Dyes and Pigments, Volume 162, March 2019, pp. 309-314
DOI:10.1016/j.dyepig.2018.10.036

Mechanophore-linked hydroxyl-terminated polybutadiene for the remote detection and quantification of mechanical stress

G. Kister[a], M. Moniruzzaman[a]*, M. Khan[a], S. Debnath[b]

[a] Centre for Defence Chemistry, Cranfield University, Defence Academy of the United Kingdom, Shrivenham, SN6 8LA, United Kingdom.

[b] Department of Chemistry, University of Illinois, Chicago, United States of America.

* Corresponding author. m.moniruzzaman@cranfield.ac.uk

Abstract

Polymers containing chromophores often exhibit mechanoresponsive behaviour, allowing the remote detection of stress in components such as rocket motors without taking the rockets out of service. Here we describe a polymer comprising a difunctional spiropyran chromophore and methyl methacrylate cross-linked with hydroxyl-terminated polybutadiene (HTPB). This polymer was developed as a sensor for the non-destructive monitoring of mechanical stress by using the force-induced colour changes as a quantitative readout. After about 40 N load was applied there was a gradual colour changes proportional to the compressive forces on the sample, as revealed by in-situ monitoring using a video camera and UV-Vis spectrometry. The tests highlighted a gradual decrease in the transmitted light intensity at 675 nm with increasing load, due to the opening of the spiropyran

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rings and their conversion to the coloured merocyanine forms. A reversible change to the initial colour occurred 72 h after the load was removed, but only under artificial fluorescent lighting, confirming that visible light is required for the ring-closing reaction. This new polymer is an ideal candidate for the remote detection of stress-induced damage in inaccessible structures or essential equipment that cannot be withdrawn from service for testing.

Keywords: Mechanoresponsive; Detection, Colour-change; Stress; Reversible

1. Introduction

Mechanophores are chemical groups that convert mechanical stress into a change in optical properties, such as the emission or reflection of light [1]. Examples include spiropyrans and spiro-oxazines, which undergo thermochromic and photochromic conversion under stress, resulting in a change from a colourless to a coloured state [1-3]. The conversion occurs when the weak spiro carbon-oxygen bond (C-O) is broken, resulting in the rearrangement of the closed spiropyran ring into a planar merocyanine structure [4] (Fig. 1).

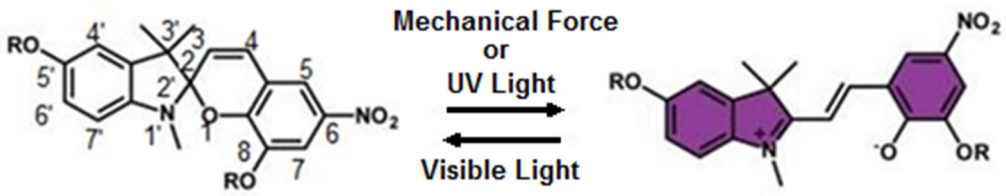

Fig. 1. Reversible colouration and decolouration in a spiro-mechanophore.

The incorporation of chromophores into polymers is desirable because the resulting materials can become mechanoresponsive, thus providing warning signs showing the site and extent of damage caused by stress and strain. This is beneficial when materials are inaccessible or cannot be withdrawn from service for regular testing, as is the case at the bond liner in rocket motors. One of the most promising mechanophores is spiropyran, which has been incorporated into poly(methylacrylate) (PMA) by single-electron transfer radical polymerization. The resulting polymers changed from colourless to pink when exposed to ultrasound because the resulting shear forces were channelled through the polymer chains to the mechanophores [3]. A rubbery spiropyran-linked PMA polymer and a glass spiropyran-crosslinked PMMA polymer tested under tensile and compressive loadings respectively, developed an intense colour change in the highly tensile stressed regions [4]. This occurred in the vicinity of the fracture in the PMA polymers, and in the centre of the bead and across the equatorial plane in the PMMA samples. The colour change in the rubbery PMA was reversed by artificial light more rapidly than in the glassy PMMA [4].

