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Improvement and tuning of the performance of light-healable coatings by variation of the monomer content

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Photo-healable epoxy crosslinked polymers were produced by combining two commercially-available epoxy monomers with a newly sythesised diamine crosslinker (APCD). The crosslinker contains a photocleavable unit in the centre which allows decrosslinking and recrosslinking of the crosslinked polymer network under different UV wavelength light. This behaviour was shown to give rise to the ability to heal a surface scratch after irradiation with 254 nm UV light, and subsequent 365 nm irradiation leads to almost complete recovery of the original coating properties. Three epoxy monomers systems were used to demonstrate the ability to tune the polymers properties without compromising the healing performance: two single epoxy polymers (APCD/PDE and APCD/BDE) were made and a third polymer made by mixing the two monomers in a 50:50 mixture (APCD/BP50). It was found that the rigid polymer had a poor healing ability compared to the flexible polymer but the 50:50 mixture polymer had the coating performance of the rigid polymer and the healing ability of the flexible polymer.

Introduction

The first self-healing polymer system was proposed just over 20 years ago[1] and in that time the field has grown immensely both in the capability and complexity of the polymers produced. The need for self-healing polymer systems has been encouraged by the global cost of maintenance and replacement of plastic and polymer coatings. Self-healing polymers allow product functionality to be restored, effectively extending the service life of a component[2, 3]. In the case of thermoset plastics, damage often requires the replacement of the component, as once cured the crosslinked structure is no longer thermally re-workable like thermoplastics. In order to heal a damaged thermoset and restore functionality two steps must occur: firstly the healing material must be able to flow into the damaged site and secondly the healing material must harden to seal the damage. There are several different technologies that approach these two steps in different ways, they can be broadly grouped into two categories: extrinsic and intrinsic[4-7].

Extrinsic healing involves the addition of healing agents into the polymer matrix, which is released upon damage of the system[8-13]. Intrinsic healing does not require the incorporation of additives into the polymer matrix as the polymer is designed in a way that the self-healing response is in-built to the chemical structure. The self-healing response arises through dynamic chemical or physical bonds which, on application of a stimulus, will cleave and allow flow of material. This approach gives rise to such desirable properties as ease of manufacture, repeatable healing and increased versatility[14-17]. Common stimuli used for intrinsically healable systems include heat, light and chemically-triggered, such as pH changes or redox reactions[18-23]. The earliest adaptations of such polymers focused on heat as the stimuli and often utilised Diels-Alder reactions as the healing mechanism with great success[24-29]. In recent years the use of light as the healing stimulus has received increasing attention due to greater reaction control and less disruptive healing treatment, with the light inducing the reversible photo-cycloaddition of moieties such as coumarin, anthracene, thymine and cinnamic acid or the reversible photo-cleavage of disulfides, allyl sulphide and trithiocarbonates[30-38].

Typically the photo-responsive moieties are incorporated into the polymer via main chain modification which results in polymers with fixed properties, limited versatility and little allowance for modification[38-41]. Herein we present the synthesis of a diamine crosslinker containing a coumarin moiety that allows a light-healing ability to be imparted to various epoxy systems via the standard thermal epoxy curing process. Through the curing of different monomers by themselves or in a mixture the properties and performance of the produced light-healable polymers can be varied with ease leading to a versatile, easily implemented and potentially universal system for producing light-healable polymers. Light-healing ability was also demonstrated to be imparted to very rigid systems by the incorporation of a slightly more flexible epoxy monomer during curing to allow the production of healable materials with little reduction in performance as a coating. As the epoxy monomers used are commercially available and require no modification before use, there is the possibility to use of many more epoxy monomers and vastly more complex mixtures as well as the potential of adding the current high performing polymers in small percentages into existing coating mixtures to provide light-healing without drastic overall structural modification.

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Experimental

Materials

7-hydroxycoumarin (Sigma-Aldrich), 3-bromopropylamine hydrobromide (Sigma-Aldrich), di-tert-butyl dicarbonate (Sigma-Aldrich), benzophenone (Merck-Schuchardt), poly(ethylene glycol) (600) diglycidyl ether (PDE) (Polysciences, Inc.) and 1,4-butanediol diglycidyl ether (BDE) (Sigma-Aldrich) were used as supplied.

Equipment/Characterisation

Photoreactions were carried out in a 40 W UVP UV crosslinker (CL-1000L) and a custom-built UV reactor equipped with 16 8W 254nm or 365 nm lamps. ^{1}H NMR and ^{13}C NMR were measured on Bruker DRX 400 spectrometer. Mass and IR spectra were recorded on Agilent 6120 Quadrupole LC/MS and Agilent Cary 630 FTIR spectrometers, respectively. DSC analysis, DMA and TGA were performed using a PerkinElmer DSC8000, PerkinElmer DMA7 and Mettler TGA/DSC1 STAR system respectively. UV-vis spectra were collected using a Shimadzu UV-1800 spectrometer. Molecular weight approximations were gathered through the use of a Tosoh EcoSEC HLC-8320GPC GPC System with Tosoh alpha 2000 and 4000 columns and calibrated with a polystyrene standard. Hardness measurements were collected on a Struers Duramin A300 durometer. Optical microscope images were taken with an Olympus GX51.

