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Review

Accelerated Microwave Curing of Fibre-reinforced Thermoset Polymer Composites for Structural Applications: A Review of Scientific Challenges

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PII: S1359-835X(18)30362-2
DOI: https://doi.org/10.1016/j.compositesa.2018.09.012
Reference: JCOMA 5181

To appear in: *Composites: Part A*

Received Date: 8 June 2018
Revised Date: 31 July 2018
Accepted Date: 10 September 2018

Please cite this article as: Ogonna Mgbemena, C., Li, D., Lin, M-F., Daniel Liddel, P., Babu Katnam, K., Thakur Kumar, V., Yazdani Nezhad, H., Accelerated Microwave Curing of Fibre-reinforced Thermoset Polymer Composites for Structural Applications: A Review of Scientific Challenges, *Composites: Part A* (2018), doi: https://doi.org/10.1016/j.compositesa.2018.09.012

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Composites Part A: Applied Science and Manufacturing, Volume 115, December 2018, pp. 88-103
DOI:10.1016/j.compositesa.2018.09.012

Accelerated Microwave Curing of Fibre-reinforced Thermoset Polymer Composites for Structural Applications: A Review of Scientific Challenges

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Abstract

Accelerated curing of high performance fibre-reinforced polymer (FRP) composites via microwave heating or radiation, which can significantly reduce cure time and increase energy efficiency, has several major challenges (e.g. uneven depth of radiation penetration, reinforcing fibre shielding, uneven curing, introduction of hot spots etc). This article reviews the current scientific challenges with microwave curing of FRP composites considering the underlying physics of microwave radiation absorption in thermoset-matrix composites. The fundamental principles behind efficient accelerated curing of composites using microwave radiation heating are reviewed and presented, especially focusing on the relation between penetration depth, microwave frequency, dielectric properties and cure degree. Based on this review, major factors influencing microwave curing of thermoset-matrix composites are identified, and recommendations for efficient cure cycle design are provided.

Keywords: microwave curing, thermosetting polymers, depth of penetration, dielectric constant, fibre-reinforced polymer composite

Nomenclature

Parameter	Definition
f	Microwave radiation frequency
$f(\alpha)$	Cure kinetics model function
k	Curing rate constant in Arrhenius expression
v_p	Microwave speed in polymer
t	Time (duration)
A	Material constant (frequency factor) in Arrhenius expression
C_{ijkl}	Material constant matrix
D_p	Depth of microwave penetration
E	Activation energy in Arrhenius expression
$\bar{E}$	Electric field intensity
E^*	Conjugate of electric field strength
H	Concentration level
P_{av}	Average power
Q	Microwave energy
R	Gas constant (=1.987 cal K^{-1} mol^{-1} or 8.314 J K^{-1} mol^{-1})
T	Absolute temperature in Kelvin (K)
T_c	Cure temperature
T_g	Glass transition temperature
α	Degree of cure
ε_{ij}	Strain tensor
ε_0'	Permittivity of free space (8.8514×10^{-12}F/m)

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ε'	Relative dielectric constant
ε_e''	Effective loss factor or relative loss factor
σ	Effective conductivity
σ_{ij}	Stress tensor
$tan\,\sigma$	Loss tangent coefficient

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1 Introduction

Advanced Composites provide opportunities to tailor material properties and manufacturing processes in order to achieve ultra-light, high-performance, environment-friendly engineering structures—reducing fuel consumption and emissions and helping combat climate change [1]. Polymer composites are playing an indispensable role in different industries. Fibre-reinforced polymer (FRP) composites are light-weight materials with high strength-to-weight ratio and their properties can be tailored for modern high performance structural applications

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allowing for efficient engineering solutions to severe and varying operating conditions e.g. dynamic and impact events on composite aircrafts [2, 3]. Different types of fibres and polymers ranging from glass to carbon fibres are currently being used in composites materials. The aerospace sector currently holds the largest share (nearly 40%) of the global composite market with its distinctive certification requirements for advanced high performance composites [4, 5] which makes it one of the top markets for carbon fibre use. Superior rigidity and functional properties distinguish high performance polymer composites, usually reinforced by carbon fibres, from other composites with their intense use for transport, energy efficiency, property tailoring. The global polymer composites market is expected to generate an income in excess of £30 billion in 2021 at the compound annual growth rate of 5.1% from 2016 to 2021 [6], with current global end-product market size of £70 billion as estimated in [7] and market share of Europe, North America and Asia at 24%, 37% and 32%, respectively [8]. The composites industry has experienced high penetration into key markets, including automotive and aerospace sectors, and has been identified as one of the key pervasive technologies for future manufacturing according to the UK Department for Business, Innovation & Skills [9, 10]. These factors are the main driving force behind the ongoing global substitution for metals in order to mitigate the attendant problem of climate change [11, 12]. This is more evident in aerospace sector than other sectors, which is the major source of stratospheric pollution [13, 14] e.g. via ten tons of CO_2 emission per 1000km (approximately per one hour flight) [15]. The aerospace industry provided ample opportunities for the expanding maintenance, repair and overhaul (MRO) market with the introduction of new aircrafts such as the Boeing Dreamliner 787, Airbus A350 XWB, and Bombardier CS-100, with more than 50% composites by weight being used in their primary structure [16].

Moreover, growing demand for polymer composites in critical structures gave rise to an urgent need for a reliable and rapid composite repair and fastener-less joining, e.g. adhesive bonding especially in the maintenance, repair and overhaul (MRO) sector in aerospace [5]. It is currently accepted that efficient polymer processing in composites and bonded joints are paramount to critical structural applications as they offer flexible geometry, property tailoring and improved strength-to-weight ratios which lead to improvements considering environmental impact [11, 12]. In adhesively bonded structures, the quality of the bonded composites has a strong relationship with the variabilities caused by process parameters such as temperature, curing duration and rate [17]. Therefore any variation in curing of thermoset polymers can potentially behave as defect precursor to the polymer integrity in the form of either weak (low-strength) or kissing bonds [18-20]. The latter one can dramatically lower down the adhesion properties [18]. Structures containing zero-thickness bond deficiencies which could be a result of improper cure are difficult to assess. This becomes important in relation to large bond areas where non-uniform temperatures and curing may exist.

Rapid curing as a tool for energy saving and mass production is not new: various types have been explored for industrialisation such as radiation cure at ambient temperature (electron beam, UV) and at high temperature (infrared, laser, microwave) [21, 22], and conventional conduction/convection thermal curing (induction, ultrasonic, resistance heating). However, curing process-induced degradation seems inevitable no matter what technique is used implying that a fully controlled processing cycle should be designed that also depends on the geometric features and composite material (e.g. carbon and epoxy). For instance, the presence of weak bonds introduced by rapid conventional curing, at twice the specified rate, can lead to >40% reduction in the ultimate failure load of adhesively bonded single-lap joint with 25mm x 25mm bond area [18, 23]. This drawback can become critical in structural applications and a barrier to the growth of rapid polymer processing e.g. in aerospace MROs where the average duration for in-service composite repair to perform successfully at the flight line takes 15 hours according to Commercial Aircraft Composite Repair Committee (CACRC) [24]. The presence of fibre reinforcements such as carbon can also influence temperature gradient through the thickness and thus the depth of penetration, which can become widespread in a rapid conventional heating. If a controllable accelerated curing

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process with high depth of penetration (e.g. microwave) at a structural scale is developed via controlling this gradient, it could have a significant economic impact on composites manufacturing and operations (e.g. aircraft manufacturers and airlines), particularly those running short duration domestic flights [25].

This review will focus on the identification of major challenges with energy-saving high-volume microwave processing technique for thermoset composites via addressing the state-of-the-arts in academic researches and industrial applications. A framework to address the underlying knowledge behind accelerated microwave curing of polymer composites in critical structures is lacking in many review articles which has been central to shaping the current review. Microwave processing has frequently been presented as a means of rapidly heating/curing resins or FRP composites in a highly homogenous volumetric manner when it is compared to conventional heating [26-28]. It therefore appears well-recommended to use for the curing of resins either in isolation or as part of reinforced composites during production, or as a means of curing sections of polymer bonds, and therefore for bonded joints. However, the mechanical performance of resins can deteriorate due to microwave exposure [29-33] and the presence of carbon fibres that prevent penetration, suggesting that microwave is not currently a reliable means for the manufacturing of high performance composite structures. These issues with the quality of microwave processed composites, in association with variabilities caused by curing parameters (e.g. radiation parameters, curing time and temperature) dictate a requirement for fully controllable microwave curing. Therefore, the information collated by this review will be analysed to determine the interactions between microwave energy, temperature gradient, penetration depth and the curing state so as to gather principle scientific basics for design of a microwave curing procedure. The analysis will be used for the development of concluding remarks for proposing an in-situ controlled rapid microwave processing.

2 Fibre-reinforced thermoset composites cure

2.1 Thermoset polymer cure

The term ‘curing` in thermosetting polymers refers to the transition of liquid resin and hardener components to a solid vitrified material [34]. Curing is initiated when the components are stoichiometric and physically mixed together. Polyester, phenolic and epoxy resins are among the mostly used thermoset polymers with epoxy popularly used in high performance composite structures.

Epoxy is mainly referred to as a chemical group comprised of two carbon atoms bonded to an oxygen atom. Epoxy curing is an exothermic process where heat is released during the chemical reaction [34-36]. The heat level applied to the epoxy mixed with hardener cure accelerator is related to the strengthening of the material by cross-linking of polymer chains which can be achieved by conventional heating, electron beams, chemical additives or accelerated curing (e.g. microwave, radiofrequency, ultra-violet radiation [22]). Simple epoxy is a three-member ring structure which is referred to as alpha-epoxy or 1,2-epoxy with R as C-H groups as is shown in Figure 1(a). Epoxy molecules are normally neutral electrically however possess a dipole moment (uneven electric charge) with partial negative charge ($-\delta$) at oxygen side and consequently positive ($+\delta$) at the other sides.

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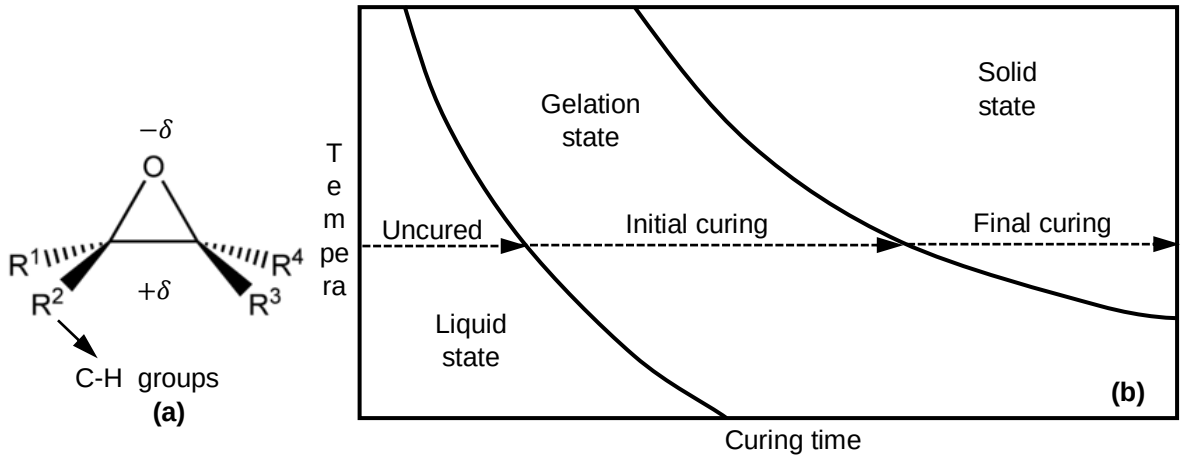


Figure 1: (a) Generic structure of alpha-epoxy or 1,2- epoxy with R as C-H groups [36], (b) epoxy curing process

The glass transition temperature (T_g) is the characteristic temperature at which thermoset polymers changes from a rigid, vitreous material to a rubbery material [34]. At curing temperature above T_g, phase transition occurs while curing at below T_g temperatures leads to vitrification. It changes the polymer's rheological properties from a Newtonian fluid to a rubbery or a vitrified viscoelastic solid as schematically illustrated in Figure 1(b).

