THERMALLY INDUCED SELF-HEALING CAPABILITY OF EPOXY AND POLYURETHANE RESINS

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Abstract

Intrinsic self-healing epoxies and polyurethanes containing D-A adducts, in addition to conventional epoxy and isocyanate precursors, have been prepared. The recovery capability of the resins have been verified by means of morphological observation, micromechanical and optical analysis. The fracture rims, micro-cracks and scratches were evident before treatment, while the defects disappear after thermal healing, resulting in recovered material. Likewise, nanoindentation and brightness measurements showed recovery ability, promoted by suitable heat treatments.

1. Introduction

Self-healing polymers are a class of smart materials able to recover after sustaining damage. The original approach of extrinsic self-healing process relies on monomer-filled capsules [1], tubular [2] or vascular systems [3][4], dispersed throughout the polymer matrix as healing agent storage.

A more innovative approach is referred as intrinsic self-healing and uses homogeneous polymers containing Diels-Alder (D-A) precursors [5][6][7][8][9]. An healing method based on this reversible reaction uses a bismaleimide solution dispensed at the damage site of an epoxy-amine thermoset containing furan functional pendant groups [10]. Otherwise, the reaction of a suitable diene/dienophile pair can lead to monomers including D-A adducts, which could be directly incorporated in the polymer backbone. The D-A adducts can be added through a multi-step process, where first the dienophile of the D-A precursor is fixed in an irreversible epoxy-amine bond, then it is added to diene through D-A reaction in solution to obtain the reversible network [11].

In this study, in order to optimize the compatibility with the already used production processes, the implementation of the hybrid network, consisting of a stable crosslinkage and a thermolabile one, has been obtained in a single step, choosing curing condition compatible with the D-A raction temperature. In such a way, the Diels-Alder reactive groups are directly available at the fracture site and the crosslinked resin overcomes the single-use limitation of traditional self-healing systems and can undergo multiple temperature-dependent healing cycles.

2. Materials

Intrinsic self-healing epoxies and polyurethanes, containing bifunctional D-A adducts, have been prepared by Diels Alder reaction, a reversible chemical process involving the interaction between diene and dienophile functionalities. Both for epoxy and isocyanate D-A adducts, 2-furfuryl group was employed as diene and bismaleimide as dienophile.

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2.1. Epoxy 2Ph2Epo D-A adduct

Epichlorohydrin, furfuryl alcohol, tetrabutylammonium bromide, 1,1’methylenedi-4,1-phenylene-bismaleimmide, 4,4’-Diaminodiphenylmethane (DDM), O,O’-Bis(2-aminopropyl) polypropylene glycol-block-polyethylene glycol-block-polypropylene glycol (Jeff 500) were purchased from Sigma Aldrich and used as received. DGEBA (commercial name EC01), with Epoxy Equivalent Weight of 185-190 g/eq was kindly supplied by Elantas S.p.A.. Furfuryl glycidyl ether was prepared according to the procedure proposed by de Almeida [12]. In order to synthesize the 2Ph2Epo D-A adduct (**Figure 1**), 1,1’methylenedi-4,1-phenylene-bismaleimmide was dissolved in chloroform and then furfuryl glycidyl ether was added to the solution. The reaction mixture was kept under stirring at 70°C for 12 hours and after column chromatography of the crude, 2Ph2Epo D-A adduct was isolated in 96% yield.

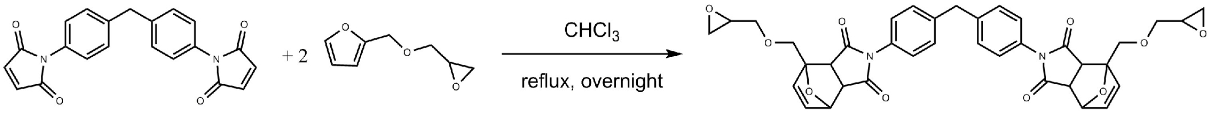

Figure 1. Synthetic scheme for 2Ph2Epo D-A adduct.

The epoxy blend, containing both 2Ph2Epo D-A adduct and DGEBA, was crosslinked with DDM and Jeff 500 as curing agents (**Figure 2**), in stoichiometric proportions and the curing reaction performed at 90°C for 24 hours in order to achieve complete conversion.

