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Self-Healing in Epoxy Thermoset Polymer Films Triggered by UV Light

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Abstract

Self-healing of damaged structures can occur in three processes: capsule-based healing, vascular healing and intrinsic healing of polymers. The latest concept has a tremendous potential to repair damaged polymers and composite structures. Until now self-healing of composite materials has been addressed using capsule based resin with an initiator that polymerises in the damaged region. In this study, self-healing behaviour of cured epoxy thermoset resins modified with an epoxy-functionalised photoresponsive azobenzene molecule has been addressed by UV light without the use of any resin capsules or other component that is not chemically joined with the composites. The study was executed by nanoindentation and atomic force microscopy (AFM). Artificially damaged thermoset films exhibited good self-healing behaviour under UV irradiation only. This effect is attributed to the intrinsic healing mechanism triggered by UV-induced *trans*→*cis* isomerization of the azobenzene chromophore which enables the damaged polymeric matrix to recover.

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1. Introduction

Shape memory polymers (SMP) or self-healing materials are smart materials, capable of regaining their original shapes from a distorted or damaged forms after being exposed to appropriate stimuli such as chemicals, heat, moisture or light [1]. In most circumstances heat is the main driving force that triggers the repair of damage. Heating

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of the deformed polymer structures above their glass transition temperature [2] (T_g) or melting temperature [3] (T_m) can activate matrix movement to the damaged regions resulting in shape recovery or self-healing of the damaged structures. The application of light as stimulus to trigger the shape memory effect has been also well studied [2, 3, 4]. Thermoset polymers with photoresponsive crosslinks cinnamic groups, demonstrated a shape memory effect attributed to the elastic contraction of the polymer chain segments that was activated upon UV irradiation [4]. Rodriguez *et al* [5] reported on the shape memory assisted self-healing (SMASH) polymers, which are polymers with reversible plasticity (shape memory properties) and able to close and rebond cracks after thermal treatment.

Azobenzene is one of the most abundant light-responsive molecules, known for its ability to change its optical and physical properties under appropriate stimuli [6]. These changes are attributed to the reversible and repeatable isomerisation of the azobenzene chromophores. Irradiation with UV light converts the thermodynamically more stable *trans* azobenzene to its less stable *cis* form. Exposure to heat, visible light or storage in the dark induces the recovery of the *cis* isomers to their *trans* counterparts. The geometrical and polarity changes that occur through this conversion can be transferred into macroscopic level, when the azo molecules are attached to a polymeric backbone, and affect the whole polymeric matrix properties.

Very recently, azobenzene was found to be a light-powered healing material for wearable electrical devices [7]. Repetitive recovery of a damaged electrical conductor was achieved only by UV light illumination. The authors attributed this effect to the photoisomerisation of azobenzene which endorsed the whole polymer matrix to undergo bulk diffusion even below its T_g or T_m . Yamamoto *et al* [8] demonstrated that azobenzene-doped gel can endorse self-healing characteristics driven by photoisomerisation. Despite self-healing behaviour has been reported in azobenzene-based gel and soft polymers, no report has been found in the public domain on self-healing behaviour of azobenzene-based rigid and toughened resins. In this study we report on the physical changes that occur in a photoresponsive epoxy-based 3D cross-linked network containing azobenzene as backbone after exposure to UV radiation. The healing and shape recovery of this stimuli-responsive thermoset is being analysed by nanoindentation and Atomic Force Microscopy (AFM). We are the first to report light triggered self-healing behaviour in an azobenzene-based rigid thermoset network confirmed the isomerisation of azobenzene chromophores by transmission spectroscopy.

2. Experimental Methods

2.1. Materials

Difunctional epoxy-based azobenzene resin (4,4'-diglycidylazobenzene) was synthesised according to literature [9]. This azobenzene crosslinker was selected due to the presence of its oxirane functional groups, which favour its miscibility with common epoxy resins (Bisphenol) and can be cured with commercially available hardeners to give rise to a matrix that can drive microscopic changes after isomerisation. For these studies 10% w/w azobenzene resin were mixed with a common biresin system Biresin® LS Resin and F4 Hardener (100 parts epoxy/18 parts hardener) supplied by Sika®. The mixture was cured in a mould at 80 °C for 2 hours. Reference samples, free of azobenzene-based resin were also prepared under the same conditions. The dimension of the cured specimens was 10 cm x 3.5 cm with a thickness ranging between 3-5 mm.

2.2. Techniques

A CM-700D spectrophotometer Konica Minolta was used for recording the films' spectra in order to determine the *cis* and *trans* isomeric compositions before and after UV irradiation. The spectra were collected every 10 nm in the wavelength range of 400-700 nm.