Synthesis of coumarin-based crosslinked polymers

Synthesis of N-Boc-3-bromopropylamine[42]

Di-*tert*-butyl dicarbonate (11.61 g, 53.2 mmol) and triethylamine (14.9 mL, 106.4 mmol) were stirred together in methanol:acetonitrile (1:1, 56 mL) for 15 minutes at room temperature. 3-bromopropylamine hydrobromide (6.57 g, 30 mmol) was dissolved in methanol:acetonitrile (1:1, 28 mL) and the solution added dropwise to the reaction flask over 2 hours whilst stirring at room temperature. The reaction solution was then evaporated to dryness and the residue dissolved in ethyl acetate (60 mL), washed with water (5x20 mL), dried over MgSO$_4$ and concentrated under vacuum to produce N-Boc-3-bromopropylamine in high purity as a yellow oil (6.51 g, 27.35 mmol, 91%); ^{1}H NMR (400 MHz, CDCl3) δ 1.44 (s, 9H), 2.04 (m, 2H), 3.26 (m, 2H), 3.43 (t, 2H), 4.66 (s(amine), 1H) ppm; ^{13}C NMR (100 MHz, CDCl3) δ 27.6, 28.6, 31.0, 32.9, 39.2, 156.2 ppm; IR (ATR) 3360, 2979, 2942, 2882, 1689, 1247, 1150, 779 cm^{-1}; MS (ESI) m/z (%) 239.04 ([M+H]$^+$, 100), 241.04 ([M+H]$^+$, 80).

Synthesis of tert-butyl (3-((2-oxo-2H-chromen-7-yl)oxy)propyl)carbamate (Boc-APC)[43]

7-hydroxycoumarin (2.31 g, 14.26 mmol) and potassium carbonate (3.10 g, 37.50 mmol) were stirred in acetone (90 mL) for 15 minutes. N-Boc-3-bromopropylamine (3.57 g, 15.00 mmol) was added and the mixture heated under reflux for 24 hours. The mixture was filtered, the filtrate evaporated to dryness, the resultant oil dissolved in chloroform (40 mL), washed with water (3x20 mL), dried over MgSO$_4$ and evaporate to dryness. The resultant residue was dissolved in chloroform and precipitated from hexane to afford Boc-APC in high purity (3.69 g, 11.60 mmol, 79%); ^{1}H NMR (400 MHz, CDCl3) δ 1.38 (s, 9H), 1.86 (m, 2H), 3.09 (q, 2H), 4.10 (t, 2H), 6.28 (d, 1H), 6.92 (d, 1H), 6.95 (dd, 1H), 7.62 (d, 1H), 7.99 (d, 1H); ^{13}C NMR (100 MHz, CDCl3) δ 27.8, 28.5, 31.1, 31.9, 37.9, 54.0, 66.4, 101.6, 112.7, 128.9, 143.6, 156.0, 156.2, 161.4, 162.2 ppm; IR (ATR) 3354, 2974, 2933, 2882, 1699, 1610, 1507, 1230, 1159, 1120, 831 cm^{-1}; MS (ESI) m/z (%) 342.13 ([M+Na]$^+$, 25).

Synthesis of di-tert-butyl (((6,7-dioxo-6,6a,6b,7,12b,12c-hexahydrocyclobuta[1,2-c:4,3-c']dichromene-3,10-diyl)bis(oxy))bis(propane-3,1-diyl))dicarbamate (Boc-APCD)

Boc-APC (8.69 g, 27.20 mmol) and benzophenone (0.99 g, 5.45 mmol) were dissolved in ethyl acetate (90 mL) and the resultant solution irradiated with 365 nm UV light in a UV reactor for 23 hours. The resultant mixture was evaporated to dryness, the residue stirred with diethyl ether (50 mL) and filtered to afford Boc-APCD in high purity (7.25 g, 11.36 mmol, 84%); ^{1}H NMR (400 MHz, CDCl3) δ 1.45 (s, 18H), 1.99 (m, 4H), 3.33 (m, 4H), 3.73 (m, 2H), 3.87 (m, 2H), 4.02 (t, 4H), 4.71 (s(amine), 2H), 6.63 (d, 2H), 6.71 (dd, 2H), 7.01 (d, 2H) ppm; ^{13}C NMR (100 MHz, CDCl3) δ 28.4, 29.5, 37.9, 40.0, 43.6, 66.2, 103.4, 112.3, 112.5, 128.5, 152.0, 156.0, 159.8, 166.1 ppm; IR (ATR) 3366, 2974, 2926, 2876, 1776, 1749, 1686, 1624, 1509, 1247, 1165, 1116, 1006, 834 cm^{-1}; MS (ESI) m/z (%) 661.27 ([M+Na]$^+$, 100).

Synthesis of 3,10-bis(3-aminopropoxy)-6a,6b,12b,12c-tetrahydrocyclobuta[1,2-c:4,3-c']dichromene-6,7-dione (APCD)

Boc-APCD (0.60 g, 0.95 mmol) was dissolved in DCM (4 mL) to which was added 1.25M HCl in methanol (1.5 mL, 1.88 mmol) whilst cooling in an ice bath. After 2 hours at room temperature the solution was evaporated to dryness. The residue was then purified by reverse phase column chromatography with 75:25 methanol:water to produce APCD in high purity (0.36 g, 0.81 mmol, 86%); ^{1}H NMR (400 MHz, d^6-DMSO) δ 1.97 (m, 4H), 2.91 (t, 4H), 3.62 (m, 2H), 3.93 (t, 4H), 4.61 (m, 2H), 6.29 (q, 2H), 6.38 (d, 2H), 6.81 (d, 2H), 7.92 (s(amine), 4H); ^{13}C NMR (100 MHz, d^6-DMSO) δ 27.3, 36.6, 38.1, 51.6, 101.9, 104.6, 118.3, 127.9, 156.7, 158.5, 172.7 ppm; IR (ATR) 3344, 2948, 2883, 1702, 1613, 1593, 1518, 1431, 1288, 1159, 1123, 1023, 978, 833 cm^{-1}; MS (ESI) m/z (%) 439.19 ([M+H]$^+$, 100).