The colour changes in spiropyran-linked PMA and PMMA polymers under mechanical loading were attributed to the stress-induced reaction of the spiropyran during elongation, and the position of the spiropyran molecule in relation to the polymer was shown to strongly influence the resulting colour changes [4]. The maximum transfer of force from the polymer to the mechanophore was achieved when two polymer chains were connected to oxygen atoms at positions 5′ and 8 (in Fig. 1), on the opposite sides of the

spiropyran molecule, whereas minimal transfer occurred when the polymer chains were on the same side or when only one chain was attached [4]. The most suitable attachment points for maximum force transfer are found at positions 5′ and 8, positions 1′ and 8 and positions 1′ and 6 in Fig. 1 (referred to as SP1, SP2 and SP3) [5]. The SP1 and SP2 sites are both mechanoresponsive and photoresponsive, whereas the SP3 site is mechanoresponsive alone. Reversible conversion to the merocyanine form occurs most rapidly in SP3-linked polymers but the repeatability of mechanical activation in SP3-linked polymers is limited due to damage in the overstressed polymer chains. Increasing the mol% of SP3 site within the polymer resulted in a stiffer material with a lower glass transition temperature and an earlier threshold strain for the activation of the spiropyran without influencing the threshold stress for activation. Force-induced activation of the spiropyran C-O covalent bond in polymeric systems and the subsequent colour changes could be used for the development of novel mechanical force sensors [6,7].

When spiropyran was covalently incorporated into PMMA, a slight change in fluorescence within the elastic domain was observed, the spiropyran-merocyanine conversion rate increased significantly above the sample yield strength, and the increase in the conversion rate slowly decreased to a plateau at high strain rates [8]. The conversion rate also increased in relation to the tensile strain applied to the polymer, reflecting the higher stresses developed by the polymer at increasing strain rates. More intense fluorescence was also produced by polymers subjected to low strain rates because more time was allowed for the spiropyran-merocyanine conversion. In addition, the temperature influenced the

spiropyran-merocyanine conversion rate during tensile loading. The rate increased at low temperatures due to the higher stress in the polymer under these conditions. However, maximum conversion was observed in polymers tested at ≥90°C. Spiropyran mechanophores have also been incorporated into other polymers such as polyurethane, polycaprolactone and polyolefins to assess their potential applications [9-11]. Although force-induced colour changes were observed, the amount of stress/strain in relation to colour intensity was not reported and this needs to be established before such polymers can be used for the non-destructive monitoring of stress in practical applications, such as the design of rocket motors.

Here we report the stress-induced gradual colour changes in a cross-linked polymer comprising hydroxyl-terminated polybutadiene (HTPB), methyl methacrylate and a spiropyran monomer. Compressive loading was applied to the polymer, and the colour change was monitored in-situ using a camera and a UV-Vis spectrometer. An optical fibre probe was used to convey the light to the spectrometer in order to monitor the colour change remotely. This approach could be used to extract information about the integrity of polymers in inaccessible structures.

2. Experimental methods

2.1. Synthesis and characterisation of the mechanophore materials

The synthesis of the difunctional spiro-monomer 1′,3′,3′- trimethyl-6-nitrospiro [chromene-2,2′-indoline] 5′,8-diol was carried out according to the reaction scheme shown in Fig. 2 [4,12].

