



biblio.ugent.be

The UGent Institutional Repository is the electronic archiving and dissemination platform for all UGent research publications. Ghent University has implemented a mandate stipulating that all academic publications of UGent researchers should be deposited and archived in this repository. Except for items where current copyright restrictions apply, these papers are available in Open Access.

This item is the archived peer-reviewed author-version of:

Title Development of optimized autonomous self-healing systems for epoxy materials based on maleimide chemistry

Authors Billiet, Stijn; Van Camp, Wim; Hillewaere, Xander K. D, Rahier Hubert, Du Prez Filip E.

In: Journal, Volume (Issue), pages, year. *Polymer*, 53(12), 2320-2326 (2012)

Optional: http://ac.els-cdn.com/S0032386112002984/1-s2.0-S0032386112002984-main.pdf?_tid=3c77b0ea-2cb4-11e2-bf0b-00000aab0f27&acdnat=1352716519_c86a6cf9dffc6179e90c4df0a639bba

To refer to or to cite this work, please use the citation to the published version:

Authors (year). Title. *journal Volume(Issue)* page-page. Doi

Billiet, Stijn; Van Camp, Wim; Hillewaere, Xander K. D, Rahier Hubert, Du Prez Filip E. (2012). Development of optimized autonomous self-healing systems for epoxy materials based on maleimide chemistry . *Polymer* 53(12), 2320-2326. Doi 10.1016/j.polymer.2012.03.061

Development of Optimized Autonomous Self-Healing Systems for Epoxy Materials Based on Maleimide Chemistry

By *Stijn Billiet^a*, *Wim Van Camp^a*, *Xander K.D. Hillewaere^a*, *Hubert Rahier^b* and *Filip E. Du Prez^{a*}*

[a] Stijn Billiet, Dr. Wim Van Camp, Xander K.D. Hillewaere, Prof. Filip. E. Du Prez
Department of Organic Chemistry, Polymer Chemistry Research Group, Ghent University,
Krijgslaan 281, S4-bis, B-9000 Ghent, Belgium

[b] Prof. Hubert Rahier
Vrije Universiteit Brussel, Faculty of Engineering, Departement of Materials and Chemistry
(MACH), Physical Chemistry and Polymer Science (FYSC)
Pleinlaan 2, B-1050 Brussel, België.

* corresponding author: Prof. Filip E. Du Prez
Tel.: +32 9 264 45 03/44 89 (secr.)
Fax: +32 9 264 49 72.
E-mail address: filip.duprez@ugent.be

Abstract: Maleimide chemistry involving amines and thiols is presented and evaluated for the design of autonomous self-healing epoxy materials. Model reactions show that amines react rapidly with maleimide compounds at room temperature *via* the Michael addition reaction. Moreover, thiols and maleimides react readily in the presence of a tertiary amines that are present in the epoxy material. The maleimide conjugation reaction with residual amines in the epoxy material ensures chemical bonding of the newly formed network with the original materials during crack healing, while in the crack plane, multifunctional thiols react with difunctional maleimides to fill the crack area. Healing efficiencies are evaluated using the tapered double cantilever beam (TDCB) test method with manual injection of the healing agents, revealing a maximum healing efficiency up to 121 % for EPON 828 epoxy material. Furthermore, the use of maleimide chemistry has also been evaluated for self-healing applications towards a cold-curing resin that is currently used for infusion of wind turbine blades (RIM resin). While the healing efficiency is strongly dependent on the type of epoxy material, the average maximum peak load for fracture after healing is roughly the same for all tested epoxy materials.

Keywords: Self-healing, Autonomous, Maleimide, Epoxy resin, Thiol

1. Introduction

Throughout their lifetime, polymeric materials and coatings are susceptible to mechanical damage such as wear, degradation, and microcracking, all of them reducing the mechanical properties of these materials. To overcome these limitations, a rapidly emerging field of research has resulted in materials that can repair crack damage in an autonomous fashion (without any stimulus or human intervention), referred to as self-healing materials.[1-12]

The microencapsulation approach, pioneered by White *et al.* for the healing of epoxy materials,[13] is by far the most studied self-healing (SH) concept in recent years. Microcapsules that are incorporated in the polymer composite material contain the self-healing agents (monomers or network precursors) that can (co)polymerize or cross-link upon rupture of the capsules as a result of mechanical damage.[6-7, 13-14] The healing efficiency in this particular microcapsule-based self-healing system is dependent on several factors including (1) monomer stability in the absence of a catalyst and the polymerization kinetics[15-16], (2) mechanical properties of the newly formed polymer in the crack plane,[17-18] and (3) chemical compatibility and stability of the catalyst within the matrix.[19-20]

Despite increased research activities, the current research related to self-healing epoxy materials has been mainly limited to a few types of chemistries that will be briefly reviewed in the next paragraph: (1) ring opening metathesis polymerization (ROMP) based systems with dicyclopentadiene and Grubbs' catalyst, (2) poly(dimethylsiloxane) (PDMS) based systems, (3) solvent-based healing systems, and (4) epoxy-based healing systems.

The healing chemistry that was originally developed by White *et al.* was based on encapsulated dicyclopentadiene (DCPD) that starts to polymerize by ring opening metathesis polymerization (ROMP) when the DCPD comes into contact with the ruthenium/Grubbs' catalyst that is dispersed in the epoxy matrix.[13] Although DCPD is a cheap and readily available healing agent, the Grubbs' catalyst is not, and is toxic. Moreover, the catalyst shows a limited stability and reactivity due to prolonged exposure to oxygen [21], moisture and the amine curing agent, while the monomer is prone to autopolymerization.[20] To overcome some of these issues, Cho *et al.* reported on poly(dimethylsiloxane) (PDMS) based self-healing materials.[22] The polycondensation reaction of hydroxyl-terminated siloxanes and alkoxy silanes is catalyzed by organotin compounds that are less expensive, less toxic, and proceed in the presence of moisture, which makes this approach more suitable for practical applications. However, as the polymerized healing agent is not structurally similar to the

polymer matrix, improvement of the interfacial compatibility between the healing agent and the substrate (crack surface) was desired. As a result, a diglycidyl ether bisphenol A based epoxy resin was encapsulated, along with an imidazole-metal complex as a latent hardener.[23] As the main drawback, the system requires external heat to promote the imidazole complex to dissociate into its reactive species, and can thus not be classified as an autonomous one.

