

Cranfield University

Rosalba Rizzieri



**Rubber Particle Cavitation in Toughened
Poly(methyl methacrylate)**

School of Industrial and Manufacturing Science

PhD Thesis

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2001



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Supervisor: Professor C.B.Bucknall

January 2001

ABSTRACT

Theoretical and experimental investigations were performed on multiphase polymers; especially rubber toughened (RT) poly(methyl methacrylate) (PMMA) to explore cavitation in the rubbery phase.

The main objectives of this project:

- i. To identify experimental methods to effectively detect rubber particle cavitation.
- ii. To relate intrinsic toughness with rubber properties (e.g. rubber type, particle morphology, rubber content, particle size).
- iii. To study the relationships between different pre-treatments, and control the onset of cavitation.

Thermal contraction measurements, dynamic mechanical analysis, creep and fracture tests were the techniques adopted. Results from those different methods were examined, compared, and related to a specifically devised mathematical model. They were found consistent.

Thermal contraction measurement presents valuable information about the progress of cavitation after pre-strain. It shows extensive rubber cavitation at low longitudinal strain (about 2 – 3%), which is sufficient to produce permanent damage, not recoverable by annealing.

Dynamic mechanical procedure estimates the resistance of the soft phase to cavitation in response to mechanically and thermally generated stresses. It can be used to detect distributions of stress and strain within the soft phase after cavitation. The dynamic mechanical tests, supported by electron microscopy, provide further insight into the cavitation mechanism. It is suggested that a complete failure of the rubber will allow any internal stresses to relax, and the rubber glass transition temperature (T_g) to become independent of the tensile stress on the specimen. If the particles remain intact, the loss peak will shift to lower temperature with increasing triaxial tension as the rubber free volume increases in response to a growing dilatational volume strain. To any in-between state, regarding rubber phase partial failure, will correspond a loss peak in the temperature range defined by T_g of the stretched rubber and the one of the relaxed rubber (upper limit).

A major advantage is that thermal contraction measurements and dynamic mechanical tests provide an observation method for the onset of cavitation as a separate process, without the complications that arise when shear yielding or multiple crazing occur at the same time.

Analysis based on the energy-balance model suggested multiple cavitation as a possible mechanism for complex particle morphology (e.g. salami or hard-soft-hard core-shell). These results are consistent with experimental data.

Tutti i grandi sono stati bambini una volta.
(Ma pochi di essi se ne ricordano).

*Antoine de Saint Exupéry,
Il Piccolo Principe*

Ai bambini
Margherita, Arianna e Giacomo
e a Matteo, quando era bambino.

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NOTATION

Explanation of symbols

a	notch length
A	cross-sectional area
B	thickness of a sample
D	particle diameter
E	storage modulus (elastic modulus)
$\mathbf{E}$	strain tensor
f	volume fraction of voids
F	deformation gradient
G	shear modulus
G	strain energy release rate
G_c	fracture energy
ΔH	activation energy
k	Boltzmann constant
K	bulk modulus
K	stress intensity factor
K_c	fracture toughness
L	outer shell radius
L	length of a sample
n	number of voids
P	pressure
r	void radius
R	particle radius
Q	shell radius
t	time
T	temperature
T_g	glass transition temperature
U	energy
Δv	volume strain

V	volume
W	energy density
W	width of a sample
Y_c	yield stress in compression
Y_t	yield stress in tension
α	thermal coefficient of expansion (linear)
β	thermal coefficient of expansion (volume)
δ	phase angle
ε	strain
ϕ	volume fraction
Γ	surface energy
λ	extension ratio
μ	coefficient of viscosity
ν	Poisson's ratio
ρ	rubber density
σ	stress
τ	shear stress
ω	angular frequency

Clarification of acronyms

ABS	acrylonitrile butadiene styrene polymer
BCS	butylacrylate-co-styrene copolymer
CSPE	chlorosulphonated polyethylene
EPDM	ethylene propylene diene monomer copolymer (rubber)
EVA	ethylene vinyl acetate copolymer
HIPS	high impact polystyrene
PB	polybutadiene
PC	polycarbonate
PMMA	polymethyl methacrylate

POM	polyoxymethylene
PP	polypropylene
PS	polystyrene
PSAN	poly(styrene-co-acrylonitrile)
PVC	polyvinyl chloride
C	continuous
CS	core shell
HSH	hard soft hard
I	intermediate
RT	rubber toughened
S	salami
CTE	coefficient of thermal expansion
DMTA	dynamic mechanical thermal analysis
LEFM	linear elastic fracture mechanics
TEM	transmission electron microscopy
3PB	three point bend
SENB	single edge notched bend

CHAPTER 1

GENERAL INTRODUCTION

1.1. Background

The mechanism of rubber toughening remains the subject of many current studies and the leading researchers in this field still do not completely agree. This thesis is based on the view that the rubbery (or soft) phase plays a fundamental role in the toughening mechanism of multiphase polymers. Under critical conditions, such as a triaxial stress field at the tip of a sharp crack, especially at low temperatures and high strain rates (impact), the behaviour of the rubber is decisive. To improve toughness, the energy absorption at the crack tip must be maximised; the yield zone must be enlarged without reducing the yield stress too much. Yielding is not enough to ensure toughness, but the yield zone must be able to stabilise and grow. The role of rubber cavitation is therefore of major importance because:

- i. The soft rubbery phase must be able to cavitate to allow yielding (in preference to fracture). Cavitation promotes shear bands or crazes, or both in the neighbouring rigid matrix.
- ii. Once cavitated, the rubber must be able to contribute to strain hardening (to stabilise and allow the yield zone to grow). This can be achieved by stopping shear bands or crazes growing into catastrophic cracks and by promoting the initiation of new dilatational yielding. Thus, the yield zone expands into regions previously at a lower strain.

The resistance to cavitation increases when particle sizes are reduced [Bucknall et al. 1994]. The smaller the particle size the higher the stress required to cavitate, so that the level at which crack propagation becomes catastrophic is easily reached. Cavitation also becomes more difficult when the shear modulus of the rubber increases [Bucknall et al. 1994]. Therefore, an intensification of cross-linking (e.g. oxidation, ageing) or a stronger chemical structure of the rubber phase, a decrease in temperature or an increase in strain rate, all make cavitation more difficult. On the other hand, hole formation can

be promoted by reducing the surface energy of the rubber, for example by adding liquids (e.g. silicone oil) [Bucknall et al. 2000a].

The second point (ii), strain hardening is fundamental. Cavitation only, without strain hardening simply makes the material more vulnerable and weak. Therefore, good interfacial adhesion between rubber and matrix, to avoid debonding, is very important in the participation of the rubber in the toughening process. If the particle undergoes full debonding from the matrix (i.e. all the chemical bonds at the rubber-matrix interface break), strain hardening is no longer effective. Dispersion of the particles is also relevant for homogenous plasticity (i.e. shear bands and crazes uniformly distributed). Furthermore, complex rubber particle morphologies are more efficient than plain rubber particles in the strain hardening process. Rubber particles with one or more hard inclusions (so called 'salami' or 'hard-soft-hard core-shell' rubber particles) allow the soft phase to stretch between the walls of rigid polymer to which it is attached. The greatest effectiveness comes from having a large proportion of the rubber phase highly strained (by fibrillation) and uniformly distributed so that it sustains very high stresses. Hence, this makes the toughening process very efficient.

1.2. Research goal and objectives

The aim of the present thesis is to use new experimental techniques to achieve a better understanding of the toughening mechanisms that are responsible for the observed improvement in impact strength in rubber-toughened (RT) polymers. A specific objective is to relate structure (rubber particle size, interface adhesion, etc.) to the intrinsic toughness. Several different types of RT polymethyl methacrylate (PMMA) samples were available for this study.

Since it is believed that cavitation plays a fundamental role in the toughening process in RT-PMMA, special attention will be given to this phenomenon. An attempt is made to examine the influence of various mechanical and thermal pre-treatments (pre-straining, cooling, annealing, etc) on the deformation and fracture behaviour of RT-PMMA.

The present investigation also takes a step forward in the development of a cavitation model, first introduced by Lazzeri and Bucknall [1993], which establishes a criterion to initiate and expand voids in RT-polymers. It follows the work of Ayre [1999], Zhang [1993], Lazzeri [1991] and Bucknall at Cranfield University. An essential contribution in the development of the multiple-cavitation model presented in Chapter 3 comes from Deseri [1999]. Relevant scientific discussions were held during periodic meetings with Julia Higgins and Alberto Saiani (Imperial College, London), Athene Donald (Cavendish Laboratories, Cambridge), Roy Moore, Rob Bailey and Gordon Emmerson (ICI, Wilton), Ian Robinson and Ian Fraser (Ineos, Wilton) involved in a common ICI-supported research.

1.3. Survey of the thesis

The improvement in toughness of a two-phase system is an important subject requiring a wide knowledge of deformation and fracture processes in polymers. The role of Chapter 2 is to give an outline of the mechanisms of deformation, yield and fracture in homopolymers and rubber-modified polymers. However, most of this subject is still under investigation and some researchers in the field do not fully share the same points of view.

In Chapter 3, attention is focused on improving a pre-existing cavitation model based on an energy-balance criterion [Lazzeri and Bucknall 1995]. Results of calculations presented in the literature introduce difficulties in defining uniquely the contribution of rubber particle structure to the intrinsic toughness of RT-polymers. Results suggest that multiple-cavitation is theoretically and experimentally possible for complex rubber particle morphologies, such as ‘salami’ or ‘hard-soft-hard core-shell’ particles.

Experimental methods used to investigate the cavitation behaviour for a list of RT-PMMA materials are presented in Chapter 4.

New experimental techniques are compared with traditional methods in Chapter 5, to monitor continuously void formation from the early stages, and to separate rubber particle cavitation from other deformation mechanisms (e.g. dilatational shear yielding

or crazing) of the surrounding matrix. Several types of rubber particles that feature different morphologies and sizes, and various mechanical and thermal pre-treatments (i.e. pre-straining, cooling and annealing) have been separately investigated. Cavitation measurements were also performed on RT-PMMA containing different kinds of rubber and for a varying range of rubber contents.

Chapter 6 discusses these experimental and theoretical studies, drawing conclusions about the factors that influence the cavitation process.

Chapter 7 reviews the achievements of this work in relation to previous knowledge, possible future implications and suggested developments.

CHAPTER 2

DEFORMATION, YIELD AND FRACTURE OF TOUGHENED POLYMERS

2.1. Introduction

Several glassy thermoplastics like polyvinyl chloride (PVC), polymethyl methacrylate (PMMA) and polycarbonate (PC) possess good properties such as good tensile strength and effective chemical resistance, e.g. for PMMA excellent optical properties and for PC clarity and toughness. Therefore these polymers are very important materials for electrical, automotive, mechanical and chemical engineering applications. They can be used for numerous purposes, such as materials handling, instrumentation, plumbing and sanitary ware and packaging [Kroschwitz 1990]. A disadvantage of many rigid thermoplastics is that at ambient temperature (about 20°C) they tend to break in a brittle manner when surface or internal defects (e.g. scratches, extraneous inclusions) are present, and they can be notch sensitive. When a material behaves in a brittle manner, the crack tip deformation rate is high and energy dissipation occurs only in a localised area around the crack tip, so that the total energy dispersed during fracture is low. This fragility can be responsible for limiting the applications of various plastic materials.

Since glassy polymers suffer from these problems, in order to use them in structural applications they are generally toughened with a small amount of rubber, i.e. incorporating a second elastomeric phase into the glassy matrix. The addition of rubber phase has proved to be a very effective solution to enhance the toughness of various brittle and semi-brittle polymers such as PVC, PC, PMMA, polystyrene (PS), nylon and epoxy resins. The rubber phase is generally blended or copolymerised with the matrix to ensure a good interface between the two phases. The advent of rubber modified polymers increased the market for plastics since the early nineteen fifties. High impact PS (HIPS) was one of the first rubber toughened polymers, followed by acrylonitrile-butadiene-styrene (ABS) and many others.

Modified polymers can behave in a more ductile manner; in particular, they can form large damage zones that can prevent unexpected catastrophic fracture. The techniques utilised to toughen polymers vary depending on the nature of the matrix and the rubber. Choosing the right rubber (type, morphology) and the right blending conditions (matrix-rubber interface adhesion, volume fraction of modifier) is essential to produce a better material. There have been broad types of studies and research on the toughening mechanisms of many rubber-modified plastics to try to find the appropriate recipe to make tougher and stronger materials. For example, if the rigid matrix is PMMA, the main deformation mechanism seems to be shear yielding and the best toughening comes from a defined blend morphology (structure, volume fraction, size and type of rubber particles) [Heim et al.1993], as specified below. It is also found that an increase in toughness can be achieved in brittle polymers through the addition of a rigid phase such as silica particles that have a higher elastic modulus than the matrix [Young and Lovell 1991]. In this case, the presence of the particles makes crack propagation more difficult. However, the increase in toughness is not as significant as in the case of rubber toughening.

The main toughened polymers studied during this programme were modified by adding rubber particles. Several authors, including Bucknall [1977, 1997, and 2000], Newman [1978], Kinloch and Young [1983], Lovell et al. [1993] have reviewed the literature on rubber toughening. Inclusion of small rubber particles in the glassy polymer matrix is a very common way of achieving a high degree of toughness. Merz et al. [1956] first proposed a theory of toughening by means of rubber particles in HIPS. Rubber particles, holding together the opposite faces of a growing crack were able to absorb energy. According to this theory, the amount of energy absorbed in the impact equals the sum of the energy required to fracture the glassy matrix and the work to break the rubber particles. Micro-cracks were responsible for stress whitening and for the low density of HIPS under stress. However, this theory could not explain the differences in fracture behaviour among toughened polymers based on different matrices.

Newman and Strella [1965], from mechanical property and optical microscopy studies on ABS, suggested that the role of rubber particles was to promote yielding in the

matrix, which could absorb more energy than rubber particle deformation and breaking. However, this idea could not explain elongation without necking. The absence of yielding or cavitation from optical microscopy studies on rubber modified epoxies conducted by Kunz-Douglas et al. [1980] advanced the idea that rubber particles play the role of bridges between the fracture surfaces as the crack grows through the material, so that the elastic energy stored in the rubber particles during deformation and its dissipation at rupture was the cause of the increased toughness. For many rubber toughened polymers it has been demonstrated that particles can cavitate during deformation and this process can trigger other damage mechanisms [Bubeck et al. 1991, Lovell et al. 1994]. Many scientists now believe that rubber particle cavitation promotes crazing, shear yielding, or both in the matrix to allow yielding rather than fracture. Moreover cavitation, stretching and tearing of the rubber phase is considered fundamental to strain hardening to stop shear bands or crazes growing into catastrophic cracks and to permit the yield zone to stabilise and expand, increasing fracture resistance by absorbing and dissipating energy.

Chen and Mai [1998] used a three-dimensional finite element analysis model to show that under a triaxial state of stress, cavitated or debonded rubber particles were able to initiate extensive plastic deformation in the surrounding matrix, while intact particles, with high bulk modulus, were able to sustain the triaxial stress and limit the development of plastic deformation. Several researchers [Yee and Pearson 1986, Parker et al. 1990, Wu and Mai 1993] also investigated experimental evidence in rubber-modified epoxies and PC, finding that rubber cavitation, relieving constraints at the tip of a crack in high triaxial tension, was followed by extensive matrix shear yielding. They concluded that cavitation not only can reduce the hydrostatic tension in the matrix, but it can also promote the initiation of multiple crazing. In the case of fibrillated rubber particles, they can also help to sustain loading and stabilise crazes [Bucknall 1994], as described below.

The contribution of rubber particles to fracture energy, due to stretching, cavitation and void expansion, is fundamental for glassy polymers. Rubber cavitation, matrix crazing and shear yielding have been identified as the major toughening mechanisms for

polymers [Bucknall 1997, Riew and Kinloch 1993 and 1996] and the significance and correlation of these processes is still the subject of various studies. A lot has been written about the factors that influence toughness in rubber modified polymers. Rubber particle size, particle volume fraction, rubber-matrix interface adhesion and rubber stiffness are known to play a major role to improve toughness [Bucknall 2000].

- An increase in volume fraction of rubber particles results in a growth in impact toughness, but it is responsible for a reduction in stiffness.
- Small ($\sim 0.1 \mu\text{m}$) rubber particles have been found to be less likely the cause of craze formation than large ($\sim 0.5 \mu\text{m}$) particles in ABS [Donald and Kramer 1982], while small particles are more effective at initiating shear yielding. Therefore, an equal distribution of small and large rubber particles can promote deformation by shear yielding and crazing, and craze propagation can be controlled by shear bands and large particles to give better toughness in ABS. The optimum particle dimension depends on the deformation mechanisms of the matrix. When the matrix deforms mainly by crazing larger particles are preferred, whereas, if shear yielding is the predominant deformation process, small particles are better. Since PMMA, at low strain rate, deforms primarily by shear yielding, the best particle size was found to be ranging between 200 and 250 nm [Wrotecki et al. 1991]. Dompas et al. [1994] also proved that particle sizes smaller than 150 nm diameter did not promote toughness in modified PVC.
- It has been shown that interfacial adhesion between matrix and rubber particles must be good to enhance toughness. Therefore, big particles, that present more easily debonding during deformation than small particles [Pearson and Yee 1991] need to be treated to improve interfacial adhesion.

The morphology of rubber particles is also crucial. Most of the RT-PMMA samples studied in the present thesis show a hard-soft-hard core-shell (HSH CS) rubber particle morphology. An outer layer of PMMA blended with the matrix contains a layer of rubber that encloses a glassy core of the same material of the matrix. The particle diameter should be smaller than the wavelength of light and the rubber should have identical refractive index to that of the PMMA, to maintain the transparency and the optical properties of the PMMA. Lovell et al. [1993] investigating several types of RT-

PMMA containing HSH CS rubber particles concluded that they were tougher than RT-PMMA containing simple rubber particles. The presence of a high modulus glassy material, as the core of the particles, seemed to be the reason for more efficient toughening. It is also suggested [Bucknall et al. 2000b, and present thesis] that complex particle morphologies improve toughness allowing different levels of strain within the rubber phase, by partial cavitation (fibrillation and stretching of fibrillated rubber among the rigid core or inclusions and the matrix). While HSH CS have had most of the attention in the experimental part of this work, a complete theoretical analysis of HSH CS toughening has still to be performed. Pure rubber particles are instead studied by Bucknall et al. [1994] in a first qualitative analysis of cavitation theory, that is deeply discussed and developed in Chapter 3. Lazzeri and Bucknall [1993, 1995] have modelled the formation of a cavity in a rubber particle on the basis of an energy balance criterion. Other models discussing the nature and the procedure of void initiation from various researchers [Fond and Schirrer 1996, Dijkstra 1993] have helped the understanding of this complex process. Even so, the mechanisms of toughening and knowledge of the deformation processes are still a subject of interest and investigation.

2.2. Deformation

While cavitation is a very important deformation mechanism and its investigation is the research goal of the present study, knowledge of visco-elastic and plastic (shear yielding and crazing) deformation processes that can lead to a macroscopic failure of the specimen are essential.

Polymeric materials are made of complicated conformations of long molecular chains. For this reason the deformation behaviour of polymers is a difficult subject and still not well understood. If a blend material is considered, the deformation behaviour is governed by the morphology and properties of the matrix polymer and the ones of the toughening agent, apart from test conditions, specimen geometry and preparation. Many of these parameters may not remain constant during deformation, e.g. the temperature may rise locally due to plastic deformation, the geometry may change and the morphology may vary too.

The initial part of a stress-strain curve of a polymeric material under uniaxial loading presents time-dependent elastic behaviour, and may be followed by time-dependent plastic deformation. Four elastic parameters are normally used to describe the elastic behaviour of an isotropic solid; they are the Young's modulus (E), the shear modulus (G), the Poisson's ratio (ν) and the bulk modulus (K). They are related through the formulae:

$$G = \frac{E}{2(1+\nu)} \quad K = \frac{E}{3(1-2\nu)} \quad (2.1)$$

The elastic properties of polymers are very sensitive to temperature and rate of load application during the test. In general, it is found that the effect of increasing the loading rate upon properties such as E , has the same effect as decreasing the temperature [Young and Lovell 1991] during the test. Polymer molecular chains are adaptable: they can change conformation and locally accommodate the occurring deformation. This peculiar behaviour gives polymers visco-elastic properties, i.e. they display both elastic and viscous types of behaviour. Hooke's law, $\sigma = E\varepsilon$, describes linear elastic relationship: the extension is instantaneous and directly proportional to the applied load. Newton's law, $\sigma = \eta d\varepsilon/dt$, expresses linear viscous behaviour (η being the viscosity): the extension rate is proportional to the applied load.

Generally, a linear visco-elastic behaviour follows the Boltzmann superposition principle [Young and Lovell 1991]. For example, in creep, for a linear visco-elastic material each loading step independently contributes to the final deformation so that the overall deformation can be determined from the sum of the strains due to each loading step, as shown in Figure 2.2.1. It is convenient to model the linear visco-elastic properties of polymers with a mechanical analogy. Combinations of linear springs of modulus E (which follow Hooke's law) and viscous dashpots of viscosity η (which obey Newton's law) can be adopted. Figure 2.2.2 illustrates three models: in the Maxwell one spring and dashpot feature a series connection, in the Kelvin/Voigt approximation they are in parallel. The standard linear model is the one that achieves

the best representation of the visco-elastic behaviour in polymers: it includes a linear spring connected in parallel to a subsystem consisting in a spring and dashpot in series.

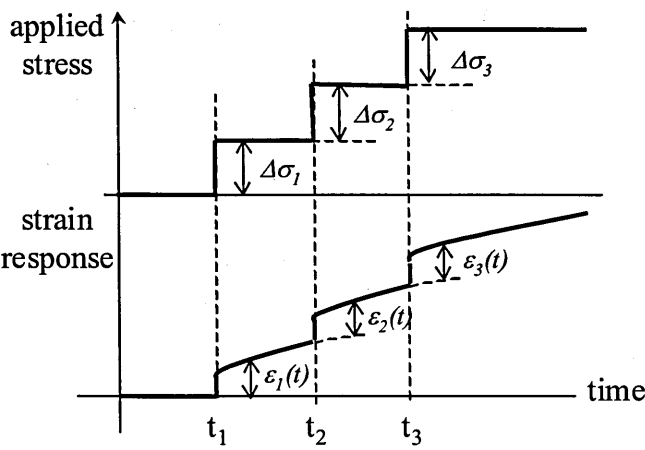


Fig. 2.2.1 Creep behaviour of a linear visco-elastic material subjected to a series of loading steps (after Ward [1983])

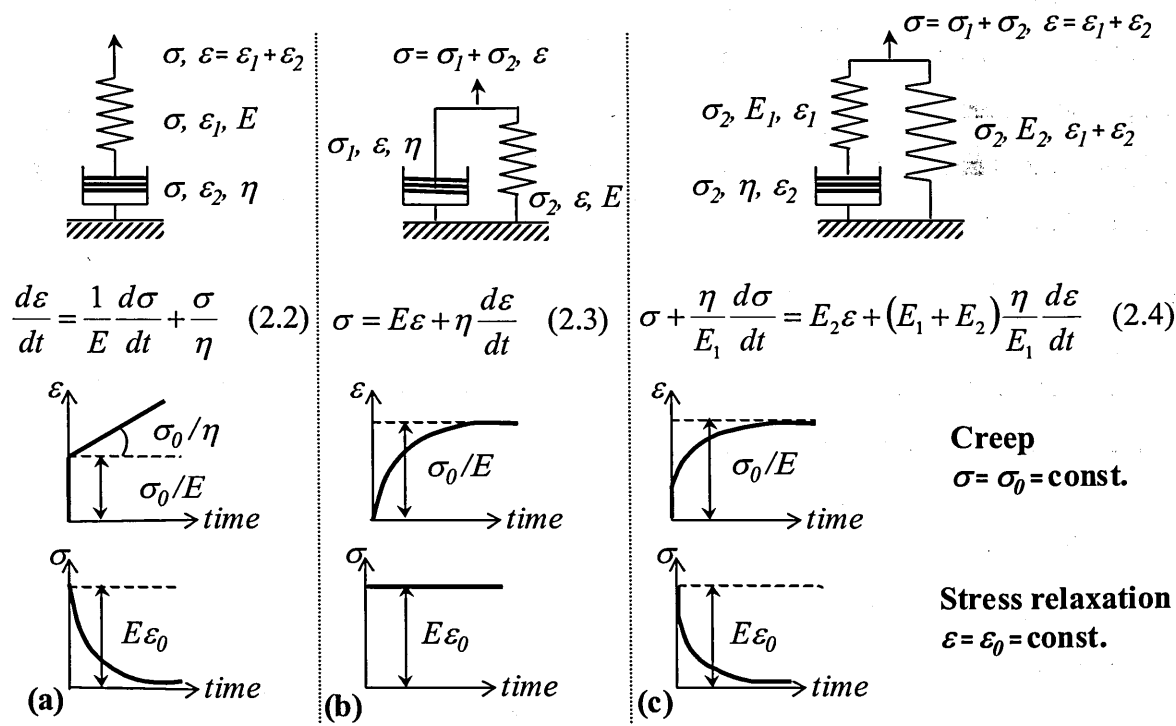


Fig. 2.2.2 Above: schematic representation of the mechanical models used to characterise visco-elastic polymers. Below: the behaviour of the models under different types of loading: creep (constant stress, σ_0) and stress relaxation (constant strain, ϵ_0). (a) The Maxwell model, (b) the Kelvin/Voigt model, (c) the Standard linear model.

The Maxwell model can be simply described by equation (2.2) in Fig. 2.2.2 [Ward 1983]. In case of creep, the stress is kept constant and equation (2.2) becomes:

$$\frac{d\varepsilon}{dt} = \frac{\sigma_0}{\eta} \quad (2.5)$$

The strain increases linearly with the time. For visco-elastic materials the strain increases rapidly at first, but slows down with time. On the other hand, in case of stress relaxation the strain is fixed and equation (2.2) becomes:

$$\frac{d\sigma}{\sigma} = -\frac{E}{\eta} dt \quad (2.6)$$

Integrated with the initial condition at $t = 0$, $\sigma = \sigma_0$ gives:

$$\sigma = \sigma_0 e^{-\frac{Et}{\eta}} \quad (2.7)$$

The stress decreases exponentially with time and it relaxes completely after a long time. Thus, the Maxwell model expresses the stress relaxation of a polymer, but only to a first approximation. A polymer does not undergo a full relaxation, because of molecular chain rearrangements.

The Kelvin/Voigt model can be described by equation (2.3) in Fig. 2.2.2. In case of creep, equation (2.3) becomes:

$$\frac{d\varepsilon}{dt} + \frac{E\varepsilon}{\eta} = \frac{\sigma_0}{\eta} \quad (2.8)$$

Differentiation gives:

$$\varepsilon = \frac{\sigma_0}{E} \left(1 - e^{-\frac{Et}{\eta}} \right) \quad (2.9)$$

that represents a good approximation for the behaviour of a polymer. A polymer does not present a constant strain after a long time, but the strain slowly increases because of molecular motions.

The standard linear model where a Maxwell element and a spring are in parallel is described by equation (2.4) in Fig. 2.2.2. In this case the model represents, to a first approximation, polymer behaviour under any loading condition. Real visco-elastic behaviour of polymer materials is more complicated and can be expressed by more complex models (e.g. various Maxwell elements in parallel or a large number of Voigt elements in series). Figure 2.2.3 represents a visco-elastic response, typical for polymers, that is a combination of elastic (time independent), anelastic (time dependent, but recoverable) and viscous (time dependent and non-recoverable) behaviour [Ferry 1980].

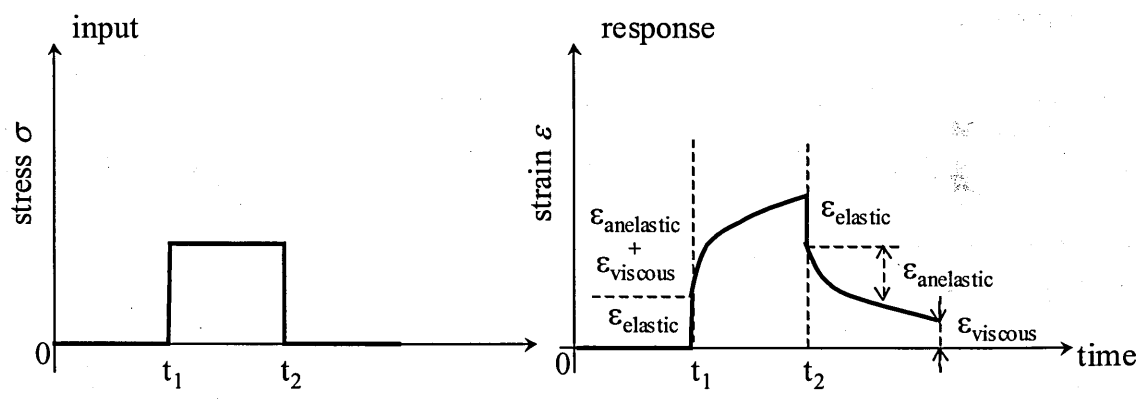


Fig. 2.2.3 Variation of stress and strain with time for a visco-elastic material due to response to loading and unloading conditions.

The viscous response for polymers at temperatures below the glass transition temperature (T_g) is generally insignificant and they essentially show the elastic and anelastic deformation. If there is enough time for molecular relaxation to occur, a small deformation may disappear due to the regeneration of molecular kinks. Moreover for polymers the visco-elastic behaviour is strongly temperature dependent. In fact, increasing the temperature makes the molecules spread due to thermal expansion

(volume thermal expansion), in addition a rise in temperature accelerates relaxation processes in the material.

A particular case of time dependent deformation that is fundamental for experimental work described in this thesis is the harmonic oscillation. Briefly below are described the parameters used to address dynamic visco-elastic properties. If a body is for example subjected to an oscillating sinusoidal strain $\varepsilon(t) = \varepsilon_0 \sin(\omega t)$ of angular frequency ω , where ε_0 is the maximum amplitude of the strain, the resulting stress, for a linear visco-elastic material, is also sinusoidal and out of phase (an angle δ ahead) with the applied strain (Figure 2.2.4):

$$\sigma(t) = \sigma_0 \sin(\omega t + \delta) = (\sigma_0 \cos \delta) \sin \omega t + (\sigma_0 \sin \delta) \cos \omega t \quad (2.10)$$

The strain lags behind the stress by a phase angle δ .

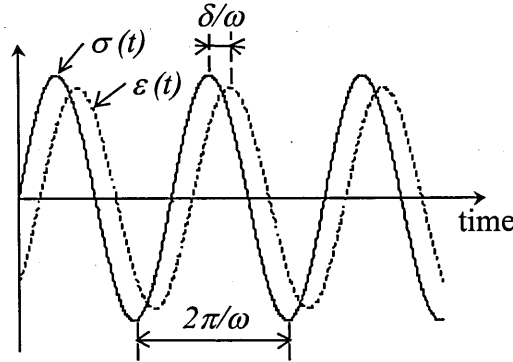


Fig. 2.2.4 Variation of stress and strain with time for a visco-elastic material

From equation (2.10) the stress consists of two components: the term $(\sigma_0 \cos \delta)$ is in phase with ε and the term $(\sigma_0 \sin \delta)$ is 90° out of phase. The stress σ has the same angular frequency ω as ε , but is out of phase to a degree that depends on the relative magnitude of these terms. Equation (2.10) can be conveniently written as:

$$\sigma(t) = \varepsilon_0 [E' \sin(\omega t) + E'' \cos(\omega t)] \quad (2.11)$$

where E' represents the in phase component, $\frac{\sigma_0}{\varepsilon_0}(\cos \delta)$, and E'' the term 90° out of phase, $\frac{\sigma_0}{\varepsilon_0}(\sin \delta)$. Adopting a complex representation the dynamic strain (ε^*), stress (σ^*) and elastic modulus (E^*) can be rewritten as:

$$\varepsilon^* = \varepsilon_0 e^{i\omega t}, \quad \sigma^* = \sigma_0 e^{i(\omega t + \delta)}$$

$$E^* = \frac{\sigma^*}{\varepsilon^*} = \frac{\sigma_0}{\varepsilon_0}(\cos \delta + i \sin \delta) = E' + iE'' \quad \text{with} \quad \tan \delta = \frac{E''}{E'} \quad (2.12)$$

where δ is the loss angle, i.e. the relative angular displacement of the stress and strain, as shown in Figure 2.2.4. E' denotes the real part of the modulus. It symbolises the storage modulus (a measure of the energy stored in the system), E'' is the imaginary part of the modulus. It represents the loss modulus (related to the energy dissipated in the system).

In case of fixed temperature, the values of E' , E'' and $\tan \delta$ for a polymer are extremely influenced by the frequency or the rate at which the load is applied during the test. It has been found experimentally that $\tan \delta$ and E'' are usually small at very low and very high frequencies and they show a peak at some intermediate frequency [Young and Lovell 1991]. E' instead is high at high frequencies when the polymer behaves as a glass and it is low at low frequencies when it behaves as a rubber. At intermediate frequencies (visco-elastic region) E' changes rapidly, when E'' and $\tan \delta$ show a peak [Young and Lovell 1991]. It is possible to associate E'' and $\tan \delta$ peaks to particular types of molecular motion in the polymer. For example, when the temperature of a polymer is close to the glass transition temperature (T_g) and the applied frequency corresponds to the natural frequency of main chain rotation a considerable degree of damping occurs in the material. The frequency at which the transition (E'' and $\tan \delta$ peaks) occurs increases as the testing temperature increases. If the applied frequency is held constant, the transition can be observed by varying the testing temperature. It is

normally easier to keep the frequency constant and vary the temperature, as it has been for dynamic mechanical tests performed during this study. Molecular motion coming from different phenomena, such as rotation of side groups (secondary transition), can also be detected from dynamic mechanical tests.

The presence of rubber particles in glassy polymers leads to stress concentrations due to mechanical deformation or thermal deformation, or both, that can promote shear yielding or crazing around the particles so that the polymer absorbs a large amount of energy. There are two main mechanisms responsible for plastic deformation in the matrix of toughened polymers: shear yielding and crazing. Depending on the material and on the stress state, these two mechanisms can operate separately or simultaneously. However, plastic deformation can be completely recovered if a large enough relaxation time is permitted or the specimen is annealed at a temperature close to the T_g of the material.

2.2.1. Yielding

Yielding is a kind of plastic deformation process that approximately involves no volume change, but does produce distortions in shape. The nature of yielding depends on the geometry of the sample and the applied stresses.

The most characteristic manifestation of yield occurs in polymer specimens under tensile load applied at constant rate. Figure 2.2.5 shows a schematic stress-strain curve for a ductile polymer (for example PE). In the initial part of the curve (AB) the stress is proportional to the strain (linear-elastic behaviour) and homogeneous deformations occur. As the strain increases the slope of the curve drops until the stress reaches a maximum at point B. In the sample there is a localised reduction in cross-section (neck formation) and a permanent plastic deformation takes place. This is called the yield point, after which further elongation brings a drop in load (strain softening), BC zone. For polymers it is difficult to define the yield point because permanent plastic deformation can occur before the maximum stress. It is even possible that some polymers do not present necking or strain softening. In the CD zone the neck expands along the specimen and the stress slowly grows (strain hardening). At high elongation

segments of the molecular chains rotate towards the direction of the stress, thus increasing the molecular density and diminishing further intermolecular motion.

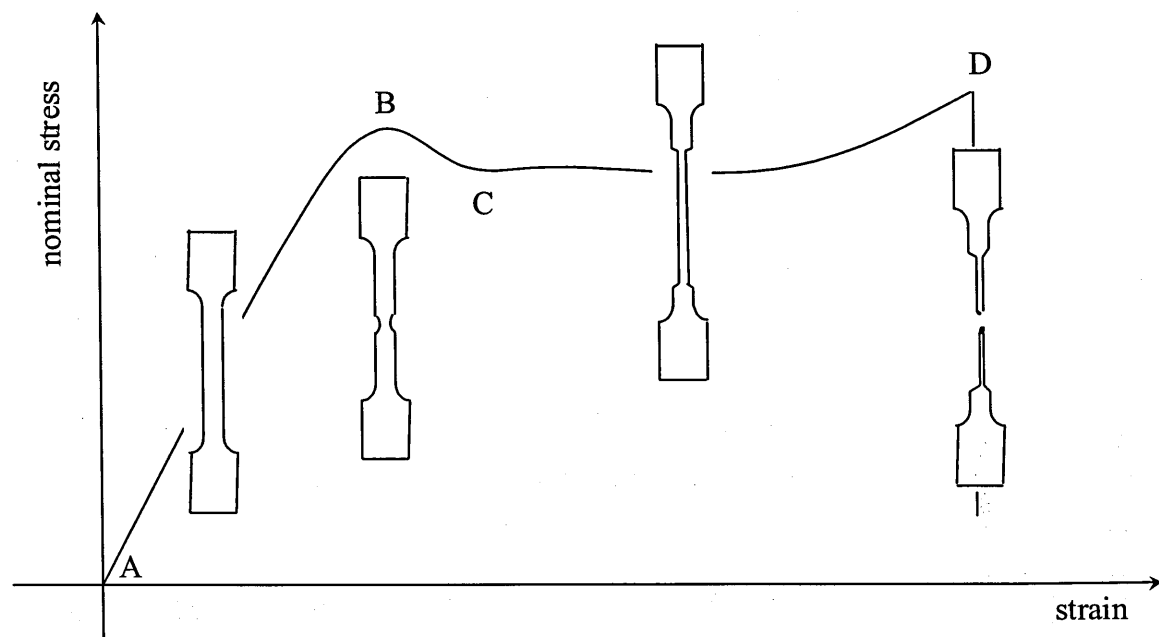


Fig. 2.2.5 Typical stress-strain curve for a ductile polymer and changes in shape during tensile loading at constant testing rate.

Yielding is well understood for crystalline materials in which planes of atoms slide over one another to new equilibrium positions. Yield in glassy materials is still under investigation. It is known that under applied stress the structure undergoes a rearrangement that persists after unloading. Interatomic or intermolecular bonds are overcome and replaced by almost equivalent bonds after yield deformation [Crist 1997]. Yielding operates to activate molecular motions, which are restricted to shear bands [Kramer 1975, Brown 1983]. Yielding and strain softening have been abundantly investigated and many theories have been proposed in the past [Eyring 1936, Robertson 1966, Argon 1973]. As an activated process, where molecule or a chain segments have to overcome a potential energy barrier to jump from one equilibrium position to another, yielding is rate and temperature dependent and can be described using the kinetic theory [Eyring 1936, Bauwens et al. 1974]. Most yield theories in polymers are based on the kinetic theory, where deformation is a rate process favoured by shear stress and temperature. This situation is represented by the Eyring equation:

$$\dot{\epsilon} = \dot{\epsilon}_0 e^{-\frac{\Delta H}{kT}} \sinh\left(\frac{V\sigma}{kT}\right) \quad (2.13)$$

where $\dot{\epsilon}$ is the plastic strain rate, $\dot{\epsilon}_0$ a constant, k the Boltzmann constant, T the temperature, ΔH the activation energy and V the activation volume. The deformation of a polymer at strain rate $\dot{\epsilon}$ is modelled as a thermally activated process that depends on both ΔH and V , as shown in Figure 2.2.6.

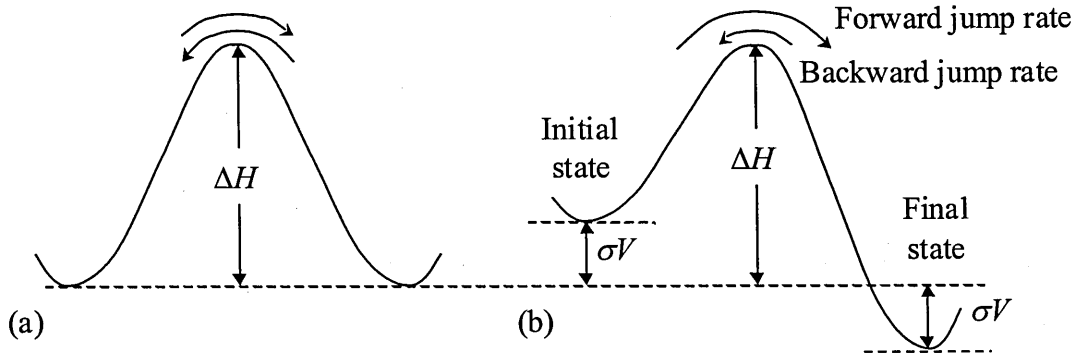


Fig. 2.2.6 Eyring model of solid flow. Before (a) and after (b) the stress is applied.

Thermal energy enables molecules or chain segments to move randomly within the material, in any direction. In the absence of stress only the ones with enough thermal energy are able to overcome the barrier. If a stress σ is applied the chains tend to move in the direction of the stress. The mechanical energy ($V\sigma$) produces a reduction of the activation in the direction of the stress ($\Delta H - V\sigma$) and an increase of the same amount in the activation energy for chain motion in the reverse direction ($\Delta H + V\sigma$). This leads to the equation (2.13), where the stress σ is the local stress acting on the molecular segment considered. It has been found that the Eyring equation can be applied to a variety of polymers over a very wide range of strain rates from creep to rapid deformation. In equation (2.13), $\dot{\epsilon}_0$ is a factor containing an entropy term (ΔS) which depends on the initial structure. The main contribution to ΔS is due to local chain movements allowed by temperature [Escaig 1984]. Since an increase in temperature can lead to significant increase in vibration amplitude of monomer units in polymers, the

role of ΔS is not negligible. If $V\sigma \gg kT$, i.e. close to the yield point, equation (2.13) becomes:

$$\dot{\epsilon} = \frac{\dot{\epsilon}_0}{2} e^{-\frac{\Delta H - \sigma V}{kT}} \quad (2.14)$$

In inhomogeneous materials, such as rubber toughened plastics, the stress varies from point to point, e.g. an applied uniaxial tensile stress results in high triaxial tensile stresses near the particle equators [Bucknall 1986]. Therefore, the kinetics accelerates the deformation process in the highest stress concentration regions. This is taken into account by multiplying the applied stress by a scalar stress concentration factor γ to obtain the local stress, where $\gamma = 1$ applies for unmodified materials.

Equation (2.14), valid near the yield point, leads to an expression for the variation of yield stress with temperature and strain rate:

$$\sigma_Y = \sigma_0 + \frac{kT}{V} \log \left(\frac{2\dot{\epsilon}_Y}{\dot{\epsilon}_0} \right) \quad (2.15)$$

where σ_0 is the yield stress at 0 K ($\sigma_0 = \frac{\Delta H}{V}$).

From equation (2.15) it can be seen that σ_Y increases linearly with $\log(\dot{\epsilon}_Y)$. Even if the above equation can fit experimental data well, and for many polymers this approach is valid, the physical meaning of the activation volume and energy is still under discussion. Furthermore, the activation parameters ΔH , ΔS , V are not constant for polymers, where the molecular density may change from point to point. Bucknall [1986] proposed that V may represent the product Ad , where A is the area of the molecule over which the stress operates, and d is the distance through which the stress takes the molecule to the top of the energy barrier.

In equation (2.15), σ_Y is the critical stress for yielding, which depends on material properties and on the proportion of different stress components. Yield is generally

associated with the maximum stress (σ_M), as specified above, so that strains imposed below σ_M are recoverable (elastic or visco-elastic), while plastic strain occurs at σ_M and beyond σ_M . Yield criteria use stress-strain data from uniaxial and multiaxial tests to define when yield occurs in a general loading situation. Some simple criteria have been developed, mainly with metals in mind, but they can, with some reservations, be used for polymers. There are two principal criteria for shear yielding:

I. Tresca criterion: yielding occurs if half of the difference between the maximum and the minimum principal stresses in the material reaches a certain critical shear stress τ_Y :

$$\frac{1}{2}(\sigma_1 - \sigma_3) \geq \tau_Y \quad (2.16)$$

where σ_1 , σ_2 and σ_3 are the principal stresses ($\sigma_1 > \sigma_2 > \sigma_3$), τ_Y is the shear yield stress. From considering a simple tensile test in which $\sigma_2 = \sigma_3 = 0$, equation (2.16) predicts that yield occurs when the applied tensile stress $\sigma_1 = 2\tau_Y$. In the three-dimensional stress diagram the Tresca criterion is represented by a hexagonal cylindrical surface with an axis that forms equal angles with the co-ordinate axes.

II. von Mises criterion: yielding occurs when the second invariant of the deviatoric stress tensor reaches a critical value σ_Y :

$$\sqrt{\frac{1}{2}[(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_1 - \sigma_3)^2]} \geq \sigma_Y \quad (2.17)$$

In the case of pure shear $\sigma_1 = -\sigma_2$ and $\sigma_3 = 0$, equation (2.17) forecasts yielding to occur when the applied tensile stress $\sigma_1 = \frac{\sigma_Y}{\sqrt{3}}$ and the yield stress in pure shear is equal to $\frac{1}{\sqrt{3}}$ of that in tension. In the three-dimensional stress diagram the von Mises

criterion is represented by a cylinder with radius $\frac{\sqrt{2}}{3}$ times the uniaxial yield stress and an axis which forms equal angles with the co-ordinate axes. The two criteria are presented in Figure 2.2.7 for the special case where $\sigma_3 = 0$.

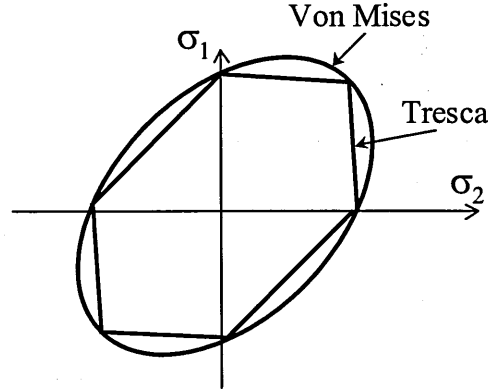


Fig. 2.2.7 Cross-section of Tresca and von Mises yield surfaces for plane stress deformation.

For polymers the yield stress is generally smaller under tension (σ_Y) than under compression (σ_C), and the ratio of σ_Y to τ_Y is less than 2. Tresca predicts that yield occurs at the same values of applied stress in tension and compression with $\sigma_Y = \sigma_C = 2\tau_Y$, whereas von Mises, while again expecting tensile and compressive yield stresses to be the same, gives their value as $\sqrt{3}\tau_Y$. Von Mises criterion is therefore more useful than the simple Tresca criterion, but still does not fit yield data for polymers.

The hydrostatic stress, which is not considered in Tresca and von Mises criteria, must be taken into account. Tresca criterion has been modified in the Mohr-Coulomb criterion and von Mises in the parabolic and conical criteria [Ward 1983]. The Coulomb criterion, originally proposed for the slip of soils, says that slip occurs when the shear stress τ_Y exceeds a value given by $(\tau_C - \mu\sigma_N)$ with τ_C a 'cohesive' stress, μ the equivalent of a coefficient of friction and σ_N the normal stress acting on the slip plane. This expression gives a higher shear yield stress in compression (σ_N is negative) than

in tension. When the Coulomb criterion is combined with the von Mises criterion the resulting modified version of the von Mises criterion can describe better the yield process in polymers. In general, for many polymers (e.g. PS and PMMA), the modified von Mises criterion gives a better fit to the experimental data. The pressure-modified von Mises criterion can be rewritten in terms of the shear yield stress:

$$\tau_Y = \tau_Y^0 - \mu P \quad (2.19)$$

with P the applied hydrostatic pressure, given by:

$$P = \frac{\sigma_1 + \sigma_2 + \sigma_3}{3} \quad (2.20)$$

where μ is a coefficient of increase in critical shear stress with pressure, i.e. the coefficient of friction of the polymer sliding against itself, and τ_Y^0 the yield stress in pure shear (under zero pressure):

$$(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2 \geq 6(\tau_Y^0 - \mu P)^2 \quad (2.21)$$

where τ_Y^0 depends on temperature, strain and thermomechanical history of the material. In the three-dimensional stress diagram the pressure-modified Tresca criterion is represented by a hexagonal pyramid and the von Mises criterion becomes a cone.

The criteria mentioned above are macroscopic continuum criteria. They try to predict the stress at which yield occurs, but do not take any account of the mechanism by which yield happens. A polymer for which yielding is the main mechanism, such as polyethylene terephthalate (PET) and PC, in impact presents a high crack initiation energy, but a low crack propagation energy. Many polymer blends with highly entangled, crosslinked or semicrystalline matrices develop high toughness when yielding take place. Though Newman and Strella [1965] proposed that rubber toughening is due to shear yielding in the matrix, their theory did not explain density changes and elongation without necking. For rubber particle toughened polymers,

cavitation has been found to be essential to promote extensive shear yielding deformation in the matrix [Yee et al. 1993, Yee and Pearson 1986, Wu and Mai 1993]. Parker et al. [1990] demonstrated the necessity for rubber cavitation to happen before yielding to enlarge the plastic zone and increase fracture toughness.

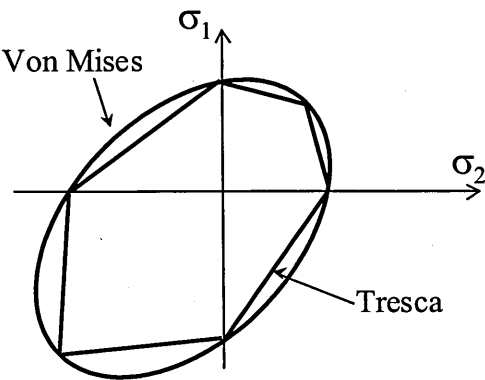


Fig. 2.2.8 Cross section of Tresca and von Mises modified yield surfaces for $\sigma_3 = 0$.

Sue and Yee [1988] experimentally observed in RT-polymers that shear yielding initiates at the equators of particles, then shifts towards the pole around the interface and finally is localised to form shear bands in the direction of $\pm 45^\circ$ to the applied tensile stress.

2.2.2. Crazeing

Crazing is a localised plastic deformation process accompanying volume dilatation that it is often observed in glassy and semi-crystalline polymers. Crazes consist of many connected voids, partially separated by highly orientated polymer fibrils. The presence of the voids explains the volume dilatation accompanying crazing. Crazes grow normal to the major principal tensile stress. For this reason the fibrils are aligned with the stress, as shown in Figure 2.2.9. The fibrils are bundles of polymer chains that bridge the voids preventing a single big crack. Hence, fibrils possess some load bearing capacity and the craze surfaces can also be highly loaded. In fact, specimens largely crazed through their cross-section are still able to support high load. If some of the fibrils break because of increasing stress or time under load, the stress applied on the remaining fibrils increases

and the transformation from crazes to a macroscopic crack accelerates. Under compression or upon annealing crazes tend to retract and disappear.

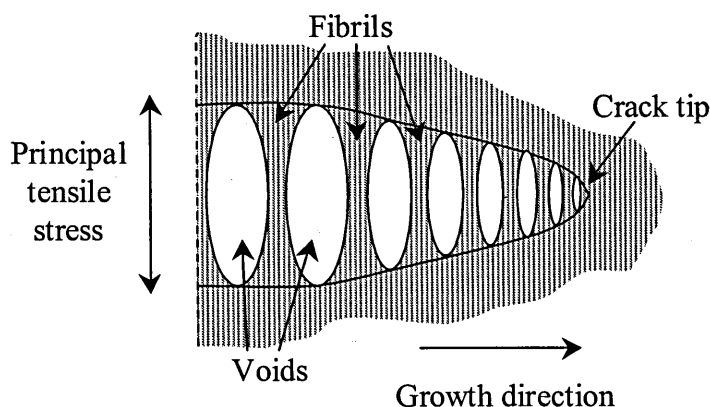


Fig 2.2.9 Schematic representation of the internal structure of a craze.

Crazes in glassy polymers can initiate from the surface, due to heterogeneity at the surface of the sample (scratches, notches), or from the inside, due to interior structural defects (voids, impurities, inclusions, e.g. rubber particles). The initiation points of crazes are points of stress concentration [Argon 1975], where the local stress field is high. Many materials, including PS, PMMA, PC, PVC and polypropylene (PP) can form crazes. The structure of crazes, their thickness and fibril diameter, depends on the material and test conditions [Donald and Kramer 1982, Huang and Brown 1988]. Rates of crazing and craze structure also depend on temperature and stress applied on the material, molecular weight, molecular orientation, thermal history of the material and on the environment surrounding the sample (solvent crazing).

Argon and Salama [1977] introduced a meniscus instability model of craze growth based on comparing the polymer at a crack tip with a liquid. The concept was then developed by Kramer [1984], who considered the bond breaking energy required in order to allow the polymer to fibrillate. Donald and Kramer [1982] made a big contribution to our understanding of the structure of crazes in glassy polymers. They found a connection between chain contour length between entanglements (l_e) and the stress needed for craze formation σ_c ; if l_e decreases σ_c increases. When l_e is very short, shear yielding is found to be the deformation process of the material instead of crazing.

Since crazing is a localised process it is generally associated with brittle behaviour, while shear yielding is considered a ductile deformation process. Therefore, the transition from crazing to shear yielding is important in the fracture of toughed polymers.

