Rigid epoxy networks with very high intrinsic fracture toughness using a piperazine-based in-situ polymerization strategy

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Abstract

Various fillers and thermoplastics are often added to thermoset epoxies to improve toughness, but this may compromise their other properties or make synthesis difficult. In this study, brittle crosslinked epoxy networks are significantly toughened through in-situ polymerization of epoxy using piperazine, which reacts at moderately low temperatures in a catalyst-free one-pot method. Dynamic mechanical properties and nanoscale morphology suggest the mechanism for improved toughness is higher yielding near the crack tip due to increased molecular weight between crosslinks. The resulting toughness (K_{IC}~2.12 MPa√m, G_{IC}~1.96 kJ/m^2) is higher than any other unfilled all-epoxy materials found in the literature.

Keywords: thermoset epoxy; thermoplastic epoxy; fracture toughness

1. Introduction

Thermosetting epoxy resins are widely used for high-performance applications due to their thermal

stability, high stiffness and strength. However, their very brittle nature has led to various strategies for improving the fracture toughness (K_{IC}, G_{IC}), including soft and hard fillers or thermoplastic particles [1-7]. Phase separation results in crack bifurcation and thus increases toughness, with G_{IC} increasing by as much as 7.5 times (1.5 kJ/m^2, 10 wt% PMMA copolymer) [4]; however, extensive phase separation between the thermoplastic and epoxy matrix can negatively affect other properties [3,4]. To improve compatibility of the chemical structures, thermoset epoxy networks have been filled with thermoplastic epoxies synthesized using aniline and alkylamine, but K_{IC} only reached a maximum of 1.5 MPa√m (15 phr loading) [8,9]. Achieving higher toughness while maintaining stiffness and strength requires a new approach involving the synthesis of a highly compatible chemical structure [1,10].

In this study, for the first time, a facile in-situ polymerization method is proposed, wherein the aromatic diamine crosslinker is partially replaced with piperazine—a cyclic secondary diamine—and thermoplastic epoxy phases are formed with a chemical structure nearly identical to the host epoxy network (Fig. 1(a)). This results in exceptional fracture toughness in a model bisphenol-A epoxy/aromatic amine system, much higher than previous reports of similar materials in the literature. These results are expected to have significant impact on epoxy-based composites and coatings for a variety of applications.

2. Materials and methods

2.1 Materials and synthesis

Bisphenol A epoxy monomer (DGEBA, 340.42 g/mol), piperazine anhydrous (PZ, 86.14 g/mol), and

4,4'-methylenedianiline (MDA, 198.26 g/mol) were used as-received. The in-situ polymerized alloy (All-E) contained DGEBA:MDA:PZ at the molar ratio 4:1:2 so that 50 mol% of DGEBA was reacted with PZ and MDA each. For comparison, a fully crosslinked epoxy network (Ts-E) and a fully linear epoxy thermoplastic (Tp-E) were also synthesized by reacting DEGBA with MDA (molar ratio 2:1) or PZ (molar ratio 1:1), respectively. For Tp-E, PZ was mixed into DGEBA by centrifugal mixing then poured into a Teflon mold and polymerized at 80 °C. Ts-E and All-E were synthesized by mixing MDA into DGEBA by repeated centrifugal mixing and degassing at 80 °C, then the mixtures were poured into Teflon molds and cured at 120, 150, and 180 °C for 2 hr each; for All-E, PZ was added before the last cycle of centrifugal mixing and degassing The resulting 5 mm-thick plates were cut into specimens for three-point bending ($100\times10\times5$ mm^3) and single-edge notch bending (SENB) specimens ($50\times10\times5$ mm^3).