In order to reach a more autonomic epoxy-based self-healing system, a polythiol curing agent (pentaerythritol tetrakis(3-mercaptopropionate)) was separately encapsulated, allowing curing at room temperature.[24] Microcapsules containing amine hardeners were also investigated, but the encapsulation of amines although possible [25]remains challenging.[26]

Microcapsules containing solvents have also been explored for use in self-healing polymer composites.[27] The release of solvents upon damage locally swells the matrix and promotes the mobility of functional groups to entangle and react across the crack plane. The proposed strategy was further improved by mixing a part of epoxy resin with the solvent, which combines the solvent healing effect and additional crosslinking reactions.[28]

‘Click’ chemistry, as introduced by Sharpless [29], was also proposed as healing mechanism. Binder *et al.* [30-32] made use of azide-alkyne chemistry to heal a poly(isobutylene) matrix. In this process, a liquid polymer was successfully used as a reactive compound.

In a recent contribution, Zhang *et al.* have explored the use of glycidyl methacrylate (GMA)–loaded microcapsules for making a self-healing epoxy material.[33] As GMA is a low viscosity liquid chemical, it combines two healing actions: solvent effect on one hand, and chemical reactions with unreacted functionalities in the matrix *via* the reactive epoxide groups and double bonds on the other hand. This promising concept was shown to be effective for cold-curing epoxy materials (EPON 828). At the same time, it broadened the spectrum of possible healing agents as the nucleophilic addition reaction of double bonds as a healing chemistry was reported for the first time. However, as a result of the reactive nature of the applied methacrylate group, the shelf-life of the healing agent is limited at relatively high temperature or the monomer may polymerize during the high curing temperatures when the synthesis of high-end composite materials, which require a curing temperature between 120 and 180 °C, is targeted. For the same reason, one may look for compounds that have an even higher boiling point than GMA (189 °C) to prevent high pressures in the microcapsules during these curing steps and thus prevent microcapsule breakage or leakage.

In view of increasing the industrial feasibility for the widespread use of microcapsule-based self-healing thermosets and composites, we have explored and evaluated the use of maleimide chemistry for the application in autonomous self-healing epoxy materials. Maleimides were already extensively used in self-healing as a member of the Diels-Alder reaction with furan compounds.[34-37] On the other hand, maleimides are known as well to react at room temperature with amines *via* the Michael addition reaction. Moreover, maleimides also react with thiols, while the presence of a tertiary amine catalyst tremendously speeds up the reaction.[38] As tertiary amines as well as unreacted amines are present in epoxy materials, maleimide chemistry has been considered as a promising chemical strategy for self-healing materials. Moreover, maleimides show a low tendency to homopolymerize and have very high boiling points, which is important in view of surviving the high curing temperatures or the use of self-healing materials in harsh conditions. As far as we know, a healing chemistry using maleimide conjugation reactions has not been reported yet.

In this contribution, we have evaluated the use of maleimide chemistry for two different types of epoxy materials. First, the proposed strategy was applied to EPON 828, which is considered as a reference material for cold-curing epoxy materials in self-healing applications and it still remains the most investigated matrix in the field. Then we have extended the same methodology to an epoxy material, RIM 135, that is currently widely used for high-end applications. For example, Owens Corning and PPG use it as a benchmark resin for glass fibre properties testing.[39-40] Due to its extremely low viscosity, it is currently widely used in the European market as a cold-curing resin for infusion of large wind turbine blades. Those blades are typically made of low temperature curing thermoset resins with glass fibre reinforcement. In the past, polyester and vinylester were the standard resins, but epoxy resins are increasingly used because of their superior mechanical properties and of the environmental problems like styrene emission styrene emission problems with other materials. This application is particularly interesting for self-healing composites, because wind turbine blades have to withstand biaxial variable amplitude fatigue loadings for 20 or more years. In an early stage, the fatigue damage typically leads to fibre/matrix debonding and small matrix cracks in the composite.[41-44]

Another important topic in the self-healing field is to expand the variety of polymer materials and composites that are capable of healing. Although most of the self-healing approaches have been focusing on the epoxy systems, a few recent reports show the interest in the

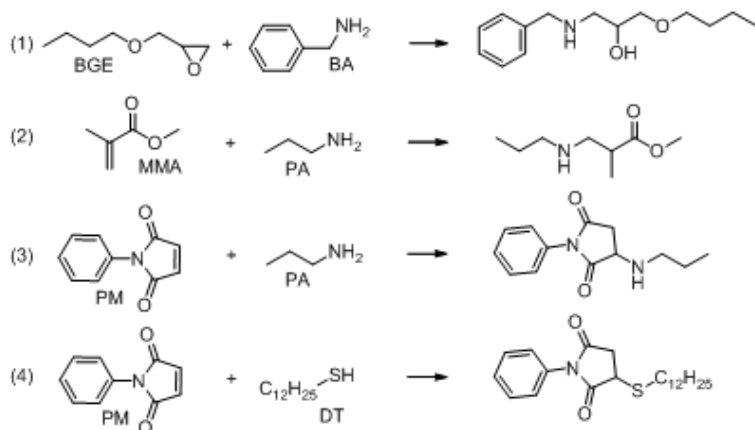
exploration of other systems and chemistries.[45-49] The improvement of self-healing strategies and the extension to other materials requires to broaden our approach and to move away from the currently applied types of chemistry. From this point of view, our current research aims to broaden the specific chemistries that are currently applied in the microencapsulation approach for epoxy materials. The encapsulation process itself is currently being optimized in our research group.

2. Results and Discussion

2.1. Model study for the kinetics of maleimides and amines/thiols at room temperature

In order to check the feasibility of the proposed maleimide chemistry for self-healing applications, we have first performed a detailed study of the reaction kinetics at room temperature of monofunctional maleimides with amines and thiols. As the lifetime of a material is dependent on the result of crack growth vs. crack repair, reaction kinetics are of utmost importance. At the same time, we have compared the maleimide – amine/thiol conjugation reaction kinetics with those of the glycidyl methacrylate – amine reactions that were proposed by Zhang *et al.*[33]

Glycidyl methacrylate reacts with amines via the reactive epoxide group as well as via the methacrylate functionality (C=C bond). In order to assess the contribution of each reactive group, we have selected two model compounds, each containing the respective reactive group. Butyl glycidyl ether (BGE) was chosen as a model compound for the epoxide group, while methyl methacrylate (MMA) was chosen as a model compound to assess the reactivity of the C=C bond (see Scheme 1, reaction (1) and (2)). Both compounds were reacted with a primary amine and the conversion was monitored by ^1H NMR. For the maleimides, the aromatic phenylmaleimide (PM) was monitored as a model compound (Scheme 1, reaction (3)). In the case of MMA and PM, the aliphatic, monofunctional propylamine (PA) was chosen as the amine to mimic the reactivity of the the primary amine groups of diethylene amine (DETA), while in the case of BGE, benzyl amine (BA) was chosen to prevent overlap of the ^1H NMR signals. All reactions were performed in *m*-cresol to ensure similar reaction conditions as with the aromatic maleimides used later on.



