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Autonomous Self-Healing of Epoxy Thermosets with Thiol-Isocyanate Chemistry

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Thiol-isocyanate chemistry, combined with a dual capsule strategy, is used for the development of extrinsic self-healing epoxy materials. It is shown that the amine groups present in the matrix both serve as a catalyst for the addition reaction between a thiol and an isocyanate and as a way to covalently link the healed network structure to the surrounding resin. The tapered double cantilever beam (TDCB) geometry is used for evaluating the recovery of the fracture toughness at room temperature after different healing times. Using manual injection of the healing agents into the crack, a healing efficiency up to 130% is obtained for the EPIKOTE 828/DETA epoxy material. On the other hand, when two types of microcapsules, one containing a tetrathiol reagent and the other a low toxic isocyanate reagent, are incorporated into this epoxy thermoset (20 wt%), a recovery of more than 50% is reached. The influence of parameters such as the amount and core content of the microcapsules on the healing efficiency is investigated. Furthermore, the thiol-isocyanate chemistry is also tested for an industrial cold-curing epoxy resin (RIM 135/RIMH 137).

1. Introduction

Self-healing polymers and composites have experienced an exponential growth in research and development since the first concepts of Dry[1] and White[2] were published more than a decade ago. Just like the human body, these materials are capable of repairing damage sustained during their lifetime without direct human intervention. As reviewed by us recently, both extrinsic and intrinsic self-healing systems were developed, for which the healing ability is provided respectively by an external healing agent, added to the matrix material, or by the material itself through reshuffling of physical or chemical bonds.[3,4] However, in spite of the very broad range of methods and chemistries used in polymers and composites,[5] only a small part has found its way to industrial applications.

In the case of extrinsic self-healing materials, an extensive range of thermosetting systems and chemistries with varying performances has been investigated. While recognizing that multiple self-healing systems reach high healing efficiencies (>90%) at room temperature,[6–11] are able to demonstrate increased fatigue lifetime[12–15] and are used in industrially interesting fibre-reinforced composite materials,[16–19] we also noticed potential issues that might explain the industrial restraint. These mainly include the toxicity of the used chemicals, a low stability of the healing system at higher temperatures or ambient conditions, the usage of expensive compounds or too slow healing for crack propagation to be arrested.

For example, in the concept where a ring-opening metathesis polymerization (ROMP) is used as the main network forming reaction,[2] a ruthenium-containing Grubbs' catalyst is required. Unfortunately, these types of catalysts are prone to oxidation in the presence of air or moisture and are inherently expensive.[20] Although very good healing efficiencies over 90% were obtained at room temperature, the catalyst remains the limiting factor for commercial exploitation. Several efforts were made to improve the Grubbs system, for example by encapsulating the catalyst in wax for protection[7] or by switching to a tungsten hexachloride ROMP catalyst.[21] In the first case, a lower catalyst amount could be used to yield the same recovery of over 90% due to its enhanced stability. In the latter case, a much lower healing efficiency of 20% was obtained.

Also in the azide-alkyne concept proposed by Binder et al.,[11] a metal-containing catalyst is necessary for the reaction to proceed. Using multifunctional alkynes in combination with polymeric multi-azides and a copper(I)-ligand catalyst, a recovery of over 90% was reached. Although these catalysts are far cheaper and more stable than Grubbs' catalysts, they are still easily oxidized,[22,23] limiting their long-term use in polymer applications.

Several systems obtaining similar high healing efficiencies make use of nucleophilic addition reactions to epoxide or ene functionalities. Amines were combined with epoxy resins by White and co-workers[10] and with maleimides by our group.[24] Although the use of amines as healing agents showed great

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DOI: 10.1002/adfm.201400580

potential as strong nucleophiles, the encapsulation of amines still proves to be difficult due to their reactivity and hydrophilicity. A first successful attempt was made by Sottos et al., using interfacial polymerization with isocyanates to form the polyurea shell and resulting in microcapsules with an estimated amine core content of 55 wt%.[25] However, no self-healing materials were generated using these microcapsules. To our knowledge, amines could only be encapsulated in higher amounts through infiltration of hollow microspheres.[10] Unfortunately, the reverse diffusion of the amine out of the microcapsules was noticed at elevated temperatures. Despite significant improvements presented in a very recent manuscript,[26] limited reverse diffusion is still present. On the other hand, thiols are easier to encapsulate, but they only possess a similar nucleophilicity to amines when deprotonated. Nevertheless, combinations with epoxy resins,[9] acrylates[27] and maleimides[24] have been investigated.

In the thiol-epoxy system, as introduced by Yuan et al.,[9,28,29] the tetrafunctional thiol pentaerythritol tetrakis(3-mercaptopropionate) (TetraThiol) was combined with an epoxy resin in a two-capsule system. The deprotonation of the thiol was achieved by infiltrating the TetraThiol microcapsule with a low molecular weight tertiary amine catalyst, which is required for fast self-healing. Full recovery was obtained with this system after 1 day at room temperature. The system also worked at lower temperatures (down to −10 °C) and already reached over 80% recovery after 3 h. However, the liquid tertiary amine is still present in the healed network and can leach out.

Klumperman et al. combined this TetraThiol with either a bifunctional acrylate or norbornene.[27,30] In both cases, DMPA was added as a photo-initiator for the radical thiol-ene addition reaction, although the reaction also proceeds without the UV activation or catalyst. Only partial recovery of scratches in PMMA coatings was reported, most likely due to the delivered healing agent volume being too low for the large crack.