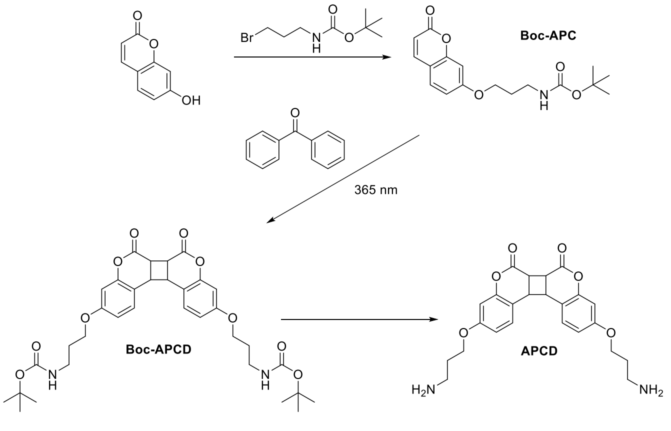

Figure 1: Synthesis scheme of new diamine crosslinker, APCD.

Preparation of APCD crosslinked epoxy polymers

The synthesis of three thermoset systems is shown in this work, all of which involve commercially-available epoxy monomers crosslinked by the newly synthesised crosslinker APCD. These polymers are APCD with PDE, APCD with BDE and APCD with a 50:50 mole percent mixture of PDE and BDE and are denoted APCD/PDE, APCD/BDE and APCD/BP50 respectively. The 50:50 mixture of epoxy monomers was used to demonstrate the tunability of the polymers mechanical properties without compromising the healing performance imparted by the photoreversible crosslinker. APCD was mixed with the desired epoxy monomer composition in a stoichiometric ratio of 2:1 of epoxy to crosslinker, along with a few drops of methanol to aid solubility. The solution was then applied to a glass slide and cured overnight at 100 °C under vacuum to drive off the methanol. The reaction scheme for APCD/PDE is presented in Figure 2 and the curing was confirmed by IR as detailed below.

Results and Discussion

Characterisation of APCD crosslinked epoxy polymers

The resultant polymers were analysed using several techniques to determine key thermal properties, confirm the intended behaviour under UV light and observe their light-healing ability.

Thermal Property Analysis

The first step after the polymers were synthesised was to determine the decomposition temperature of these materials using TGA. From the TGA curves presented in Figure 3, the polymer showed a slight decrease in weight up to 80 °C which is attributed to the loss of residual methanol from the curing stage. For APCD/PDE, decomposition of the material passed 10% mass loss at 320 °C, which is well above the common service temperatures of epoxy of 150 °C[44]. APCD/BDE gave a much lower decomposition temperature of 234 °C however APCD/BP50 displayed a decomposition temperature of 265 °C, the lower temperatures may be due to the increased strain from the short BDE making the bonds more susceptible to oxidation.

The curing of the epoxy monomer with the synthesised crosslinker was further investigated by comparison of the IR spectrum of the crosslinker and epoxy mixture with the mixture after heating at 80 °C for 6 hours. As shown for APCD/PDE & APCD/BDE in Figure 4, the signal for the epoxy group which appears at 914 cm^{-1} is reduced and the hydroxyl peak increases as the monomer cures[45]. The same behaviour was observed for all three polymers and hence the curing of the polymers for upwards of 6 hours was deemed sufficient for complete crosslinking. The polymers were then subjected to a post curing step wherein they were heated to 100 °C for another 6 hours and any further curing observed by further changes in the IR spectrum. All three polymers showed negligible changes in the IR spectrum after this additional heating cycle, suggesting 80 °C was a sufficiently high curing temperature.

The ideal curing temperature for the mixture of the crosslinker and the epoxies were then determined by DSC and the results shown in Figure 3. For APCD/PDE, an exothermic event at 12.2 °C indicated the curing temperature of the mixture, but does not appear as strong as expected due to an endothermic event occurring at a nearby temperature partially overlapping the curing curve. The endothermic event can be attributed to the melting of the unreacted PDE epoxy monomer. However for the other two polymer mixtures the exothermic events indicating the curing are clearly visible; APCD/BDE shows a curing event at 69.7 °C and APCD/BP50 exhibits two curing events, at 11.9 °C and 75.0 °C corresponding to the reaction of the two epoxy monomers present and agrees with the curing temperatures seen in the single epoxy polymers. These results coupled with the post curing results justify the use of 100 °C as a curing temperature to ensure the maximum amount of crosslinking for all three epoxy systems.