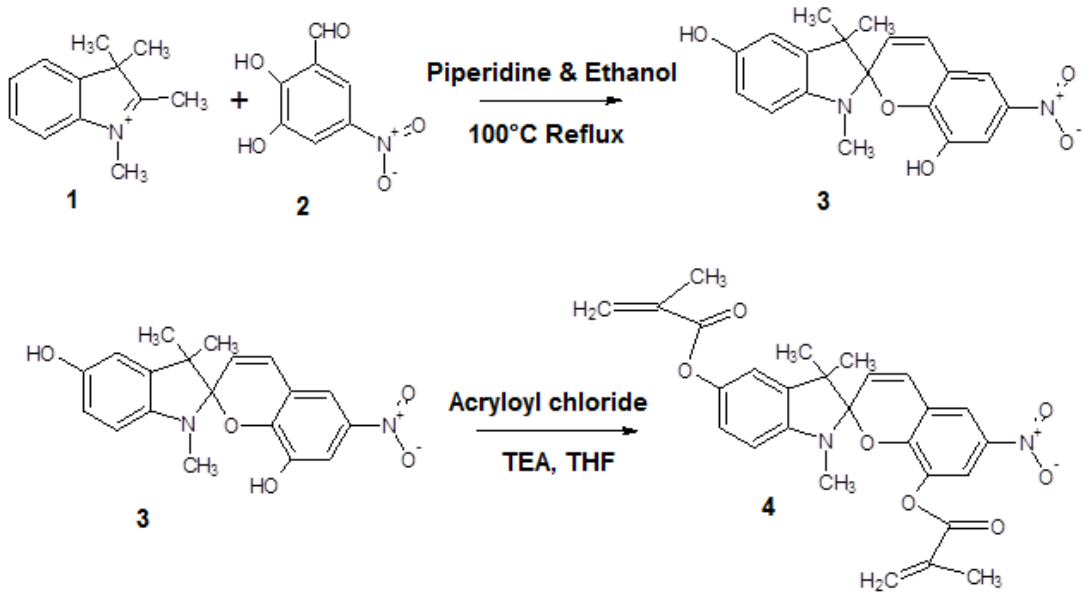

Fig. 2. Reaction scheme for the synthesis of the difunctional spiro-monomer.

The final spiropyran-linked HTPB polymer (SP_1-MMA-$HTPB_5$) was produced by mixing 56 mg (1% w/w) of the brown-coloured solid 1′,3′,3′-trimethyl-6-nitrospiro[chromene-2,2′-indoline]-5′,8-diylbis (2-methylacrylate) with 5.35 ml (91% w/w) methyl methacrylate, 250 mg (5% w/w) HTPB and 150 mg (3% w/w) 2,2′-azobis(2-methylpropionitrile) in a flat-bottom polymerisation flask. The mixture was degassed and heated at 70 °C overnight to yield a brown colour polymer coded as SP_1-MMA-$HTPB_5$.

2.2. Compression loading and colour change monitoring

Cuboid SP_1-MMA-$HTPB_5$ samples (10 x 6 x 3-6 mm) were tested by compression loading using a Zwick 1445 mechanical testing device. The load was applied at a rate of 1 mm min^{-1} and was limited to 195 N because the maximum capability of the load cell was 200 N. The colour change in the SP_1-MMA-$HTPB_5$ during compression loading was monitored using either a video camera or a UV-Vis spectrometer. When using the video camera, one side of the sample was illuminated using a Photonic PL2000 bright light source and a Watec digital colour camera was used to record the image on the other side of the sample. When using the spectrometer, the colour change was recorded via optical fibres (Fig. 3). Light emitted by a tungsten halogen lamp (LS-1 Ocean Optics, wavelength range 360–2500 nm) was transmitted to one side of the rectangular samples via a 4-mm diameter optical fibre probe (fabricated in-house using Fiberguide multimode UV-Vis silica optical fibres). The probe was placed 1–2 mm away from the sample surface. The light transmitted through the samples was collected by another optical fibre probe (Fig. 4) that was connected to a UV-Vis spectrometer (USB2000+ Ocean Optics) operating in the wavelength range 350–1000 nm. The collecting optical fibre probe was place about 2 mm from the other sample. The images and spectra of the light passing through the samples were recorded continuously when loading was applied to the samples and the data were transferred to a computer.

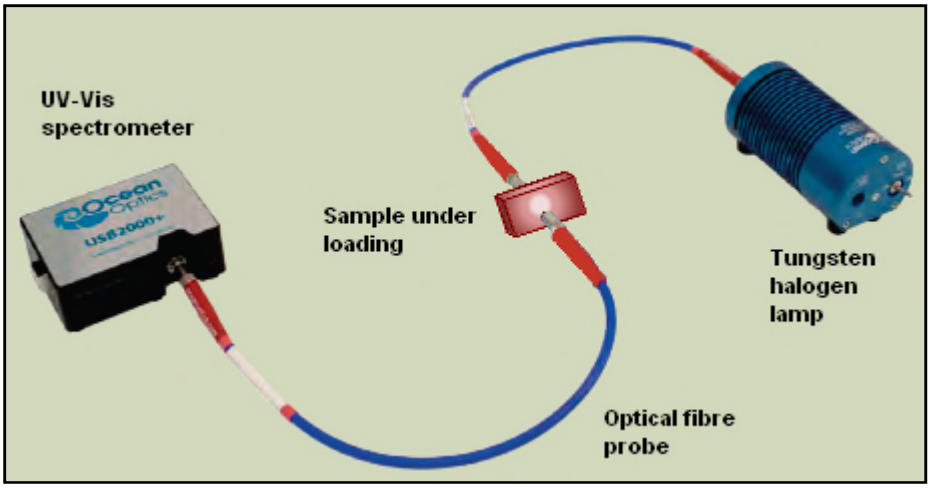

Fig. 3. General set-up for monitoring the colour change in mechanophore materials.