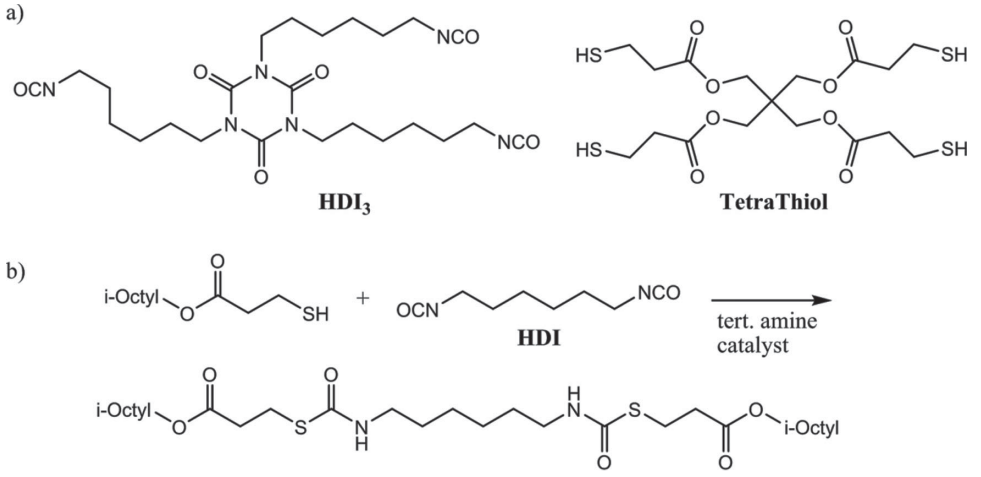
In a comparative study performed in our group, it was demonstrated that maleimides are much more reactive towards nucleophiles than epoxides or acrylates.[24] In order to form networks through a thiol-maleimide Michael addition, the TetraThiol was combined with bifunctional aromatic maleimides. Since the bismaleimides are solid, these were solubilized in m-cresol, due to the limited solubility in other solvents and because m-cresol inhibits homopolymerization of the maleimides. Nevertheless, this solvent is toxic and unfavorable for industrial applications. Although this chemistry showed a similar recovery to the thiol-epoxy system with manual injection, no microcapsules were reported.

In this research, we aimed to tackle some of the disadvantages mentioned above by developing a fast healing system, which uses low toxic, thermally stable and inexpensive healing agents and at same time is efficient in the presence of moisture or air. A thiol-isocyanate healing chemistry, new to the field of self-healing, is presented. Thus, a tetrafunctional thiol was combined with multifunctional isocyanates to form strong polythiourethane-based networks. The kinetics of this thiol-isocyanate reaction were investigated and the healing agent mixture was in first instance manually injected into the crack area. In a second step, the healing agents were encapsulated and the microcapsules were dispersed in an epoxy matrix. The influence of parameters such as the amount and core content of the microcapsules on the healing efficiency was studied.

2. Results and Discussion

2.1. Selection and Stability of Healing Agents

In order to assess the healing potential of the thiol-isocyanate chemistry, the adhesive bonding capability of several monomer mixtures was first tested qualitatively. Pentaerythritol tetrakis(3-mercaptopropionate) (TetraThiol, **Scheme 1**a) was selected as a thiol due to its high thermal stability (thermogravimetric analysis (TGA) curve in Supporting Information, Figure S1),[31] availability, functionality and its former use in self-healing applications.[9,27–30] The thiol functionality is also stable up to at least 2 years when kept under ambient atmosphere and at room temperature, as confirmed by NMR and LC-MS measurements. This TetraThiol compound was



Scheme 1. (a) HDI isocyanurate trimer (HDI_3) and pentaerythritol tetrakis(3-mercaptopropionate) (TetraThiol); (b) model reaction of HDI with isooctyl 3-mercaptopropionate, catalyzed by a tertiary amine.

combined with four commercially available bifunctional isocyanates. Methylene diphenyl diisocyanate (MDI), toluene-2,4-diisocyanate (TDI), isophorone diisocyanate (IPDI) and hexamethylene diisocyanate (HDI) were mixed with TetraThiol in a 1:1 ratio of functional groups, inserted between two smooth epoxy plates and allowed to react at room temperature without any applied pressure. Two types of epoxy compositions were used to obtain these plates: the EPIKOTE 828 epoxy resin and diethylenetriamine (DETA) were mixed in equimolar amounts (100:11 weight ratio) and cured for 1 day at 25 °C and 1 day at 40 °C in a silicon mold, while the RIM 135 resin was combined with the RIMH 137 hardener in an equimolar 100:30 weight ratio and cured for 1 day at 40 °C and 16 h at 80 °C. This RIM formulation is used for the infusion of wind turbine blades.

The adhesion was then evaluated manually at different time intervals, distinguishing liquid adhesion from adhesive bonding by the reacted network. The aromatic isocyanates MDI and TDI most likely were too reactive towards the thiol leading to early precipitation. As a consequence, further diffusion and reaction of monomers were hampered, resulting in a weak network. This problem did not occur with the aliphatic isocyanates IPDI and HDI, since these are less reactive compared to the aromatic ones.[32] In fact, the IPDI-TetraThiol network did not solidify completely, even after 10 days. HDI on the other hand showed promising results with some adhesive bonding already occurring after 8 h, while the plates can no longer be detached after 2 days as a result of the formation of a strong polythiourethane network. The resulting network has a glass transition temperature of 60 °C as measured with DSC (Supporting Information, Figure S3), which is in the same order of magnitude as the used epoxy materials. However, HDI is considered toxic with an LD50 (oral, mouse) of 350 mg kg^{-1},[33] which would be an issue in further industrial applications. Since the HDI isocyanurate trimer (HDI_3, Tolonate HDT-LV, Scheme 1a) is approximately ten times less toxic[34] and widely used in industrial context, this trifunctional isocyanate was additionally tested and further applied. This trimer is often used in coating formulations where strict Volatile Organic Compound (VOC) limits are used. A second advantage of HDI_3 over HDI is its thermal stability, important for high-end epoxy applications. While TGA measurements already indicated a 2% weight loss for HDI at 75 °C under nitrogen atmosphere, this weight loss was only reached at 198 °C for the trimer. TGA measurements under ambient atmosphere yielded similar results (Supporting Information, Figure S1 & 2).