2.2 Cure of high performance structures

The temperature and duration of heat flow through the structure required for curing depends on the process requirements and the structural performance such as requirements for durability or ductility (e.g. see aircraft structural needs in [37]). Curing is an irreversible time-dependent and progressive molecular reaction process which normally requires heat energy to conduct through the structure, the energy introduced either by conventional heating or radiation via raise in molecular mobility [38].

An effective curing cycle design requires setting up the time–temperature–pressure profile to be able to achieve the optimal degree of cure (denoted by α), and therefore the ultimate strength of the structure is achieved [39]. Degree of cure denotes the concentration percentage of molecular groups cross-linked during cure (Figure 1(b)). α is then zero for an uncured state of polymer, and $\alpha \to 1$ for a fully vitrified material normally determined by differential calorimetry scanning (DSC). The ultimate strength of the polymer matrix and the quality of its bond with reinforcement (e.g. carbon) at the end of the curing process is strongly correlated with the final optimal α. The effect of material mismatch is then required to be accurately evaluated and the process parameters properly controlled to produce efficient transfer of heat e.g. via coupled thermoanalytical measurement (e.g. DSC) and cure kinetics modelling. The degree of cure is independent of the process that has resulted in cross-linking, and thus can be used for the study of microwave curing.

The electromagnetic radiation cure mechanisms differ from thermal mechanisms in that curing is initiated by ionic or free radical intermediates formed by high energy electromagnetic radiation [21, 40], e.g. via gamma or X-ray radiation, while high temperature curing of two-component resin systems requires hardener or catalyst combination with the primary resin to induce cross-linking. Thermal conductivity and associated processing issues are therefore negated with such cure techniques. A successful example is the electron beam curing used to cure thick components in a filament winding layer-wise process [41]. However, the high electromagnetic energy and associated development and implementation costs of electron beam and gamma/X-ray curing reduce the cost effectiveness of these routes. This type of production and transfer of heat, which is necessary for a thorough reaction, can be performed more rapidly providing the heat absorbed at different locations

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and by different materials (e.g. in the presence of carbon and epoxy in composites or in a bonded composite joint).

2.3 Kinetics models for efficient cure cycle design

Recommending on efficient process cycle design either for conventional or accelerated cure for structural applications requires cure kinetics modelling. The cure kinetics models of thermosets, reported and reviewed in several papers [42-44], for predicting variation of cure state in thermoset polymers fall into two main categories: phenomenological models and mechanistic models. In this article, the authors are intent to describe the most efficient models and their parameters used for polymer composite cure simulation, so as to address the most appropriate ones for accelerated curing.

The phenomenological model describes the characteristics of the reaction kinetics but ignores the complexities involved in the reactions and the contributions of each reactant occurring at a molecular level therefore creates timely efficient numerical tools for process engineers and designers. This category is popular for thermosetting resin process modelling. On the contrary, the mechanistic models require more kinetic parameters to explain the complexities of the curing reactions in molecular scale. Mechanistic models provide more accurate predictions and interpretations of the curing process than the phenomenological models [44, 45] but are more complicated to implement usually at a molecular scale, and do not offer efficient simulations for relatively large structures. They are limited to use in molecular scale while the phenomenological model can be applied to relatively large structures.

In contrary to the phenomenological models, the mechanistic models are broadly varied, and have the advantage of interpreting the curing process without the complexities of rigorous experimentation but they are complex in theory. To date, several mechanistic models have been proposed using the concept of free radical polymerisation e.g. proposed in [46-48], in which polymerisation involves separate initiator molecules to grow the polymer chain. The phenomenological models normally predict the degree of cure as function of the energy provided for cross-linking in a polymer composite (activation energy denoted by E). This is independent of the source of energy, and as such can be adopted for microwave curing e.g. proposed in [49].

Based on the phenomenological models, the main constitutive material expressions for curing are the degree of cure rate equation and the rate of reaction equation so-called Arrhenius, equations (1) and (2) respectively, given by [50-56]:

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{1}$$

where $\alpha = \Delta H / H_{total}$ is the conversion or the degree of cure, and dimensionless ($0 \leq \alpha < 1$) with H being the reaction exothermal energy, and $f(\alpha)$ is the kinetic model function that can be calibrated experimentally. k is the rate constant (sec^{-1}), and can commonly be given by

$$k = Aexp\left(\frac{-E}{RT}\right) \tag{2}$$

where A is the exponential term constant or frequency factor (sec^{-1}), E is the activation energy (kcal mol^{-1} or kJ mol^{-1}) quantifiable from the Friedman method [57, 58], and R the gas constant (1.987 cal K^{-1} mol^{-1} or 8.314 J K^{-1} mol^{-1}). The absolute temperature is denoted by T in Kelvin (K). Equation (1) has been adapted to use for microwave curing modelling in [49] where has shown accurate prediction of the resin cure state at microwave exposure. To put it phenomenologically, one may solve a differential equation with a specific order depending on the $f(\alpha)$ expression to work out α as function of activation energy, temperature and material constants. The activation energy is however not obliged to be specific to heating mechanisms, and thus can be linked to any sources such as microwave or ultraviolet lights, likewise α.

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2.4 Quantification of cure state in a microwave curing process

The attention in this section is paid mainly to the determination of cure kinetics state in a microwave process based on existing evidences. Cure state determination is extremely important to ascertain the requisite conditions for curing, to optimise the microwave curing process specifications such as curing time frame, and to determine the optimum degree of cure [39]. Such determination can be the indication of solidification (rigidity) state of the cured material, and as such can correlate uneven structural scale polymer curing during microwave to the phenomenons occurring in microscale. Epoxy microwave curing in particular can be measured using thermoanalytical techniques such as DSC, dynamic mechanical thermal analysis (DMTA), field emission gun scanning electron microscopy (FE-SEM), Fourier transform infra-red (FTIR) spectroscopy and Raman spectroscopy [39, 59-66]. This paper does not intend to turn its focus on introduction of these methods however it should be noted that the methods are used to characterise material properties and cure characteristics in laboratory coupon level, and not used for in-situ structural measurements. The major limitation with most of the measurement methods is that they are quite expensive, laboratory based and are not well suited for industrial-scale applications e.g. for in-service composite bonding, through-the-thickness curing measurement or for complex geometries. A number of techniques have been used in low technology readiness level (TRL) industrial scale for in-situ curing measurement of a structure in process such as viscosity measurements of the resin as a function of control parameters (e.g. duration), ultrasonic method for measurement of resin flow velocity and dielectric spectroscopy. These techniques have not yet been developed for high TRL applications, and are very limited in terms of being applied to multi-material scenarios (e.g. composites) or complex geometries. The lack of a reliable curing state measurement technique in situ is a major barrier towards designing of controlled efficient microwave process for composites.

Many epoxy manufacturers propose a range of curing temperature and duration from which the user can select for optimal performance [39, 67, 68]. However, there are certain limitations that should be taken into consideration such as the geometry, substrates, thermal mass concerns, maximum operating temperature (not exceeding the limiting T_g), heating duration and the maximum increase in temperature rate. The latter two factors are the main focus in this review as controlling those leads to *acceleration* in curing process.

Acquiring fundamental knowledge of accelerated curing process at molecular level is an ongoing research (e.g. in [18, 69]). Recently, the sum frequency generation vibrational spectroscopy (SFG) has been employed to investigate activities at molecular level in situ. SFG is a nonlinear optical technique for investigating surfaces and interfaces that are exposed to laser beam. It has the capability of investigating polymeric chemical structures in their molecular interactions by monitoring orientation, spread, functional groups, hydrogen bonding formation and diffusion [69, 70]. This has been a great achievement as structural applications necessitate complete reaction of all molecular groups in the resin to achieve a fully cured product with highly branched molecular structure. To achieve this, the curing temperature is suggested held constant and the curing duration is properly selected and applied for an accelerated curing process otherwise the reduction in mechanical strength will become significant, i.e. >30%. If the temperature, (T_c), is selected well above T_g, the process becomes chemically kinetic driven, thus the curing time must be limited to keep the mixture in a solid viscoelastic state. Moreover, the curing duration plays a significant role to allow for full process (Figure 1(b)), in order to reach the final product mechanical state. Therefore, it is important for the structural designer to specify the maximum allowable service temperature to which an application should be subjected by adjusting T_g [72]. In addition to the findings from cure measurement techniques, designer may always consider the limitations imposed by T_g and heating rate as deterministic parameters for an optimal accelerated curing cycle design.

Navabpour et al. [73] investigated the cure of RTM6 epoxy resin system using a conventional differential scanning calorimeter and a microwave-heated calorimeter, using two curing methods, dynamic and isothermal. RTM6 cured isothermally showed similar cure times and final degree of cure using both conventional and microwave heating methods, suggesting similar curing mechanisms using both heating methods. However dynamic curing suggested different curing mechanisms using thermal and microwave heating (Figure 2). It was shown using near-infrared spectra (Figure 3) obtained during dynamic curing that the difference is due to amine groups, compared to the epoxy-hydroxyl reaction, reacted more rapidly in the microwave curing than in the conventional curing of the resin.