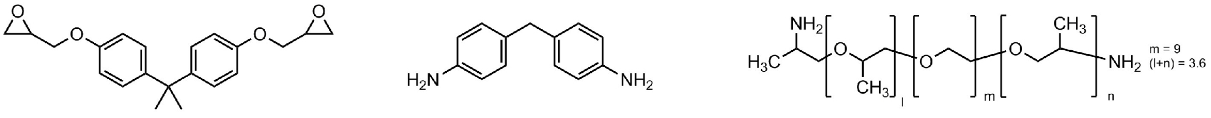

Figure 2. Additional resin components: DGEBA, DDM, Jeff 500.

The coexistence of thermally stable and thermo-reversible networks is required for the formation of a hybrid polymer architecture with robust self-healing capabilities and overall mechanical stability. The complete miscibility of all resin constituents allows the homogeneous distribution of different moieties in the resin network.

2.2. Isocyanate 2Ph2isoCyan D-A adduct

Furfuryl isocyanate, 1,1’methylenedi-4,1-phenylene-bismaleimmide, poly(ethylene glycol) 400 (PEG 400) were purchased from Sigma Aldrich and used as received; Niax catalyst PM-40 was purchased from Momentive. Isocyanate 2Ph2isoCyan D-A adduct had been synthesized starting from two commercial precursors, such as furfuryl isocyanate and 1,1′-(Methylenedi-4,1-phenylene)bismaleimide, in dry dichloromethane under inert atmosphere to avoid premature hydrolysis of isocyanate functionalities. The reaction was carried out at 50°C and after column chromatography of the reaction crude on silica gel, the product (**Figure 3**) was isolated in 50% yield.

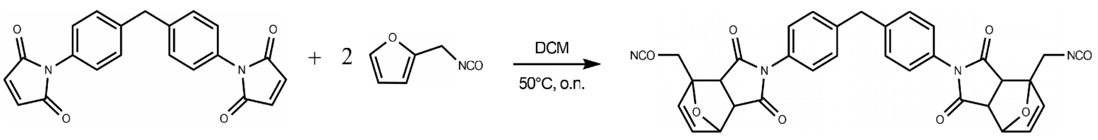

Figure 3. Synthetic scheme for 2Ph2isoCyan D-A adduct.

Step-growth polymerization catalysis of 2Ph2isoCyan D-A adduct and PEG 400, in the presence of catalytic amount of commercially available Niax catalyst, afforded a novel linear polyurethane, bearing both thermally reversible D-A moieties and flexible ethereal chains in polymer backbone. This preparation was performed under inert atmosphere and in refluxing dry dichloromethane for 2-3 hours; then, the curing agent (glycerol) was added to the reaction mixture containing the *in-situ* generated

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isocyanate-terminated prepolymer, affording in this way a cured polyurethane (**Figure 4**). PEG 400 was chosen to ensure high chain mobility and to afford softness to the structures where it have to be included, while a slight excess of 2Ph2isoCyan D-A adduct was used to produce an isocyanate-terminated polyurethane amenable to be cured with an active hydrogen compound such as glycerol. Step polymerization events occurred at relative low temperature first of all to preserve Diels Alder functionalities and to minimize side-reactions involving the generation of allophanate linkages that can increase branching, cross-linking, and so viscosity [13] [14] [15] that made difficult both the melt process and the removal of these side products.

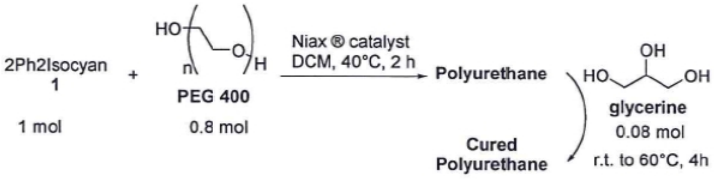

Figure 4. Synthetic scheme for polyurethane assembly.

3. Results and Discussions

The recovery capability of both epoxy and isocyanate based materials has been verified by means of morphological observation, performed by Olympus BX 51M, equipped with Linkam THM600 hot stage. Scratches and fractures have been produced on a cured sample, and morphological assessment of self healing recovery behavior has been observed during a suitable heat treatment.

The fracture rims (**Figure 5-a**), micro-cracks (**Figure 5-b**) and scratches (**Figure 6-a**) were evident before treatment, while the defects disappear after thermal healing: 20 minutes at 140°C for epoxy resin (**Figure 5-c**), and 15 minutes at 80°C for polyurethane (**Figure 6-b**), resulting in recovered material.