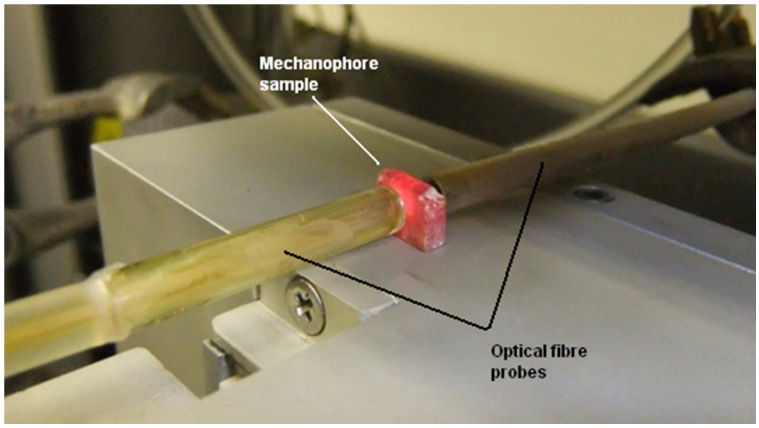

Fig. 4. Detailed set-up for monitoring the colour change in mechanophore materials by means of optical fibre probes.

3. Results and discussion

3.1. Colour change monitored by video camera

SP_1-MMA-$HTPB_5$ samples were subjected to compressive loading while a video camera was used to record light transmitted through each block. The stress induced an optical change in the samples as a function of the compressive load, resulting in the appearance of a bright red colour. The colour change is almost linearly dependent on the applied force (Fig. 5). Significant observable colour change occurred at loads above 50 N. Due to the imperfect cuboidal shape of each specimen, the dark colour was gradually observed on one side of the specimen (left side in the pictures). This was due to a gradient of internal compressive stresses within the sample, with higher stresses on the left side than the right. The colour change progressed along the specimen length as the compressive load increased because of the gradual formation of internal stresses. As stated earlier, the colour change in the samples was associated with the rupture of the spiropyran C-O bond and the formation of conjugated merocyanine [4].

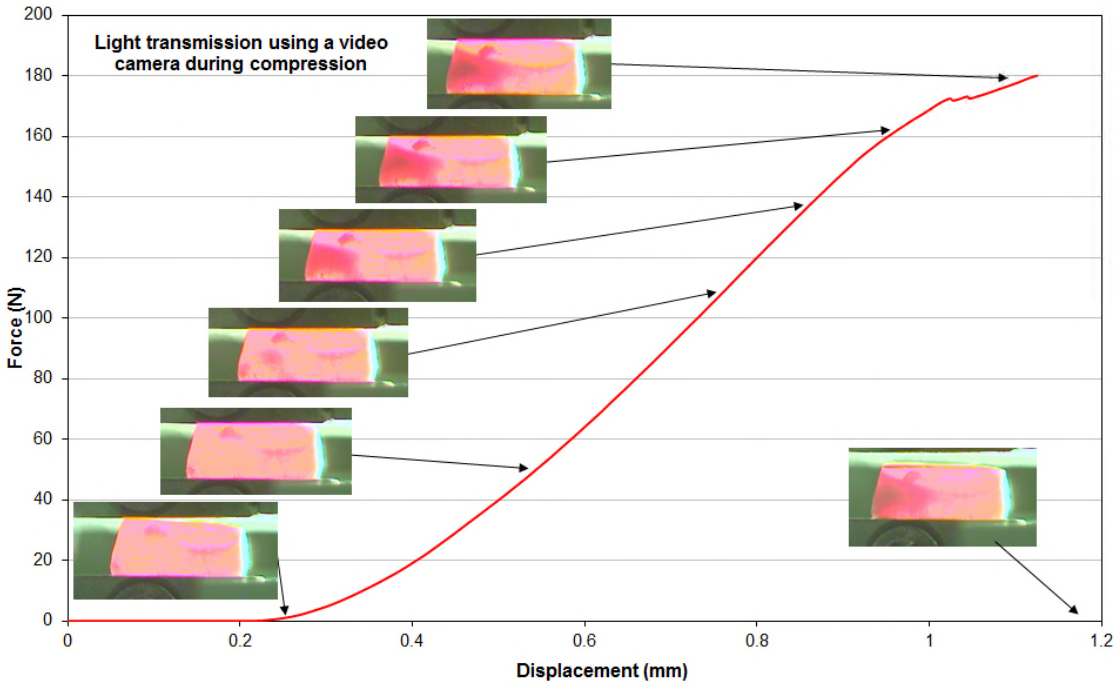

Fig. 5. Colour changes in SP_1-MMA-$HTPB_5$ during compressive loading.

