Polymer 74 (2015) 254–261

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Self-healing thermoplastic-toughened epoxy

A.R. Jones [a, b], C.A. Watkins [c, b], S.R. White [d, b], N.R. Sottos [c, b, *]

[a] Department of Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, 1206 W. Green St., Urbana, IL, 61801, USA
[b] Beckman Institute for Advanced Science and Technology, 405 N. Mathews, Urbana, IL, 61801, USA
[c] Department of Material Science and Engineering, University of Illinois at Urbana-Champaign, 1304 W. Green St., Urbana, IL, 61801, USA
[d] Department of Aerospace Engineering, University of Illinois at Urbana-Champaign, 104 S. Wright St., Urbana, IL, 61801, USA

ARTICLE INFO

Article history:
Received 15 May 2015
Received in revised form
15 July 2015
Accepted 19 July 2015
Available online 21 July 2015

Keywords:
Thermoplastic-toughened epoxy
Self-healing
Microcapsule

ABSTRACT

A thermoplastic resin poly(bisphenol A-co-epichlorohydrin) (PBAE) is blended with a high glass transition temperature (T_g) epoxy matrix to serve as both a toughening additive and a healing agent in combination with an encapsulated solvent. Microcapsules are coated with poly(dopamine) (PDA) to improve the thermal stability and retain the core solvent during curing at 180 °C. The fracture toughness of the high T_g epoxy (EPON 828: diamino diphenyl sulfone) is doubled by the addition of 20 wt % PBAE alone and tripled by the addition of both microcapsules and the thermoplastic phase. Self-healing is achieved with up to 57% recovery of virgin fracture toughness of the toughened epoxy. Healing performance and fracture toughness of the self-healing system remain stable after aging 30 days. The relative amount of thermoplastic phase and the presence of solvent-filled microcapsules influence the storage modulus, T_g, and healing performance of the polymer.

1. Introduction

Self-healing material systems are designed to repair damage autonomously, without external intervention. Healing strategies vary from requiring some external intervention (i.e. heat or pressure) to fully autonomous systems that possess the ability to heal without intervention. To date, three primary types of healing strategies have been demonstrated including microcapsule, microvascular, and intrinsic approaches [1]. For microcapsule-based systems, healing agents are sequestered in microcapsules, which are dispersed in a host matrix. Healing is triggered by damage that ruptures the embedded microcapsules, releasing the healing agents and promoting the formation of new material within the damaged area. Microvascular systems sequester the healing agent(s) within a network of microchannels enabling continuous and/or repeated delivery during repetitive damage. Intrinsic approaches are predicated on reversible bonding (e.g. hydrogen, ionic) to provide self-healing functionality.

Previous microcapsule-based systems have lacked stability at the manufacturing temperatures common for commercial epoxies and composites (ca. 121 °C to 177 °C). For autonomous healing in high performance composites, the encapsulated healing agents must react at room temperature (during healing), but resist degradation or premature reaction during the curing of the host matrix material [2]. The selection of a healing chemistry that fulfills these two competing requirements remains a significant technical challenge. In prior work, exposure of self-healing materials to high temperatures during postcure regularly reduced healing performance. Mangun et al. [3] reported ca. 52% recovery of fracture toughness with a poly(dimethyl siloxane) healing chemistry in an epoxy matrix postcured at 100 °C for 1 h. However, a higher postcure temperature of 177 °C for 4 h reduced the healing efficiency to 28%. Jin et al. [4] achieved higher healing efficiencies (ca. 80–90%) with a multi-capsule amine/epoxy healing chemistry. However, a postcure of 121 °C for 1 h decreased healing to ca. 30–40% recovery. By tuning the healing chemistry, Jin and co-workers drastically improved performance to 90% recovery after a postcure of 150 °C for 6 h, but only achieved 60% recovery after a postcure of 177 °C for 3 h [2]. Zhang et al. [5,6] also developed an amine/epoxy healing chemistry, but observed a reduction from 60% to 40% healing efficiency after modest heat treatment temperatures (max. 80 °C). Yaun et al. [7] reported high healing efficiencies (ca. 100%) after thermal postcures (up to 180 °C for 4 h) and heat treatments (up to 250 °C) by using a high loading of amine/mercaptan and epoxy microcapsules in several different epoxy systems, with fracture toughnesses ranging from 0.5 to