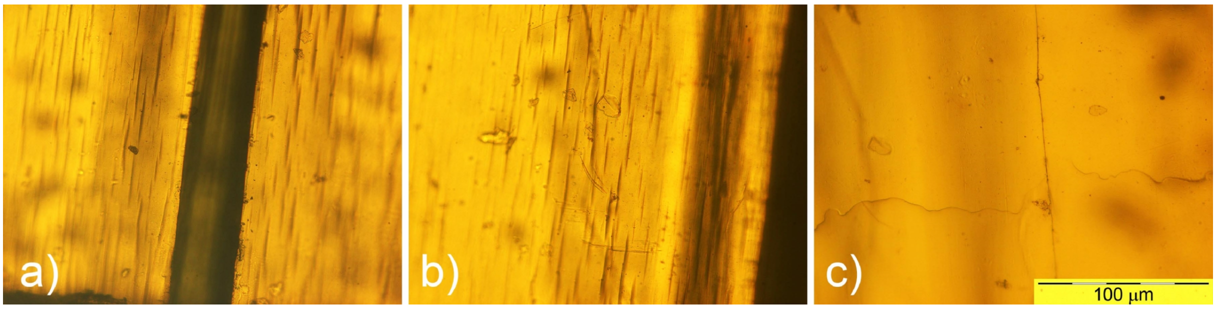

Figure 5. D-A epoxy resin. a) fracture rims; b) microcracks at fracture rims; c) healed fracture.

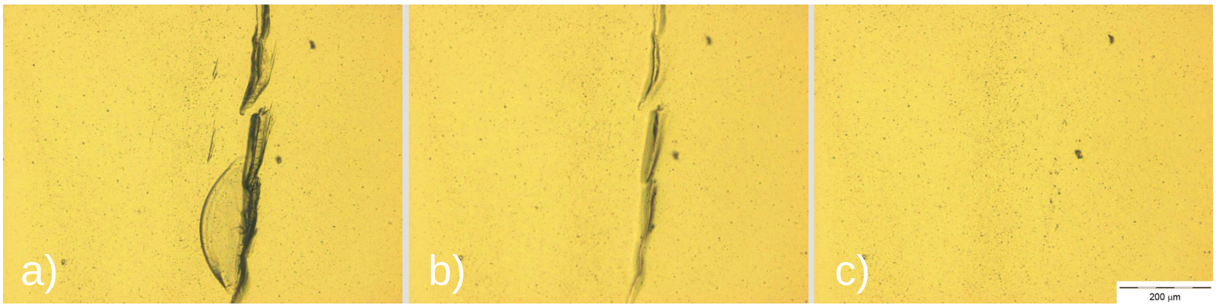

Figure 6. D-A PU resin: a) scratched surface, b) surface after 5 minutes thermal treatment, surface after 15 minutes thermal treatment.

Thermal stimulus is able to trigger the r-DA reaction increasing local molecular mobility and activating the healing process. After complete recovery of morphological damage, a further thermal treatment promotes direct D-A recombination reaction and leads to network mending, thus restoring resin mechanical properties.

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Nano-indentation and quasi-static stress-strain tests and have been carried out on 2Ph2Epo65 to evaluate the healing efficiency of the material. Elastic modulus (E) was calculated from the load vs displacement data. NanoTest Platform produced by Micro Materials Ltd has been used. This instrument monitors and records the dynamic load and displacement of a three-sided pyramidal diamond indenter Berkovich tip with a radius of about 100 nm. All data were corrected for thermal drift and instrument compliance and subsequently analysed with the Oliver and Pharr method [16]. Elastic modulus was calculated by nanoindentation tests in load controlled mode: ten different indentation loads ranging from 50 mN to 250 mN were performed. At the maximum load a depth of about 6000 nm has to be measured, less than 10% of sample thickness (about 500 μm), in order to avoid the substrate interference. Results are shown in **Table 1**.

Table 1. Reduced Modulus [GPa] and Elastic Modulus [GPa] of 2Ph2Epo65.