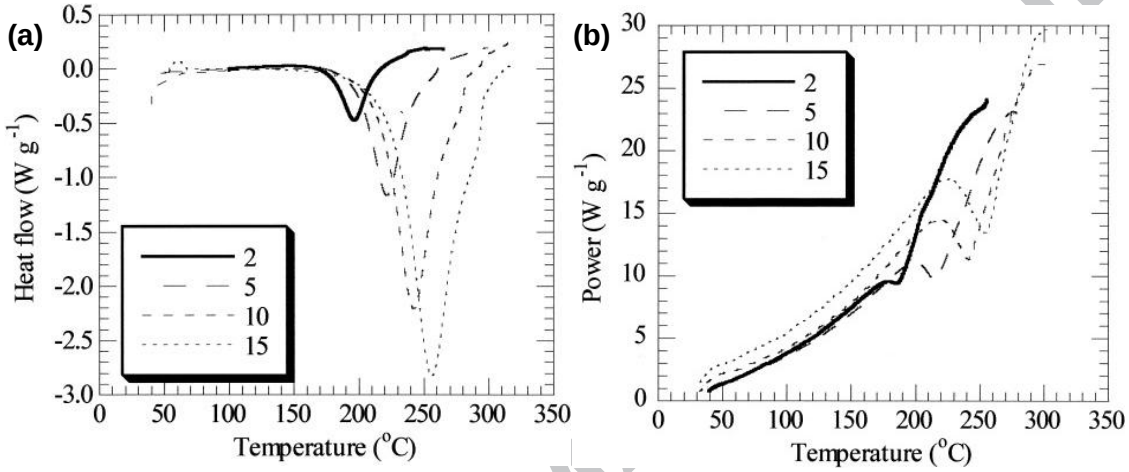


Figure 2: Heat flow characteristics of dynamically cured RTM6 epoxy using (a) conventional thermal heating and (b) microwave heating, at different heating rate (2,5,10,15 °C/min) [73]

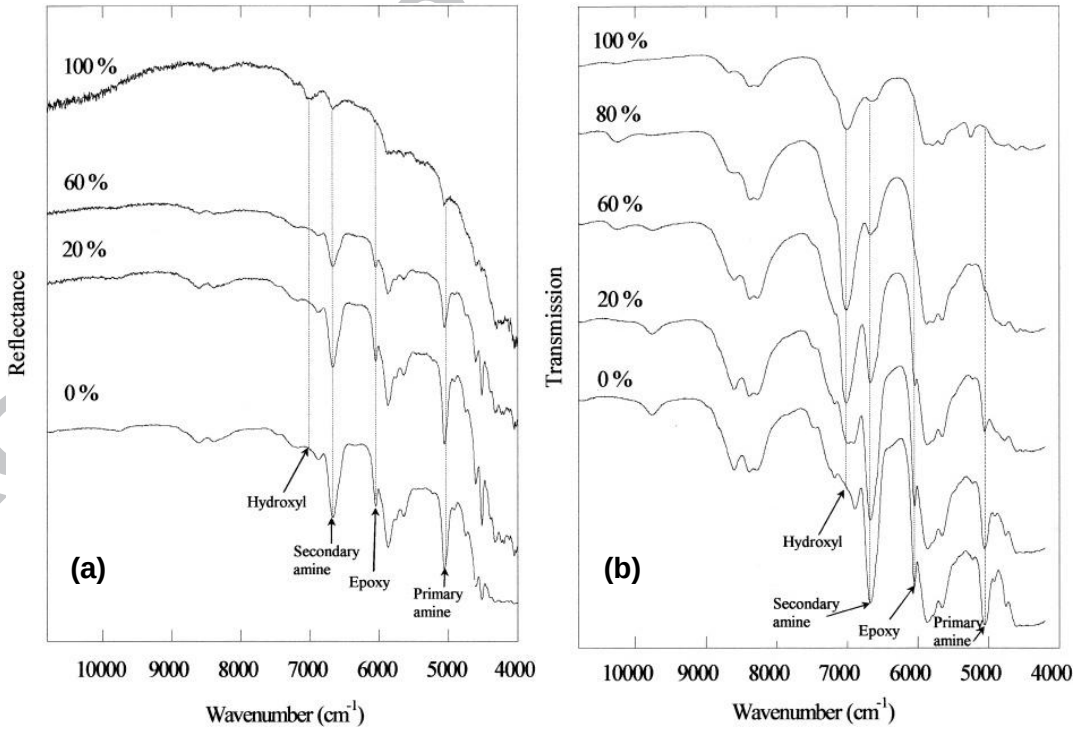


Figure 3: Near-infrared spectra for dynamically cured RTM6 epoxy using (a) conventional thermal heating and (b) microwave heating, at different degree of cure [73]

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3 Accelerated curing of thermoset polymers and composites

3.1 Existing methods

Accelerated curing of thermoset composites was first introduced in the late 90s in response to the growing market for structural integration and bonding using thermosetting polymers in semiconductors, microelectronics and aircraft industries. Conventional heating and radiation curing are two main approaches adopted for use with thermoset matrix composites. However, the proposed processes for accelerated curing (already addressed in literature [21]) are varied, each revealing benefits and limitations as detailed below. The electromagnetic spectrum for the radiation types listed below, and possible effects from each type in molecular scale, is schematically shown in Figure 4 [74].

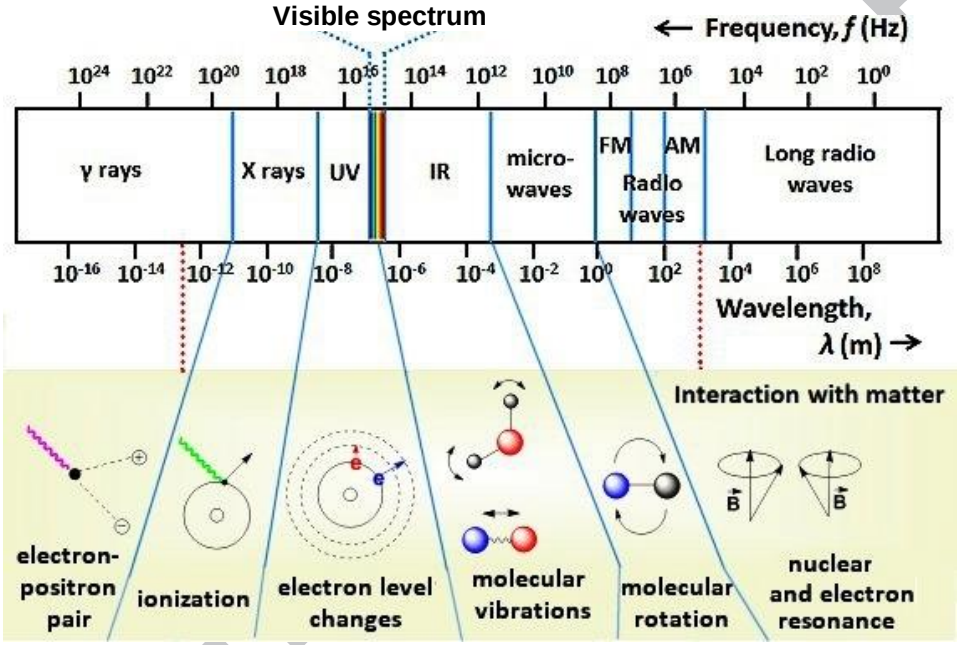


Figure 4: Electromagnetic spectrum for each radiation type and molecular scale effects [74]

Conventional rapid heating: In this method, the rate of temperature rise is increased until the temperature reaches the specified curing temperature such as the authors' examinations on the aerospace grade thermoset epoxy adhesive tape, FM94® [18, 20]. The process must be controlled to avoid mechanical degradation. The study on single-lap adhesively bonded composite joints which investigated curing the bond adhesive (Cytec FM94® adhesive tape) at twice as the specified heating rate showed both the load carrying capacity and the strain-to-failure reduction by approximately 40% from the bond processed according to the adhesive specification.

Electron beam radiation: In this method, beams of electrons are used to bombard the polymer surface and transmit sufficient kinetic energy to initiate the curing process via decomposition of radiation-sensitive polymers [40, 75-77]. The method is an excellent alternative to out-of-autoclave method. However, this method is reported to cause poor interface bonding between matrix and fibres in reinforced composites, and therefore, introduces low mechanical properties.

Gamma or X-rays (ultra-high energy, frequency at order of $>10^7$GHz, wavelength of $<10^{-5}$ mm): This method has been in use since the 1970s and is mostly employed for composites with relatively high thickness ≥300mm [78, 79]. The depth of the radiation penetration is high, however the method requires longer curing times than the electron beam approach due to lower dose rates, resulting in ionisation or ionic polarisation (Figure 5) which differs from a dipolar polarisation. The major challenge associated with the method is the high risk of

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exposure to radioactivity which makes a health and safety barrier for the adaptation of the technology.

Ultraviolet (UV) radiation (high energy, frequency at order of $>10^6$GHz, wavelength of $<10^{-4}$ mm): Thermoset curing using UV radiation is an economic, cost saving, energy efficient and environmental friendly process [80-82]. However, its application is limited to thin structures due to low depth of penetration of the radiation in epoxy/composite. In most recent applications, the UV radiation is normally used in open mould processes and with thin UV transparent composites [22, 23, 82].

Infra-red radiation (medium energy, frequency at order of $>10^3$GHz, wavelength of $<10^{-1}$ mm): This method is based on the conversion of electromagnetic wave energy to heat by resonance vibration of molecules [83, 84]. The method is both adaptable and controllable. Different coupled polymeric groups such as CH, CH_2, CH_3 and C-C can vibrate in response to the radiation frequency. The bulk of the vibrating frequencies are within the short wave and medium infrared region above 1.5µm. Most of the electromagnetic energy is absorbed on the surface of the material due to strong molecular vibrational bombardments. This limits the depth of its penetration into polymer matrix [28, 85].

Microwave and radiofrequency heating (medium energy, frequency at order of >1GHz, wavelength of $<10^3$ mm): Microwave heating is known as the most efficient volume-heating process due to its excellent depth of penetration in polymers [29]. Its process can be tuned with the use of high efficient dielectric nanomaterials in polymers in order to boost micro-level heating at molecular scale [31, 65, 86, 87]. Dielectric nanomaterials can efficiently absorb radiation and convert it to molecular vibrations/rotations via dipole moments, mainly as a result of dipolar polarisation (Figure 6). The vibrations can then add to the heating level in polymer surrounding the nano-materials by friction mechanism [86].

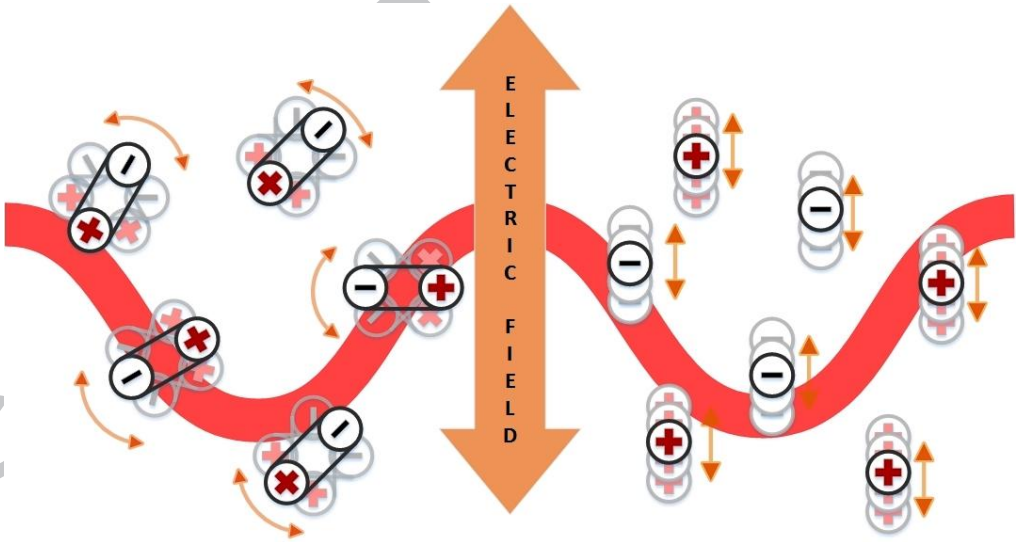


Figure 5: Schematic illustration of dipolar polarisation versus ionic polarisation as two different dielectric heating mechanisms (e.g. in an epoxy polymer) occurring due to low and high electromagnetic radiation, respectively [88]

