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Investigation of interpenetrating polymer networks for self-healing applications

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ABSTRACT

Self-healing techniques can enhance the durability and reliability of thermosetting polymer systems. This research discusses thermally induced healing of Interpenetrating Polymer Networks (IPNs) with varying percentages of linear polymer. An *in situ* sequential IPN system was developed using diglycidyl ether of bisphenol A (DGEBA) cured with 4,4′-methylene biscyclohexanamine as the cross-linked phase and poly(methacrylated phenyl glycidyl ether) (pMPGE) as the linear polymer phase. It was hypothesized that upon healing, diffusion of linear polymer to the crack interface could aid in crack healing. The polymer network without linear polymer had a healing efficiency of 52% after the first healing cycle, dropping to 25% after the fourth healing cycle. IPNs with varying amounts of pMPGE had healing efficiencies ranging from 40% to 52% after the first healing cycle. Healing efficiencies dropped to 27–39% after the fourth healing cycle. The incorporation of linear polymer allowed for greater retention of healing efficiency over consecutive healing cycles.

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1. Introduction

Polymers are susceptible to damage in the form of cracks induced by thermal and mechanical fatigue as well as static and impact loading. While critical modes of damage are application specific, once cracks have formed within polymeric materials, the integrity of the structure is compromised and the product lifetime may be significantly shortened. In recent years there has been increasing interest in self-healing materials that can recover mechanical properties to mitigate loss of performance due to microcrack formation and propagation. This can be achieved autonomously or via an external force like heat or change in pH [1–4]. Self-healing materials offer the potential of longer product lifetimes and increased safety. These materials could be of particular use in structures that are at present impractical or impossible to repair.

A variety of self-healing techniques have been reported to date. Research focused on thermoplastic crack healing was performed in the late 1970s and early 1980s [5–9]. The two main methods of self-healing investigated today consist of: (1) Incorporating a healing agent within a polymer network, whether with microcapsules, hollow fibers, or microvascular networks [1,10–12] and (2) Relying on the inherent ability of physical or covalent interactions to reform bonds across a crack interface [2,13–15].

The goal of this research was to develop an *in situ* forming interpenetrating polymer network (IPN) of a mobile linear polymer within a cross-linked polymer. The physical properties and healing ability of the IPNs were investigated. This work is motivated by previous work by the authors on healing of unmodified epoxy–amine thermosets [16]. Fully reacted stoichiometric formulations of epoxy–amine thermosets were capable of recovering up to 68% of the fracture load. Healing of thermoset-thermoplastic composites has been previously demonstrated [17–19]; however, these systems consisted of a preformed thermoplastic phase that was blended with the thermosetting resin. One strategy uses a highly miscible linear polymer and epoxy thermoset [17] while the other uses a phase-separated blend of epoxy and poly(ε-caprolactone) [19]. Healing efficiencies of up to 77% were reported for the miscible system, and values for the phase-separated system exceeded 100% under certain conditions. Healing of IPNs is intriguing because it is a solid-state approach to strength recovery. Unlike encapsulation methods, no liquid-filled phases are included within the system, potentially simplifying processing and making healing possible for applications where liquid-based healing is not appropriate.

It should be noted that all solid-state healing approaches require external heating. Additionally, there is no inherent ability to sense damage. Plaisted et al. demonstrated that the incorporation of electromagnetic (copper) elements within fiber-reinforced composites provided damage sensing as well as a method for heating [20]. Park et al. induced healing by applying electrical current to a carbon-fiber reinforced polymer, using the carbon fibers themselves as heating elements [21]. While both groups focused on healing of a reversibly cross-linking network, this technique could also be applied to healing of IPN networks within a fiber-reinforced composite. Since pressure could not necessarily be applied to a composite structure in the field, it is important that cracks are detected and healed while still on a very small scale where intimate contact between the crack surfaces is still possible.

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Damage in polymers and fiber-reinforced polymers may consist of microcracks or larger scale damage, depending on the crack-forming event. Fatigue-induced damage often presents as microcracks that, over time, propagate and coalesce to form macroscale cracks. Larger open cracks can also result from impact. These larger cracks have greater volumes and surfaces that are not in contact with each other, making their repair more difficult and better suited to liquid-based healing systems. The healing approach reported herein is appropriate for healing of microcracks within polymers or fiber-reinforced polymers, preventing crack propagation to larger scale catastrophic damage.

The following report contains the first example of a healable thermoset-thermoplastic composite in which monomers for both phases are combined, and polymerizations proceed sequentially and independently of each other. As a result, this system could provide improved processing properties and single pot curing, making it a good candidate as a resin system for fiber-reinforced polymers.

2. Material and methods

2.1. Materials

Diglycidyl ether of bisphenol A (DGEBA) with $n = 0.13$ (EPON 828, Miller-Stephenson), 4,4′-methylene biscyclohexanamine (PACM, Air Products), phenyl glycidyl ether (PGE, Sigma–Aldrich), and methacrylic acid (Sigma–Aldrich) were used as received. AMC-2 (Aerojet Fine Chemicals), a chromium-based esterification catalyst, and hydroquinone (99%, Sigma–Aldrich) were used as received for methacrylation. Trigonox 239A initiator (45 wt.% cumyl hydroperoxide, 45 wt.% carboxylic ester, 10 wt.% cumyl acid, Akzo-Nobel) and CoNap-All (OM Group), a cobalt naphthenate catalyst containing 6 wt.% cobalt, were used to induce thermoplastic polymerization.