Specimen Type	Nanoindentetion test	
	Reduced Modulus [GPa]	Elastic Modulus [GPa]
As prepared	5.55	4.89
Heat-treatment @ 120°C, 30 min	2.96	2.60
Additional heat-treatment @ 90°C, 24 h	4.65	4.10

According to Zheng *et al.* [17] elastic modulus measured by depth sensing indentation could be invariantly higher than tensile test by a value of 5-20%. Results reveal that a satisfactory morphological and mechanical recovery has been achieved suggesting very promising application in the field of adhesives, coatings and structural materials.

The uncured 2Ph2isoCyan system was applied on steel substrate, previously coated with opaque acrylic paint. The polyurethane coating was dissolved in CH_2Cl_2/AcOEt and dispensed on the surface by a spray gun. PU on metal sheet was subsequently cured in oven at 65 °C for 24 hours, resulting in a crosslinked PU film with a thickness of 80-100 µm.

PU coating on metal sheet was scratched by an abrasive rubber, then a healing cycle (20 minutes at 90°C) was applied by a hot stage linked to the optical microscopy: the images (magnitude 5X), recorded during the *in situ* heat-treatment and reported in **Figure 7**, show a significant decrease of the opacity as a result of the healing-cycle.

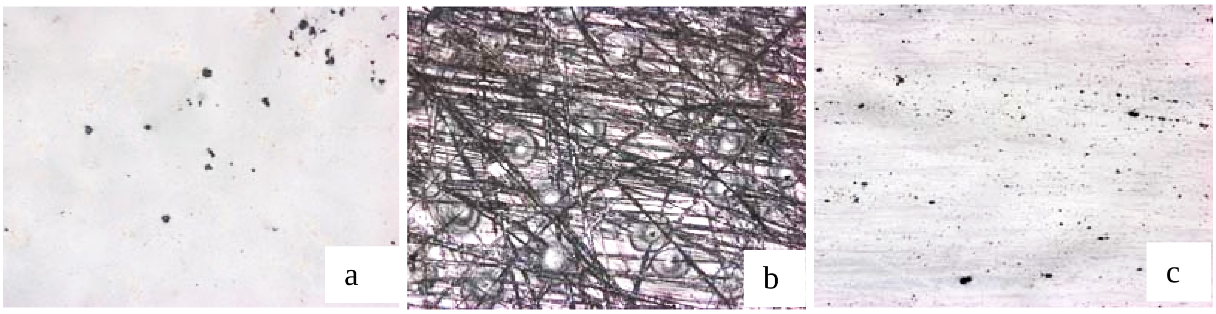

Figure 7. PU coating on metal sheet: virgin surface, b) scratched surface, b) scratched surface after healing treatment.

Optical properties as color and gloss, measured by the sphera gloss spectro-guide BYK-Gardner and shown in **Table 2**, confirme morphological observation.

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Table 2. Gloss [GU] and color (L*, a*, b*) values.

Specimen Type	Gloss	Color		
	[GU]	L*	a*	b*
Virgin	+84.8	88.8	1.3	5.0
Scratched	+4.0	88.9	1.2	5.2
Healed	+80.5	89.4	1.4	6.2

Both **Figure 7** and **Table 2** prove the self-healing capability of synthesised D-A polyuretane. The scratches, evident in **Figure 7b**, are almost completely recovered after the thermal treatment (20 minutes at 90°C) promoting self-healing. Damage and healing cycle have clearly visible effects on the gloss of surface: the value drops from 84.8 for virgin sample to 4.0 after damage, and rises to 80.5 after the thermal treatment.

3. Conclusions

This paper reports the preparation and characterization of two different crosslinked systems, containing Diels-Alder adducts.

In the case of epoxy system, the self-healing properties have been induced by the presence of 2Ph2Epo, crosslinked with a mixture of aromatic/aliphatic tetrafunctional amines. The cured sample is characterised by a crosslinked structure, exhibiting a T_g at 92°C.

The self-healing behavior was confirmed by optical analysis and nanoindentation on a crosslinked sample. A proper thermal treatment at temperature higher than rD-A threshold allowed good recover of damage, consisting in fracture and small cracks.

In the case of Diels-Alder polyurethane containing 2Ph2isoCyan, self-healing after scratch damage was also confirmed. The sample surface was restored after proper treatment, and gloss value similar to pristine sample was achieved.

The coexistence of thermally stable and thermo-reversible covalent bonds allowed the formation of a hybrid polymer architecture with robust self-healing capabilities and overall mechanical stability.

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