Henkee and Kramer [1984] found that with low entanglement density the material deforms by crazing. Meanwhile the resistance against crazing increases if the number of entanglements increases. When the entanglement density is high enough, the material deforms via shear yielding. Crazing and shear yielding can coexist for a medium entanglement density.

Berger and Kramer [1988] investigated how test conditions (temperature and strain rate) influence the transition from crazing to shear yielding. They demonstrated that shear yielding is more sensitive to a change in test conditions than crazing. The transition can also be promoted by changing the stress state, e.g. PS and other brittle materials, which deform by crazing in a tensile test, show shear banding under compression. Craze can form only under tensile conditions because crazing is a dilatation process. It is now generally accepted that crazes form more easily under a high triaxial stress [Donald 1997]. The same material that unnotched can deform by shear yielding, if notched can form crazes.

Figure 2.2.10 shows a failure envelope for PMMA under biaxial stress from Sternstein and Ongchin [1969]. Under biaxial tension (first quadrant) crazing is the predominant deformation mechanism, while under biaxial compression (third quadrant) only shear yielding is allowed.

Crazing and shear yielding are simultaneously possible if the stress is below the fracture stress and $\sigma_1 > 0$ and $\sigma_2 < 0$ or $\sigma_1 < 0$ and $\sigma_2 > 0$ (second and fourth quadrant). The intersections of the yielding and crazing envelopes determine the ductile to brittle transition. Increasing temperature or decreasing strain rate can also change the fracture from brittle to ductile.

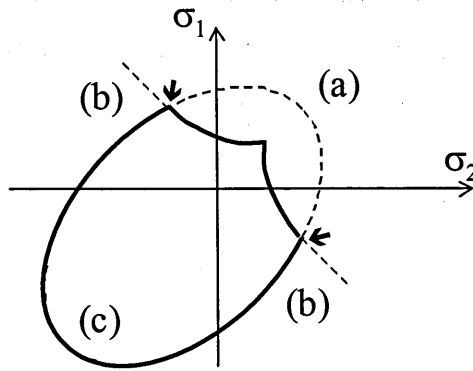


Fig. 2.2.10 Schematic representation of failure envelope for PMMA under biaxial stress. The deformation process can be (a) only crazing, (b) crazing and shear yielding at the same time, (c) only shear yielding.

Bucknall et al. [1972] also observed shear bands forming simultaneously and interacting with crazes, from kinetic studies based on time-dependent volume changes on different blends (e.g. PVC blended with ABS). They suggested that shear bands could terminate crazes by acting as barriers to craze expansion or propagating from the tip of a growing craze.

2.3. Fracture

Polymers undergo fracture in many different ways depending upon their structure and the conditions of testing. Some glassy polymers (e.g. PMMA) tend to be rather brittle and break at relatively low strains with very little plastic deformation, whereas semi-crystalline polymers are generally more ductile. However, the majority of polymers are brittle under certain conditions and ductile when these conditions change (e.g. by increasing the temperature). For example, PMMA at low temperatures fails mainly in a brittle manner, and the specimen breaks when its maximum load (σ_M) is reached, generally at a low strain. Above room temperature, it gets more ductile with increased yielding. In this case the yield point is usually lower than σ_M and the specimen fails at high strain (brittle-ductile transition) [Ward 1983]. Fracture in polymers is also influenced by strain rate. For example, nylon at room temperature fails in an increasing ductile manner when strain-rate decreases [Young and Lovell 1991].

The brittle-ductile transition temperature (T_b) and the yield stress (σ_y) are sensitive to the structure of the material. T_b increases with increasing crosslinking or crystallinity, while it decreases with the addition of plasticizers to the polymer. The brittle-ductile transition is also sensitive to the presence of defects (scratches, cracks or notches increase T_b) so that a notched sample can fail in a brittle manner at a temperature at which it would otherwise be ductile. Moreover when rubber is blended with a glassy matrix the T_b of the blend is generally lower than that of the unmodified matrix and stress whitening usually becomes visible over the entire fracture surface and not just ahead of the notch, as in the case of brittle fracture. It is believed that one cause of stress whitening is cavitation of the rubber phase [Ramsteiner and Heckmann 1985] and that T_b decreases with increasing rubber content.

The fracture of brittle polymers can be explained by the Griffith theory [1920]. Griffith first assumed that the presence of defects is the reason why the strength of materials is less than what one would expect on the basis of theoretical predictions of the cohesive forces between atoms or molecules. The defects act as stress concentrators to initiate crack growth. This concept is the basis of fracture mechanics. There are two different parameters that characterise fracture mechanics.

One principle, which originated from Griffith, is a thermodynamic fracture criterion that is valid for elastic materials. A stable crack in a specimen held in tension ($\varepsilon = \text{constant}$) grows only if the stored strain energy released during growth is higher than the crack surface energy (i.e. the energy required to create two new fracture surfaces U_f). In the rare case of pure brittle fracture, i.e. when no plastic deformation takes place, only the energy U_s necessary to overcome atomic and molecular cohesion forces during crack propagation is considered, whereas, in most materials, fracture is accompanied by plastic deformation and its contribution (U_p) must be taken into account. The crack propagates when the strain energy release rate G exceeds a critical value G_c (also called fracture energy), that is the sum of U_s and U_p [Williams 1984]. G_c is an intrinsic material property that should be valid for different specimen geometries and crack forms.

The second parameter permits the crack to grow only if the stress intensity around the crack tip goes beyond a critical value (K_c). The stress distribution in the vicinity of the crack tip is characterised by the stress intensity factor K . For a plate with a sharp crack of length a and a stress (σ_n) applied normal to the crack plane:

$$K = Y \sigma \sqrt{a} \quad (2.22)$$

Y is a numerical factor which depends on the ratio of the crack length a to the width W of the specimen. For example, for a short, through-thickness crack in the centre of a large uniaxially stressed plate, $Y = \sqrt{\pi}$. Since many Y factors have been tabulated, K_c can be measured from the fracture stress in one geometry and used to predict the fracture in another. The stress-intensity factor, K , thus represents a single parameter that includes both the effect of the stress applied to a sample and the effect of a crack of given size in a sample. K_c is the critical stress intensity factor for the onset of crack growth. It is a material property independent of specimen size and geometry, also called fracture toughness since it characterises the resistance of a material to crack propagation.

The two critical fracture parameters are related for linear elastic materials by the Young's modulus E and the Poisson's ratio ν , as follows:

$$K_c^2 = E G_c \quad \text{in plane stress} \quad (2.23)$$

$$K_c^2 = \frac{E G_c}{1 - \nu^2} \quad \text{in plane strain} \quad (2.24)$$

For polymers, E depends upon the rate of testing and it may not be easy to determine the strain-rate for the fracture. This involves measurements of dC/da , the variation of specimen compliance C with crack length, where C is defined as the ratio of the displacement of the ends of the specimen to the applied load.

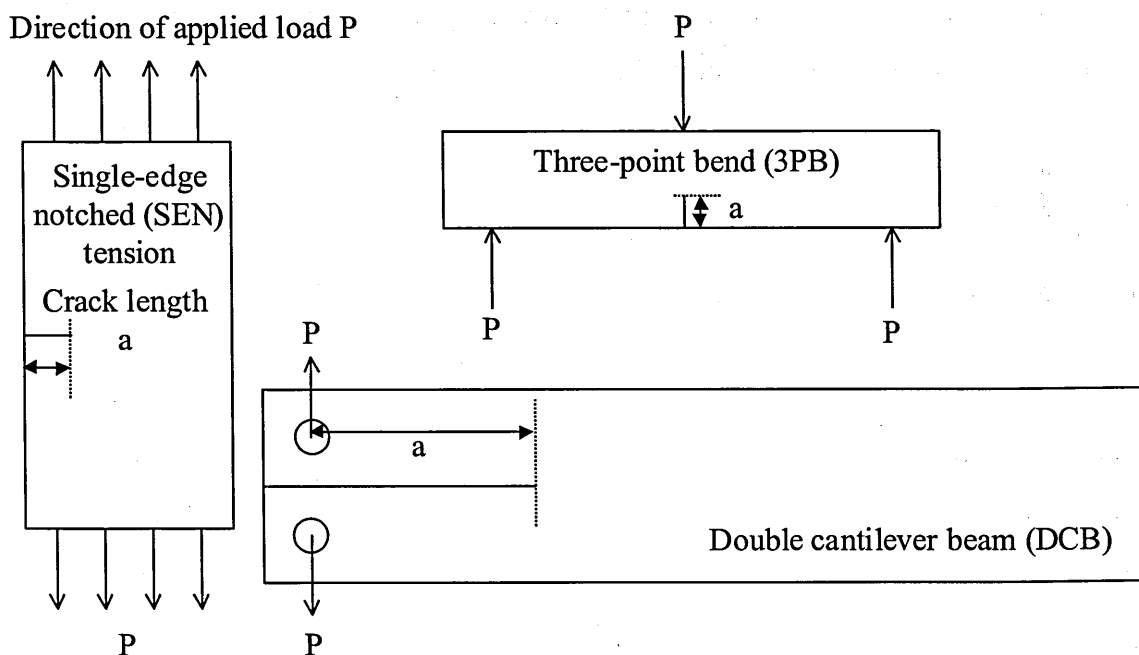


Fig 2.3.1 Various types of fracture mechanics specimen.

Figure 2.3.1 illustrates some common fracture test specimens, where the sizes, shapes and loading geometries are very different, but linear-elastic stress analysis revealed a big similarity. The stress-concentration effect of a sharp crack is so dominant that near the crack tip the stress distributions are almost identical in every case. The tensile stress σ across the crack line at a small distance r ahead of the tip increases with $\frac{1}{\sqrt{r}}$

($\sigma = 2\sigma_n \sqrt{\frac{a}{r}}$) to infinity as the tip is approached [Timoshenko and Goodier 1951], but the product $\sigma\sqrt{r}$ remains constant. Therefore K , which is proportional to $\sigma\sqrt{r}$, completely describes the magnitude of stresses which act to open the crack.

Both the thermodynamic and stress-field criteria provide a good quantitative correlation of the fracture behaviour of brittle polymers such as PS and PMMA, but these approaches are valid for linear-elastic materials only, where the region of plastic deformation around a crack is small compared to the size of the crack. The plastic zone at the crack tip where the energy is dissipated is also called the process zone. For a material that obeys the simple von Mises criterion, the process zone size can be

estimated from Irwin's equations [1958] as the radius r_p at which the crack tip stress field, determined by K , initiates yield:

$$r_p = \frac{K_c^2}{2\pi\sigma_Y^2} \quad \text{in plane stress} \quad (2.25)$$

$$r_p = \frac{K_c^2}{6\pi\sigma_Y^2} \quad \text{in plane strain} \quad (2.26)$$

The bigger the process zone is, the tougher is the material. However linear-elastic fracture-mechanics (LEFM) remains valid only if r_p is smaller than any dimension of the specimen. It is recommended [Williams 1990] for fracture toughness testing that both thickness B of the specimen and the crack length a exceed the following value:

$$B, a > 2.5 \frac{K_c^2}{\sigma_Y^2} \quad (2.27)$$

From equations (2.25) and (2.26) it can be seen that plane strain conditions reduce the extent of yielding at the crack tip. In fact when all three principal stresses are tensile the shear stresses generated are lower. Since plastic flow in plane strain is more limited than in plane stress, fracture toughened values in plane strain will be low. Large enough specimen dimensions relative to the plastic zone can ensure plane strain conditions around the crack tip. Polymers may raise special problems corresponding to the assumptions made in the stress analysis: i.e. small strains, linear behaviour and time-dependent modulus. Recently, the development of new methods has extended the use of fracture mechanics to elastic-plastic conditions which are associated with lower strength materials, smaller section sizes and lower load ratings. When the size of the plastic zone exceeds the limit for a linear stress-strain behaviour others methods, e.g. J-integral [Crouch 1993], R-curve, essential work of fracture [Clutton 1994] can be employed to investigate fracture. A study of toughened plastics test techniques has been reviewed by Williams [1984, 1990, and 1997], Crouch [1993], Clutton [1994], Hale [1995] and Pavan [1996]. They discussed and developed the application of elastic fracture mechanics, 'J' testing and essential work test methods.

The J integral represents the energy available for crack propagation and it can be seen as a measure of the difference in potential energy between two identical samples which undergo the same loading conditions, but have different crack lengths. Therefore, if the material behaves in a linear-elastic manner the parameter J coincides with G . The protocol for the J integral procedure prescribes that many specimens with identical crack lengths are loaded to different displacements to obtain several amounts of crack growth Δ_a , where J represents the area under the load-displacement curve. By plotting J versus Δ_a the resistance curve, also called the R curve, is obtained and the value of J at crack initiation (J_c) corresponds to the intersection of the R curve with the line ($J_{0.2}=2\sigma_Y \Delta_a$) with $\Delta_a = 0.2$ [McCrum 1997].

An alternative procedure to the J integral for ductile materials consists of measuring the total essential work of fracture, W_f . W_f can be considered as the sum of the essential work of fracture (W_e) carried out in the region where the fracture takes place and the non-essential work of fracture (W_p) done where plastic deformation occurs, such that:

$$W_f = W_e + W_p = w_e l t + w_p \beta l^2 t \quad (2.28)$$

Where l is the ligament length, t the specimen thickness and β a shape factor related to the form of the plastic zone. w_e is defined as the work required for the creation of unit area and is therefore proportional to the fracture surface, w_p depends on the shape and the volume of the plastic zone surrounding the fracture surface.

CHAPTER 3

RUBBER PARTICLE CAVITATION MODEL

3.1. Introduction

The mechanisms of rubber toughening in glassy polymers have been under active investigation for many years [Schmitt and Keskkula 1960, Bucknall and Smith 1965]. They have been the subject of much controversy in the literature and are still not completely understood.

Observations made by different authors on HIPS, ABS [Schmitt and Keskkula 1960, Bucknall and Clayton 1972, Bubeck et al. 1991], rubber-toughened (RT) nylons [Dijkstra 1994, Lazzeri 1991], RT-PMMA [Lovell et al. 1991] and RT-epoxy [Yee and Pearson 1986, Sue 1991] have emphasised the role of rubber particles either as initiators or as accelerators of matrix deformation mechanisms. Newmann and Strella [1965] also believed that the main energy-absorbing component of a rubber-toughened plastic was yielding in the matrix. It is now generally accepted that rubber particles are able to initiate or accelerate matrix deformation once they have cavitated. Cavitation promotes matrix plasticity, so that the fracture resistance of the rubber modified material increases [Bucknall 2000]. Rubber particle cavitation is important in particular in the crack tip region where the stress field is triaxial. Parker et al. [1990] observed in toughened polycarbonate blends that deformation in front of a crack tip occurs initially by rubber particle cavitation and then by enhanced shear yielding. The formation of voids in the rubber phase makes the particle less resistant to deformation. This promotes dilatational shear yielding or multiple crazing or both in the surrounding matrix at reduced stresses. Bubeck et al. [1991] detected by 'real-time SAXS' (small-angle X-ray scattering) studies, in HIPS and other toughened thermoplastics, that part of the observed dilatation was due to a process that came before crazing deformation. This non-crazing dilatation process was attributed to rubber cavitation.

Evidence of multiple voids and fibrillation of the rubber phase has been widely observed by various researchers [Bucknall 2000]. In the case of fibrillation of the rubber

within the particle, the system undergoes a significant degree of strain hardening [O'Connor et al. 1997, Bucknall 2000]. Strain softening followed by strain hardening is fundamental to increased toughness. Rubber cavitation before yielding has been considered very probable when high triaxial states of tensile stress are achieved inside a particle. For this situation mechanical stresses and/or thermal stresses could be both responsible. While thermal stresses do not produce damage in the matrix, mechanical loading could add yielding and crazing to the cavitation process. On cooling the particle, the rubber will tend to contract. However, being well bonded to the matrix, the particle is partially prevented from contracting and becomes subjected to a dilatant stress. The opening of a cavity is then likely, since it produces a local decrease in the hydrostatic component of the stress [Lazzeri and Bucknall 1995].

There are different types of cavitation depending on the particle morphology. The fracture surface of a simple system consisting of spherical rubber particles in an epoxy resin matrix, when examined in the scanning electron microscope, shows single holes in the rubber, Figure 3.1.1a [Kinloch 1997]. Cavitation in a high-impact polystyrene (HIPS) containing 'salami' rubber particles with hard polystyrene sub-inclusions embedded in a continuous matrix of cross-linked rubber, results in a craze-like morphology. The rubber fibrils extend between sub-inclusions and between sub-inclusions and matrix, as shown in Figure 3.1.1b [Bucknall 2000]. Rubber fibrillation is also possible in three stage particles with a rigid core, a rubbery inner shell and a thin outer shell strongly grafted to the rigid matrix, Figure 3.1.1c. The rubber fibrils form bridges between the rigid core and outer shell of matrix so that they can stretch and the rubber particles expand until strain hardening stabilises the voids.

Cavitation is now well known to be possible even under simple cooling if the magnitude of the thermal contraction stress is high enough to allow the nucleation of voids [Humme et al. 1976, Morbitzer et al. 1982]. Thermal contraction and expansion tests [Bucknall et al. 2000a] show that the elastic stresses generated during cooling can be sufficient to initiate voids in the rubber particles. Void formation is generally observed when the elastic tensile strain in the matrix or the linear thermal contraction in the rubber is between 0.4% to 1.0%, which means that the volume strain within the rubber

phase is probably in the range 1% and 3% [Lazzeri and Bucknall 1993]. The critical volume strain needed for cavitation is very small ($<1\%$) [Bucknall 1997], so that neither large strains nor yielding are necessary before cavitation.

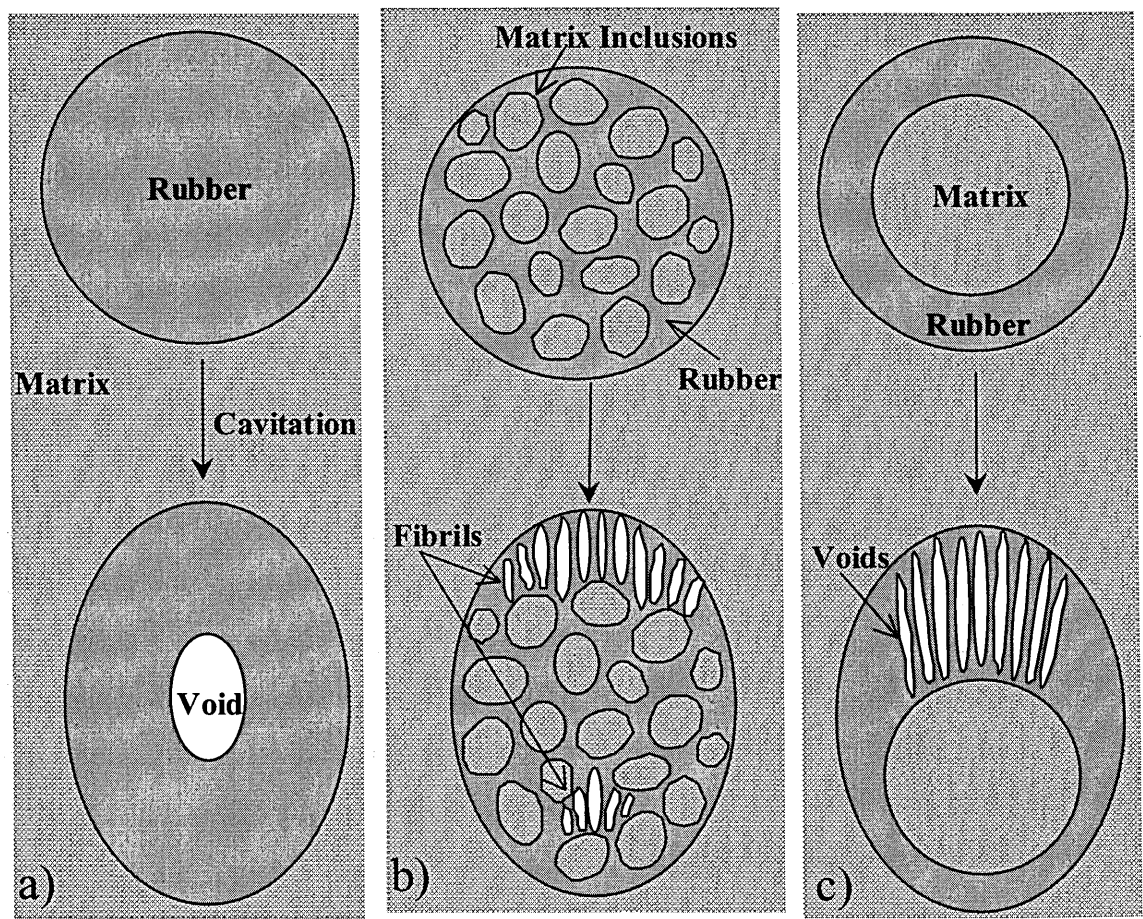


Fig.3.1.1 Illustrative representation before and after cavitation of: a) a spherical rubber particle in a continuous glassy matrix; b) a ‘salami’ rubber particle; c) a core-shell HSH (hard-soft-hard) rubber particle.

However, cavitation of the rubber particles appears to promote conditions that release energy-absorbing mechanisms in the matrix and improve toughening. Under certain conditions, yielding of the matrix may occur even in the absence of cavitation [Cheng et al. 1992, Lazzeri and Giuliani 1997]. In any case, a quantitative understanding of the cavitation process is fundamental to explaining mechanisms of deformation and fracture of rubber modified plastics, including toughened versions of epoxy resins, polyamides and other craze-resistant polymers.

3.2. Background of the Model

As noted above, several authors have observed cavitation within the rubber particles of toughened polymers and some have pointed out that voids begin at an early stage in the deformation process. For this reason a quantitative model of cavitation and its effects on yielding and formation of dilatational bands has been developed by Bucknall and co-workers [Lazzeri and Bucknall 1993, Lazzeri and Bucknall 1995, Bucknall et al. 1994, Ayre 1999].

a) Cavitation in metals and polymers

In the past, dilatation bands have been observed mainly in metals, especially at crack tips, and a relevant theory has been developed by Gurson and others [Gurson 1977, Thomason 1991] for a porous ductile metal. This theory adopts a continuum approach to materials undergoing plastic deformation accompanied by void formation. The Gurson model analyses plastic flow in a porous medium by assuming that the material behaves like a homogeneous continuum. Therefore, the effect of the voids is averaged throughout the volume. The main difference between the Gurson model and classical plasticity is that in Gurson's analysis the yield surface exhibits a strong hydrostatic stress dependence, while classical plasticity assumes that the yielding is independent of hydrostatic stress. A strain softening term is introduced [Anderson 1995]. Although there are many similarities between ductile metals and polymers, there are also important differences. Cavitation in metals generally originates from defects or hard inclusions and voids grow as a result of plastic deformation of the metallic matrix. In toughened plastics, cavitation originates within the rubber phase and the mechanism responsible for cavitation is essentially elastic [Lazzeri and Bucknall 1995]. Whereas cavitation in metals often causes a reduction in ductility because the voids coalesce even at low strains, cavitation in polymers produces a hardening and strengthening orientation allowing energy absorption. The Gurson model has been adapted by Lazzeri and Bucknall [1993] to take into account the effects of mean stress on cavitation, yielding and deformation behaviour of polymer containing pre-existing voids.

b) Rubber-like materials

Matrix-rubber interactions complicate the analysis of rubber particle cavitation in toughened plastics. Several authors have treated the problem of cavitation in rubber-like materials, considering a simpler system, for example bulk rubber, and providing a first development in the analysis of cavitation. Gent and co-workers [Gent and Lindley 1959, Gent and Tompkins 1969] analysed the phenomenon of failure in bulk samples of rubber, and carried out experiments on a rubber cylinder subjected to tensile loading. They assumed that void formation in the bulk samples takes place as the result of elastic expansion of precursor cavities. Therefore, a critical load for failure was related directly to the elastic modulus of the rubber. These pre-existing defects were considered as spherical cavities with a diameter between 0.5 μm and 1 mm, expanding to an indefinitely large size under increasing negative pressure. Gent and Wang [1991] proposed an energy criterion to determine the critical internal pressure required to grow a void. They found a strong dependence of this pressure upon the initial size of the void. This pressure is higher for smaller precursor void sizes, and the analysis was not valid for voids smaller than 1 μm in diameter. In rubber-modified systems, the rubber particles often have diameters well below 1 μm , therefore analyses based on pre-existing defects bigger than 1 μm in the rubber are unrealistic.

Other authors [Horgan and Pence 1989] described models where non-linear elasticity, i.e. dealing with large strains, has been taken into account. In 1969, Gent and Tompkins considered rubber materials with pre-existing cavities and, in addition to a non-linear elastic bulk energy, they introduced a surface energy term.

3.3. Cavitation model overview

The first quantitative model for rubber particle cavitation including a surface energy term was introduced by Lazzeri and Bucknall [1993] and then developed by Bucknall et al. [1994], Ayre [1999], Bucknall et al. [2000a]. The model is essentially an extension of the work of Gent and Wang, who analysed the criteria for void growth in a macroscopic block of rubber containing pre-existing voids, as described above. Instead of assuming the presence of large voids, the Lazzeri and Bucknall model identifies the

nuclei for cavitation with the small voids that constitute the free volume of the rubber. The model assumes also that the voids form within an elastomeric continuum. Recent studies of cavitation induced by cooling below 0°C have provided experimental evidence to support this proposal [Bucknall and al. 2000a]. Positron annihilation lifetime spectroscopy (PALS) shows that the free volume in polybutadiene at 23°C is made up of voids with diameters in the range of 0.5 to 0.8 nm [Bartoš et al. 1997].

In the model, an energy balance approach based on thermodynamic principles is employed to describe the cavitation phenomenon. Provided that there is a minimum energy $U_r < U_0$, where U_0 is the initial energy of the intact particle, the resulting void is thermodynamically stable; this is a necessary condition for cavitation. In its simplest form, the model considers the rubber particle as an isolated system so that the internal energy of the cavitated particle must be lower than the energy of the intact particle, to allow void formation. When the void expands within the rubber particle, the energy stored in the particle is released. The elastic energy stored in an isotropic rigid material consists of a shear energy component and a dilatational one. In the model, only the dilatational strain energy is considered; the strain component responsible for changing the volume but not the shape of the material. In fact the model considers the surface of the rubber particle as being fixed while the hole expands, so that the volume occupied by the rubber decreases and the volume strain energy is released. While the hydrostatic stress in the rubber is positive, the more the hole grows, the bigger is the amount of energy released through relaxation of volume strain in the rubber phase. This energy is then required to form a new void surface of area $4\pi r^2$ and to stretch the rubber surrounding the void.

The initial energy condition, with no void formation, was expressed as:

$$U_0 = \frac{4}{3} \pi R^3 W = \frac{2}{3} \pi R^3 K_p \Delta_v^2 \quad (3.1)$$

W is the stored volumetric strain energy density: $W = \frac{\sigma_m \Delta_v}{2} = \frac{K_p \Delta_v^2}{2}$. K_p denotes the bulk modulus of the rubber particle and Δ_v is the volume strain ($\frac{\Delta V}{V}$), which is proportional to the mean stress σ_m (the average of the three principal stresses). The model considers the rubber particle as spherical in shape (Figure 3.3.1) with an initial radius R_0 that increases to R when the particle is subjected to the volume strain Δ_v and is then held constant during the formation of a spherical void of radius r , so that no energy is exchanged between particle and matrix as the void expands. Furthermore, it is assumed that the formation of the hole is an instantaneous process, with the hydrostatic tension on the particle as the driving force for cavitation.

The total energy of a particle with a single void formed at its centre is given by:

$$U_r = \frac{2}{3} \pi K_p R^3 \left(\Delta_v - \left(\frac{r}{R} \right)^3 \right)^2 + 4 \pi r^2 \Gamma + 2 \pi r^3 G_r F(\lambda_f) \quad (3.2)$$

$$U_r = U_{volume} + U_{surface} + U_{stretch}$$

where Γ is the surface tension of the rubber, and G_r is the rubber's shear modulus, and $F(\lambda_f)$ is a function of the rubber extension ratio λ_f at failure, $F(\lambda_f)$ is taken as 1.0 [Lazzeri and Bucknall 1993]. It can be seen that the total energy of the rubber particle (U_r) is determined by three terms:

- U_{volume} volumetric strain energy of the rubber phase
- $U_{surface}$ surface energy of the cavity
- $U_{stretch}$ shear strain energy term that represents the energy to stretch the rubber biaxially around the hole up to failure plus the energy to tear the rubber around the hole as it is formed. This term explains the importance of cross-linking in the rubber phase in determining toughness.

Each of these energy terms is shown separately in Figure 3.3.2, in which the normalised energy of the particle U/U_0 is plotted against void size for a homogeneous rubber particle of radius $R = 0.1 \mu\text{m}$. The values for the properties of the rubber and the matrix

are representative of a rubber-toughened PMMA at 23°C and are listed in Table 3.3.1 [Brandrup and Immergut, 1989]. The initial applied volume strain Δ_v is taken as 0.5%.

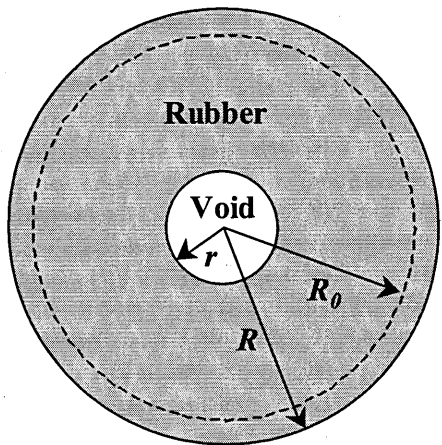


Fig. 3.3.1 Schematic representation of a simple homogeneous spherical rubber particle used in developing the cavitation model.

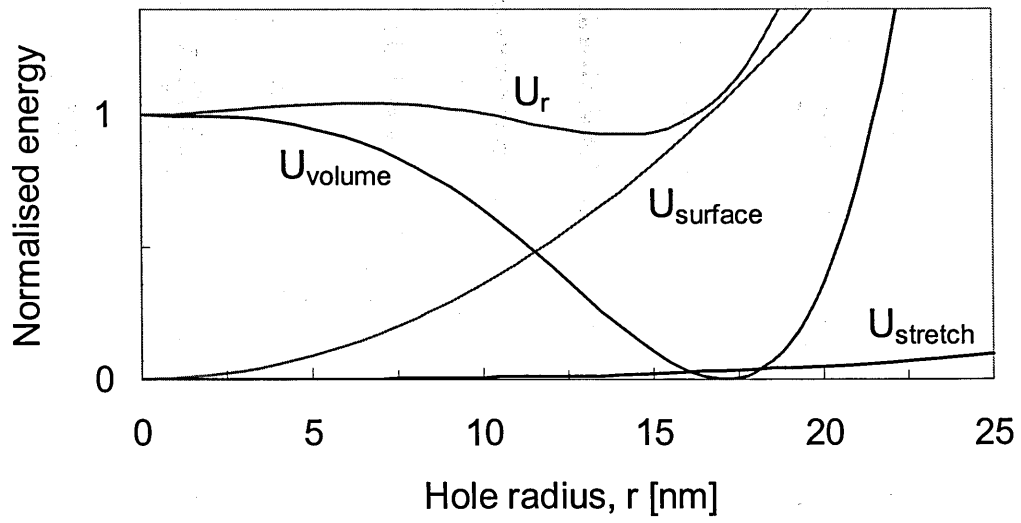


Fig. 3.3.2 Relationship between normalised volume energy, normalised surface energy, normalised stretch energy and normalised total energy versus void size in a rubber particle, calculated using equation (3.2) and data given in Table 3.3.1.

As the radius r of the cavity increases, the volume strain in the rubber phase gradually decreases to reach zero when the density of the rubber achieves its equilibrium. After equilibrium, the more the void grows the more the strain energy increases. The rubber,

constrained by a fixed outer radius R , undergoes compressive strain when the void increases. Since the surface energy term ($U_{surface}$) always increases as the void expands, as does the stretching energy term ($U_{stretch}$), the minimum of the total energy (U_r) of the rubber particle is not zero. In this case, the rubber particle at equilibrium keeps an energy due to the contributions of the surface and the stretching energy terms.

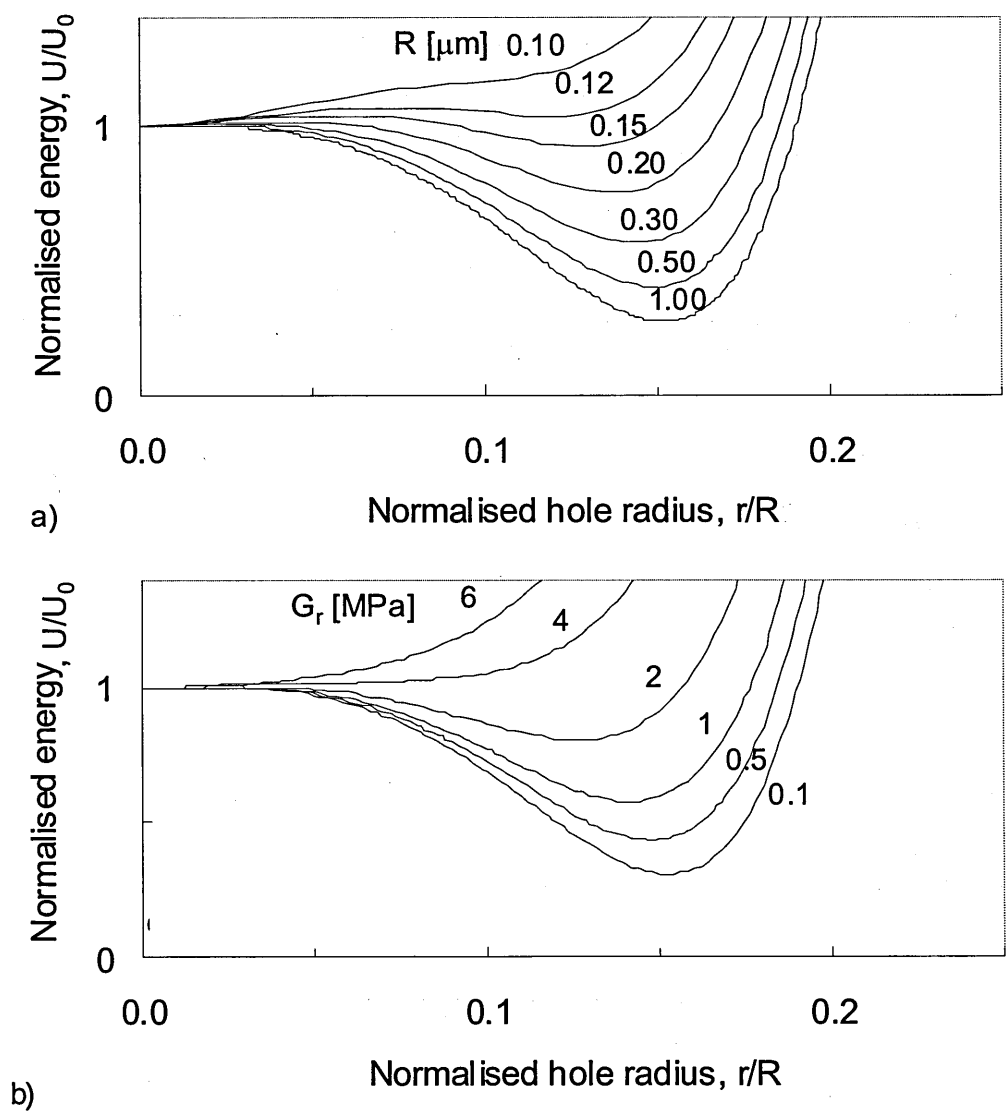


Fig. 3.3.3 Relationship between normalised total energy and void size, calculated using equation (3.2), and data given in Table 3.3.1, a) for a range of particle sizes R [from 0.1 to 1.0 μm] and b) for a range of rubber shear moduli G_r [from 0.1 to 6 MPa].

Numerous factors influence the energy balance e.g. rubber particle size, rubber shear modulus and rubber surface energy. At a specified volume strain, there is a critical

particle size, below which cavitation cannot occur, so that the largest particles will cavitate first, as shown in Figure 3.3.3a. The rubber will become more difficult to cavitate if the rubber shear modulus (G_r) increases, as shown in Figure 3.3.3b. The increase in G_r could be due to cross-linking, or to cooling into the temperature zone of the rubber-glass transition temperature.

A combination of the cavitation model with the shear yielding model developed by Lazzeri and Bucknall [1993] is reviewed in the cavitation diagram, Figure 3.3.4. The diagram describes the interaction between cavitation, shear yielding and fracture. The effects of materials characteristics (particle size, morphology, rubber content, particle-matrix adhesion) and test conditions (strain rate, temperature and specimen geometry) on the deformation behaviour are summarised by the cavitation diagram. The dilatation yield criterion given by Lazzeri and Bucknall [1993] is a combination of the modified von Mises equation for a solid material with the modified Gurson equation for a ductile material containing a volume fraction f of voids:

$$\sigma_e = \sigma_0 \sqrt{\left(1 - \frac{\mu \sigma_m}{\sigma_0}\right)^2 - 2f \cosh\left(\frac{3\sigma_m}{2\sigma_0}\right) + f^2} \quad (3.3)$$

where σ_e and σ_m are the von Mises equivalent stress and the mean stress respectively; μ is a materials constant and σ_0 represents the yield stress under pure shear conditions ($\sigma_m = 0$).

For a RT-PMMA containing 40% by volume of rubber particles for the case $f = 0$ the yield envelope defines an upper-bound curve. Above the upper-bound curve shear yielding occurs even when there is no cavitation. The yielding envelope for $f = 0.4$ defines a lower-bound curve, below which no yielding occurs, and the material behaves elastically. The dotted lines in the diagram indicate the stress state; uniaxial ($\sigma, 0, 0$), equi-biaxial ($\sigma, \sigma, 0$) and triaxial ($\sigma, \sigma, 2\nu\sigma$). The triaxial state of stress represents stresses acting on the crack plane in the plane-strain zone of a crack tip, where cavitation has a strong effect on yielding. The diagram also indicates the effect of particle size. Larger particles will need only a low mean stress to cavitate within the

elastic region under uniaxial, biaxial or triaxial states of stress. For smaller particles, a higher mean stress is necessary to cavitate. More details on the cavitation diagram are given in Appendix A.

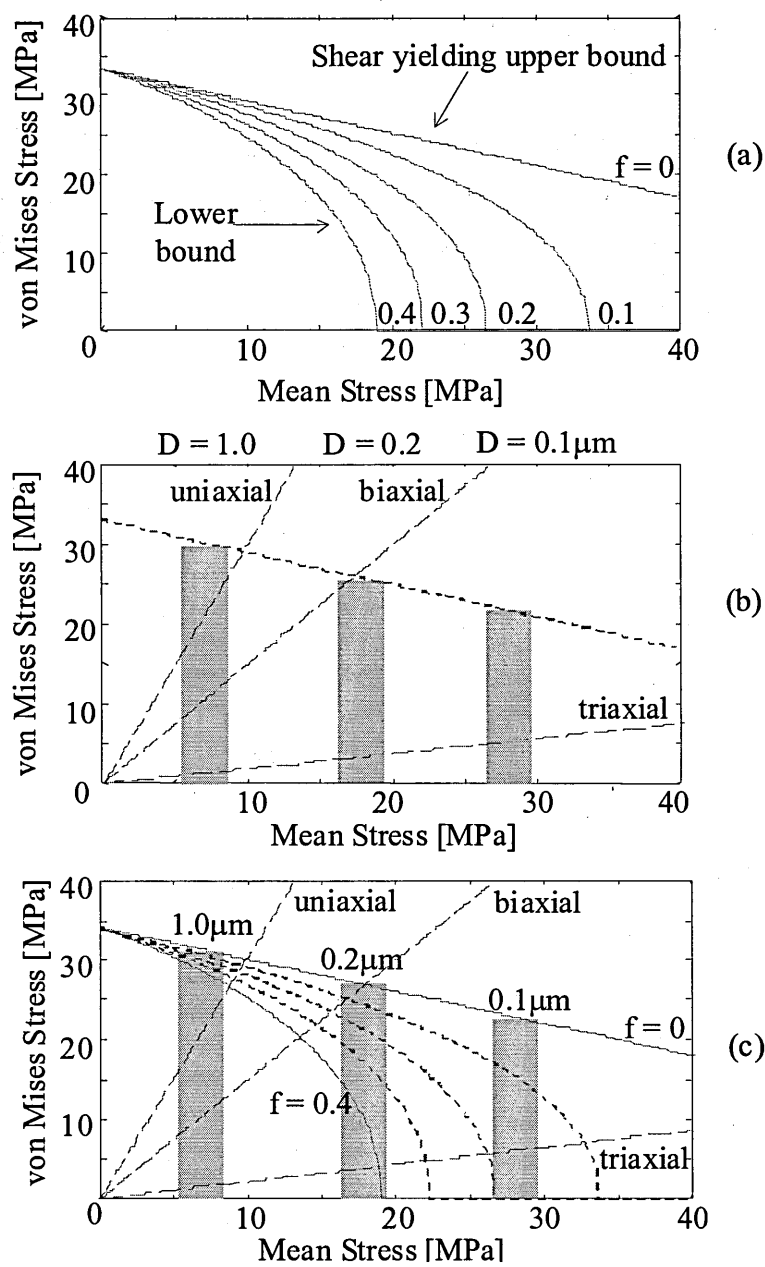


Fig. 3.3.4 Schematic cavitation diagram for a RT-PMMA with 40 vol. % of rubber particles: a) yield envelopes at various volume fractions of cavitated rubber particles; b) uniaxial, biaxial and triaxial state of stress and shifts in the mean stress at cavitation upon reduction of the rubber particle sizes (D in μm); c) combination of a) and b).

To establish the cavitation model expressed by equation (3.2) numerous simplifying assumptions were made. Several authors developed the model in its general form by considering new energy terms. Bucknall et al. [1994] introduced an additional term for the work done by the matrix as the void expanded. This term derives from elastic interactions between the particle and the surrounding matrix, so that when the void expands some of the volumetric strain energy stored in the matrix is released to the particle. The rubber-toughened polymer was treated as a set of concentric spherical elements in a rubber particle of radius R surrounded by a concentric matrix shell of radius Q , as illustrated in Figure 3.3.5. The two phases were assumed to be homogeneous, isotropic and well bonded to each other.

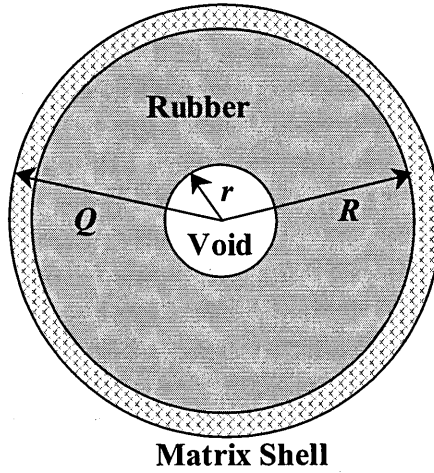


Fig. 3.3.5 Schematic representation of a spherical rubber particle surrounded by a concentric rigid matrix shell.

Calculations were based upon the elastic behaviour of a spherical shell under uniformly distributed internal and external tensile stresses P_R and P_Q acting normally to the surfaces. This standard problem in mechanics was solved using the elastic analysis for small strains ($\leq 1\%$) of Reismann and Pawlik [1980]. The radial displacement $x(q)$ within the matrix at a distance q ($R \leq q \leq Q$) from the centre of the sphere is given by:

$$x(q) = \frac{(P_R R^3 - P_Q Q^3)q}{3K_m(R^3 - Q^3)} + \frac{(P_R - P_Q)R^3 Q^3}{4G_m(R^3 - Q^3)q^2} \quad (3.4)$$

The volume strain in the matrix shell at a radial distance R (at the rubber-matrix interface) is given by:

$$\Delta_{vm} = \frac{3x(R)}{R} = \frac{P_Q - P_R\phi}{K_m(1-\phi)} + \frac{3(P_Q - P_R)}{4G_m(1-\phi)} \quad (3.5)$$

where $\phi = \left(\frac{R}{Q}\right)^3$ is the volume fraction of the rubber particles in the polymer. The volume strain of the rubber particle, acting as a simple sphere under external negative pressure P_R is $\Delta_{vp} = \frac{P_R}{K_p}$.

Another contribution comes from Ayre and Bucknall [1998], who developed the model further by considering the volumetric strain energy deriving from differential thermal contraction and not only from mechanical loading contributions. For example, if the specimens are cooled rapidly from the melt (i.e. during injection moulding) internal stresses appear because of different cooling rates between core and skin. Also, differences in the volumetric coefficient of thermal expansion between the matrix, β_m , generally a glassy polymer, and the rubber particle, β_p , generate thermal stresses in the material at any temperature (T) below the glass transition temperature of the matrix (T_{gm}). This produces a strain mismatch given by $\Delta_v(\beta_m - \beta_p)$, where $\Delta_v = T - T_{gm}$. Since the matrix and the particle are well bonded, the thermal volume strain mismatch is given by:

$$\Delta T(\beta_m - \beta_p) = \Delta_{vp} - \Delta_{vm} \quad (3.6)$$

Substituting the expression for Δ_{vm} (3.5) and Δ_{vp} into equation (3.6), it is clear how the internal stress acting on the rubber particle, P_R , depends upon mechanical loading (P_Q) and differential thermal contraction (ΔT):

$$\Delta T(\beta_m - \beta_p) = P_R \left(\frac{1}{K_p} + \frac{4G_m\phi + 3K_m}{4G_mK_m(1-\phi)} \right) - P_Q \left(\frac{4G_m + 3K_m}{4G_mK_m(1-\phi)} \right) \quad (3.7)$$

Ayre and Bucknall [1998] also applied the model to a modified system, closer to reality in the case of RT-PMMA: a core-shell rubber particle, with rubbery shell that encloses a rigid glassy core. In this case the bulk modulus of the particle in equation (3.2) and the coefficient of volumetric expansion in the volume strain formula (3.6) must take into account the rigid core. The problem was solved using the Boyce et al. [1987] analysis based on the Chow [1978] method, as follows:

$$K_p = K_r \left\{ 1 + \frac{\left(\frac{K_c}{K_r} - 1 \right) \phi_c}{1 + \left(\frac{K_c}{K_r} - 1 \right) (1 - \phi_c) \left(\frac{1 + \nu_r}{3(1 - \nu_r)} \right)} \right\} \quad (3.8)$$

which can be simplified to a volume-weighted average:

$$K_p = \frac{K_r K_c}{K_c(1 - \phi_c) + K_r \phi_c} \quad (3.8a)$$

$$\beta_p = \beta_r \left\{ 1 + \frac{\frac{K_c}{K_r} \left(\frac{\beta_c}{\beta_r} - 1 \right) \phi_c}{1 + \left(\frac{K_c}{K_r} - 1 \right) (1 - \phi_c) \left(\frac{1 + \nu_r}{3(1 - \nu_r)} \right) + \phi_c} \right\} \quad (3.9)$$

which simplifies to:

$$\beta_p = \beta_c \phi_c + \beta_r (1 - \phi_c) \quad (3.9a)$$

where the subscripts p , c or r stand for the particle, the rigid core and the rubber shell respectively, and ϕ_c is the volume fraction of the core with respect to the particle. The rubber-toughened polymer was then treated as a four-stage system: concentric spherical

elements of a glassy core of radius C , a rubber shell of outer radius R , a matrix shell of outer radius Q surrounded by an outer shell of rubber-toughened bulk material of radius L (where $L \gg Q$), as illustrated in Fig. 3.3.6.

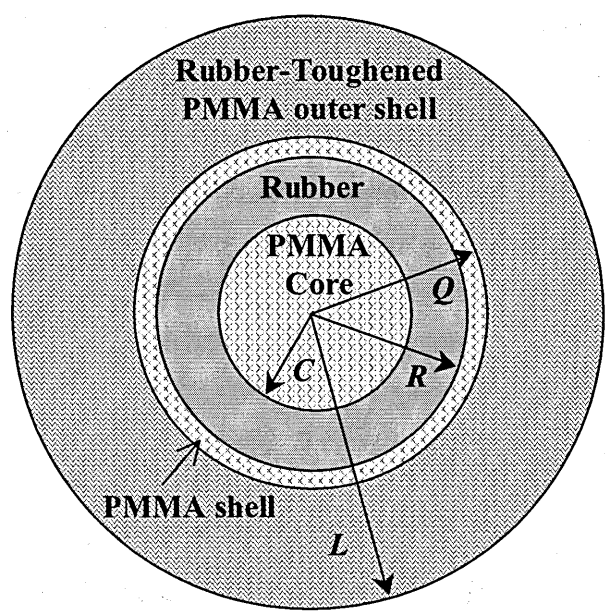


Fig. 3.3.6. Schematic representation of a spherical, core-shell HSH (hard-soft-hard) rubber particle surrounded by a rigid matrix shell and an outer shell of rubber-toughened bulk material.

	PMMA	Pure rubber	Rubber particle	Outer shell of bulk material
Bulk modulus, MPa	$K_m = 4000$	$K_r = 2000$	$K_p = 2600$	$K_L = 3500$
Shear modulus, MPa	$G_m = 1100$	$G_r = 0.1$	$G_p = 0.1$	$G_L = 800$
Radius, μm	$Q = 0.15$	$R = 0.1$	$R = 0.1$	$L \gg Q$
Vol. coefficient. of thermal expansion, K^{-1}	$\beta_m = 2.5 \times 10^{-4}$	$\beta_r = 6 \times 10^{-4}$	$\beta_p = 4.4 \times 10^{-4}$	
Surface energy, J m^{-2}		$\Gamma_r = 0.03$		
Poisson's ratio	$\nu = 0.37$	$\nu_r = 0.499$		
Vol. fraction of core			$\phi_c = 0.4$	

Tab. 3.3.1: Typical property values for the glassy matrix (PMMA) and the rubber (polybutadiene-co-styrene) [Brandrup and Immergut 1989] and calculated properties for the rubber particle and the outer shell composite from equations above.

The properties of the outer shell are an average of the properties of the rubber and the matrix in proportion to the volume fraction of the rubber with respect to the rubber-toughened polymer.

Calculations show that by considering the interactions between the particle and the surrounding system, the energy balance model becomes more representative of experimental conditions. However, in experimental tests, void formation requires larger volume strains than those predicted by the model. The high resistance to cavitation exhibited by rubber toughened polymers has been the driving force for further investigation and development of the model.

3.4. Model developments

There are many explanations for the discrepancy between critical conditions for cavitation predicted by the original model and evidence of cavitation from experimental tests. Many restrictions of the model are here considered and explored.

First of all, the energy-balance model is based upon the thermodynamic criterion that the energy released during void formation must exceed the energy needed to form the void; it does not take into account any kinetic effects. It does not consider the rate at which voids form. The most recent evidence, which has been discussed above, indicates that the condition $U_r < U_0$ for the void to be thermodynamically stable is a necessary, but not a sufficient, condition for cavitation. Bucknall et al. [2000a] looked more closely at the energy-balance model and took into account a small energy barrier to the growth of voids from the size expected in the free volume. The model predicts a maximum in the energy U_r of a cavitated particle that occurs at small values of void size (r). In equation (3.2) at small r the surface energy term in r^2 increases more rapidly than

the volumetric energy term $\left(\Delta_v - \left(\frac{r}{R} \right)^3 \right)^2$ decreases. Because of that, the total

cavitation energy shows a maximum at small void size, Figure 3.4.1. The height of the energy-barrier is determined by the surface-to-volume ratio.

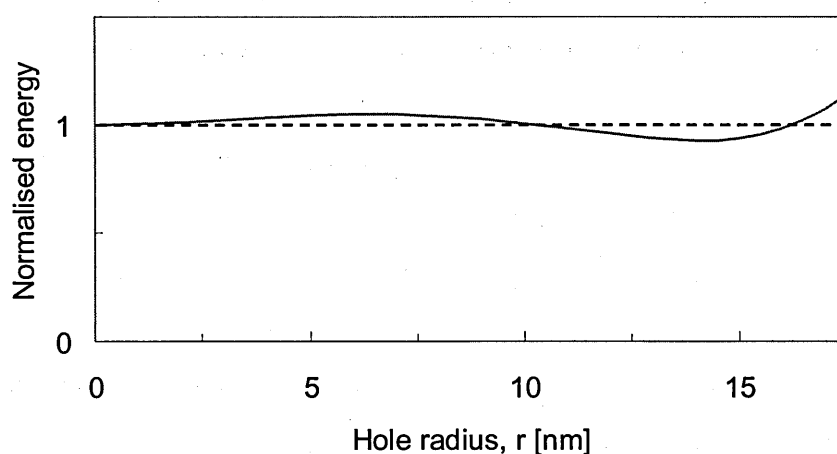


Fig. 3.4.1 Maximum (energy barrier) in the normalised total energy versus void size in a rubber particle, calculated using equation (3.2) and data given in Table 3.3.1.