A nanohardness tester from CSM Instruments SA (2034 Peseux, Switzerland) with a Berkovich (triangular-based pyramid) diamond indenter was used for stiffness and hardness measurements of the specimens before and after UV irradiation. For each sample 3 replicates were performed with approximately 10 scans in each replica, applying a maximum load of 5 mN, a pause time of 30 s, and loading and unloading rates of 10 mN/min.

The actual depths of indents created manually using a common diamond scribe and a pin were studied before and after UV irradiation by AFM analysis. The AFM Digital Instruments Dimension™ 3000 SPM with a NanoScope IIIa controller (Veeco instruments, Santa Barbara, California, USA) and a NanoScope IIIa software (version 4.42r4) was used. Tapping mode was employed across the surface of the samples at a frequency of 1 Hz.

To achieve a complete conversion of the *trans* azobenzene to the *cis* isomer, the specimen films were mounted on the sample holding platform of the indenter and irradiated *in-situ* for 1 hour using a M2100 Novacure light source equipped with a 320-390 nm filter. An irradiation time of 1 hour was chosen to permit the *trans* to *cis* isomerisation to take place throughout the thickness of the films and also to allow for the relaxation of the polymer matrix. The intensity of the irradiation was arbitrary chosen to 1000 mW/cm². The distance between the specimens and the light guide was chosen to 12 mm in order to expose maximum area of the specimen to UV light. The existence of any thermal effect that could possibly be occurring after UV irradiation was eliminated by allowing the samples to cool for 1 hour before being subjected to tests. Temperature rise in the films due to UV irradiation was measured by embedding a thermocouple in the films' and found to be 5 °C. It was observed that the specimens reached the room temperature within 10 min of suspending the irradiation.

3. Results and Discussion

3.1. Photoresponsive behaviour of the azobenzene-based films

The initial goal of this study was to demonstrate whether or not the azobenzene molecule, as seen in Figure 1, are capable of undergoing reversible isomerisation within the crosslinked-tough polymer matrix.

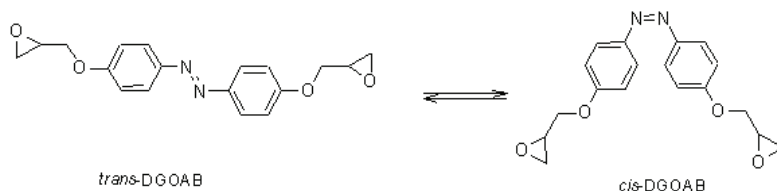


Fig. 1. *Trans* and *cis* isomeric forms of 4, 4'-diglycidylazobenzene (DGOAB).

A widely used method to investigate the azobenzene isomerisation in solutions or within thin films (<1 mm) is UV/Vis spectroscopy [10]. Peris *et al* [11] have reported the reversible photoisomerisation of the 4,4'-DGOAB in solution, determined by UV/Vis absorption spectroscopy. Azobenzene molecules have high molar extinction coefficient [12], consequently well-defined UV/Vis absorption spectra cannot be recorder with thick films. Therefore the UV/Vis absorption spectroscopy was not employed for the characterisation of photoisomerisation. The use of reflectance spectrophotometer was found to be suitable to record the photoisomerisation in thick films (>1 mm), as the colour of the films changed visually from dark yellow to orange. Figure 2 illustrates the reflectance spectra of a 10% DGOAB epoxy film before and after UV and visible irradiation.

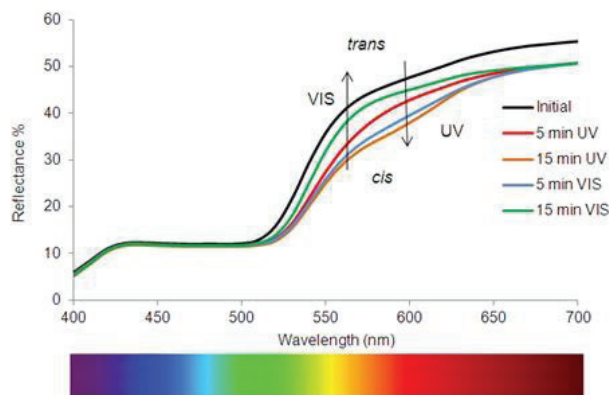


Fig. 2. Reflectance spectra of a 10% azobenzene-based epoxy cured film pre- and post-irradiation.