The reversibility of the colour change was confirmed by monitoring the surface of the illuminated samples after removing the compressive load, while the samples remained between the grips of the testing machine. As shown in Fig. 6, the intensity of the red colour in the sample gradually decreased with time until complete disappearance after 72 h. The reversible change primarily occurred during the day, when the sample was illuminated by standard laboratory lights (fluorescent tubes, wavelength range 390–780 nm). In contrast, there was no significant colour change during the night when the samples remained in the dark. This confirms that the open spiropyran ring closes in response to visible light. A similar reverse conversion was observed in spiropyran-linked PMA after 6 h exposure to fluorescent lights [4]. The longer time required for reverse conversion in our HTPB polymer may indicate that HTPB inhibits the closure of the spiropyran ring. Furthermore, the time required to decolourise the PPMA-based

mechanoresponsive polymer we investigated may be longer than the equivalent process for a softer PMA-based polymer due to the presence of methyl group in PMMA, which makes the polymer harder (glass transition temperature = 85ºC for PMMA compared to ~10ºC for PMA). This would restrict the rotation of the merocynine as it reverts to the closed form.

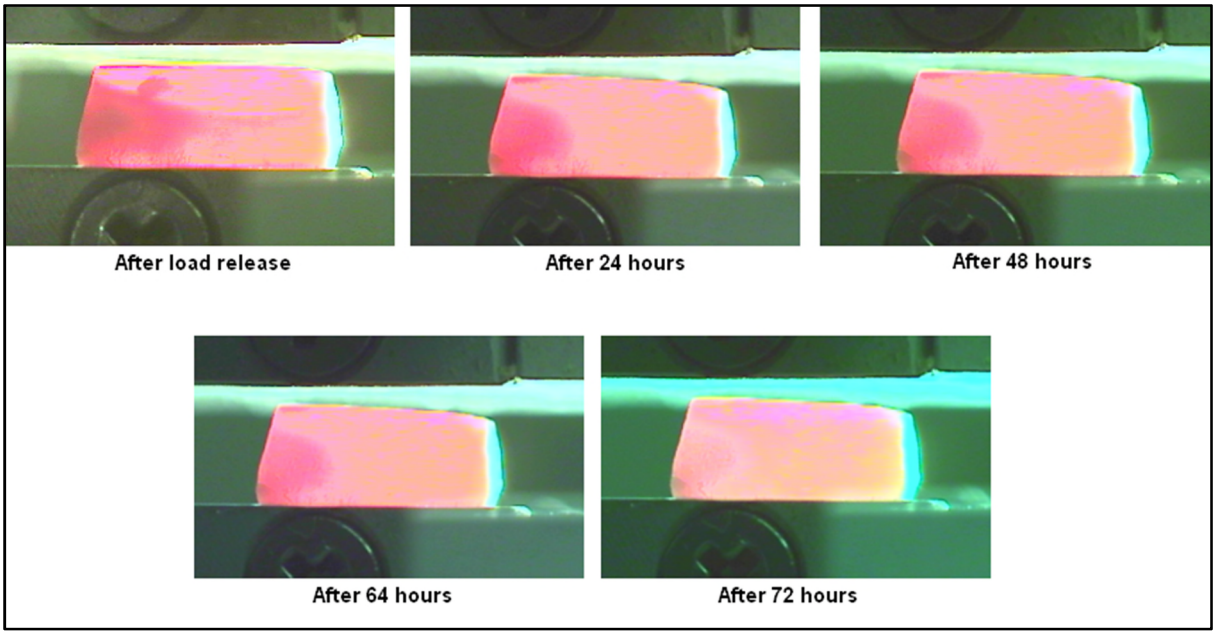

Fig. 6. Colour decay in SP_1-MMA-$HTPB_5$ as a function of time after removing the compressive load.