2.2 Characterization

Three-point flexural tests (ASTM D790) and SENB tests (ASTM D5045) were performed on an electromechanical testing machine at a crosshead speed of 1 mm/min. Fracture morphology was observed by optical microscope (OM) and atomic force microscope (AFM). Dynamic mechanical analysis (DMA) was performed in double-cantilever mode under N_2 atmosphere over a temperature range -100–200 °C and frequency range of 0.01–100 Hz. Differential scanning calorimetry (DSC) was performed under N_2 atmosphere over a temperature range 0–200 °C at a heating/cooling rate of 10 °C/min. The chemical structure of the polymers was determined by FTIR and NIR over the range 500-8000 cm^{-1}.

3. Results and discussion

3.1 Polymer structure and dynamics

Minor amounts of unreacted epoxide groups and secondary amine groups were found in Tp-E, representing the terminal groups of chain ends and suggests the molecular weight is moderately high (Fig. 1(b)), but such peaks were not observed for Ts-E or All-E. Tp-E shows a higher content of CH_2 groups due to the presence of piperazine, while Ts-E and All-E show higher aromatic content due to MDA.

Thermal and mechanical properties of the epoxy polymers are summarized in Table 1. The molecular weight between crosslinks (or entanglements) was estimated from rubber elasticity theory ($M_c = 3\rho RT/E'$) [11], revealing larger M_c as PZ content increases. This is reflected by the T_g, or the α-relaxation, which decreases with PZ content due to less constraint. The β-relaxation associated with the motion of small chain segments—such as hydroxyl or methylene groups, cyclic amines, and phenylene rotation—occurs at higher temperature as the crosslink density increases due to the conformation constraint caused by chemical crosslinks (Fig. 1(c)). This relaxation process strongly influences the room-temperature mechanical properties, and are determined by both the chemical structure and nanoscale morphology [1,10,12]. The aliphatic structure of PZ is likely the source of lower β-relaxation temperature and higher β-relaxation energy barrier, since it is the main variable. Unlike most epoxy-based blends employing thermoplastic phases [1-7], no phase separation was expected or observed for All-E since the chemical structures of all three epoxy polymers are similar, with differences in the physical morphology arising

from different values of M_c. The flexural modulus (E_b) decreases with PZ content, since the crosslink density (ν_e) strongly effects the network stiffness. However, flexural strength (σ_b) is highest for the alloy All-E due to the improved plastic deformation ability of long chains between crosslinks, whereas Ts-E is too brittle to reach higher flexural stresses before reaching a critical fracture strain. Higher ν_e results in higher stiffness, but not necessarily higher strength [11]. This is reflected by the linear relationship between flexural toughness (U_f, measured by the area under the stress-strain curve) and K_{IC} (Table 1).

3.2 Fracture toughness

Fig. 1(e) summarizes the fracture properties of the polymers in this study. Ts-E shows low toughness (0.83 MPa√m) typical of MDA-cured epoxy networks [6,10], while Tp-E is tougher (3.59 MPa√m) than common thermoplastics such as PA6 or PMMA due to its hybrid aromatic/aliphatic backbone structure. Incorporating this chain structure into the MDA-cured epoxy vastly improves the network's toughness by over 150%, which far exceeds other reports on thermoplastic epoxy-modified networks [2-4] and PES-modified DGEBA/MDA networks [5,6]. The fracture surfaces from SENB tests revealed extensive plastic deformation extending from the notch tip in Tp-E (Fig. 2(a)). Ts-E was predictably brittle with a small process zone near the notch tip followed by a mirror-like surface, and All-E was similar except for more plastic deformation in the notch tip vicinity. However, AFM observation of the nanoscale morphology in the mirror-like region far away from the notch tip revealed increasing surface roughness (R_a) with PZ content. This is due to the increase in M_c, which results in a higher degree of yielding ahead of the crack

tip and thus increased toughness [1,4,9-12]; the correlation between G_{IC} and R_a is shown in Fig. 2(b). This mechanism is further corroborated by DMA results. A strong correlation was observed between the activation energy barrier for β-relaxation and K_{IC} (Fig. 2(b)), suggesting that greater energy is dissipated through segmental motions of longer epoxy chains containing flexible PZ moieties [12]. This yield-based intrinsic toughening mechanism is illustrated in Fig. 2(c). See the Supporting Information for details on the determination of fracture toughness and E_β.