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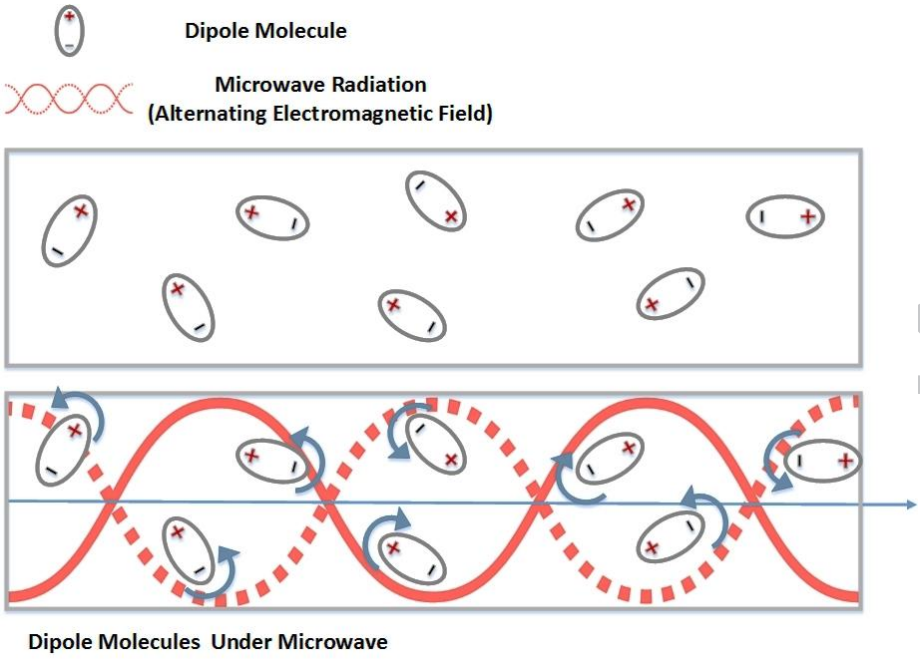


Figure 6: Schematic of a material with dipole molecules (e.g. epoxy, water, dielectric nanomaterials) subjected to an alternating electromagnetic field (arrows represent applied dipole moments on dipole molecules for alignment according to the field, solid-line wave)

3.2 Evidence on challenges with microwave thermoset polymer and composite cure

Figure 7 shows the schematic for microwave heating of functionalised graphene nanoribbons (GNR) in thermoset polymers functionalised by poly(propylene oxide) (PPO) to rapidly cross-link the polymer matrix [87]. Using mechanical testing carried out on conventional oven cured and microwave cured specimens, it was found that microwave-assisted localised heating is a promising technique to significantly improve the mechanical properties of polymer reinforced sandstone for wellbore reinforcements, i.e. the microwave cured specimens showed higher yield stress, compressive strength and toughness compared to conventional cured specimens.

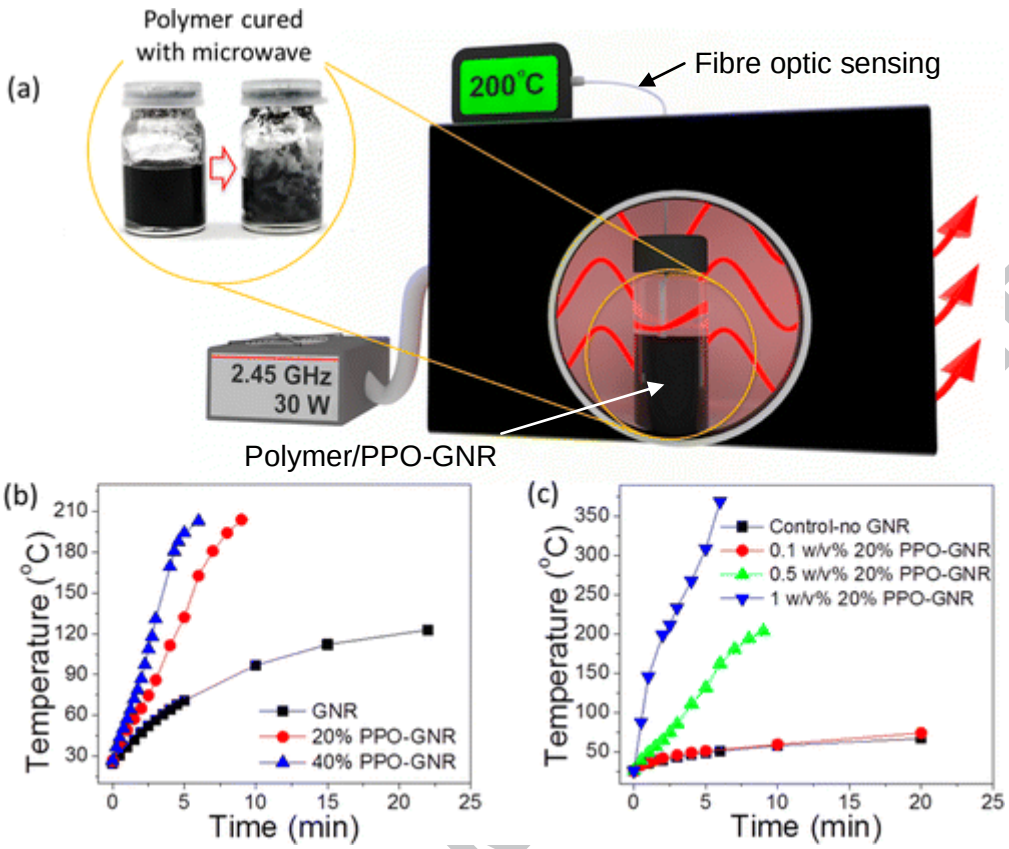


Figure 7: Microwave-assisted curing of polymer/PPO-GNR suspensions [87]. (a) Illustration of the microwave-assisted polymer curing system using a waveguide and an in situ temperature monitor with a photograph of the polymer/PPO-GNRs suspension before and after microwave curing. (b) Microwave heating profile of GNR, 20%-PPO-GNR, and 40%-PPO-GNR suspensions. (c) Microwave heating profile of the polymer/PPO-GNR suspension containing different amounts of 20%-PPO-GNR.

The research has shown a promising technology in rapid cross-linking the polymer matrix using PPO functionalised GNRs, and thereby increasing its mechanical resilience. However, care should be taken with microwave exposure as it may also degrade the matrix at the verge that leads to mechanical degradation of the polymer structure [86]. The research in [86] evidenced such degradations in dielectric enhanced epoxies using nanomaterials, 1.0wt% Fe_3O_4 nanoparticles in epoxy resin (Figure 8) exposed three minutes to 100W single-mode microwave exposure. Also, in a very recent research in [89] on the effect of microwave radiation on the interfacial adhesion properties between epoxy and carbon fibres in a carbon composite material, serving microwave recycling, the authors have observed carbon fibre surface deterioration due to extreme exposure to microwave in which temperature reached 600°C under 100W power (Figure 9).

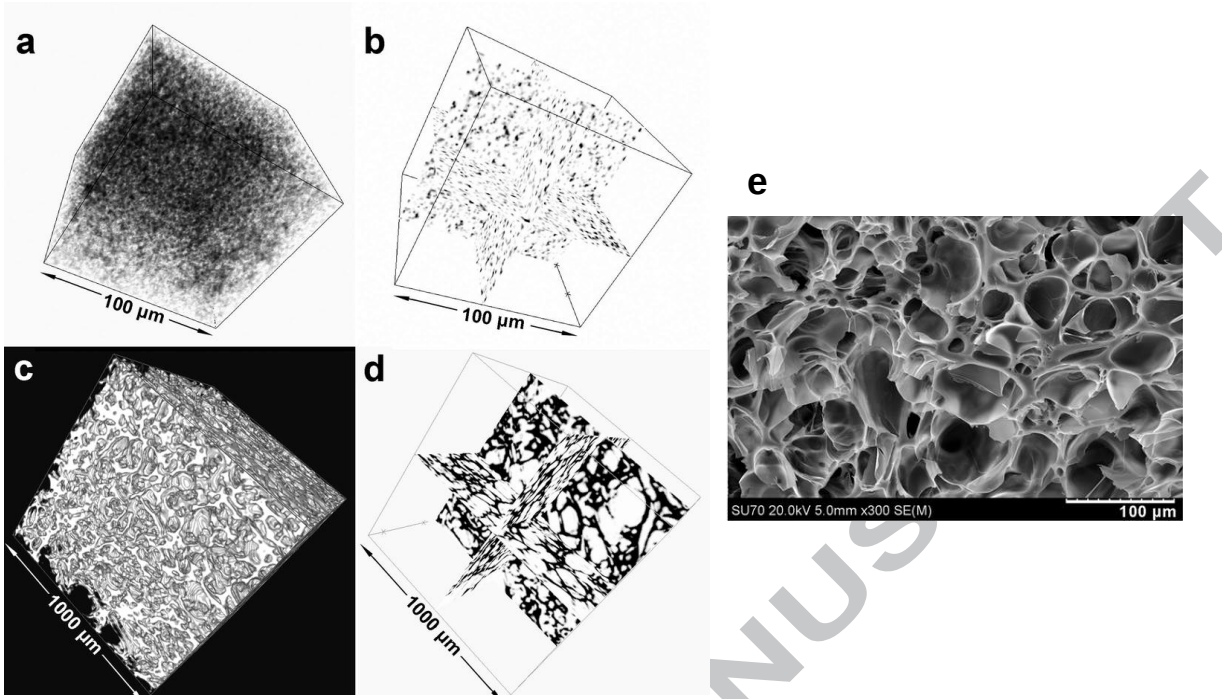


Figure 8: 3D degradation pattern in cured nanocomposite adhesive (1.0wt% Fe_3O_4 nanoparticles in epoxy resin); (a-b) before and (c-d) after microwave 3min exposure at 100 W, 2.45 GHz, (e) the FESEM magnified image of (c-d) [86]

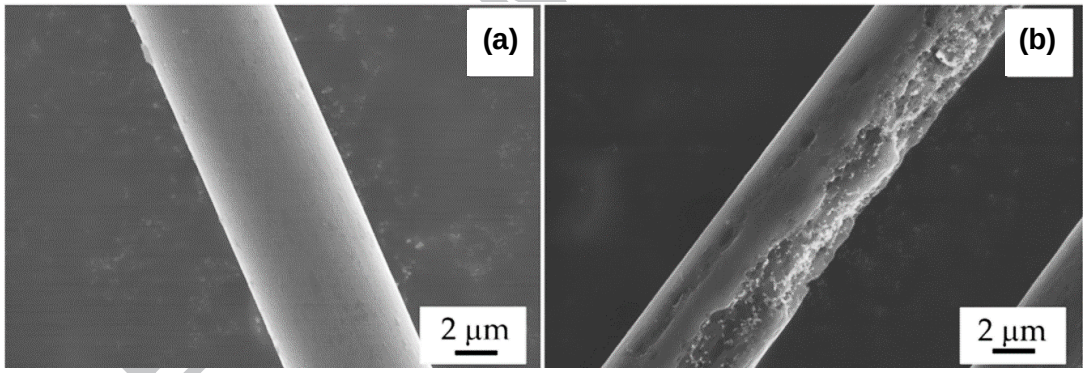


Figure 9: FE-SEM images of microwave recycled carbon fibres at (a) 500°C and (b) 600°C [89]

However, several studies have conducted on successful (without degradation) accelerated curing of epoxy resins by means of controlled microwave heating [29, 30, 33, 66, 90-98]. As reported in [99] microwave heating offers distinctive advantage of having a controlled selective and volumetric heating at a reduced duration compared to thermal rapid heating which is a time and energy consuming process. A number of researches also claimed other advantages over thermal curing such as providing uniform temperature distribution and low temperature gradient through the thickness [33, 91].

