MENDABLE PROPERTIES OF DIELS ALDER THERMOSETS: THE INFLUENCE OF BACKBONE FLEXIBILITY AND CROSSLINKING DENSITY

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Abstract

A family of thermosetting epoxy resins has been prepared and characterized, containing a pair of Diels-Alder (D-A) adducts in the epoxy precursor backbone. The D-A adducts can be reversibly cleaved and reformed [1] under the appropriate thermal conditions, and this feature has been exploited to produce intrinsically self repairing materials since the pioneering work of Wudl and coworkers in the 2002 [2]. The present work has been focused to investigate the effects of different structural features, such as average number of crosslinking functionality and molecular flexibility of epoxy precursors, on the efficiency of healing process to recover the pristine material properties after mechanical damage. High crosslinking density and molecular stiffness improve mechanical performances such as elastic modulus and glass transition temperature, but on the other hand they hinder the capability of self healing. Therefore, this paper aims to elucidate the insights of self-healing phenomena and relate them to molecular structure of thermosetting precursors.

1. Introduction

IUPAC defines thermosets as infusible, insoluble network obtained by prepolymers cured by the action of heat or suitable radiation [3].

Curing reaction significantly improves material's mechanical properties, providing enhanced chemical stability and heat resistance. As a consequence, thermosets find extensive application in many enginering fields including reinforced composites, adhesives and sealants, encapsulants for electronic devices and coatings [4, 5]. Thermosetting polymers can be hardly replaced by thermoplastics in a wide range of applications, especially related to high performance engineering materials in the automotive and aero-space areas. Nevertheless, thermosets suffer from certain limitations related to their three-dimensional molecular architecture: they are almost impossible to reuse and recycle, they inherently exhibit brittle and fragile behavior, which increase the risk of fatigue failure during loading. In addition, they do not offer intrinsic repairability, as a consequence of reduced chain mobility with respect to thermoplastics, so widely used for reprocessing and repairing. [6].

Irreversible damages, such as microcracks and delaminations can significantly reduce the load carrying ability of thermosetting resins. Their intrinsic capability to recover from mechanical damages is inherently limited by reduced molecular mobility after thermosetting reaction. Therefore, the goal of developing self-healing thermosets is quite a challenging task.

In the last decades, self-healing polymers and composites have been extensively investigated. So far, two main categories of self-healing mechanisms have been developed: the extrinsic or autonomous healing and the intrinsic or external stimuli healing.

In the first case, the occurrence of mechanical damage ruptures microcontainers, in the shape of capsules or fibrils, embedded in the crosslinked matrix and containing un-reacted liquid monomer. The flowing monomer can flood the small fracture volume and autonomously react between the fracture surfaces and repair the damage. Several disadvantages are known related to the extrinsic healing

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mechanism, the main one being the difficulty to healing multiple damages occurring on the same location.

For the intrinsic self-healing materials, cracks can be repaired by the thermosetting matrix itself, due to physical and chemical interaction at the broken interfaces.

A number of thermally reversible reaction have been exploited to prepare self-healing materials, such as those involving alkoyamine moieties [7], esters [8], disulfide groups [9], and Diels-Alder adducts [2].

Since the pioneering work of Wudl and co-workers, most of the recent studies on intrinsic self-healing thermosets have been focused on polymerization precursors containing Diels-Alder adducts. The diene/dienophile couple constituted by furan/maleimide adduct is the most suitable systems, exhibiting a [4+2] cycloaddition D-A reaction predominant at temperature lower than 90°C, while the rD-A reaction is taking place at temperature higher than 120-130°C [2, 10-11].

In this work a family of epoxy precursors was prepared, starting with D-A precursors 2Ph2Epo and 2Ph4Epo, crosslinked with tetrafunctional amines (see table 1).

The two epoxy precursors differ in the molecular linkages between the same furan/maleimide central D-A adduct, providing different mobility during self-healing treatment.

This paper discussed the preparation of intrinsic self-healing features of crosslinked epoxy resins, comparing the damage mending efficiency with molecular stiffness and mobility of Diels-Alder adducts formed during fracture and/or healing thermal treatments.