Scheme 1: Model reactions in *m*-cresol for a comparison of the reactivity of amines with (1) epoxide, (2) methacrylate and (3) maleimide functionality, respectively. (4) Model reaction for a comparison of the reactivity of thiols with maleimide functionality.

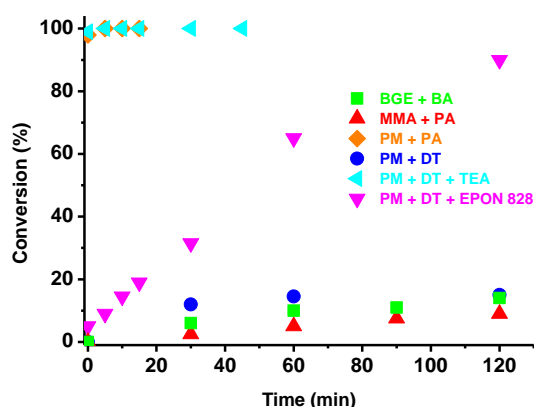


Figure 1: Reaction kinetics at room temperature of the reaction of BGE and BA (■), MMA and PA (▲), PM and PA (◆), PM and DT (●), PM and DT catalyzed by TEA (◀), and PM and DT catalyzed by grinded EPON 828 epoxy material (▼).

As can be noticed from Figure 1, maleimides are more reactive towards amines than the epoxide or methacrylate groups. The reaction of PM with PA (Scheme 1, reaction (3)) reaches full conversion after 10 min, while the reaction of BGE and BA (Scheme 1, reaction (1)) reaches only 14 % conversion after 120 min, and only 10 % of the C=C bonds react with PA after 120 min (Scheme 1, reaction (2)). The high reactivity of maleimides may show faster healing rates and hence increase the rate of crack healing vs. crack propagation.

In a similar way, we have also investigated the reactivity of thiols with maleimides, using PM and dodecanethiol (DT) to mimic the reactivity of the used multifunctional thiols (Scheme 1, reaction (4)).[50] As can be seen in Figure 1, the reaction proceeds rather slowly, reaching 15 % of maleimide conversion in 120 minutes. However, the use of a tertiary amine

catalyst (NEt_3) dramatically increases the reaction rate[51] and 100% conversion is reached in less than 10 minutes. An identical reaction with grinded epoxy material added as the catalyst (average size of the particles $\pm 100 \mu\text{m}$) reached 90 % of conversion of the maleimide functionalities in 120 minutes, clearly demonstrating the ability of the tertiary amines in the epoxy material to catalyze the thiol-maleimide reaction.

2.2 Healing strategy

Since the above described model reactions have demonstrated that the maleimide-amine reaction proceeds faster than the epoxide-amine or methacrylate-amine reaction, the former reaction shows a promising chemical strategy for application in self-healing materials. Consequently, we propose a healing strategy based on maleimide and thiol compounds on one hand, and amine species that are present in the epoxy material on the other hand.

Actually, one can make a distinction between the bulk area of the crack and the crack interface (Figure 2) in a damaged epoxy material. At the crack interface, residual (unreacted) amines, that arise from the incomplete curing reaction of the matrix, can react with maleimide compounds. The covalent bond will ensure a chemical bonding of the newly formed network and the original epoxy material. Moreover, it has been shown that the use of an excess of amine hardener during the synthesis of the epoxy material can result in an important contribution to the healing reaction.[33] On the other hand, in the bulk area of the crack, a healing reaction can occur by reaction of thiols with the maleimide compounds. These reactions are catalyzed by the tertiary amines that are present at the crack interface, as has been shown in the model reaction of PM and DT catalyzed by grinded EPON 828 epoxy material, which obviously contains tertiary amines at the surface (see Figure 2). Moreover, polythiols have been encapsulated for the use in self-healing materials before,[24, 52-53] mostly as an alternative to polyamines that are more difficult to encapsulate.[26, 54]

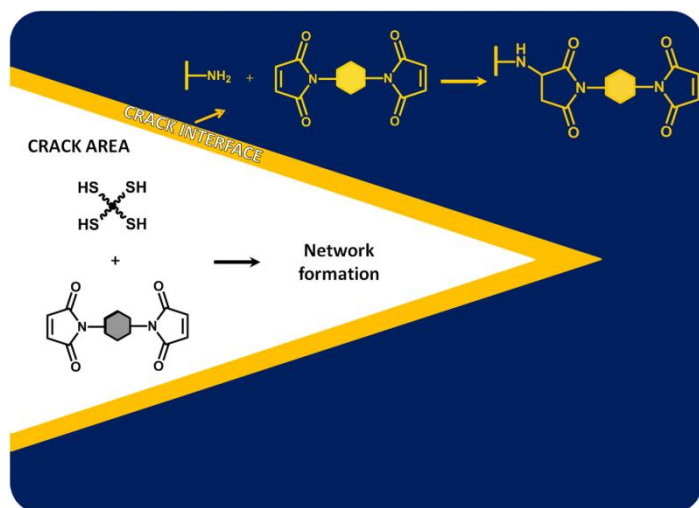
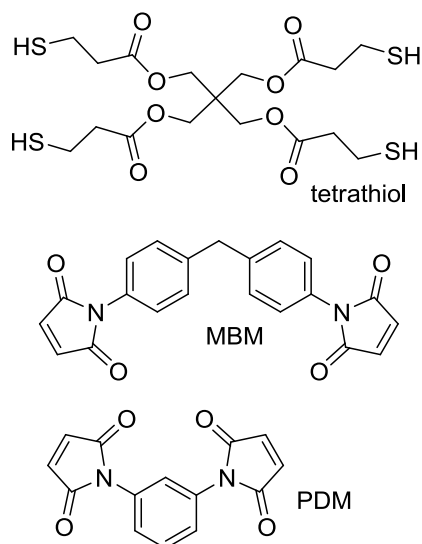


Figure 2: Schematic depiction of a crack in the epoxy material. At the crack interface, a reaction can occur between unreacted amine functionalities at the crack interface and maleimide compounds as the healing agents, ensuring covalent bonding of the newly formed material and the original material. In the crack area, multifunctional thiols and maleimides form a network.

As we aim to form a crosslinked material in the crack plane, we propose the use of multifunctional compounds. A polythiol with four functionalities (pentaerythritol(3-mercaptopropionate)) was chosen for its high functionality and flexibility, high boiling point and earlier demonstration of its successful encapsulation for self-healing epoxy materials. For the multifunctional maleimides, we have chosen two difunctional maleimides: 1,1(methylenedi-4,1-phenyl)bismaleimide (MBM) that has a central bisphenyl moiety, and *N,N'*-(1,3 phenylenedi)maleimide (PDM) that contains a phenyl group (see Scheme 2). The structural similarities should ensure a good compatibility of the newly formed material with the original material. As both maleimide compounds are solid compounds, they are solubilized in *m*-cresol that was chosen because of the lack of solubility of the bismaleimide in other solvents. Moreover, *m*-cresol has some advantages such as its high boiling point (203 °C), its hydrophobic nature that will facilitate the microcapsule production via an ‘oil-in-water’ microencapsulation process and the ability to act as an inhibitor for the homopolymerization of bismaleimides, a possible side reaction that would limit the shelf-life of the healing agent. All of the mentioned healing agents are stable for a long period when stored in a dry and cool place. The maximal solubility of MBM and PDM was determined as 30 and 15 wt%, respectively.