Another potential issue with isocyanates is their stability in the presence of moisture. Over time, nucleophilic addition of water to the isocyanate will occur with the formation of an unstable N-substituted carbamic acid. With release of CO_2 and heat, the carbamic acid decomposes to form amines which can also participate in the healing reaction and actually react faster with other isocyanates than thiols. In that case, strong polyurea bonds are formed. Therefore, we believe that moisture has no negative influence on the network formation. The amine-isocyanate reaction is also responsible for covalent linkage of the healed network to the surrounding epoxy matrix via residual amine groups.

2.2. Kinetic Study of Thiol-Isocyanate Reaction

Since rapid inhibition of crack propagation leads to smaller crack volumes to be healed, a fast healing reaction is favorable. Therefore, a kinetic study of the thiol-isocyanate reaction was performed using online FTIR spectroscopy and microcalorimetry measurements.

For the online infrared study, the peak areas of both the isocyanate and thio-urethane carbonyl stretches (2278 and 1675 cm^{-1}, respectively) were monitored in situ during the reaction. HDI was combined with isooctyl 3-mercaptopropionate, a model compound with a thiol functional group similar to TetraThiol (Scheme 1b), but with only one functionality to avoid crosslinking and subsequent precipitation of the product. A concentration of 0.5 M in chloroform was used. When both reagents were mixed together in a 1:1 ratio of functional groups and allowed to react for 1 h, little to no reaction was observed. As shown in **Figure 1**, the isocyanate carbonyl stretch absorption remained constant and no formation of thio-urethane groups was detected. The prominent absorption peak of the ester carbonyl stretch of the monofunctional thiol at 1727 cm^{-1} was used as a reference, since the peak intensity should remain constant during the reaction. If any solvent evaporated as a result of the release of reaction heat, the intensity of this peak would increase because of the change in concentration.

On the other hand, when 5 mol% of *N,N*-diisopropylethylamine (DIPEA) was added as a model catalyst after one hour, the thiol-isocyanate reaction immediately proceeded to full conversion in less than 7 min. This can be seen clearly in both the decrease and increase in peak intensity of the isocyanate and thio-urethane carbonyl stretches respectively. This is similar to what has been described earlier in literature for the thiol-isocyanate combination with tertiary amines.[35,36]

Since the epoxy matrix contains a vast amount of tertiary amines, a similar experiment was performed with this material as a catalyst (Figure 1). Therefore, the epoxy plates described above were in first instance ground to a powder with an average granule size of ±100 µm. A large amount of EPIKOTE

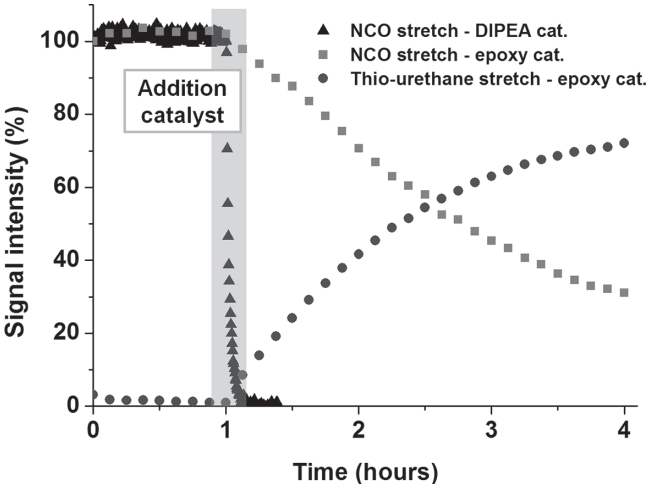


Figure 1. Online FTIR 2D plot of the model reaction of hexamethylene diisocyanate with isooctyl 3-mercaptopropionate, catalyzed by *N,N*-diisopropylethylamine (DIPEA) or the epoxy matrix powder.

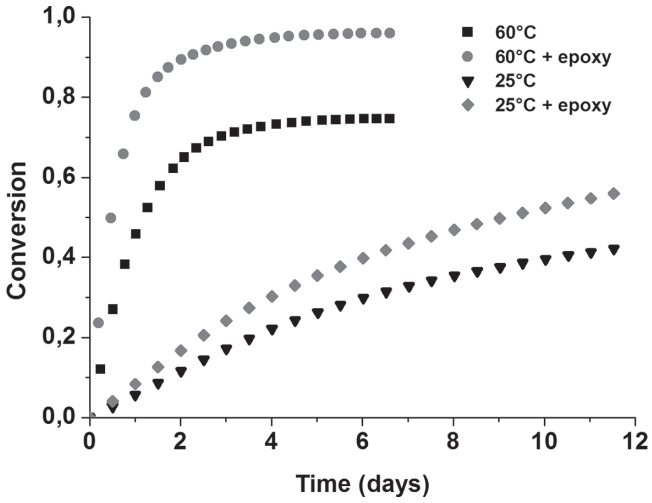


Figure 2. Comparative microcalorimetry study of the thiol-isocyanate reaction of TetraThiol with HDI_3 at 25 and 60 °C without catalyst and catalyzed by the epoxy matrix powder (EPIKOTE 828).