To allow the void to become large enough to expand without restraint the energy barrier must be crossed. The observed high resistance of rubber particles to cavitation is therefore explained, at least in part, by the kinetics of the voiding process. The height of the energy barrier controls the rate of void formation. A certain amount of thermal and/or mechanical energy is required to overcome the barrier. Equation (3.2) [Bucknall et al. 2000a] shows that the height of the barrier is reduced when the rubber develops dilatational stresses due to differential cooling or/and mechanical loading. When the material is cooled, the rate of void formation increases progressively and cavitation becomes an easier process, as emphasised in many cooling experiments. Data from thermal contraction and expansion tests on ABS [Bucknall et al. 2000a, Bucknall 2000] support the suggestion that kinetic effects control cavitation. A trace of silicone oil (1% by volume) was melt compounded with ABS to promote rubber particle cavitation, because of its low surface energy. In this case the volume-temperature curve on heating was different from the one on cooling, providing the evidence of an energy barrier to overcome both opening and closing of voids.

Another limitation of the model is the assumption of a simple spherical rubber particle, because in many toughened plastics the particles are not plain homogeneous rubber spheres. Ayre [1999] examined the most common morphologies of rubber particles, directing his attention in particular towards differences in their thermal expansion

behaviour. A particle containing many glassy sub-inclusions will experience lower thermal strains than a solid rubber particle. Even the bulk modulus of the particle and hence the volume strain energy will be affected by the presence of sub-inclusions. The equivalent expressions for the thermal expansion coefficient and the bulk modulus of a core-shell rubber particle appear in equations (3.8) and (3.9) above. These formulae could be used for more complex particle morphologies, e.g. ‘salami’ particles. Ayre [1999] concluded that rubber particles containing glassy cores are less susceptible to thermal mismatch. Particles of complex morphology could be used to reduce thermal strains inside the material and so prevent cavitation. On the other hand, the volume strain energy released during cavitation is higher, because of the increased equivalent bulk modulus, so that for a given degree of cooling the material might cavitate more easily. Indeed equation (3.8) can be rewritten as: $K_p = \frac{K_r K_c}{K_c - (K_c - K_p)\phi_c}$, where the difference $(K_c - K_p)$ is positive. If the volume fraction of the core (ϕ_c) increases, the effective bulk modulus of the particle (K_p) increases too. Consequently, if K_p increases, from equation (3.2) the volume strain energy released during cavitation increases, so that the chance of void formation becomes higher.

An important point that will be amply developed below is that multilayer particles, which have rigid cores embedded in the rubber, present evidence of multiple cavitation. Rubber particles with complex morphology, containing one or more rigid sub-inclusions, such as ‘core-shell’, ‘onion-skin’ and ‘salami’ particles are regularly used to toughen commercial plastics [Bucknall 1977]. When rigid inclusions are closely spaced, the expansion of the initial void is restricted, and it is more likely that additional void formation and expansion will occur within the same rubber particle. Multiple cavitation is confirmed by electron microscopy studies, which show that complex rubber particles rarely form single cavities. Typically, they contain many apparently discrete voids, which are often separated by rubber membranes and constrained by the presence of rigid polymer cores or sub-inclusions. In several micrographs of HIPS with ‘salami’ rubber particles, fibrillation has been observed in the rubber phase, where the fibrils are separated by voids or cavities [Soares 1994]. This phenomenon is not addressed by the simple energy balance equation (eqn 3.2), which considers the formation and expansion

of a single void, but this does not correspond to reality in many cases. It is therefore necessary to examine extensions of the model, which could account for the observed behaviour. However, in homogeneous rubber particles, the formation of a second or successive void requires that the specific surface energy Γ_r of the voids should increase rapidly with void size. The effects of a variable Γ_r on multiple void formation are examined below.

3.5. A model for multiple-cavitation

The possibility that several holes can be formed in a first step of the cavitation process instead of one has been analysed by the author of the present thesis in close co-operation with Deseri [Deseri 1999] and Bucknall [1999 and 2000].

A brief analysis of equation (3.2) shows that a single void is always more stable than two voids of the same total volume, since two voids have a larger surface area. However, this conclusion is based on the assumption that the specific surface energy Γ_r of the rubber is independent of void size (Figure 3.5.1): for most calculations, it is assumed that $\Gamma_r = \sim 35 \text{ mJ m}^{-2}$, which is the measured value for polybutadiene. However, if the resistance to void growth (which is determined by Γ_r) could increase rapidly with void size, then the formation of two or more voids per particle might become possible. In the case of multiple-cavitation, the effects of the surface energy term become extremely important, causing the particle to resist expansion much more strongly than is predicted by the energy balance model involving a single void. Therefore, in order to model multiple cavitation the surface energy Γ_r is made an increasing function of void radius r , while the exact form of Γ_r is chosen on the basis of mathematical convenience. Physically, this suggestion is quite realistic, because in a cross-linked rubber it becomes progressively more necessary to break chemical bonds as the cavity expands. This bond rupture effect must be added to the contribution of ordinary van der Waals forces in calculating Γ_r . A similar approach has been adopted by Kramer in discussing the energy needed to form craze fibrils in glassy polymers [Kramer, 1984]. For example, at the scale of 1 nm, there is no need to consider bond rupture, and the surface energy of cross-linked polybutadiene can be compared with that

of the polymer before cross-linking, 35 mJ m^{-2} . When bond rupture is taken into account, the value might rise to 80 mJ m^{-2} .

The following discussion examines the predictions of the energy-balance model, equation (3.2), for the case in which Γ_r increases in a prescribed way with r [Bucknall, 1999, 2000 private communication]. The important requirement is that the function Γ_r should in turn be concave, then convex, then concave as shown in Figure 3.5.1 (i.e. that the gradient of the curve of Γ_r against r should first increase, then decrease, and then increase again). A function is convex when the chord joining any two points on the graph of the function lies above the curve [Ledermann and Vajda, 1985]. In the development of the modified model the mathematical approach has been forced to justify essential physical considerations, as described below.

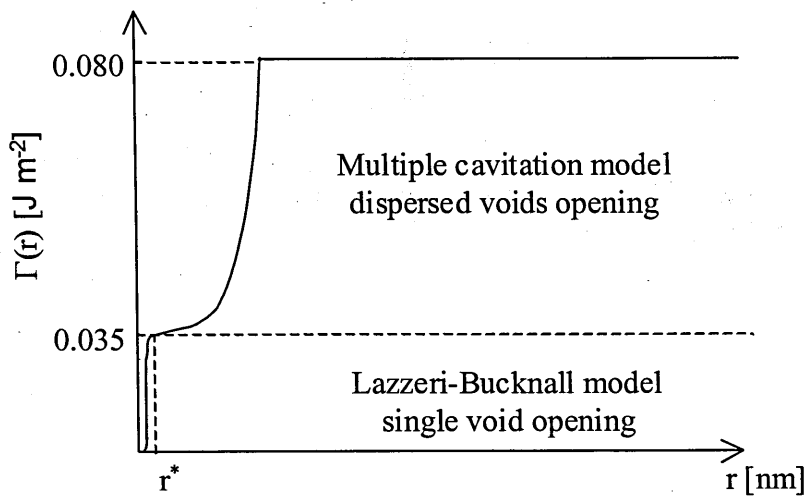


Fig.3.5.1 Illustrative representation of the surface energy term Γ_r , where r^* is the natural radius of a free volume void.

A one-dimensional model for a stretched bar [Del Piero and Truskinovsky 1999], which treated the (Helmholtz) free energy as the sum of a convex term for the bulk and a non-subadditive term for the surface, was proposed to explain the nucleation of a finite number of fractures. A general development of the one-dimensional model for fracture due to Braides and Coscia [1993] was taken into account in Del Piero and Truskinovsky's analysis. The modification of the energy-balance [Lazzeri and Bucknall, 1993] model is in the same spirit of one proposed by Del Piero and Truskinovsky.

3.5.1. Description of model

The model is energetically based and it is an extension of the one proposed by Lazzeri and Bucknall [1993] discussed above. The original Lazzeri-Bucknall model provides a clear and simplified constitutive law suitable for homogeneous particles. An homogeneous particle exhibits just one void (undergoing nucleation and expansion). In the modified model presented here, there is a proposal for developing a simplified model suitable for the description of the observed behaviour of inhomogeneous particles. An inhomogeneous particle, with a complex morphology, might form more than one void (as a result of nucleation, constrained expansion, limitation on growth and nucleation of new voids). Complicated morphologies, where, for example, the void might initially be spherical, but subsequently change to a different shape (*e.g.*, to an oblate spheroid), owing to the proximity of rigid sub-inclusions or of the surrounding matrix, are considered. The fundamental assumption is that once the first void has been formed, it must be prevented from growing further. Even with a variable Γ_r , this condition would not be very realistic for a homogeneous rubber particle. Therefore, an inhomogeneous ‘equivalent’ rubber particle is considered, where the cavities are stabilised to produce the steeply rising surface energy term at a certain void diameter. To take into account a rubber particle with a complicated morphology, a mathematical limitation on void growth is introduced here. To understand whether this model can predict multiple cavitation, attention has been focused mainly on the mathematical aspects of this complicated process.

In considering the assumptions made for the Lazzeri-Bucknall model, a quantity defined as the Helmholtz free energy density U_n^* per unit volume, divided by the bulk modulus of the rubber (i.e. $\frac{U_r}{\frac{4}{3}\pi R^3 K_r}$) is introduced for straightforwardness of calculation. For

n identical spherical cavities, this is taken as the sum of three terms:

$$\text{a) bulk term: } \frac{1}{2}(\Delta_v - n\phi)^2 \quad (3.10)$$

where $\phi = (r/R)^3$, r is the radius of the equivalent void and R the radius of the particle.

$$\text{b) surface term: } \begin{cases} 3n \left(\frac{\Gamma_1}{R K_r} \phi^{\frac{2}{3}} + \frac{\beta}{K_r} \phi^2 \right) & \text{for } 0 \leq \phi \leq \phi_r \\ \Gamma_2 & \text{for } \phi > \phi_r \end{cases} \quad (3.11)$$

where Γ_1 is the specific surface energy required to open the first void, ϕ_r is the maximum volume fraction of voids allowed by the full relaxation of the stress in the rubber phase, Γ_2 is the specific surface energy required to fully relax the stress (i.e. the void expands to the point where the void closure forces are negligible). The Γ_2 threshold is strongly dependent on the morphology of the particle. β is a constitutive parameter governing the growth of the specific surface energy from its minimum value ($\beta = 2(\Gamma_2 - \Gamma_1)/R$). Not all the parameters appearing in (3.11) are independent, and conditions relating β and ϕ to Γ_1 , Γ_2 and R can be established. The complete calculations are discussed in Appendix B.

$$\text{c) stretch term: } \frac{3}{2} n \phi \frac{G_r F(\lambda_f)}{K_r} \quad (3.12)$$

The overall energy density for n cavities is then given by:

$$U_n^* = \frac{1}{2} (\Delta_v - n\phi)^2 + 3n \left(\frac{\Gamma_1}{R K_r} \phi^{\frac{2}{3}} + \frac{\beta}{K_r} \phi^2 \right) + \frac{3}{2} n \phi \frac{G_r F(\lambda_f)}{K_r} \quad \text{or} \quad (3.13)$$

$$U_n^* = \frac{1}{2} (\Delta_v - n\phi)^2 + n \left(\gamma \phi^{\frac{2}{3}} + \bar{\beta} \phi^2 + \xi \phi \right)$$

where $\gamma = \frac{3\Gamma_1}{R K_r}$, $\bar{\beta} = \frac{3\beta}{K_r}$ and $\xi = \frac{3}{2} \frac{G_r F(\lambda_f)}{K_r}$ for simplicity.

This approach will be used to investigate the possibility for the system to allow the nucleation of a new void, when the previous void is already nucleated and stabilised, instead of the expansion of the pre-existing cavities.

If a cavitated configuration with n voids is considered, the criterion for the formation of the next cavity is:

$$\text{Nucleation: } U_{n+1}^* \leq U_n^* \quad (3.14)$$

Where U_n^* and U_{n+1}^* are the values of the energy before and after cavitation respectively. The stable cavitated configuration is achieved when the energy reaches its global minimum. This occurs when the stationary condition of the energy is satisfied at the level of n voids, i.e.

$$\text{Equilibrium: } \frac{dU_n}{d\phi} = 0 \quad (3.15)$$

By taking into account (3.15) and the limit condition (3.14) with $=$ in place of $\leq$, we get expressions for both the critical volume strains at cavitation $\Delta_v^{(n)}$ and the corresponding ϕ :

$$\Delta_v^{(n)} = \xi + [n + 2(1 + 2\bar{\beta})] \left(\frac{2\gamma}{3(1 + 2\bar{\beta})} \right)^{\frac{3}{4}} \quad (3.16)$$

$$\phi = \frac{\Delta_v - \xi}{n + 2(1 + 2\bar{\beta})} \quad (3.17)$$

$$\phi = \left(\frac{2\gamma}{3(1 + 2\bar{\beta})} \right)^{\frac{3}{4}} \quad (3.18)$$

The range of variation in the volumetric coefficient of thermal expansion α_v for rubbers is from $2.1 \cdot 10^{-4}$ to $2.4 \cdot 10^{-4} \text{ } ^\circ\text{C}^{-1}$. For $R = 100 \text{ nm}$, $K_r = 2 \text{ GPa}$, $F(\lambda_f) = 1$, $G_r = 0.4 \text{ MPa}$, $\Gamma_1 = 35 \text{ mJ m}^{-2}$, $\Gamma_2 = 80 \text{ mJ m}^{-2}$, we have $\phi = 2.3 \cdot 10^{-3}$.

To make a full comparison between the experimental results and the predictions of the model there is the need to know the stress versus volume-strain relationship at each stage of cavitation. To do this, the relationship between the mean stress and the volume strain can be deduced by differentiating U_n^* :

$$\sigma_n(\Delta_v) = \frac{U_n^*}{d\Delta_v}$$

$$\frac{U_n^*}{d\Delta_v} = \xi + \frac{2 \left[n\bar{\beta} + 2(1+2\bar{\beta})^2 \right]}{n+2(1+2\bar{\beta})} \hat{\phi}(\Delta_v) + \frac{2}{3} \gamma \frac{n}{n+2(1+2\bar{\beta})} \left(\hat{\phi}(\Delta_v) \right)^{\frac{1}{3}} \quad (3.19)$$

for $n=0,1,2,3$, where $\hat{\phi}(\Delta_v) = \phi = \frac{\Delta_v - \xi}{n+2(1+2\bar{\beta})}$.

The critical stress is given by:

$$\bar{\sigma}_n = \sigma|_{\Delta_v = \Delta_v^{(n)}} = \xi + \frac{n(1+4\bar{\beta}) + 4(1+2\bar{\beta})}{n+2(1+2\bar{\beta})} \left(\frac{2\gamma}{3(1+2\bar{\beta})} \right)^{\frac{3}{4}} \quad (3.20)$$

The stress intervals between two subsequent cavitations can be easily calculated to be:

$$\bar{\sigma}_{n+1} - \bar{\sigma}_n = - \frac{2(1+\bar{\beta})}{(n+1+2(1+2\bar{\beta})) (n+2(1+2\bar{\beta}))} \left(\frac{2\gamma}{3(1+2\bar{\beta})} \right)^{\frac{3}{4}} \quad (3.21)$$

The jump in the stress is negative when the $n+1^{st}$ cavity nucleates, and the difference $\bar{\sigma}_{n+1} - \bar{\sigma}_n$ decreases as n increases; it is bounded from above by $\bar{\sigma}_0 - \bar{\sigma}_1$.

With increasing dilatational volume strain Δ_v , the mean (hydrostatic) stress in the particle rises to a maximum, then falls as the first void is formed. If the specific surface energy Γ_r of the void increases sufficiently rapidly with r , a further increase in Δ_v will

be accompanied by a rise in mean stress within the rubber phase, leading eventually to the formation of a second void. The process will then be repeated as Δ_V increases. In Figure 3.5.2 the behaviour of the overall stress is plotted as a function of the applied volume strain. This corresponds to the function defined by the relation (3.20), and reproduces the expected sawtooth behaviour. Each drop in the stress arises at the corresponding volume strain, and the stress can decrease to zero only if the threshold Γ_2 of the surface energy is achieved.

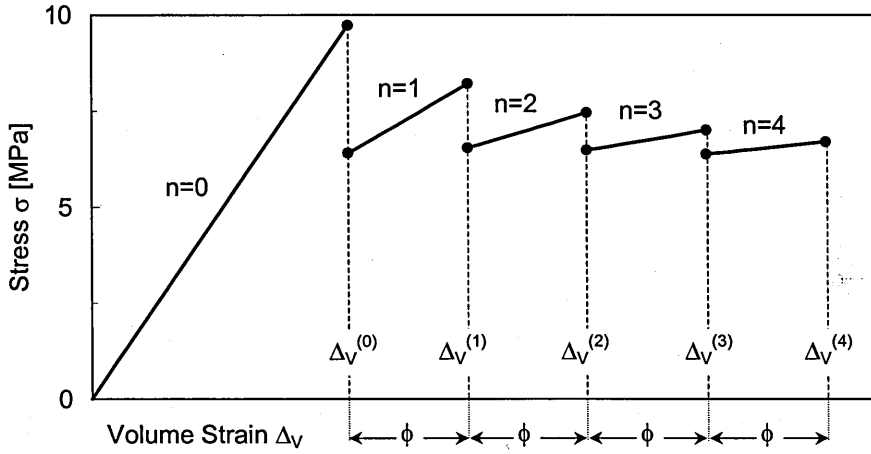


Fig. 3.5.2 Overall stress and critical volume strains, which are equally spaced, calculated from equation (3.20).

Predicted critical volume strains are equally spaced, forming a discrete set of values, each corresponding to a stable configuration of the particle, as shown in Figure 3.5.2.

3.5.2. Comparison between the modified model and the fundamental Lazzeri-Bucknall model

1st) Calculations show that the critical volume strain for the first cavity ($n=0$) is higher for the modified model than for the Lazzeri-Bucknall (LB) model:

$$\Delta_V^{(0)} = \xi + 2 \left(1 + 2\bar{\beta}\right)^{\frac{1}{4}} \left(\frac{2}{3} \gamma\right)^{\frac{3}{4}} > \Delta_V^{(LB)} = \xi + \left(\frac{2}{3} \gamma\right)^{\frac{3}{4}} \quad (3.22)$$

2nd) The void radius for the modified model is lower:

$$r = R \left(\frac{2\gamma}{3(1+2\bar{\beta})} \right)^{\frac{1}{4}} < r^{(LB)} = R \left(\frac{2}{3} \gamma \right)^{\frac{1}{4}} \quad (3.23)$$

3rd) In the new model the critical volume strains $\Delta_v^{(n)}$ are equally spaced (Figure 3.5.2):

$$\Delta_v^{(n+1)} - \Delta_v^{(n)} = \phi \quad (3.24)$$

4th) The critical mean stress to generate the first cavity is bigger in the modified model:

$$\sigma_n = \xi + 2(1+2\bar{\beta})^{\frac{1}{4}} \left(\frac{2}{3} \gamma \right)^{\frac{3}{4}} > \sigma_n^{(LB)} = \xi + 2 \left(\frac{2}{3} \gamma \right)^{\frac{3}{4}} \quad (3.25)$$

3.6. Scattering of the rubber particle density

Dynamic mechanical tests on several toughened polymers, including ABS, HIPS and RT-PMMA, have shown a linear increase in the glass transition temperature of the rubber (T_β) with increasing compressive stress. However, tests carried out under superimposed tension have proved much less reproducible in some toughened polymers, notably ABS and RT-PMMA. Data show that there are large variations in stress and strain between (and possibly within) individual rubber particles. In some RT-PMMA specimens, application of tensile stress produces a double peak, clearly demonstrating that point. On the evidence of the DMTA data, cavitation does not always produce a reproducible state of stress in the rubber phase. The confirmed large scatter in the temperature of the secondary loss peak is examined in Chapters 4 and 5. This scatter is associated with the formation of voids in a fraction of the rubber particles, and the consequent change in density and relaxation behaviour of the rubber phase. In some experimental results the levels of scatter appear to be particularly high and this can be attributed to the formation of several cavities within each rubber particle.

For the sake of simplicity, the unstretched, intact particle is treated as a reference configuration, and the constant density of the material in this state is denoted by ρ_0 . Furthermore, it is assumed that the particle undergoes homogeneous deformations, and the current configuration is taken as a particle with one fully developed cavity. The density of the rubber is here denoted by ρ . The model predicts a scattering of the density, and this can be easily demonstrated by invoking the theorem of conservation of mass. When only smooth deformations occur, i.e. with no cavitation, the theorem implies that:

$$\rho_0 = \rho \det \mathbf{F} \quad (3.26)$$

where $\mathbf{F}$ is the gradient of the deformation, and the determinant of $\mathbf{F}$ gives the change in volume from the reference configuration. Because cavitation of rubber particles occurs at “very small” strains, $\mathbf{E}$ denotes the infinitesimal strain tensor:

$$\det \mathbf{F} \cong 1 + \text{tr } \mathbf{E} = 1 + \Delta_V \quad (3.27)$$

Thus, from (3.26) and (3.27) the density of the rubber relative to the current configuration becomes:

$$\frac{\rho}{\rho_0} = \frac{1}{1 + \Delta_V} \quad (3.28)$$

Equation (3.28) for $0 \leq \Delta_V < \Delta_V^{(0)}$ i.e. before the first critical volume strain is reached,

gives $1 \geq \frac{\rho}{\rho_0} > \frac{1}{1 + \Delta_V^{(0)}}$, by setting:

$$\left(\frac{\rho}{\rho_0} \right)_{(-)}^{(0)} = \frac{1}{1 + \Delta_V^{(0)}} \quad (3.29)$$

Then $\frac{\rho}{\rho_0}$ when $\Delta_V = \Delta_V^{(0)}$ the elastic strain is $\Delta_V^{(0)} - \phi$ so that the first void is formed:

$$\left(\frac{\rho}{\rho_0}\right)_{(+)}^{(0)} = \frac{1}{1 + \Delta_v^{(0)} - \phi} = \frac{\rho}{\rho_0} \quad (3.30)$$

By computing the difference $\left\|\frac{\rho}{\rho_0}\right\|^{(0)} = \left(\frac{\rho}{\rho_0}\right)_{(+)}^{(0)} - \left(\frac{\rho}{\rho_0}\right)_{(-)}^{(0)}$ the jump in density corresponding to the nucleation of the first void is:

$$\left\|\frac{\rho}{\rho_0}\right\|^{(0)} = \frac{\phi}{(1 + \Delta_v^{(0)})(1 + \Delta_v^{(0)} - \phi)} \cong \phi \quad (3.31)$$

which has been obtained after employing a Taylor's expansion and neglecting higher order terms. The symbol $\|\cdot\|$ represents the jump in the scattering behaviour.

When the prescribed volume strain is increased in such a way that $\Delta_v^{(0)} \leq \Delta_v < \Delta_v^{(1)}$, then the relative density changes according to (3.29), with $\Delta_v^{(0)}$ replaced by $\Delta_v^{(1)}$ and ϕ replaced by $\hat{\phi}(\Delta_v)$, which is the void volume fraction determined by the attained volume strain, i.e.

$$\left(\frac{\rho}{\rho_0}\right)_{(+)}^{(0)} \geq \frac{\rho}{\rho_0} > \frac{1}{1 + \Delta_v^{(1)} - \hat{\phi}(\Delta_v^{(1)})} = \left(\frac{\rho}{\rho_0}\right)_{(-)}^{(1)} \quad (3.32)$$

A straightforward calculation on the expansion of a spherical cavity in a particle subjected to constant radial displacement in linear elasticity shows that $\hat{\phi}(\Delta_v) = \phi$, i.e. the void in its stable configuration has a negligible expansion (Appendix C). Thus, when Δ_v approaches its second critical value (equation with $n = 1$) the corresponding relative density becomes:

$$\left(\frac{\rho}{\rho_0}\right)_{(-)}^{(1)} \cong \frac{1}{1 + \Delta_v^{(1)} - \phi} = \frac{1}{1 + \Delta_v^{(0)}} = \left(\frac{\rho}{\rho_0}\right)_{(-)}^{(0)}. \quad (3.33)$$

This means that after the first jump, the relative density of the rubber phase decreases back to its original value before nucleation. By iterating the procedure explained above, it can be shown that at each critical volume strain the (positive) discontinuity of the density remains constant even though the critical volume strains increase in value. The behaviour of $\frac{\rho}{\rho_0}$ as a function of Δ_v is represented in Figure 3.6.1.

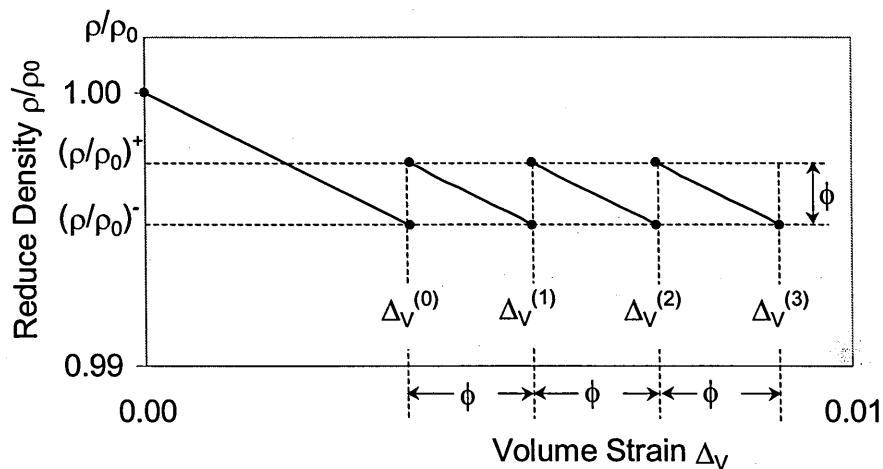


Fig. 3.6.1 Density scattering of the rubber, calculated from the equations above.

3.7. Scattering of the α -transition temperature

A linear relationship is used to predict the behaviour of the α -transition temperature of the rubber as the density changes. Indeed, if α_v ($\alpha_v = 3\alpha_L$ and $7\times 10^{-5} \leq \alpha_L \leq 8\times 10^{-5} \text{ K}^{-1}$) indicates the volumetric expansion coefficient of the rubber, we have that:

$$\frac{\rho}{\rho_0} = \alpha_v (T - T_0) \tag{3.34}$$

where T_0 is the (constant) temperature of the rubber particle in the reference configuration and T is the current temperature.

The jumps in the α -transition temperature corresponding to the critical volume strains are then easily obtained by inverting equation (3.34) i.e.

$$\|T\| = \alpha_v^{-1} \left\| \frac{\rho}{\rho_0} \right\| = \frac{\phi}{\alpha_v} \quad (3.35)$$

Because the range of variation of α_v for rubbers is from 2.1×10^{-4} to $2.4 \times 10^{-4} \text{ K}^{-1}$, if the values of R , K_r , Γ_1 , Γ_2 are the ones listed above (after equation (3.18)), from equation (3.31) $\left\| \frac{\rho}{\rho_0} \right\| = \phi = 2.3 \times 10^{-3}$; with these values equation (3.35) predicts a range of variation for $\|T\|$ of between 9.6°C and 11°C . The order of magnitude of $\|T\|$ measured for a RT-PMMA (HSH CS-250-40) is 6°C [Bucknall et al., 2000a], as shown in Figure 3.7.1.

Using this model, a relationship is established between multiple cavitation of the rubber particles and the observed scatter in the loss peak temperature. In view of these relationships, it is not surprising that the overall values of T_β observed in dynamic mechanical tests on ABS and RT-PMMA are subject to wide variations when the tests are conducted under superimposed tensile stress.

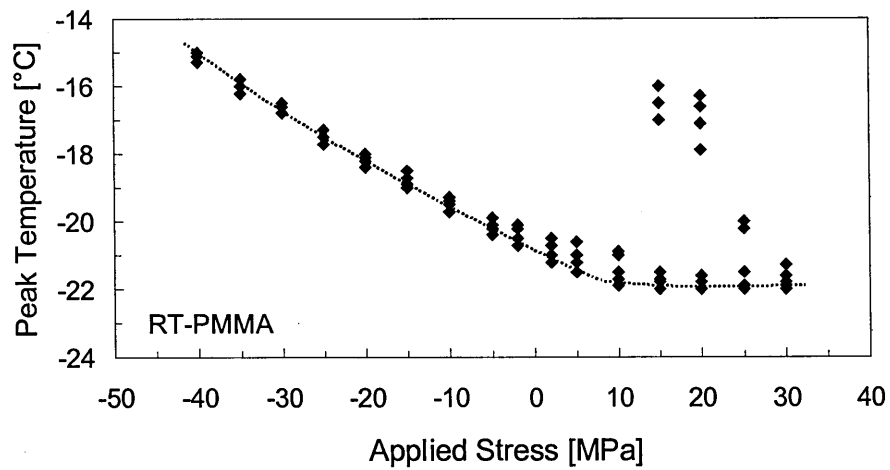


Fig 3.7.1 Temperature scattering, from DMTA experimental data for HSH CS-250-40.

This might be due to the fact that during a tensile test not all the particles cavitate at the same time, but many particles just stretch under the tensile stress, whereas others cavitate. In this case the upper value of the rubber density of all the stretched and cavitared rubber particles would be reduced.

CHAPTER 4

EXPERIMENTAL DETAILS

4.1. Introduction

This chapter contains a list of the materials tested during the present research, a general description of their properties and details of specimen preparation techniques. A description of the experimental conditions can also be found below. The approaches selected for this study include dynamic mechanical thermal analysis (DMTA), coefficient of thermal expansion (CTE) measurements, creep and three-point-bend (3PB) tests. Particular attention will be given to the dynamic mechanical thermal analysis technique. The detection of cavitated rubber particles in RT-PMMA was compared with that of cavitated rubbery layers in POM in order to investigate the role of cavitation in multiphase polymers. Other materials like ABS and PC/PB were tested to prove the accuracy of the DMTA results. The behaviour of RT-PMMA compounded with silicone oil was examined. The influence of pre-strain and cooling on the mechanical properties of RT-PMMA was also investigated. Transmission electron microscopy (TEM) was used in support of the other experimental results. Experimental details will be presented separately in each section dealing with experimental results.

4.2. Materials

Several materials were analysed in this study to obtain a wide range of information about initiation and development of cavitation and the relationship between cavitation and mechanical properties. The polymers used in this research were based mainly on blends of hard polymethyl methacrylate (PMMA) and rubber particles (or layers) as toughening agents (RT). The rubber toughened PMMA (RT-PMMA) materials are described below and schematised in Table 4.1.1.

Particle		Rubber		T/O ¹	Moulding	Short name ³		
morphology	diameter [nm]	content wt %	modifier ²					
hard soft hard core shell	127	18	BCS	T	injection	CS-127		
	130					CS-130		
	176					CS-176		
	186					CS-186		
	200					CS-200		
	203					CS-203		
	250	25	EVA		compression	CS-250-25		
		40				CS-250-40		
	salami intermediate continuous salami	very variable				2	O	S2-EVA
						4		S4-EVA
6						I6		
8						C8		
4			S4-EPDM					
4			S4-CSPE					

Tab. 4.1.1: Properties of the RT-PMMA materials used in this research

¹) T: transparent, O: opaque.

²) Rubber modifier: BCS: poly butylacrylate-co-styrene
EVA: ethylene vinyl acetate
EPDM: ethylene propylene diene monomer
CSPE: chlorosulphonated polyethylene

³) Short name: CS: HSH core-shell, S:salami
C:continuous, I:intermediate
127..250: particle size (diameter nm)
25, 40: rubber contained (wt%)

Other materials, including a polyoxymethylene (POM), an acrylonitrile-butadiene-styrene (ABS), a polycarbonate toughened with polybutadiene (PC/PB) and a vulcanised rubber were used for purposes of comparison and to establish confidence in

the DMTA test results. Silicone oil was also used to compound with RT-PMMA. The general details of the above materials are listed below.

4.2.1. RT-PMMA

Several series of RT-PMMA were examined during this study. The details of these materials are listed in Table 4.1.1. Fourteen RT-PMMA materials supplied from the Acrylics Division of ICI plc were studied.

Two RT-PMMA materials (CS-250-40 and CS-250-25) arrived as granulated materials. They were first dried and then compression-moulded into square plaques measuring $240 \times 240 \times 4$ (or 6) mm³. The other RT-PMMA blends were received already moulded. Six of them (CS-127, CS-130, CS-176, CS-186, CS-200, CS-203) were injection moulded film-gated plaques ($150 \times 150 \times 4$ mm³), in which the direction of the flow was clearly defined by the position of the sprue and the film gate, as illustrated in Figure 4.2.1. The remaining six RT-PMMA materials were received in the form of compression moulded plaques ($115 \times 115 \times 6$ mm³ square plaques shaped by a flexible rubber gasket).

Eight of the RT-PMMA materials contained hard-soft-hard core-shell rubber particles (labelled CS). They comprised a hard glassy PMMA core surrounded by a rubbery inner shell and an outer shell of PMMA as illustrated in Figure 4.2.2. The outer shell was grafted to the rubber to ensure good adhesion between the modifier particles and the PMMA matrix, and the rubber shell was grafted to the core.

A TEM micrograph of a core-shell CS-127 is reported in Figure 4.2.3.

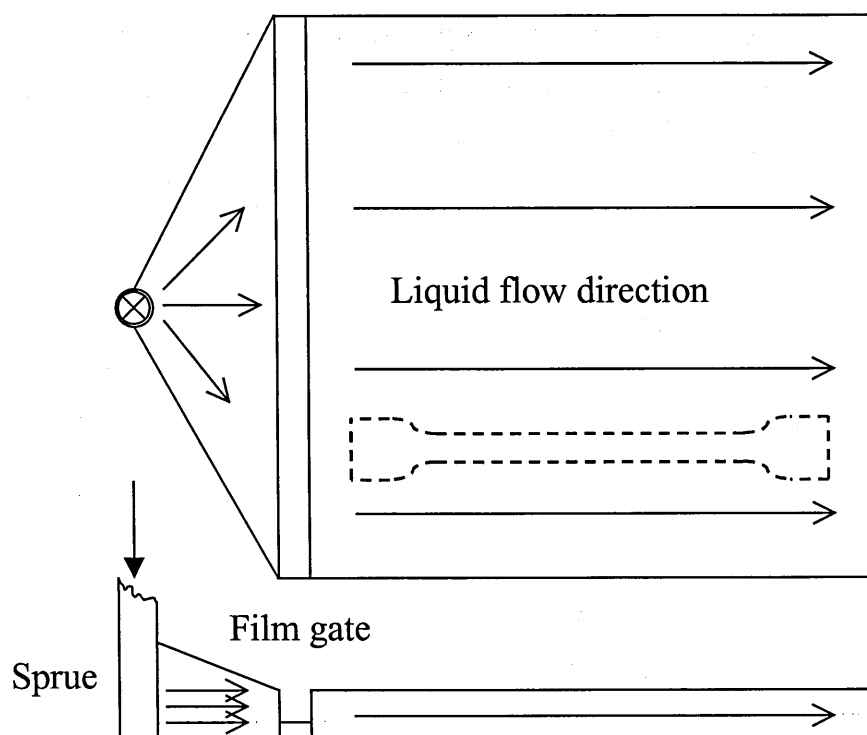


Fig. 4.2.1 RT-PMMA injection moulded plaque, components and flow direction.

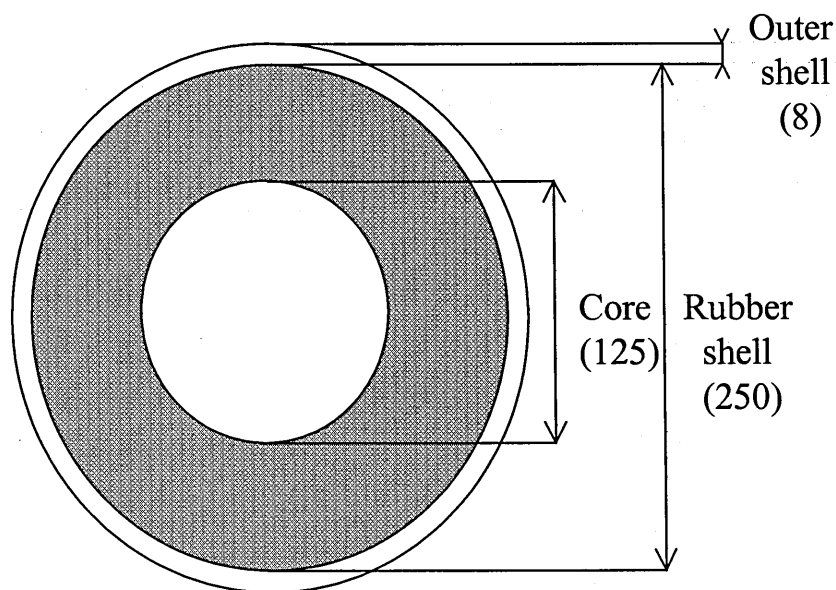


Fig. 4.2.2 Typical HSH core-shell rubber particle. In brackets are the dimensions (in nm) of a CS-250-40 material taken as an example of a rubber core-shell particle.

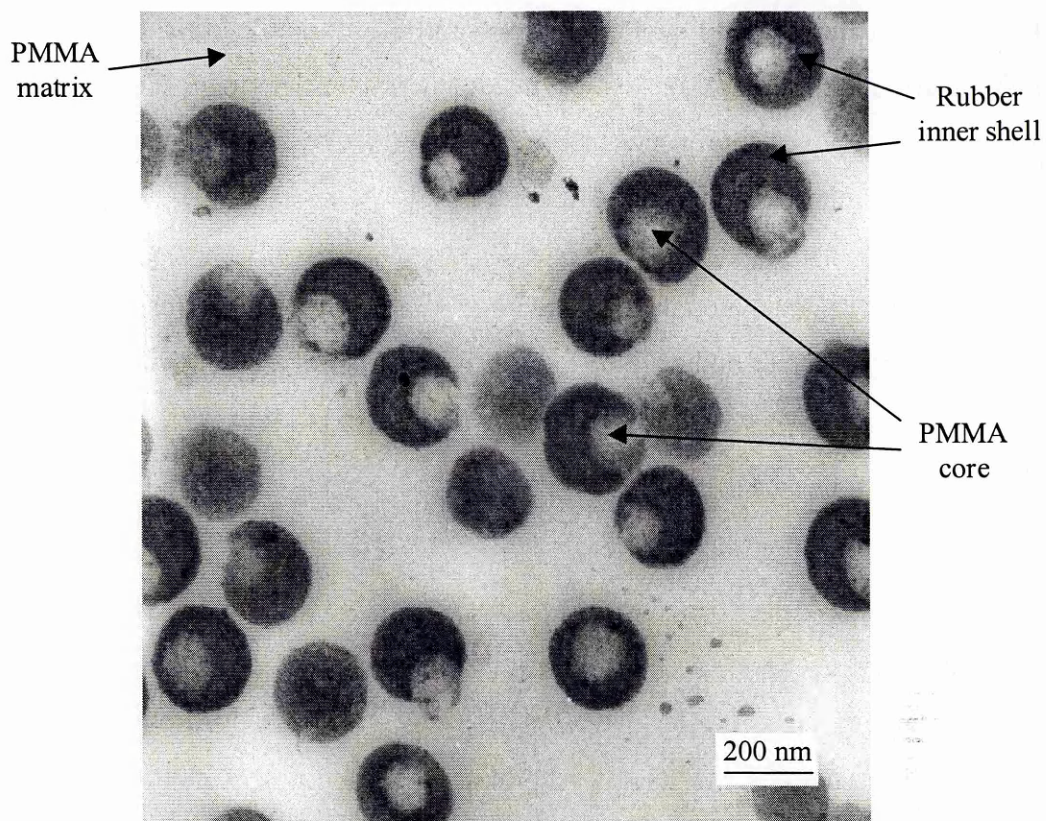


Fig. 4.2.3 TEM micrograph of a HSH core-shell RT-PMMA (CS-127)

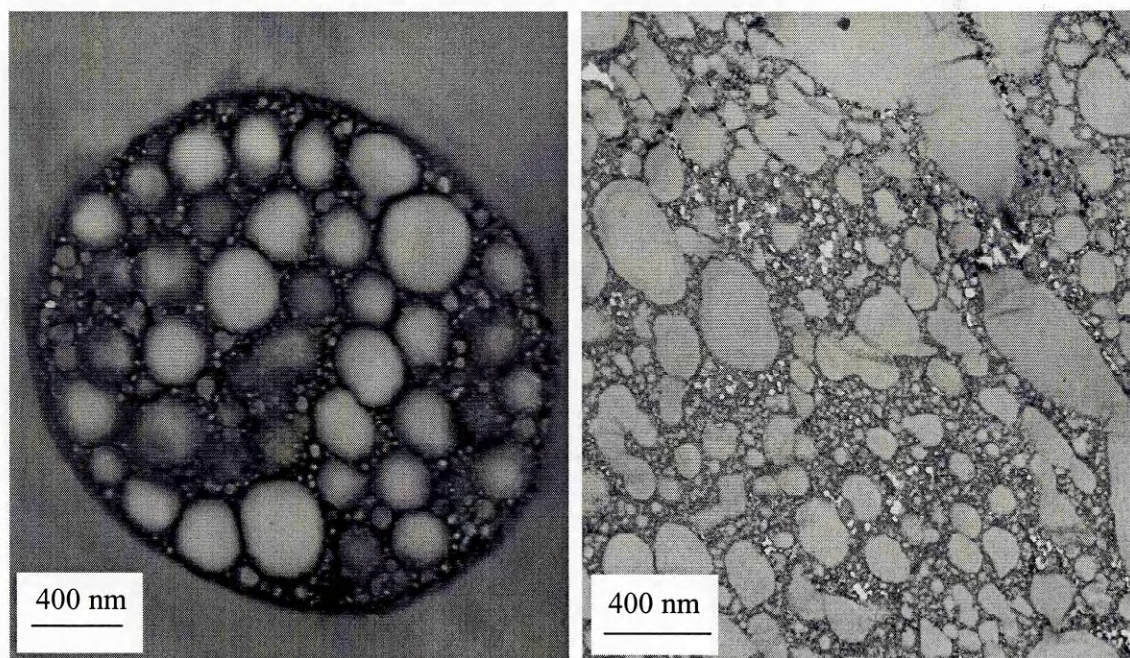


Fig. 4.2.4 TEM micrograph of a salami RT-PMMA S4-EPDM (left) and a continuous RT-PMMA C8.

Four RT-PMMA materials had rubber-like salami particle morphology (labelled S) with a chaotic distribution of hard inclusions inside the rubber particle. The particles' dimensions were very variable inside the PMMA matrix. A general salami particle is shown in the TEM micrograph in Figure 4.2.4, left.

Two types of RT-PMMA materials presented a morphology consisting of intermediate (labelled I) and continuous rubber (labelled C), with layers of rubber dispersed inside the PMMA matrix, as shown in the TEM photo in Figure 4.2.4, right.

4.2.2. POM

A POM manufactured by Hoechst, known also as polyformaldehyde or acetal homopolymer, was also studied. The POM contains crystalline lamellae separated by thin layers of 'amorphous' POM, which is rubbery above its glass transition temperature ($T_g \sim -70^\circ\text{C}$). This material was injection moulded at Cranfield University [Amonpong 1999]. The mould had a box shape as illustrated in Figure 4.2.5.

The samples were machined from the lateral wall in the direction of the flow.

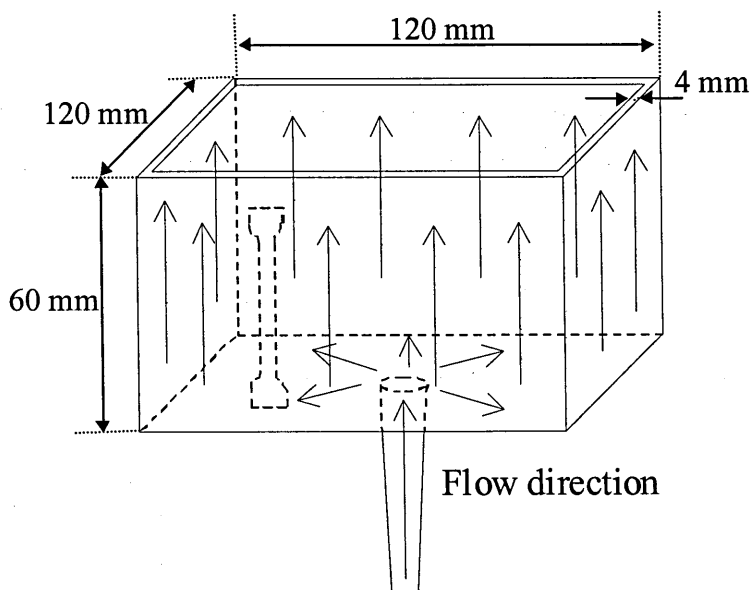


Fig. 4.2.5 Injection moulded box of POM.

4.2.3. Supporting materials (ABS, PC-PB, Rubber and Silicone Oil)

ABS and PC-PB materials were used in this study as multiphase materials to prove the instrumental accuracy in DMTA tests. ABS was compression moulded into plaques at Cranfield University. PC-PB arrived as injection moulded bars.

Vulcanised rubber from a racing bicycle inner tube was also tested in DMTA experiments. The specimen had a cylindrical shape as shown in Figure 4.2.6.

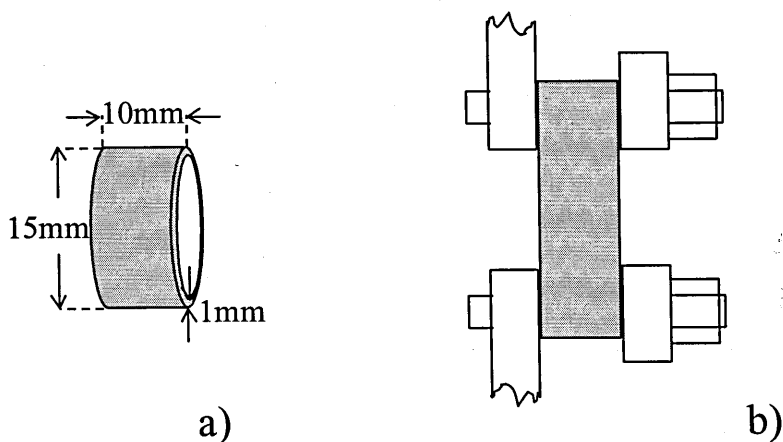


Fig. 4.2.6 Inner tube: (a) vulcanised rubber sample; (b) in tensile DMTA configuration.

A RT-PMMA (CS-250-40) was compounded using a Werner Pfleiderer twin screw extruder (ZSK 30M9) with 0.1% and 1% (vol.) silicone oil (Dow Corning 510/50cS silicone fluid). The blends were then granulated and compression moulded into plaques.

4.3. Processing: compression moulding

The RT-PMMA CS-250-25 and CS-250-40 were compression moulded from pellets using the following procedure.

Before moulding, the RT-PMMA granules were dried overnight in vacuum at 80°C to avoid bubble formation and the material was then slowly cooled back to room temperature under vacuum. The amount of material used in each moulding was roughly 10% greater than the amount needed to fill the mould, to ensure adequate mould filling and to prevent void formation.

A Moore compression-moulding machine was used to prepare the plaques. The mould consists of two 4mm thick polished chromium plated steel plates of dimensions $300 \times 300 \times 3 \text{ mm}^3$, and one 4mm (or 6 mm) thick metal frame moulding chase of dimensions $250 \times 250 \text{ mm}^2$. The metal plates were heated to 80°C and coated with a film lubricant of water-based release agent, Frekote Aqualift C200, to facilitate polymer flow and prevent sticking. Typically, 250 g of granular material was then moulded in the pre-heated press at 220°C for 5 minutes without applying any pressure. In this stage the material was melted and allowed to reach thermal equilibrium with the mould. Then a pressure of 4 MPa was gradually applied to force the air out of the chase and ensure consistent plaque quality. The pressure was maintained for 10 minutes before leaving the press to cool down slowly ($0.5^\circ\text{C min}^{-1}$) to room temperature. In some cases an annealing procedure (at 115°C for 3 hours) was used to relieve stress and to achieve an equilibrium structure.

4.4. Specimen preparation

Several shapes of specimens were machined to suit the varied test procedure. The specimens were machined from compression and injection moulded plaques.

For tensile dumbbell specimens a band saw was first used to make rectangular strips. Then the samples were machined using an ICI air-compressor router. Fine metallographic grinding papers (P600 and P1200) were used to remove the surface irregularities and polish the surface smoothly, to avoid surface stress concentrations during testing. Specimens were left for at least 24 hours at room temperature before testing. Specimens for creep tests were also annealed at 110°C for 2 hours before testing. These precautions allowed the relaxation of any internal stresses caused by the machining.

The cross-sectional dimensions of the gauge length were measured as the average of three readings at different places along the length. The samples were carefully polished

to obtain the same second decimal number (in mm) for the three readings. Dumbbell tensile specimens were used in tensile, creep and tensile DMTA tests.

Rectangular samples for compression testing were cut from the central section of the dumbbell tensile bars, using a low speed rotary saw with paraffin as a lubricant and coolant, to ensure that the compression faces were parallel. The parallelism of the test pieces, especially of the end faces, was rigorously controlled to avoid bending or buckling, especially in long samples (100 mm) used for CTE. Compression specimens were used in CTE and DMTA tests.

Samples for three point bending (3PB) LEFM tests were cut using a milling machine from unstrained rough blanks and from the central section of dumbbell pre-strained tensile bars. The samples were in the form of single edge notched bend (SENB) specimens. The rectangular block was V-notched using a rotating cutter, to give a notch tip of less than 50 μm . The notch was subsequently sharpened by dropping a weight from a set height onto a new razor blade positioned at the tip of the V-notch to provide a crack with a normal tip radius of 1 μm . The razor blade-notch technique has been developed after many attempts at several heights for the same material (CS-250-40). The best height from which to drop the weight (95 g) has been found to be about 12 cm from the top of the razor blade, as shown in Figure 4.4.1. A microscope was used to measure the initial crack length; it was important that both sides of the specimen were measured in order to accommodate asymmetric crack geometry which sometimes arises after razor tapping. The V-notch length was roughly 0.47 times the width (W) of the sample and the final notch length (a) was kept in the range: $0.45 W < a < 0.55 W$. Fractured specimens were examined to determine the length of the initial notch depth and those outside these specifications were rejected.

Rubber samples were cut from the bicycle inner tube with sharp scissors.

Shapes and dimensions of all the samples used in this study are summarised in Table 4.4.1.

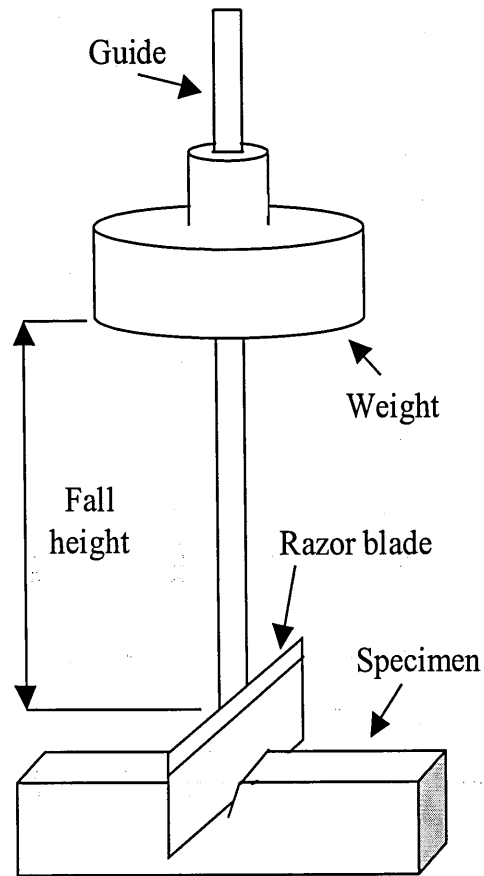
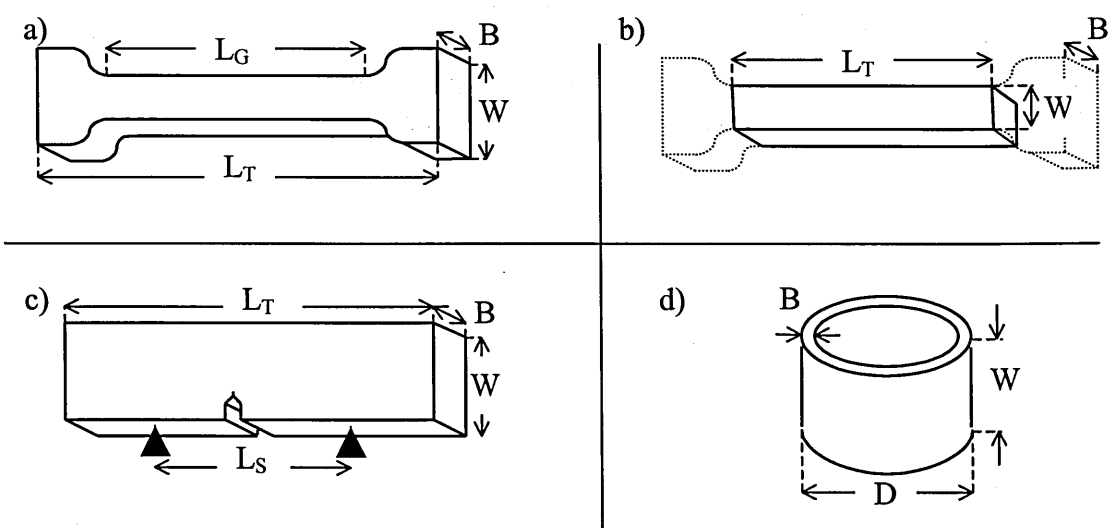


Fig. 4.4.1 Schematic representation of the razor-notch apparatus: a weight of about 95g was dropped from a height of almost 12 cm to the top of the razor blade.