Scheme 2: Healing agents pentaerythritol(3-mercaptopropionate) (tetrathiol), 1,1(methylenedi-4,1-phenyl)bismaleimide (MBM), and *N,N'*-(1,3 phenylenedi)maleimide (PDM).

2.2. Quantification of the healing efficiency: Tapered Double Cantilever Beam (TDCB) tests

In a next step, the effectiveness of the proposed chemistry for self healing applications was determined by the quantitative Tapered Double Cantilever Beam (TDCB) test method. TDCB samples with a long moulded groove of 47 mm were used to evaluate the self-healing ability, according to the protocol described by White et al.[13] With this test, TDCB samples were pulled until crack formation occurred, which results in a maximum load that the virgin material can resist. Note that at this stage of the research, the various healing agents are manually injected in the crack plane. 30 μ L of a combination of healing agents (equimolar amounts of MBM and tetrathiol, MBM and DETA, PDM and tetrathiol, PDM and DETA, respectively, see experimental part for details) was then injected in the crack plane, the sample unloaded, and allowed to heal at 25 °C for 3 or 5 days. The same test was then repeated to obtain the maximum load that is necessary to break the healed sample. The ratio of these two values is defined as the healing efficiency.[55] The TDCB tests are applied to two types of epoxy materials: EPON 828 and RIM 135 resin (vide supra). For the latter material, we have also evaluated the effect of the use of excess hardener during the epoxy material preparation.

2.2.1. EPON 828 epoxy material

In the case of the EPON 828 resin, an equimolar distribution of resin and diethylene amine (DETA) hardener is used (100/12 w/w ratio of resin/hardener). Using the usual temperature program for curing the matrix material (24 h at room temperature, followed by 24 h at 40 °C),

a DSC study (see figure 3) revealed a conversion of the epoxide groups of 85 %.[56] As equimolar amounts of the amine hardener were used, 15 % of the initial amine functionalities (most likely secondary and some primary amines) have not reacted and are still available to take part in the healing reaction. During the curing process, the vitrification of the mixture will hamper higher conversions because of diffusional constraints. After the curing process used in this study, the T_g of the epoxy material is 56 °C, while after a heating cycle up to 200 °C to ensure complete curing, the T_g rises to about 130 °C. This can best be seen in the reversing heat capacity curve where only the heat capacity is retrieved while the reaction exotherm is retrieved in the non-reversing curve (not shown).

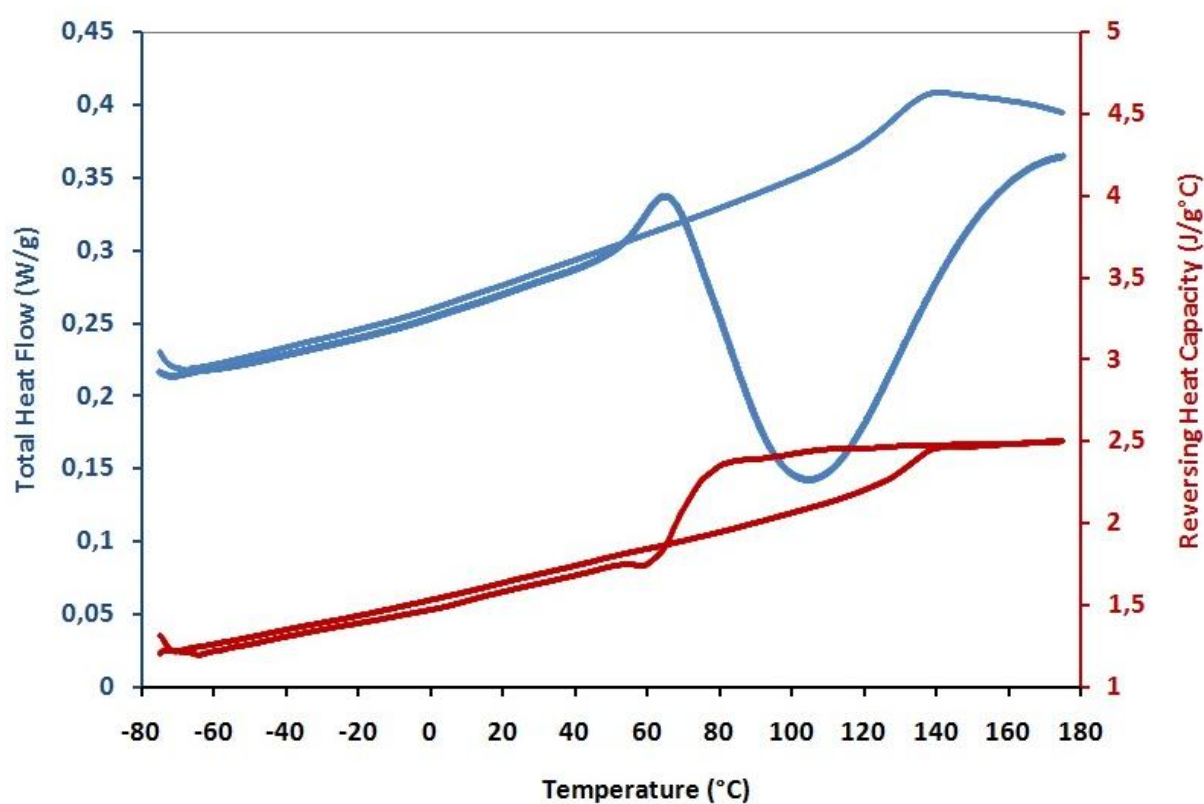


Figure 3: MDSC thermograms (amplitude = 0.5°C and period 60 sec) of the cured EPON 828 resin. 1st heating showing the T_g (55.85°C) after the standard cure procedure followed by the residual reaction. 2nd heating(128.55°C) showing the final T_g after full cure. Curves are shifted vertically for clarity.