However, reinforcements such as carbon should prevent penetration in composites as they absorb the radiation due to their inherent dielectric characteristics, normally higher than the characteristics of the polymer. So, they may act like radiation shielding through the thickness of a FRP composite. Heating occurs as a result of molecular interactions with the electromagnetic field as was schematically shown in Figure 4 and Figure 6. This is used for polymeric and other materials (e.g. ceramics) however it requires a highly controlled process for uniform exposure that mitigates carbon fibre shielding that prevents through-thickness uniform exposure, as well as avoiding hot spots produced by highly localised heating.

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3.3 Dielectric properties of composites

Dielectric materials generally possess either permanent or induced dipoles which act as a capacitor when positioned between two electrodes. Charge is stored on the material without any electromagnetic activation field (e.g. microwave) [100], known as materials having low characteristic electrical and thermal conductivity [101]. However, recent studies reveal that the dielectric properties of polymers can efficiently be enhanced by dielectric additives such as dielectric nanomaterials [102, 103]. These polymers have been used in several tailored applications such as medical devices, aerospace, high voltage applications and microelectronics [29, 65, 104]. Conventional polymers usually have low dielectric constants requiring an activation field (e.g. electric or magnetic) to increase dielectric mobility (via molecular polarisation), that may provide sufficient kinetic energy for cross-linking and therefore for curing. In general, dielectric properties of dipolar materials e.g. thermoset polymers can be described from a combination of two main electromagnetic properties: the (electric) permittivity and the (magnetic) permeability [105]. These properties are highly sensitive to the presence of dielectric e.g. metallic nano-particles with high microwave absorption properties [106-109], and can also be affected by sample preparation [49, 56, 110-115], moisture [116-118], and temperature [119, 120]. There has also been a slight confusion of using different terms as 'dielectric constant' in different literatures. Some of these terms are related and can be used alternatively to represent the dielectric capability of material subjected to an activation field. Three key dielectric properties have been identified by this review as categorised below:

Dielectric Constant (ε') (also known as electric permittivity): This represents the ability of the material to store a charge e.g. when it is used as capacitor, and thus represents the polarity of material molecules in an electric field. ε' is a dimensionless value, and can be measured according to the procedures described in ASTM D150, ASTM D2520, or IEC 60250.

Dissipation Factor ($\boldsymbol{\varepsilon''}$) (also known as loss factor and dielectric loss): This is the measure of the loss rate of the field energy dissipated by dielectric mobility (polarisation) of the material. The higher the dielectric loss, the less output field energy, and thus the higher microwave absorption. $\boldsymbol{\varepsilon''}$ is dimension-less, and its measurement procedure is described in ASTM D150, ASTM D924-15 and IEC 60250. This is the main parameter which defines the rate and effectiveness of curing as a result of high frequency molecular mobility at an electromagnetic (e.g. microwave) exposure. The factor is strongly correlated with the level of radiation energy that a polymer can absorb [86]. This parameter and ε' can be characterised via a network vector analyser (VNA) in which the field absorption, reflection and transmission level of the materials is quantified.

Dielectric Strength (also known as breakdown voltage): This is the maximum electric field a material can tolerate before failure physically at its breakdown level [86]. It is a key limiting property for applications with high radiation or electric current level. The unit for the dielectric strength is volts per metre (V/m), and it is measured according to ASTM D149 or IEC 60243.

In order to justify the loss mechanisms, the dielectric constant for a dielectric material takes the complex form, ε^*:

$$\varepsilon^* = \varepsilon' \pm j\varepsilon'' \tag{3}$$

where the imaginary part ε'' is the effective (or relative) dielectric loss factor representing the ability of the material to dissipate microwave energy e.g. an indication on how much of energy is converted to other types of energy rather than electric in the material in response to microwave exposure. The complex permittivity is the main parameter which describes the level of heat generation due to interaction of microwave radiation with the material. This accounts for dipolar relaxation loss as well as conduction, and Maxwell-Wagner losses at relatively low frequencies. The Maxwell-Wagner loss generally refers to interfacial polarisation occurring in electrically inhomogeneous systems e.g. FRP composites or nano-

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modified epoxies. The loss occurs when an electric current passes through interfaces between two different dielectric media (e.g. nanomaterial and epoxy matrix), and because of their different conductivities, surface charges pile up at the interfaces. This is a function of temperature, moisture content, material density and electric field direction.

Another common way to represent the ability of material to absorb and convert electromagnetic energy to heat energy is the so-called loss tangent which is defined as:

$$\tan\delta = \varepsilon''/\varepsilon' \quad (4)$$

Materials possessing $\tan\delta > 0.5$ are referred to as high microwave absorbing and thus can efficiently be processed via dielectric microwave heating.

3.4 Microwave heating based on dielectric properties

Microwaves are electromagnetic waves with frequency bandwidths of 100MHz to 300GHz and wavelengths spanning from 1m to 1mm, respectively. Microwaves are orderly and polarised compared to visible waves, and obey the law of optic physics, and can be absorbed, transmitted or reflected depending on dielectric properties of the material at which the waves colliding. The absorption level is controlled by ε'', the dielectric loss. Microwave heating is in the form of radiation in which energy is dissipated volumetrically as a result of the interactions between the material(s) and microwaves at molecular scale [85]. Microwave dielectric heating has been employed in a variety of applications such as vulcanisation of rubber [121], heating of foods [122, 123] and bonding of composites [30, 86, 90, 98]. Epoxies may be cured by absorbing microwave energy from a high frequency field and converting it to heat energy via molecular vibrations/rotations in the presence of an alternating field (Figure 6). The prevailing mechanism for dielectric heating is dipolar loss, also referred to as re-orientation loss mechanism. If a dielectric material with permanent dipoles is subjected to an alternating electromagnetic field (or an alternating electric current which produces an alternating expanding and collapsing magnetic field), the dipoles will vibrate intensely but will find it difficult to conform to the high-speed reversals in the field, i.e. there may be delays in the molecular rotating (back and forth) response. This phenomenon is important as it leads to power dissipation in the dielectric material as a result of the phase lag with the field. The lag causes delay in energy absorption, heat conversion and hence results in non-uniform curing across the material. This makes the microwave process significantly material and geometry dependent, and is the first fundamental challenge relating to microwave curing control for a thermoset polymer composite. If the structure is thick or has a complex geometry, this lag and its heating delay at different locations will contribute to the introduction of non-uniform heating in the structure. To elaborate the physics of the challenge further, a concise theoretical background of such microwave absorption in dielectric materials is presented below.

The classical Debye theory and Lamberts law describes microwave heating of a dielectric material, i.e. materials with molecular dipolar response [99, 124]. The microwave energy absorbed by a dielectric material is expressed according to Lamberts law given by:

$$Q = \sigma|\bar{E}|^2 = 2\pi f \varepsilon_0' \varepsilon' (\tan\sigma)\overline{E}^2 \quad (5)$$

where Q is the microwave energy, σ is the effective electrical conductivity, $\bar{E}$ is the field intensity, f is the microwave frequency, ε_0' is the permittivity of free space, air (8.8514×10^{-12} F/m) and ε' is the dielectric constant that quantifies the stored and transmitted energy from material. $\tan\sigma$ is the loss tangent coefficient, a geometry dependent parameter, and $\bar{E}$ is the electric field intensity.

Equation (6) approximates the volumetric power dissipated during microwave radiation [99, 124]:

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$$P_{av} = \pi f \varepsilon_0 \varepsilon_e'' \int (E^* . \overline{E}) dV \quad (6)$$

where P_{av} is the power averaged over the volume of the material, and E^* is the conjugate of electric field strength.

The depth of penetration (D_p) can be calculated as function of the dielectric characteristics and the applied power which can be used as the basis for thickness/size limit value for a specific polymer curing application. The calculations may be used directly for homogenous materials but for polymer composites, one may use numerical analysis to be able to obtain D_p in the presence of reinforcements such as carbon fibres. D_p indicates the depth at which the power density decreases to approx. 1/e or 37% of its initial value, and expressed as:

$$D_p = \frac{\lambda}{2\pi\sqrt{2\varepsilon'}\sqrt{\left(1+\left(\frac{\varepsilon''}{\varepsilon'}\right)^2\right)^{1/2}-1}} \quad (7)$$

where λ is the free space wavelength of incident radiation. This clearly indicates the direct relation between depth of penetration and the wavelength (alternatively frequency), e.g. for microwaves D_p can become smaller than the thickness of the material to be processes and leads to non-uniform radiation/heating distribution. It is noteworthy that the implementation of equation (7) is not complicated for designing a polymer curing cycle based on D_p, and parameters ε' and ε'' (characterised by VNA), however not for a multi-material system with varying thickness, material (e.g. for fibre-matrix composite) and morphology (e.g. UD or woven carbon fibre pre-pregs). Numerical analysis would be useful to relate the microwave penetration equation to the cure kinetics model described in section 2.1 in order to predict the degree of cure for a carbon FRP composite.

4 Challenges with microwave curing for structural applications

Evidences based on existing literature for non-uniform and/or improper microwave curing of polymers and composites are presented in this section, followed by classification of major challenges existing in such evidences.

4.1 Non-uniform microwave curing evidences

4.1.1 Non-uniform microwave curing in dissimilar material systems

Boey and Yap [29] investigated the effect of three curing agents, 4,4'-diaminodiphenylsulfone (DDS), 4,4'-diaminophenylmethane (DDM) and meta-phenylene diamine (mPDA) on curing of diglycidyl ether of bisphenol-A (DGEBA) – as an structural epoxy Aradite GY6010 – using microwave curing and thermal heating. Microwave curing was done between 200W-600W power at 2.45GHz frequency. Their results showed that although microwave heating takes shorter curing time to attain the optimal achievable degree of cure and T_g, compared to thermal curing, these values can remarkably be lower or higher than the values obtained from thermal curing depending on the curing agent used. This highlights the sensitivity of rapid cross-linking mechanism to the molecular mobility (and not the depth of microwave penetration), and thus highlights the sensitivity of selection of a suitable curing agent for a microwave process.

In another study [65] on use of silica-coated carbon nanotubes (CNTs) in epoxy for microwave curing rate enhancement, it was found that the amount of pores and void content in samples cured by microwave were higher than those cured from thermal heating that has not fully been justified what has caused the pores and voids. This phenomenon is not only specific to curing epoxies but also evident from the research in [86] carried out on post-cured epoxy exposure, while localised microwave heating was boosted by inclusion of dielectric

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nanoparticles (observed by 3D X-ray computed tomography as shown in Figure 8). A new cure cycle may be required specific to such applications, i.e. using dielectric nanomaterial for microwave absorption enhancement. Answering these questions would require scientific studies of microwaving mechanisms at molecular level at both epoxy bulk and epoxy-nanomaterial interface before a rapid process cycle is realised at full (macro) scale. Also, the presence of carbon fibres can prevent microwave penetration [29-33, 94]. Overcoming the challenges with the exposure of dissimilar materials (e.g. agents, nano-fillers, carbon) would not, alone, lead to an efficient uniform cure, and process control (e.g. radiation power) such as that presented in the following section is also a necessity.