828 powder (1.5 g versus 4.37 g of thiol) was added to the reaction mixture to simulate the crack surface area to crack volume ratio in the targeted self-healing application. Upon addition of the powder, the isocyanate carbonyl stretch steadily decreased until a conversion of 60% was reached after 3 h. When twice the amount of epoxy powder (3 g) was used, the conversion after 3 h increased to 70%. This experiment clearly indicates the catalytic effect of the epoxy matrix on the thiol-isocyanate reaction. As a consequence, tertiary amines should not necessarily be incorporated in the microcapsules.

This catalytic effect was confirmed in an additional microcalorimetry study where TetraThiol was reacted with the HDI trimer in the absence of any solvent. When the TetraThiol-HDI_3 reaction was monitored over time at 25 °C without a catalyst, a low reaction rate was observed (**Figure 2**). Therefore, these compounds cannot be encapsulated in one single capsule.

On the other hand, adding EPIKOTE 828 epoxy powder to the same mixture increased the reaction rate significantly, again demonstrating the catalytic effect of the matrix. As can be seen in Figure 2, a similar conversion of 25% was reached after 3 days with 'epoxy catalyst' as after 5 days without catalyst. In a second test, the influence of temperature on the reaction was investigated. Heating the TetraThiol-HDI_3 mixture to 60 °C without the presence of a catalyst resulted in a quite significant increase in reaction rate. After 3 days, a reaction conversion of 71% was obtained. An even larger increase was noticed when the epoxy powder catalyst was added (93% conversion after 3 days). It is important to mention that in the latter case, the vitrification temperature of the epoxy powder of 56 °C[24] is exceeded. Part of the increase in measured reaction heat could thus be caused by further curing of the epoxy powder.

2.3. Synthesis of Microcapsules

Microcapsules containing Tetrathiol in the core were synthesized according to an optimized procedure reported by Zhang et al. in 2008.[31] In an interfacial polycondensation process, melamine-formaldehyde (MF) walled microcapsules containing TetraThiol with 0–10 wt% methyl benzoate as a viscosity lowering solvent were prepared. Microcapsule sizes were analyzed using a combination of optical microscopy, scanning electron microscopy (SEM) and a particle sizer, showing a mean diameter of 150 µm (**Figure 3**a). With a rough outer shell and a smooth inner shell, the morphology is similar to the earlier described microcapsules.[37–39] Using Soxhlet extraction with acetone for 2 days, core contents were determined to be 75–85 wt% of the total microcapsule weight. The microcapsules were stable up to at least one year.

Microcapsules containing HDI trimer were synthesized according to a procedure recently developed in our group.[40] The work was inspired by the work of Yang and coworkers,[41,42] using the interfacial polymerization between an active isocyanate present in the core and an active amine present in the water phase, obtaining a polyurea walled microcapsule with HDI_3 in the core. Smooth microcapsules with a mean diameter of 150 µm were obtained (Figure 3b), containing up to 70 wt% in HDI_3 core. As can be seen in the graph, agglomerates were also formed after the sieving step. In a separate study performed by our group, the isocyanate capsule stability in water has been investigated.[40] The results indicated that the isocyanate containing microcapsules only lose a significant part of their core (>10 wt%) after a period of two days when immersed in water. In this study, it has been shown that one day of aqueous immersion could be compared to one month of

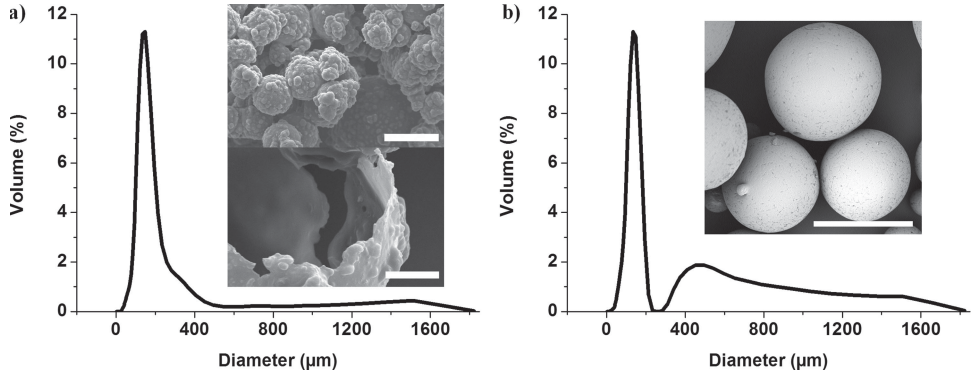


Figure 3. (a) TetraThiol microcapsules – SEM (scale bar top: 50 µm and bottom: 10 µm) and particle size distribution; microcapsules were broken to show the shell thickness in the bottom figure; (b) HDI_3 microcapsules – SEM (scale bar 90 µm) and particle size distribution.