The first spectrum was collected from a non-irradiated film, which had previously been stored in the dark, assuming that the film contained 100% *trans* azobenzene. The film was then irradiated with UV light and reflectance spectra were recorded periodically. After 5 and 15 min of exposure, a decrease in the intensity of reflectance at 570 nm (yellow colour) was noticed. This was attributed to the *trans*→*cis* isomerisation. Further irradiation beyond 15 min demonstrated no change to the reflectance spectra suggesting complete conversion of *trans* isomers to their *cis* counterparts on the surface of the thick films. It was observed that complete *trans*→*cis* isomerisation involved a maximum decrease in reflectance of 23% for 10% mol azobenzene loading. Similar conversion of *trans* to *cis* isomerisation was reported previously [13].

Subsequent irradiation with visible light for 5 and 15 min demonstrated the opposite effect. As seen in the spectra (Figure 2), the reflectance of the film increased with irradiation time, confirming a full recovery of the *cis* isomers to the *trans* counterparts. Quantitative analysis of the reflectance spectra confirmed that a 95% *cis*→*trans* isomerisation was achieved within 15 min irradiation by visible light. It should be noted that reflectance spectra recorded on a reference film with no azobenzene showed no changes in the reflectance upon irradiation by UV or visible light suggesting that the intensity changes of the transmission spectra in the former samples were caused by the isomerisation of azobenzene.

3.2. Nanoindentation analysis of the azobenzene-based thermosets

After confirming that the azobenzene underwent reversible isomerisation in a crosslinked tough resin, further investigation into possible mechanical property changes and self-healing behaviour, triggered by photoisomerisation was conducted on the specimens using nanoindentation and optical microscopy analysis. Nanoindentation tests were performed on the pristine and subsequently UV irradiated azobenzene film and the results are tabulated in Table 1. The stiffness of the films did not show any significant changes after UV irradiation, which possibly indicated that the resins had no significant fatigue. On the other hand, the hardness of the films decreased (by 26%) from 255.62 MPa to 188.67 MPa, which is in agreement with the literature value [14].

Table 1. Nanoindentation data of azobenzene films before and after UV irradiation.

Sample history	Stiffness (GPa)	Hardness (MPa)
Initial (10% AB/ epoxy resin) film	3.73 ± 0.11	255.62 ± 31.45
UV irradiated (10% AB/ epoxy resin) film	3.75 ± 0.10	188.67 ± 19.77

The most appealing phenomenon in this part of work is the change in size and shape of the indents during UV irradiation. After indentation of the specimens the images of the indents before and after irradiation were captured by optical microscope connected to the indentation equipment. Figure 3 shows three indentation marks that were generated on the epoxy resin film containing 10% azobenzene before and after UV irradiation. Upon UV irradiation the three visible indents in the unirradiated specimen (Figure 3a) almost disappeared (Figure 3b) suggesting shape recovery with associated healing of the indents.

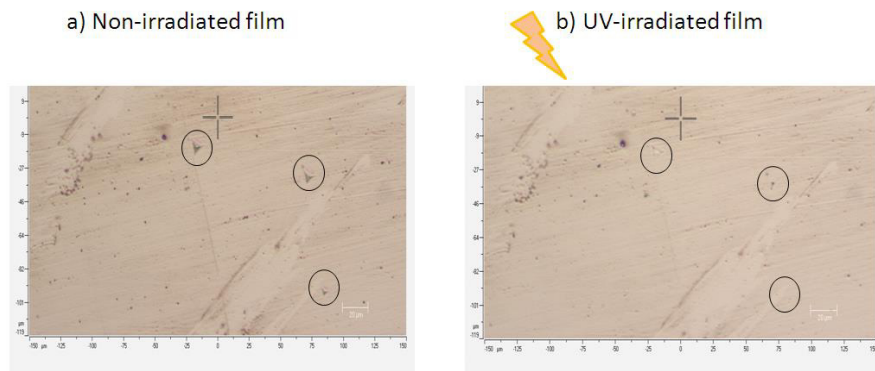


Fig. 3. Images of 3 indentation marks of an azobenzene-based epoxy film a) before and b) after UV irradiation