Samples for:	Shape and Type	Width W [mm]	Thickness B [mm]	Total Length L_T [mm]	Gauge Length L_G [mm]
Tensile Pre-straining CTE	Dumbbell a)	CTE:10 3PB:13	4 6	150	65
Tensile DMTA tests	Dumbbell a)	3	4	45	20
Creep tests	Dumbbell a)	3	4	80	40
CTE tests	Rectangular b)	3	4	100	-
Compression DMTA tests	Rectangular b)	3	4	15	
3PB tests	SENB c)	12	6	60	Span length L_S 48
Tensile rubber DMTA tests	Cylindrical d)	10	1	Diameter D 15	-



Tab. 4.4.1 Shapes and dimensions of specimens used in this study

4.5. Test methods

A description of the test techniques and equipment used during this research is developed below.

4.5.1. Dynamic Mechanical Thermal Analysis (DMTA)

Tests were carried out using a specialised dynamic mechanical thermal spectrometer (the Eplexor DMTA machine) manufactured in Germany by Gabo Qualimeter GmbH. This technique was used to characterise the temperature and shape of the relaxation peak, $\tan \delta$.

4.5.1.1. Apparatus

This instrument is capable of performing measurements of dynamic mechanical properties at small load amplitudes, i.e. dynamic modulus and loss over a wide range of temperatures, while subjecting the specimen to static load of up to 1500 N in tension or compression. A schematic diagram is shown in Figure 4.5.1.

4.5.1.2. Theory

Dynamic mechanical tests characterise materials through monitoring the sample stiffness and therefore molecular mobility. The kind of molecular movement in the different materials depends on the internal structure and on experimental parameters (temperature, frequency, etc.). This behaviour is defined in terms of the visco-elastic properties of the materials. The results of DMTA tests are normally expressed in terms of a complex dynamic modulus, and a phase angle δ .

In both tension and compression tests, static and dynamic stresses were applied independently to the specimens in a direction parallel to the length of the bar. A static load was applied to the specimens and was held constant between intermittent periods when dynamic loading was applied.

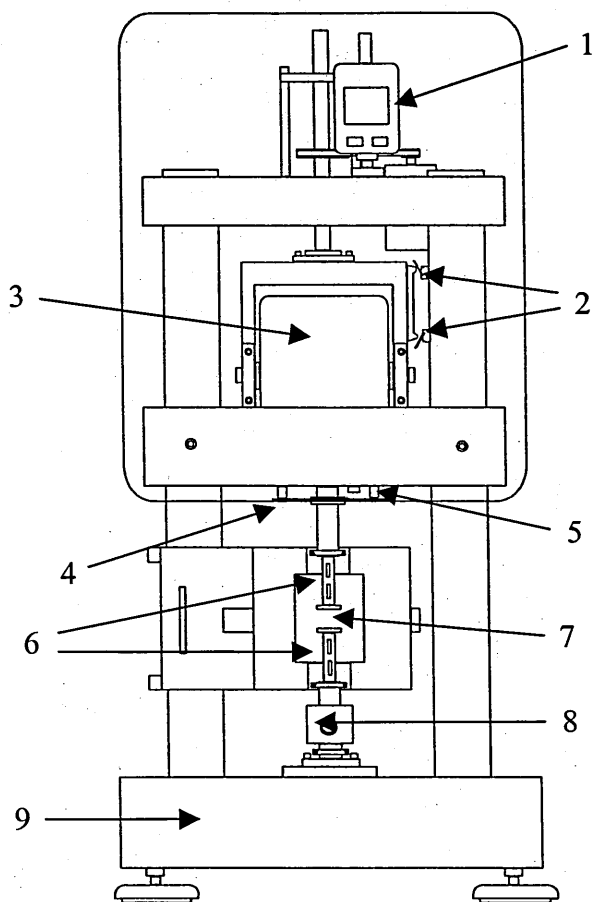


Fig. 4.5.1 Schematic diagram of the Eplexor DMTS apparatus. 1) Static displacement transducer (strain range 0.005 to 35 mm), 2) Limit switches, 3) Vibrator (frequency range 0.1 to 100 Hz), 4) Blade spring, 5) Eddy current displacement transducer (dynamic strain range 0.0025 to 3 mm), 6) Clamps, 7) Temperature control chamber (temperature range -150°C to 500°C), 8) Force transducer (force range 1 N to 1500 N), 9) Frame.

An oscillatory stress (or strain, depending upon the test arrangement) of angular frequency ω was generated in the specimen:

$$\sigma(t) = \sigma_0 \sin \omega t \quad (4.1)$$

Owing to the time-dependent properties of the polymer the resultant response is also sinusoidal but is out of phase with the stress:

$$\varepsilon(t) = \varepsilon_0 \sin (\omega t + \delta) \quad (4.2)$$

The stimulus lags behind the response by a phase angle δ .

A force transducer measured the dynamic force with the sample between the transducer and the magnetic drive and, from the calculation of the cross-section area A_0 (from B and W), the machine calculated the dynamic stress (σ_a).

An eddy current displacement transducer measured the dynamic strain amplitude (ε_a). The machine calculated the dynamic modulus:

$$|E^*| = \sigma_a \varepsilon_a^{-1} \quad (4.3)$$

and from the measured phase angle (δ) the machine calculated $\tan \delta$:

$$\tan \delta = E'' / E' \quad E' = |E^*| \cos \delta \quad E'' = |E^*| \sin \delta \quad (4.4)$$

where E' is the real (in-phase) part of the modulus, which is also called the storage modulus, and corresponds to a recoverable or stored energy term; E'' is the imaginary part of the modulus also called the loss modulus, which corresponds to an energy dissipation and so is irrecoverable. $\tan \delta$, which is proportional to the ratio of energy dissipated / energy stored, is also called the loss tangent or damping factor. $\tan \delta$ is therefore related to the molecular mobility and the position of $\tan \delta$ peak is taken as equal to the glass transition temperature (T_g).

4.5.1.3. Test conditions

Tensile and compression were the test configurations used in this study. In the thermostat of the DMTA machine the samples were cooled well below the rubber's glass transition temperature (T_g) at a rate of $10^\circ\text{C min}^{-1}$ with a minimum holding force applied in order to maintain the sample in the correct position and prevent buckling. When the chosen starting temperature was reached, the static pre-load was applied and a sinusoidal mechanical strain was imposed. The amplitude and phase of the resultant displacement were then measured.

Testing was carried out in the temperature sweep mode, using a thermal rate of $1^{\circ}\text{C min}^{-1}$ over the temperature range. Measurements were collected every 2°C and the tests were conducted at a frequency of 1 Hz at a dynamic strain amplitude ranging from $\pm 0.1\%$ to $\pm 0.2\%$.

4.5.2. Coefficient of Thermal Expansion (CTE) measurements

Thermal contraction and expansion experiments were carried out using the Gabo Eplexor, the same machine used for DMTA tests with an appropriate setting. The thermal correction factor of the instrument was set to zero. The clamps were removed from the temperature control chamber, so that the total length could be used for the specimen. The sample's dimension was chosen to be long enough to record sensitively the changes in length due to contraction and expansion and to fit the temperature chamber, but not to be too long, to avoid buckling. The test setting is shown in Figure 4.5.2.

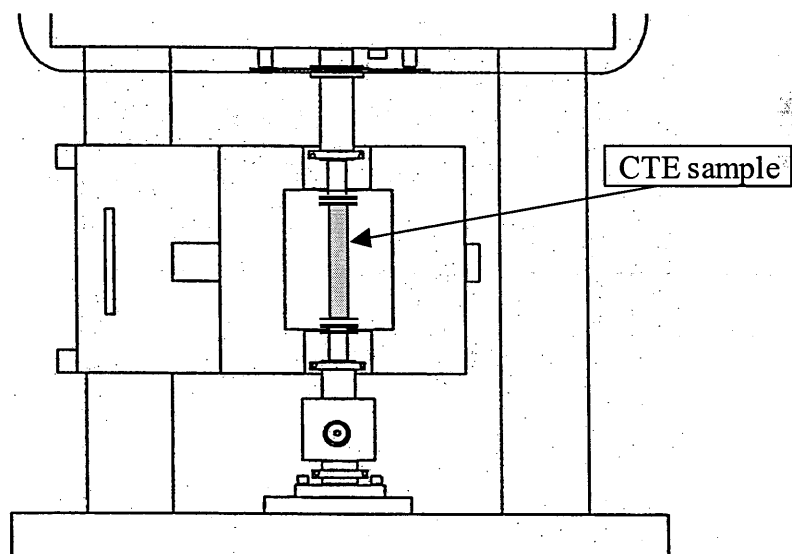


Fig. 4.5.2 Schematic setting in the temperature control chamber for a CTE test

The dimensions of the specimens were $4 \times 4 \text{ mm}^2$ cross section by 100 mm length. A holding force of 2 N was chosen to maintain the sample straight. The DMTA is programmed to work simultaneously under static and dynamic control. 1 N for the dynamic load and 5 N for the static one were chosen. After each measurement the

dynamic and the static forces were removed. The temperature range was set to be from +50°C to –60°C at a thermal ramp rate of 1°C min⁻¹ for the cooling and the expansion tests.

4.5.3. Fracture Mechanics: LEFM

The toughness of the materials was characterised using a linear elastic fracture mechanics (LEFM) analysis to determine K_{IC} and G_C at fracture initiation. Tests were performed on SENB specimens (as shown in Table 4.4.1) and test procedures followed the European Structural Integrity Society (ESIS) protocols [Williams 1990, Pavan 1996].

All the experiments were conducted at a constant temperature of 23°C maintained in the room by an air-conditioned system. LEFM tests were conducted in 3PB, as represented in Figure 4.5.3, either on a Rosand Instrumented Falling Weight Impact apparatus (for high rate tests) or an Instron universal-testing machine (model 6025) (for lower rate testing). The tests were performed with the central loading nose travelling at a constant speed of 1 m s⁻¹ for high rate tests and 10 mm min⁻¹ for lower rate tests.

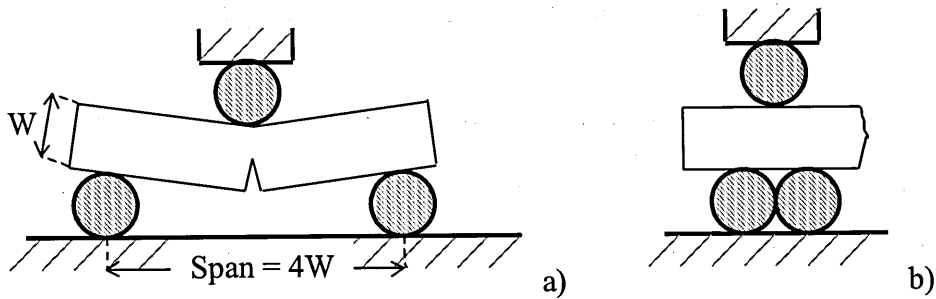


Fig. 4.5.3 (a) Schematic 3PB test configuration and (b) indentation correction.

During the course of the test a force-displacement curve was obtained and this enabled the force and energy absorbed by the specimen at crack initiation to be calculated. An indentation energy correction procedure (Figure 4.5.3b) was also performed for the G_C determination in order to remove the effects of machine compliance and indentation of the supports into the material (as detailed in the ESIS protocols). Because dynamic

effects cause special problems in high-rate fracture testing, mechanical damping was provided, as shown in Figure 4.5.4.

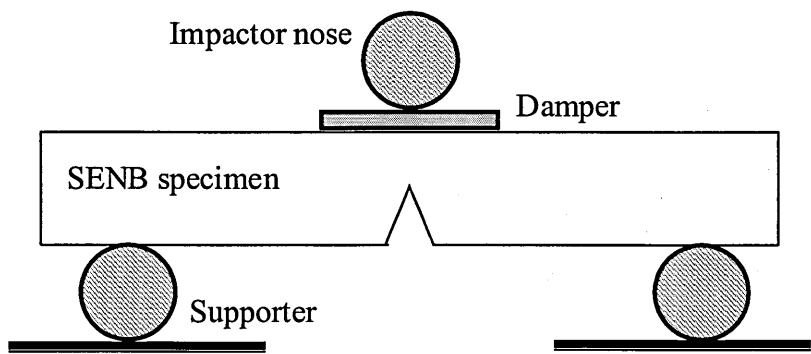


Fig. 4.5.4 Schematic presentation of bending rig with damper.

The impact test will provide a force-time signal with large associated stress waves, that make it almost impossible to analyse the curve for peak force and absorbed energy, unless some mechanical damping is applied to the SENB specimens. In this work natural rubber from gloves (1 mm thick) was used for the damping, as suggested in an ICI internal report [Bailey et al. 1997]. Calculation of the LEFM parameters followed the ESIS protocols.

4.5.4. Tensile tests

Tensile tests were carried out with the Instron universal testing machine for tensile strength tests and pre-straining tests on CS-250-25 and CS-250-40. Strength values were found at a crosshead speed of 1 mm min⁻¹ and 5 mm min⁻¹, at a temperature of 23°C, following the test method ASTM D 638M-93 metric. The yield stress in tension was taken at the peak of the load-displacement curve as an average of at least four samples. Test specimens were in the form of standard dumbbells.

Pre-straining tests were conducted only on CS-250-40 samples, in preparation for CTE and creep tests. The pre-straining tests were conducted in the tensile configuration at a cross-head speed of 0.5 mm min⁻¹ at 23°C for strains of 0.5%, 1%, 1.5%, 2%, 3% and 4%. Tests were carried out by loading the specimens to different strains and holding constant the extension for 5 minutes. At the end of this period, the specimens were

unloaded at the same cross-head speed of 0.5 mm min^{-1} , and removed from the testing machine. Creep tests were started on these pre-strained specimens between 2 and 10 minutes after unloading. Longitudinal strains were accurately measured with a contact extensometer supplied by Instron using a gauge length of 25 mm. The strained specimens were then divided into two groups. Half of the total samples prepared for the TEM and creep tests were then tested and the remaining half were annealed at 110°C for 2 hours and left cooling overnight before testing.

4.5.5. Creep tests

Creep tests were also conducted on CS-250-40 samples with the Instron universal testing apparatus in the tensile configuration. During the course of the test the load was maintained constant at 26 MPa, the temperature was also checked carefully to keep it constant at 23°C . Creep data were determined by observing changes in the strain with time, under a constant load. The strain was measured using an Instron extensometer.

4.6. Electron microscopy (TEM)

A scanning transmission electron microscope (STEM), Phillips CM20 was used to investigate size, dispersion, morphology and cavitation of rubber particles in RT-PMMA.

The samples were prepared for TEM in blocks of dimensions $4 \times 4 \times 4 \text{ mm}^3$ cut from the specimen using a low speed rotary saw and adopting paraffin as lubricant and coolant. The area of interest was then chosen as the end of the bar, which was trimmed into a pyramid shape using a Reichert-Jung Ultramicrotome fitted with a glass knife. Then the tip of the pyramid was cut off to produce a specimen measuring $0.5 \times 0.5 \text{ mm}^2$. The samples were placed in a sealed chamber and stained for 24 hours with ruthenium tetroxide [Montezinos D. et al. 1985, Ohlsson B. et al. 1990] as a penetrating staining agent for polybutylacrylate rubber particles. The samples were then sectioned from the top of the stained pyramid using the ultramicrotome fitted with a 35° angled diamond knife. These slides of a constant thickness of 80 nm were cut into a water reservoir and

then floated onto a copper grid and air-dried naturally. The sequence of steps in the sample preparation technique is described below in Figure 4.6.1.

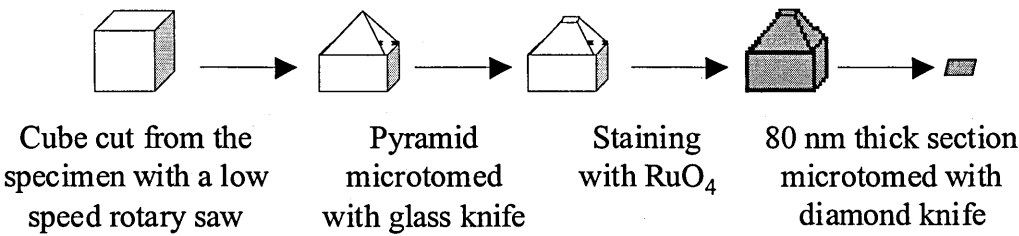


Fig. 4.6.1 Sequence of steps for preparation of TEM samples technique

The prepared ultrathin sections were mounted in the TEM specimen holder and an accelerating voltage of 120 kV was selected. Micrographs were taken of the specimens viewed and the negative films were then developed and printed to be analysed.

CHAPTER 5

EXPERIMENTAL RESULTS AND DISCUSSION

5.1. Cavitation in multiphase polymers

By incorporating a dispersed soft phase into a rigid polymer, either at the polymerisation stage or during melt processing, the impact properties of the rigid polymer can usually be improved. The role of the second phase is to promote the initiation and development of localised matrix deformation, which mainly involves dilatational processes such as voiding or craze formation. Any voiding mechanism in the soft phase of multiphase polymers could be considered as a source of weakness and damage, whereas there is increasing evidence that toughness depends upon cavitation of the rubber phase. When the modifier is represented by rubber particles and they are all intact and well bonded to the matrix, they may produce only limited yielding in the material, especially at the tip of a sharp notch. However, if the particles start to cavitate, the formation of dilatational shear bands and/or crazes can promote an extensive yield zone ahead of the crack tip [Bucknall 2000]. In fact the formation of small voids in the rubber phase results in the relief of the triaxial stresses ahead of a notch or a running crack. Therefore, the size of the plastic zone can be increased significantly and tough behaviour can also be observed under impact conditions [Dijkstra 1993]. Recently, Chen and Mai [1998] confirmed the important role of rubber cavitation in the toughening process. They used three-dimensional large deformation elastic-plastic finite element analysis to show that rubber particles or voids interact with the crack-tip much more strongly than with each other. While intact rubber particles can maintain the triaxial stress plane-strain condition, because of their high bulk modulus, the cavitated rubber or debonded particles promote extensive plastic deformation at high triaxial stresses, i.e. ahead of the crack tip or notch. They concluded that, if the bulk moduli of the rubber and the matrix were of the same order of magnitude, the hydrostatic tension inside the rubber particles could be high enough to promote cavitation prior to matrix shear yielding. The hydrostatic tension inside the rubber particles is proportional to their bulk modulus and so it gets easier to cavitate as this modulus is raised.

It is now believed that the morphology of the particles plays an important role in the deformation mechanism of rubber toughened polymers. It has been found [Young and Lovell 1991] that complex rubber particle morphology can lead to a significantly more efficient toughening process. For some particular rubber particle morphologies, such as soft particles with hard inclusions, the cavitated rubber phase seems to be able to stretch and then strain-harden so that the yield zone becomes larger [Bucknall 2000]. A range of very different morphologies can be observed in rubber particle toughened polymers. The particles may consist of pure bulk rubber or may have inside them one core or more inclusions or inner shells of glassy polymer, as shown in Figure 5.1.1.

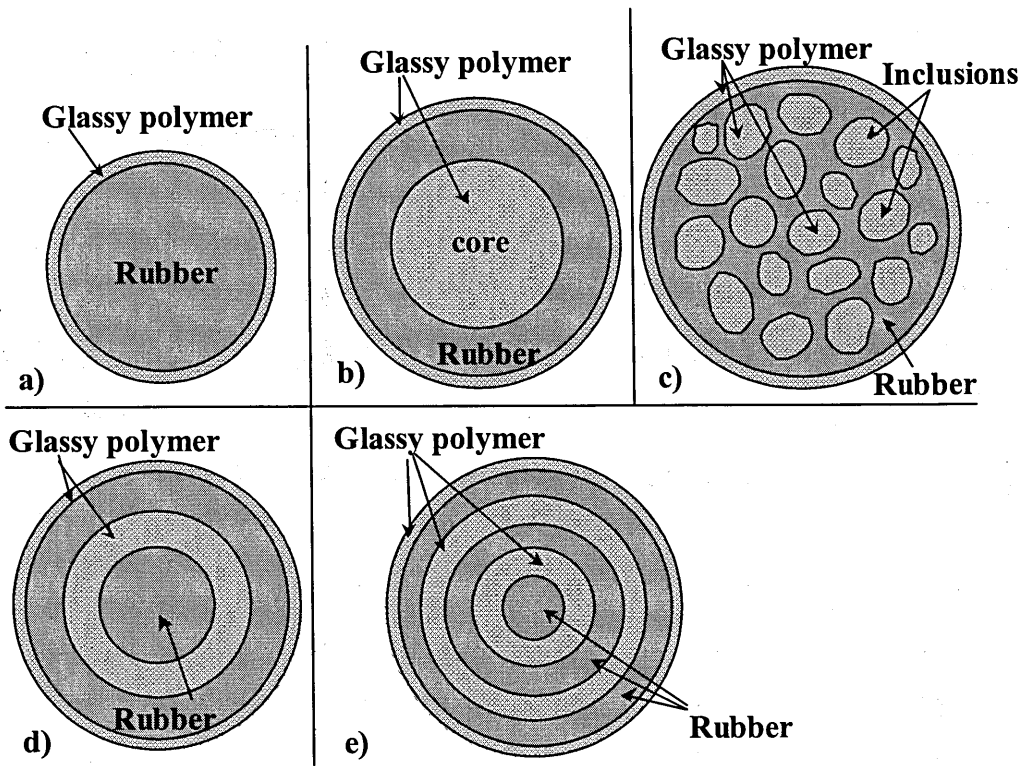


Fig.5.1.1 Schematic representation of different particle morphologies: (a) simple solid rubber particle, (b) hard-soft-hard core-shell (HSH-CS), (c) salami (S), (d) soft-hard-soft core-shell (SHS-CS), (e) onion skin (O) rubber particle.

The rubber particles are called ‘hard-soft-hard core-shell’ (HSH-CS) if they have one single rigid core, ‘salami’ (S) if they contain many rigid inclusions, ‘soft-hard-soft core-shell’ (SHS-CS) if they have one rigid shell, and ‘onion skin’ (O) when there are more than one rigid shells. The morphology and the behaviour of these particles are discussed

in Chapter 4 and also in the present Chapter. The rubber particles in Figure 5.1.1 present an outer layer of glassy polymer that should be blended with the matrix.

The development of the theoretical model for rubber particle cavitation and its effects upon toughening processes, such as yielding in the matrix, have been the subject of several recent studies. These models and the cavitation model covered here provide better understanding of the cavitation process, but experimental data are required for their validation. Since void initiation seems to be the trigger for the plastic deformation mechanism [Bucknall 1997], candidate experimental methods are ones capable of monitoring void formation from the beginning. So far, only the light scattering technique has been successfully adopted for this analysis [Géhan and Schirrer 1999]. However, there are many limitations regarding this technique; in particular, only transparent or translucent blends can be studied. Even in these cases the method is effective only during the early stages of cavitation, where the specimen has not yet become opaque.

Alternative experimental methods were explored during this study in order to find evidence of rubber cavitation. Several treatments designed to promote the onset and the expansion of voids in the rubber through various degrees of damage (i.e. changes in the microstructure due to tensile strain, cooling and annealing) were also considered. Since cavitation affects rubber toughened polymers by generating whitening and causing changes in volume and in the mechanical properties, any method capable of detecting these modifications could be suitable. Transmission electron microscopy (TEM), dynamic mechanical thermal analysis (DMTA), coefficient of thermal expansion (CTE) measurements, creep and fracture mechanics (LEFM) tests, have been simultaneously adopted and comparisons have been made.

5.2. Electron microscopy evidence

Optical and electron microscopy have made a major contribution to our knowledge of the main deformation mechanisms in polymers. Strong evidence of crazes, shear bands and cavitation either inside the rubber particles or at the particle-matrix interface has

been found by optical and electron microscopic studies [Kinloch et al. 1983, Michler 1985, Yee and Pearson 1986, Wu and Mai 1993].

Scanning electron microscopy (SEM) works by scanning an electron beam so that both secondary (low energy) and backscattered (rather higher energy) electrons are detected to form an image. Secondary electrons principally provide topographic information. Therefore, they are used to study the fracture surfaces of polymers, whereas backscattered electrons can give atomic number contrast. Usually the fracture surfaces of polymers are coated with a conducting material (e.g. carbon or gold). SEM analysis can present various inconveniences; in particular damage can be caused by the high-energy electron beam (possible mass loss and crosslinking). When the sample is inhomogeneous (due to crystallinity or the presence of second phase particles, as in RT-materials) it is not always possible to distinguish the nature of the deformation mechanism.

Transmission electron microscopy (TEM) generates images based on electron transmission through a section of the material. Ultrathin sections ($\leq 100\text{nm}$ thickness) are required, and samples are generally obtained by microtoming. Again, the drawback of this 'destructive' approach is that additional damage may occur during the sectioning, and relaxation of stresses may take place. Polymers, especially RT-polymers, are often stained for two main reasons:

- i. The stain can distinguish between different regions helping the interpretation of the image. For example, osmium tetroxide (OsO_4) or ruthenium tetroxide (RuO_4) have been widely used in the study of RT-thermoplastics, since they stain the rubber particles and not the matrix. During the present study the stain RuO_4 has been preferred because of its high effectiveness with RT-PMMA [Ayre 1999].
- ii. The stain also hardens the material by crosslinking unsaturated bonds, which increases the modulus of the rubber phase. For this reason the polymer becomes less susceptible to knife damage during sectioning.

One of the problems of using thin films is that their stress state is different from that of bulk samples, and the nature of the deformation may be altered. Some efforts have been made to study the deformation processes by observing bulk specimens or their sections directly under the microscope, but mainly they have been unproductive for the following reasons:

- ♦ In SEM if new surfaces open up, which have not been coated with a conducting layer, they become electrically charged, obstructing the image.
- ♦ In SEM and TEM the stress state at the free surface is generally different from the one in the bulk sample, due to loss of constraints.
- ♦ In TEM the thin section may suffer beam damage
- ♦ Even if thicker sections can be examined under the TEM, as a consequence of its high voltage [Michler 1985], they are still far from the true deformation behaviour of bulk samples and the problems associated with beam damage may still be present.

Even so, most of the published experimental information about rubber cavitation has been based on optical microscopy [Pearson and Yee 1989], SEM [Kinloch 1997] and TEM.

During the present study TEM has been adopted to visualise the structure of thin microtomed sections of RT-PMMA. TEM has been primarily used to examine the rubber morphology and investigate evidence of cavitation. It was sometimes possible to follow the deformation processes. For example, Figure 5.2.1 shows an electron micrograph of a RuO₄ stained RT-PMMA section, after tensile fracture. The RuO₄ stains the rubber regions dark by depositing ruthenium in areas containing the rubber. It should be noted that only three layers can be visualised (the PMMA core, the inner rubber shell and the surrounding PMMA matrix), since the outer layer of the particle is PMMA and is blended with the matrix. There is chemical graft-linking between the different layers in the rubber particle that assures a good adhesion.

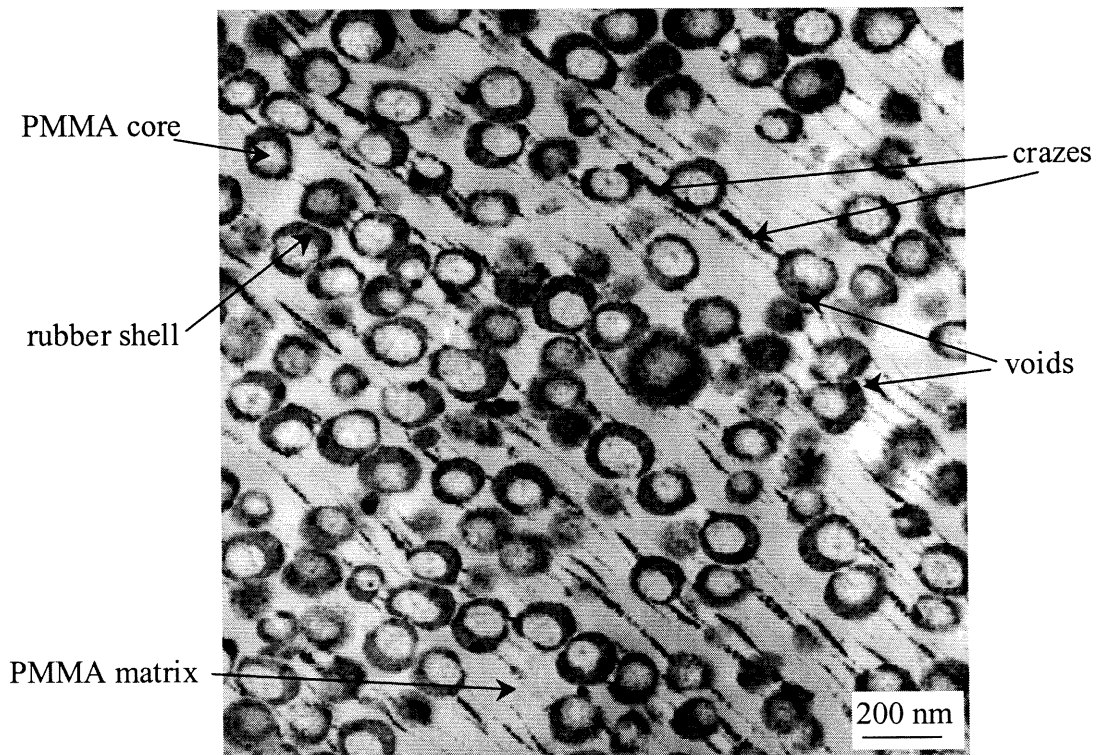


Fig. 5.2.1 Transmission electron micrograph of RuO_4 stained longitudinal section of tensile fractured RT-PMMA specimens, (courtesy of AJ Barwick, ICI).

Crazes can be observed coming from both the equators of the HSH core-shell rubber particles and in between close neighbour particles. These crazes seem to extend between, and even through, rubber particles. A thorough inspection shows darker areas inside some rubber shells, which are voids. These dark spots may form because the stain accumulates inside the holes and different techniques for preparation of thin sections visualise voids differently. Thin sections of specimens to be observed under the TEM can be prepared in three ways.

- a) Thin polymer films may naturally be manufactured this thin (about 100 nm thick). This is very rare, and does not apply to the present project, because here the attention is focused on degree of damage in ultrathin sections from macroscopic test specimens.
- b) The small pyramidal-shaped blocks cut from test specimens are stained before microtoming. This technique has been adopted in Cranfield University. When the

transmission electron micrograph shows evidence of cavitation, the holes appear as bright voids (white spots).

- c) The already microtomed sections are stained just before being observed in the TEM. In this case the small voids are filled with RuO_4 and they look like black spots in the micrographs. This technique has been used in the ICI laboratory.

If the stress and strain used to deform the polymers are so large that void formation in the rubber particles is accompanied by extensive yielding or crazing in the surrounding matrix, the exact role of cavitation in the toughening mechanism could be obscured. This explains why the majority of the TEM RT-PMMA pictures are here taken from slightly damaged test samples.

5.2.1. RT-PMMA morphology

Under TEM the morphologies of all the RT-PMMA specimens covered in this study were observed.

Figure 5.2.2 presents two micrographs of a HSH CS-130-18 (Table 4.1.1 Chapter 4) core-shell RT-PMMA material as moulded. It can be noted that the PMMA cores are rarely in the centre of the rubber particle.

Figure 5.2.3 shows micrographs of a continuous (C8 in Table 4.1.1 Chapter 4) RT-PMMA that has not been subject to any mechanical or thermal deformation process. The bright spots on the photos are voids, probably caused by electron beam damage or microtoming artefacts. It is very complicated to explain the formation of such voids when so many variables in the imaging analysis play fundamental roles.

Figure 5.2.4 reports two TEM photos of an undeformed (S4-EPDM) RT-PMMA with salami rubber particle morphology. The salami particles in the material were of a large variety of dimensions. The micrograph on the left, showing a whole particle, the smallest found in many analysed sections, that has been taken at the same TEM enlargement as the other one, which presents only a fraction of an entire particle.

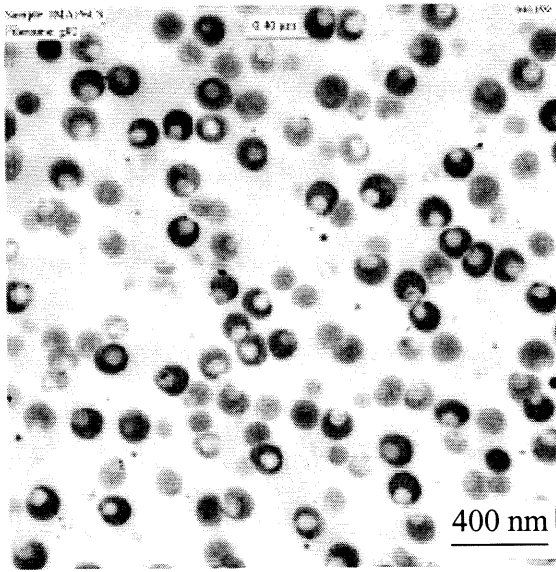
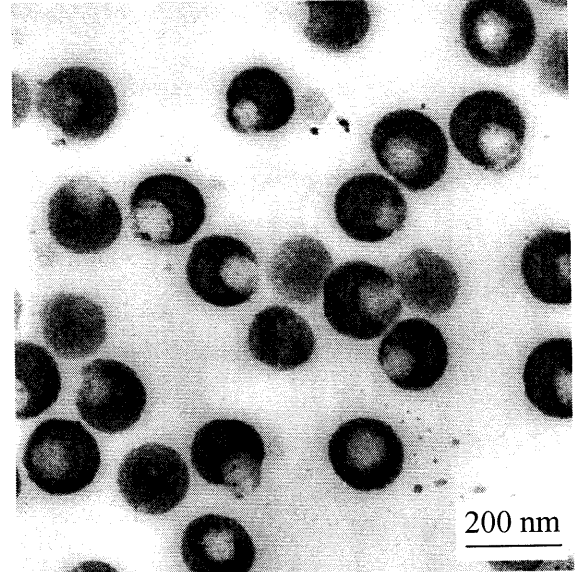


Fig. 5.2.2 TEM differently enlarged micrographs of an undeformed (HSH CS-130-18) RT-PMMA.

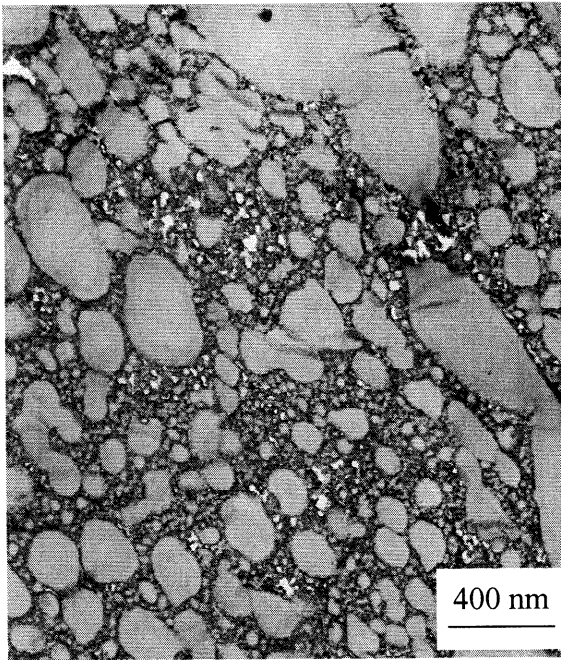
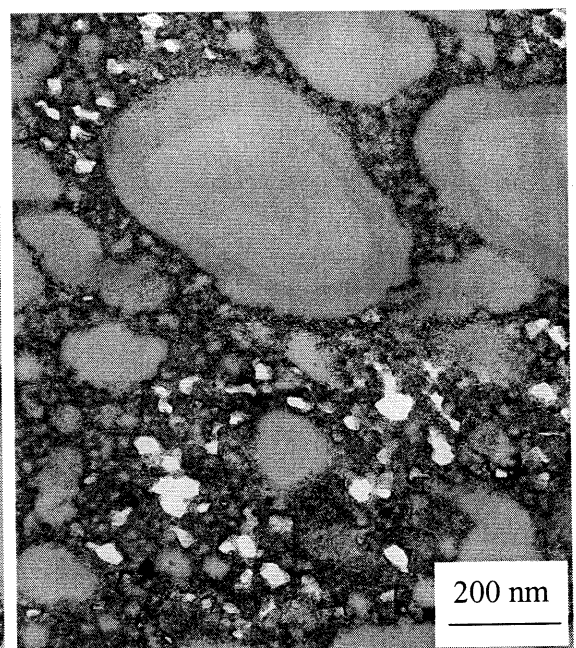


Fig. 5.2.3 TEM differently enlarged micrographs of an undeformed continuous (C8) RT-PMMA.

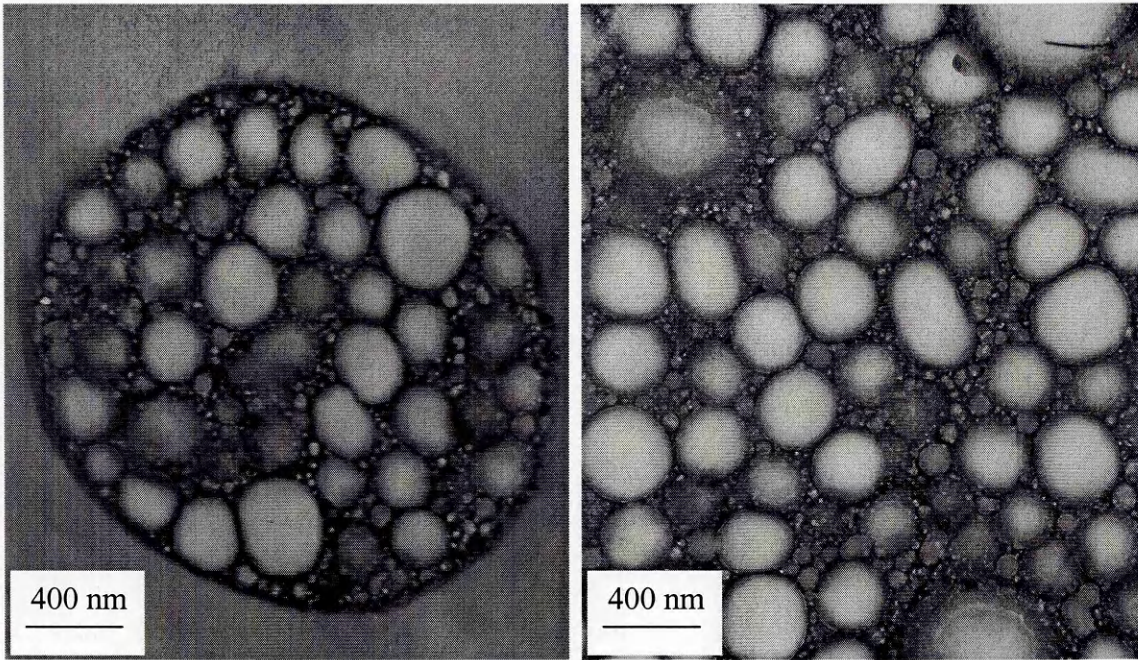


Fig. 5.2.4 TEM micrographs of an undeformed salami (S4-EPDM) RT-PMMA, showing the variety of particle dimensions.

5.2.2. Evidence of cavitation in RT-PMMA

Evidence of cavitation has been hunted essentially in HSH core shell rubber particles. These polymers have been the predominant kind of RT-PMMA materials tested during the current project.

Figure 5.2.5 compares cavitated HSH CS-250-40 RT-PMMA samples, after (a) being pre-strained at about 6% strain, and (b) after cooling to -90°C under a constant tensile stress of 30 MPa. The main differences are not only the level of damage that the materials present in the pictures ((a) shows particle cavitation and craze formation, (b) only particle cavitation), but also the distinct visualisation of voids in the rubber shell. Micrograph (a) was taken at Cranfield University, where the sections were stained before microtoming. It illustrates voids as bright marks, whereas, photo (b), taken at the ICI laboratory (staining after microtoming), presents them as a concentration of black dots in the rubber shell.

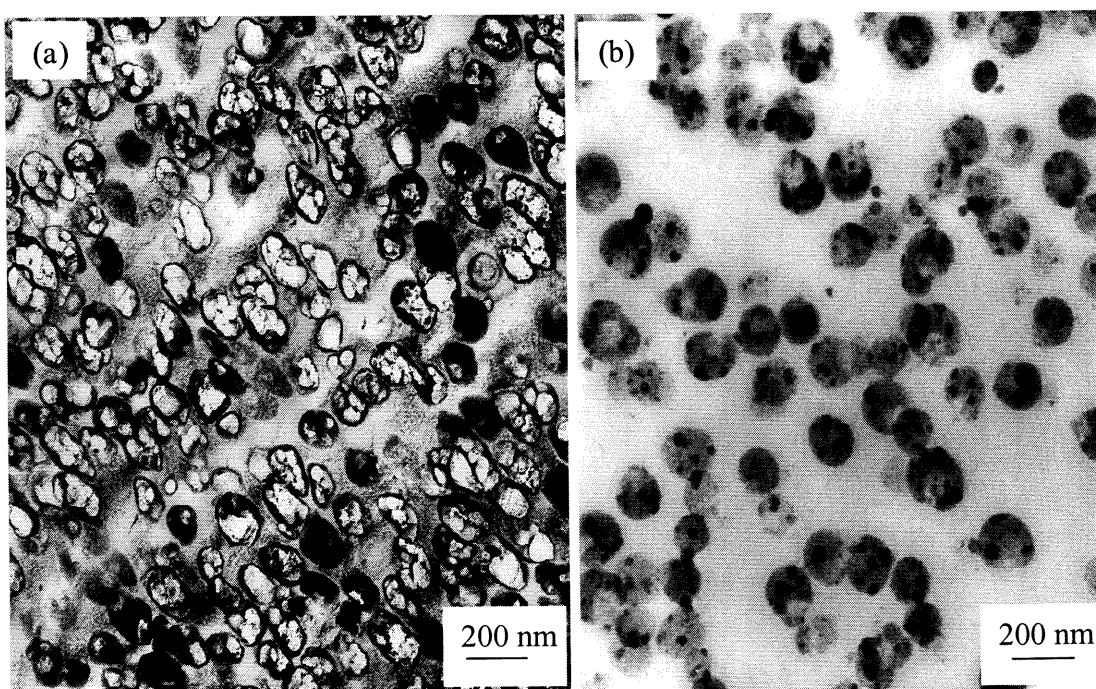


Fig.5.2.5 TEM micrographs of cavitated (HSH CS-250-40) RT-PMMA. Micrographs taken at Cranfield University, after pre-straining at about 6% strain, (a), and at the ICI laboratory after cooling to -90°C under a constant tensile stress of 30 MPa, (b).

The thin dark ‘strings’ in Figure 5.2.6 are considered a proof of rubber fibrillation in core-shell particles, after the specimen has been pre-strained at about 6% strain. Multiple void formation in complex rubber particle morphology has been confirmed also by the energy-balance model development (Chapter 3). Moreover, various authors in the past found TEM evidence of fibrillation in complicated rubber particle morphologies, for example in HIPS with salami particles [Bucknall 2000].

Figure 5.2.7 presents cavitated rubber particles in a pre-strained (below 4%) HSH CS-250-40 RT-PMMA. The holes appear to form a ‘line’ pattern of voided particles.

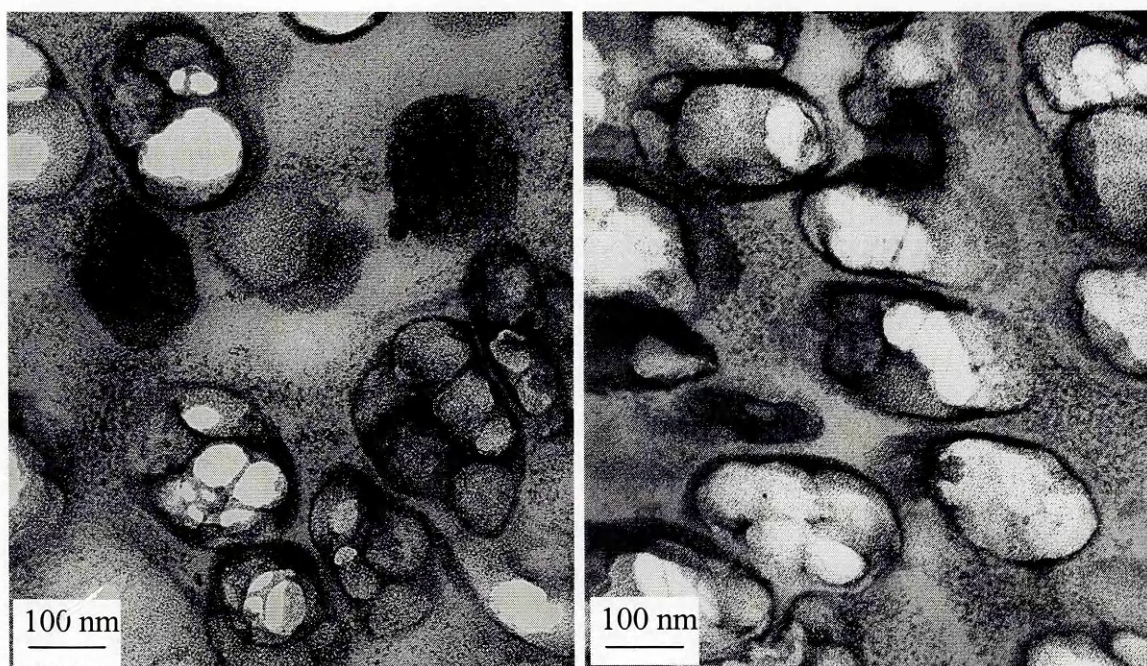


Fig. 5.2.6 TEM micrographs of cavitated and fibrillated (HSH CS-250-40) RT-PMMA specimens pre-strained at about 6% strain.

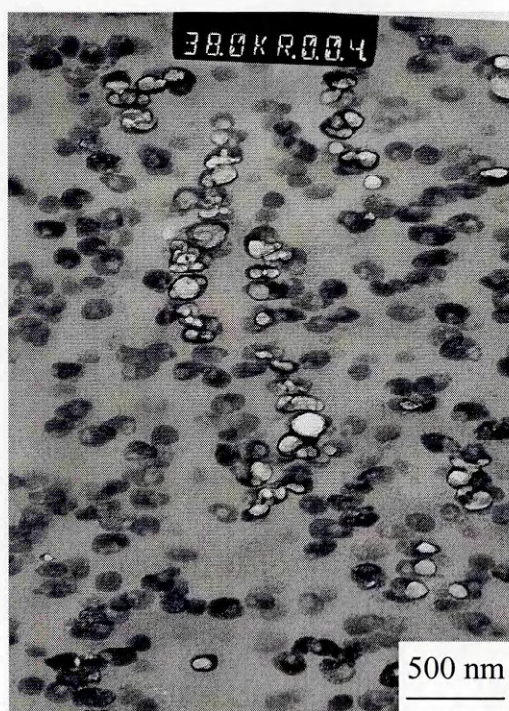


Fig. 5.2.7 TEM micrograph of cavitated particles of a pre-strained (below 4%) (HSH CS-250-40) RT-PMMA.

Figure 5.2.8 reports two micrographs of HSH CS-250-40 RT-PMMA samples after being stretched to yield at different speeds. When the load has been applied at low speed (1 mm min^{-1}), the particles do not present any evidence of cavitation and there is no crazing in the matrix (a). It is suggested that rubber particles at such low loading rates have enough time to deform and to adjust to the stress distribution, so that no major damage occurs, whereas, if the loading rate increases (50 mm min^{-1}), drastic damage (cavitation and crazing) occurs in the material (b). This evidence supports the theory that cavitation is a trigger for plastic deformation in the matrix.

In Figure 5.2.9 HSH CS-250-40 RT-PMMA specimens are compared before (a) and after (b) cooling at -90°C under constant tensile applied stress of 30 MPa. It can be observed that a large amount of cavitation takes place after cooling and stretching have been applied simultaneously. DMTA is the test under investigation here. The specimen during DMTA tests is cooled and a constant static load, below the yield point of the material, is at the same time applied to it.

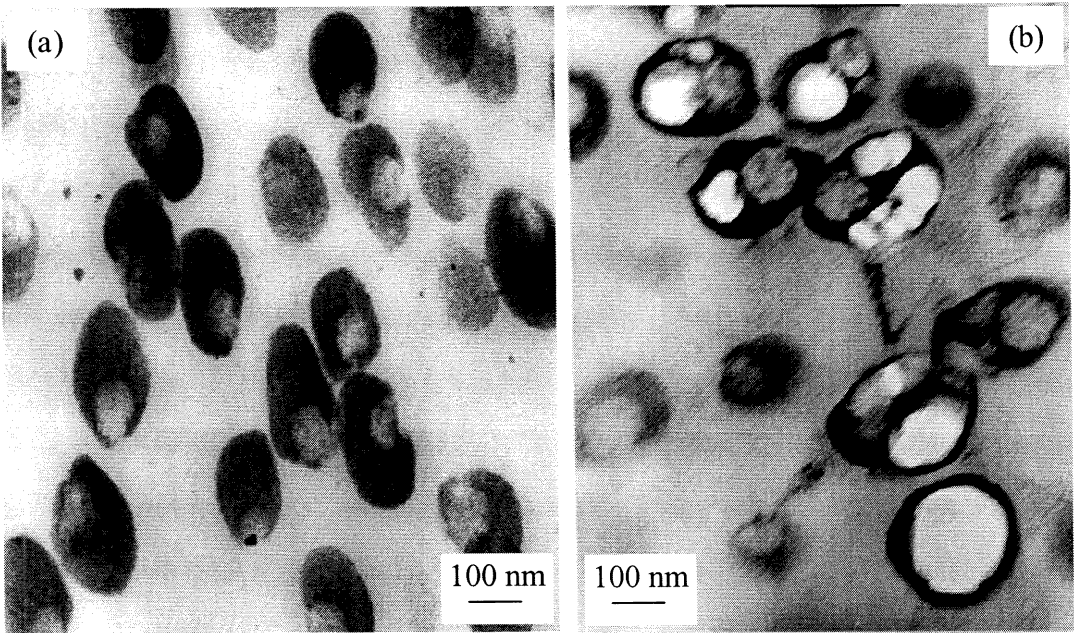


Fig. 5.2.8 TEM micrographs of tensile stretched RT-PMMA samples at applied load rate of (a) 1 mm min^{-1} and (b) 50 mm min^{-1} .

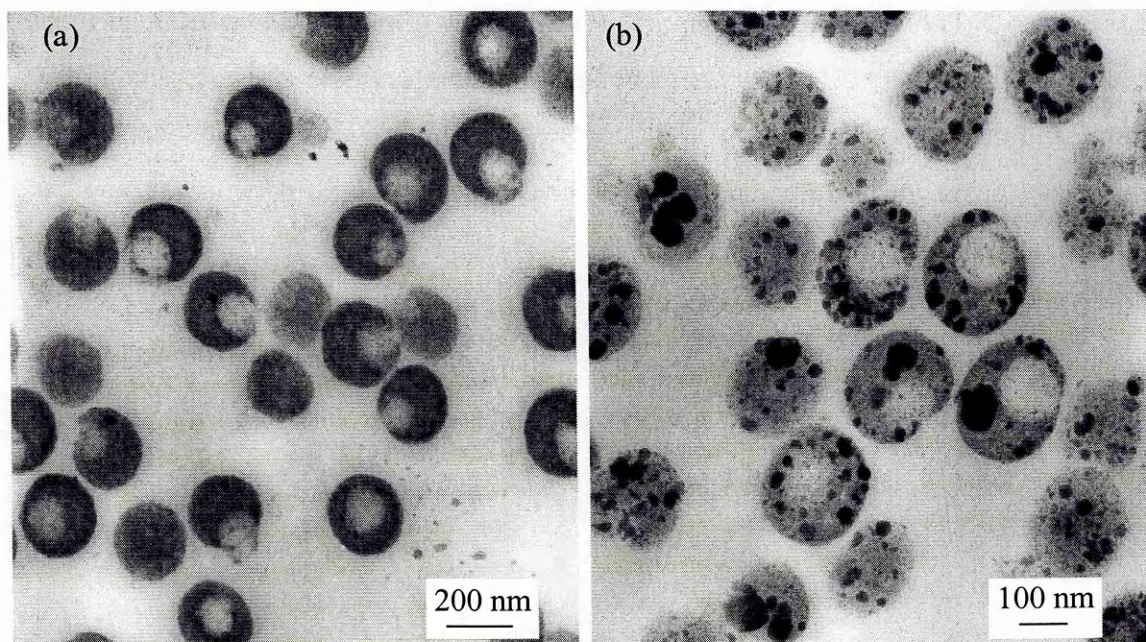


Fig. 5.2.9 TEM micrographs of a (HSH CS-250-40) RT-PMMA samples (a) before and (b) after cooling to -90°C under a constant tensile stress of 30 MPa.