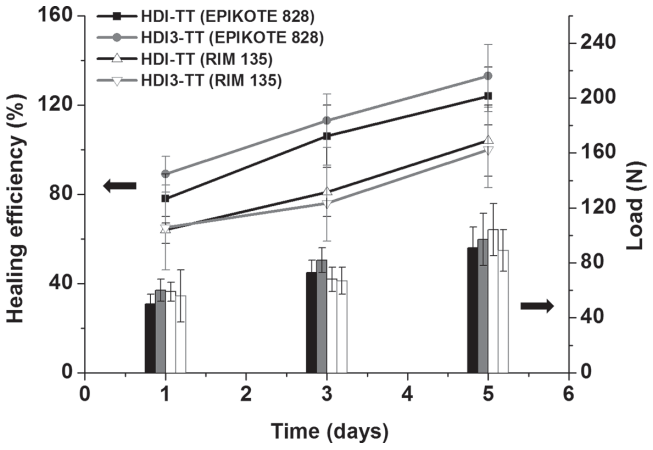


Figure 4. Healing efficiency and healed load after 1, 3, or 5 days at 25 °C, combining TetraThiol with HDI or HDI_3 as healing agents in EPIKOTE 828 or RIM 135 epoxy material.

exposure to air and ambient conditions, thus indicating a long shelf life.

2.4. Quantification of Healing Efficiency

Since the thiol-isocyanate chemistry showed great potential for healing epoxy materials, the extent of its healing capability was examined using the Tapered Double Cantilever Beam (TDCB) test. In accordance with the protocol proposed by White et al.,[6,43] a tapered epoxy sample with a side groove (47 mm in length) and a thickness of 2.5 mm in the groove was used. A precrack was generated by tapping the sample onto a fresh razor blade following the ASTM D4045 standard. As indicated by Schön et al. for PMMA fracture analysis,[44] this is the method introducing the least residual stress at the crack tip, thus resulting in more consistent fracture toughness values.

In a first stage, virgin epoxy material was loaded until fracture, followed by manual injection of the optimal mixture of TetraThiol with HDI or HDI_3 into the crack area (30 µL, 1:1 ratio of functional groups). After removal of excess of healing agent, these samples were clamped and allowed to heal for 8 h, 1, 3 or 5 days at 25 °C. This was then followed by a second fracture test. About 10 samples were tested for every healing time, using both the EPIKOTE 828 and RIM 135 epoxy material. The efficiency of healing fracture damage was determined by the ratio of the healed over the virgin peak load to fracture, as this equals the ratio of the measured fracture toughness after and before healing in the TDCB geometry[45] and thus gives an indication of the recovery of the resistance to fracture. A healing efficiency of 61 ± 7% was obtained after 8 h for the EPIKOTE 828 matrix material. As can be seen in **Figure 4**, this recovery increases over time, reaching up to 89% after 1 day, 113% after 3 days and 133% after 5 days. No further increase was noticed after 10 days. The reason for the healing efficiency exceeding 100% is two-fold: on one hand, a healed polythiourethane network with a greater resistance to fracture is formed, and on the other hand, the sample is forced to break into this newly formed network because of the side groove in the TDCB geometry. It is also clear that the RIM material renders lower healing efficiencies (Figure 4), although 100% is still reached after 5 days. This is ascribed to the fact that the healed peak load to fracture is compared to a higher virgin peak load for the RIM 135 matrix (84 ± 8 N versus 60 ± 7 N for the EPIKOTE 828 material). The network formation is not influenced by the difference in both epoxy materials, since the healed peak load values are not significantly different for both matrices (Figure 4). This is valid for both the HDI- and HDI_3-TetraThiol combination.

Diffusion problems, which could potentially occur with the healing agents in the crack, have also been investigated. When TetraThiol was added on top of HDI_3 without mixing, the reaction only took place at the interface of both viscous liquids, which was observed visually as a steadily growing solid layer in between the liquid phases. Although the diffusion occurs over several millimeters, which is exceeding the distance between microcapsules in the self-healing epoxy, it is still slow. Thus, in spite of the healing agents being completely miscible in one another, spontaneous mixing is hampered by their high viscosities (500 and 1300 cP for TetraThiol and HDI_3 respectively).

A potential solution to this diffusion issue is the addition of a compatible, high boiling solvent to lower the viscosity of both compounds. Methyl benzoate, having a low toxicity and a boiling point of 200 °C, was selected as a suitable solvent for both healing agents. When increasing amounts of this solvent are mixed with TetraThiol and HDI_3, the viscosity is drastically reduced (**Figure 5**a). In order to have an equal distribution of

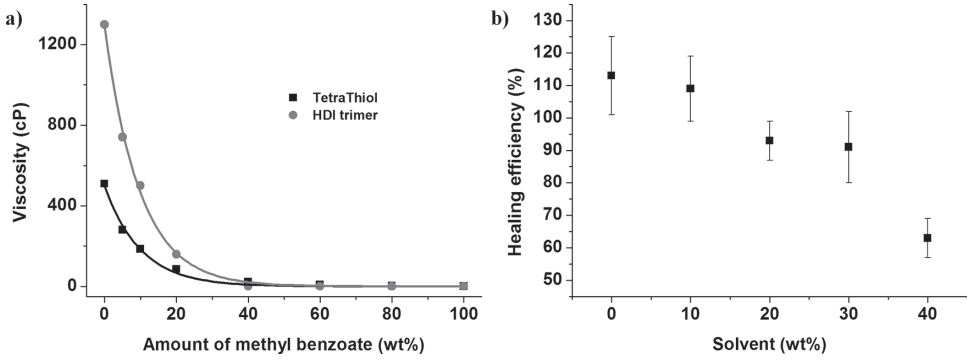


Figure 5. (a) Viscosity of TetraThiol and HDI_3 with increasing percentage of methyl benzoate as a solvent. (b) Decrease in healing efficiency in EPIKOTE 828 samples with increasing amount of methyl benzoate after 3 days of healing via manual injection.

both healing agents into the crack, a similar viscosity would be favorable. As can be seen from the graph, this is the case when 10 and 20 wt% of methyl benzoate is added to TetraThiol and HDI_3 respectively, rendering a viscosity of 185 and 160 cP.