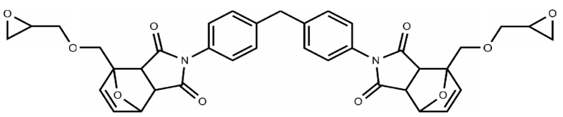
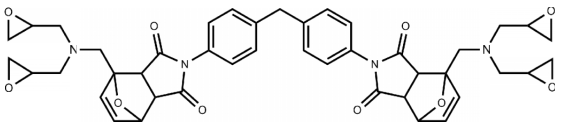
While the non-covalent interactions of supramolecular chemistry have long been utilized for their inherently reversible nature, they are far weaker than their covalent counterparts. It is therefore desirable when designing a structural healable polymeric material to take advantage of reversible and stronger covalent bonds. Intrinsic self-healing ability of materials based on thermally reversible Diels-Alder (DA) reaction between furan and maleimide moieties has been already established. The diene and dienophile components of this reaction can be altered to a number of functionality, and thus the reaction is an extremely versatile tool in polymer chemistry.

2. Materials and Methods

2.1. Mendable thermoset based on Diels-Alder adducts

Structural formulae of available epoxy precursors are presented in table 1. The 2Ph2Epo is the reference self healing epoxy, characterized by the presence of two oxirane rings and two Diels Alder adducts. The introduction of two additional functional groups has been used to obtain a molecular network with higher crosslinking density.

Table 1. Diels Alder epoxy precursors

Acronym	Molecular structure	Molecular weight (gmol^{-1})
2Ph2Epo		666.68
2Ph4Epo		776.84

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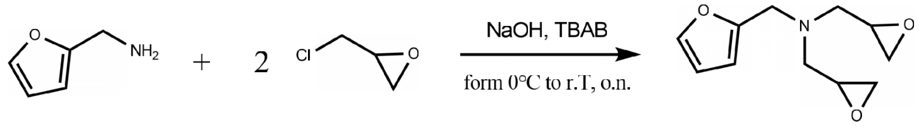
Epichlorohydrin, furfuryl amine, 1,1’methylenedi-4,1-phenylene-bismaleimmide, 4,4′-Diaminodiphenylmethane (DDM), O,O′-Bis(2-aminopropyl) polypropylene glycol-block-polyethylene glycol-block-polypropylene glycol (Jeff 500), chloroform, acetonitril NaOH were purchased from Sigma Aldrich and used as received. Diglycidyl ether of bisphenol A (DGEBA) with an Epoxy Equivalent Weight of 185-190 g/eq was kindly supplied by Elantas S.p.A. with commercial name of EC01.

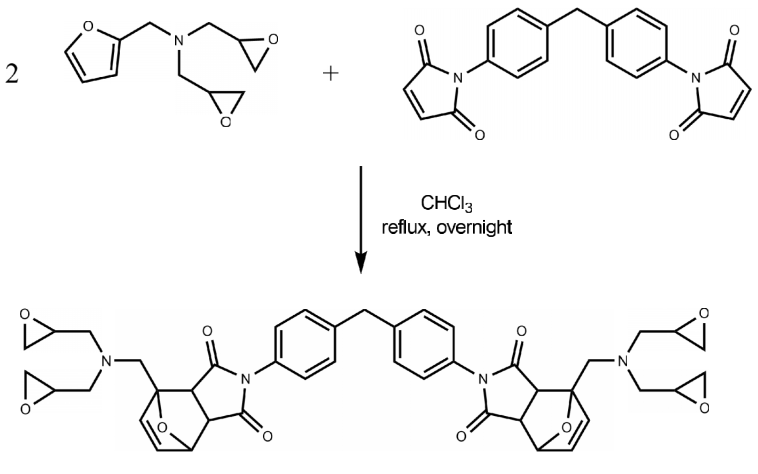
Synthesis of 2Ph2Epo:
The synthesis of 2Ph2Epo has already been described by the authors in a previous paper [12].
NMR: Characteristic peak of DA adduct (δ~5.5) appear, in which two carbon atoms change from sp^2 to sp^3 hybridization (double peak slightly split for the formation of the two stereoisomers, endo and exo, with the former overwhelming the latter).