Two possible reasons may result in this healing effect. Firstly the photoinduced heating of the films that may induce the matrix movement driving the healing process of the indent. However, we have carried out a similar experiment on a rigid network film with no azobenzene and found no changes to the indents after exposure to UV light. Furthermore the T_g of the cured films without and with azobenzene chromophores was found to be 81 °C and 83 °C, respectively. The UV irradiation on the films for 1 hour with an intensity of 1000 mW/cm² found to have increased the temperature by 5 °C from room temperature (20 °C), and it is impossible to increase the chain motion at such a low temperature (25 °C) to initiate healing of the indents. Thus the possibility of photothermal healing can be eliminated. The second possible reason may be driven by the photoisomerisation of azobenzene chromophores in the cured resin. It has already been shown in Figure 2 that UV irradiation of azobenzene-based specimens triggers the *trans* to *cis* isomerisation of azobenzene. Therefore it is more likely that the photoisomerisation of azobenzene (*trans*→*cis*) triggered the healing effect. The justification of this effect is that isomerisation of azobenzene initiates the motion of the polymeric chains pushing the polymer matrix towards the void regions to trigger healing of the indents. Although a complete healing effect in an azobenzene-based softer polymer and gel has been previously reported [8, 14] we are the first to report the self-healing behaviour in 3D crosslinked tough matrix triggered by photoisomerisation.

3.3. AFM analysis for self-healing behaviour of the azobenzene-based thermosets

Nanoindentation analysis indicated the healing behaviour of the indent qualitatively but the extent of healing and depth changes before and after irradiation remained undefined. Therefore AFM analysis of pre- and post-irradiated thermoset specimens that were scratched by a diamond tip scribe and a pin, was carried out for quantitative analysis. Initially the reference thermoset with no azobenzene was scratched with a diamond tip scribe and depth of the scratches was measured before and after 1 hr UV irradiation as shown in Figure 4. 3D images of the cured epoxy resin films (Figure 4) containing two scratches of 56 nm and 105 nm showed no depth change after UV treatment suggesting no significant shape recovery or healing. This is expected as the healing would have happened in the reference sample only if healable stimuli such as Diels-Alder reaction, hydrogen bonded supramolecular network, and ionic liquids [15] were present in the matrix or the matrix was heated above its T_g or melting temperature; such an agent or stimuli was not included in this tested reference specimen.

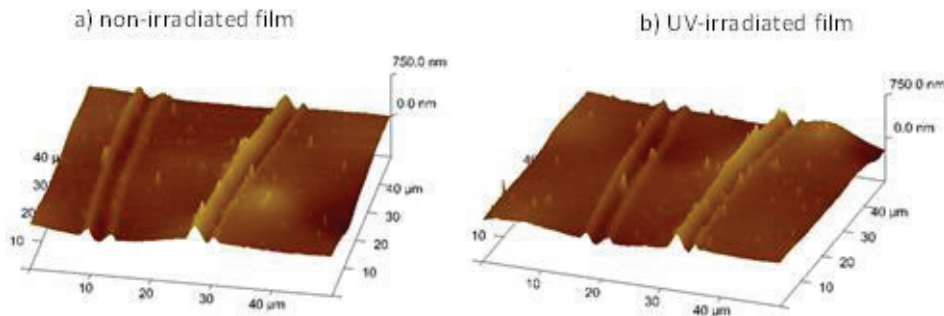


Fig. 4. 3D AFM topographic images of two scratches on an epoxy resin film (reference sample) a) before and b) after 1 hour UV irradiation.

Further investigation into the healing ratios of thermoset films containing 10 % mol azobenzene was carried out before and after UV irradiation on films scratched at various depths and their changes are shown in Table 2. Profile measurements were taken along a fixed line at the deepest point of the scratches before and after irradiation in order to avoid error from the measurement. The percentage of healing was calculated using the following equation, where d_i is the initial depth (nm) before irradiation and d_{UV} the depth (nm) after 1 hour exposure to UV light.

$$HR = \frac{(d_i - d_{UV})}{d_i} \times 100\%$$

Table 2. Depths and healing ratio data obtained by AFM measurements on 10% mol azobenzene-based cured specimens.

Sample history	Scratch 1	Scratch 2	Scratch 3	Scratch 4	Pinhole
Initial depth (d_i , nm)	947.80	400.19	771.65	132.39	2675.01
Depth after 1hr UV irradiation (d_{UV} , nm)	430.07	127.62	208.46	37.36	1607.49
Healing ratio (HR, %)	55%	68%	73%	72%	40%

Azobenzene-based epoxy thermosetting films were analysed under the same experimental conditions as the reference sample with the exception of larger penetration depths compared to the reference films. Figure 5 depicts 3D images of the azobenzene-based cured specimen before and after exposure to UV light. The scratches with initial depth of 948 nm and 400 nm became smoother upon UV irradiation for 1 hr. A recovery of about 55% and 68% was obtained in the 948 nm and 400 nm-deep scratches, respectively. Similarly, two additional scratches with depths of 772 nm and 132 nm were created, as shown in Figure 6 (unirradiated) and subjected to UV radiation for 1 hr. Figure 6b shows a healing behaviour of about 73% for the 772 nm-deep scratch and 72% for 132 nm scratch after exposure to UV light. The observed healing effect is attributed to the *trans*→*cis* photoisomerisation of the azobenzene which triggered the polymer chain motion followed by matrix diffusion to the free volumes, which in this case are scratches. The AFM results are consistent with the nanoindentation results suggesting that healing is driven by photoinduced matrix diffusion triggered by isomerisation.