5.3. Evidence of cavitation from dynamic mechanical thermal analysis tests

Dynamic mechanical thermal analysis (DMTA) methods are widely used in the polymer industry because of the improved understanding of DMTA technique and the availability of reasonably priced instruments. DMTA tests give much information on the relaxation processes for polymers, e.g. the modulus and damping factor over a wide range of temperature and frequency. It is also useful in cure studies for thermoset materials and in testing the physical ageing of thermoplastics [Bucknall 2000]. However, DMTA tests have been used during the present project to investigate rubber particle cavitation in multiphase polymers, mainly in RT-PMMA.

In DMTA, it is the sample stiffness and loss that are being measured. The sample stiffness generally depends upon its modulus of elasticity and its geometry or shape. The modulus, defined as the stress per unit area divided by the strain resulting from the applied force, is a measure of the material's resistance to deformation. For polymers, which exhibit time-dependent deformation, data on modulus must be accompanied by information about the time under load or frequency to which they refer. It is for this

reason that DMTA becomes an important instrument of investigation of relaxation behaviour of polymers. The DMTA technique applies a periodic stress or strain to a sample and measures the resulting strain or stress response. Due to the time-dependent properties, the resultant response is out of phase, by the angle δ , with the applied stimulus, as it has been mentioned in Chapter 4. The behaviour of polymers can then be described in terms of the complex modulus (E^*), defined as the instantaneous ratio of the stress/strain, and given by the sum of an in-phase or elastic response (E'), that is the recoverable or stored part of E^* , and an out-of-phase or viscous response (E''), that expresses the irrecoverable or dissipated part of E^* , as shown in the illustrative Figure 5.3.1.

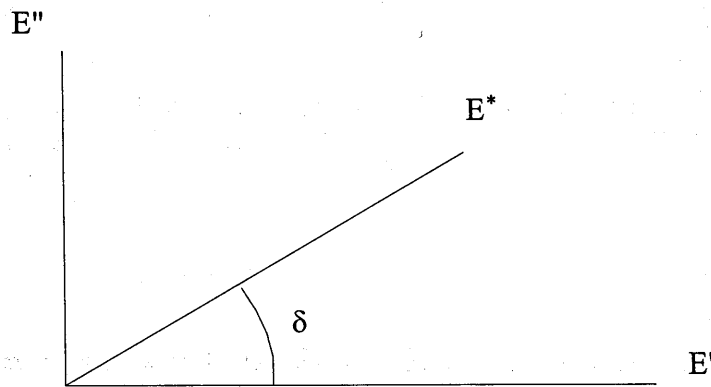


Fig. 5.3.1 Schematic illustration of the relationship between E' , E'' , E^* and δ .

δ is the measured phase lag between the applied stimulus and the response. $\tan \delta$ is called the loss tangent. The phase angle δ between the applied dynamic (sinusoidal) stimulus and the specimen's response rises to a maximum at the α relaxation temperature. A peak in $\tan \delta$ value is observed because the loss modulus (E'') exhibits a peak when the relaxation temperature is approached, while the storage modulus (E') decreases. Typical DMTA test results at 1 Hz constant frequency and 30 MPa uniaxial compressive static load applied on the sample are presented in Figure 5.3.2 for (a) a PMMA and (b) a RT-PMMA (HSH CS-250-40) sample.

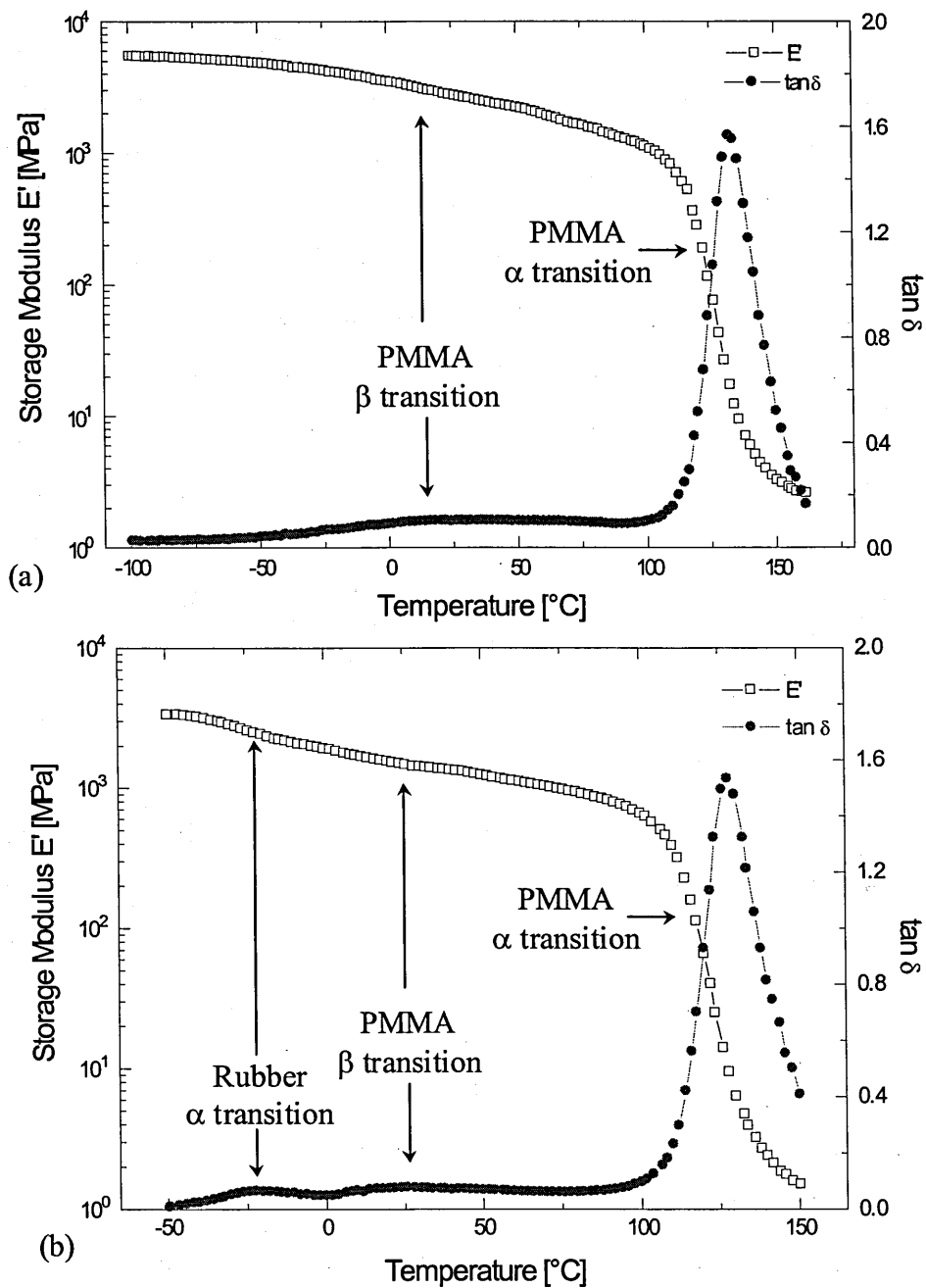


Fig. 5.3.2 Storage modulus and $\tan \delta$ versus temperature for a PMMA, (a), and a RT-PMMA (HSH CS-250-40) sample, (b). The tests were carried out at 1 Hz constant frequency and 30 MPa uniaxial compressive static load applied on the samples.

The storage modulus decreases during the α transition of the rubber at about -25°C (in Figure 5.3.2) and it decreases again during the β transition of the PMMA at around

20°C. It continues to fall gradually up until the α transition of the PMMA, at about 120°C (in Figure 5.3.2), where it drops dramatically. No further loss processes occur until the material decomposes. Primary and secondary transitions are accompanied by a peak in $\tan \delta$ curve. A broad peak indicates the β relaxation of PMMA that interferes with a sharper $\tan \delta$ peak, corresponding to the α relaxation of the rubber. Generally the position of the rubber $\tan \delta$ peak is taken as an indication of the position of the glass transition temperature of the rubber (T_{gr}). A much higher relaxation peak is typical of the primary α transition of PMMA, generally assumed as the position of the PMMA glass transition temperature (T_{gPMMA}). Figure 5.3.3 represents the two $\tan \delta$ peaks corresponding to (a) the β relaxation of the PMMA and (b) the β relaxation of the PMMA coupled with the α relaxation of the rubber in a RT-PMMA (S4-EPDM, Table 4.1.1 Chapter 4).

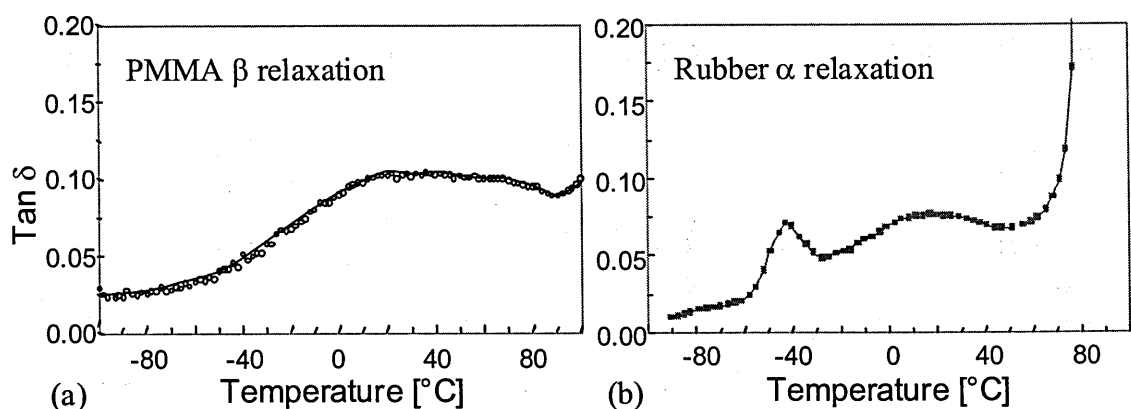


Fig. 5.3.3 $\tan \delta$ versus temperature for a PMMA (a), and a RT-PMMA (S4-EPDM) sample (b). The tests were carried out at 1 Hz constant frequency and 10 MPa uniaxial compressive static load applied on the samples.

The assumption to locate the position of the glass transition temperature at the peak of $\tan \delta$, must take into account many variables of the system that influence that position. For example, the frequency at which the stimulus is applied; the faster the stimulus is applied the less time the molecules have to respond to it, and the peak shifts to higher temperature. Even the applied load will effect $\tan \delta$ location; the higher is the pressure applied on the sample, the less is the space for molecules to move so that again $\tan \delta$ peak should shift to higher temperature [Ferry 1980]. The temperature at which the

rubber $\tan \delta$ peak in a RT-PMMA reaches a maximum is affected by the sloping baseline of the β relaxation in the PMMA matrix. Therefore, the ‘absolute’ position of the rubber $\tan \delta$ peak (assuming that other variables of the system remain unchanged during different tests) is obtained subtracting the apparent β -PMMA $\tan \delta$ sloping baseline from the test results, as shown in Figure 5.3.4.

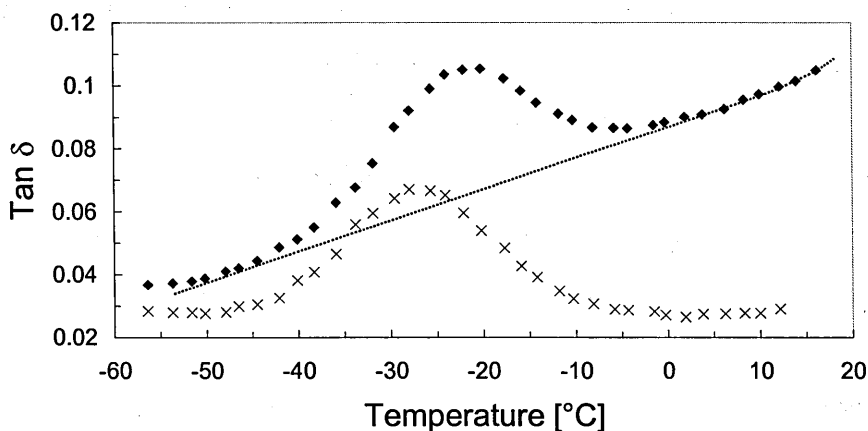


Fig. 5.3.4 (♦) rubber $\tan \delta$ peak result for a RT-PMMA (HSH CS-250-40) from a DMTA test. (x) the same peak after the subtraction of the β -PMMA $\tan \delta$ peak sloping baseline (---).

Since the scope of the present study is to compare the rubber $\tan \delta$ peak shift with applied static load, the values considered for the position of the peaks are simply taken from test results (maintaining the frequency constant).

During the present study, the DMTA method was adopted mainly to investigate cavitation in RT-PMMA. The adoption of DMTA to detect cavitation is based upon earlier work by Lin et al. [1998], in which dynamic mechanical tests were used to detect cavitation in the rubber particles of a standard HIPS. Their analysis is based upon the simple principle that the temperature of the rubber’s α relaxation peak is affected by the loading conditions imposed on the rubber. DMTA tests were conducted at constant frequency of 1 Hz, at increasing temperature from well below the rubber T_{gr} to room temperature and at constant static load applied. The samples were, thus, subjected to a mechanical load in addition to thermal stresses. Shifts in the rubber $\tan \delta$ peak,

considered as molecular energy dispersion mechanisms, were monitored at different static load applied on the samples. Because the rubber α relaxation is affected by the loading condition on the rubber, a comparison between the $\tan \delta$ peaks measured from tests made at different applied load was then established. In principle, by increasing the compressive loading, and so increasing the hydrostatic pressure on the rubber particles, the rubber density increases and the rubber free volume decreases to cause the α relaxation to happen at higher temperatures. This is because the molecules need more energy to overcome the intermolecular forces for chain vibration and rotation [Ferry 1980]. On the other hand, under tensile loading conditions the α relaxation peak temperature is expected to occur at lower temperature because the intermolecular forces are reduced due to the increase in intermolecular distance. Figure 5.3.5 reports DMTA data for a RT-PMMA (HSH CS-127-18) under increasing uniaxial compression loading at 10, 30 and 40 MPa, and under uniaxial tensile loading at 30 MPa. It can be noted that $\tan \delta$ peak shifts clearly to higher temperature while increasing compressive loading and it shifts to lower temperature under tensile loading.

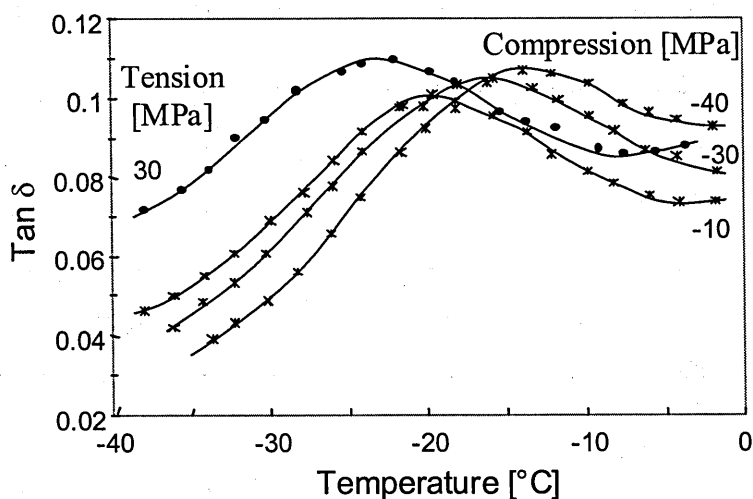


Fig. 5.3.5 Dynamic loss curves for RT-PMMA (HSH CS-127-18) specimens tested at 1 Hz constant frequency, and under different superimposed uniaxial stresses of 30 MPa (tension) and -10, -30, -40 MPa (compression). Under compression the secondary loss peak moves to higher temperatures, whereas under tension the peak shifts to lower temperatures.

The following materials were investigated using DMTA under uniaxial compressive and tensile loading condition.

5.3.1. RT-PMMA

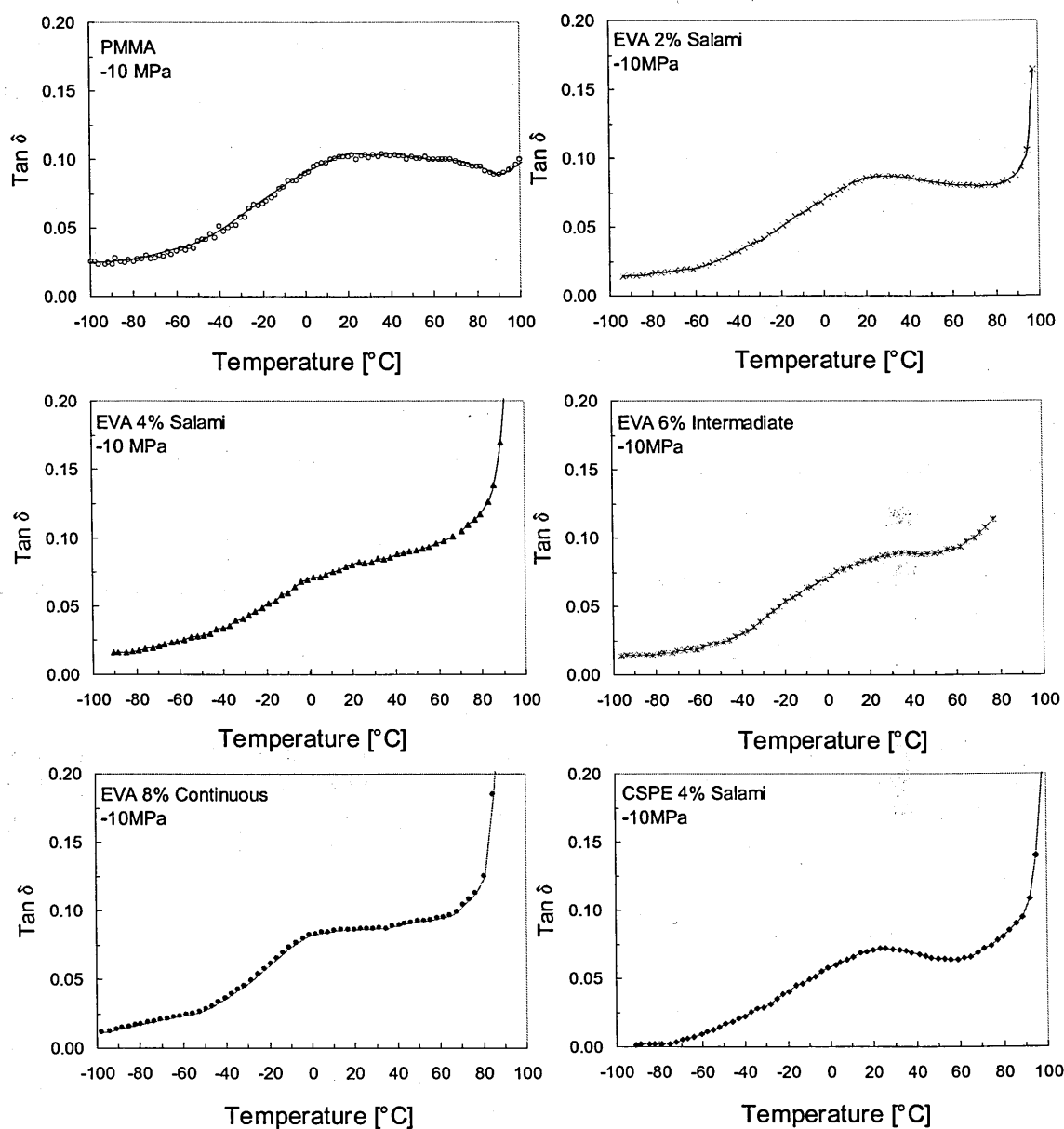


Fig. 5.3.6 Comparison between DMTA tests made on PMMA and RT-PMMA materials at low rubber content, showing the β -PMMA transition peak for PMMA and the β -PMMA transition peak coupled with the rubber tan δ peak for various types of RT-PMMA.

Rubber relaxation of various compression moulded RT-PMMA samples was investigated using DMTA under applied compression stress of 10 MPa. Some of the RT-PMMA (S2-EVA, S4-EVA, I6-EVA, C8-EVA, S4-CSPE, Table 4.1.1 Chapter 4)

the rubber content was too low to show a clearly distinct $\tan \delta$ peak. As shown in Figure 5.3.6, the rubber $\tan \delta$ peak is hidden by the broad β -PMMA relaxation peak and no distinction can be made.

However, a RT-PMMA (S4-EPDM) with a low rubber content showed a distinct rubber $\tan \delta$ peak at about -40°C . Under 10 MPa static load applied on the specimen, first in compression and then in tension, the rubber $\tan \delta$ peak presented a temperature shift of approximately 3°C . No further analysis was carried out on these materials. Figure 5.3.7 reports a comparison between 10 MPa compressive and tensile stresses applied on S8-EVA and S4-EPDM. No significant changes or distinct peaks can be seen in the S8-EVA results, even if S8-EVA had the same rubber particle morphology (salami) and higher rubber contents (8% in volume) than the S4-EPDM (4% in volume). The only known difference was in the type of rubber.

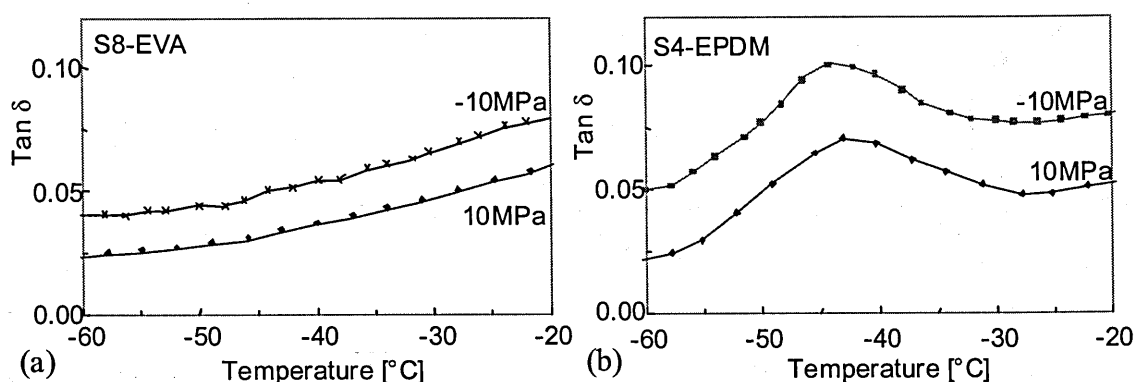


Fig. 5.3.7 DMTA results at applied uniaxial stress in compression (-10 MPa) and tension (10 MPa) for (a) S8-EVA and (b) S4-EPDM.

A small number of tests have been carried out on injection moulded hard-soft-hard core-shell (HSH CS) RT-PMMA samples having different rubber particle diameters ranging from 127 to 203 nm and 18 % wt. rubber content. The tests were conducted under 10 and 20 MPa applied stresses. A shift of roughly 5°C in the rubber $\tan \delta$ peak temperature was observed by increasing the rubber particle sizes (Figure 5.3.8). Increase in rubber particle size produces a decrease in rubber relaxation temperature.

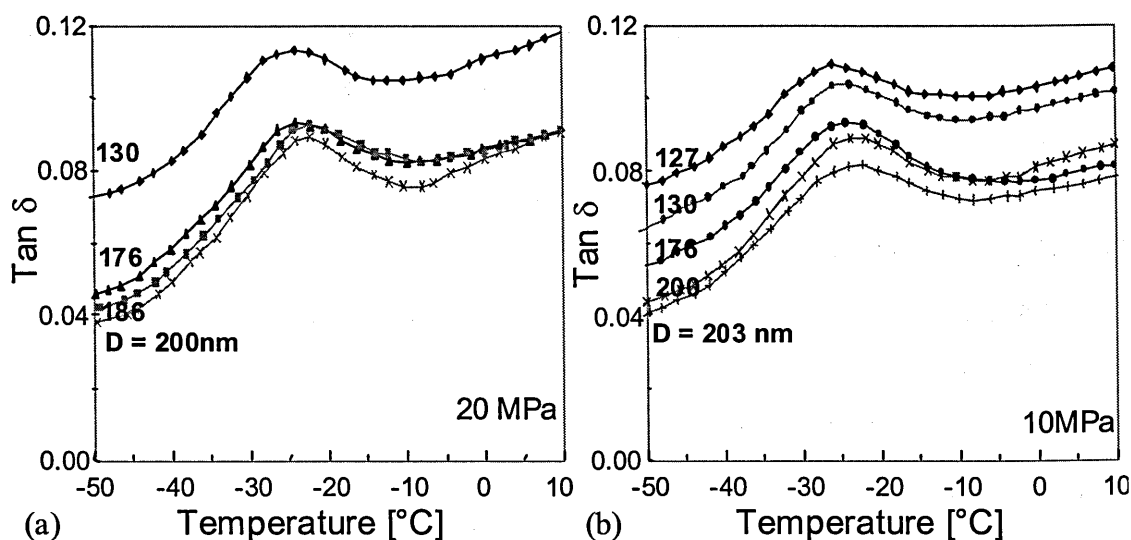


Fig. 5.3.8 Tan δ peak versus temperature plot for RT-PMMA (a) HSH CS-130-18, HSH CS-176-18, HSH CS-186-18, HSH CS-200-18 DMTA tests under 20 MPa tensile applied stress, and (b) HSH CS-127-18, HSH CS-130-18, HSH CS-170-18, HSH CS-200-18, HSH CS-203-18 DMTA tests under 10 MPa tensile applied stress.

The HSH CS RT-PMMA containing rubber particle of 127 nm diameter was tested under a full range of applied compressive and tensile stresses (from 40 MPa compression to 35 MPa tension, equivalent to a variation of 25 MPa hydrostatic pressure), as illustrated in Figure 5.3.9. This material exhibits a relationship between the rubber α relaxation temperature and applied pressure essentially linear, over the entire static loading range investigated. Higher tensile stresses produced in the specimens crazing and yielding. The total peak shift of 11°C results in a pressure dependence shift of 0.44°C/MPa.

A linear behaviour is expected from a one phase polymer or a multiphase polymer where both phases are intact and well bonded one to the other. It is possible that some rubber toughened plastics undergo neither cavitation nor debonding. In these cases, the pressure-temperature dependence of the rubber α -relaxation peak is linear over the entire test range of uniaxial static loads [Bucknall et al. 2000b], signifying that the rubber remains intact and firmly bonded to the matrix. Similar behaviour can be observed in various toughened plastics, for example ABS (Figure 5.3.18), rubber-toughened epoxy and rubber-toughened PC (Figure 5.3.17) [Ayre 1999]. Therefore, if no voids are present in the rubber phase or debonding is not occurring between rubber

and matrix, the stresses applied are fully transmitted and the density of the rubber changes on application of superimposed axial stresses, causing a linear shift in the glass transition of the rubber. Under compression the relaxation occurs at higher temperatures. Conversely, under superimposed tension the loss peak shifts to lower temperatures, as shown in Figure 5.3.5 and 3.9 for HSH CS-127-18.

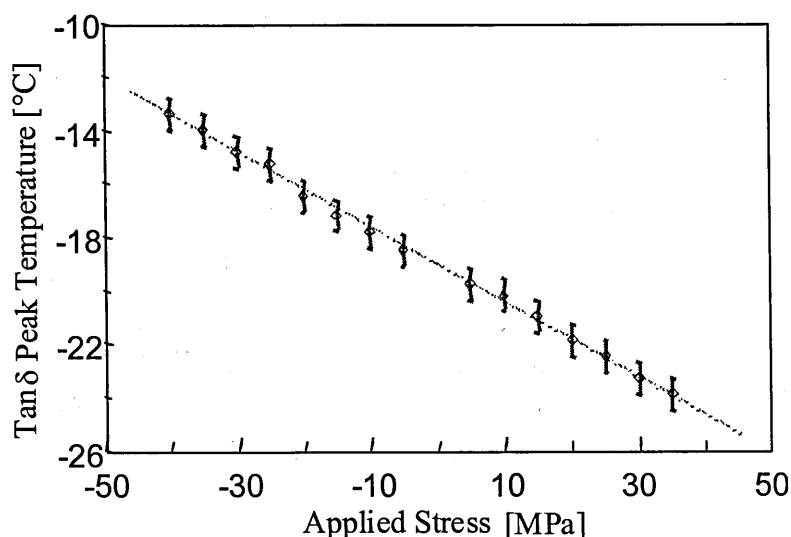


Fig. 5.3.9 Effects of superimposed static loading upon the temperature of the secondary loss peak in RT-PMMA(HSH CS-127-18) with core-shell particles of 127 nm diameter. The pressure-temperature dependence of the rubber α -relaxation peak is linear over the entire test range of uniaxial static load. Showing scatter bars.

Most of the DMTA tests were performed on compression moulded RT-PMMA samples with hard-soft-hard core-shell rubber particle morphology, rubber particle diameter of about 250 nm and rubber content of 40% in weight (HSH CS-250-40). Under applied compressive stresses, tests done on different specimens were very reproducible (Figure 5.3.10a), showing an approximately linear pressure dependence of the rubber relaxation on applied stress (Figure 5.3.12). On the other hand, under applied tensile stresses, the test results were more scattering and the temperature of the $\tan \delta$ maximum varies from specimen to specimen (Figure 5.3.10b). Sometimes, under tension, the rubber $\tan \delta$ peak presents a splitting in two, as shown in Figure 5.3.11.

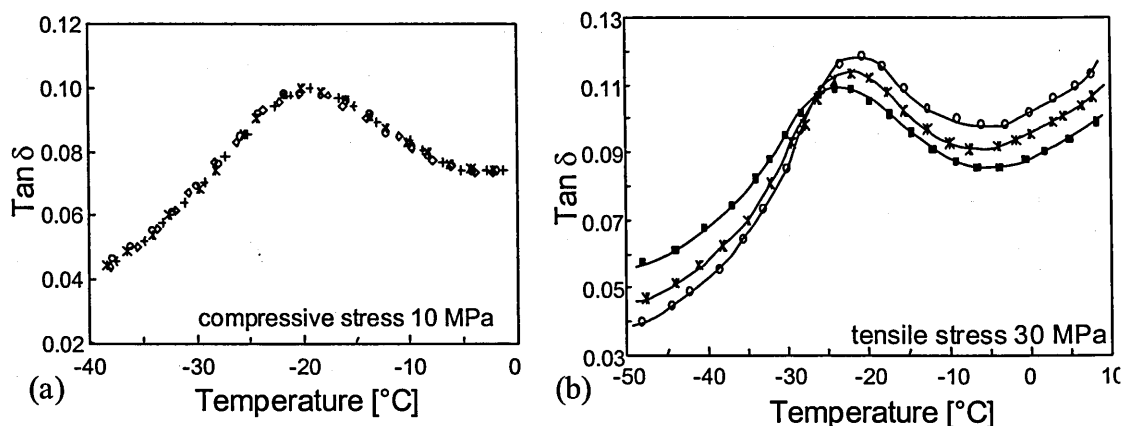


Fig. 5.3.10 Four different samples of RT-PMMA (HSH CS-250-40) tested under uniaxial compression (10 MPa), (a), and 3 different samples tested under uniaxial tension (30 MPa), (b).

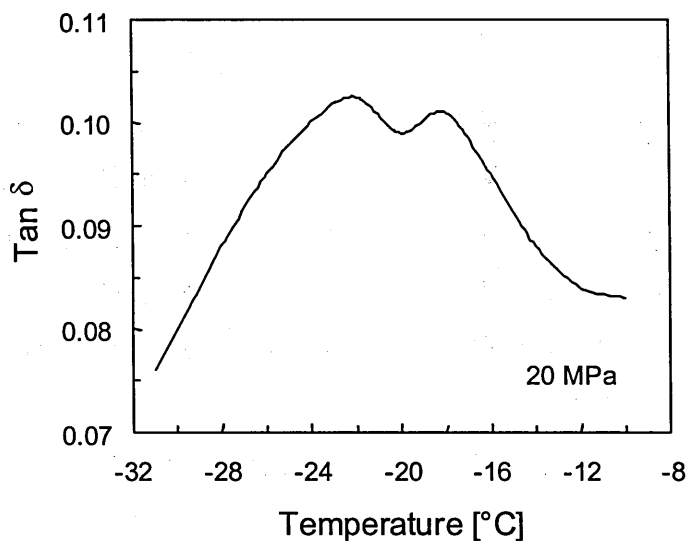


Fig. 5.3.11 Splitting of the low temperature loss peak under a superimposed axial tensile loading of 20 MPa due to incomplete cavitation of the rubber in RT-PMMA (HSH CS-250-40).

Under applied compressive static stresses from 40 to 5 MPa (a range of 12 MPa in hydrostatic pressure) $\tan \delta$ peak temperature shifts 6°C , resulting in a pressure dependent shift of $0.5^{\circ}\text{C}/\text{MPa}$ (Figure 5.3.12). However, under applied tensile stresses from 10 to 30 MPa, the rubber α relaxation turned out to be scattering. Some of the peaks lay at a constant temperature insensitive to increased tensile stresses, while others peaks were spread out at higher temperatures. Previous authors may have considered

this variability to be the result of experimental error and therefore unimportant. It is now believed that the difference in variability from tension to compression is due to changes in the properties of the material on application of tensile stress.

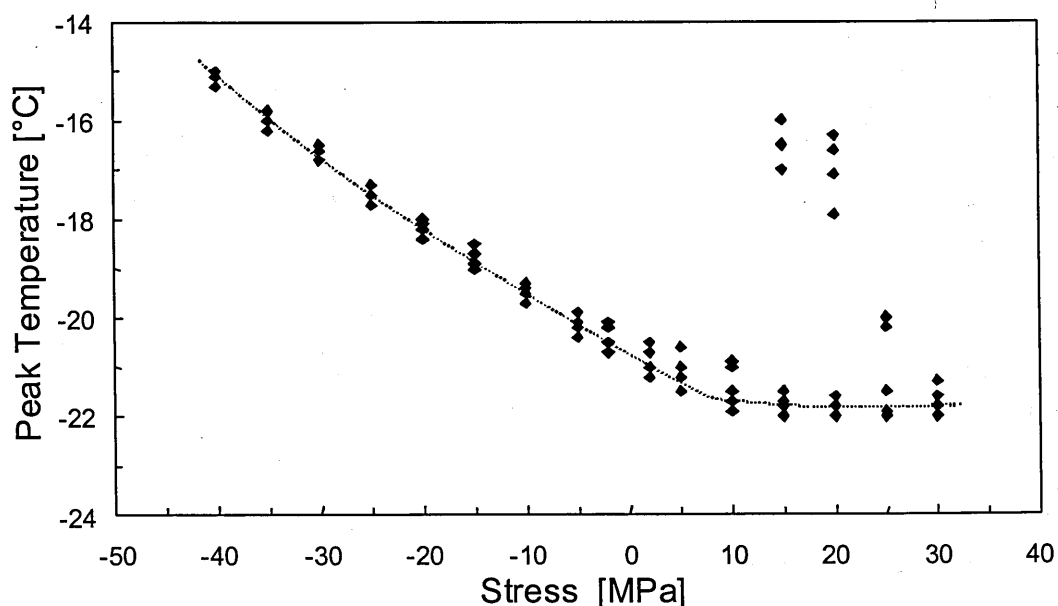


Fig. 5.3.12 Effects of superimposed static loading upon the temperature of the secondary loss peak in RT-PMMA(HSH CS-250-40) with core-shell particles of 250 nm diameter. The low temperature peak shows a scatter from specimen to specimen under uniaxial tensile stress.

The case where the pressure-temperature dependence of the α -relaxation peak is non-linear over the test range of uniaxial static tensile load is the one of major interest in this work. RT-PMMA with core-shell rubber particles 250nm in diameter is an example of a material exhibiting this behaviour.

In order to characterise this change in behaviour, dynamic loss data for different specimens, all tested at the same superimposed stress level, were compared at -20°C . The reason for choosing this temperature is that -20°C is close to T_{α} for all specimens, although in only a few cases does T_{α} lie exactly at -20°C . The results of this comparison are illustrated in Figure 5.3.13, which emphasises the contrast in dynamic mechanical behaviour between specimens tested in compression and specimens tested in tension.

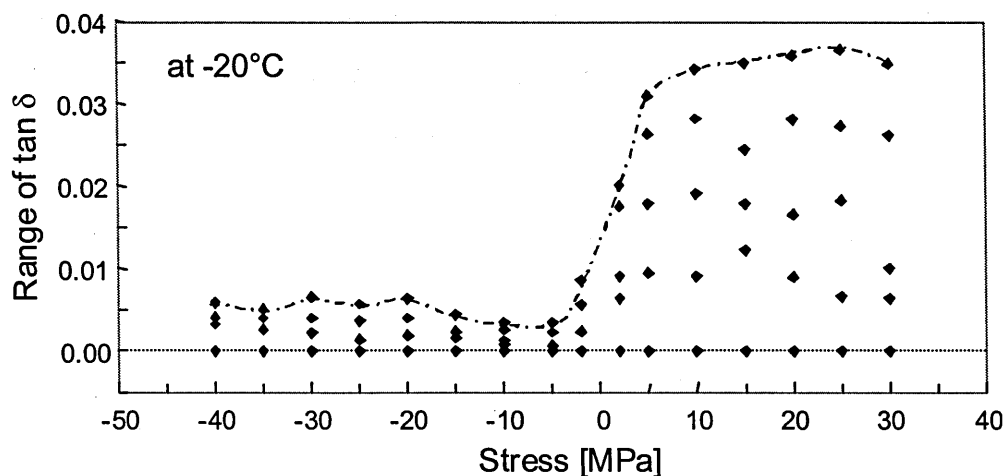


Fig. 5.3.13 Effects of superimposed static stresses upon the variability of the loss peak, expressed as the difference between the highest and lowest values of $\tan \delta$, in sets consisting of five specimens each, at -20°C . RT-PMMA (HSH CS-250-40) (from Bucknall et al. 2000b)

The variability observed above is in contrast to the consistency observed in loss curves for HIPS by Lin et al. [1998] and for RT-Nylon by Ayre [1999] under tensile loading: for these materials T_α was independent of tensile stress, with no indication of specimen-to-specimen variability.

A similar phenomena, as the split into two of the loss peak (Figure 5.3.11) observed under superimposed tensile stress, was also reported by Morbitzer et al. [1982] and Humme et al. [1976] in ABS. It is suggested that the two peaks correspond to the presence of two distinct populations of rubber particles, revealing different levels of cavitation, and therefore different stresses and strains in the rubber phase [Bucknall et al. 2000b]. The first loss maximum, on the low temperature side of the double peak, could be due to intact particles, which are able to sustain the load. Morbitzer et al. [1982] attributed the second maximum to debonded, and therefore unloaded particles, but in the light of more recent work [Bucknall et al. 2000b] it is more possible that at least some of the observed shifts are due to internal, complete or partial, cavitation of the rubber phase.

It is now a little clearer why the dynamic mechanical behaviour of some RT-PMMA studied during the present thesis is so variable when static tensile stresses are superimposed upon the dynamic loads required for the measurements.

DMTA test results on similar compression moulded RT-PMMA (HSH CS-250-25) samples, with a lower rubber content (25% wt instead of 40%), presented an analogous behaviour. The pressure dependence of the rubber peak was investigated just after moulding, after annealing, after yielding and after yielding and annealing. Different pre-treatments influenced the rubber α relaxation behaviour under applied compressive and tensile stresses (from 40 MPa compression to 30 MPa tension), as shown in Figure 5.3.14. After moulding and after annealing the material presented an approximately linear behaviour under applied compression, whereas the behaviour in tension featured a low correlation with the applied stress. After tensile yielding the scattering increased, and double peaks appeared even under applied compression. Annealing after yielding had the effects of reducing the spreading in peak temperature values.

These results suggest that in Figures 5.3.12 and 5.3.14 the series of dispersed peaks above the approximately linear behaviour following the compression data, indicate a broad distributions of internal stresses in the rubber phase. It has been advanced the hypothesis [Bucknall et al. 2000b] that scattered rubber $\tan \delta$ peaks, especially at higher tensile stresses or after tensile yielding (Figure 5.3.14), could be due to fibrils of rubber that are differently stretched between core and matrix, and some are approaching their breaking point. According to this interpretation, the peaks at higher temperature in specimens subjected to 15 MPa tensile stress or more, are due either to less highly stretched fibrils or to partially relaxed intact rubber layers in partially cavitated shells. The total volume of intact rubber regions of this kind in any given specimen will necessarily decrease as overall tensile strains increase, thereby increasing the local volume strains in individual particles, so that fibrillation spreads throughout the materials. Evidence of double peaks and scattering in the compression data region of yielded polymers is attributed to the presence of small voids that open up under the dilatational stresses, that the rubber still undergoes under compressive applied loading.

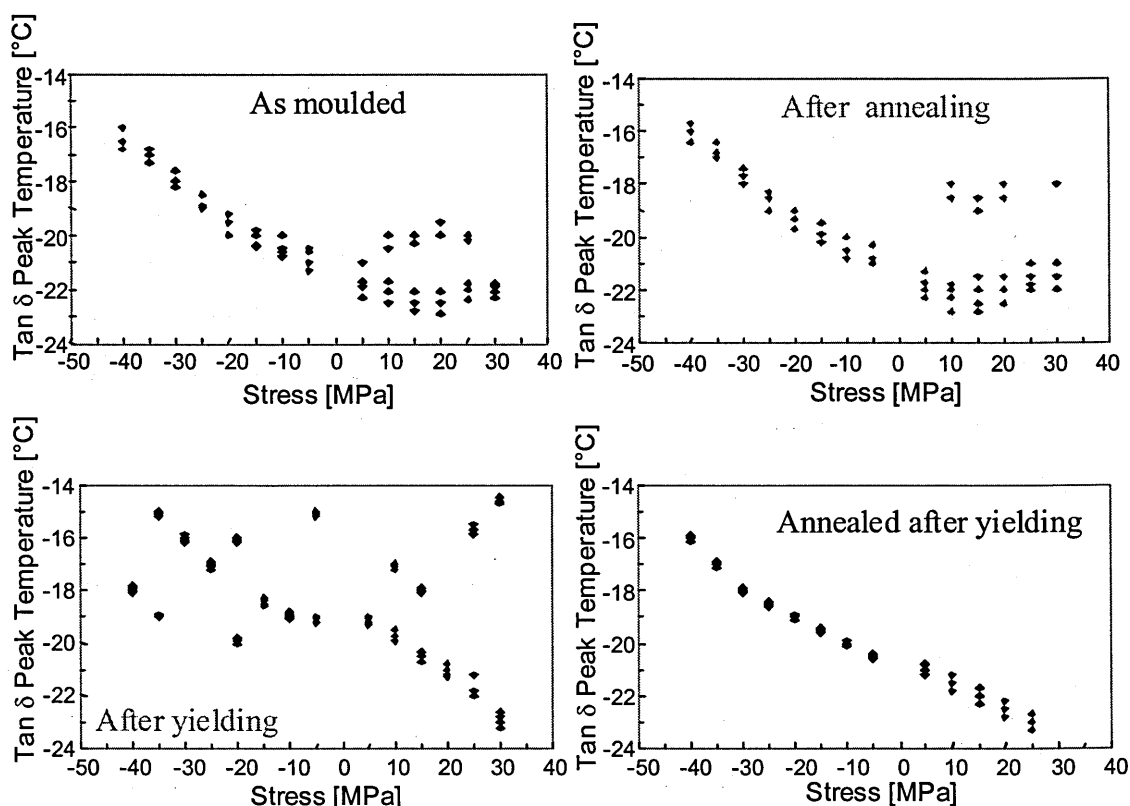


Fig. 5.3.14 Effect of applied stress on the $\tan \delta$ peak temperature for the rubber phase in RT-PMMA (HSH CS-250-25) after different treatments.

5.3.2. Rubber

Vulcanised butyl rubber was tested using DMTA to characterise the amount of $\tan \delta$ peak shift under increasing applied tensile strain. Tests were carried out at 1 Hz constant frequency and uniaxial constant tensile strain ranging from 30% to 175%. Plots of $\tan \delta$ versus temperature show, in Figure 5.3.15, clear distinct peaks in the temperature range from -35°C to -60°C . Figure 5.3.16 reports $\tan \delta$ peak temperature versus uniaxial tensile strain, showing a difference of 140% uniaxial strain resulting in peak shift of 25°C .

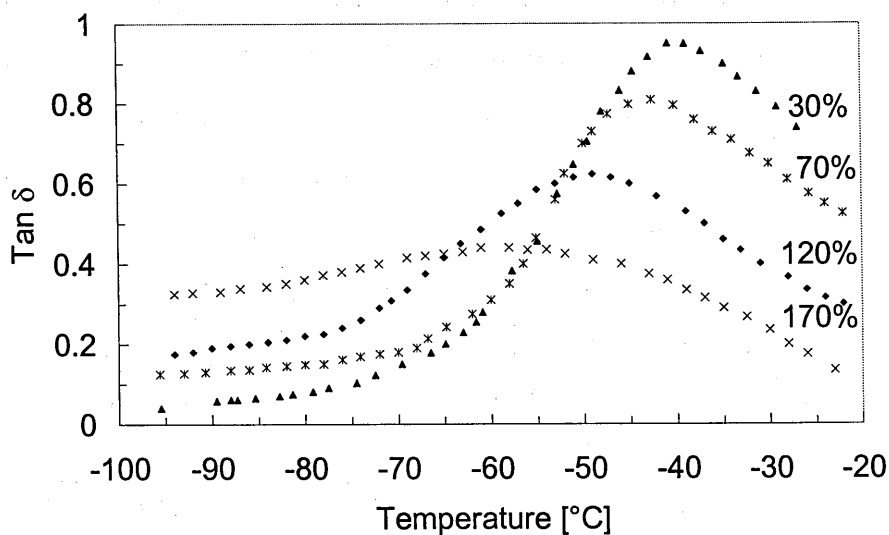


Fig. 5.3.15 Shift of $\tan \delta$ peak for vulcanised butyl rubber with increasing tensile strain.

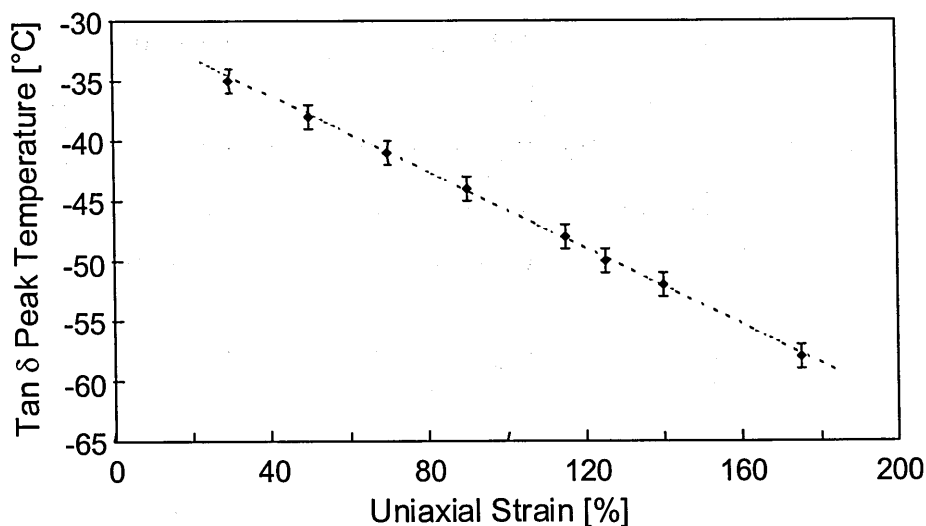


Fig. 5.3.16 Relationship between loss peak temperature and tensile strain for vulcanised butyl rubber. Showing error bars.

5.3.3. PC-PB and ABS

Samples from injection moulded bars of polycarbonate toughened with polybutadiene rubber particles (about 200 nm diameter) (PC-PB) were subjected to DMTA tests. A small number of repeat measurements were made. The main issue was to investigate the

instrumental accuracy in DMTA tests. Rubber α relaxation peaks were consistent with DMTA results from Ayre [1999] on the same PC-PB material. Test results gave a linear behaviour between applied stress and rubber $\tan \delta$ peak over the loading range from 40 MPa uniaxial compression to 40 MPa uniaxial tension stress. Rubber $\tan \delta$ peaks plotted against temperature present sharp and distinct peaks in Figure 5.3.17a. The shift in $\tan \delta$ peak temperature over the entire loading range is presented in Figure 5.3.17b. It can be noted that a difference of 80 MPa uniaxial static loading (equivalent to 27 MPa hydrostatic pressure) results in peak shift of 7°C that can be associated to a pressure dependent shift of 0.26 °C/MPa.

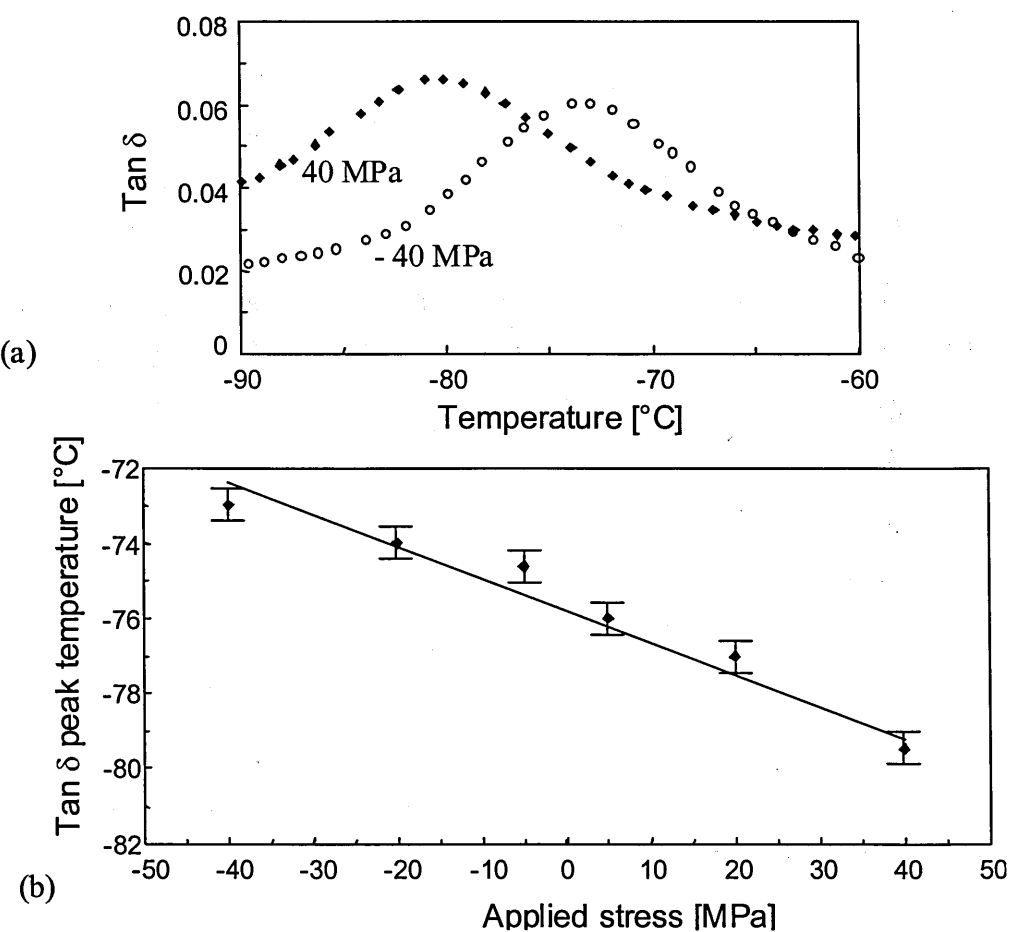


Fig. 5.3.17 PC-PB rubber α relaxation peaks under different static loading conditions, 40 MPa uniaxial tensile stress ($\blacklozenge$) and 40 MPa uniaxial compressive stress ($\circ$), (a). Rubber α relaxation peak temperature shifts with applied static load (b). Showing scatter bars.

Samples from compression moulded plaques of transparent acrylonitrile-butadiene-styrene (ABS), containing 25% in volume of PB rubber particles (about 100 nm particle diameter) were tested using the DMTA. Even in this case the rubber α relaxation peaks were found coherent with the results from Ayre [1999]. Figure 5.3.18a presents DMTA results for 40 MPa applied uniaxial compression and tension. The plot of $\tan \delta$ peaks against applied stress gave an approximately linear behaviour over the whole loading range from 40 MPa uniaxial compression to 40 MPa uniaxial tension stress, as shown in Figure 5.3.18b. In this case a difference of 27 MPa hydrostatic pressure results in peak shift of 9°C, i.e. a pressure dependent shift of 0.33 °C/MPa.