4.1.2 Non-uniform microwave curing at constant microwave power

In [90], the influence of microwave heating on the compressive strength of carbon epoxy composites (aerospace grade carbon T800; 60% volume fraction) was studied on the specimens cured at constant 100W, 133W and 167W microwave powers (using a 2.45GHz fixed frequency Nanjing Sanle microwave), in comparison with those cured at 180°C for two hours using the specified conventional curing cycle. The specimens were then analysed using FTIR. Figure 10 shows the temperature variation at different microwave power levels against exposure duration. Expectedly at 167W (the highest power examined), the time required to reach stable temperature was shorter (approx. 10min). However surprisingly at 100W, the temperature could not reach at or above the specified 180°C within the 25min duration from which the temperature raise is negligible, having been offered a saturation temperature level as function of microwave power. But *why such temperature limit level cannot be pushed up, nonetheless of the existence of continuous exposure*? The attributions to provide answer to this question is elaborated below.

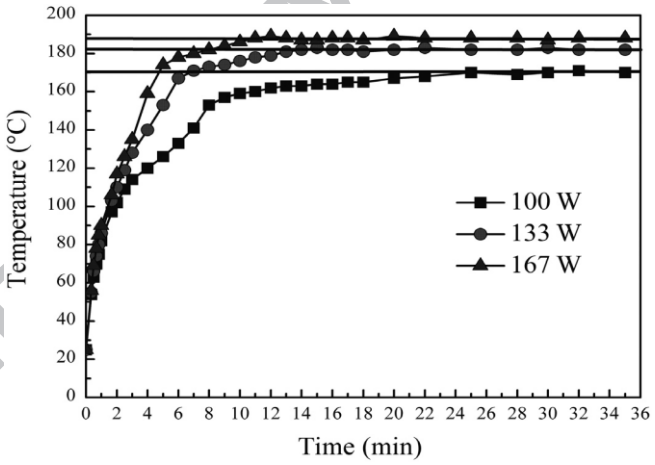


Figure 10: Temperature profiles for carbon fibre-reinforced epoxy composite laminates at different power levels during microwave heating [90] .

The FTIR results of the uncured, thermally cured and microwave cured samples examined in [90], indicating the characteristic peaks of epoxy molecular groups, are shown in Figure 11. The microwave sample was cured at 100W for 50min followed by 133W at 90min. At the wave number of 908cm^{-1} corresponding to the vibration of epoxy ring molecules, the *intensity* of the peak becomes weak and almost identical for both thermally cured (curve b) and microwave cured specimens (curve c) as opposed to the uncured epoxy specimen (curve a). This indicates that the epoxy groups participated in the curing reaction, and completely react the same in the two methods. This is verified by the reductions of the peaks at 1630cm^{-1} (featuring N-H in-plane bending vibration). A further look at peaks 1365cm^{-1} (featuring bis-methyl symmetric deformation vibration of bisphenol-A) and 510-400cm^{-1} (featuring partial fingerprint region) and the substantial shift of the peak at 800-825cm^{-1}(C—H inplane bending vibration on benzene ring) reveals that microwave curing has caused a small change in the cross-links, and as such the network structures obtained by the two

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curing methods are different. According to this study, microwave heating has insignificant influence on the molecular structure of the ultimate cured products from pre-preg carbon epoxy composite material which attributes to the saturation level in Figure 10 where temperature is not increased with increasing exposure duration at constant power unless the power is increased. However, this achievement could not necessarily be generalised to other carbon epoxy composites due to the apparent difference in microwave absorption characteristics of multi-material systems e.g. different dielectric constants.

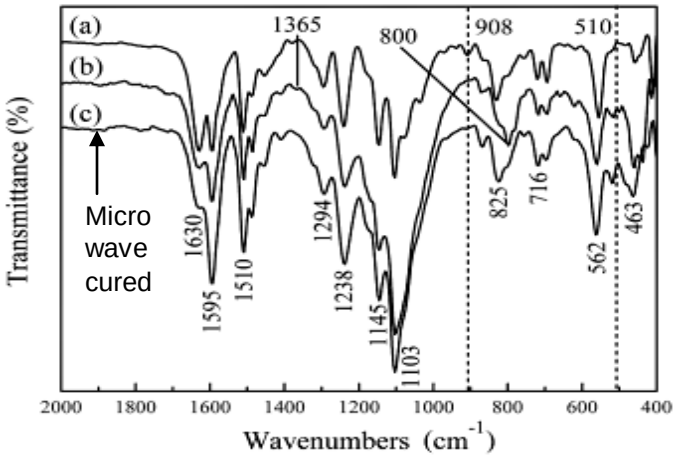


Figure 11: FTIR spectra of uncured specimen (curve a), thermally cured specimen (curve b) and microwave cured (curve c) specimens [90]

Relying on microwave power increase to increase temperature and therefore to accelerate curing is not always the best solution based on literature:

A separate study in [94] on the accelerated synthesis of epoxy-acrylate resin system using microwave processing, reduced the reaction time from two hours to few seconds [94] via dramatic power increase. However it was reported that the excessive exposure has had adverse effect on the compressive strength of the material post-microwave as the exposure introduced porosity and degraded the epoxy matrix [86, 90, 91]. Note that no dielectric nanomaterial was used in [94], neither in [65, 86] but the epoxy was still degraded via porosities induced by excessive microwave heating power.

4.1.3 Non-uniform microwave curing of thick structures

Moreover, Esposito et al. [39] studied relatively thick carbon epoxy composite laminates subjected to autoclave curing (in accordance to manufacturer recommendations) and microwave curing. The study showed that the laminate experiences overheating at the central region of the laminates. The laminates involved in that study were cut-sectioned at the overheated region, and were subjected to interlaminar shear strength (ILSS) testing. The results in comparison with those obtained from thin laminates showed a significant reduction in the ILSS for the overheated thick material (53MPa, 46MPa and 36MPa for 6mm, 17mm and 25mm respectively). This has been along with the inverse trend in laminate's central temperature i.e. the temperature increased with the increasing thickness from 91°C for the thinnest to 159°C for the thickest specimen.

The studies highlight the fact that geometric features must be taken into account along with the material constants (e.g. in [90]) for designing of an optimum microwave curing cycle for a composite structure. The material architecture (e.g. UD or woven reinforcements) should also be influential in the efficiency of microwave process as it locally changes the dielectric characteristics and absorption capacity. This complicates the cycle design as many parameters will be involved. However dielectric properties can be obtained for specific

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material-architectures, as characterising parameters for efficient microwave cycle design (described in section 3.4).

Therefore, the mechanical performance of polymers can deteriorate due to microwave exposure The evidences with the quality of microwave processed composites, in association with variabilities caused by curing parameters (e.g. radiation parameters, curing time and temperature) dictate a requirement for fully controllable microwave curing. According to literature data collated by this review, a number of main challenges (outlined below) contradict the common belief that microwave produces a homogenous cure though it is so-called a volumetric heating tool, identified in various studies.

4.2 Scientific challenges:

4.2.1 Challenge 1 – Thermal conductivity of resins:

Thermosets and liquid resins are microwave transparent, and therefore appear well suited for microwave processing. Microwave radiation also serves rapid curing, and improves resin stability [21]. Relevant researches in literature (e.g. [28, 125]) on structural scale polymer specimens, however, revealed that while the oven's microwave radiation profile may be uniform, the specimens' temperature are far from uniform due to non-uniform microwave absorption by the material. Also, temperature rise at constant power is limited by a temperature threshold, the maximum reachable temperature [90]. It is reasoned that the relatively low thermal conductivity of the material results in heat build-up at the specimen centres leading to hot spots. Such effects may also result from changes in the dielectric properties of the material during curing i.e. dielectric mobility is reduced during the vitrification process of a curing thermoset polymer. Thermal conductivity will also be influenced during cure. Such factors, as well as introducing the possibility of increased exothermic reactions, will limit the rate at which pure resins of a significant volume can be microwave cured. It is also important to ensure that the complete sample is fully cured without damaging some areas of the resin due to extreme exposure as observed in a number of researches [31, 86, 94].

4.2.2 Challenge 2 – Microwave shielding:

A second issue with microwave curing of FRP composites is the influence of the presence of carbon fibre on the penetration depth and on the ε'' parameter (see section 3.3) i.e. the dielectric loss due to interfacial polarisation, which can prevent the direct exposure of material beyond a certain thickness being directly 'heated' by the microwaves, as well as the effects of material thickness, fibre content and morphology. The ability to monitor temperatures at multiple locations within composites would provide valuable information which could aid microwave curing strategies e.g. using infrared or fibre optic sensing [126].

4.2.3 Challenge 3 – Microwave arcing:

Many studies related to mechanical performance of microwave cured thermoset composites have looked up the undesirable effects caused by carbon fibre arcing (due to the distinguished strong microwave absorption properties by carbon) during microwave curing of composites, and consideration in microwave power control has been taken to avoid such phenomenon [28, 90, 127-130] while maintaining the nominal post-cure structural integrity comparable to that of composites cured by conventional heating. The absorption occurs due to molecular mobility in dipolar (e.g. epoxy) and microwave absorbing materials (e.g. carbon). The difference in energy dissipation via absorption and the microwave exposure will result in transmission of the energy partially through the material either in a similar or dissimilar medium. In a conductive medium (e.g. carbon) such transmission can occur between molecules apart but relatively close [131]. In the case of a high microwave exposure such release level is high and causes arcing phenomenon.

The studies are also extent to the arcing occurring in the presence of carbon nanoparticles, nanotubes and graphene wherever carbon material is present [132-135]. Microwave arcing

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may introduce severe localised damage to both composite and its manufacturing equipment (e.g. vacuum bagging), and raises huge health and safety concerns.

Xu et al. [90] used powers lower than 180W to avoid arcing during a microwave vacuum bagging (pressure of 0.1MPa) of 3mm-thickness epoxy composite panels at ~60% carbon volume fraction, using a fixed frequency (2.45 GHz) WZD1S-03 microwave oven supplied by Nanjing Sanle Ltd. Kwak et al. [28] managed to reach 1000W microwave without arcing for curing of 2.4mm-thickness (polyacrylonitrile)-based carbon epoxy (Gurit) composite panels at 1.8 g/cm^3 fibre density, using a 12 magnetron, fixed frequency (2.45 GHz) Vötsch Industrietechnik GmbH that employs magnetron firing sequence to avoid arcing. Some researchers have taken further considerations to pre-apply epoxy material to cover carbon fibre ends/edges prior to curing to avoid arcing (e.g. see [28, 127, 128]).