3.2. Colour change monitored by UV-Vis spectrometry

Having observed qualitative colour changes in the SP_1-MMA-$HTPB_5$ samples during compressive loading and unloading, we repeated the experiments but this time monitored the material's behaviour by UV-Vis spectrometry in order to collect quantitative data. The white light passing through the samples was collected using a 4-mm diameter optical fibre probe connected to the spectrometer. The transmitted light spectra as collected using the optical fibre probe are plotted

against the compression load in Fig. 7. A transmission peak was observed in the red-light region at ~675 nm. The intensity of the transmitted light declined gradually with increasing load up to the fixed maximum load of 195 N (reached ~55 s after starting the test). This means that the amount of light absorbed by the samples increased with the applied force, suggesting the progressive formation of more coloured species corresponding to the opening of the spiropyran ring and conversion to the merocyanine form.

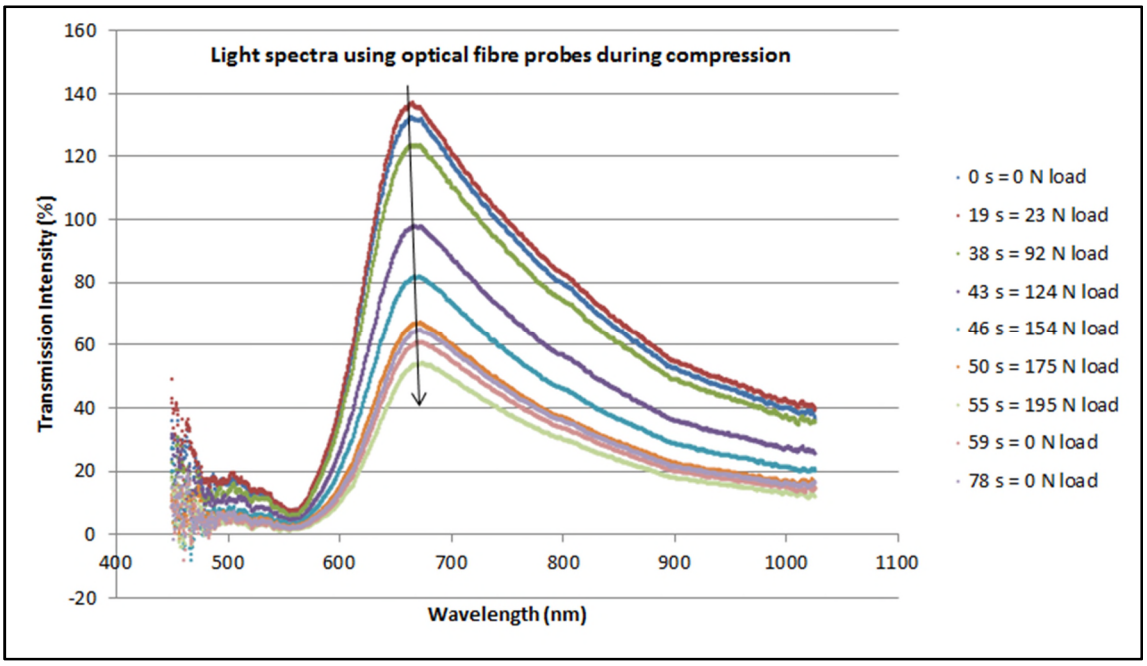

Fig. 7. SP_1-MMA-$HTPB_5$ UV-Vis transmission spectra as a function of loading force.

As observed qualitatively using a camera, the transmission intensity rapidly decreased when a threshold in the compressive load was applied to the sample. This is shown in Fig. 8 where the transmission intensity at the spectrum peaks is plotted as a function of the load. The transmission intensity remained constant until about 40 N load was applied (Fig. 8) but after this value the intensity started

decreasing indicating that a minimum load of 40 N had to be applied to the sample to initiate the spiropyran ring opening reaction. After about 70 N load, the transmission intensity decreased linearly confirming that all the spiropyran molecules were not converted to their open forms immediately. Another SP_1-MMA-$HTPB_5$ sample was subjected to two successive compressive loading test. During the second test, we observed a small (<2%) decrease in light transmission at 675 nm. This indicated that most of the spiropyran rings were opened during the first loading test, and there was not sufficient time for them to revert to the closed form before the second test. Optical fibres were used as sensing platforms to monitor the change in fluorescence arising from the opening of the spiropyran ring under both thermal stimuli and illumination. The spiropyran molecules were incorporated into sol-gels placed between two multimode optical fibres, or doped within the core of PMMA optical fibres, or applied as a coating on PMMA optical fibres [13-15]. Microstructured optical fibres have been used to monitor the fluorescence emanating from the opening of the spiropyran isomer incorporated in liposome vesicles under the influence of zinc ions [16]. This suggests that any stress-induced debonding in a rocket motor bond liner exposed to heat/cool cycles could be monitored by applying mechanoresponsive polymers to rocket motor cases and monitoring the colour changes. A colour chart as a function of stress would indicate the amount of stress a rocket motor experiences during storage or transportation in a cold environment, thus offering the benefit of non-destructive and low-cost damage assessment without disrupting the line of services as the current assessment technique requires an indiscriminate X-ray scanning by taking the missiles out of service.