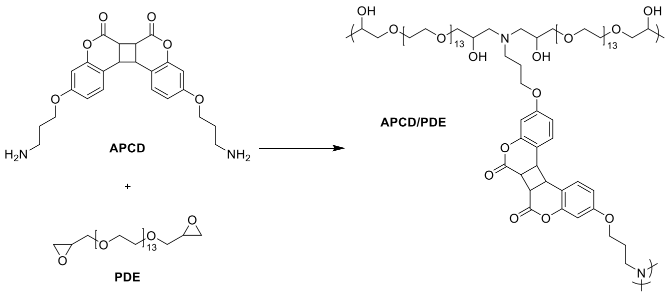

Figure 2: The subsequent reaction of the synthesised diamine crosslinker with PDE to produce the crosslinked epoxy polymer APCD/PDE.

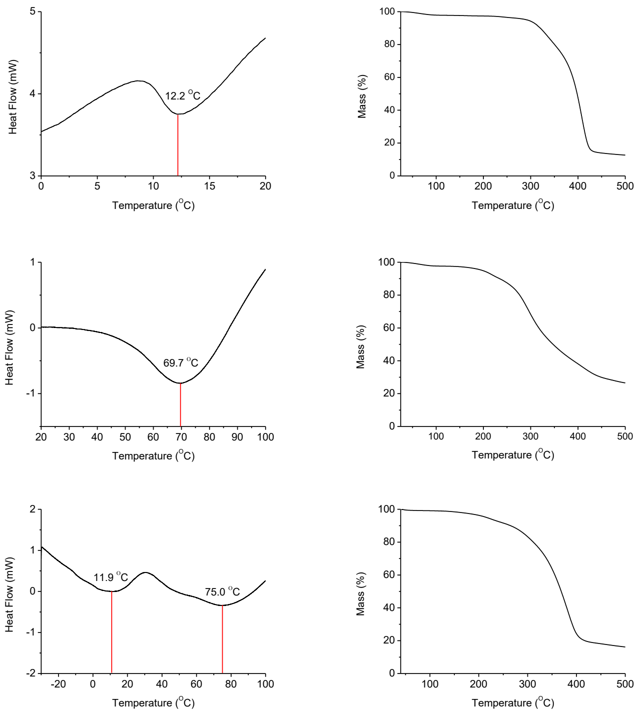

Figure 3: DSC curing curve (left) of a mixture of unreacted APCD and the respective epoxy monomers and TGA (right) of the crosslinked polymers for APCD/PDE (top), APCD/BDE (middle) and APCD/BP50 (bottom). Heating rate of 2 °C/min was used for DSC and 10 °C/min for TGA.

The three crosslinked polymers were tested using DMA to determine their respective glass transition temperatures in the crosslinked state. The values determined from these measurements are shown in Table 1 and as expected the relatively soft PDE polymer displays a low value compared to the other two. However, although the BP50 polymer value falls between the two single epoxy polymers it is much closer to the BDE value than expected, suggesting the incorporation of the BDE monomer has a dominating effect on the mechanical properties of the polymer. The values observed for the BDE and BP50 polymers are very promising as they fall either side and close to the T_g of the common automotive coating material PMMA which is 105 °C and the values for all polymers are above that of another common coating material PET (65 °C)[46].

Decrosslinking and Recrosslinking of crosslinked epoxy polymers

As the light-healing ability imparted by the photoreversible crosslinker arises from the decrosslinking of the material via the bisection of the crosslinker within the polymer by <280 nm UV light and subsequent reformation of the crosslinker with >320 nm UV light (as depicted in Figure 5) it is paramount to confirm and determine the extent to which this reaction occurs[47, 48]. This mechanism indicates that the coatings will be stable in sunlight as <280 nm light is almost non-existent in ground level sunlight as it is absorbed by the atmosphere suggesting minimal decrosslinking would occur. Also as >320 nm is very prevalent in sunlight it may also be utilised in the recrosslinking process[49].

The decrosslinking of the epoxy polymers was first monitored by IR and performed by irradiating a thin, glass-mounted polymer sample with 254 nm UV light in the stated UVP UV crosslinker. The relative peak positions and intensities were monitored and can be seen to change as decrosslinking occurs (Figure 6). The observed trends were found to be consistent for both of the polymers APCD/PDE and APCD/BDE. The peak at 1720 cm^{-1} corresponding to the coumarin carbonyls can be seen to increase in intensity and shift as the dimer is cleaved due to a new environment for the carbonyl. A peak appears at 1616 cm^{-1} indicating the formation of coumarin double bond as the cyclobutane undergoes reverse cycloaddition. The peak at 1528 cm^{-1} decreases as the cyclobutane disappears as this peak arises from the C-H bonds of the cyclobutane ring in the dimer. It is important to note that the majority of the signals remain relatively unchanged indicating the structure of the rest of the polymer is unaffected by the UV light irradiation[50].

The photoreversibility process can be readily monitored using UV-vis spectroscopy, as it allows the observation of the formation and loss of the coumarin double bonds as shown in Figure 5. The mixture of the crosslinker and the respective epoxy monomers were dissolved in methanol and spin-coated onto a quartz square which allowed measurement by UV-vis spectroscopy through the use of a cuvette shaped mount for the coated quartz square. During irradiation of the sample with 254 nm UV light, a peak can be seen at 328 nm (Figure 7a); this peak corresponds to the coumarin double bonds that are formed during the dimer scission[50]. After the UV-vis spectra peak absorbance plateaued, the sample was then irradiated with 365 nm UV light to induce the reformation of the coumarin dimer. Figure 7b shows that, as expected, the reformation of the dimer required more energy than the scission as the irradiation dose displayed on the spectra is a factor of 100 greater in both cases. Significant reformation of the broken dimers was achieved, with the more flexible PDE-based polymer yielding the greater reformation; the 365 nm irradiation gave reformation of 72% and 63% of the broken dimers for APCD/PDE and APCD/BDE respectively.