Synthesis of 2Ph4Epo:
Epichlorohydrin (1 mol) was stirred and heated to 40°C in a 250 ml round-bottom flask equipped with a condenser. Furfuryl amine (0.5 mol) was added dropwise and the reaction mixture was stirred for 5 h at 40°C, then cooled down to room temperature. Aqueous sodium hydroxide (160 ml, 50%w/v NaOH) was added slowly. The reaction proceeded for additional 12h at 30°C. NaCl was extracted with water from the organic phase, and the solvent evaporated under vacuum. The liquid was further purified by flash-chromatography on a silica gel column using a 8/2 chloroform/acetonitrile mixture as the eluent. Glycidyl furfuryl amine was isolated in 80% yield (scheme 1).



Scheme 1. Synthetic scheme for furfuryl amine alkylation with epichlorohydrin and NaOH

1,1’methylenedi-4,1-phenylene-bismaleimmide (12.3 mmol) was dissolved in chloroform (10-12ml) in a 250 ml round-bottom flask equipped with a refrigerant. To the solution was added glycidyl furfuryl ammine (27 mmol) and the flask was heated to 70°C. The progress of the reaction (scheme 2) was monitored by thin layer chromatography (TLC) and the reaction mixture was kept under stirring at 70°C for 12h. The product was purified by flash-chromatography on a silica gel column using 8/2 chloroform/acetonitrile mixture as eluent.
NMR: Characteristic peak of DA adduct (δ~5.5) appear, in which two carbon atoms change from sp^2 to sp^3 hybridization (double peak slightly split for the formation of the two stereoisomers, endo and exo, with the former overwhelming the latter).



Scheme 2. Synthesis of the DA adduct 2Ph4Epo from 1,1’methylenedi-4,1-phenylene-bismaleimmide and furfuryl diglycidyl amine

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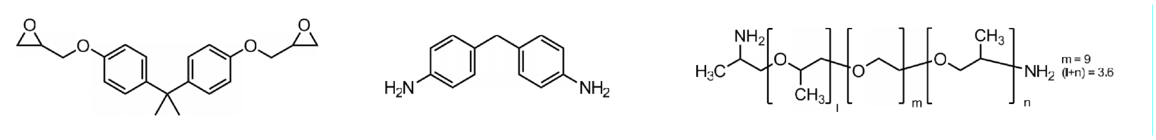
Crosslinked sample preparation

The Diels-Alder epoxy *2Ph2Epo, 2Ph4Epo,* and their mixture with DGEBA were crosslinked using stoichiometrically balanced DDM and Jeff 500 as curing agents (see Scheme 3) at 90°C for 24 hours. The sample composition is reported in the following table 2.

Table 2. Crosslinked sample composition.

Acronym	*DA epoxy* (mole)	*DGEBA* (mole)	*DDM* (mole)	*Jeff500* (mole)
2Ph2Epo100	1.00	-	0.30	0.20
2Ph2Epo65	0.65	0.35	0.30	0.20
2Ph4Epo100	1.00	-	0.60	0.40
DGEBA100	-	1.00	0.30	0.20



Scheme 3. Molecular structures of DGEBA, DDM and Jeff 500

2.2. Experimental characterization

DSC: differential scanning calorimetry was performed with Q1000 TA Instruments, in the presence of nitrogen purge at 10°C/min.

NMR: ^{1}HNMR analysis, recorded in d_6-DMSO (Bruker avance 400) on a sample previously purified by column chromatography, confirmed the product structure.

Optical microscopy: the ability to recover scratch damage was evaluated by means of morphological analysis. Optical microscopy was performed by Olympus BX 51M, equipped with Linkam THM600 hot stage

Nanoindentation: 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 [13].

3. Results and Discussions

A homologous (homogeneous) family of epoxy resins containing Diels-Alder adducts was synthesized and analysed to investigate the self-healing capability of this class of thermosetting materials. The precursors were prepared with the aim to elucidate the role of main structural parameters, such as molecular stiffness and crosslinking density, on the intrinsic mending properties of cured networks. Therefore, the epoxy precursors were synthesized (see table 1) differing for number of functional groups and flexibility of linkers between epoxy groups and central core containing D-A adducts.

The first epoxy precursor investigated was 2Ph2Epo, a bifunctional epoxy with a molecular weight of 666.68 gmol^{-1}. To induce the self-healing capability, two identical dienes (furfural derivatives) were capped on a bismaleimide dienophiles, resulting in a symmetrical epoxy compound containing two Diels-Alder adducts.

