



Material Behaviour

Selection of healing agents for a vascular self-healing application

A. Cuvellier^{a,*}, A. Torre-Muruzabal^a, G. Van Assche^a, K. De Clerck^b, H. Rahier^a^a Physical Chemistry and Polymer Science (FYSC), Department of Materials and Chemistry, Faculty of Engineering, Vrije Universiteit Brussel (VUB), Pleinlaan 2, B-1050 Brussels, Belgium^b Fiber and Colouration Technology Research Group, Department of Textiles, Faculty of Engineering and Architecture, Ghent University, Technologiepark 907, 9052 Ghent, Belgium

ARTICLE INFO

Article history:

Received 29 May 2017

Accepted 11 July 2017

Available online 12 July 2017

Keywords:

Self-healing polymer

Vascular network

Autonomous

Epoxy-amine

Glass transition temperature

ABSTRACT

To increase the durability and reliability of thermosets, self-healing via a vascular network, is developed. A judicious choice of healing agents proves to be necessary to achieve the best recovery of properties. Four low viscosity two-component epoxy-amine healing systems were compared, to check which glass transition temperature range would be best to recover mechanical properties (T_g ranging from -8 to 68 °C). Interdiffusion experiments show that all systems react sufficiently slowly at room temperature to allow interdiffusion of epoxy and amine over more than 1 mm before the diffusion is stopped by vitrification. Swelling tests revealed that most of the selected healing agents diffuse into the surrounding matrix and swell it. This might be beneficial for crack closure and improved adhesion between healing system and matrix. Flexural tests demonstrated that, the higher the glass transition temperature of the fully cured healing system, the higher the healing capability.

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1. Introduction

Thermosetting polymers and polymer composites have seen a significant increase in use over recent decades due to main advantages such as light weight, good processability and chemical stability under atmospheric conditions. Despite their success, reliability and durability are still problematic for structural applications due to the creation of microcracks as a consequence of mechanical stress and cyclic thermal fatigue in these brittle polymers. This emphasizes the need for self-healing polymers that are able to repair themselves in an autonomous way and recover their initial functionality when the healing mechanism is triggered by a crack formed in the matrix [1–3].

The self-healing mechanism can be extrinsic or intrinsic. When extrinsic, the healing mechanism is based on healing agents, pre-embedded in capsules [3–8], hollow fibres [9–11] or vascular networks [12–15], that can be carried rapidly to the damaged site. When a crack forms it triggers the delivery of the healing agents and allows autonomous healing without manual intervention [1,16]. When intrinsic, the self-healing mechanism is inherent to the chemical nature of the polymer and doesn't require major external

input such as vasculcs, but generally an external stimulus (heat [17,18], light [19,20], etc) is required, often making the system non-autonomic.

Capsule-based self-healing systems are by far the most studied, but have a few important drawbacks, such as the inability of repeated healing at a given location [21,22], the large size of the capsules (10–1000 μm) [23] and the large volume fraction of microcapsules needed to heal cracks at an early stage. Moreover, achieving the required dispersion of the microcapsules and/or the catalyst to cover the whole substrate can be problematic [24]. In contrast, vascular networks permit repeated healing in the same location, and allow the healing agents to reach more distant points of the substrate, thus increasing the available volume of healing agent to repair a crack, and could in principle replenish the system. Some vascular systems with channel diameters between 200 μm and 2.5 mm have been discussed in literature [12,25,26]. The large channels, however, reduced the mechanical properties of the material.

The overall objective is the development of an autonomous self-healing polymer that uses a vascular network of submicron (830 ± 130 nm) channels. In this paper, the focus will be on the selection of a two-component epoxy-amine healing chemistry to autonomously self-heal an epoxy thermoset. Although epoxy-amine systems for self-healing [7,27,28] have been extensively studied, only few studies compared several epoxy-amine pairs [29],

* Corresponding author.

E-mail address: Audrey.Cuvellier@vub.be (A. Cuvellier).

and to our knowledge none studied the influence of T_g of the healing system on the healing capability, when autonomic healing at ambient temperature. The healing agents are combined in healing systems for which the glass transition temperatures at full cure ($T_{g, x=1}$) are below, around and above room temperature, to study the influence of the $T_{g, x=1}$ of the healing system on the healing capability. $X = 1$ indicates that full conversion is reached, and thus that at least one of the reagents is depleted.

2. Materials

Triethylenetetramine (TETA), poly(propylene glycol) diglycidyl ether (PPGDE) and trimethylolpropane triglycidyl ether (TMPTE) were purchased from Sigma Aldrich, Jeffamine D 230 polyetheramine (JEFF D230) and Jeffamine D 400 polyetheramine (JEFF D400) were from Huntsman. These epoxy resins and amines were used in different combinations for the healing systems. The chemical structure, purity, viscosity and molar mass of the healing agents are given in Table 1. The original epoxy thermoset matrix was prepared using RIMR 135 Epikote resin (mainly contains diglycidyl ether of bisphenol A) and RIMH 137 Epikure curing agent (mainly contains alkyletheramines and isophorone diamine) in a 100:30 weight ratio, both purchased from Hexion. Food-grade pullulan with a molar mass of 200 kDa and a density of 1.85 g cm^{-3} , kindly provided by Hayashibara Biochemical Laboratories Inc., was used to prepare electrospun submicron polysaccharide fibres.