The decrosslinking of the epoxy polymers by irradiation can be further understood by monitoring the solubility of the material after irradiation. Glass mounted insoluble crosslinked samples were irradiated with 254 nm UV light for set times whilst soaking in methanol allowing the material to dissolve as the UV light cleaved the crosslinks forming the soluble linear chains and/or oligomers. The samples were dried and weighed after each interval with the solutions collected and analysed by GPC to determine the molecular weight of the liberated fragments. Figure 8 shows the mass lost from the polymers with increasing irradiation time as well as the GPC chromatograms of the solutions. The chromatograms of the solutions collected before irradiation all show a broad peak corresponding to low molecular weight oligomeric material as well as a sharp peak indicating unreacted epoxy monomer from the slight excess of epoxy added during the curing process, which is observable at 17.5 min for PDE and 18.5 min for BDE.

Table 1: Glass transition temperatures (T_g) of the three polymers as measured by DMA.

	APCD/PDE	APCD/BDE	APCD/BP50
T_g (°C)	65.7	107.4	99.5

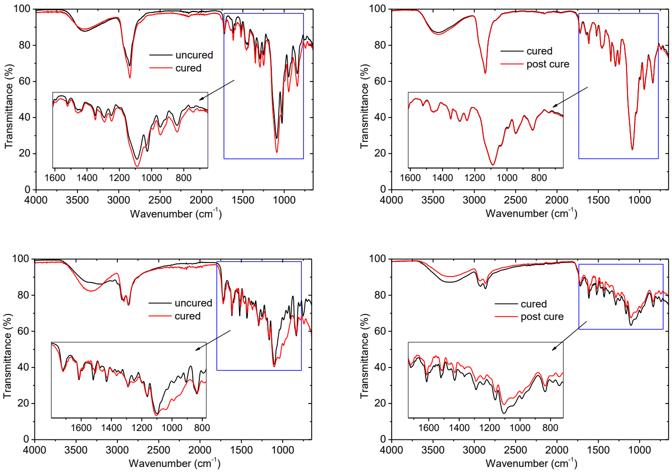

Figure 4: Monitoring of the curing process by IR (left) and the post-curing study (right) for the epoxy polymers APCD/PDE (top) and APCD/BDE (bottom).

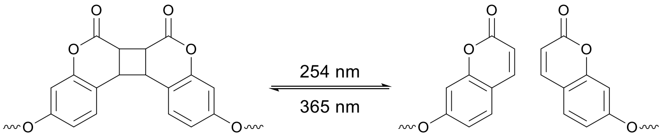

Figure 5: Decrosslinking and recrosslinking of the polymer by the scission and reformation of the cyclobutane ring in the coumarin dimer.

After irradiation a broad peak is present which is of much higher molecular weight than the broad peak observed in the before irradiation chromatogram indicating that the irradiation has broken down the crosslinked polymer into soluble linear chains and oligomers; the M_n of the broad peaks were found to range from around 1000 – 6000 g/mol after UV irradiation.

After the solubility test the polymer solutions were combined and dried to allow analysis by DSC and NMR. The DSC would yield a T_g of the decrosslinked state allowing for further understanding of the healing process of the polymer and the NMR would inform whether the rest of the polymer structure is maintained under the UV treatment. The DSC curves, shown in Figure 9, exhibited T_g values of 7.9 °C and 22.1 °C for APCD/PDE and APCD/BDE respectively; when the T_g is lower than room temperature then there is a greater potential for the polymer to be able to heal at room temperature. As the crosslinks are cleaved by the UV light, if the linear chains and oligomers formed are above their T_g they are able to flow and can heal the damage; a lower T_g of these collected portions would then suggest better healing performance, being either the potential to heal at room temperature or the expediency of the healing process. The NMR of the soluble chains from the APCD/PDE solubility test (Figure S1) show that during the decrosslinking process the backbone of the PEG epoxy polymer remains intact as the signal at 3.52 ppm, which corresponds to the CH_2 moiety of this backbone, remains unchanged. This is important as the polymer can only be photoreversible if only the coumarin dimers are cleaved as they can be reformed with the 365 nm light, however if there is UV light induced degradation of the other bonds in the polymer they cannot be reformed by the 365 nm irradiation rendering the polymer with a shorter life-span. The NMR of the dissolved polymer does not exhibit the characteristic signals from the cyclobutane of the coumarin dimer, which appear at 3.62 ppm and 4.61 ppm, confirming that the solubility of the polymer is due to decrosslinking of the polymer by coumarin dimer scission and not another fragmentation process. Another point to notice is the lack of a signal for the epoxy group in the dissolved chains NMR, which appears as multiplets at 2.61 and 2.74 ppm in the monomer NMR, instead exhibiting peaks corresponding to the CH_2s of the opened epoxy ring adjacent to the amine linkage. This further indicates that the liberated chains were once part of the crosslinked structure.