However, this approach also has some disadvantages. Firstly, the addition of methyl benzoate to the HDI_3 microcapsules results in a faster loss of core content over time, most likely due to solvent swelling of the polyurea shell. Secondly, the maximum healing efficiency that can be obtained decreases with increasing amount of solvent (Figure 5b). This was measured using manual injection of the healing agent mixture with 10 to 40 wt% of methyl benzoate added compared to the amount of TetraThiol. When more than 10 wt% of methyl benzoate was used, the healing efficiency dropped significantly. The drop can be fully explained by the decrease in amount of healing agent present in the crack and a potential plasticizing effect of the solvent leading to a weaker network. To minimize this negative impact, microcapsules were used containing the TetraThiol in combination with a small amount (5–10 wt%) of the viscosity-lowering solvent.

The effect of temperature was also investigated, since the microcalorimetry analysis showed that the reaction rate significantly increases with temperature. At least 4 EPIKOTE 828 samples were healed with the HDI_3-TetraThiol combination for 3 days at 40 and 60 °C. The slight increase to 40 °C significantly improved the recovery from 113 ± 12 to 126 ± 3%, while the increase to 60 °C resulted in a decrease in healing efficiency to 98 ± 14%. Both results could be explained by an increase in thiol-isocyanate reaction rate. First, the effect of heating on the healing reaction must be distinguished from the devitrification effect of the epoxy material. Therefore, a blank epoxy sample was clamped without healing agents added and subsequently left at 40 and 60 °C for 3 days each. Temperatures of 40 and 60 °C are below and just above the vitrification temperature of 56 °C.[24] At both 40 and 60 °C, no recovery in fracture toughness was recorded after 3 days. Thus, the observed temperature effect on the healing efficiency in the manually healed epoxy samples is fully related to an increase in the thiol-isocyanate reaction rate. This means that the recovery increase at 40 °C can be explained by a higher conversion after 3 days. On the other hand, the decrease at 60 °C could be explained by a further increase in reaction rate, hampering monomer diffusion due to fast gelation. Since in this case the vitrification temperature is exceeded, the reduction in residual free epoxide and amine groups at the crack surface might also have an influence.

The capability of the reaction to proceed at lower temperatures was also tested. When 5 EPIKOTE 828 samples were healed with the HDI_3-TetraThiol combination for 3 days at −2 °C, a significant healing efficiency of 50 ± 6% was recorded. Although this value is much lower than the recovery at 25 °C, it shows that the system is also capable of healing at low temperatures, e.g., during cold periods.

In a next step, the two types of microcapsules, one containing the TetraThiol and the other the HDI_3, were used to generate a fully autonomous, self-healing system. The microcapsules are only added to the EPIKOTE 828 material around the crack area in the TDCB geometry by using a silicon insert while casting.[43] MF microcapsules with a TetraThiol-methyl benzoate core were mixed with polyurea microcapsules with an HDI_3 core in a 1:1 ratio of thiol-isocyanate groups. After the first fracture test, the samples were clamped and allowed to heal for 5 days at 25 °C (at least three samples per composition).

The best results were obtained using TetraThiol microcapsules with a core content of 75–85 wt%, while the isocyanate capsules had a content of 70 wt%. With a microcapsule loading of 20 wt%, up to 54% of the original peak load to fracture was recovered, meaning that the healed peak load exceeded 40 N. From this healing efficiency value, it is already clear that the healed peak load is compared to an enhanced virgin peak load, as a result of a reinforcing effect of the microcapsules. As described by Brown et al.,[46] microcapsules tend to strengthen the epoxy material through increased hackle markings and subsurface microcracking. Furthermore, asymmetric tail formation is noticed in the crack plain. As can be seen from **Figure 6**a, the virgin peak load increases with a higher amount of microcapsules. Figure 6b shows the tail formation in the wake of two microcapsules. If the fracture toughness recovery is compared to the virgin peak load of the unloaded epoxy material (60 N),[2] a healing efficiency up to 69% can be calculated. This healing efficiency is lower than the results obtained using manual injection because several additional parameters play an important role: the microcapsule spatial distribution, the microcapsule fracture behavior, the flow and mixing of the healing agents in the crack as mentioned before and the resulting healing agent volume delivered to the crack. X-ray Computed Tomography (CT) scans of the crack surface showed that some delamination of the isocyanate microcapsules occurred (Supporting Information, Figure S4). These capsules could be distinguished from the TetraThiol microcapsules due to a difference in electron density. As a result, we believe that the isocyanate volume delivered to the crack is too low, which is considered to be the main reason for the decrease in healing efficiency.