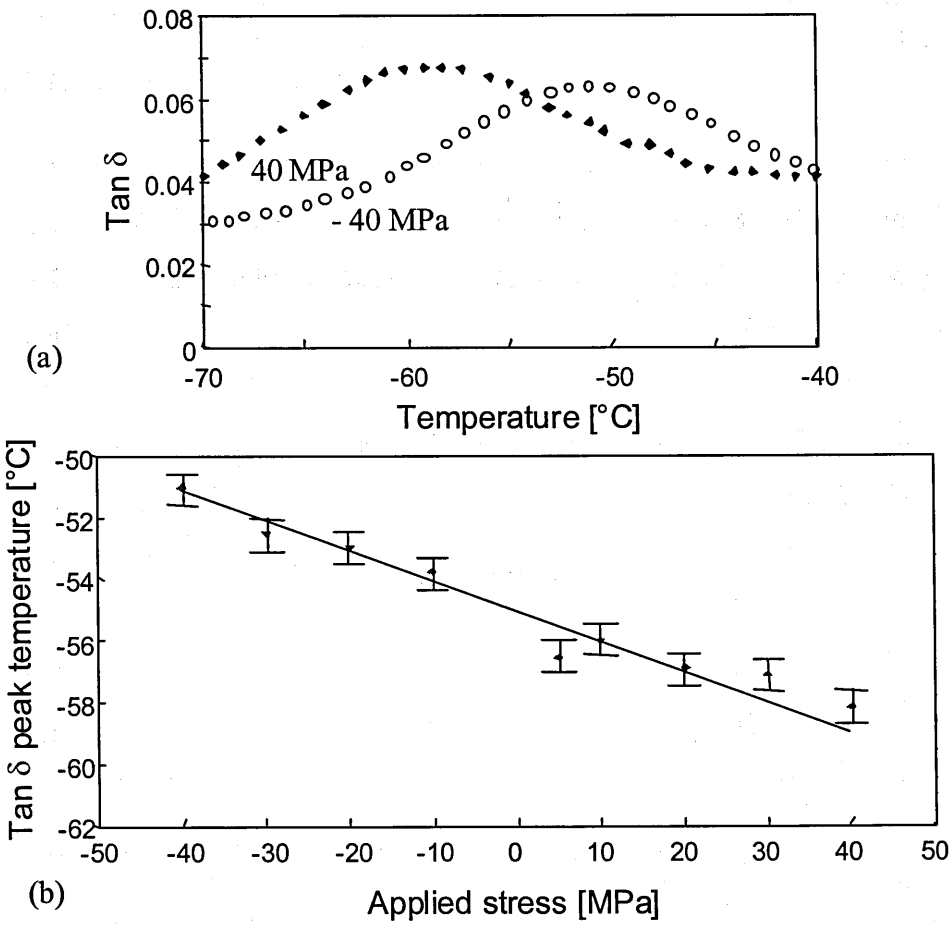


Fig. 5.3.18 ABS rubber α relaxation peaks under different static loading conditions. (a) Data obtained under 40 MPa uniaxial tensile stress ($\blacklozenge$) and 40 MPa uniaxial compressive stress ($\circ$). The minus sign indicates compression stresses. (b) Shifts of the $\tan \delta$ temperature peak with applied stress, showing error bars for the difficulty in indentifying the exact position of each peak.

5.3.4. POM

A semi-crystalline polyoxymethylene (POM) was studied to support DMTA as a valuable technique to investigate cavitation in multiphase materials. A clearly resolved peak was found in the range -60°C to -70°C , for the amorphous phase [Brandrup and Immergut 1989]. The plot of $\tan \delta$ and storage modulus versus temperature is presented in Figure 5.3.19.

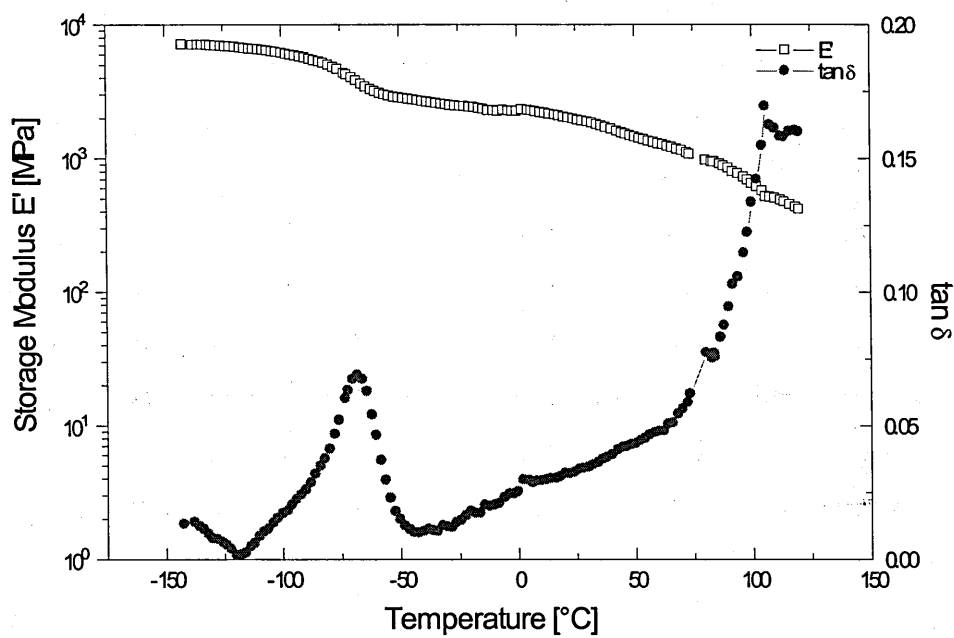


Fig. 5.3.19 Storage modulus and $\tan \delta$ versus temperature for a POM sample. The tests were carried out at 1 Hz constant frequency and 30 MPa uniaxial compressive static load applied on the samples.

The results for a full range of tests carried out at different applied stress are graphically presented in Figure 5.3.20. A change in slope of the loss peak versus stress curve is observed as the superimposed stress varies from compression to tension. This case could be considered as a particular case of the situation described for the RT-PMMA (HSH CS-250-40 and HSH CS-250-25). Figure 5.3.20 shows a little scatter under superimposed tension, but a drastic change in behaviour between compression and tension. In compression, the loss peak temperature is a strong function of the applied

stress, whereas in tension the slope is much lower. The discontinuity occurs near 0 MPa applied stress. However, this pattern of behaviour cannot be attributed to instrumental problems, because several other multiphase materials give a linear relationship with no discontinuity, as presented above(Figure 5.3.9).

To explain the discontinuity it has been suggested that the combination of thermal contraction stresses and tensile loading are enough to cause cavitation in the rubbery, non-crystalline phase of POM. The cavitation process will leave domains of rubbery material in which the tensile stresses are reduced. Nevertheless, the data show that the application of tensile stress to the cavitated domains produces a downward shift in loss peak temperature. It has been proposed that the soft material remains mechanically connected to the adjacent crystalline material in these domains (as in crazes), and thus responds to tensile loading [Bucknall et al. 2000b]. In this material, attempts to obtain evidence of void formation using TEM have so far been unsuccessful.

A similar pattern of behaviour is to be expected in other semi-crystalline polymers, and these experiments on POM might provide an insight into the deformation and fracture of all semi-crystalline polymers. However, many of them (e.g. PE) are more difficult to study using this approach because of their low yield stresses or very low T_{α} s.

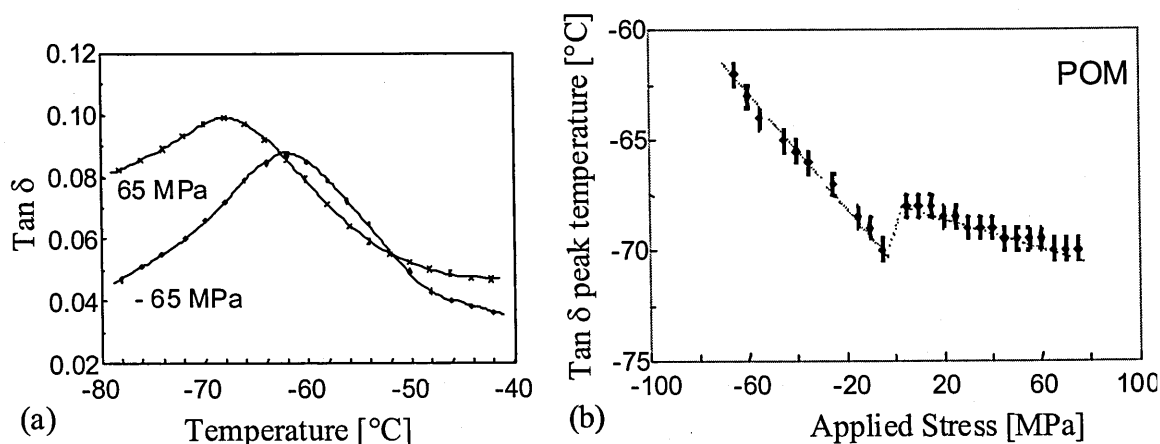


Fig. 5.3.20 Loss peaks for the amorphous glass transition in POM, under ± 65 MPa axial stress, (a) Effects of axial stress on loss peak temperature for POM, showing error bars. There is a drastic change in behaviour between compression and tension, (b).

5.4. Evidence of cavitation from coefficient of thermal expansion (CTE) measurements

Bucknall et al. [2000a] measured thermal contraction and expansion in poly(styrene-co-acrylonitrile) (PSAN) and ABS. They found that in PSAN contraction and expansion were linear and reversible, while in some ABS materials the volumetric expansion gave an irreversible contraction curve with an S profile. During subsequent heating and cooling, expansion and contraction were linear, whereas after annealing, they again showed the same S-shaped curve. The same behaviour was observed in another type of ABS blended with silicone oil. This non-linearity is believed to be due to cavitation of the rubber particles. Void formation during the thermal contraction process promotes relaxation of the tensile stresses induced by differential thermal contraction in the rubber phase. The relaxed rubber particles are therefore unable to contribute to the following thermal expansion and a fall in the coefficient of thermal expansion is observed.

It was also observed from the non-linear behaviour of ABS that the temperatures at which cavitation initiates are well below those predicted by the Lazzeri-Bucknall (LB) energy-balance model [1995]. The LB model shows that void formation and expansion in the rubber becomes thermodynamically possible (i.e. the total energy decreases) when the dilatational volume strain reaches a critical value. Since the thermal expansion coefficient of the rubber is much higher than that of the matrix, purely cooling the blend below the glass transition temperature of the matrix (T_{gm}), as little as 20K [Ayre and Bucknall 1998], causes a substantial volume strain due to differential thermal contraction. This could be enough to cause cavitation in the rubber phase. However, Bucknall et al. [2000a] noted that rubber particles are more resistant to cavitation than is predicted by the thermodynamic criterion. They attributed this discrepancy to the presence of an energy barrier, which had to be exceeded in order to achieve void formation, and which determines the rate at which free-volume voids expand. The model shows that when moderate values of volume strain are applied to the particle, the total energy $U(r)$ of a spherical particle containing a spherical void of radius r , reaches a maximum at very small void size r , followed by a minimum at much bigger r . The condition $U(r) < U(0)$ is a necessary but not sufficient condition for cavitation to occur

and attention has to be focused on the energy barrier at low r . It was concluded that cooling the ABS and/or blending it with silicone oil was sufficient to reduce the energy barrier and promote cavitation. When the material is cooled, the volume strain energy in the rubber particle increases and the peak of the energy barrier therefore decreases. The presence of silicone oil has the effect of reducing the surface energy of the blend and thus decreasing the height of the energy barrier. The two effects together, cooling and dropping the surface energy induce a fall in the energy barrier peak until the void is able to overcome the barrier and is allowed to expand. Since 0.4 nm seems to be the average void size for the free volume in the rubber [Bartoš et al. 1997], it is reasonable to assume that cavities in the rubber can expand from pre-existing free-volume voids.

The present work follows the method first developed by Ayre [1999] to detect rubber particle cavitation using measurements of thermal contraction and expansion. The experimental materials used for this study were a plain PMMA and transparent rubber toughened RT-PMMA (HSH CS-250-40) samples. The RT-PMMA contains 40 wt% of HSH-CS rubber particles having a solid PMMA core, an acrylic rubber shell, and a PMMA outer shell. Specimens of RT-PMMA were subjected to various mechanical and thermal pre-treatments aimed to introduce voids into the rubber particles. Tensile dumbbell specimens, cut from a 3 mm compression moulded sheet, were first polished with fine metallographic grinding papers (P600 and P1200), and afterwards annealed at 115°C for 3 hours. The polishing process is an efficient method for eliminating surface scratches and thus surface stress concentrations during the test. Annealing allows the relaxation of any internal stresses caused by the machining. These samples were then pre-strained to extensions of 0%, 0.5%, 1%, 1.5%, 2%, 3% and 4%, and half of the pre-strained samples were subsequently annealed. Thermal contraction and expansion experiments were then made on these specimens after different pre-treatments, to determine whether cavitation had taken place in the rubber phase.

Rectangular bars were cut from the central sections of pre-strained only and annealed pre-strained dumbbell tensile samples. The dimensions of the specimens were 4×3 mm² cross section by 100 mm length. The parallelism of the samples was carefully controlled to avoid bending or buckling. Thermal expansion measurements were carried out using

the same instrument used for DMTA tests, with an appropriate setting, as illustrated in the Chapter 4. The clamps were removed from the temperature control chamber, and the thermal correction factor of the machine was changed to zero. The samples were long enough to record perceptively the changes in length due to contraction and expansion and to fit the total length of the temperature chamber. A holding force of 2 N was needed to maintain the sample straight and, since the machine can work only under simultaneous static and dynamic control, the smallest possible dynamic load of 1 N was then chosen. For a cross section of $4 \times 3 = 12 \text{ mm}^2$, 0.083 MPa dynamic stress was applied on the specimens during the measurements. As the Young's modulus of the blend was approximately 2000 MPa, the specimen was subject to a dynamic strain of roughly $\pm 0.004\%$, which is considerably smaller than the measured changes in length. The temperature range was set to vary from $+60$ to -60°C with a temperature ramp rate of 1°C min^{-1} , for the cooling and the expansion tests.

Table 5.4.1 represents a list of the specimens studied, giving the degree of pre-strain (a) and pre-strain and annealing (b) to which they had been subjected before testing. The linear coefficients of thermal expansion (CTE) measured from the slopes of the diagrams, the linear CTE calculated from equation 4.3 below, and the volume fractions ϕ of 'intact' rubber particles (where 'intact' refers to rubber particles that contribute fully to the contraction and expansion behaviour of the blend), calculated from equation (5.4.4), are also recorded for cases (a) and (b).

In principle, the potential of this experimental technique is straightforward. If a glassy polymer that contains well bonded, intact rubber particles is cooled, the CTE of the blend is higher than the CTE of the simple glassy polymer. This happens because the rubber phase features a larger CTE than the matrix. The difference in CTE leads to the generation of increasing internal stresses between the two phases when they are cooled from the glass transition temperature of the matrix (T_{gm}) to the glass transition temperature of the rubber (T_{gr}). Above T_{gm} any stresses generated would be relieved by matrix relaxation. Below T_{gr} the rubber will be in a glassy state and assume the typical CTE of a glassy polymer, so that there is no further increase in internal stress. At intermediate temperatures, cooling forces the rubber to contract faster than the

surrounding matrix, resulting in a state of tension. Therefore the CTE of the modified polymer will be higher than that of the pure matrix. If the rubber particles are debonded or cavitated, they do not fully participate in the increase of CTE. Hence the rubber will be unable to take the total strain and the matrix will be partially or fully relieved from the previous constraint. This depends on the degree of damage affecting the rubber.

	Material	PMMA	RT-PMMA (HSH CS-250-40)						
	% pre-strain	—	0	0.5	1	1.5	2	3	4
(a)	CTE (10^{-6} K^{-1})								
	Calculated	67*	95	—					
(a)	CTE (10^{-6} K^{-1})								
	Measured	70	100				80		
(a)	ϕ								
	Calculated	—	0.45				0.18		
(b)	CTE (10^{-6} K^{-1})								
	Measured	70	100					80	
(b)	ϕ								
	Calculated	—	0.45					0.18	

Tab. 5.4.1: List of materials, % of pre-strain, and comparison between the linear CTE measured from the graphs (between the T_g of the rubber and the T_g of the PMMA) and calculated from equation (5.4.3). Volume fraction of intact rubber particles ϕ calculated from equation (5.4.4). (a) for pre-strained samples, (b) for annealed after pre-straining samples. * value is obtained from the literature [Brandrup and Immergut 1989].

Three cases can be recognised:

- i. If the rubber particles are completely detached over the whole interface between rubber and outer rigid shell, they make no contribution to the CTE of the blend during cooling. In this case the matrix can contract freely.
- ii. If the particles are cavitated and rubber fibrils still form bridges between regions of the rigid phase (core with outer shell), their contribution to the CTE of the blend

decreases with increasing size and/or number of voids in the rubber. In this case the matrix is less sensitive to the presence of the rubber.

- iii. Any combination of i and ii produces a partial relaxation and the matrix is only locally free to expand.

The expression for the volumetric CTE of the modified polymer (β_{mp}), when rubber and matrix behave elastically is given by Boyce et al. [1987] as a combination of the volumetric CTEs of the matrix (β_m) and the particle (β_p):

$$\beta_{mp} = \beta_m + K^* \phi (\beta_p - \beta_m) \quad (5.4.1)$$

where ϕ is the volume fraction of intact rubber particles, and K^* the bulk modulus of the blend:

$$K^* = \frac{4 G_m K_p + 3 K_m K_p}{4 G_m K_m (1 - \phi) + K_p (4 G_m \phi + 3 K_m)} \quad (5.4.2)$$

The approximation $K^* = 0.8$ applies when assuming typical values of $K_m = 4$ GPa, $G_m = 1$ GPa, $K_p = 2$ GPa and $0.1 < \phi < 0.4$. Equation (5.4.1) then becomes:

$$\beta_{mp} = \beta_m + 0.8 \phi (\beta_p - \beta_m) \quad (5.4.3)$$

$$\phi = \frac{\beta_{mp} - \beta_m}{0.8 (\beta_p - \beta_m)} \quad (5.4.4)$$

To calculate ϕ for a partially-cavitated RT-PMMA it is first necessary to calculate β_p for the composite HSH CS rubber particle from the following simplified equation [Ayre 1999]:

$$\beta_p = \beta_c \phi_c + \beta_r (1 - \phi_c) \quad (5.4.5)$$

Considering the outer hard shell as part of the PMMA matrix, the problem then reduces to calculating the volumetric coefficient of thermal expansion (CTE) β_p for a particle with a spherical PMMA core and a concentric rubber shell. Assuming the core occupies 50% of the total volume (where ϕ_c is the volume fraction of core in the particle) and taking typical volumetric CTE values as $\beta_m = 2 \times 10^{-4} \text{ K}^{-1}$ for the matrix and $\beta_r = 7 \times 10^{-4} \text{ K}^{-1}$ for the acrylic rubber shell [Brandrup and Immergut 1989], the resulting CTE of the particle is: $\beta_p = 4.7 \times 10^{-4} \text{ K}^{-1}$. This value was used in equations (5.4.3) and (5.4.4) to calculate β_{mp} for the RT-PMMA, with $\beta_m = 2 \times 10^{-4} \text{ K}^{-1}$, $K_p = 2 \text{ GPa}$, $G_m = 1 \text{ GPa}$, $K_m = 4 \text{ GPa}$, and assuming $\phi = 0.4$. Linear CTE values listed in Table 5.4.1 are calculated by considering the RT-PMMA as an isotropic material, for which the relationship between linear (α) and volumetric (β) expansion coefficients is $\beta = 3\alpha$. As shown in Table 5.4.1, this calculation achieves a good correspondence with the experimentally measured linear CTE expansion and contraction data.

Table 5.4.1 reports the volume fractions of ‘intact’ rubber particles ϕ calculated from equation (5.4.4). The values of β_{mp} measured from the experimental tests for each pre-treated sample are displayed in Figure 5.4.6 and 5.4.7 (assuming again $\beta = 3\alpha$).

5.4.1. Properties of PMMA

The PMMA tested during this study was a transparent glassy polymer with a relatively high modulus. Considering the stress-strain curve obtained under uniaxial tension, as shown Figure 5.4.1, the stress is approximately linear up to the point of failure at $\epsilon \approx 2\%$.

Uniaxial thermal contraction/expansion tests were carried out over the temperature range from 50°C to -60°C . Thermal contraction and expansion data for PMMA were linear and completely reversible with temperature, as shown in Figure 5.4.2. A straight-line fitting (least squares method) has been applied to the experimental data. The linear CTE (α) for PMMA can be estimated from the slope of the straight line in Figure 5.4.2. A good comparison is then established between the measured linear CTE and the typical value [Brandrup and Immergut 1989] quoted in Table 5.4.1.

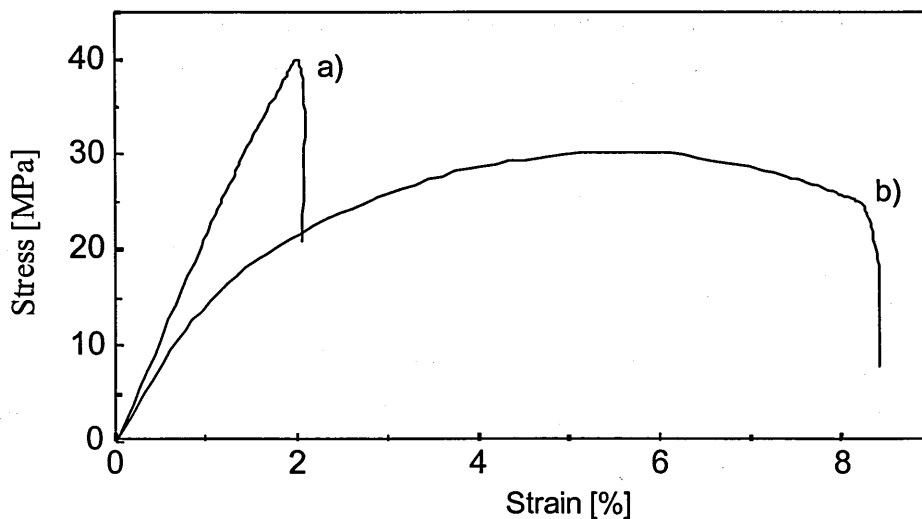


Fig. 5.4.1 Comparison between stress-strain curves for (a) a plain transparent PMMA and (b) a transparent RT-PMMA with 40 wt% HSH-CS rubber particles.

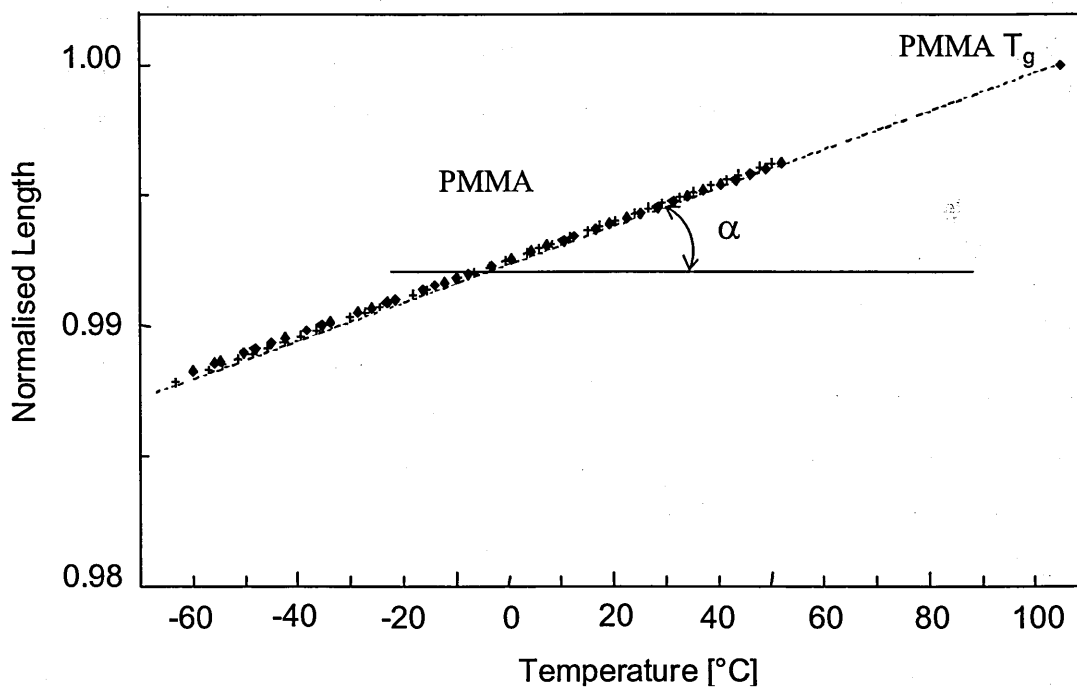


Fig. 5.4.2 Thermal contraction (♦) and expansion (+) data for PMMA, over the temperature range from 50°C to -60°C. The reference length is defined at 105°C (taken as the T_g of the PMMA). The slope of the dotted line defines the measured linear CTE of PMMA given in Table 5.4.1.

5.4.2. Properties of RT-PMMA (HSH CS-250-40)

The RT-PMMA (HSH CS-250-40) chosen for this study was also transparent, and the refractive index of the rubber had been chosen to match that of the matrix. However, the presence of HSH-CS rubber particles at a concentration of 40% by weight causes a considerable reduction in Young's modulus, as shown in Figure 5.4.1.

The locations of the glass transition temperatures of the two phases, which govern the thermal contraction and expansion behaviour of RT-PMMA, were determined using DMTA, as shown in Figure 5.4.3. The $\tan \delta$ curve identifies two distinct peaks, a small one (a) at around -20°C and a bigger one (b) at roughly $+105^\circ\text{C}$.

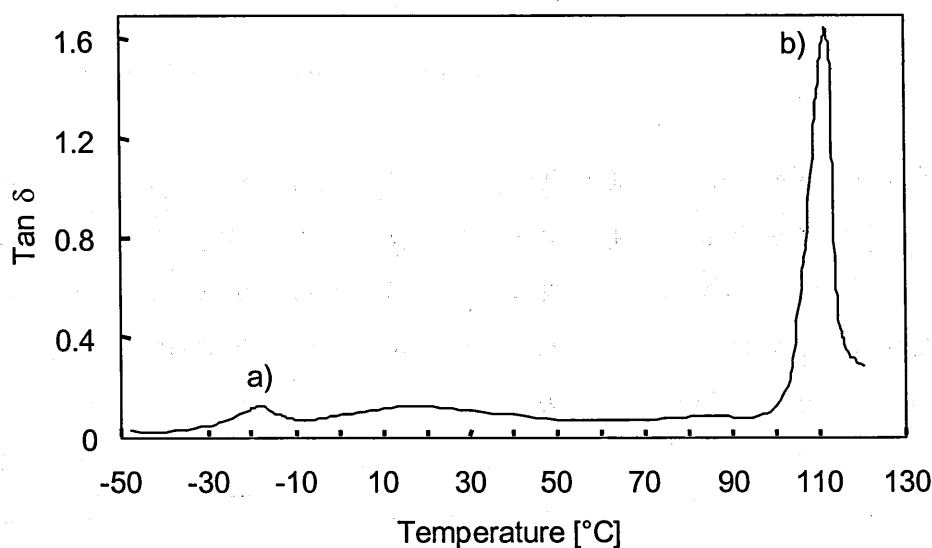


Fig. 5.4.3 Dynamic loss curve for a HSH CS-250-40 showing the $\tan \delta$ peak temperatures for (a) the rubber phase and (b) the glassy matrix polymer. The test was carried out at 1 Hz and 0.4 % static strain applied to the sample.

The thermal contraction data presented here are all normalised with respect to the (extrapolated) reference length of the sample at 105°C , which is taken as the T_g of PMMA. Thus, the reference length corresponds to the length at the current temperature divided by the length at 105°C (i.e. $L(T)/L(T_{g\text{PMMA}})$).

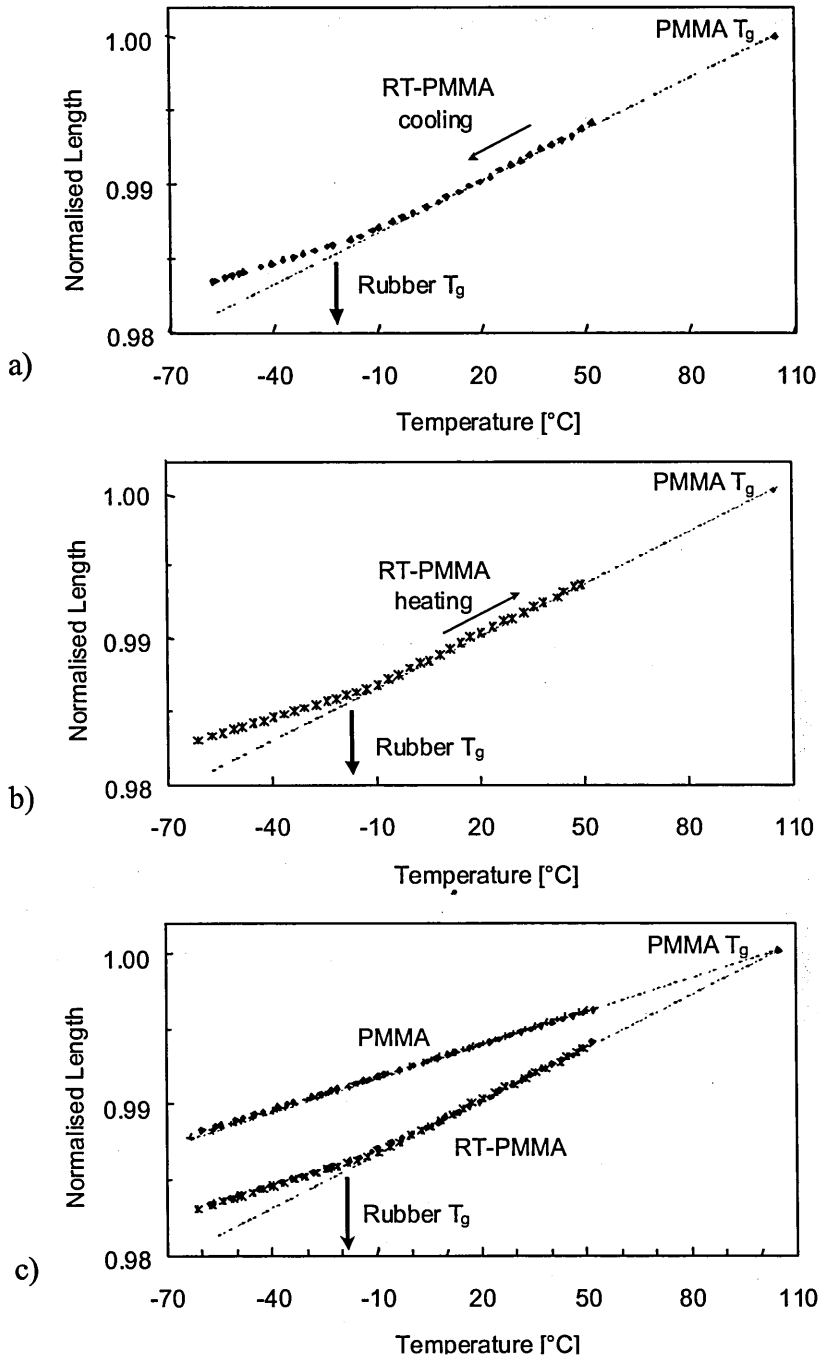


Fig. 5.4.4. Thermal contraction (a) and expansion (b) experimental results for RT-PMMA (HSH CS-250-40) and comparison (c) between PMMA and RT-PMMA, over the temperature range from 50°C to -60°C. Experimental data are normalised to the glass transition temperature of PMMA ($T_g = 105^\circ\text{C}$). The thermal contraction coefficient of the blend RT-PMMA is greater than that of pure glassy PMMA.

Results showing an increase of CTE in RT-PMMA (HSH CS-250-40) are given in Figure 5.4.4. It can be assumed that the PMMA matrix is soft and fully relaxed at its T_g .

and the stress acting on the particle-matrix interface are zero. For this reason, the dimensions of RT-PMMA specimens are also normalised as $L(T)/L(T_{gPMMA})$.

Thermal expansion and contraction data for RT-PMMA (HSH CS-250-40) are reversible (Figures 5.4.4a and b), but their paths diverge from the PMMA curve as the temperature decreases, Figure 5.4.4c. The coefficient of thermal expansion of the RT-PMMA is higher, because the rubber has a much higher CTE than the PMMA. The unstrained RT-PMMA presented an increase in CTE of approximately 45% compared with the CTE of PMMA. The curve in Figure 5.4.4c exhibits a sharp bend in the proximity of the glass transition temperature of the rubber (T_{gr}). The RT-PMMA and PMMA thermal contraction and expansion diagrams become parallel below -20°C , where both phases are then glassy. Since in this case, the RT-PMMA has received no pre-treatment other than normal cooling in the compression-moulding machine, the cavitation of the rubber particles is expected to be at a minimum. This is confirmed by calculations of the linear CTE of the RT-PMMA, listed in Table 5.4.1, based on equation (5.4.3) and on the assumption that the particles are intact ($\phi = 0.4$).

5.4.3. Effects of RT-PMMA blended with silicone oil

Following Bucknall et al. [2000a] project on ABS blended with silicone oil, a transparent grade of RT-PMMA (HSH CS-250-40) was compounded with 1% and 0.1% by volume of silicone oil. The blended and granulated material was then compression moulded into plaques and machined in rectangular specimens for CTE measurements.

RT-PMMA specimens containing 1% (volume) silicone oil were opaque. Measurements carried out on those samples present a negligible variation in CTE, as presented in Figure 5.4.5. On the other hand, comparison between CTE measurements on RT-PMMA and RT-PMMA with 0.1% (volume) shows a slight difference (Figure 5.4.6). Samples with 0.1% (volume) silicone oil were still transparent. Because of the limited numbers of specimens tested and because of the small variation in CTE, the small difference in CTE has been mainly attributed to machine inaccuracy. Even so, it is advised that a further study is needed on the possibility that a small volume of silicone

oil added to the RT-PMMA could cause a reduction in CTE due to cavitation of the rubber phase under cooling.

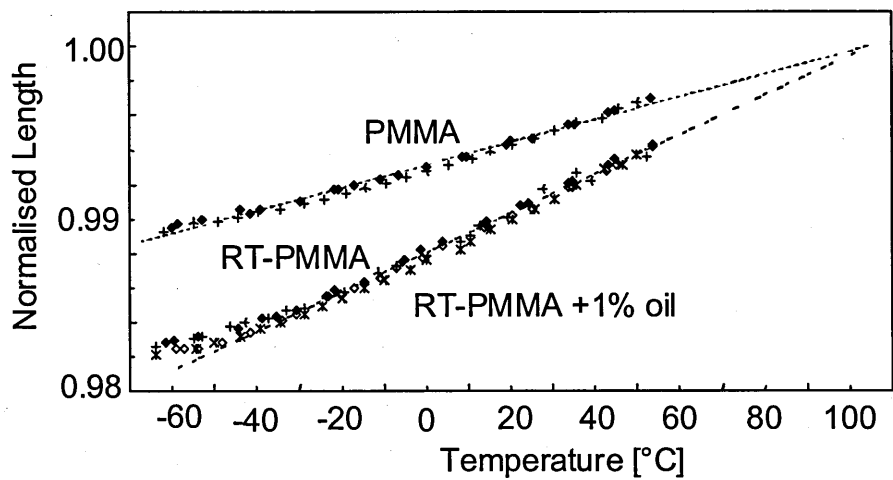


Fig. 5.4.5 Thermal contraction and expansion experimental results over the temperature range [50°C to -60°C] for PMMA, RT-PMMA (HSH CS-250-40) (cooling ♦, heating +) and the same RT-PMMA blended with 1% volume of silicone oil (cooling ◊, heating ×).

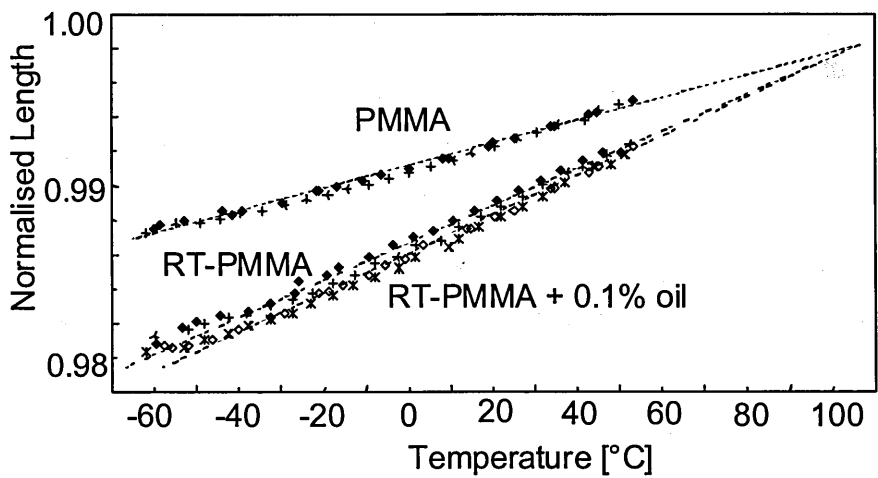


Fig.5.4.5 Thermal contraction and expansion experimental results for PMMA, RT-PMMA (HSH CS-250-40) (cooling ♦, heating +) and the same RT-PMMA blended with 0.1% volume of silicone oil (cooling ◊, heating ×).

5.4.4. Effects of different rubber concentrations and rubber particle sizes

Figure 5.4.7 compares CTE data for a RT-PMMA containing 18% wt of HSH CS rubber particles with 170 nm particle diameter (HSH CS-170-18) and a RT-PMMA with 40% wt of HSH CS, 250 nm diameter rubber particles (HSH CS-250-40). As expected, the CTE for the RT-PMMA poorer in rubber content is lower. Measured linear CTE for HSH CS-250-40 and HSH CS-170-18 are 100 and 90 10^{-6} K^{-1} , respectively. The volume fraction of rubber particles in HSH CS-170-18 calculated using equation (5.4.4) gives a value of $\phi = 0.32$.

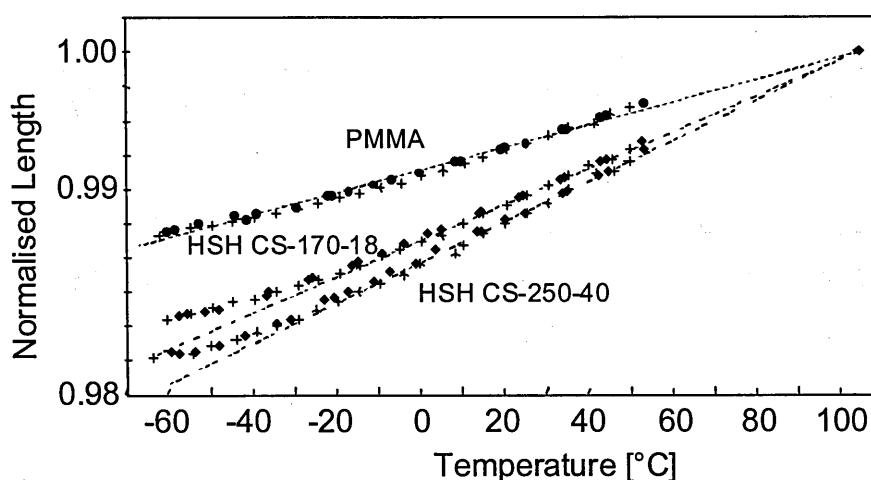


Fig. 5.4.7 Thermal contraction and expansion experimental results for PMMA, HSH CS-170-18 and HSH CS-250-40 (cooling $\blacklozenge$ and heating $+$).

CTE data for RT-PMMA samples with the same HSH CS rubber particle morphology, but different rubber particle diameter, ranging between 130 and 200 nm are reported in Figure 5.4.8. The effects of changing rubber particle sizes from 130 to 200 nm are very limited on the measure of CTE.

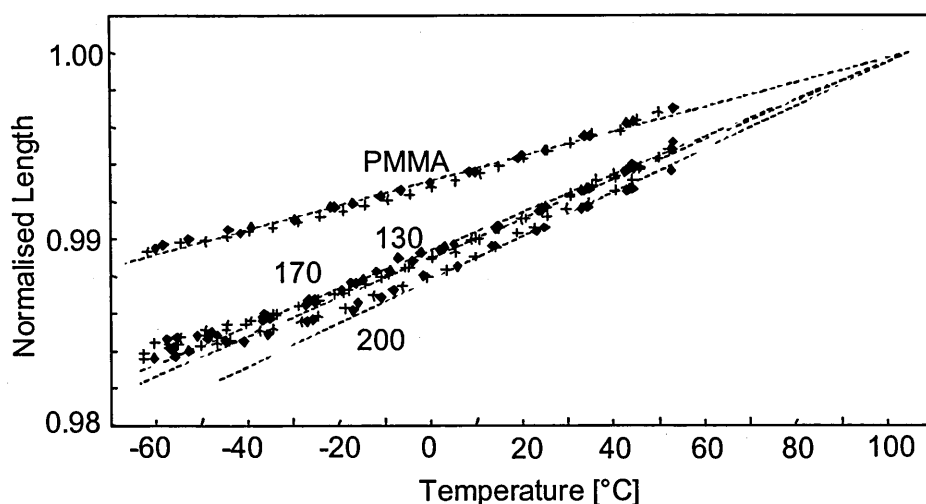


Fig. 5.4.8 Thermal contraction and expansion experimental results for PMMA, HSH CS-130-18, HSH CS-170-18 and HSH CS-200-18 (cooling $\blacklozenge$ and heating $+$).

5.4.5. Effects of pre-straining on RT-PMMA

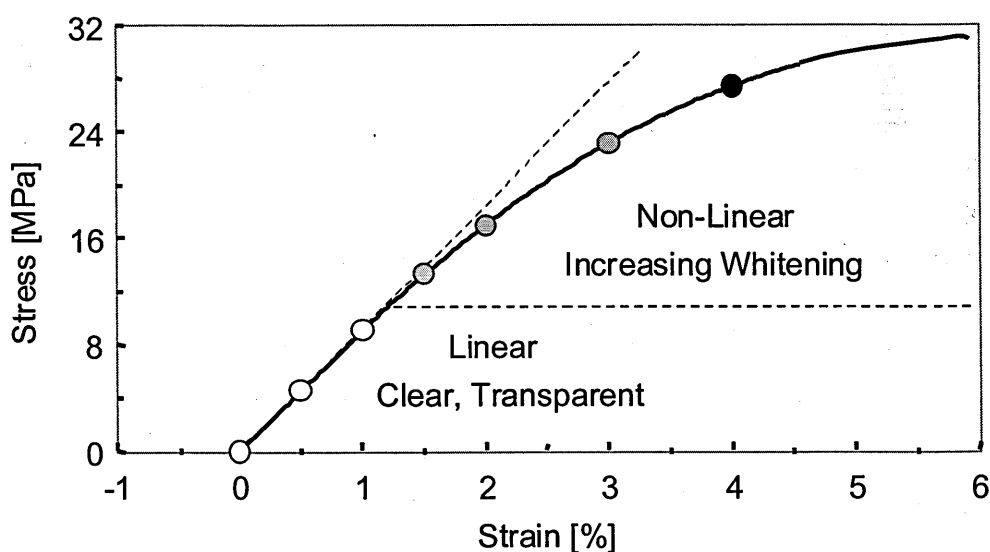


Fig. 5.4.9 Stress-strain curve for a transparent RT-PMMA (HSH CS-250-40) tested at a constant strain rate of 1 mm min^{-1} under uniaxial tensile loading, with notes on changes in transparency (from completely transparent $\bigcirc$ to completely opaque $\bullet$).

Some RT-PMMA (HSH CS-250-40) specimens were subjected to various mechanical and thermal pre-treatments aimed at introducing voids into the rubber particles. Thermal contraction and expansion experiments were then performed on these specimens to

determine whether cavitation had taken place. The stresses induced by differential thermal contraction are released when the particles cavitate, thereby allowing the RT-PMMA to expand. In this case, rubber particle cavitation can be monitored by measuring the thermal contraction and expansion behaviour.

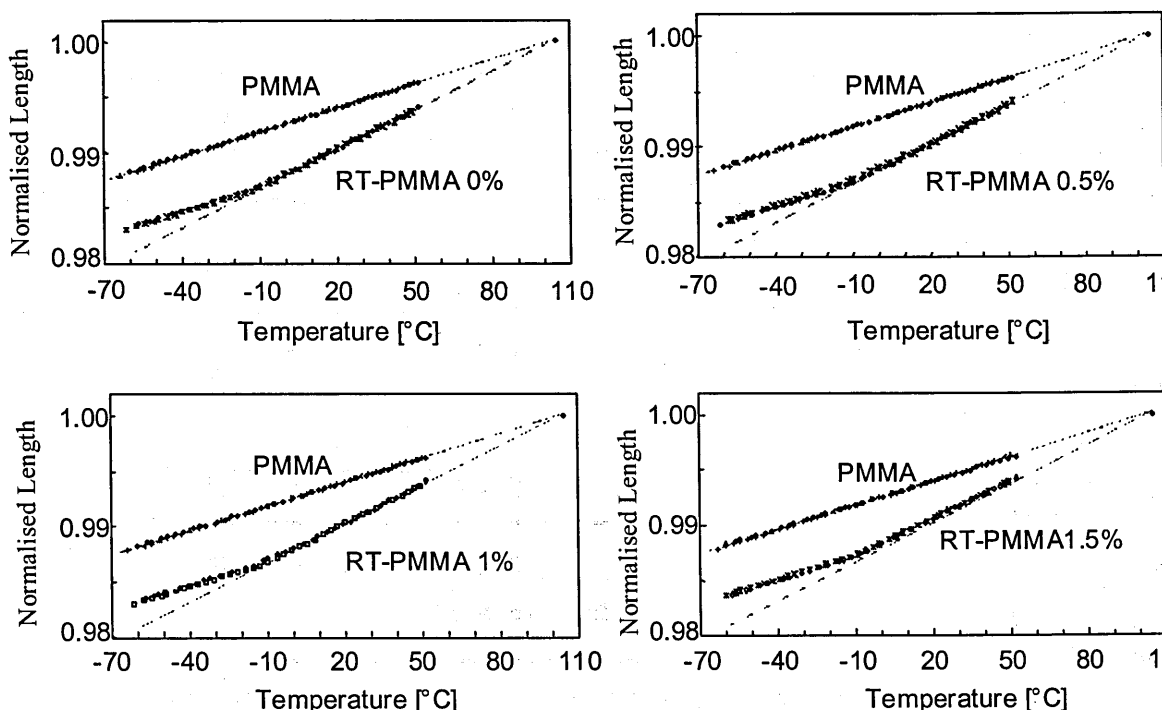


Fig.5.4.10 Comparison between thermal contraction and expansion experimental data for PMMA and RT-PMMA (HSH CS-250-40) pre-strained to 0%, 0.5%, 1% and 1.5%. Normalised length = $L(T)/L(T_{gPMMA})$.

For strains lower than 1.2%, the polymer remains transparent and features an approximately linear stress-strain relationship (Figure 5.4.9). Beyond this point, visible diffuse whitening is observed, and the slope of the stress-strain curve decreases, as the Young's modulus is reduced. At $\epsilon = 4\%$, most of the gauge length of the specimen is opaquely white. The change in transparency for RT-PMMA samples under uniaxial tensile load is shown in Figure 5.4.9.

The transition in transparency can be explained by assuming that small regions inside the materials have undergone a modification in refractive index. Four different possibilities satisfy this phenomenon:

- I. cavitation of the rubber particles;
- II. debonding of the rubber particles;
- III. multiple crazing;
- IV. any combination of the above three features.

Figure 5.4.10 shows that pre-straining by 0.5%, 1.0% or 1.5% has little or no effect upon the expansion/contraction behaviour of RT-PMMA, indicating that no significant cavitation has taken place in the rubber particles. However, there is a marked change in behaviour when the pre-strain is raised to 2.0%, Figure 5.4.11. The coefficient of expansion drops, becoming much closer to that of PMMA, as indicated in Table 5.4.1. Increasing the pre-strain to 3% or 4% produces little further change in thermal behaviour, suggesting that the cavitation process reached saturation at a pre-strain of 2%. Nevertheless, the coefficient of thermal expansion does not fall to the low level of plain PMMA (Figure 5.4.12). Damage in the rubber particles, cavitation or debonding limits the ability of the rubber to contribute to the CTE of the blend.

The probable explanations for this discrepancy can be sought in different hypotheses. The first possibility that comes obviously to mind is that some of the entire populations of particles remain intact, even at the 'saturation' stage of pre-straining. The intact rubber particles interact with the matrix and the CTE of the blend increases above that of PMMA. The proportion of intact particles can then be detected from the measured expansion data. It is also possible that cavitated particles are not fully relaxed, and therefore continue to influence the thermal expansion/contraction behaviour of the blend. Here, the complex morphology of these rubber particles can result in the formation of stressed rubber bridges between glassy parts of the particle, so that the free contraction or expansion of the matrix is restricted. Possibly, both factors (partial cavitation and fibrillation) contribute to the overall thermal behaviour of pre-strained RT-PMMA.

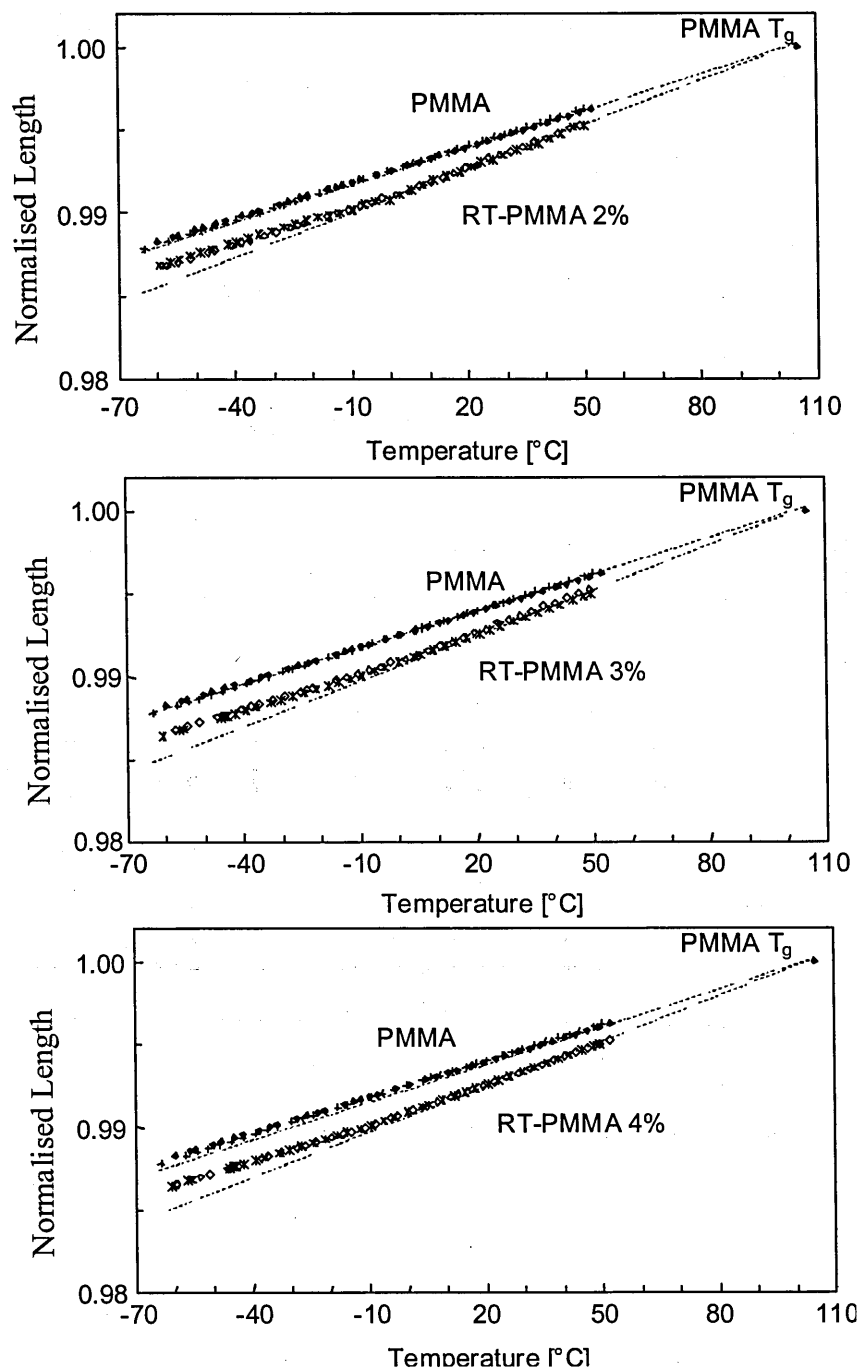


Fig. 5.4.11 Comparison between thermal contraction and expansion data for PMMA and RT-PMMA (HSH CS-250-40) pre-strained to 2%, 3% and 4%.