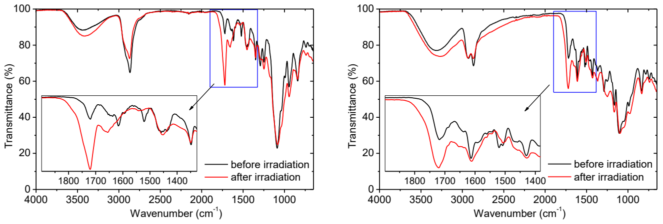

Figure 6: Decrosslinking of the epoxy polymers APCD/PDE (left) and APCD/BDE (right) monitored by IR after irradiation with 254 nm UV light.

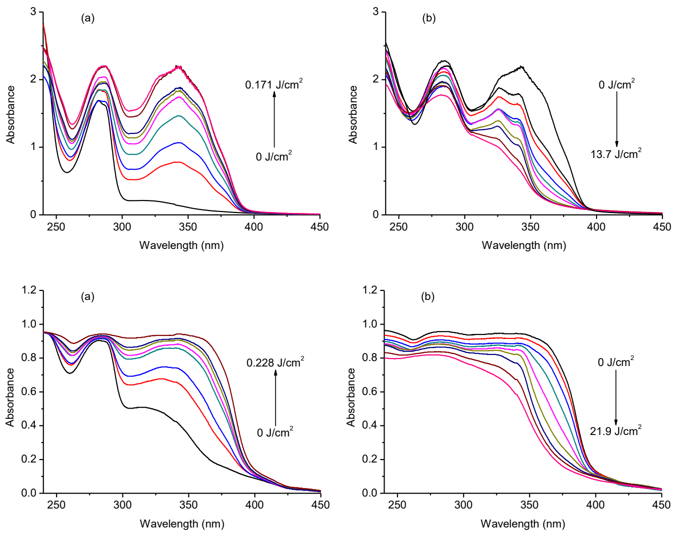

Figure 7: UV-vis monitoring of the scission and reformation of the coumarin dimer within the polymers APCD/PDE (top) and APCD/BDE (bottom) whilst irradiating (a) at 254 nm and (b) 365 nm respectively.

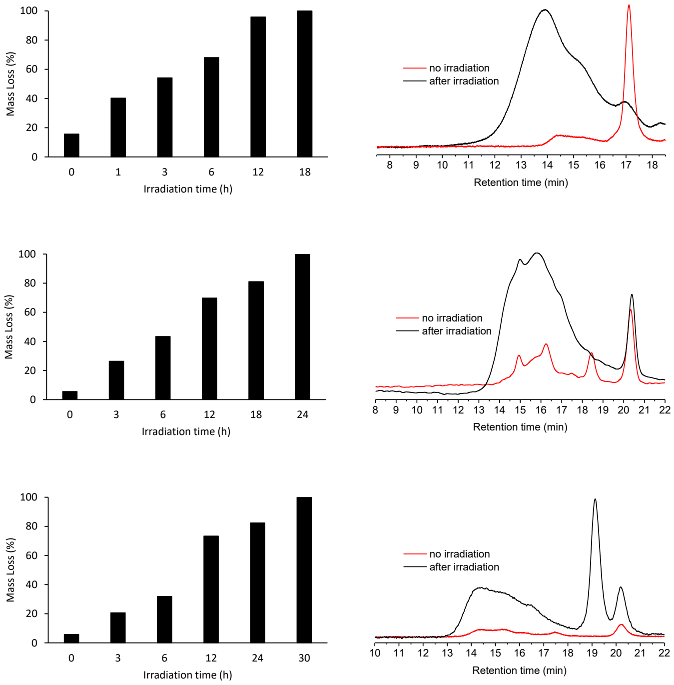

Figure 8: Mass loss from the crosslinked polymers during irradiation with 254 nm UV light and the GPC chromatograms of the soluble portion of the polymers before and after irradiation with UV light for APCD/PDE (top), APCD/BDE (middle) and APCD/BP50 (bottom). UV light doses of 12.3 J/cm^2, 16.4 J/cm^2 and 20.5 J/cm^2 respectively.

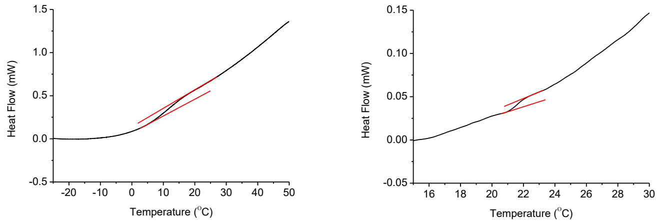

Figure 9: DSC curves of the soluble polymers and oligomers produced during irradiation of APCD/PDE (left) and APCD/BDE (right) for the solubility test.

Mechanical Property Analysis

In order to determine whether the produced polymers were suitable for the desired application as a coating, the hardness of the polymers were tested by use of a durometer. Of interest was not only the hardness of the crosslinked film but also the likely decrease in hardness after irradiation with 254 nm UV light and the possible regain of hardness with a subsequent 365 nm irradiation. The samples were initially tested to determine the crosslinked hardness after which they were irradiated with UV light and tested again to give a decrosslinked hardness value; finally the samples were tested after irradiation with 365 nm UV light to determine if the original hardness could be recovered after recrosslinking. The irradiation energies used were the same respective energies determined from the UV-vis photoreversibility study described above.