The designed molecular structure, while introducing the presence of thermoreversible D-A bonds, allows high compatibility with commercial epoxies and curing agents. Furthermore, self-healing resins based on 2Ph2Epo precursors can be used as adhesives, coatings and matrix for composites and can be cured according to conventional processing schemes.

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Chen et al. reported the occurrence of an endothermic event at temperature higher than 120°C, associated to the retro Diels Alder reaction [2]. The pristine molecular structure can be restored by annealing at 90°C.

This evidence was used to properly formulate the crosslinking mixture. In fact, the curing temperature cannot exceed the rD-A activation temperature, not to incur in the temporary scission of epoxy precursor. Analogously, the glass transition temperature of crosslinked resin cannot exceed curing temperature, in order to prevent vitrification during curing. Therefore, a mixture of aromatic and aliphatic amines was used to set glass transition temperature of crosslinked 2Ph2Epo100 resin around 90°C. Composition is described in table 2.

As already described, 2Ph2Epo100 system was cured at 90°C for 24 hours. DSC confirmed the complete conversion of crosslinking reaction by the absence of residual reactivity. Glass transition of cured resin was 94°C.

In Table 3 measured values of reduced modulus and calculated elastic modulus are reported.

Table 3. Nanoindentation tests.

Specimen Type	Nanoindentetion test	
	Reduced Modulus [GPa]	Elastic Modulus [GPa]
2Ph2Epo100	3.52	3.10
2Ph2Epo65	5.55	4.89
2Ph4Epo100	4.91	4.33

Nanoindentation was used in order to investigate the elastic modulus of cured material and self-healing proprieties. The reduced elastic modulus, E_r, was calculated based on equation (1), taking into account the effect of non-rigid indenter column:

$$E_r = \frac{\sqrt{\circledR}\ S}{2\ \ \sqrt{A}} = \left[\frac{\left(1-3_i^2\right)}{E_i}+\frac{\left(1-3_S^2\right)}{E_S}\right]^{-1} \tag{1}$$

where A is the contact area, β the geometric constant (1.034 for a Berkovich indenter) and S the unloading stiffness at maximum load. E and v are the elastic modulus and the Poisson ratio; and the subscripts “i” and “s” refer to the diamond indenter and the specimen, respectively. The E_i is 1140 GPa, $ν_i$ is 0.07 and the $ν_s$ is 0.35.

Self Healing properties.

Intrinsic self healing mechanism is triggered by the reversible character of Diels-Alder reaction. Diels-Alder bonds are weaker than other covalent bonds usually building up the crosslinked network. Therefore, upon sample breakage, they are preferentially cleaved making available diene and dienophile groups. Further thermal treatment at temperature higher than rD-A threshold completes cleavage of D-A bonds and maximizes molecular mobility, allowing the physical healing due to very effective diffusion of molecular fragments. After this initial healing stage, a further annealing at lower temperature is required to restore the pristine crosslinking density and mechanical properties by direct Diels-Alder reaction. This mechanism was responsible for scratch recovery of 2Ph2Epo100 samples, as shown in Figure 1.

Thermal treatment at 120°C for 5 minutes completely restored the damaged surface. Unfortunately, the high molecular mobility achieved in the *activated* stage produced sample deformation through material viscous flow. In fact, due to the high concentration of D-A adducts cleaved, the crosslinking density dropped and materials transformed into viscous thermoplastic.

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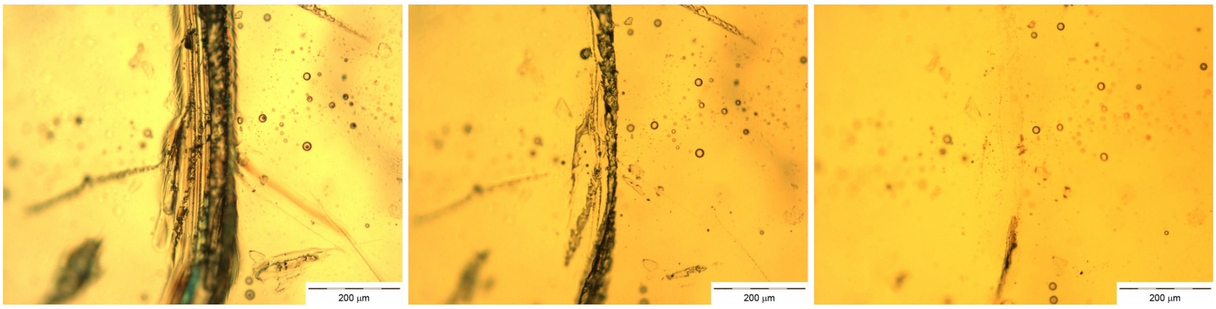