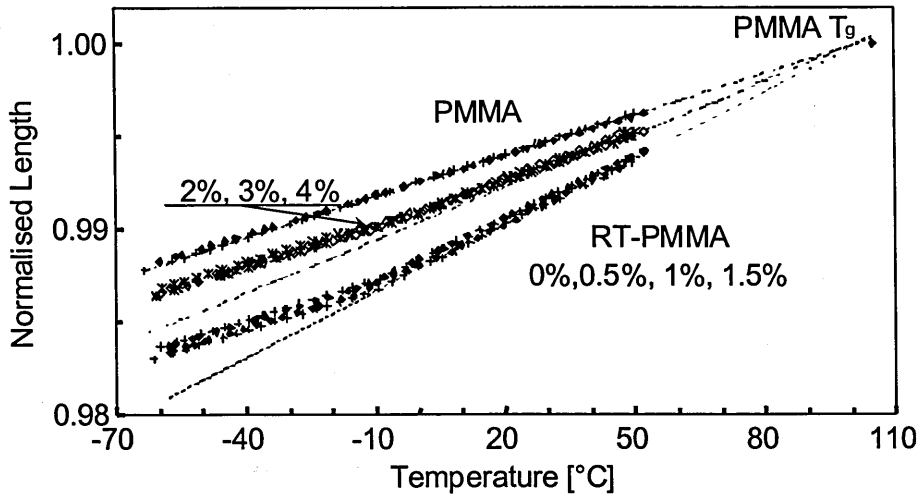


Fig. 5.4.12 Comparison between thermal contraction and expansion experimental results over the temperature range $[-50^{\circ}\text{C}, -70^{\circ}\text{C}]$ for PMMA and RT-PMMA (HSH CS-250-40) pre-strained to 2%, 3% and 4%.

It is fundamentally important to recognise that cavitation of the rubber phase does not necessarily result in the complete loss of mechanical interactions between particle and matrix. An electron microscopy study on similar HSH CS rubber particles in a PSAN matrix has shown that, on cavitation, the acrylic rubber shell forms highly-stretched fibrils connecting the PMMA core to the surrounding matrix [Starke et al. 1997]. It is therefore clear that cavitated rubber particles cannot be treated as equivalent to voids of the same size. Similar conclusions were reached in a study that used dynamic mechanical thermal analysis (DMTA) to investigate the shift of $\tan \delta$ peak for the rubber phase, as described above.

5.4.6. Effects of annealing on pre-strained RT-PMMA

Subsequent annealing eliminated the whitening produced during pre-straining, but restored the CTE to its original high value only in the case of specimens with a pre-strain of 2%. As shown in Figure 5.4.13, annealing of RT-PMMA specimens that had previously been pre-strained up to $\epsilon = 3\%$ or 4% had little effect on their thermal expansion behaviour. Here, the CTE β_{mp} remained as low as it was immediately after pre-straining. By contrast, specimens that had been pre-strained to $\epsilon = 2\%$ showed a significant degree of recovery on annealing. This evidence suggests that pre-straining beyond $\epsilon = 2\%$ introduces further damage into the rubber particles, which is not

recovered on annealing. The exact nature of this damage is not clear at present, but probably involves tearing of the rubber as the voids expand, with consequent rupture of chemical bonds. Annealing may be sufficient to close up the voids and reduce light scattering, so that the material become transparent again, but it does not eliminate the damage occurring on the scale of a few nanometres.

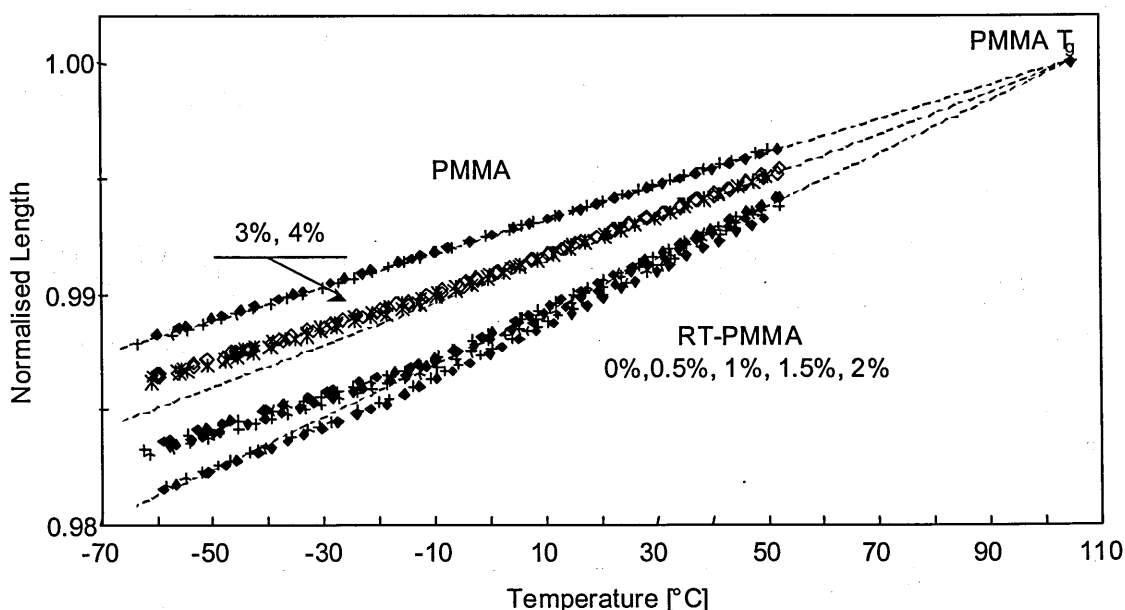


Fig.5.4.13 Comparison between thermal contraction and expansion data for PMMA and RT-PMMA annealed after being pre-strained to 0%, 0.5%, 1%, 1.5%, 2%, 3% and 4%.

The energy-balance criterion [Lazzeri and Bucknall 1995] can be employed to explain this phenomenon. A possibility is that, after annealing, small voids remain in the rubber phase of samples that were pre-strained beyond 2%. Assuming the size of the remaining voids to be larger than the critical diameter (≈ 0.8 nm) corresponding to the energy barrier peak, there is no need for them to overcome the barrier to expand. Therefore, cooling to room temperature causes enough volume strain due to differential thermal contraction for them to expand.

5.5. Evidence of cavitation from creep experiments

During the present study, creep and fracture measurements (following) were employed to have a wider point of view on the deformation behaviour of toughened plastics.

Creep investigation was based on experimental tests at a constant temperature of 23°C in uniaxial tension, involving the application of a constant load upon a uniform cross section and the subsequent measurement of the longitudinal deflection of the specimens by means of an Instron strain gauge. For the sake of simplicity the material was considered as isotropic.

A reasonable mean duration for the creep tests drove the selection of the applied load value. Figure 5.5.1 presents the acceleration in creep rates obtained on increasing the stress applied to RT-PMMA (HSH CS-250-40) specimens from 25 to 27 MPa.

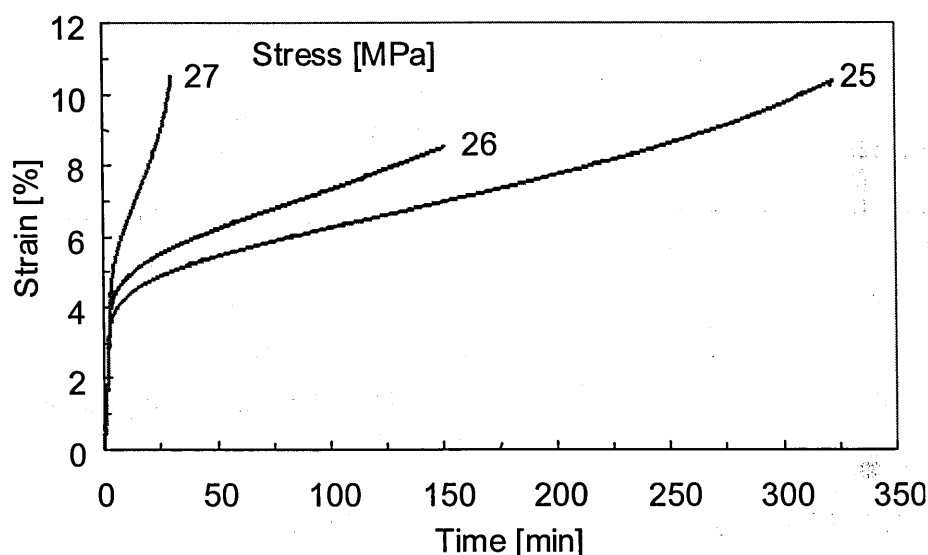


Fig 5.5.1 Creep curves for RT-PMMA (HSH CS-250-40) at 23°C, showing the effects of increasing longitudinal tensile stress from 25 to 27 MPa. No pre-strain.

Tensile creep tests were carried out on straight RT-PMMA and pre-treated RT-PMMA specimens to investigate possible correlation between rubber particle cavitation and subsequent yielding.

5.5.1. Effects of pre-straining on RT-PMMA

In order to investigate the effects of cavitated rubber particles on toughening mechanisms in RT-PMMA, specimens of HSH CS-250-40 were pre-strained at 23°C to strain values between 0.5% and 4%, and then subjected to creep tests at 23°C, under a constant tensile stress of 26 MPa. The results are presented in Figure 5.5.2.

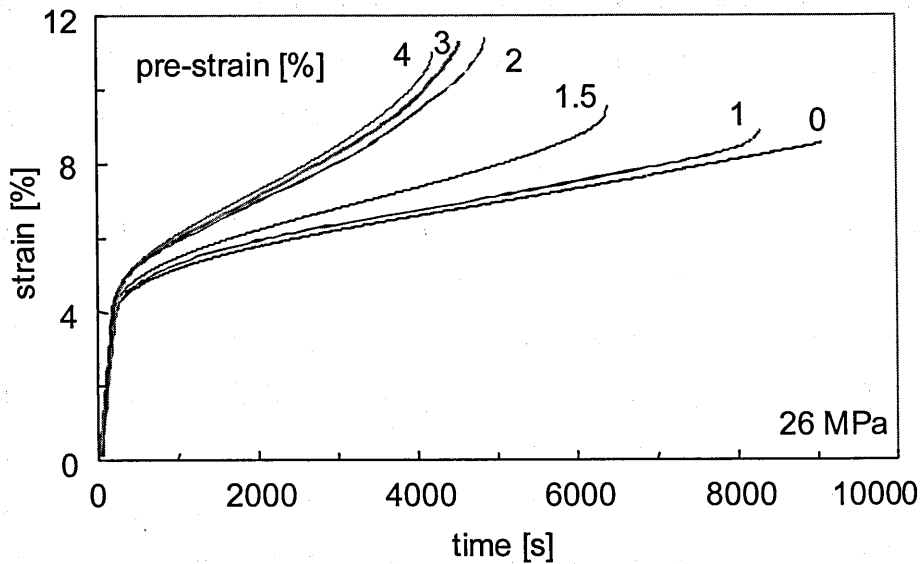


Fig. 5.5.2 Creep curves for RT-PMMA (HSH CS-250-40) at 23°C under a tensile stress of 26 MPa, showing the effects of pre-straining to 0, 1, 1.5, 2, 3 and 4%.

Pre-strains up to 1% cause a very small acceleration in the rate of deformation, but the most dramatic change occurs for pre-strain values between 1.5% and 2%. This change coincides with the change in thermal expansion behaviour, and provides further support for the view that cavitated rubber particles promote yielding in rubber-toughened polymers [Lazzeri and Bucknall 1995]. A similar effect has been reported in ABS polymers [Bucknall et al. 2000a]. Comparison with Figure 5.5.1 highlights the effect of pre-strain on creep rate acceleration in RT-PMMA specimens. Increasing the applied stress from 26 MPa to 27 MPa has a greater effect than increasing the pre-strain from 0% to 4%.

Considering $\tau_{5\%}$, the time, which a sample takes to reach 5% strain it can be observed (Figure 5.5.3) that increasing the pre-strain had the effect of reducing $\tau_{5\%}$. The drop in $\tau_{5\%}$ become sharp at 1.5 % pre-strain and a constant level is achieved beyond 2% pre-strain. Confirmation that pre-straining beyond 1% produces damage in RT-PMMA, which causes an acceleration of creep rate in subsequent tests, is presented in Figure 5.5.3, whereas, pre-straining to 2% strain or more produces a stabilisation in creep rate, indicating that any additional cavitation in the rubber particles does not affect creep kinetics. This could be because cavitation occurring at $\epsilon > 2\%$ is no more than what is

produced when a stress of 26 MPa is applied in the creep test. To relate changes in transparency during uniaxial tensile tests with decreases in creep rate for pre-strained specimens, Figure 5.5.3 presents two diagrams. Circular points of different colours, from white to black, have been added to the stress/displacement curve in Figure 5.5.3. They represent increases in whitening under growing strain. It can be seen that the strain at which the specimen starts becoming opaque corresponds to the strain at which there is a fall in the time to reach 5% strain in the creep tests.

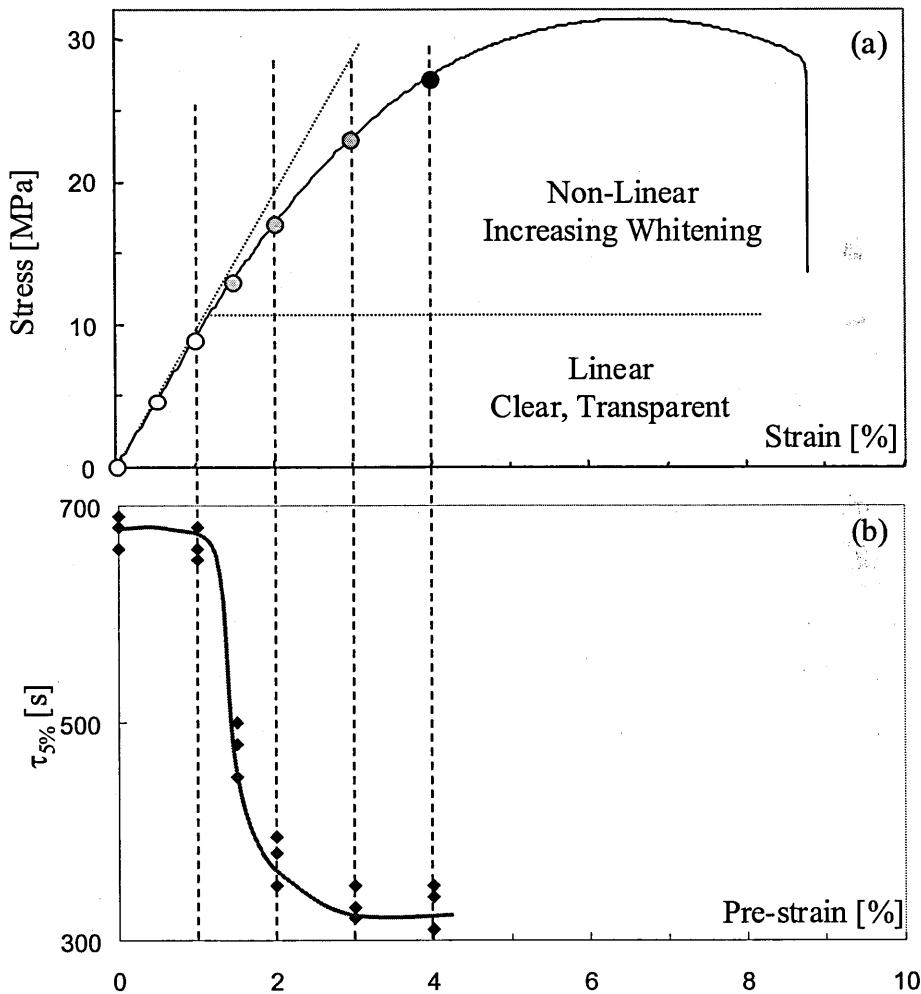


Fig. 5.5.3 Stress/strain curve for a RT-PMMA (HSH CS-250-40) under uniaxial tensile test (a), compared with the decrease in the time to reach 5% strain in the creep tests (b).

5.5.2. Effects of annealing on pre-strained RT-PMMA and cooling

Some of the RT-PMMA (HSH CS-250-40) specimens that were pre-strained had been annealed (115°C for 3 hours) until the transparency was restored in all the specimens. A few of the annealed samples were in addition cooled at -90°C for 1 hour.

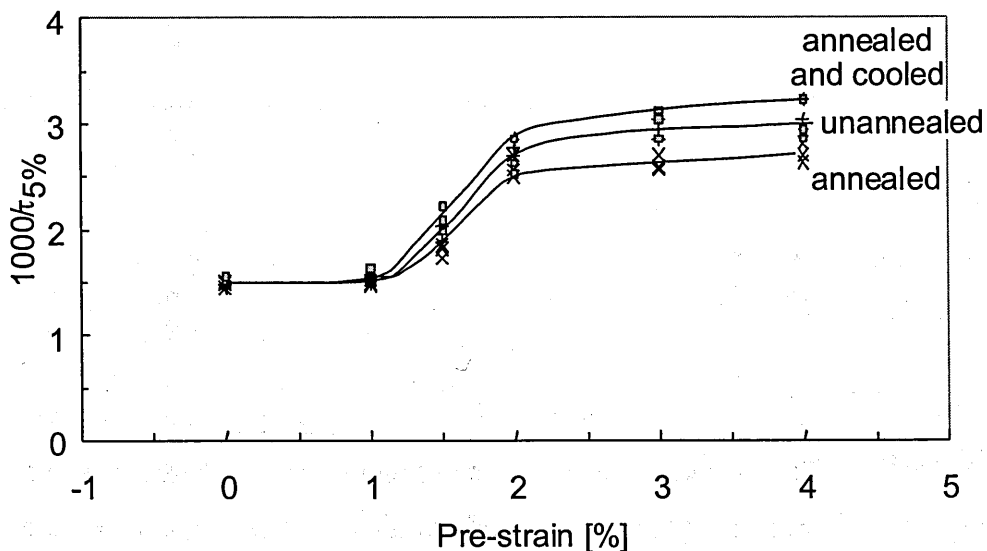


Fig. 5.5.4 Damage rate ($1000/\tau_{5\%}$) against pre-strain for various pre-treated RT-PMMA (HSH CS-250-40).

It can be observed from Figure 5.5.4 that annealing at 115°C after pre-straining slightly reduces but does not eliminate the acceleration in deformation rate, whereas, cooling after annealing increases the damage rate. It is suggested that annealing does not eliminate completely the damage created from pre-strain beyond 1.5 % strain, perhaps because some small voids still remain in the material. Cooling forces the expansion of the void driven by the differential thermal stresses acting on the material. The resulting degree of damage in the material increases.

5.6. Evidence of cavitation from fracture tests on sharply notched specimens

The most severe form of damage is a sharp crack. A parameter identifying the index of toughness is the maximum stress that can be applied before such a crack expands. This stress will depend on the geometry of the cracked body, as well as on the inherent properties of the material.

Three-point bend slow speed (10 mm min^{-1}) and impact (1 m s^{-1}) tests were carried out at 23°C on sharply-notched (Charpy-type) bars of RT-PMMA (HSH CS-250-40). Some of the RT-PMMA specimens were subjected to tensile pre-strains in the range 1–4%, and some of these pre-strained specimens were subsequently annealed at 115°C for 3 hours.

When fracture is brittle, a force/displacement curve from fracture tests at high and low speeds contains data from which linear fracture mechanics parameters can be determined for the considered material. The critical stress intensity factor (K_{Ic}) can be calculated from the force at fracture and the critical strain energy release rate (G_{Ic}) can be established from the integral of the force/displacement curve up to the point of fracture. These fracture parameters may be considered as fundamental properties of the material under test [Williams and Pavan 1995]. Linear elastic fracture mechanics (LEFM) standard protocols for the determination of K_{Ic} and G_{Ic} of polymers under low and high loading speeds have been used [Williams 1990, Pavan 1996]. Since the behaviour of RT-PMMA specimens was excessively ductile, the values of K_c and G_c did not qualify as linear elastic data. The purpose of the present investigation was to consider only a comparison between these values for various pre-treated samples. Henceforth G_c and K_c are considered as ‘apparent’ critical stress intensity factor and ‘apparent’ critical strain energy release rate, respectively.

Oscillations in the force/displacement curve induced a perturbation in impact fracture mechanics testing. These oscillations arise from dynamic effects, particularly the initial inertial loading on the specimens, as the specimen is accelerated to the speed of striker on initial contact, plus various vibrations occurring within the specimen and the system. These oscillations lead to difficulty in analysing the precise fracture point on the force/displacement curve and hence the accurate determination of the force and energy at fracture. Damping can be applied to keep the oscillations within reasonable limits, thus helping to define the underlying force/displacement curve. A minimal (1 mm thick) mechanical damping device of visco-elastic rubber material was applied to the specimen in the zone where the striker came into contact with the sample.

5.6.1. Effects of pre-straining and annealing

RT-PMMA specimens were first pre-strained in the range 1-4%. Half of the pre-strained materials were subsequently annealed at 115°C for 3 hours. All the samples were then machined and razor-notched to obtain a bar with a central sharp notch. Three point bending tests were carried out at two different speeds of applied load, 10 mm min⁻¹ and 1 m s⁻¹ (impact).

Figures 5.6.1, 5.6.2, 5.6.3 and 5.6.4 report values of apparent K_c and G_c for pre-strained and annealed pre-strained specimens, tested at 10 mm min⁻¹ and 1 m s⁻¹. For both series of tests, the apparent G_c value increased by 40-50%, while the apparent K_c value decreased by 20% with increasing pre-strain. Without pre-straining, G_c was 2 kJ m⁻² and K_c was 1.8 MPa m^{0.5} in slow bending, and 4 kJ m⁻² and 3.5 MPa m^{0.5} in impact. For specimens that had been subjected to pre-strains of 2% or more gave G_c values of 3 and 5.5 kJ m⁻², while K_c values of 1.5 and 3 MPa m^{0.5}, respectively. Annealing at 115°C reduced these enhanced G_c and K_c values in specimens that had been pre-strained to 1.5% or more, but after annealing there was still a definite increase in G_c and decrease in K_c , with increasing pre-strain.

These results demonstrate that rubber particle cavitation has a beneficial effect on toughness. It is important to note that this experiment does not reveal the full effect of rubber particle cavitation, because in a well-designed RT-PMMA a high level of cavitation is always initiated during loading by the stress field surrounding the notch tip. The effect of pre-straining is to extend the cavitated yield zone beyond the region that it naturally forms when a given fracture test is performed.

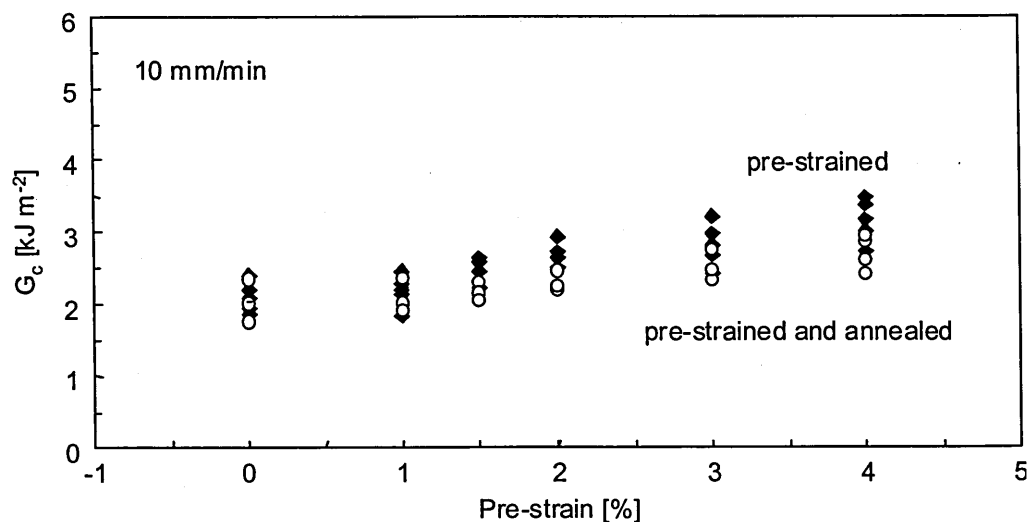


Fig. 5.6.1 Apparent G_c for pre-strained and annealed pre-strained RT-PMMA (HSH CS-250-40) specimens, from three point bending fracture tests at 10 mm min^{-1}

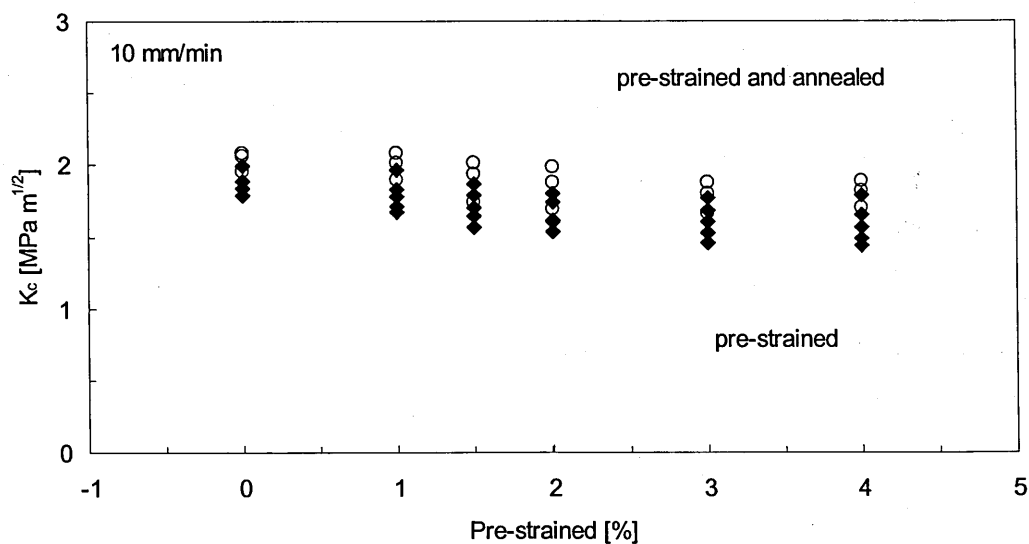


Fig. 5.6.2 Apparent K_c for pre-strained and annealed pre-strained RT-PMMA (HSH CS-250-40) specimens, from three point bending fracture tests at 10 mm min^{-1}

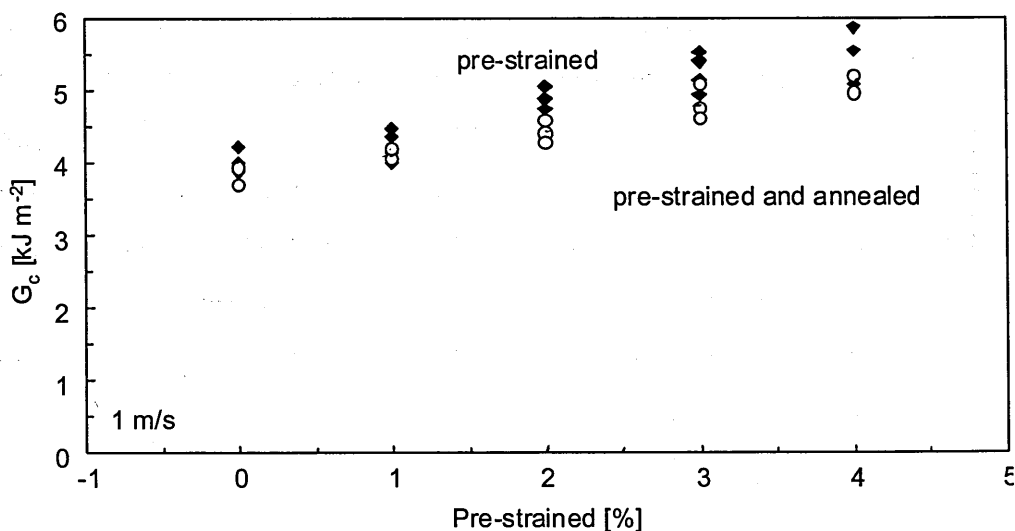


Fig. 5.6.3 Apparent G_c for pre-strained and annealed pre-strained RT-PMMA (HSH CS-250-40) specimens, from three point bending fracture tests at 1 m s^{-1}

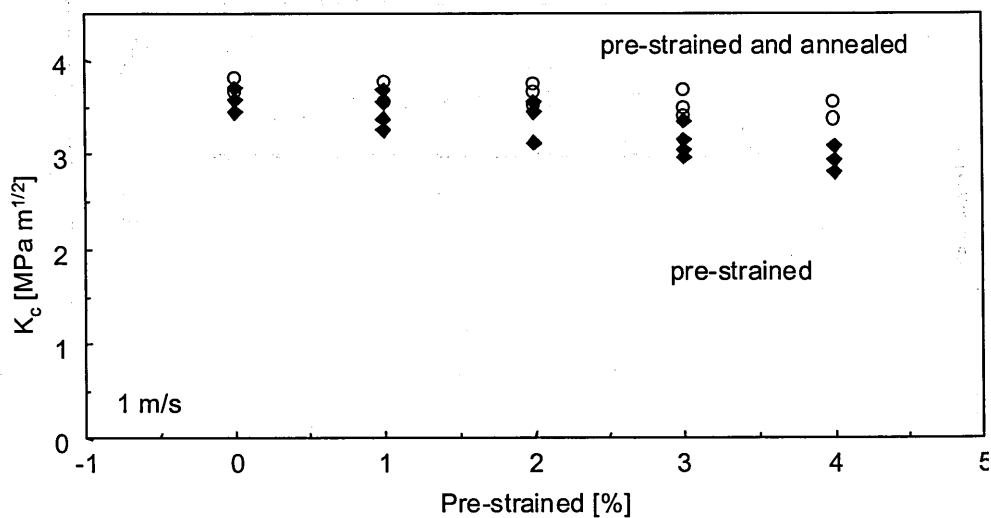


Fig. 5.6.4 Apparent K_c for pre-strained and annealed pre-strained RT-PMMA (HSH CS-250-40) specimens, from three point bending fracture tests at 1 m s^{-1} .

5.7. Comparison of the techniques used

The correlation between visual damage, thermal contraction behaviour, creep rates and fracture resistance for RT-PMMA (HSH CS-250-40) pre-treated specimens is shown in Figure 5.7.1.

A pre-strain of 1.0% has little effect on transparency, CTE, creep rate or fracture resistance. However, increasing the pre-strain to 1.5% causes some increase in light scattering, which is more intense in some parts of the gauge length than in others. The damage responsible for this light scattering causes an increase in the creep rate, but has little effect on expansion behaviour or fracture resistance. At a pre-strain of 3.0%, thermal expansion and creep behaviour have changed dramatically, while fracture resistance shows little significant variation. A further increase in pre-strain to 4.0% has little further effect on thermal contraction and creep rate, but it does increase fracture resistance, as measured by G_c .

Annealing at 115°C after pre-straining to some extent reduces the effects of pre-strain, but it does not eliminate the main pattern.

This work has established various techniques that can be used to study rubber properties and to investigate the role of rubber particle cavitation in the toughening mechanism. For a better understanding of the overall process these methods should be simultaneously adopted, so that a widespread perspective of the whole phenomenon can be obtained.

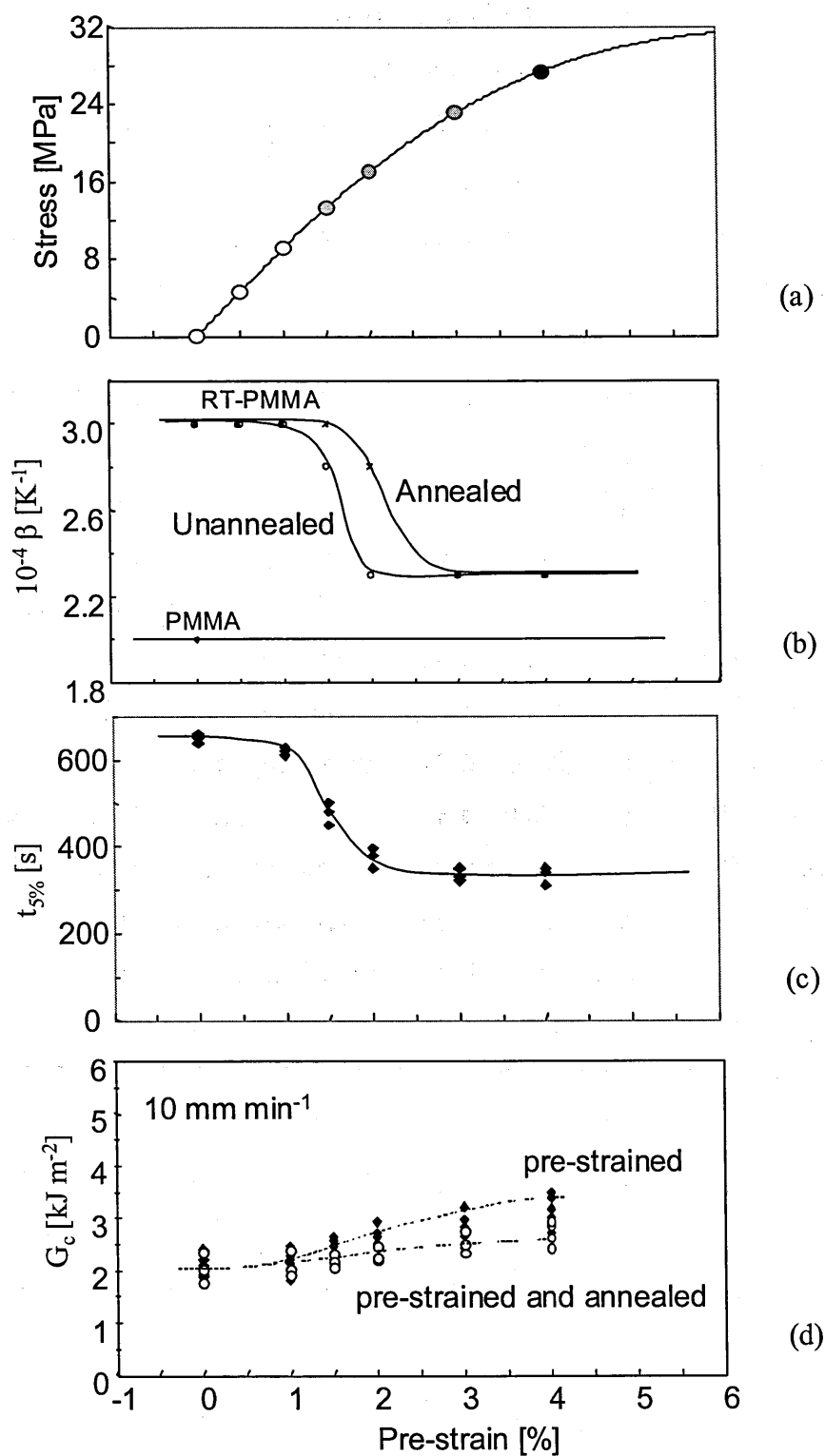


Fig. 5.7.1 Correlation between (a) visual damage under uniaxial tensile test, (b) thermal contraction behaviour, (c) time to reach 5% strain in the creep tests at 26 MPa and (d) sharp-notched fracture resistance at 10 mm min⁻¹ for a RT-PMMA (HSH CS-250-40).

CHAPTER 6

DISCUSSION

6.1. Introduction

The aim of this research is to characterise cavitation in multiphase plastics using experimental methods that are able to detect cavitation continuously from the time at which it starts to develop. Dynamic mechanical thermal analysis (DMTA) and coefficient of thermal expansion (CTE) measurements have proved to be very effective. Before the project started, very little had been published on the detection of cavitation in rubber modified polymers using indirect techniques such as DMTA and CTE investigation [Bucknall et al. 2000a, 2000b, Rizzieri et al. 2000, Ayre 1999]. In the present study, creep measurements and three-point bending fracture tests have also been taken into account and compared with DMTA and CTE results. The final aim consists in the enhancements of the energy-balance based theoretical model [Lazzeri and Bucknall 1993, 1995, Bucknall et al. 1994] to predict more effectively the conditions for multiple cavitation.

6.1.1. Why detection of cavitation is relevant

Void formation in the rubber particles has been known to be fundamental in rubber toughening of plastics for over twenty years [Bucknall 1997]. It is now well accepted that cavitation significantly contributes to the toughening mechanisms and to the fracture resistance of multiphase notch sensitive polymers. More recently, it has been recognised that rubber particle cavitation is probably a rate-controlling step in the deformation and fracture of these materials, especially under critical conditions involving sharp cracks in thick specimens [Bucknall 2000].

The formation of voids within the rubber provides the possibility of relieving the triaxial stress field in the proximity of the crack tip and enhancing plastic deformation in the matrix. In this case, the transition from plane strain to plane stress conditions will enlarge the yield zone and promote crack blunting. In most types of toughened plastics,

cavitation of the rubber particles near a crack tip is followed by shear yielding or crazing in the surrounding matrix to form dilatation bands, thereby allowing the material to yield at greatly reduced stresses.

Several research groups have detected and modelled the effects of cavitated rubber particles in promoting shear yielding near crack tips. Dilatational shear bands formed in this way have been observed in several different rubber-toughened plastics [Bucknall 1997, 2000]. Therefore, as the primary crack tip energy absorbing mechanism is related to the intense global shear yielding or shear banding between cavitated or ruptured rubber particles and to plastic void growth, void formation is essential, as a stress releasing mechanism, for notch-sensitive polymers. Strong evidence shows that rubber particle cavitation is a required precursor to internally-generated multiple crazing in toughened glassy polymers such as ABS and high-impact polystyrene (HIPS) [Yang and Bucknall 1997]. However, some researchers have reservations on this point, and are looking for further experimental evidence to resolve this issue. No theory related to the precise modifications induced by the rubber particles in the toughening of plastics is absolutely accepted.

Focusing on these developments, it is clearly important to seek a quantitative understanding of the factors controlling cavitation of the rubber phase. In order to do so, distinction and isolation of the cavitation event from the dilatational yielding, shear yielding and crazing, that occur to varying degrees and interact during the deformation of polymer blends, have to be pursued. The present study addresses this objective.

6.2. Detection of cavitation using direct methods

Previous studies of rubber particle cavitation have been based mainly on measurements of small-angle X ray scattering, light scattering, electron microscopy, or other methods in which the detection of rubber particle cavitation depends upon large-scale expansion of cavities, which may initially be less than 10 nm in diameter.

The evidence for cavitation in rubber particles that has been published so far comes mostly from optical or electron microscope studies. Optical and electron microscopy

provides information about shear yielding, crazing and rubber particle cavitation, but it is an invasive method with many limitations. Most studies are on cavities formed within the rubber phase when the polymer was subjected to large tensile stresses. These conditions nearly always produce a large amount of shear yielding and/or crazing in the surrounding rigid matrix. Consequently, these methods produce data on the initiation and development of dilatational yielding, rather than on the cavitation event itself. In fact, by the time the cavities are examined under the microscope, they have already undergone large expansions from their original equilibrium dimensions, in response to the increasing local strains in the matrix.

In polymers modified with rubber particles, the detection of cavitation using direct methods like transmission electron microscopy (TEM) or scanning electron microscopy (SEM) is not easy because of the small size of the particles and the drawbacks of these techniques. The SEM does not have the resolution to detect very small cavities, and even when the cavities are larger the image contrast between rubber, holes and hard inclusions is often not clear. TEM can resolve down to 10 nm, but the preparation technique, based on staining and sectioning often induces artificial deformation and damage in the samples. Microtoming thin slices (70 ~ 80 nm) of a soft and ductile material can end up with non-uniform thickness of the slices, local stress, shape deformation of the particles and smearing of the soft phase. To reduce these undesired effects the material can be cryotomed (like nylon at -90°C). In multiphase plastics, cooling will induce differential thermal contraction because the hard and soft phases have very different coefficients of thermal expansion. The use of a hardening agent such as osmium or ruthenium tetroxide (OsO_4 and RuO_4 , respectively) can help to reduce damage to the soft inclusions and increase the contrast between rubber and matrix. On the other hand, the stain has the disadvantage of modifying the observed results of deformation. It may cause swelling of the rubbery phase or non-uniform oxidation of the rubber. It may plasticise the matrix, thereby obscuring damage such as crazes. There is also the problem of electron beam damage, which can easily be confused with the natural deformation that is under investigation. The effectiveness of microscopy as an investigation technique is therefore limited.

Microscopy has the obvious advantage of allowing direct observation and characterisation of morphology of the cavities formed within rubber particles, but there is a clear need for alternative experimental techniques that can detect and monitor the cavitation process in itself during its early stages and induce cavitation in the rubber particles, without causing any damage to the matrix. It is concluded that the validity of direct analysis using electron microscopy is greatly enhanced when it is supported by some complementary methods.

6.3. Detection of cavitation using indirect methods

There are indirect methods of detecting cavitation that cannot distinguish void formation in the soft phase (due to either simple cavitation or fibrillation) from void formation in the rigid matrix (crazing). One example is the measurement of the volume change during tensile tests to quantify crazing and cavitation, which are both dilatational processes. Shear deformation is to a first approximation a constant volume process; therefore, the axial strain is compensated by the lateral strain. Dilatational processes like crazing and cavitation can occur without a significant change in cross-sectional area. Thus a graph of volume strain plotted against axial strain features a gradient of 1 if the deformation is entirely due to dilatational processes, and 0 if shear deformation is the only deformation mechanism. Even so, it cannot be determined which of the two voiding mechanisms is actually operating [Lazzeri 1991].

Indirect methods such as DMTA and CTE measurements are here used to obtain evidence that cavitation occurs in the rubbery phase. The success of these methods is based on the fact that they do not induce any damage other than cavitation in the rubbery phase. Therefore these techniques can be used either to create the conditions for the initiation of cavitation (by simple cooling with the CTE method, or cooling and stretching with DMTA) or to detect rubber particle cavitation if it is already present in the sample, without creating the necessary conditions for matrix deformation (shear yielding and crazing).

Creep measurements and three-point bending fracture analysis are also indirect techniques that can detect cavitation. Because the time to reach 5% strain in the creep

tests is very sensitive to pre-strain, creep experiments show a better transition from unstrained to pre-strained (cavitated rubber phase) data, than fracture tests. However, these methods involve large stresses and strains, so that not only cavitation will be present in the material. Annealing has been used to minimise plastic deformation in the matrix after pre-straining (transparency of the material was then restored). A broadly-based study, involving DMTA, CTE measurements, creep and fracture tests will give a wide viewpoint on the overall deformation process.

Void formation in the rubber requires an energy input, which is supplied by some combination of differential thermal contraction and mechanical loading. In toughened thermoplastics, volume strains in the order of roughly 1% are generated within the rubber particles simply on cooling from the T_g of the matrix (typically $>100^\circ\text{C}$) to 23°C [Ayre et al. 1998]. Under appropriate conditions, differential thermal contraction alone can be sufficient to cause cavitation, as demonstrated by Humme et al. [1976] and Morbitzer et al. [1982] in dynamic mechanical studies on ABS. Application of tensile stress to ABS produces additional dilatational volume strains of a similar magnitude in the rubber. These strains are partially or fully released when the particles cavitate.

6.4. Coefficient of Thermal Expansion (CTE) Measurements

CTE measurements are easily performed. In principle CTE technique involves simple equipment, for example any sensitive device with movable jaws for holding the sample that are capable of registering small changes in length, and an accurate thermostatic chamber which regulates the temperature of the sample. To analyse the degree of damage already present or induced in the material by the cooling it is enough to calculate the volume coefficient of expansion (β) (equivalent to three times the linear coefficient of expansion (α), which is measured from the slope of the curve of length against temperature).

In toughened plastics a significant volume strain is created in the rubber particles purely during cooling. This occurs because rubbery materials have a thermal expansion coefficient approximately three times larger than glassy plastics. During cooling a

rubber particle tries to contract more than the surrounding matrix, which resists this modification. Consequently the rubber particle will be subject to negative hydrostatic pressure and undergo expansion, while the matrix will develop reaction forces. Differential thermal contractions generate triaxial tension in the rubber particles and cause a large increase in the coefficient of thermal expansion of RT-PMMA relative to that of the matrix PMMA. Therefore, while the pure glassy material will have a certain coefficient of expansion, the rubber-toughened polymer will have a higher thermal expansion coefficient, as discussed in Chapter 5 (Figure 5.4.4). When the hydrostatic negative pressure on the rubber particle reaches a critical value, the result can be fibrillation or void formation within the rubber, or debonding between rubber and matrix. As the rubber or the rubber-matrix interface fails, the constraint upon the material will be reduced or removed, the matrix will respond more like the pure material and the thermal contraction coefficient of the blend will decrease. This behaviour has been observed in two ABS materials by Bucknall et al. [2000a].

In most toughened thermoplastic materials, thermal strains alone appear to be insufficient to cause rubber cavitation, and there is a need for an external mechanical load. On superimposing a mechanical load, the state of tension in the rubber becomes more severe, and its effects are less able to be dissipated by relaxation than is the case with thermal stress. For this reason, pre-straining and pre-straining-annealing treatments have been adopted to investigate RT-PMMA deformation processes.

The CTEs of pre-strained and annealed RT-PMMA (HSH CS-250-40) drop closer to that of PMMA, but only for specimens subjected to a tensile pre-strain of 2% or more, whereas pre-strains of 1.5% or less do not cause a reduction in CTE. This is because the role that the rubber particles played on the CTE of the RT-PMMA, is reduced by cavitation or debonding present in the particles after pre-straining above 1.5%. Consequent annealing restored the CTE to its original value only in the case of specimens with a pre-strain of 2% or less. These results indicate that some very small residual cavities can remain in the rubber after annealing. CTE measurements (as well as creep tests) have been performed on pre-strained specimens up to 4% strain. It is suggested further work on pre-strained samples above 4%.

6.5. Dynamic Mechanical Thermal Analysis (DMTA)

The DMTA technique has been used to detect cavitation, by linking thermal contraction and mechanical loading contributions. DMTA tests apply not just differential volume strains to the sample, but tensile and compression stresses are added, revealing that a low tensile stress (as low as 2 MPa) could be enough to turn a small hole into a permanent void. In any case, mechanical work (tensile) is necessary to open pre-existing cracks. This method can so be used to estimate the volume fraction of particles that have sustained any sort of damage that induces relaxation in the rubber. By observing the position of $\tan \delta$ peak temperature versus applied stress it is possible to detect the distribution of stresses and strains within the rubber phase. DMTA results have been found to be very reproducible. DMTA is therefore a powerful technique to determine cavitation even during the early stages of void formation. A major advantage of the dynamic mechanical technique is that it provides a method for observing the onset of rubber particle cavitation as a separate process without the complications that arise when shear yielding or multiple crazing occur at the same time. For this reason even a low volume fraction of cavitated rubbery phase can be detected and estimated with accuracy in the sample.

Early works from Lin et al. [1998], Ayre [1999] and Johnson [2000] on different rubber toughened plastics, have confirmed the linear dependence of the rubber loss peak temperature upon increasing applied compression loading. DMTA results under applied tension were instead cause of many doubts. The discontinuity in pressure dependence was mainly seen at about 0 MPa (illustration in Figure 6.5.1a), raising the suspicion of inconsistency from compression to tensile experiments, because of the changing in loading configuration.

The present study, for the first time, shows a clear linear behaviour from compression to tension of the rubber $\tan \delta$ peak temperature versus applied load (Figure 6.5.1b). A significant number of tests (3 or 4 tests at the same test conditions), with a good level of data reproducibility, have been carried out on RT-PMMA (HSH CS-127-18), reporting an approximately straight line. Moreover, the present thesis suggests an explanation to the possibility of finding $\tan \delta$ peak temperature above the baseline of the linear loss

temperature-pressure relationship (Figure 6.5.1c). DMTA tests on RT-PMMA (HSH CS-250-40 and HSH CS-250-25) report a large scattering in loss temperature data. Sometimes the rubber $\tan \delta$ peaks were split in two. However more evidence and proof to confirm and develop this study are advised.

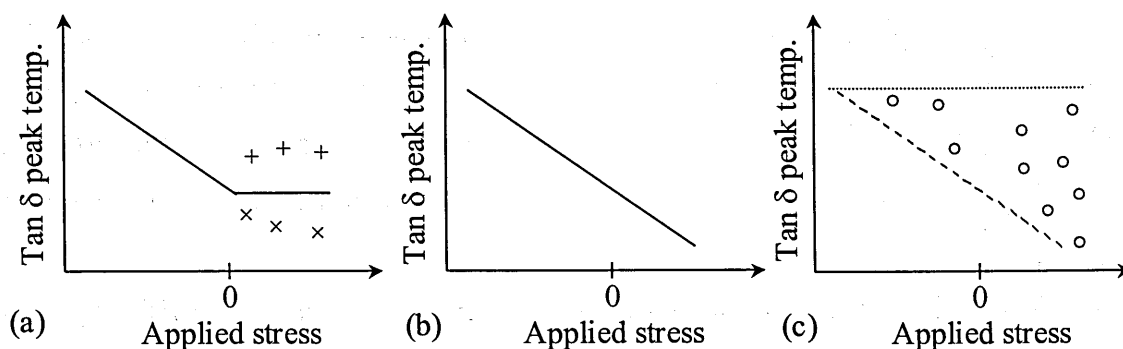


Fig. 6.5.1 Schematic illustration showing developments in DMTA results for toughened polymers under applied loading. (a) Early work by Lin [1998], Ayre [1999] and Johnson [2000], (b) and (c) results from the present study.

In principle, the relationship between the rubber relaxation temperature and the pressure is linear. However, while expecting a linear relationship, any deviation from linearity can be correlated with relaxation due to damage in the soft phase. If the triaxial stress due to thermal contraction, dilatational stress and mechanical work is released through debonding or complete cavitation, or it is only partially released through incomplete cavitation or fibrillation of the particles, the rubber $\tan \delta$ peak should shift to higher temperatures. In case of complete failure of the rubber the corresponding $\tan \delta$ peak moves to the T_{gr} of the relaxed rubber. When cavitation or fibrillation occur in some or all of the rubber particles, the state of stresses in the rubber phase is no longer uniform throughout the specimen, but varies from particle to particle. In some cases, DMTA tests show a double peak, representing both damaged and intact particles. In this case $\tan \delta$ peak could be anywhere between the glass transition temperature of the relaxed rubber and the glass transition temperature of the fully stretched rubber, as shown in Figure 6.5.1.

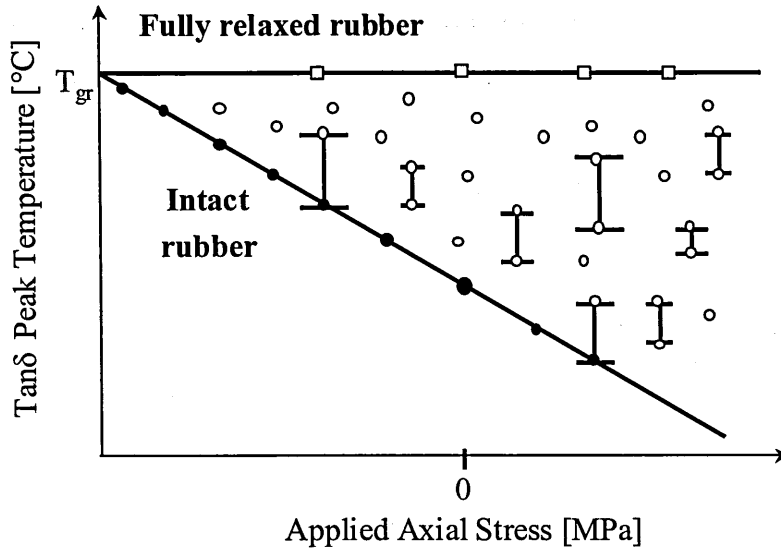


Fig. 6.5.2 Schematic diagram showing the effects of rubber particle cavitation upon loss temperature, where the cavitated rubber is fully relaxed (horizontal line); partially relaxed and fibrillated (white spots between the horizontal line and the oblique line, in this case double peaks are represented with error bars), or undamaged and highly stretched (black spots on the oblique line).

Evidence of rubber $\tan \delta$ peak scattering and presence of double peaks in the compression region of applied stresses, have been found for a RT-PMMA (HSH CS-250-25) tested after yielding (Figure 5.3.14, Chapter 5). Pre-straining to 4% in tension caused a very large scatter in T_{gr} values, indicating a wide distribution of internal stresses in the rubber phase. In that way, DMTA has been used to detect distributions of stress and strain within the rubber phase after the onset of cavitation in the particles. It could also provide valuable information about the progress of cavitation under increasing applied loads. In Figure 6.5.2, white spots and double peaks in the compression region, have been considered to be due to cavitation of pre-existing voids, introduced by tensile yielding. Subsequent annealing drastically reduced the scatter to a very low level (Figure 5.3.14, Chapter 5), while CTE measurements registered no changes in CTE of annealed pre-strained samples above 2%. Small cavities may remain in the rubber phase after annealing, so that they still contribute to the rubber relaxation under applied compression, but they do not support thermal expansion measurements.

In order to understand the complex relationship between applied stress and observed loss peak temperatures, especially under tensile loading, it is helpful to employ a

schematic diagram comparing the relaxation behaviour of intact rubber particles (i.e. well bonded and void-free core-shell particles) with that of the bulk rubber, as in Figure 6.5.3.