As it can be seen in Table 2, two of the three polymers created exhibited initial hardness values in the range of 20 – 30 HV, this suggests they may be suitable for the targeted coating application as the commonly used coating material PMMA exhibits a value of around 20 HV[51, 52]. They also showed the softening and hardening behaviour in response to the 254 nm and 365 nm irradiation respectively, as predicted above. APCD/PDE was seen to soften the most significantly of the three after decrosslinking with the hardness decreasing by 40%, however it was also seen to regain the greatest amount of hardness upon recrosslinking having recovered 88% of the lost hardness. This behaviour compared to the other two polymers can be attributed to the high flexibility of the PEG chain which results in the material being soft when decrosslinked and allows for the higher degree of recrosslinking as the chains can more readily flow and allow local registration of adjacent coumarin double bonds, as shown in the photoreversibility study above. APCD/BDE was only able to recover ca. 60% of the lost hardness after recrosslinking which agrees strongly with the photoreversibility study conducted earlier in this paper which showed that no more than 65% of the coumarin dimers reform during the recrosslinking stage. However APCD/BP50 had a ca. 80% regain of the lost hardness after recrosslinking which also agreed with the recrosslinking percentage of 72% demonstrated by UV-vis. This increase compared to the BDE polymer may be due to the relatively higher flexibility of the BP50 allowing for more coumarin dimers to align and dimerise during 365 nm irradiation. The hardness value of APCD/BP50 also fell in between that of the single-epoxy polymers satisfying the goal to have the ability to vary the mechanical strength of the polymers by implementing a mixture of monomers. However the value is closer to that of BDE which further suggests that the percentage of BDE monomer used strongly dictates the mechanical properties as was found to be the case with the T_g results. It is important to note that the polymers hardness always remained close to or above 20 HV, which means that even in the decrosslinked state necessary for healing to occur the polymer is still adequately strong for a coating material suggesting no compromise of functionality would occur during or after healing treatment when in service.

Light-healing of crosslinked epoxy polymer

The light-healing of the polymers were conducted on several glass slide mounted samples. The samples were scratched using a razor blade and the scratch dimensions and healing capability were monitored by optical microscopy (OM), the typical scratch depth produced from this method was evaluated by observing the cross-section of some scratched samples and was seen to be between 80 – 200 µm (Figure S2). The healing of the scratched samples was induced by exposure to 254 nm UV light in deliberate intervals to find the necessary minimum time required to heal the inflicted damage.

A sample of APCD/PDE polymer was inflicted with a 9 µm wide scratch and irradiated as described above. The damage was seen to completely heal after 16.4 J/cm^2 of 254 nm irradiation at room temperature; the healing process is shown in Figure 10. The same process was conducted on several APCD/BDE samples but healing was unfortunately not observed (Figure S3). This was attributed to the shorter nature of the BDE epoxy monomer compared to the PDE causing limited mobility and reduced propensity for flow of the polymer chains upon decrosslinking. However the increased mechanical strength of the APCD/BDE polymer was of great interest and hence the APCD/BP50 polymer was developed to leverage the mechanical properties of the BDE-based epoxy and the healing ability of the PDE-based epoxy. Samples of APCD/BP50 were prepared and tested in the same fashion as outlined above (Figure 11). The scratch was 18 µm in width and was also seen to heal at room temperature after irradiation of 19.9 J/cm^2. This result proved that the use of a mixture of monomers to form APCD/BP50 was effective in forming a polymer that had improved healing ability over the APCD/BDE but also greater mechanical strength than that of APCD/PDE. It also opens up the possibility to investigate to what extreme the BDE fraction of the monomer mixture can be used while still achieving room temperature healing upon irradiation.

One of the key benefits of the intrinsic healing approach is the ability to heal repeatedly in the same region, as the polymers in this report are designed following this approach it is important to demonstrate this ability. The sample of APCD/PDE seen to heal a scratch was recrosslinked with 21.9 J/cm^2 of 365 nm UV light, which was 1.5 times the energy found in the UV-vis photoreversibility study to give the maximum amount of recrosslinking. After this recrosslinking treatment another surface scratch was imposed on the sample perpendicular to the initial scratch and then irradiated at room temperature to induce healing, the healing of the second scratch was monitored and shown in Figure 10. It was observed that the secondary scratch of 16 µm was able to be healed at room temperature with a similar irradiation dose necessary to the dose required for healing of the initial scratch (16.4 J/cm^2 and 21.9 J/cm^2 respectively) demonstrating the repeatable healing ability of these polymers.

To observe the effect of temperature on the healing process another damaged sample of both APCD/PDE and APCD/BP50 polymers were created and irradiated with UV light, however the polymer was maintained at 60 °C during this irradiation (Figure S4 and S5). The damage was seen to be healed with 6.17

J/cm^2 and 4.11 J/cm^2 of irradiation respectively which was much lower than that required at room temperature and unexpectedly resulted in the BP50 polymer healing quicker than the PDE polymer in contrast to the room temperature trial. The heat is seen to aid the light-healing process by increasing the flowability of the decrosslinked polymer allowing the chains to move into the damage site faster than at room temperature. In addition, as the penetration of UV light into the polymer may limit the decrosslinking of the subsurface material, the increased flowability of the surface chains at a higher temperature may enable the exposure of further underlying material more quickly as the decrosslinked chains move from the surface into the site of the damage.