* Corresponding author. Beckman Institute for Advanced Science and Technology, 405 N. Mathews Ave., Urbana, IL, 61801, USA.
E-mail address: n-sottos@illinois.edu (N.R. Sottos).

http://dx.doi.org/10.1016/j.polymer.2015.07.028
0032-3861/

1.0 MPa $m^{0.5}$.

Higher cure temperatures lead to improved mechanical properties, such as fracture toughness and elastic modulus of epoxy, which are critical for aerospace and other high performance applications. Fracture toughness is commonly increased through the addition of fillers or a thermoplastic phase [8,9]. Thermoplastic phases have also been used to repair crack damage upon heating [10]. Hayes et al. blended the thermoplastic poly(bisphenol-A-co-epichlorohydrin) (PBAE) with epoxy to achieve 70% recovery of fracture toughness after a heat treatment of 130 °C for 1 h [11]. Luo and co-workers reported fast recovery (8 min) using a poly-(caprolactone) thermoplastic additive and exposure to a temperature of 190 °C [12]. Pingkarawat et al. have reported up to 200% recovery of interlaminar fracture toughness in carbonfiber reinforced composites with poly[ethylene-co-(methacrylic acid)] (EMMA) following a heat treatment of 150 °C for 30 min [13]. Each of these systems demonstrated high healing performance, but only after external heat treatment.

In this work, we use the thermoplastic additive PBAE to simultaneously toughen and self-heal, with the aid of an encapsulated solvent, ethyl phenyl acetate, in a high temperature cured epoxy. High temperature capsule stability is achieved through the use of a high boiling point solvent, ethyl phenyl acetate (EPA), and a robust coating of poly(dopamine) (PDA) on the microcapsules. A damage event triggers the rupture of microcapsules, releasing the solvent (EPA) into the crack plane. Locally, the thermoplastic dissolves and redistributes in the damage region, followed by diffusion and eventual evaporation of the solvent. To characterize this healing event, we vary healing cycle time and thermoplastic loading. The combination of a thermoplastic additive and an encapsulated solvent is a motif that can be translated to other thermosetting matrices to achieve synergistic toughening and self-healing.

2. Experimental

2.1. Materials

Urea, ammonium chloride, resorcinol, formalin (37 wt % formaldehyde), octanol, dopamine hydrochloride, ammonium persulfate, sodium phosphate monobasic monohydrate, sodium citrate dihydrate, ethyl phenyl acetate (EPA), diamino diphenyl sulfone (DDS), and poly(bisphenol A-co-epichlorohydrin) (PBAE) were purchased from Sigma Aldrich and used as received. Ethylene maleic-co-anhydride (EMA) copolymer (ZeMac E400, Vertellus) was prepared in a 2.5% w/v aqueous solution and used as a surfactant. Desmodur L75 was generously supplied by Bayer as a polyurethane prepolymer. EPON 828 epoxy resin was purchased from Miller–Stephenson. Araldite LY 8605 epoxy resin and Aradur 8605 hardener were purchased from Huntsman.

2.2. Synthesis of microcapsules

Capsules were prepared using a double shell wall technique previously described by Caruso et al. [14]. In this technique, polyurethane prepolymer (Desmodur L75) undergoes a rapid interfacial polymerization forming the inner shell wall, which is followed by an in situ polymerization of urea and formaldehyde. An aqueous solution of surfactant (EMA) and shell wall formers (urea, ammonium chloride, and resorcinol) was prepared and the pH was adjusted to 3.5 by dropwise addition of sodium hydroxide. The core material was comprised of ethyl phenyl acetate (EPA) and 0.05 g of Desmodur L75 per mL of EPA. The core solution was then slowly added to the aqueous solution and allowed to emulsify for 20 min at 400 rpm. Formalin was added to the encapsulation mixture and the temperature of the control bath was slowly ramped to 55 °C at 1 °C/min for 4 h. After the reaction was complete, the microcapsules were recovered by filtration and sieved to be between 75 and 250 μm in diameter.