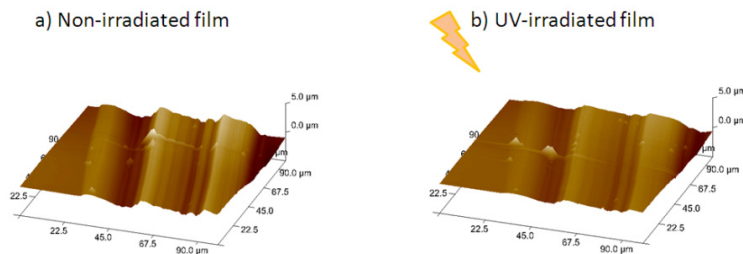


Fig. 5. 3D AFM topographic images of two scratches on a 10% azobenzene-based epoxy resin film a) before and b) after 1 hour UV irradiation.

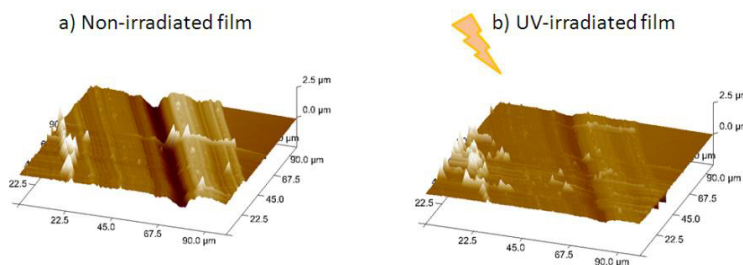


Fig. 6. 3D AFM topographic images of two extra scratches on a 10% azobenzene-based epoxy resin film a) before and b) after 1 hour UV irradiation.

In order to evaluate the effect of the nature of scratches on the film surface a further indent was created on a thermosetting specimen using a pin as shown in Figure 7. The initial depth of the pinhole was about 2.7 mm, however the first few micrometres of the pinhole edge were analysed due to the configuration of the AFM. Upon UV irradiation the pinhole healed by about 40% which is smaller than the degree of healing observed in less deep

scratches (Figure 4 and 5). The smaller recovery could have several reasons such as UV light intensity drop in the deeper surface and matrix diffusion was decelerated or the available matrix around the hole is not enough to fill bigger hole in a rigid structure within the dose time used in this investigation.

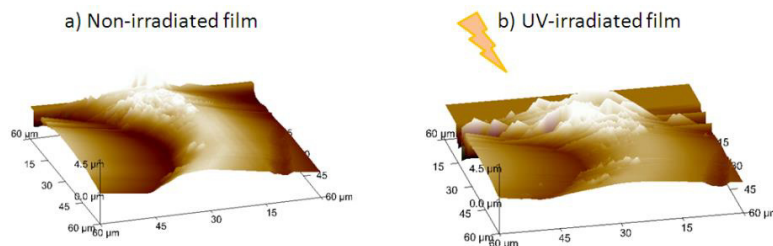


Fig. 7. 3D AFM topographic images of a pinhole on a 10% azobenzene-based epoxy resin film a) before and b) after 1 hour UV irradiation.

4. Conclusions

Self-healing of polymers and composite structures is an important phenomenon. For the first time we have demonstrated UV-light triggered self-healing behaviour in 3D crosslinked rigid solid structure made by curing an azobenzene epoxy modified phenolic resin without incorporating any healing stimuli such as Diels-Alder reaction, hydrogen bonded supramolecular network, and ionic liquids or heating the materials above their glass transition or melting temperature. It was observed that the indents created during nanoindentation experiments healed upon irradiation by UV light without causing any fatigue to the mechanical properties of the thermoset films, as confirmed by unaffected stiffness after irradiation. It was also found that the hardness was decreased by about 26% by UV irradiation. The authenticity of the healing behaviour was confirmed by AFM analysis of 3D topographic images. This light driven healing of the thermosets was driven by *trans* to *cis* isomerisation of azobenzene chromophores, which triggered the matrix diffusion to the scratched regions of the films. Reflectance spectroscopy analysis confirmed the *trans* to *cis* isomerisation. This finding suggests that azobenzene-based epoxy resins could have potential applications in shape memory recovery or damage repair by self-healing process.

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