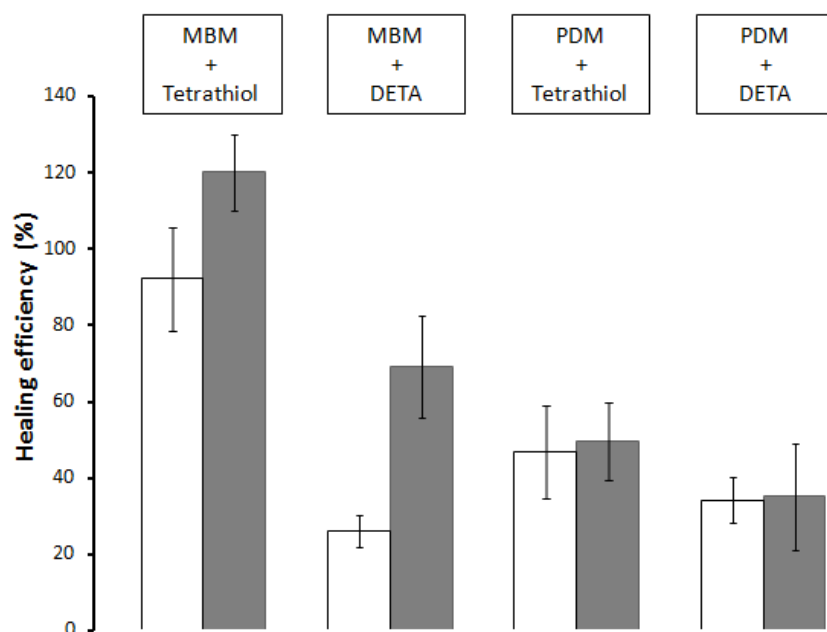


Figure 4: Healing efficiency for the healing of EPON 828 epoxy material with various mixtures of healing agents at 25 °C for 3 days (white bars) and 5 days (grey bars), respectively. All the specimens were cured at an equimolar ratio of DETA hardener to epoxy resin (12/100, w/w).

Figure 4 shows the healing efficiency for the healing of the EPON 828 epoxy material with 4 mixtures of healing agent for 3 and 5 days at 25 °C. The healing efficiency shows the average value of a minimum of 10 to 15 specimens, with the corresponding standard deviation. This standard deviation can be assigned to small variations in the precrack and deviations of the crack plane. These values are in accordance to previous reports in which TDCB has been used to test self-healing materials.[27, 55] The results clearly show a difference between the various mixtures of healing agents, while also the time allowed for healing shows to be an important parameter. The MBM compound results in a higher healing efficiency compared to PDM (maximum of 121 % compared to 51 % after 5 days, respectively). The combination of maleimides with tetrathiol results in a higher healing efficiency than the combination with DETA (121 % vs. 70 %). These results show effective healing, with the combination of tetrathiol with MBM as the most effective healing agent combination.

2.2.2. RIM 135 epoxy material

The RIM 135 epoxy resin is a combination of bisphenol A diglycidylether (DGEBA) and 1,6-hexanediol diglycidylether. The hardener RIMH 137 is mainly composed of alkyl ether amine and isophorone diamine.

When using an equimolar ratio of resin to hardener (100/30 w/w resin/hardener) in the case of RIM 135 epoxy material, and using the usual temperature program for curing (24 h at 40°C, followed by 16 h at 80 °C), a DSC study revealed a complete conversion of the epoxides.

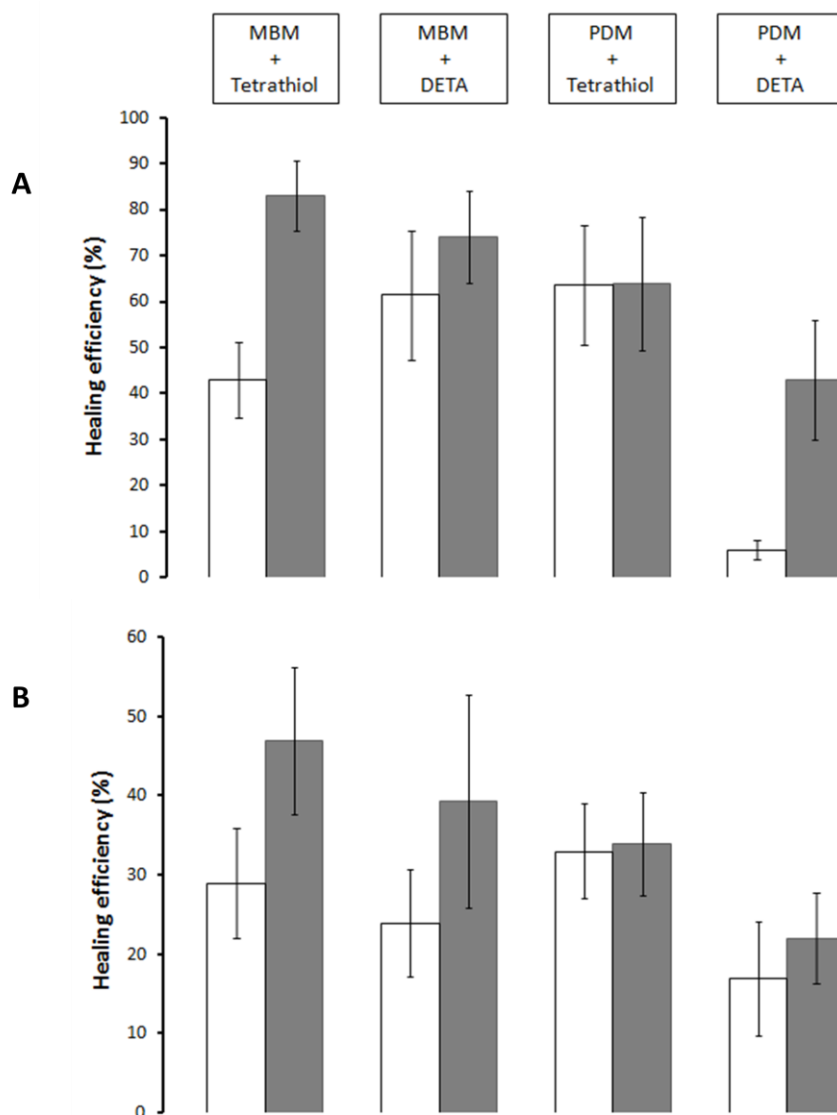


Figure 5: Healing efficiency for the healing of RIM 135 epoxy material with various mixtures of healing agents at 25 °C for 3 days (white bars) and 5 days (grey bars), respectively. (A) specimens were cured at an equimolar ratio of epoxy resin to RIMH 137 hardener (100/30, w/w). (B) specimens were cured at an excess ratio of epoxy resin tot RIMH 137 hardener (100/50, w/w).

Indeed, the T_g of the epoxy material after the applied curing process and after a heating cycle up to 200 °C was found to be identical, i.e. 76 °C. As equimolar amounts of the amine hardener were used, the amine functionalities have reacted during the curing program. Thus, the RIM epoxy material that results from curing of an equimolar ratio of resin to hardener (100/30 w/w) does not contain a significant amount of unreacted amines, and hence no residual amine functionalities at the crack surfaces that can help in chemically linking the epoxy surface to the self healing agent.