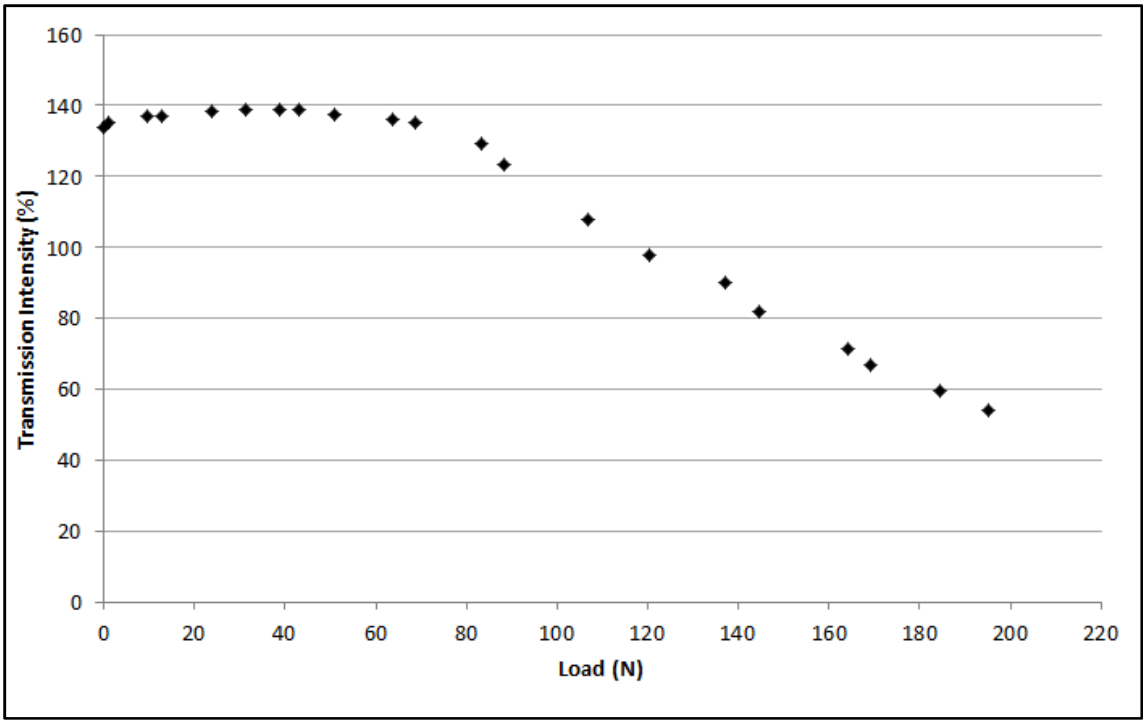

Fig. 8. Variation of the transmission intensity at the 675-nm peak as a function of loading force.

4. **Conclusions**

We have developed a mechanoresponsive HTPB polymer with spiropyran and methyl methacrylate that changes colour when subjected to compressive loading. The compressive force-induced colour change was monitored using a video camera and by UV-Vis spectrometry. During compression, a change in colour was observed in highly stressed areas of the sample and a minimum load of 40 N was required to initiate the ring opening reaction. The colour change was characterised by an increase in the absorption band at ~675 nm as more compressive loading was applied. This absorbance band is attributed to the opening of the spiropyran ring in response to the mechanical stress: the higher the load, the more intense the colour and the weaker the light transmission at 675

nm. The spiropyran-merocyanine conversion was reversible under fluorescent light over a period of hours. This means such force–induced coloration could be used for the non-destructive assessment of stress in polymeric/composite materials, including rocket motors.

Acknowledgments

This work was supported by the Centre for Defence Enterprise and Defence Science and Technology Centre (DSTL) [grant number DSTLX1000081514].

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2018-10-21
Elsevier
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