To ensure the healing observed occurred due to the photo-opening and closure of the coumarin moiety within the polymer, a heat control experiment was performed to determine if the healing was due to the proposed light-triggered mechanism or due to heating the system alone. A scratched sample of both the successfully healed polymers, prepared in the same way as outlined above, was exposed to a temperature of 60 °C for the same times as used in irradiation to heal the respective materials and the scratch dimensions monitored in the same fashion. The scratches on the two polymers were seen to remain relatively unchanged through the heating process, hence the healing of the polymer can be specifically attributed to the UV light treatment and the photoreactions of the coumarin moiety in the diamine crosslinker.

Table 2: Vickers hardness (HV) measurement results for the three states of the polymers.

	APCD/PDE	APCD/BDE	APCD/BP50
Crosslinked	14.2	30.7	26.2
Decrosslinked	8.5	21.4	17.8
Recrosslinked	13.5	26.6	24.1

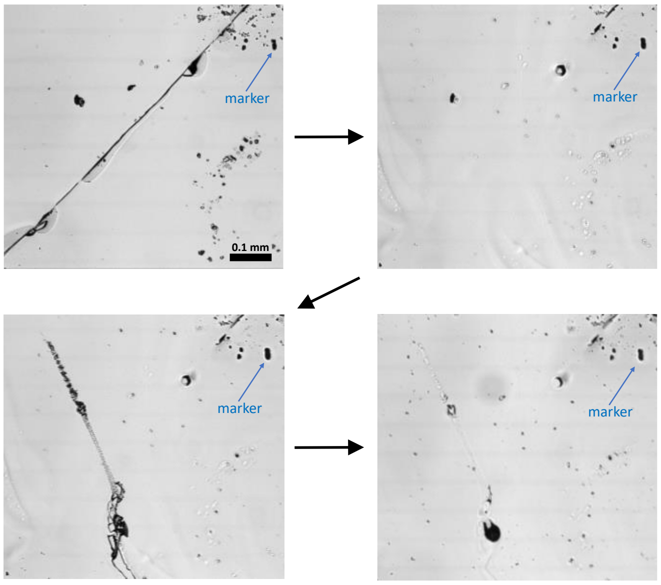

Figure 10: OM images of the light-healing of a scratch on the surface of polymer APCD/PDE and the subsequent healing of a second perpendicular scratch on the same sample, with scratch widths of 9 μm and 16 μm respectively.

Conclusions

The use of a new diamine crosslinker containing the photo-responsive coumarin moiety has been shown to impart light-healing properties to unmodified and commercially available epoxy monomers through the common thermal epoxy cure process. The use of a mixture of two commercially-available monomers, PDE and BDE, to form a light-healable polymer that outperformed the polymers made from the single epoxy monomers was also demonstrated.

The reversible photocycloaddition reaction of the coumarin moiety within the crosslinked epoxy polymer was confirmed by UV-vis and FT-IR demonstrating the desired cleavage and reformation of the crosslinker which gives rise to the light-healing ability observed.

Light damage to the epoxy polymers surface, in this case scratches, were shown to be healed by the irradiation of the polymer with 254 nm UV light at room temperature for two of the produced epoxies, APCD/PDE and APCD/BP50. The successful healing of the APCD/BP50 polymer suggests that the presence of the longer PDE chain in the formulation can vastly improve the light-healing performance of the polymer and should stimulate interest in the use of this monomer in different ratios with not only the currently studied BDE monomer but other rigid epoxy monomers.

The ability of these polymers to heal substantial surface damage through the exposure to UV light at room temperature coupled with the hardness values obtained being comparable to that of PMMA indicates that they satisfy our goal of creating light-healable epoxies that are suitable for the targeted coating application, in particular APCD/BP50 which surpasses the hardness of PMMA while still possessing the ability to heal at room temperature via irradiation alone.

Further work is being conducted to demonstrate the ability to impart light-healing abilities to more epoxy monomers using the newly developed crosslinker and also the investigation of further applications beyond light-healing for the current suite of polymers based on the observed capability of the polymers developed herein.

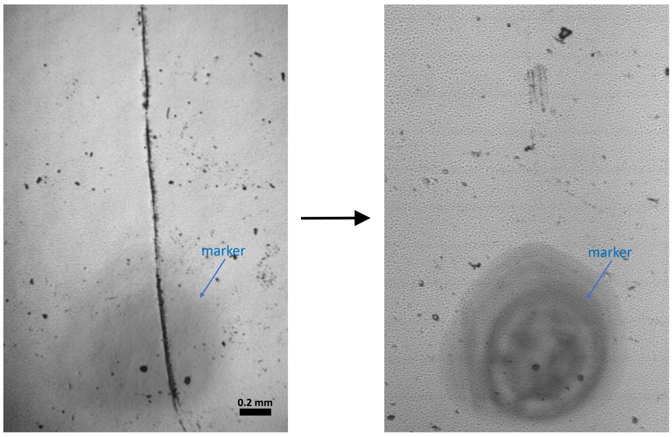

Figure 11: OM images of an 18 μm scratch on the surface of the polymers APCD/BP50 before (left) and after (right) irradiation with 254 nm light at room temperature.

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High-performing crosslinked epoxy coatings that possess room temperature self-healing ability by use of a newly synthesised dynamic diamine crosslinker.