2.2. Polymer synthesis

Methacrylated phenyl glycidyl ether (MPGE) was synthesized by the reaction of PGE with 1.01 times the stoichiometric amount of methacrylic acid. The reaction was conducted in the presence of 1 wt.% AMC-2 and 0.05 wt.% hydroquinone for 1 h at 70 °C and 2 h at 90 °C [22,23].

The IPNs were prepared with varying amounts (0–40 wt.%) of MPGE added to a stoichiometric mixture of DGEBA and PACM. Polymerization of MPGE required 1.5 wt.% Trigonox and 0.375 wt.% CoNap with wt.% of both referring to amount of MPGE. Components were combined and cast to produce polymer blocks.

The *in situ* IPN was synthesized sequentially. Reaction mixtures were pre-cured at room temperature (~23 °C) for 2 h. In this stage, MPGE was reacted to form linear polymer dissolved in epoxy and amine monomers. The system was then cured at 80 °C for 2 h and post-cured at 175 °C for 1 h to achieve full reaction of epoxide and amine groups [16,24]. A schematic of the *in situ* sequential IPN curing process is shown in Fig. 1. The degree to which the polymers are formed sequentially is discussed later.

2.3. Fourier transform infrared (FT–IR) spectroscopy

FT–IR spectroscopy was performed using a Nicolet Nexus 670 Spectrometer with a deuterated triglycine sulfate (DTGS) detector and KBr beam splitter. The resolution was set at 8 cm^{-1} and 32 scans were taken per spectrum. Epoxide group consumption was monitored using the characteristic peak at 4528 cm^{-1} [16]. The peak at 6160 cm^{-1} was used to monitor methacrylate group reaction [25].

2.4. Dynamic mechanical analysis

Glass transition temperatures (T_gs) were measured using a Dynamic Mechanical Analyzer (DMA, TA Instruments model 2980) in single cantilever bending mode with sample dimensions 35 mm × 12.8 mm × 3.2 mm. Tests were conducted at a heating rate of 2 °C min^{-1} from room temperature to 200 °C, an oscillating frequency of 1.0 Hz, and an amplitude of 15 μm. T_g was defined as the peak in the loss modulus curve of the second testing cycle.

2.5. Soxhlet extraction

Soxhlet extraction was conducted to determine the solvent soluble fractions, such as polymerized MPGE (pMPGE), of the IPN [26]. This information was compared with the amount of MPGE used in the IPN in order to ascertain the potential mobility of the linear polymer phase. Fully cured samples were finely ground, placed in a porous cellulose thimble, and extracted in tetrahydrofuran (THF, Sigma–Aldrich). Samples were removed after 4 h, dried and then weighed. The difference between initial and final weights is expected to be the amount of mobile pMPGE available for healing via diffusion across a crack surface.

2.6. Modified compact tension mechanical testing

Compact tension specimens of dimensions 14 mm × 15 mm × 6 mm were prepared in accordance with ASTM D5045-99. Specimens were modified from this standard with the addition of a crack-arresting hole drilled at a distance of 3.5 mm from the notched end. This modification provides improved realignment of crack surfaces during healing [27] and is representative of the microscale cracks that solid-state healing systems, such as the ones tested, are designed to heal. A pre-crack was formed in virgin samples by lightly tapping a sharp razor blade in the base of the notch.

Prior to healing, virgin specimens were loaded to failure using an Instron 8872 with a 1 kN load cell at a crosshead speed of 0.10 mm min^{-1}. Four specimens were tested for each condition. The maximum load (P_0) was recorded. Fractured specimens were healed in a Carver Laboratory Press at 165 °C and 13 MPa for 1 h

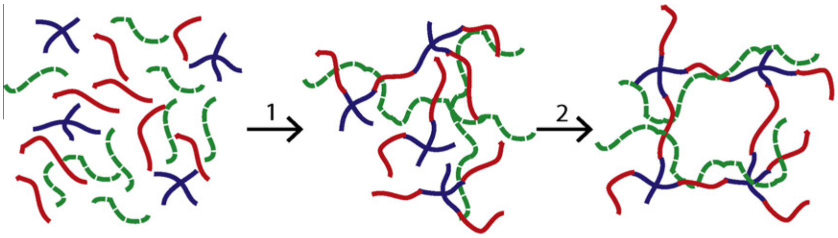

Fig. 1. Synthesis of the *in situ* sequential IPN network. Left: Monomers are mixed together, with green dashed lines representing MPGE, red lines representing DGEBA, and blue crosses representing PACM. Middle: All MPGE is reacted and some of the cross-linked polymer has formed. Right: The cross-linked network fully forms. Conditions: 1. 23 °C 2 h, 2. 2 h 80 °C, 1 h 175 °C. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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