Dry microcapsules were subjected to a second process, in which a coating of poly(dopamine) (PDA) was uniformly deposited on the outer shell, following a process described by Kang et al. [15]. Ammonium persulfate was used to oxidize the catechol moieties in dopamine hydrochloride, thus producing quinine which polymerizes to form PDA. Microcapsules (3 g) were added to 36 ml of buffer solution (pH = 7.0), 0.66 g of dopamine hydrochloride, and 0.66 g of ammonium persulfate. The reaction was allowed to continue for 24 h at room temperature under agitation. Capsules were again recovered by filtration.

2.3. Characterization of microcapsules

The microcapsule size distribution was obtained by image analysis of a minimum of 200 microcapsules. Scanning electron microscopy (SEM) was used to examine shell wall morphology. The thermal stability of the microcapsules was first evaluated using thermogravimetric analysis (TGA). TGA was performed by ramping the temperature from room temperature up to 180 °C at 10 °C/min

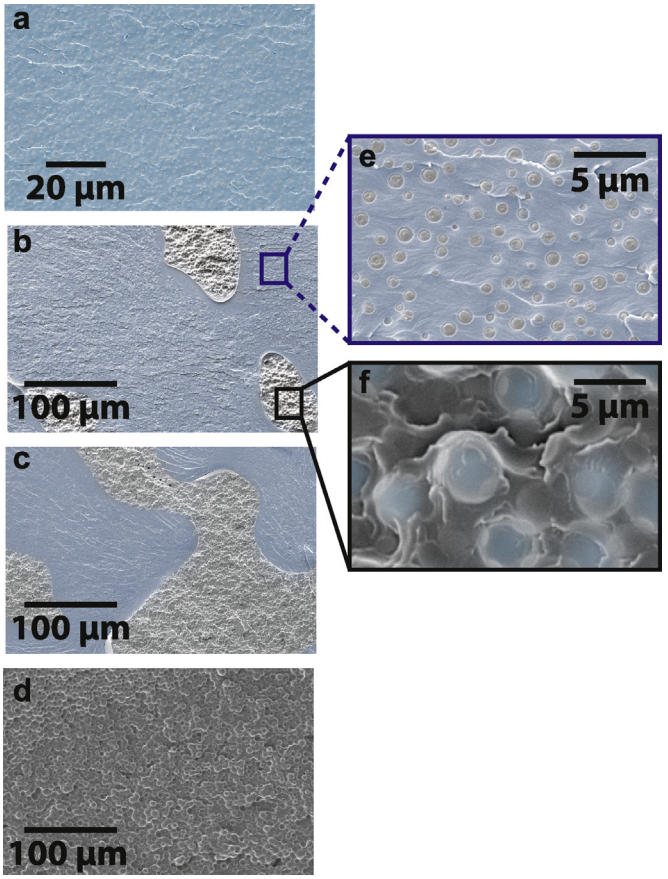

Fig. 1. Phase morphology of thermoplastic/epoxy blends. SEM images of the fracture surface morphology (epoxy = blue, PBAE = gray) with increasing wt % PBAE: (a) 10 wt % PBAE, (b) 15 wt % PBAE, (c) 20 wt % PBAE, and (d) 25 wt % PBAE. At 10 wt % PBAE, small thermoplastic particulates were dispersed in an epoxy matrix (shown at a higher magnification in (e)). As the wt % of PBAE increased, bi-continuous phase separation was observed with both thermoplastic particulates in an epoxy matrix (e) and phase inversion, consisting of epoxy regions coated with a thermoplastic matrix (f). Phase inversion increasingly dominated the surface morphology until full phase inversion was observed at 25 wt % PBAE. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)