In a next step, the microcapsule loading in the EPIKOTE 828 epoxy material was lowered to 10 and 15 wt% to further

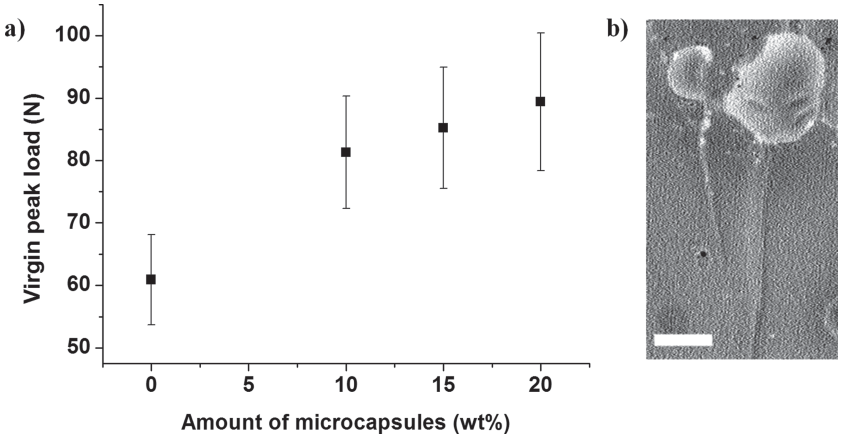


Figure 6. (a) Reinforcing effect of the microcapsules on the EPIKOTE 828 epoxy matrix. (b) Scanning electron micrograph of tail formation in the wake of two microcapsules (scale bar 40 μm).

investigate the influence of the healing agent volume. Again, at least 3 samples were used per composition and healed for 5 days at room temperature. In both cases, an average healing efficiency of only 30% was reached due to a lower healing agent volume delivery to the crack. To further confirm this, the core content of the isocyanate microcapsules was lowered while retaining a microcapsule loading of 20 wt%. When HDI_3 microcapsules with a core content of 40, 50, and 60 wt% were used, healing efficiencies of respectively 13, 26, and 39% were obtained.

3. Conclusion

A tetrafunctional thiol was combined with hexamethylene diisocyanate and its isocyanurate trimer to provide self-healing in epoxy matrix materials. These healing agents were selected based on their adhesive capability, low toxicity and thermal stability. The thiol-isocyanate nucleophilic addition reaction is fast enough to ensure fast inhibition of crack propagation. In the presence of a tertiary amine catalyst, the reaction proceeds to full conversion within minutes. When the amine-containing epoxy matrix was used as a heterogeneous powder catalyst, a significant increase in reactivity was noticed as well in comparison to the thiol-isocyanate mixture without any tertiary amine. The healing potential of the thiol-isocyanate combination was screened using manual injection of the HDI- or HDI_3-TetraThiol mixture into the cracked epoxy material. Up to 133% of recovery in fracture toughness was measured after 5 days, with 61% already being reached after 8 h.

Two different commercial epoxy matrices were tested and yielded similar recovered peak loads. In a next step, both the TetraThiol and HDI trimer were encapsulated with high core contents in a melamine-formaldehyde or polyurea shell respectively. These microcapsules were then embedded in the EPIKOTE 828 epoxy material to provide self-healing properties, yielding a recovery up to 54% after 5 days. Although further optimization would be required to increase this healing efficiency, a new self-healing chemistry has been successfully introduced, approaching the stringent demands of industry concerning toxicity, stability and costs and providing a healing system that is still efficient when moisture or air is present.

4. Experimental Section

4.1. Materials

Diisocyanate (IPDI, Aldrich, 98%), 4,4′-methylenebis(phenyl isocyanate) (MDI, Aldrich, 98%), toluene-2,4-diisocyanate (TDI, Aldrich, 95%), hexamethylene diisocyanate (HDI, Sigma, ≥99%), pentaerythritol tetrakis(3-mercaptopropionate) (TetraThiol, Aldrich, >95%), isooctyl 3-mercaptopropionate (Sigma-Aldrich, ≥99%), N,N-diisopropylethylamine (DIPEA, Sigma-Aldrich, 99%), diethylenetriamine (DETA, Sigma-Aldrich, 99%), EPIKOTE 828 LVEL epoxy resin (Low viscosity, Momentive Specialty Chemicals GmbH), RIM 135 epoxy resin (Momentive Specialty Chemicals GmbH) and RIMH137 (Momentive Specialty Chemicals GmbH) were used as received. The EPIKOTE 828 LVEL resin is a bisphenol A/epichlorohydrin derived epoxy resin with a MW ≤ 700 g mol^{-1}. The RIM 135 epoxy resin is a combination of bisphenol A diglycidylether and 1,6-hexanediol diglycidylether. The RIMH 137 hardener is mainly composed of low MW poly(propylether amine) (MW ≈ 230 g mol^{-1}) and isophorone diamine. The isocyanurate-based hexamethylene diisocyanate trimer (HDI_3, Tolonate HDT-LV) was kindly provided by Vencorex Chemicals and used as received. Solvents were purchased from Acros and used without purification.

4.2. Instrumentation

Online Fourier-Transform InfraRed (FTIR) spectroscopy: was conducted using a React-IR 4000 Instrument (Mettler Toledo AutoChem ReactIR) equipped with a diamond ATR probe.

Microcalorimetric Measurements: were performed on a TAM III (TA Instruments). Approximately 1 g of the different mixtures was placed in the equipment and kept at isothermal conditions while the reaction heat flow was recorded.

Thermogravimetric Analyses (TGA): were performed on a TGA/SDTA851e equipment (Mettler-Toledo). The samples were heated from 25 to 800 °C at a rate of 10 °C min^{-1} under nitrogen or ambient atmosphere. The thermograms were analyzed with the STARe software from Mettler-Toledo.

Differential Scanning Calorimetry (DSC): thermograms were recorded using a Mettler-Toledo DSC 1/700 instrument with an FRS5 sensor and Automatic Sample Robot. Nitrogen gas was used as purge gas. Liquid nitrogen was used to cool the system. The samples were studied in standard 40 µL aluminum sample pans and at a scan rate of 10 °C min^{-1}. The thermograms were analyzed with the STARe software from Mettler-Toledo.