3. Experimental

3.1. Preparation of the vascularised thermosets

The vascular network was prepared by embedding electrospun sacrificial polysaccharide (pullulan) fibres into the thermoset epoxy matrix. To electrospin the fibres, the polymer solution (25 wt% of pullulan) was pumped with a flow rate of 1 mL h^{-1} through a nozzle with an inner diameter of 1.024 mm. The tip to collector distance was 20 cm and the voltage was varied between 15 and 30 kV. The setup is composed of a voltage source (Glassman High Voltage Series EH30P3), an infusion pump (KD Scientific Syringe Pump Series 100), and a grounded collector plate, and is operated in a climate chamber (Weiss WK 340/40). The solution was electrospun at $23 \pm 1.5 \text{ }^\circ\text{C}$ and $50 \pm 3\%$ relative humidity. For the thermoset epoxy matrix, RIMR135 and RIMH137 were mixed for about 10–15 min and degassed under vacuum. Mats of electrospun

polysaccharide fibres were placed in the mould in between peel plies and glass fibre meshes. Next, the fibre mats were impregnated with resin by vacuum-assisted resin transfer. The composites were cured for 24 h at ambient temperature and subsequently post-cured for 15 h at $80 \text{ }^\circ\text{C}$ to obtain an epoxy with a glass transition temperature of $87 \text{ }^\circ\text{C}$. After curing, samples of the required dimensions were cut from the cured composite plate ($300 \text{ mm} \times 300 \text{ mm} \times 3 \text{ mm}$). The polysaccharide fibres were dissolved by immersing the composite pieces in water under stirring, leaving a network of interconnected submicron channels behind (Fig. 1). More details can be found in Ref. [30]. The samples discussed in this paper contained 9 vol% of channels that were $830 \pm 130 \text{ nm}$ wide. Samples of virgin (non-vascularized) epoxy thermoset were prepared using the same curing conditions and cut to the required size.

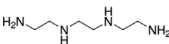
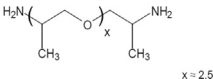
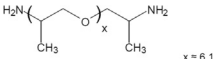
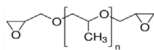
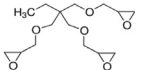
3.2. Methods

DSC experiments were performed on a DSC Q2000 from TA instruments. Nitrogen was used as a purge gas, with a flow rate of 50 mL min^{-1} . A T4P calibration was performed using sapphire, and temperature and enthalpy were calibrated using indium.

To measure the glass transitions at full cure ($T_{g, x=1}$) of the healing systems, samples were cured 4 days at room temperature and 15 h at $50 \text{ }^\circ\text{C}$. For the TETA/TMPTE system, an additional post cure of 5 h was done at $80 \text{ }^\circ\text{C}$ to reach full cure. Determination of $T_{g, x=1}$ was done using a modulated temperature experiment with a modulation amplitude of 0.25 K and period of 30 s, at a heating rate of 2.5 K min^{-1} from $-70 \text{ }^\circ\text{C}$ to $100 \text{ }^\circ\text{C}$.

Microcalorimetry experiments were performed under isothermal conditions at $25 \text{ }^\circ\text{C}$ using a TA Instruments TAM III. To study the reaction kinetics, samples of mixed healing agents (mass between 1 and 1.15 g) were introduced into 4 mL glass ampoules. When performing microcalorimetry, the sample was first introduced in an equilibration position for 15 min, and then moved into the measuring position inside one of the microcalorimeter channels. The data points recorded over the first 45 min are considered unreliable due to the slow response of the device. For fast reactions, this implies a non-negligible amount of heat flow is not correctly measured, which is why the estimated initial heat flow value is obtained by extrapolation for the first hour of reaction. This heat is then added to the measured heat, determined by integration. From this value (in J.g^{-1}), the heat of reaction (kJ.mol^{-1}), is calculated by dividing by the concentration of reactive functional groups (epoxy or N-H) in mol.g^{-1} of the healing agent that will be depleted first.

Table 1
Structure, molar mass (g.mol^{-1}), viscosity (mPa.s) and purity of the different healing agents.

Abbreviation	Structure	Molar mass (g.mol^{-1})	Viscosity (mPa.s)	Purity (%)
TETA		146	20	70
JEFF D230		230	9	Min 97%
JEFF D400		430	22	Min 97%
PPGDE		380	30–60	n.a.
TMPTE		302	120–180	n.a.

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