4.2.4 Challenge 4 – Microwave cavity:

Most of the literature on microwave curing of epoxy thermoset composites present their results in terms of duration of exposure and microwave power along with the effects on laboratory scale thermos-analytical data. This has been addressed repeatedly in literature [92, 136-138], and has been attributed to the change in material system. An important factor often ignored, and is often down to trial and error, is the size and nature of the microwave cavity which become extremely important in relatively large scale applications, e.g. microwave curing a 25-ply 3mm thickness carbon FRP composite (representative of an aircraft fuselage skin [2]). The design for multi-mode ovens becomes very complicated, while single-mode ones are designed based on solutions of the electromagnetic field equations for a given applicator geometry. A systematic geometric requirements for efficient microwave curing has briefly been addressed only in a few articles (e.g. in [139]). As the size of the microwave cavity increases, the number of possible resonant modes also increases. Consequently, multi-mode ovens are usually much larger than one wavelength e.g. 10cm. For a rectangular cavity, the recommended mode equation for the resonant frequencies is [139]:

$$f_{nml} = v_p \left(\left(\frac{l}{2a}\right)^2 + \left(\frac{m}{2b}\right)^2 + \left(\frac{n}{2d}\right)^2 \right)^{0.5} \quad (8)$$

where f_{mnl} is the resonant frequency, v_p is the microwave speed, n, m, l are the number of half-sinusoidal variations in the standing wave pattern along the x, y and z-axes in a cavity/oven, and a, b, and d are the dimensions of the cavity in the x, y, and z directions. These factors play a critical role in the energy transmitted to the specimen. The authors have conducted a simple experiment to observe the effects from such factors using two different cavities (CEM ovens):

Cylindrical fully cured aerospace grade Hysol 9396 epoxy specimens (ϕ25mm×25mm) were subjected to microwaves in a) a relatively small microwave oven (approximately 300 milli-litre, single-mode cavity) with the test specimen located at its centre to ensure it was located at the maximum standing wave amplitude, and b) in a multi-mode microwave oven with a 55litre cavity with the specimen located at its centre (the multi-mode cavity had rotating table to promote a more uniform exposure to radiation energy across the specimens). Both microwave systems supplied by CEM were operated at 50W with a frequency of 2.45GHz. Gradual heating was focused to avoid exothermal conditions, which is why higher powers were avoided, also to avoid degradation via creation of voids [94]. The surface temperatures of the specimens in both experiments were recorded using fibre optic sensors. Figure 12 compares temperatures at the specimen surface in the small and large cavity. A significant difference in surface temperature is evident between the two scenarios with the cured resin in the smaller cavity reaching temperatures of 300^{o}C in 5-6 minutes causing visible hot spots, and eventually total degradation. The surface temperature of the resin specimens in the larger cavity, with constant power and frequency, barely rises. Figure 12 reveals that even if the specimens are subjected to exposure over the course of an hour, surface temperature hardly reaches 60^{o}C.

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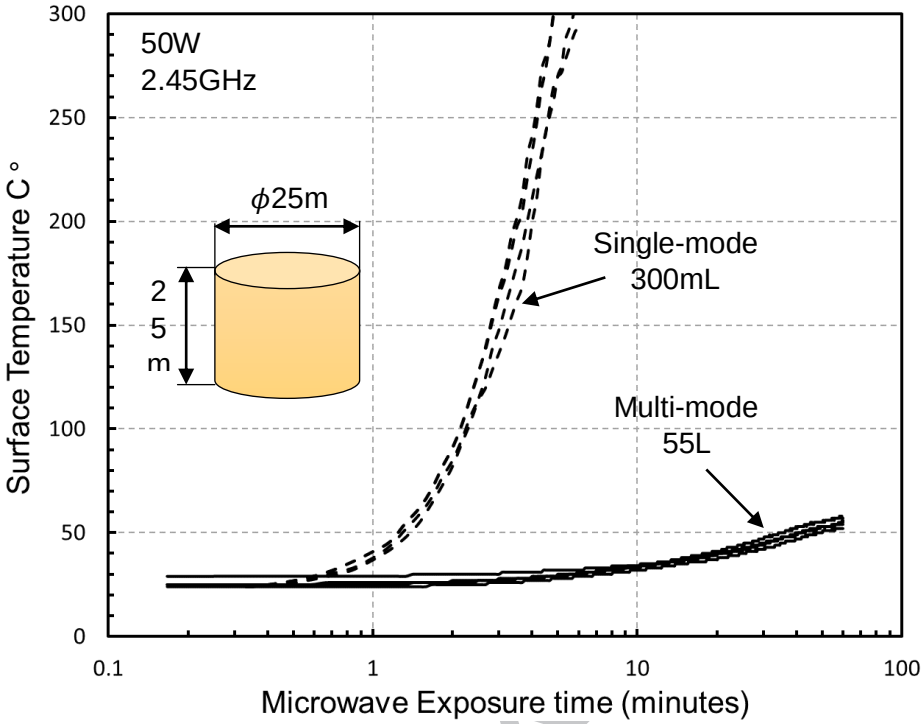


Figure 12: Epoxy specimens subjected to 50W and 2.45GHz in a 300mL single-mode and 55L multi-mode cavity

Note that this was a general observation on the results from the two cavities with different resonant frequency, equation (8). Without relevant information, such as the power density, or information regarding the power absorbed by the specimens as function of the resonant frequency, i.e. equation (6), or uniformity of the field in the cavity, it is difficult to precisely relate the temperature rise to physical attributes of the specimen in micro-scale level. The expression suggested in [139], equation (8), provides the appropriate cavity size requirements for efficient heating.

It has widely been reported that microwave curing produces uniform heating throughout the volume of a specimen, rather than simply heating the specimen via conduction heating [91,99]. Poor heat transfer and non-uniform thermal conductivity in conventional heating results in greater heat being experienced by the outer surface of thick sections as opposed to the centre of the specimen. This effect is mitigated in microwave heating as all parts of the specimen are exposed at once, theoretically speaking. However, equation (7) suggests that the depth of penetration is wavelength (frequency) dependent, and hence the process cannot simply be suggested for relatively thick specimens, as it can be for thin ones. Also, in connection with challenge 1, the centre of materials can reach a temperature much higher than the surface temperature as result of poor thermal conductivity of polymers.

The exposure of epoxy specimens in the 55L cavity (Araldite 1564 epoxy/Aradure 3486 hardener, fully cured by conventional heating and confirmed by DSC analysis) to microwaves at 100W resulted in the centre of the specimen deteriorating after 20 and 30 minutes. The specimens are shown in Figure 13(a). Note that the outer surface is trading heat energy via convection with environment, thus remains under-heated (unburnt). Throughout this exposure, the measured temperature of the specimen surface was no greater than 90^{o}C, also measured via fibre optic sensing. This was 10^{o}C lower than that used to initially cure the specimen, and suggests that the temperature at the specimen centre was significantly higher. It is reasoned that although the specimens may have experienced uniform volumetric heating, the poor thermal conductivity increases local temperature at the centre of the specimen relative to the specimen edge which had the

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ability to lose heat to the surrounding environment. A solution to this problem may therefore be to combine microwave heating with simultaneous conventional heating (e.g. via tooling) to ensure uniform heating in such cases. Such hybrid heating has been used to uniformly heat ceramics in the research proposed in [140, 141]. Nevertheless, this method was largely used to overcome the non-uniform heating experienced by the non-uniformity of the multimode microwave furnaces in use in [140]. Figure 14 show the schematic illustration of uniform heating as result of microwave-conventional combined heating. This method may aid uniform curing of thick specimens with poor thermal conductivity.

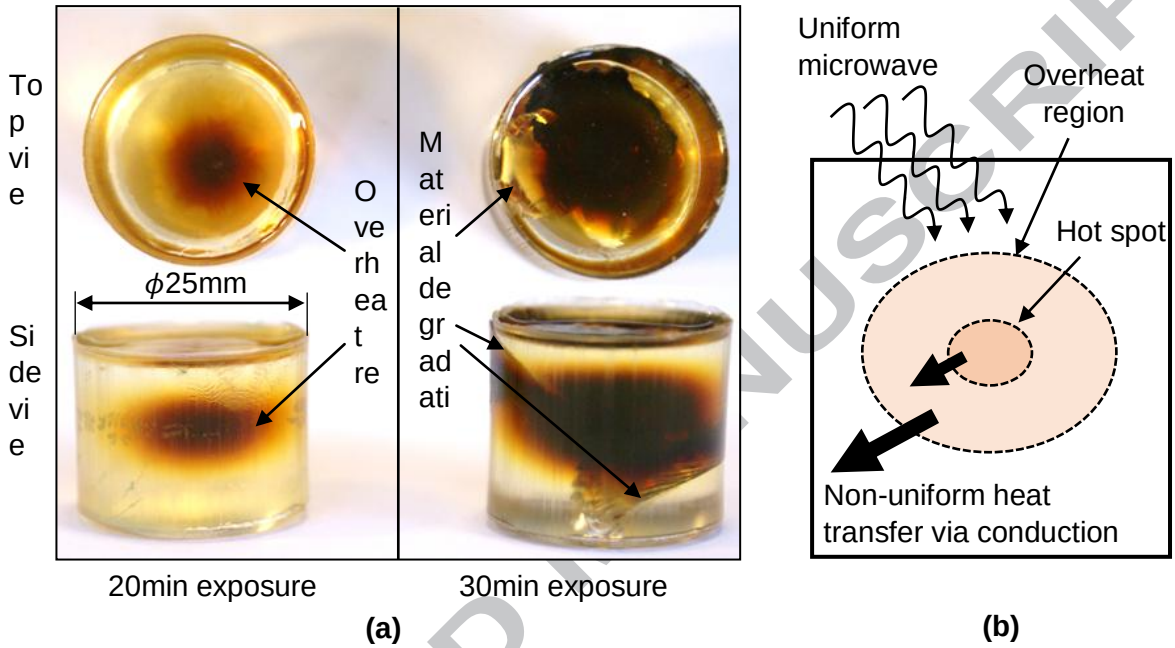


Figure 13: Microwave overheat degradation; (a) epoxy specimens subjected to 100W power (55L cavity), (b) schematic of proposed heat transfer and microwave radiation interaction at uniform microwave exposure (length of big arrows represents heat transfer level via conduction)

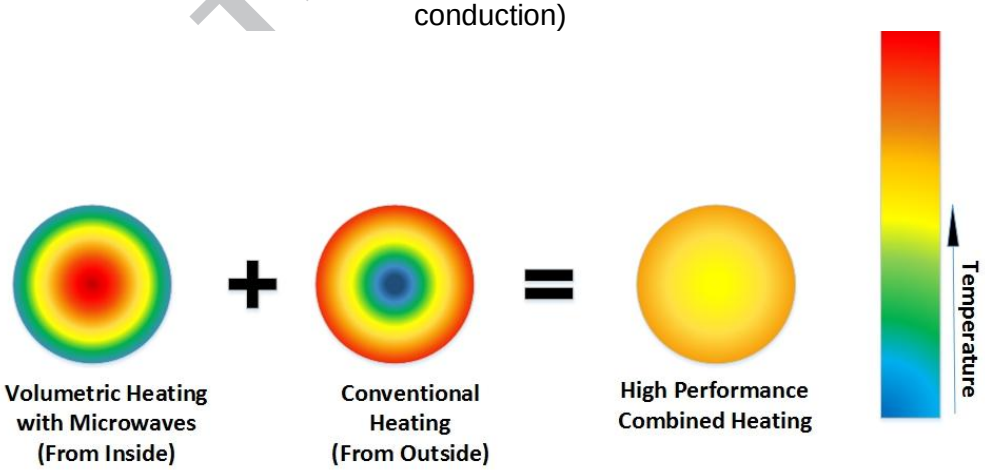


Figure 14: Uniform heating as result of microwave-conventional combined heating

4.2.5 Challenge 5 – Microwave radiation characteristics:

Another major drawback addressed for microwave heating, in conjunction with geometric features of its cavity and to-be-cured structure, is the non-uniform power distributions within the microwave cavity which results in 'hot spots' (microwave antinode regions receiving maximum microwave amplitude and therefore maximum heating as shown in Figure 15). This factor is in part often reduced by either rotating the subject on a turntable or

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alternatively by using mode stirrers, rotating reflectors used to change the distribution of the electromagnetic field in the cavity.