Figure 5A shows that also in this case, the MBM curing agent performs better. The difference resulting from the use of tetrathiol or DETA is less clear in this case. Healing efficiencies after 5 days are slightly higher than after 3 days. When compared to the healing efficiencies of

EPON 828 material, the healing efficiency for the RIM material is generally lower with a maximum healing efficiency of about 85 %.

We also have investigated the effect of using an excess ratio of hardener for the preparation of RIM 135 epoxy material (100/50 w/w resin/hardener), as this material will bear unreacted amine functionalities at the crack surface, which will be able to react with the maleimide healing agents. In this case, the T_g of the material after the curing process is 48 °C; this value remains identical after a heating cycle up to 200 °C, revealing that all epoxy functionalities have reacted. Figure 5B shows the healing efficiency for various mixtures of healing agents at 25 °C for 3 days (white bars) and 5 days (grey bars), respectively. Also in this case, MBM reveals to be a more efficient healing agent than PDM. However, the healing efficiencies are lower than in the case of EPON 828 and RIM with an equimolar ratio of hardener to resin.

2.2.3. Average peak load vs. healing efficiency

Although the healing efficiencies for the epoxy material EPON 828 are higher than the values for the corresponding RIM (100:30 and 100:50) epoxy material, one should note that the healing efficiency is a relative value, and is influenced by the strength of the original material. For this reason, it is of interest to evaluate the maximal force that is needed to break the healed material. The white bars in Figure 6 represent the maximal peak load to break the various virgin epoxy materials. The average maximal peak load to break the virgin sample is 58 N in the case of EPON 828, 80 N in the case of RIM (100:30), and 120 N in the case of RIM (100:50). It is clear that EPON 828 is an intrinsically weaker material than RIM (100:30) and RIM (100:50). However, note that the high apparent strength of the RIM (100:50) arises from plastic deformation of the RIM material due to its relatively low T_g (48 °C). The grey bars in Figure 6 represent the maximal peak load to break the healed material. The various epoxy materials were healed for 5 days at 25 °C with a combination of tetrathiol and MBM, as this showed to be the most effective healing agent combination. It should be noted that the average maximum peak load to break the healed specimens is not very different (around 62 N), irrespective of the virgin material. Taking into account this average value, the healing efficiency for EPON 828 is 121%, 90 % for RIM (100:30) and 48 % for RIM (100:50). Thus, although the maximum peak load is nearly the same, the healing efficiency decreases dramatically as a result of the high maximum load to break the original material.

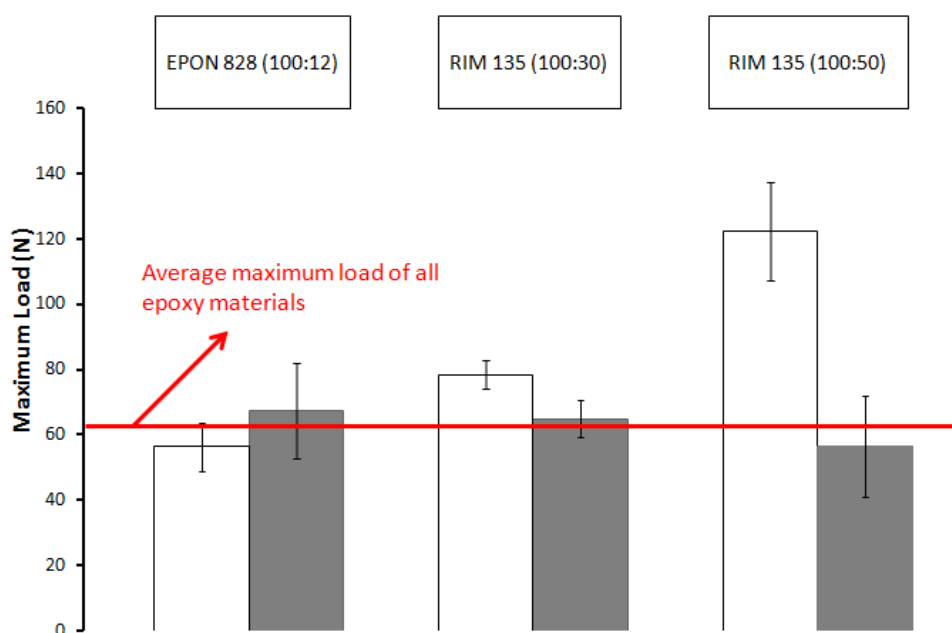


Figure 6: Overview of the maximal peak load to break various epoxy samples. The white bars represent the maximal peak load to break the original material. The grey bars represent the maximum peak load to break the healed material. The horizontal line shows the average maximum peak load for all healed specimens (irrespective of the original material). The specimens were healed with a healing agent combination of MBM and tetrathiol for 5 days at 25 °C.

3. Conclusions

An alternative chemistry based on the Michael addition between bismaleimides and amines or thiols was developed for the self-healing of epoxy materials. The proposed healing reaction was characterized *via* an extensive kinetic study of monofunctional model compounds. This study led to the selection of multifunctional healing agents that were tested for their healing efficiency of various epoxy materials *via* the ‘tapered double cantilever beam’ (TDCB) test method, with manual injection of the healing agents (30 μ L). For EPON 828, an average healing efficiency of 121 % was reached with the healing agent combination MBM + tetrathiol. Moreover, we have extended the self-healing testing towards resins that are currently used as a cold-curing resin for infusion of large wind turbine blades. In this case, we have also investigated the effect of unreacted amine functionalities in the epoxy material by using an excess of hardener to resin. Also in the case of the RIM resin, the combination of MBM + tetrathiol was found to be the most promising healing agent. It reached healing efficiencies going from 80 % (equimolar) to 50 % (excess amine hardener) after a healing period of 5 days at room temperature. However, the healing efficiency was found to be strongly dependent on the type of epoxy material, while the absolute average maximum peak load for fracture after healing was found to be roughly the same for all epoxy materials.

Further research is focusing on the encapsulation of maleimide compounds in microcapsules. At the same time, we are exploring other chemical strategies to further optimize the healing chemistry and investigate the possibility for the application of these concepts in state-of-the-art materials for daily applications.