Figure 1. Scratch recovery for 2Ph2Epo100. 10 X magnification. From left to right: @ room temperature; @ 120°C; after 5 min @ 120°C.

The occurrence of this phenomenon is not desiderable if self-healing materials has to be used for structural application, such as matrix for reinforced composites or adhesives. Therefore, the concentration of cleavable bonds has to be reduced by the introduction of thermally stable epoxy precursor, such as DGEBA.

The 2Ph2Epo65 system, containing 65% of D-A epoxy and 35% of DGEBA (see table 2) was prepared to prevent viscous flow of material when rD-A reaction occurs.

DSC analysis confirmed a Tg of 90°C and the lack of residual reactivity for completely crosslinked 2Ph2Epo65 system. Self healing capability of 2Ph2Epo65 was reported in figure 2: the scratch damage completely disappeared after 30 minutes at 120°C, restoring the pristine surface.

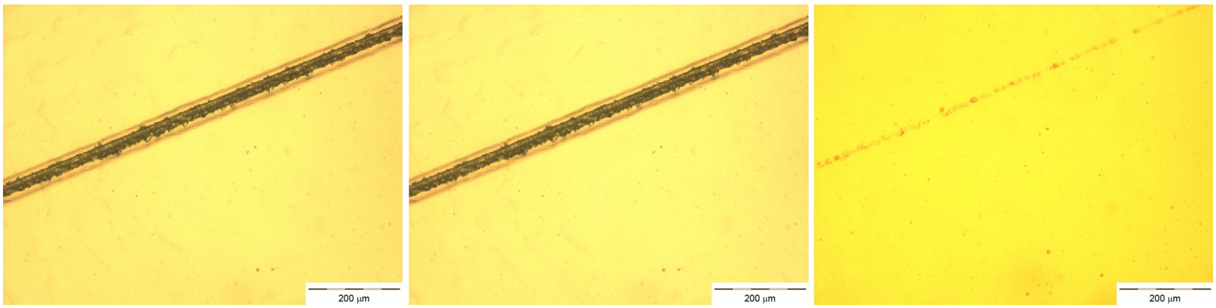

Figure 2. Scratch recovery for 2Ph2Epo65. 10 X magnification. From left to right: @ room temperature; @ 120°C; after 30 min @ 120°C.

A different approach to prevent viscous flow of materials during the high temperature stage is to use Diels-Alder epoxy adduct with higher functionality. The presence of four reacting epoxy group for each precursor molecules (2Ph4Epo) increases the crosslinking density with respect to bifunctional epoxy, when the same tetrafunctional curing agents are used.

System 2Ph4Epo100 was prepared according to table 2 and cured at 90°C 24 hours. DSC analysis confirmed a Tg of 95°C and the lack of residual reactivity for crosslinked 2Ph4Epo100 system.

The increased molecular stiffness introduced by multifunctional epoxy groups (see table 1) prevented the network to achieve sufficient molecular mobility for damage healing. As a consequence, morphological and mechanical damages were not recovered.

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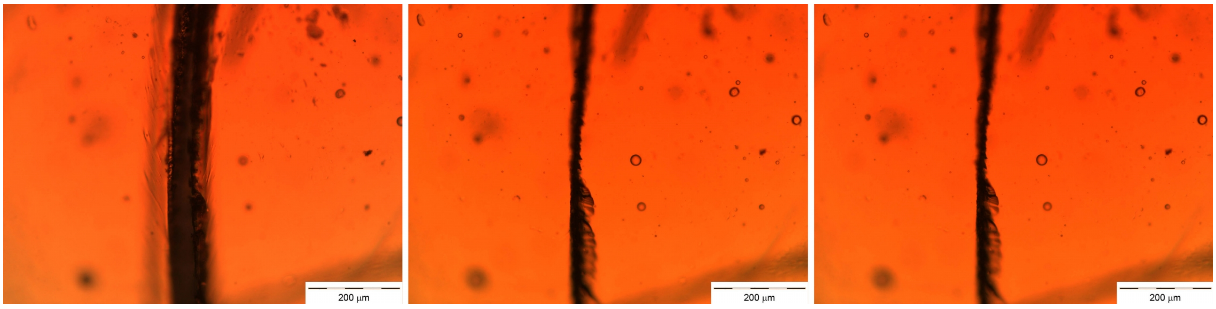