Tapered Double Cantilever Beam (TDCB): load-displacement curves were recorded with a Tinius Olsen H10KT testing machine equipped with a HTE-5kN load cell. A displacement rate of 0.3 mm/min was used. The data were analyzed with Tinius Olsen Test Navigator software.

Viscosimetry: was performed using a Brookfield Digital Viscosimeter Model DV-II with spindle 4 (rod, 3 mm diameter) from the Brookfield LV Spindle Set.

Particle Size Analysis: Average particle sizes and dispersities of the microcapsules were measured by laser diffraction using a Beckman Coulter LS 200 instrument (0.2 to 2000 µm range).

Scanning Electron Microscopy (SEM): Pictures were recorded with a TM-3000 Hitachi tabletop microscope, using Leit adhesive Carbon Tabs (12 mm) from Agar Scientific.

Micro-CT: The scanner used in this work was built inside a shielded room to ensure a maximum flexibility of the set-up.[47] The X-ray tube of this high-resolution CT scanner is a FXE-160.50 dual head open type source from Feinfocus. For the scans, the transmission head was used with an accelerating high voltage of 100 kV and an electron current of 80 mA. 1800 projections were made at a resolution of 5.1 µm and an illumination time of 1000 ms per frame, with two frames per projection. The detector used was a VARIAN Paxscan 2520 V with 14 bit dynamic range and CsI scintillator.

Microencapsulation Experiments: were carried out in double-walled cylindrical glass reactors (250 mL, Radleys) equipped with an external circulating heating bath (Julabo F-12 unit), and a three-bladed teflon overhead turbine stirrer fitted at approximately 2 cm from the bottom of the reactor vessel (Cowie Ltd.) typically running at 450 rpm. Homogenization of the emulsion was carried out with a T 18 basic ULTRA-TURRAX, high performance disperser by IKA. Six speed ranges are available, from 3500 rpm (speed 1) till 24 000 rpm (speed 6).

4.3. Synthesis

Synthesis of Microcapsules: Melamine-formaldehyde walled microcapsules containing TetraThiol in the core were synthesized following the procedure reported by Zhang et al.[31] After collection, the microcapsules were washed with deionized water and acetone, dried under vacuum at 45 °C overnight and afterwards sieved through 500 µm pores to remove agglomerates. Polyurea walled microcapsules

containing HDI trimer in the core were synthesized by interfacial polymerization.[40] After collection, the microcapsules were vacuum dried at 45 °C overnight, generally yielding agglomerates that could be separated with gentle pressure without damaging the capsules. Again sieves with 500 μm pores were used to remove remaining agglomerates.

Core Content Determination: The core content of the microcapsules containing TetraThiol was determined by Soxhlet extraction with acetone for 2 days and NMR, using methyl benzoate as a reference. The NMR spectra were recorded on a Bruker AVANCE 300 spectrometer. The spectra were analyzed with the ACD/Spec Manager software from ACD/Labs. The core content of the microcapsules containing HDI trimer was determined on a React-IR 4000 Instrument (Mettler Toledo AutoChem ReactIR) equipped with a silicon ATR probe (SiComp, optical range 4400–650 cm^{-1}).

Synthesis of Epoxy Materials: EPIKOTE 828 LVEL epoxy resin is mixed with DETA in an equimolar 100:11 weight ratio, RIM 135 resin is mixed with RIMH 137 in an equimolar 100:30 weight ratio. After homogeneous mixing, the air was 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.[6,43] The EPIKOTE 828 mixture is cured for 1 day at 25 °C and 1 day at 40 °C, while the RIM 135 mixture is cured for 1 day at 40 °C and 16 h at 80 °C.

4.4. Quantification of Healing Efficiency

Tapered Double Cantilever Beam test samples were used for the quantification of the healing efficiency. In accordance with the protocol introduced by White et al.,[6,43] a tapered epoxy sample with a side groove (47 mm in length) and a thickness of 2.5 mm in the groove was used. A precrack was generated by tapping the TDCB sample onto a razor blade, which was inserted into the notch of the TDCB specimen. The samples were then pin loaded at a displacement rate of 0.3 mm min^{-1}.[6] The specimens were loaded until failure occurs, resulting in the peak load necessary to break the virgin sample. If multiple peak loads were obtained, the average was used as the load to failure for the TDCB sample. When broken, healing agents can be delivered to the crack, either by manual injection of the healing mixture or by the use of microcapsules. In the case of manual addition, 30 μL of healing agent was injected in the crack plane and both crack surfaces were brought into contact by gentle clamping. For the microcapsule containing TDCB samples, only the clamping step was required. The healed samples were stored at 25 °C for the designated period and then broken at the same displacement rate to calculate the healing efficiency, which is defined as the ratio of the average peak load of the healed sample over the average peak load of the same virgin sample. At least 3 samples were tested for each composition.

Supporting Information

Supporting Information and a short video demonstrating the self-healing capability of the capsule-containing epoxy thermoset is available from the Wiley Online Library or from the author.

Acknowledgements

The authors would like to thank Tom Bultreys and Veerle Cnudde from the Centre for X-Ray Tomography at Ghent University (UGCT, Department Geology and Soil Science) for the X-ray CT measurements. The authors acknowledge the Strategic Innovative Materials (SIM) project, supported by the Agency for Innovation through Science and Technology (IWT), for financial support. Filip Du Prez also acknowledges the Belgian Program on Interuniversity Attraction Poles initiated by the Belgian State, Prime Minister's office (Program P7/05) and the European Science Foundation – Precision Polymer Materials (P2M) program.

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Received: February 19, 2014
Revised: May 15, 2014
Published online: July 10, 2014

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