4. Experimental

Materials: Butyl glycidylether (BGE, Aldrich, 95%), benzyl amine (BA, Acros, 99,5%), diethylene triamine (DETA, Aldrich, 99%), phenylmaleimide (PM, Aldrich, 97%), propylamine (PA, Acros, 98%), 1-dodecanethiol (DT, Fluka, 97%), pentaerythritol(3-mercaptopropionate (Tetrathiol, Aldrich, 95%), triethylamine (TEA, Acros, 99%), 1,1(methylenedi-4,1-phenyl)bismaleimide (MBM, Aldrich, 95%), N,N'-(1,3 phenylenedi)maleimide (PDM, Acros, 97%), EPON 828 epoxy resin (Low viscosity, Momentive Specialty Chemicals GmbH), RIM 135 epoxy resin (Momentive Specialty Chemicals GmbH) and RIMH 137 hardener (Momentive Specialty Chemicals GmbH) were used as received. The RIM 135 epoxy resin is a combination of bisphenol A diglycidylether (DGEBA) and 1,6-hexanediol diglycidylether.[57] The RIMH 137 hardener is mainly composed of low MW poly(propylether amine) (MW \approx 230) and isophorone diamine. Solvents were purchased from Acros and used without purification.

Model study for the kinetics of the reaction of amines and epoxide/C-C double bonds: PA (0.44 ml – 5.28 mmol) is added to MMA (0.56 ml – 5.26 mmol) in *m*-cresol (10 wt%) in a glass (10 ml) vial as reference for the reactivity of amines on the double bond of GMA. As a reference for the epoxide group in GMA, BA (0.43 ml – 3.96 mmol) is added to BGE (0.57 ml – 3.99 mmol) in *m*-cresol (10 wt%). ¹H-NMR is used to follow conversions of the mentioned reactions.

Model study for the kinetics of the reaction of maleimides and amines/thiols: PM (0.208 g – 1.20 mmol) is dissolved in *m*-cresol (1.72 ml – 10 wt%), at room temperature, in a glass (2 ml) vial. The vial is put in the ultrasonic bath for a short time to ensure that a homogeneous solution is obtained. In this solution PA (0.1 ml – 1.20 mmol) or DT (0.285 ml – 1.20 mmol) is added. For the reaction with DT, a reaction was conducted without catalyst, with TEA (17 μ l – 0.122 mmol) as a catalyst, or EPON 828 as a catalyst (0.125g - 100:12 wt% - grinded,

average size of grains $\pm 100 \mu\text{m}$), respectively. Conversion of the maleimide functionality was monitored by $^1\text{H-NMR}$.

Stock solutions of healing agents: MBM (0.385 g – 1 mmol) is dissolved in *m*-cresol (1.24 ml – 25 wt%) in a glass vial (2 ml), followed by addition of tetrathiol (190 μl – 0.5 mmol) or DETA (108 μl – 1 mmol), respectively. Alternatively, PDM (0.268 g – 1 mmol) is dissolved in *m*-cresol (1.60 ml – 15 wt%) in a glass vial (2 ml), followed by addition of tetrathiol (190 μl – 0.5 mmol) or DETA (108 μl – 1 mmol), respectively.

Synthesis of epoxy materials: EPON 828 resin is mixed with DETA in a 100/12 (equimolar) weight/weight ratio, RIM 135 resin is mixed with RIMH 137 in a 100/30 (equimolar) or 100/50 (excess hardener) weight/weight ratio. After homogeneous mixing, air bubbles are removed by applying high vacuum for 5 minutes. The solution is then poured in a silicon mold with specific dimensions to produce the Tapered Double Cantilever Beam (TDCB) samples.[55] The filled molds are cured at different temperatures - EPON 828 (1 day at 25°C and 16 hours at 40 °C) and RIM 135 (1 day at 40 °C and 16 hours at 80°C).

TDCB testing: A precrack was made in the TDCB sample with the aid of a razor blade, which was inserted into the groove to the TDCB specimen and tapping it into the moulded notch starter. The samples were then clamped on the tensile testing machine to be stretched at a speed of 5 $\mu\text{m}/\text{sec}$.[55] The specimens were loaded until failure occurs, resulting in the peak load to break the virgin sample. For healing of the samples, 30 μl of healing agent was manually injected in the crack plane and the samples were clamped together to ensure a good contact of the healing agent to the crack surface. The healed samples were stored at 25°C for 3 or 5 days and then broken at the same initial opening speed to calculate the healing efficiency, which is defined as the ratio of the maximum peak load of the healed sample to the maximum peak load of the virgin sample. The average value of minimum 5 samples was taken to get accurate results.

Instrumentation: ^1H NMR spectra were recorded with a Bruker AVANCE 300 (300 MHz) FT-NMR spectrometer. Differential Scanning Calorimetry (DSC) thermograms were recorded using a TA Instruments Q2000 DSC with autosampler option and Refrigerated Cooling System (RCS). Nitrogen gas was used as purge gas. The samples were studied in TAI Tzero Hermetic Aluminum sample pans and a scan rate of 10K/min. TDCB tests were conducted on

a Tinius Olsen H10KT with a load cell of 5000 N. The load-displacement curves were analyzed with the aid of the Test Navigator software.

Acknowledgements

Stijn Billiet thanks the Agency for Innovation by Science and Technology in Flanders (IWT) for a PhD scholarship. W. Van Paepeghe (Ghent University) and D. Van Hemelrijck (Vrije universiteit Brussel) are acknowledged for the scientific discussions. W. V. C. thanks the Research Foundation – Flanders (FWO) for a postdoctoral research fellowship. F. D. P. acknowledges the Belgian Program on Interuniversity Attraction Poles initiated by the Belgian State, Prime Minister's office (Program P6/27), and the European Science Foundation – Precision Polymer Materials (P2M) program for financial support.

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

References

1. Norris BC and Bielawski CW. *Macromolecules* 2010;43(8):3591-3593.
2. Williams KA, Dreyer DR, and Bielawski CW. *MRS Bulletin* 2008;33(08):759-765.
3. Caruso MM, Davis DA, Shen Q, Odom SA, Sottos NR, White SR, and Moore JS. *Chemical Reviews* 2009;109(11):5755-5798.
4. Wudl F and Murphy EB. *Progress in Polymer Science* 2010;35:223-251.
5. Mauldin TC and Kessler MR. *International Materials Reviews*;55(6):317-346.
6. Syrett JA, Becer CR, and Haddleton DM. *Polymer Chemistry* 2010;1(7):978-987.
7. Hager MD, Greil P, Leyens C, van der Zwaag S, and Schubert US. *Advanced Materials*;22(47):5424-5430.
8. Blaiszik BJ, Kramer SLB, Olugebefola SC, Moore JS, Sottos NR, and White SR. *Annual Review of Materials Research*, Vol 40;40:179-211.
9. Wool RP. *Soft Matter* 2008;4(3):400-418.
10. Burattini S, Greenland BW, Chappell D, Colquhoun HM, and Hayes W. *Chemical Society Reviews*;39(6):1973-1985.
11. van der Zwaag S. *Self Healing Materials*. Dordrecht, The Netherlands: Springer, 2007.
12. Williams KA, Boydston AJ, and Bielawski CW. *Journal of The Royal Society Interface* 2007;4(13):359-362.
13. White SR, Sottos NR, Geubelle PH, Moore JS, Kessler MR, Sriram SR, Brown EN, and Viswanathan S. *Nature* 2001;409(6822):794-797.
14. Wu DY, Meure S, and Solomon D. *Progress in Polymer Science* 2008;33(5):479-522.
15. Mauldin TC, Rule JD, Sottos NR, White SR, and Moore JS. *Journal of the Royal Society Interface* 2007;4(13):389-393.
16. Rule JD and Moore JS. *Macromolecules* 2002;35(21):7878-7882.
17. Lee JK, Liu X, Yoon SH, and Kessler MR. *Journal of Polymer Science Part B- Polymer Physics* 2007;45(14):1771-1780.
18. Liu X, Lee JK, Yoon SH, and Kessler MR. *Journal of Applied Polymer Science* 2006;101(3):1266-1272.
19. Wilson GO, Caruso MM, Reimer NT, White SR, Sottos NR, and Moore JS. *Chemistry of Materials* 2008;20(10):3288-3297.