Figure 3. Scratch recovery for 2Ph4Epo100. 10 X magnification. From left to right: @ room temperature; @ 120°C; after 20 min @ 120°C.

For the sake of comparison, similar analysis was performed on DGEBA100, a crosslinked DGEBA resin cured with the mixture of DDM/Jeff500 amines. Tg of resin was also in the close range of 90°C. As expected, samples heated at 140°C, well above resin Tg, did not recover the damage induced on the scratched surface.

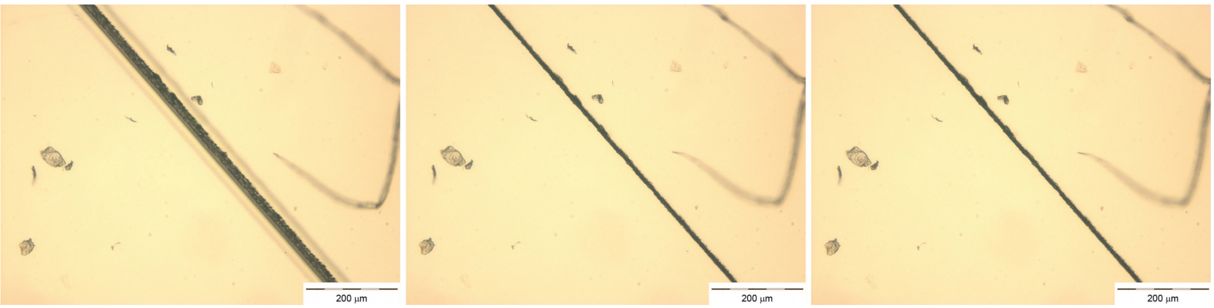

Figure 4. Scratch recovery for DGEBA100. 10 X magnification. From left to right: @ room temperature; @ 140°C; after 20 min @ 140°C.

A minor modification of scratch dimensions and features can be detected as a result of stress relaxation at temperature higher than resin Tg. Nevertheless, molecular mobility is hindered by crosslinking covalent bonds. As expected, conventional cured epoxy systems cannot recover mechanical damages.

4. Conclusions

2Ph2Epo epoxy precursor is the most promising candidate for the preparation of crosslinked self healing resins. The higher crosslinking density introduced by the use of tetrafunctional 2Ph4Epo hindered molecular mobility preventing further recovery of scratch damage. A similar behavior was evidenced for conventional epoxy resin (DGEBA100).

To take full advantage of 2Ph2Epo features, a careful balance of molecular mobility has to be achieved by proper formulation of curing mixture. If pure D-A epoxy is crosslinked with tetrafunctional amines mixture, the cleavage of thermoreversible D-A bonds during the first healing stage induces high molecular mobility. Viscous flow of materials during this stage produces unacceptable sample deformation. Therefore, a controlled amount of conventional epoxy DGEBA was introduced in the curing mixture. The reduced concentration of cleavable D-A bonds reduced viscous flow of material to a reasonable extent, still mantaining a sufficient molecular mobility to allow self-healing.

It is evident that succesfull use of this material in enginnering field such as reinforced composite or adhesive joints is based on a careful balance of conflicting properties:

a sufficient molecular mobility is required for allow intediffusion and self-healing;

dimensional stability has to be manteined to prevent complete viscous flow.

The combined use of D-A epoxy containing thermal cleavable bonds and conventional DGEBA was adopted as a practical strategy to prepare self-healing epoxy thermosets. The D-A epoxy used were

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completely miscible with conventional DGEBA and curing amines, assuring high compatibility with commercial precursors and curing schemes.

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