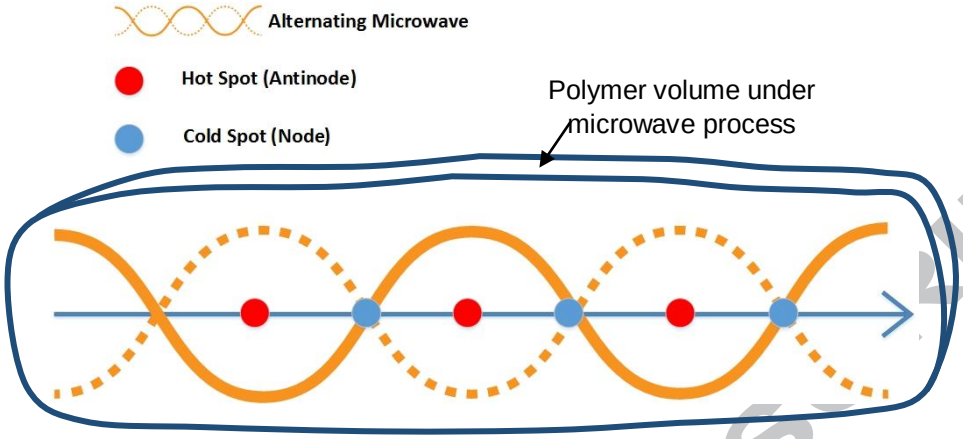


Figure 15: Creation of hot spots as result of nodes and antinodes during microwave processing of material

Both methods attempt to average the power distribution [139]. The use of multiple magnetrons has also been used to produce even better distributions [142], however care should be taken with size adjustments in the multi-mode microwave as opposed to the single mode one [143] to provide effective heating. This method is further elaborated below:

Multiple frequency microwaves can be used to produce more evenly distributed power distributions within the cavity [144]. However, variations in wavelength (λ) can influence the effectiveness of the microwave penetration (D_p in equation (7)) and can produce hot spots when attempting to cure thicker sections. Also, there is difficulty in conducting *in situ* temperature measurements in microwave processing to track down the hot spots. Conventional thermocouples were found to cause arcing and damage to the microwave source. To mitigate this problem, some researchers have used shielded thermocouples, optical fibre probes and non-contact pyrometers to determine temperatures of specimens subjected to exposure to microwave [145].

Inappropriate curing cycles resulting in incidences of exothermic peaks can degrade the polymer matrix material (via large thermal gradients in combination with poor thermal conductivity, residual stress introduction and polymer degradation), and as such be detrimental to the properties of FRP composites [146, 147]. In most industrial applications, where thin laminate pre-pregs are used for structural applications (e.g. Hexcel® pre-pregs in aerospace sector [2, 148]), the manufacturers' optimal thermal cure cycles should be followed to reduce or eliminate material deterioration which will result from exothermic events resulting in overheating of the material. The energy required to initiate an exothermic polymerisation may not readily be accessible, and may require material modification (e.g. addition of radiation absorbent nanomaterials or accelerators) to provide such energy via self-accelerating and/or stirring (auto-acceleration) [147, 149]. In general, a new cycle/modification may be required for rapid curing via microwave radiation. Therefore, relying on a temperature controlled microwave process based on recommended specifications for curing FRP composites is not sufficient to resolve the challenges mentioned.

5 Design considerations for efficient microwave curing

Composite microwave cure must overcome the aforementioned challenges with the depth of penetration, shielding effects, material thermal conductivity, void creation and exothermal events at once to be able to offer a reliable process. To overcome the challenges described above, experimental and numerical coupled researches should be carried out to provide an

efficient microwave curing cycle specific to composite material and geometric features. The results from such research can be used for the design and optimisation of a controllable microwave curing oven for FRPs using in-situ sensing (e.g. via fibre bragg grating (FBG) sensing technology [150]) and numerical electromagnetic modelling for thick complex geometries. However to overcome the aforementioned challenges in such controlled oven, the variation of temperature and strain through-the-thickness and in the plane of the pre-pregs during the cure should initially be understood. The state of cure of the microwave processed composites should be determined, e.g. via using DSC, at different microwave exposure durations and locations within the specimens, with its information being analysed against the in-situ measured data to accurately determine and quantify the interactions between microwave energy, temperature gradient (and thus penetration depth), internal strain development and the degree of cure. Moreover, the cure kinetics models described in section 2.1 can be coupled to the microwave depth of penetration via relating the energy required for polymerisation to that of required for microwave radiation. The major factors affecting efficiency and reliability of FRP composites' microwave process as identified in literature are presented in Figure 16. A coupled material-process approach (e.g. cure kinetics model and depth of penetration) should provide a predictive tool to achieve optimum microwave process and mechanical performance. This will develop an empirical correlation between dielectric properties and the degree of cure. The interaction of microwave absorption and heat transfer between fibre and matrix, and within the matrix itself also needs to be quantified which suggests a design tool for various composite systems (e.g. different materials). However, intensive experimental research is required to validate this hypothesis, and to examine microwave controlled scenarios especially for process variabilities along with processing of different FRP composites. Findings of such in-depth study will be useful for future development of closed-loop controlled in-situ microwave processing of polymer composite structures.

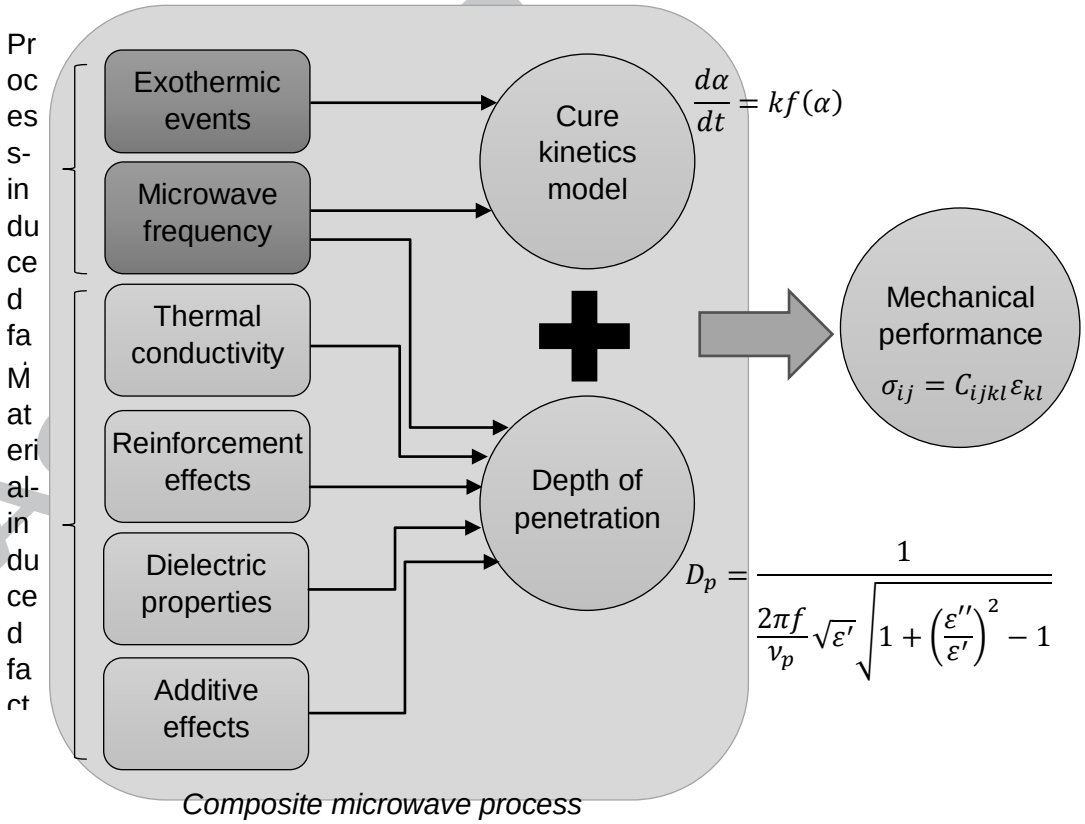


Figure 16: Major factors affecting efficiency and reliability of FRP composites microwave process

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6 Concluding remarks

Existing accelerated curing technologies were presented in this review, and the theoretical parameters influencing efficiency of thermoset composites cure via electromagnetic radiation were addressed and discussed. Details of microwave curing method and its fundamental principles were further elaborated in particular interest regarding scientific challenges in front of polymer composite microwave curing, addressed based on evidences of challenges that can be linked with the fundamental physics of a dipole molecule vibrating and polarising in response to an alternating electromagnetic field. This review considered the influence on thermosetting resins and FRP thermoset composites' performance due to variations in the curing process such as the rate of cure. Identified challenges in literature associated with efficient microwave curing process were collated, presented and discussed in detail.

In summary:

1. A thorough understanding of the dielectric properties of the thermoset resin, as well as the dielectric effects from included reinforcements (e.g. shielding and depth of microwave penetration) used in carbon fibre-reinforced thermoset composites, is required for tailoring effective microwave curing process, thus requiring highly adjustable process control parameters enabling microwave processing a broad range of combined polymer-reinforcement types.
2. Microwave curing was referred to as the most time and energy efficient process in literature despite all the challenges described in the review that correlates its process success highly with the thorough consideration of a number of parameters summarised in Challenges 1-5 and Figure 16, prior to and in situ process. The volumetric heating label for microwave shall be given a second thought specifically for relatively thick materials as the depth of penetration depends on the microwave frequency and cavity.
3. Thermoset resin's dielectric properties can be affected by the nature and type of reinforcement, sample preparation methods, temperature, and the degree of cure which will influence the epoxy's microwave absorption and therefore the level of its dissipation for heating, requiring a process parameter controlled microwave to avoid uneven curing.
4. The volume and dimensions of the cavity used for microwave processing must be considered in design of an efficient cure cycle in relation to the geometric features of FRP composites. As dimension of the cavity is fixed once a microwave oven is manufactured, focus can be made on adjustments of other remaining parameters expectedly, however designers may pursue new designs of variable cavity microwaves for efficient cure of different geometries/dimensions.
5. Non-uniform power distribution within the microwave cavity results in non-uniform heating of specimens and/or hot spots. This is linked with item 3 described above about the effect of dielectric parameters associated with thermoset polymer, and Figure 15.
6. Finally, wrong implementation of recommended curing cycles used in conventional heating for microwave curing is also responsible for the degradation of the final microwaved composite product and poor mechanical properties of the structural part via microwave heating.

Acknowledgments

The research for the review paper has received funding from the UK Engineering & Physical Sciences Research Council (EPSRC) Grant, Ref. EP/R016828/1, for Self-Tuning Fibre-Reinforced Polymer Adaptive Nanocomposite (STRAINcomp), and the UK EPSRC Grant, Ref. EP/N021975/1, for Towards Tailored Composite Bonded Repairs (BONDPAIR).

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Mgbemena, Chinedum Ogonna; Li, Danning; Lin, Meng-Fang; Liddel, Paul Daniel; Katnam, Kali Babu ...

2018-09-12
Elsevier
https://doi.org/10.1016/j.compositesa.2018.09.012
Mgbemena CO, Li D, Lin MF, et al., Accelerated microwave curing of fibre-reinforced thermoset polymer composites for structural applications: A review of scientific challenges. Composites Part A: Applied Science and Manufacturing, Volume 115, December 2018, pp. 88-103

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