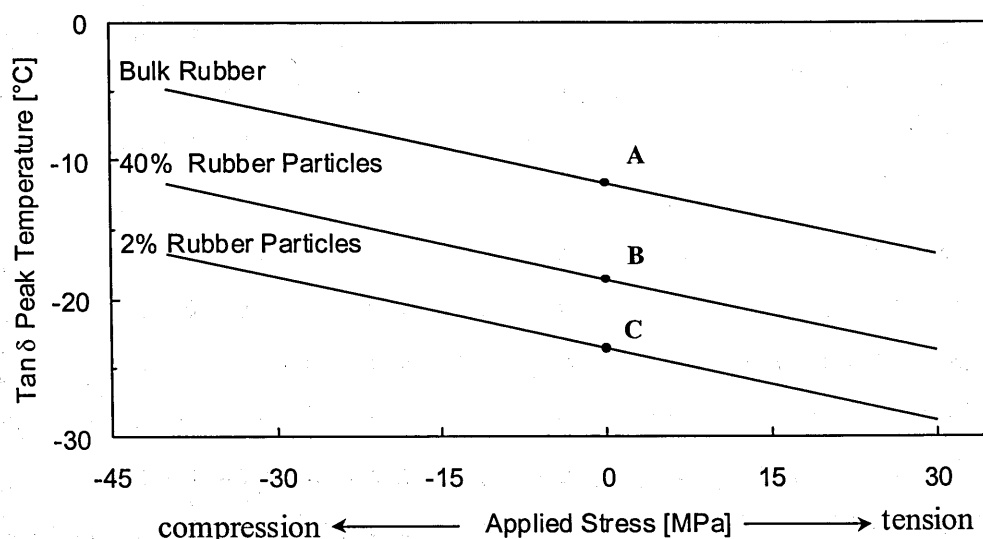


Fig. 6.5.3 Schematic diagram showing the relationship between applied mean stress and loss peak temperature for bulk rubber and for toughened polymers containing 40% and 2% rubber particles. Note that the mean ('hydrostatic') stress is one third of the uniaxial stress.

Point A defines the loss peak temperature T_{α} of the unstressed bulk rubber, which is higher than its true T_g because of the dynamic nature of the test. Considering both theoretical considerations and the work of Morbitzer et al. [1982] and Humme et al. [1976], thermal contraction can develop tensile stresses within the rubber particles causing the loss peak temperature to fall by as much as 20°C. The difference between the thermal contraction coefficient of the matrix and that of the rubber explains the location of the points B and C below A on the diagram. Point C is located below point B because of the lower concentration of rubber particles. The constraining effects of the matrix on the thermal contraction in the rubber particles become larger as the rubber content is reduced [Bucknall et al. 2000b].

In Figure 6.5.3, the lines through points A, B and C are based on the present work and that of McKinney et al. [1960]. It can be observed that quite high 'hydrostatic' pressures, in the order of 20-30 MPa (equivalent to uniaxial compressive stresses of

60-90 MPa) must be applied to the rubber blend to reduce the stress in the rubber phase to zero, and thus shift the $\tan \delta$ peak to the same temperature as point A. More generally, it can be seen that the large dilatational stresses generated in the rubber particles during cooling cause the whole T_α versus applied stress curve to shift progressively to the left as the rubber content is decreased [Bucknall et al. 2000b]. If, for example, the loss peak temperatures were plotted against the applied stress within the rubber particles, rather than the stress applied to the toughened polymer, then T_α versus stress curves for all rubber contents would lay over the curve for the bulk rubber, and pass through point A [Bucknall et al. 2000b].

An alternative way of reducing or eliminating tensile stresses in the rubber phase is to induce cavitation. As illustrated schematically in Figure 6.5.2, if the particles then become fully relaxed, they will produce a $\tan \delta$ peak at the same temperature as point A, which does not shift when the toughened polymer is subjected to tensile mean stresses (or to modest levels of compressive mean stress). If cavitation does not result in complete relaxation, the $\tan \delta$ peak will occur at a lower temperature, as shown schematically by the white circles between the lines marked 'Fully relaxed rubber' and 'Intact rubber'. The residual stress in the rubber phase may vary with applied stress.

The presence of a core in each particle could result in the formation of rubber fibrils, which are stretched out between core and shell, and therefore subject to quite high strains [Starke et al. 1997], although the mean stresses in the fibrils may be relatively small. On the basis of this evidence, it is clear that T_α for cavitated rubber particles can fall well below the relaxed-rubber line, because of large tensile strains in the fibrils, although mean stresses may be quite low (of the order of 1 MPa). The white spots in Figure 6.5.2 represent this state. Failures of the fibrils, of course, limit the extent of the downward shift in T_α .

The literature contains little information about the effects of large tensile strains on the relaxation behaviour of the rubber. Measurements on vulcanised butyl rubber have demonstrated a strong dependence of T_α on tensile strain (Figure 5.3.16, Chapter 5]. There is a downward shift of as much as 25°C on increasing the tensile strain from 30 to

175%. The direct conversion of intact rubber membranes to highly stretched fibrils would explain the data reported by Lin et al. [1998] for HIPS, and would be consistent with transmission electron microscopy observations.

6.5.1. An application of the above theory

Applying the principles above to the experimental results, it can be seen that the point at which zero axial stress is applied to RT-PMMA (point B), corresponds to a loss peak temperature of -21°C (Figure 6.5.4). The rubber phase undergoes a triaxial tension field at this point, because of differential thermal contraction due to cooling. Taking the values on Table 6.5.1 for the moduli and expansion coefficients of the rubber and PMMA phases [Brandrup and Immergut 1989], calculations [Ayre 1999] give a maximum value of +3% for the volume strain in the rubber phase, in the absence of an applied stress.

	Rubber	Matrix
Bulk Modulus: K [MPa]	2000	4000
Shear Modulus: G [MPa]	1	1000
Volumetric Thermal Expansion Coefficient: β [K^{-1}]	6×10^{-4}	2×10^{-4}

Tab. 6.5.1: Typical physical properties used for the calculation (Brandrup et al. 1989).

At this volume strain, the loss peak temperature for intact rubber particles should be about 9°C below that of the fully relaxed rubber. In other words, the estimated temperature at point A on the diagram is -12°C , as shown in Figure 6.5.4.

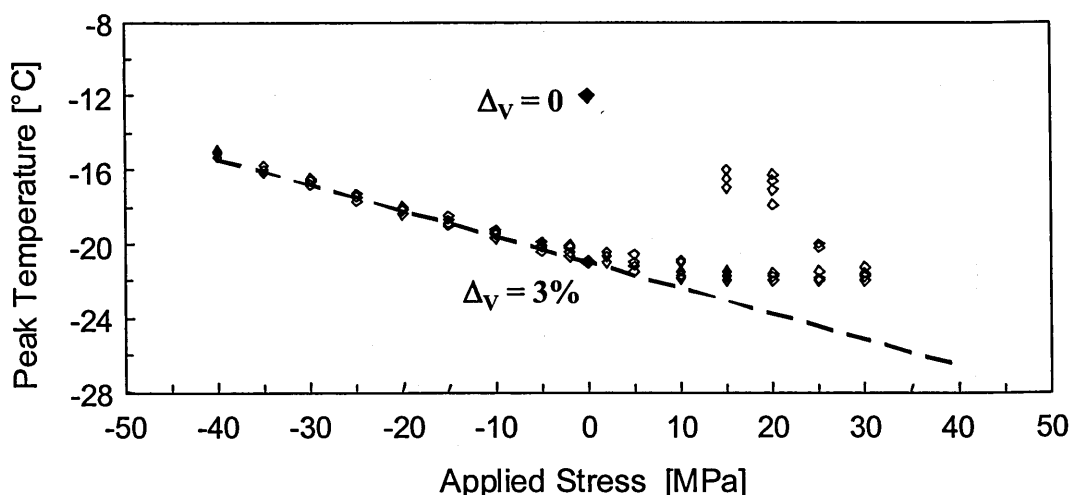


Fig. 6.5.4 Schematic diagram comparing for illustrative purposes the position of the loss peak temperature for intact rubber particles in the absence of applied stress ($\diamond$), with the data ($\diamond$) from DMTA tests for a RT-PMMA (HSH CS-250-40).

It follows that the observed loss peak temperature could rise as high as -12°C once the rubber particles have cavitated, assuming that the stresses and strains in the rubber phase fall to zero at that stage. This assumption is reasonable for some rubber-toughened plastics, but is not necessarily valid for the RT-PMMA (HSH CS-250-40) under investigation, because of its morphology. As in all transparent grades of RT-PMMA the rubber is present as a spherical inner shell which lies between a concentric spherical core of PMMA and an outer shell of PMMA, to both of which it is securely grafted. The outer PMMA shell binds the particle firmly to the surrounding matrix. Consequently, on cavitation the elastomeric shell can break up into fibrils, which connect the rigid core to the rigid matrix [Starke et al. 1997], in a similar manner to that observed in HIPS. During the early stages of cavitation, when total volume strains in the rubber particle are still in the order of 1%, only part of each elastomeric shell may be affected, with the remainder forming an intact layer connecting the core to the matrix, as illustrated in Figure 6.5.5.

However, as the strain in the neighbouring matrix increases, and especially if the matrix begins to craze, the volume strain in the particle will increase, and fibrillation of the rubber phase will spread until the whole of the shell is affected [Starke et al. 1997].

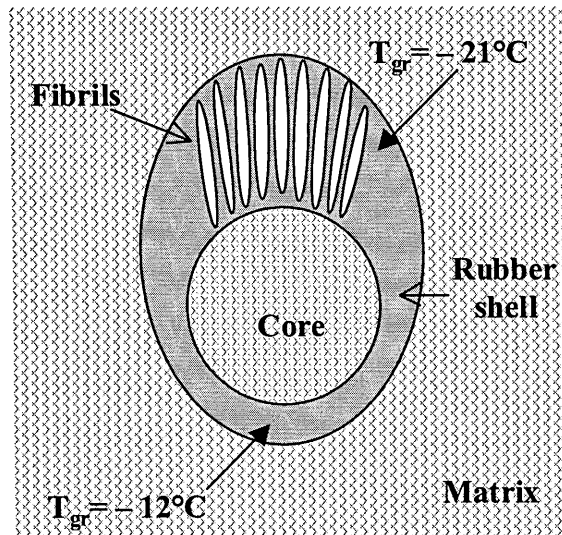


Fig. 6.5.5 Schematic representation of a rubber shell in a core shell rubber particle that is partially fibrillated and partially intact and connected to both the core and the matrix.

6.5.2. An energy-balance model for multiple cavitation

Many of the properties of rubber toughened polymers can be explained, at least qualitatively, using the energy-balance model for cavitation developed by Lazzeri and Bucknall [1993, 1995] and Bucknall et al. [1994]. In its simplest form, the model predicts the formation of one spherical void per particle, once the energy available reaches a critical level. In recent years, the development of this energy-balance model has led to an improved understanding of the cavitation process [Bucknall 1997, 2000] [Yang and Bucknall 1997] [Ayre and Bucknall 1998] [Lazzeri and Bucknall 1993, 1995] [Bucknall et al. 1994, 2000a] [Ayre 1999]. Void formation is made possible by the release of energy stored in the rubber particle itself (as volume strain energy) and in the surrounding rigid matrix.

One explanation for the variability in the rubber $\tan \delta$ peak for RT-PMMA (HSH CS-250-40 and HSH CS-250-25) could be found in electron micrographs. They show that complex rubber particles rarely form single cavities; typically, they contain many apparently discrete voids, which are often separated by rubber membranes and constrained by the presence of rigid polymer cores or sub-inclusions [Starke et al. 1997]. This scatter could be associated with the formation of voids in a fraction of the rubber

particles, and the consequent change in density and relaxation behaviour of the rubber phase. It has been suggested that the reason because the level of scatter is particularly high, especially under applied tensile stresses, is to attribute this to the formation of several cavities within each rubber particle. In complex rubber particles containing rigid sub-inclusions, morphology can limit the expansion of the initial voids, and thus provide conditions for the formation of additional voids within the same particle. This phenomenon is not addressed by simple energy-balance model, and it is therefore necessary to examine extensions of the model, which could account for the observed behaviour.

A modified version of the Lazzeri-Bucknall model, presented in Chapter 3, forecasts the successive formation of cavities within each rubber particle as the volume strain imposed on the toughened polymer increases. In this case, predicted critical volume strains are equally spaced, forming a discrete set of values, each corresponding to a stable configuration of the particle (Figure 3.6.1, Chapter 3). Using this model, a relationship is established between multiple cavitation of the rubber particles and the observed scatter in the loss peak temperature. However, it is important to note that a similar approach can be applied to the more general case. For example, the void might initially be spherical, but subsequently change to a different shape (e.g., to a spheroid), owing to the proximity of rigid sub-inclusions or the surrounding matrix. In some of these flattened voids, volumetric expansion is further restrained by craze-like fibrils spanning the gap between the walls of the void. For both of these cases, the relationship between the energy of the particle and the volume of individual voids can be of a form that promotes multiple cavitation within individual particles. Numerous examples of this phenomenon have been reported in the literature, especially in rubber particles containing a single rigid polymeric core and in the 'salami' particles that are formed in high-impact polystyrene. Further studies of the developed model are suggested to employ, in a rigorous manner, particle morphology and void shape.

CHAPTER 7

CONCLUSIONS AND OVERVIEW

A growing understanding of the precise role of the rubber particles in the toughening mechanism has developed over the past few years. Although various authors have slightly dissimilar points of view, they generally agree that rubber particle cavitation is fundamental. Cavitation allows lower yield stresses, especially under the constrained conditions at the tip of a sharp crack. The relevant role of rubber particles is to limit the stress imposed on the polymer by initiating yield and promoting strain softening. Rubber particles must have also the capacity to promote a degree of strain hardening in the material. Once the polymer has started the yield process, a homogeneous distribution of rubber particles is able to stop shear bands or crazes from degenerating into big cracks. Instead, the yield zone will substantially expand, and the energy absorption will increase a lot. The present thesis provides a better understanding of the role of cavitation in multiphase polymers, focusing attention on RT-PMMA.

Thermal contraction measurements compared the thermal contraction and expansion behaviour of PMMA and transparent RT-PMMA (hard-soft-hard core-shell, 250 nm particle diameter, 40 wt% rubber content: HSH CS-250-40) specimens after different types of pre-treatment. Coefficients of thermal expansion (CTE) and contraction (CTC) for straight PMMA and RT-PMMA were coincident. Plain PMMA gave a constant CTE $70 \times 10^{-6} \text{ K}^{-1}$, unaffected by pre-straining. Addition of rubber particles (featuring a much higher CTE than PMMA) caused a consistent increase in CTE (to $100 \times 10^{-6} \text{ K}^{-1}$, a 43% increment) inside the whole temperature range whose boundaries are the glass transition temperatures of the rubber and PMMA, T_{gr} and T_{gPMMA} respectively. At temperatures below T_{gr} both phases (matrix and rubber) are glassy and the CTE drops back to a low value ($70 \times 10^{-6} \text{ K}^{-1}$). Tensile tests on RT-PMMA show that the stress-strain curve rises steeply up to 4% strain, while whitening starts to appear at strains beyond 1.2% and yield takes place at 6% strain. Thermal contraction measurements present evidence of extensive cavitation of the rubber phase much earlier, at strains of about 2%. Specimens subjected to a tensile pre-strain of 2% or more gave a CTE of only $80 \times 10^{-6} \text{ K}^{-1}$, whereas pre-strains of 1.5% or less did not cause any change in CTE. Since cavitation (or

debonding) limits the ability of the rubber to contribute to the CTE of the blend, the fall in CTE is explained by these processes. Subsequent annealing eliminated the whitening produced during pre-straining, but restored the CTE to its original high value only in the case of specimens with a pre-strain of 2%. This result indicates that strains of 3% are sufficient to introduce damage that does not fully recover on annealing. Some very small residual cavities can remain in the rubber after annealing, leading to the reduced CTE of the blend.

Tensile creep tests at 23°C and 26 MPa tensile stress were performed on specimens pre-strained to different levels. Pre-strains of 1% had no effect on creep behaviour, but a pre-strain of 1.5% caused a significant increase in creep rate, and pre-strains of 2, 3 or 4% raised the creep rate to double its original value. Subsequent annealing caused a small reduction in the creep rates of the more highly strained specimens. These experiments demonstrate the strong influence of rubber particle cavitation on the deformation behaviour of toughened plastics

Dynamic mechanical tests were carried out over a range of temperatures on stressed specimens of various multiphase polymers. Shifts in the position of the rubber $\tan \delta$ peak (related to the position of T_{gr}) were measured to determine the effects of stresses upon the rubber phase behaviour. Under increasing compressive stress, the peak shifts to higher temperatures, because the density of the soft phase increases, and relaxation times therefore become longer. Conversely, under increasing tensile stress, the $\tan \delta$ peak should shift to lower temperatures. However, these downward shifts occur only if the rubbery phase is: (a) well bonded to the rigid phase, so that stresses are fully transmitted across the interface; (b) free from internal voids, so that the imposed volume increase is not taken up simply in expanding a void.

Tests on RT-PMMA under compression show the expected pattern of behaviour. T_{gr} increases steadily with applied constant stress. On the other hand, under tension T_{gr} remains constant or increases in an irregular way, indicating that cavitation has taken place in the rubber phase. Here the jump in T_{gr} is due to the release of internal stresses in the rubber particles, produced as a result of differential thermal contraction from

T_{gPMMA} . Cavitation allows the rubber phase to relax, affecting its density and T_{gr} . Similar results were obtained for a different RT-PMMA (HSH CS-250-25), with a lower rubber content (25 wt%) but similar morphology (hard-soft-hard core-shell). Pre-straining to 4% in tension causes the scatter in T_{gr} values to become very large, indicating a wide distribution of internal stresses in the rubber phase, while subsequent annealing reduces the scatter. The dynamic mechanical tests, supported by electron microscopy and mathematical modelling, provided further progress in understanding the cavitation mechanism. There are three possibilities.

a) Complete failure at the rubber-matrix interface (debonding). This would cause a separation of the rubber phase from the matrix, so that any internal stresses in the rubber would be relaxed, and T_{gr} would become independent of the tensile stress on the specimen. Calculations show that near -20°C the internal stresses due to differential thermal contraction should cause a depression of about 12°C in T_{gr} , provided there is no debonding or cavitation. The release of such stresses should therefore allow the $\tan \delta$ peak to shift upwards by this amount.

b) The particle remains intact, with no failure either at the interface or internally. In this case, the loss peak should shift downward with increasing applied tensile stress, as its free volume increases in response to dilatational volume strain.

c) An intermediate state, where partial failure has occurred in the rubber phase, but stresses are still transmitted to the rubber, e.g. rubber fibrillation. In this case, the loss peaks, due to the glass transition in the rubber, will lie somewhere between the high temperature defined by (a) (the T_{gr} of the unstressed rubber) and the lower temperatures defined in (b) (the T_{gr} of the stressed rubber).

None of the materials studied exhibits the behaviour defined under (a). For a transparent RT-PMMA containing small particles (127 nm diameter), low rubber content (18 wt%), and hard-soft-hard core-shell particle morphology (HSH CS-127-18), the T_{gr} shifts downwards linearly with tensile stress, indicating the rubber particles remained intact under test conditions (possibility (b)). This observation is consistent with the predictions

of the energy-balance model, that resistance to cavitation should increase when the particle size is reduced.

Results on RT-PMMA (HSH CS-250-40 and HSH CS-250-25) show a scatter of T_{gr} values under superimposed tension, corresponding to condition (c) above, where partial relaxation occurs in the rubber phase. However, in some specimens of HSH CS-250-25 that had previously yielded in tension, the scatter band was larger, and extended to include specimens that were subjected to dynamic mechanical tests in superimposed compression; in these cases, the compression was unable to close up voids that had been formed during the initial tensile test. A similar discontinuity was also observed in polyoxymethylene (POM) homopolymer, where an internal failure within the soft blocks is comparable with rubber particle cavitation in toughened PMMA. In this context, it is worth observing that the high rigidity and yield stress of POM allow us to measure the T_g of the elastomeric amorphous phase over a very wide range of superimposed stresses.

Tests on RT-PMMA containing EVA poly(ethylene-co-vinyl acetate) (salami particle morphology with 2% wt rubber content: S2-EVA, and 4% wt: S4-EVA, intermediate rubber morphology with 6% wt rubber content: I6, continuous rubber morphology with 8% wt rubber content: C8) and tests on RT-PMMA containing CSPE (chlorosulphonated-polyethylene) (salami particle morphology with 4% rubber content: S4-CSPE) showed no evidence of a low temperature relaxation peak due to the rubber phase. This relaxation might be obscured by the broad β peak due to the PMMA matrix. A material containing EPDM (ethylene-propylene-diene-monomer terpolymer) salami particles (with 4% wt rubber content: S4-EPDM) showed a prominent $\tan \delta$ peak at about -43°C , which shifted a small amount with applied stresses in the range -10 to $+10$ MPa.

Tests were also carried out on RT-PMMA materials containing hard-soft-hard core-shell particles of different diameters, ranging from 127 to 203 nm and 18% wt rubber content (HSH CS-127-18, -130-, -176-, -186-, -200-, and CS-203-18). The number of

tests completed was rather limited, but they did show evidence of an increasing resistance to cavitation with decreasing particle size.

Ultra-microtomed sections were obtained from specimens of RT-PMMA prepared by all of the polymerisation techniques covered in this study. Before microtoming, the specimens were stained with ruthenium tetroxide. Sections from unstrained and strained specimens were examined using TEM. This work showed no evidence of debonding at the interface between rubber and matrix, nor at the boundary between the rubber shell and the rigid cores, nor between the rubber phase and the rigid sub-inclusions in salami particles. However, in specimens that had been subjected to moderate or high tensile strains, there was ample evidence for cavitation within the rubber phase. Electron microscopy studies have been used mainly to characterise the blend morphology and investigate the deformation mechanism. TEM analysis always brings up doubts on any observed deformation, because it is a too invasive method (see specimen preparation). Therefore the TEM technique has been used principally for confirmation of results from other experimental work.

Three-point bend tests were carried out at 23°C on sharply-notched (Charpy-type) bars of HSH CS-250-40, at loading rates of 10 mm min⁻¹ and 1 m s⁻¹ (impact). Before cutting the specimens, the material was subjected to tensile pre-strains in the range 1% to 4%; some of the tensile specimens treated in this way were subsequently annealed above the T_g of PMMA. In both series of tests, the apparent fracture energy G_c value increased by about 50% and K_{Ic} dropped by 20% with increasing pre-strain. Annealing at 115°C reduced these improvement in G_c values for specimens pre-strained to 1.5% or more, but after annealing a distinct increase of G_c and decrease of K_{Ic} with pre-strain was still observed. Again, the results exhibit the positive effect of rubber particle cavitation on toughness. Since a high degree of rubber cavitation is always present around the notch tip (triaxial stress field) when the fracture experiment starts, G_c and K_{Ic} values are not fully representative of rubber particle cavitation. The consequence of pre-straining is to enlarge the cavitated yield zone beyond the region that it forms naturally.

A mathematical model, previously reviewed by Ayre [1999] has been developed to predict the favourable conditions for energy absorbing deformation mechanisms, such as multiple cavitation and provide support to experimental evidence. The energy-balance model [Lazzeri and Bucknall 1993] has shown in the past [Bucknall et al. 1994, Lazzeri and Bucknall 1995] that resistance to cavitation in the rubber particles depends upon their average size and size distribution, and also on the surface energy and shear modulus of the rubber phase. Shear modulus is a function of chain structure, cross-linking, temperature, and loading rate. Ayre's [1999] development of the model resulted in the inclusion of two new terms:

1. The energy stored in the rigid PMMA core and the rigid PMMA matrix
2. The strain energy generated as a result of differential thermal contraction between rubber and matrix on cooling from the T_g of the PMMA.

These principles have been applied to hard-soft-hard core-shell particles provided for this project. The present work has attempted to enhance the model featuring the possibility of forming several voids in a single rubber particle. This prediction has been confirmed during this study using DMTA, thermal contraction measurements and TEM. However, further improvements are required to achieve a better understanding of this complicated subject.

The two original experimental techniques (DMTA and thermal contraction measurements) adopted here, have proved to have a high capability of detecting cavitation in multiphase polymers. Dynamic mechanical tests under axial stress can qualitatively characterise the stress in the rubber. While debonded rubber should be stress-free except under compression, T_{gr} of intact rubber should fall linearly with increasing mean stress.

The flexibility of the thermal contraction method makes it applicable to determining whether the rubber particles have cavitated (debonded). This method has the advantage of being applicable to opaque rubber-toughened polymers, including mineral-filled polymers.

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APPENDIX A

Cavitation diagram

Cavitation diagrams were introduced by Lazzeri and Bucknall [1995] in order to describe and predict material behaviour under various loading conditions. The sequence of yield, cavitation and fracture processes are defined in terms of the von Mises σ_e and the mean stress σ_m .

A schematic cavitation diagram based upon the properties of an arbitrary polymer containing 40% in volume of rubber particles is here discussed. For clarity the deformation components contained in the diagram are first independently considered: shear yielding, particle cavitation, crazing and fracture. At the end, all the information is summarised in one comprehensive diagram.

A.1. Shear Yielding

According to the von Mises strain energy density criterion, yielding occurs where a critical value of σ_e (σ_e = von Mises equivalent stress or deviatoric stress) is reached:

$$\sigma_e = \sqrt{\frac{(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2}{2}} > \sigma_0 \quad (\text{A.1})$$

where σ_0 refers to pure shear yield stress and $\sigma_1, \sigma_2, \sigma_3$ represent the principal stresses. In polymers, the yield behaviour is largely pressure dependent, described by a modified version of the von Mises criterion (A.1):

$$\sigma_e > \sigma_0 - \mu \sigma_m = \sigma_0 - \mu \frac{\sigma_1 + \sigma_2 + \sigma_3}{3} \quad (\text{A.2})$$

where σ_m identifies the mean normal stress (hydrostatic pressure) and μ is a material constant (dimensionless pressure coefficient) related to the uniaxial yield stresses in tension Y_t and compression Y_c : $\mu = 3 \frac{Y_c - Y_t}{Y_c + Y_t}$.

McClintock [1968], Berg [1970], Gurson [1977] developed a modification for a material containing voids, where the yield behaviour is depending on the volume fraction (f) of voids:

$$\sigma_e = \sigma_0 \sqrt{1 - 2f \cosh\left(\frac{3\sigma_m}{2\sigma_0}\right) + f^2} \quad (\text{A.3})$$

Lazzeri and Bucknall [1993, 1995] combined (A.2) and (A.3) to work out yield behaviour as a function of pressure and volume fraction of voids:

$$\frac{\sigma_e^2}{\sigma_0^2} + \mu \frac{\sigma_m}{\sigma_0} \left(2 - \mu \frac{\sigma_m}{\sigma_0}\right) + 2f \cosh\left(\frac{3\sigma_m}{2\sigma_0}\right) - f^2 = 1 \quad (\text{A.4})$$

Equation (A.4) embeds the previously mentioned formulae: (A.1) $f = \mu = 0$, (A.2) $f = 0$, and (A.3) $\mu = 0$. For $\mu = 0.39$ and f in the range 0 to 0.4, the following yield condition for the cavitation diagram (σ_e versus σ_m) are given:

In Figure A.1 upper and lower bound envelopes for shear yielding define an elastic region below the lower bound, where the material has not yet reached its yield stress. In the area between the two bounds, the material is able to yield only in presence of voids that allow dilatational shear band. A plastic region, above the upper bound envelope, defines the zone where the material can yield in any case.

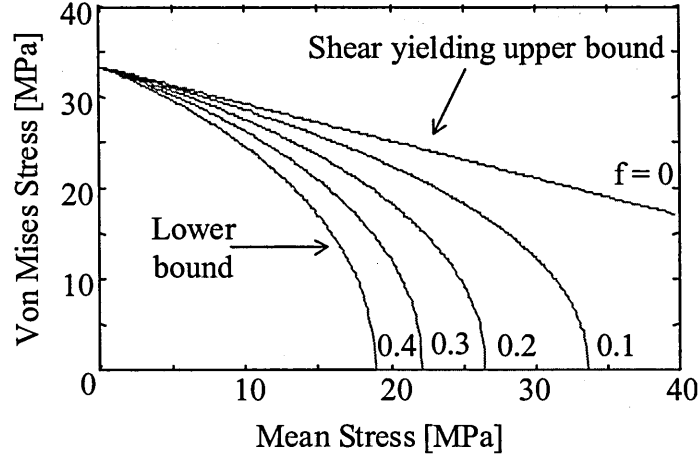


Fig. A.1 Representation of shear yield envelopes described by equation (A.4), taking f in the range 0 (no voids) to 0.4 (all particles cavitated).

A.2. Particle cavitation

Cavitation is here described as a function of hydrostatic stress only.

$$\begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \end{bmatrix} = \frac{E}{1-\nu-2\nu^2} \begin{bmatrix} 1-\nu & \nu & \nu \\ \nu & 1-\nu & \nu \\ \nu & \nu & 1-\nu \end{bmatrix} \begin{bmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \end{bmatrix}$$

where E is the elastic modulus and ν the Poisson's ratio.

In the case $\varepsilon_1 = \varepsilon_2 = \varepsilon_3 = \varepsilon$, the principal stresses $\sigma_1 = \sigma_2 = \sigma_3 = \frac{E}{1-\nu-2\nu^2} (1+\nu)\varepsilon$

and the mean stress becomes: $\sigma_m = \frac{\sigma_1 + \sigma_2 + \sigma_3}{3} = \frac{E}{1-\nu-2\nu^2} (1+\nu)\varepsilon$. Substituting

the relationship $E = 3K(1-2\nu)$, where K is the bulk modulus, the mean stress turns into: $\sigma_m = 3\varepsilon K$.

Therefore, the critical mean stress required to cause cavitation is:

$$\sigma_m = K\Delta v_c \quad (\text{A.5})$$

where Δ_{vc} is the critical volume strain calculated using equation (3.2) in Chapter 3.

Figure A.2 shows the dependence of cavitation upon rubber particle size. Those particles with lower diameter require a bigger mean stress for void formation, whereas the largest particles are expected to cavitate first.

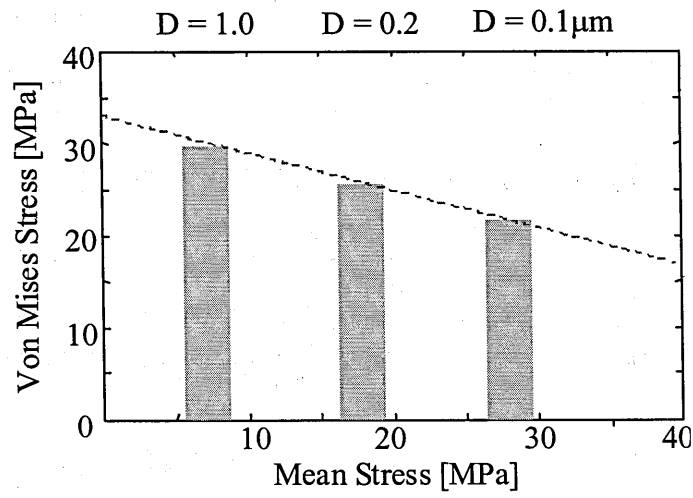


Fig. A.2 Mean stress from equation (A.5) for rubber particle cavitation for different sizes of rubber particle diameter (D). The dotted line represent the upper bound yield envelopes, from Figure A.1.

A.3. Crazing and fracture

The onset and propagation of crazes and cracks are defined here simply in terms of critical tensile stress. Crazing occurs when the principal stress reaches a critical magnitude. Three different stress states are taken as example:

i. Uniaxial tension $(\sigma, 0, 0)$, $\sigma_m = \frac{\sigma}{3}$ and $\sigma_e = \sigma$, so that $\sigma_e = 3\sigma_m$.

ii. Equi-biaxial tension $(\sigma, \sigma, 0)$ (plane stress crack tip conditions), $\sigma_m = \frac{2}{3}\sigma$ and

$$\sigma_e = \sigma, \text{ so that } \sigma_e = \frac{3}{2}\sigma_m.$$

iii. Triaxial stress ($\sigma, \sigma, 2\nu\sigma$) (plane strain crack tip conditions), $\sigma_m = \frac{2}{3}\sigma(1+\nu)$ and

$$\sigma_e = \sigma(1-2\nu), \text{ so that } \sigma_e = \frac{3}{2} \frac{1-2\nu}{1+\nu} \sigma_m.$$

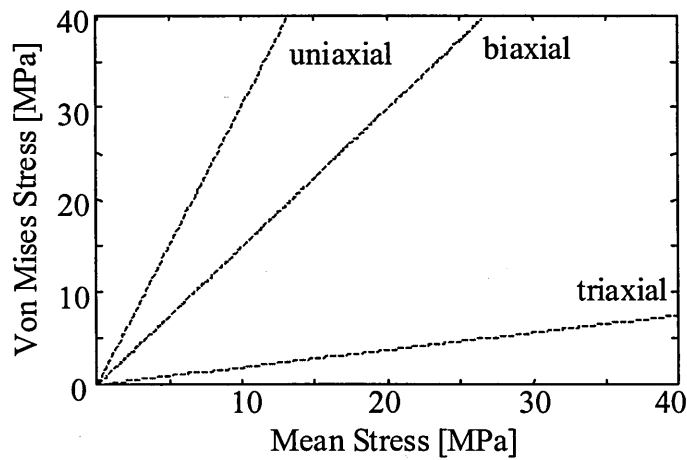


Fig. A.3 Condition for fracture in uniaxial (i), equi-biaxial (ii) and triaxial (iii) stress field.

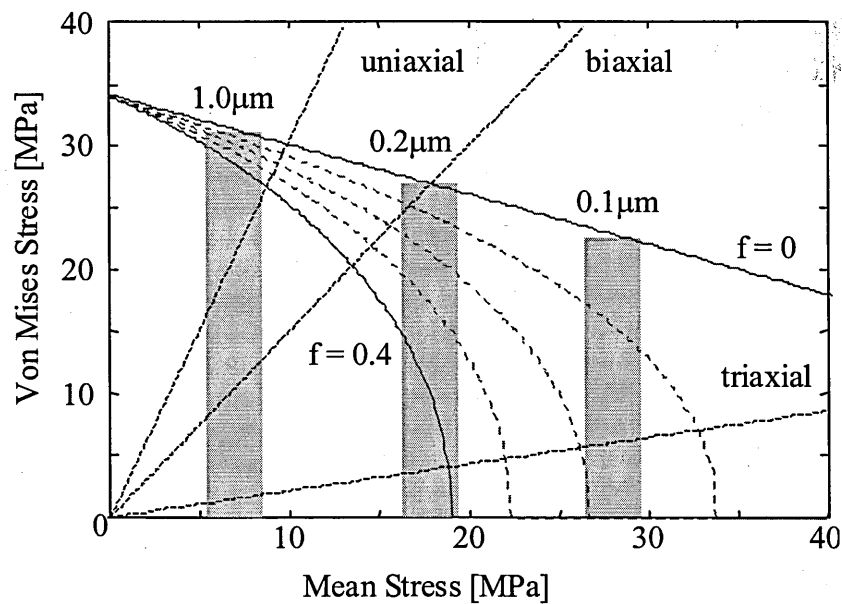


Fig. A.4 Cavitation diagram combining information from Figs. A.1, A.2 and A.3.

By comparing yield shear, cavitation and crazing in one diagram it becomes possible to observe how they interact, Figure A.4. Large particles cavitate before yielding in

uniaxial tension. The presence of voids reduces the yield stress and this depression is much smaller in uniaxial tension than at the crack tip (triaxial stress field). Particles with diameter of 0.2 μm , under biaxial stress, cavitate in the middle region and promote dilatational yielding. Particles of diameter 0.1 μm under uniaxial and biaxial stress are unable to cavitate before crazing and failure is brittle.

APPENDIX B

B.1. The Lazzeri-Bucknall (LB) model revisited

The LB model considered a spherical rubber particle of initial radius R_0 subjected to a prescribed spherically symmetric radial displacement field on its boundary. The state of deformation is homogeneous and the radial displacement grows monotonically in such a way that inertial effects are negligible. The radius of the particle increases from R_0 to R under the prescribed radial displacement, then R is held constant during the nucleation of a spherical void of radius r . The changes in the geometry of the particle from its reference configuration to its current one are meant to be ‘small’, i.e. these changes are described by means of the linearised geometry. Because the changes in the overall geometry are ‘small’, the linearization of the gradient of deformation leads, in particular, to the ‘infinitesimal’ strain tensor. The trace of this tensor accounts for its hydrostatic part, and this trace is named *volumetric strain*, denoted by Δ_v . The assumptions mentioned above allow us to treat Δ_v as a prescribed scalar (constant) field, in place of the radial displacement on the boundary of the particle in its reference configuration, as shown in Figure B.1.

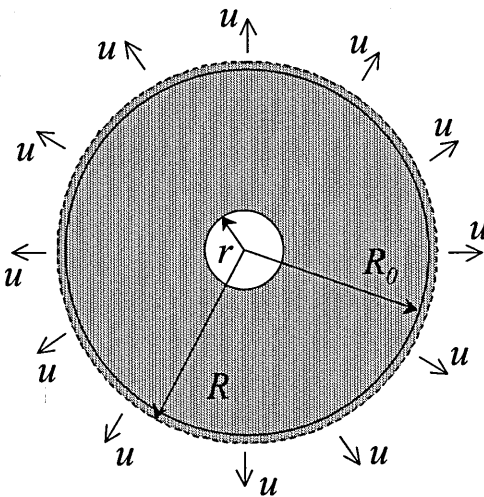


Fig. B.1 Schematic representation of a spherical particle in a symmetric radial displacement field.

Lazzeri and Bucknall made the assumption that no external work was added to the initial (Helmholtz free) energy U , as discussed in chapter 'Rubber particle cavitation model':

$$U_r = \frac{2}{3} \pi K_r R^3 \left(\Delta_v - \left(\frac{r}{R} \right)^3 \right)^2 + 4\pi r^2 \Gamma + 2\pi r^3 G_r F(\lambda_f) \quad (\text{B.1})$$

If we divide U_r by the volume strain of the particle $V_R = \frac{4}{3} \pi R^3$ and the rubber bulk modulus of the rubber K_r we get:

$$U_r^*(\phi) = \frac{U_r}{\frac{4}{3} \pi R^3 K_r} = \frac{1}{2} (\Delta_v - \phi)^2 + \phi^{\frac{2}{3}} \gamma + \xi \phi \quad (\text{B.2})$$

where:

$$\phi = \left(\frac{r}{R} \right)^3, \quad \gamma = \frac{3\Gamma}{RK_r}, \quad \xi = \frac{3}{2} \frac{G_r F(\lambda_f)}{K_r} \quad (\text{B.3})$$

In terms of the prescribed volume strain Δ_v the volume fraction ϕ of the cavity at equilibrium can be determined by taking into account two conditions simultaneously:

a) equilibrium:

which is attained if U^* is stationary with respect to ϕ , i.e. if $dU^*/d\phi = 0$; for $\phi \neq 0$ this is equivalent to writing:

$$\frac{dU_r^*(\phi)}{d\phi} = -(\Delta_v - \phi) + \frac{2}{3} \phi^{-\frac{1}{3}} + \xi = 0$$

$$3\phi^{\frac{4}{3}} - 3(\Delta_v - \xi)\phi^{\frac{1}{3}} + 2\gamma = 0 \quad (\text{B.4})$$

b) nucleation:

cavitation is possible if the value of the energy after nucleation is less than or equal to the energy before cavitation. This is the thermodynamic criterion that $U^*(\phi) \leq U^*(0)$. Thus, by evaluating (B.1) at $\phi = 0$ and by equating the expression obtained to $U^*(\phi)$ is:

$$U_r^*(\phi) = \frac{1}{2}(\Delta_v - \phi)^2 + \phi^{\frac{2}{3}}\gamma + \xi\phi = U_r^*(0) = \frac{1}{2}\Delta_v$$

$$\phi^2 - 2(\Delta_v - \xi)\phi + 2\gamma\phi^{\frac{2}{3}} = 0$$

$$\phi^{\frac{4}{3}} - 2(\Delta_v - \xi)\phi^{\frac{1}{3}} + 2\gamma = 0 \quad (\text{B.5})$$

Both equation (B.4) and equation (B.5) must be satisfied. Thus, if we subtract (B.5) from (B.4) we get:

$$2\phi^{\frac{4}{3}} - (\Delta_v - \xi)\phi^{\frac{1}{3}} = 0 \quad (\text{B.6})$$

which has the solutions $\phi = 0$ and:

$$\phi = \frac{(\Delta_v - \xi)}{2} \quad (\text{B.7})$$

The substitution of this value into equation (B.5) yields the critical value of the volume strain necessary for the nucleation of a void:

$$\left(\frac{\Delta_v - \xi}{2}\right)^{\frac{4}{3}} = \frac{2}{3}\gamma$$

$$\phi = \left(\frac{2}{3} \gamma \right)^{\frac{3}{4}} \quad (\text{B.8})$$

$$\Delta_v = \xi + 2 \left(\frac{2}{3} \gamma \right)^{\frac{3}{4}} \quad (\text{B.9})$$

If we take $K_r = 2 \text{ GPa} = 2 \times 10^9 \text{ N/m}^2$, $G_r = 0.4 \text{ MPa} = 4 \times 10^5 \text{ N/m}^2$, $R = 100 \text{ nm} = 10^{-7} \text{ m}$, $\Gamma = 0.035 \text{ J/m}^2 = 0.035 \text{ N/m}$ and $F(\lambda_f) = 1$, we get:

$$\xi = \frac{3 G_r F(\lambda_f)}{2 K_r} = 3 \times 10^{-4}, \quad \gamma = \frac{3\Gamma}{RK_r} = 5.25 \times 10^{-4}$$

$$\Delta_v = \xi + 2 \left(\frac{2}{3} \gamma \right)^{\frac{3}{4}} \cong 0.5 \% \quad (\text{B.10})$$

If we substitute the value Δ_v deduced in (B.10) into equation (B.7), where $\phi = \left(\frac{r}{R} \right)^3$, we get the expression for the critical value of the radius of the cavity:

$$r_{crit.} = R \phi^{\frac{1}{3}} = R \left(\frac{\Delta_v - \xi}{2} \right)^{\frac{1}{3}} \cong 14 \text{ nm} \quad (\text{B.11})$$

B.2. The LB modified model for multiple cavitation

The LB model has been generalised to include complex particles by introducing the concept of an equivalent homogeneous particle, which models cavitation in a multilayer rubber particle by adopting a mathematical formulation for the surface energy density Γ_r as follows:

$$\Gamma_r = \begin{cases} \Gamma_1 + r \sigma_m \phi^{\frac{1}{3}} + R \beta \phi^{\frac{4}{3}} & \text{for } 0 \leq \phi \leq \phi_r \\ \Gamma_2 & \text{for } \phi > \phi_r \end{cases} \quad (\text{B.12})$$

where Γ_1 is the specific surface energy required to open the first void and Γ_2 is the 'plateau' value of the specific surface energy at large void sizes. β is a constitutive parameter governing the growth of the specific surface energy from its minimum value to the plateau value: $\beta = 2 \frac{\Gamma_2 - \Gamma_1}{R}$.

In the void fraction $\phi = \left(\frac{r}{R}\right)^3$, r is the radius of the equivalent void and R defines the radius of the equivalent particle.

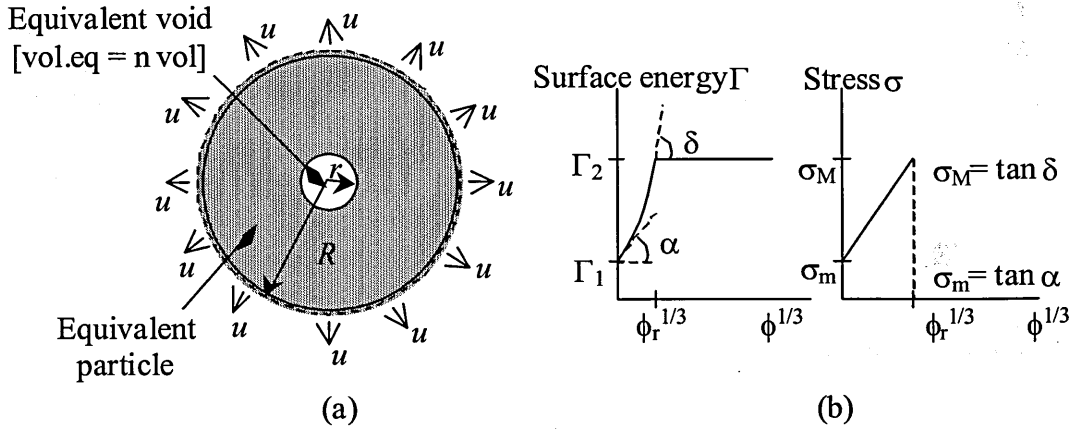


Fig. B.2 Schematic representation of a) the equivalent homogeneous spherical particle with equivalent void and b) the surface energy density (Γ) and the surface stress ($\sigma = R^{-1} d\Gamma/d\phi^{1/3}$) plotted against $\phi^{1/3}$ ($= r/R$), the volume fraction of the void with respect to the particle. Here ϕ_r defines the maximum volume fraction of voids allowed by the full relaxation of the stress.

If we put Γ_r , as defined by (B.12) into the LB model (equation (B.2)), for n cavities, we obtain, for $0 \leq \phi \leq \phi_r$:

$$U_n^* = \frac{1}{2} (\Delta_v - n\phi)^2 + n \left(\gamma \phi^{\frac{2}{3}} + \bar{\beta} \phi^2 + \xi \phi \right) \quad (\text{B.13})$$

where: $\gamma = \frac{3\Gamma_1}{R K_r}$, $\bar{\beta} = \frac{3\beta}{K_r}$ and $\xi = \frac{3}{2} \frac{G_r F(\lambda_f)}{K_r}$.

In equation (B.13), the stretch term expressed by ξ represents the state of equal biaxial tension, i.e. the minimum stress supported around the void (σ_m) as the void forms.

The equilibrium values of Δ_v are the ones at which the energy U_n^* reaches a global minimum, where the cavities are stabilised:

Equilibrium necessary condition: $\frac{dU_n^*(\phi)}{d\phi} = 0$

$$3(n+2\bar{\beta})\phi^{\frac{4}{3}} - 3(\Delta_v - \xi)\phi^{\frac{1}{3}} + 2\gamma = 0 \quad (\text{B.14})$$

Nucleation necessary condition: $U_{n+1}^*(\phi) = U_n^*(\phi) \quad \forall n = 0, 1, 2, \dots$

$$(2n+1+2\bar{\beta})\phi^{\frac{4}{3}} - 2(\Delta_v - \xi)\phi^{\frac{1}{3}} + 2\gamma = 0 \quad (\text{B.15})$$

Equations (B.14) and (B.15) have to be satisfied simultaneously. Furthermore, the equilibrium condition (B.14) can be rewritten for $n+1$ voids. Thus, if we subtract (B.15) from (B.14) evaluated for $n+1$ voids we get:

$$(n+2+4\bar{\beta})\phi^{\frac{4}{3}} - (\Delta_v - \xi)\phi^{\frac{1}{3}} = 0$$

This has the solutions $\phi = 0$ and :

$$\phi = \frac{\Delta_v - \xi}{n+2(1+2\bar{\beta})} \quad (\text{B.16})$$

If we substitute this expression for ϕ into (B.15) we have:

$$\left(\frac{\Delta_v - \xi}{n+2(1+2\bar{\beta})} \right)^{\frac{4}{3}} 3(1+2\bar{\beta}) - 2\gamma = 0 \quad (\text{B.17})$$

$$\Delta_v^n = \xi + (n+2(1+2\bar{\beta})) \left(\frac{2\gamma}{3(1+2\bar{\beta})} \right)^{\frac{3}{4}} \quad (\text{B.18})$$

Hence comparing equations (B.16) with (B.17):

$$\phi = \left(\frac{2\gamma}{3(1+2\bar{\beta})} \right)^{\frac{3}{4}} \quad (\text{B.19})$$

Corresponding to a prescribed value of Δ_v the overall stress can be obtained by substituting the equilibrium value of ϕ , given by (B.16), into (B.13) and then by differentiation of U_n^* with respect to Δ_v :

$$\sigma_n(\Delta_v) = \frac{dU_n^*}{d\Delta_v} = \xi + \frac{2(2(1+2\bar{\beta})^2 + n\bar{\beta})}{n+2(1+2\bar{\beta})} \left(\frac{(\Delta_v + \xi)}{n+2(1+2\bar{\beta})} \right) + \frac{\frac{2}{3}\gamma^n}{n+2(1+2\bar{\beta})} \left(\frac{(\Delta_v + \xi)}{n+2(1+2\bar{\beta})} \right)^{-\frac{1}{3}} \quad (\text{B.19})$$

Expression (B.19) gives the overall stress as a function of Δ_v . When Δ_v attains any critical value, given by function (B.18) the stress becomes:

$$\bar{\sigma}_n(\Delta_v) = \xi + \frac{n(1+4\bar{\beta}) + 4(1+2\bar{\beta})^2}{n+2(1+2\bar{\beta})} \left(\frac{2\gamma}{3(1+2\bar{\beta})} \right)^{\frac{3}{4}} \quad (\text{B.20})$$

When the $(n+1)^{th}$ cavity does nucleate, the stress falls sharply; indeed by evaluating (B.20) with $n+1$ in place of n , we can find the difference $\bar{\sigma}_{n+1}(\Delta_v) - \bar{\sigma}_n(\Delta_v)$:

$$\frac{\bar{\sigma}_{n+1} - \bar{\sigma}_n}{\phi} = - \frac{2(1+2\bar{\beta})}{[n+1+2(1+2\bar{\beta})][n+2(1+2\bar{\beta})]} \quad (\text{B.21})$$

From equation (B.21) we can see that the jump in stress is negative when the $(n+1)^{th}$ cavity nucleates, and also that the magnitude of this jump decreases when the number of cavities increases.

APPENDIX C

The expansion of the cavity

The radial displacement u in a sphere with one concentric spherical void is given by equation 5.7 reported in the book by Reismann and Pawlik, [pag.153, 1980], as shown in Figure C.1:

$$u(\zeta) = c_1 \zeta + c_2 \zeta^{-2} \quad (C.1)$$

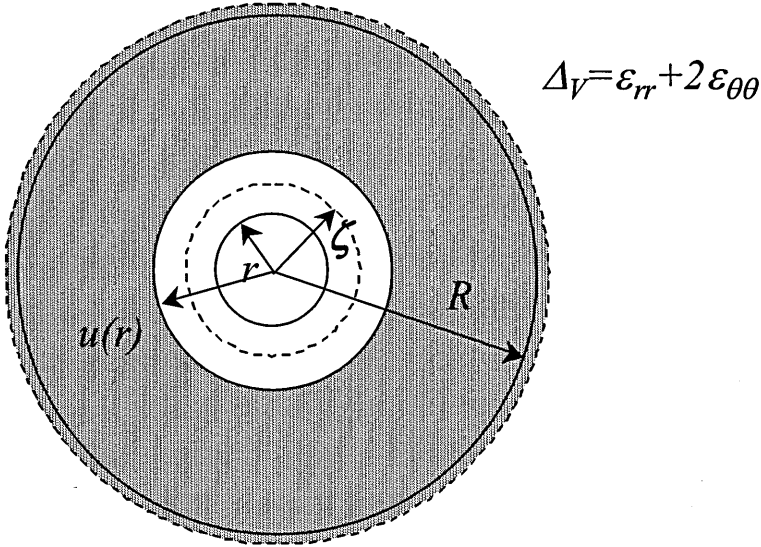


Fig.C.1 Schematic representation for the expansion of a cavity of initial radius r .

Because the volume strain on the boundary is prescribed, the boundary conditions are:

$$\epsilon_{rr}(\zeta = R) = \frac{\Delta_V}{3} \quad \epsilon_{\theta\theta}(\zeta = R) = \epsilon_{\phi\phi}(\zeta = R) = \frac{\Delta_V}{3} \quad (C.2)$$

The expressions for ϵ_{rr} , $\epsilon_{\theta\theta}$, $\epsilon_{\phi\phi}$ are :

$$\varepsilon_{rr} = \frac{d u}{d \zeta} = c_1 - 2 c_2 \zeta^{-3} \quad \varepsilon_{\theta\theta} = \varepsilon_{\varphi\varphi} = \frac{u}{\zeta} = c_1 + c_2 \zeta^{-3} \quad (\text{C.3})$$

where (C.2) and (C.3) evaluated for $\zeta = R$ yield:

$$c_1 - 2 \frac{c_2}{R^3} = \frac{\Delta_V}{3} \quad \text{and} \quad c_1 + \frac{c_2}{R} = \frac{\Delta_V}{3} \quad (\text{C.4})$$

So that $c_2 = 0$ and $c_1 = \frac{\Delta_V}{3}$. Thus

$$u(\zeta) = \frac{\Delta_V}{3} \zeta \quad (\text{C.5})$$

and the new value of the radius of the cavity is:

$$r + u(r) = \left(1 + \frac{\Delta_V}{3}\right) r \quad (\text{C.6})$$

Then the final volume fraction $\phi_F = \left(\frac{r + u(r)}{R}\right)^3$ becomes:

$$\phi_F = \left(\frac{r}{R}\right)^3 \left(1 + \frac{\Delta_V}{3}\right)^3 = \phi \left(1 + \frac{\Delta_V}{3}\right)^3 \cong \phi \quad (\text{C.7})$$

« *Experience is the name everyone gives their mistakes* » Oscar Wilde