20. Jones AS, Rule JD, Moore JS, White SR, and Sottos NR. *Chemistry of Materials* 2006;18(5):1312-1317.
21. Coope TS, Mayer UFJ, Wass DF, Trask RS, and Bond IP. *Advanced Functional Materials* 2011;21(24):4624-4631.
22. Cho SH, Andersson HM, White SR, Sottos NR, and Braun PV. *Advanced Materials* 2006;18(8):997-+.
23. Rong MZ, Zhang MQ, and Zhang W. *Advanced Composites Letters* 2007;16(5):167-172.
24. Yuan YC, Rong MZ, Zhang MQ, Chen B, Yang GC, and Li XM. *Macromolecules* 2008;41(14):5197-5202.
25. Yuan Y.C., Ye X.J., Rong M.Z., Zhang M.Q., Yang G.C., and Zhao J.Q. *ACS Appl. Mater. Interfaces* 2011;3(11):4487-4495.
26. McIlroy DA, Blaiszik BJ, Caruso MM, White SR, Moore JS, and Sottos NR. *Macromolecules*;43(4):1855-1859.
27. Caruso MM, Delafuente DA, Ho V, Sottos NR, Moore JS, and White SR. *Macromolecules* 2007;40(25):8830-8832.
28. Caruso MM, Blaiszik BJ, White SR, Sottos NR, and Moore JS. *Advanced Functional Materials* 2008;18(13):1898-1904.
29. Kolb HC, Finn MG, and Sharpless KB. *Angewandte Chemie International Edition* 2001;40(11):2004-2021.
30. Gragert M, Schunack M, and Binder WH. *Macromolecular Rapid Communications* 2011;32(5):419-425.
31. Schunack M, Gragert M, Döhler D, Michael P, and Binder WH. *Macromolecular Chemistry and Physics* 2012;213(2):205-214.
32. Sheng X, Mauldin TC, and Kessler MR. *Journal of Polymer Science Part A: Polymer Chemistry* 2010;48(18):4093-4102.
33. Meng LM, Yuan YC, Rong MZ, and Zhang MQ. *Journal of Materials Chemistry* 2010;20(29):6030-6038.
34. Chen X, Dam MA, Ono K, Mal A, Shen H, Nutt SR, Sheran K, and Wudl F. *Science* 2002;295(5560):1698-1702.
35. Chen X, Wudl F, Mal AK, Shen H, and Nutt SR. *Macromolecules* 2003;36(6):1802-1807.
36. Liu Y-L, Hsieh C-Y, and Chen Y-W. *Polymer* 2006;47(8):2581-2586.
37. Toncelli C, De Reus DC, Picchioni F, and Broekhuis AA. *Macromolecular Chemistry and Physics* 2012;213(2):157-165.
38. Mather BD, Viswanathan K, Miller KM, and Long TE. *Progress in Polymer Science* 2006;31(5):487-531.
39. Owens Corning. Industrial Customer Presentation: "High Performance Reinforcements" 2011.
40. PPG Industries Inc. "Composite Materials for Wind blades: current performance and future directions". Presented by Juan Camilo Serrano at the 2010 Wind Turbine blade workshop, Sandia National Laboratories, , July 20-21, 2010.
41. Reifsnider K.L. Introduction. *Fatigue of composite materials: Composite Material Series 4: Elsevier, 1990. pp. 1-9.*
42. Reifsnider K.L. Fatigue behaviour of composite laminates. *Fatigue of composite materials. Composite Material Series 4: Elsevier, 1990. pp. 105-180.*
43. Reifsnider K.L. Life prediction for resin-matrix composite materials. *Fatigue of composite materials. Composite Material Series 4: Elsevier, 1990. pp. 431-483.*
44. Van Paepegem W. and Degrieck J. *Composites Part A* 2001;32(10):1433-1441.
45. Wang HP, Yuan YC, Rong MZ, and Zhang MQ. *Colloid and Polymer Science* 2009;287(9):1089-1097.

46. Yang JL, Keller MW, Moore JS, White SR, and Sottos NR. *Macromolecules* 2008;41(24):9650-9655.
47. Wang X, Li G, Wei J, and Guan W. *Journal of Applied Polymer Science* 2009;113(2):1008-1016.
48. Sheng X, Mauldin TC, and Kessler MR. *Journal of Polymer Science Part a-Polymer Chemistry*;48(18):4093-4102.
49. Montarnal D, Tournilhac F, Hidalgo M, and Leibler L. *Journal of Polymer Science Part a-Polymer Chemistry*;48(5):1133-1141.
50. Chan JW, Hoyle CE, Lowe AB, and Bowman M. *Macromolecules*;43(15):6381-6388.
51. Li GZ, Randev RK, Soeriyadi AH, Rees G, Boyer C, Tong Z, Davis TP, Becer CR, and Haddleton DM. *Polymer Chemistry*;1(8):1196-1204.
52. Yuan YC, Rong MZ, and Zhang MQ. *Polymer* 2008;49(10):2531-2541.
53. van den Dungen ETA and Klumperman B. *Journal of Polymer Science Part a-Polymer Chemistry*;48(22):5215-5230.
54. Yuan L, Liang GZ, Xie JQ, and He SB. *Colloid and Polymer Science* 2007;285(7):781-791.
55. Brown EN, Sottos NR, and White SR. *Experimental Mechanics* 2002;42(4):372-379.
56. Menczel JD and Prime RB. *Thermal Analysis of Polymers: Fundamentals and Applications*. Hoboken, New Jersey: John Wiley & Sons, 2009.
57. Momentive Specialty Chemicals. Technical Data Sheet EPIKOTE Resin MGS RIM 135.