4. Conclusions

We report a facile one-pot approach to synthesizing an aromatic amine-cured epoxy network with significantly improved fracture toughness by using piperazine as a localized in-situ chain extender, creating a so-called epoxy alloy. The stiffness and T_g of the network decrease slightly with 50% molar replacement of aromatic diamine, but using the thermoplastic epoxy with a similar chemical structure to the host epoxy network prevents the large reductions commonly seen with long-chain amine additives. With further optimization of starting monomers, this approach will lead to the development of high-performance epoxy-based materials with very high toughness and stiffness.

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References

[1] J. Liu, H. Sue, Z.J. Thompson, F.S. Bates, M. Dettloff, G. Jacob, N. Verghese, H. Pham, Effect of crosslink density on fracture behavior of model epoxies containing block copolymer nanoparticles, Polymer 50 (2009) 4683-4689.

[2] J. Misumi, T. Oyama, Low viscosity and high toughness epoxy resin modified by in situ radical polymerization method for improving mechanical properties of carbon fiber reinforced plastics, Polymer 156 (2018) 1-9.

[3] A. Salazar, S.G. Prolongo, J. Rodríguez, The effect of hygrothermal conditions on the fracture toughness of epoxy/poly(styrene-co-allylalcohol) blends, Mater. Lett. 64 (2010) 167-169.

[4] H. Kishi, K. Yamada, J. Kimura, Control of nanostructures and fracture toughness of epoxy/acrylic block copolymer blends using in situ manipulation of the epoxy matrix reaction type, Polymer 176 (2019) 89-100.

[5] H. Kishi, Y-B. Shi, J. Huang, A.F. Yee, Shear ductility and toughenability study of highly cross-linked epoxy/polyethersulphone, J. Mater. Sci. 32 (1997) 761-771.

[6] N. Odagiri, H. Kishi, D. Lee, T. Okabe, A study of resin fracture toughness: Comparison of particle-toughened thermosetting resin and micro phase-separated thermosetting resin, Mater. Syst. 37 (2020) 29-35.

[7] X. Zhao, Y. Li, W. Chen, S. Li, Y. Zhao, S. Du, Improved fracture toughness of epoxy resin reinforced with polyamide 6/graphene oxide nanocomposites prepared via in situ polymerization, Compos. Sci. Technol. 171 (2019) 180-189.

[8] T. Yang, R. Wang, X. Hou, J. Cheng, J. Zhang, Morphology and high-performance of in-situ self-assemble epoxy resin with side aliphatic dangling chains, Mater. Lett. 166 (2016) 150-153.

[9] D. Chen, J. Li, Y. Yuan, C. Gao, Y. Cui, S. Li, H. Wang, C. Peng, X. Liu, Z. Wu, J. Ye, A new strategy to improve the toughness of epoxy thermosets by introducing the thermoplastic epoxy, Polymer 240 (2022) 124518.

[10] Y.G. Hsu, K.H. Lin, T.Y. Lin, Y.L. Fang, S.C. Chen, Y.C. Sung, Properties of epoxy-amine networks containing nanostructured ether-crosslinked domains, Mater. Chem. Phys. 132 (2012) 688-702.

[11] M. Sharifi, C.W. Jang, C.F. Abrams, G.R. Palmese, Toughened epoxy polymers via rearranged network topology, J. Mater. Chem. A 2 (2014) 16071-16082.

[12] C.L. Soles, A.B. Burns, K. Ito, E. Chan, J. Liu, A.F. Yee, M.S. Tyagi, Importance of sub-nanosecond fluctuations on the toughness of polycarbonate glasses, Macromolecules 53 (2020) 6672-6681.

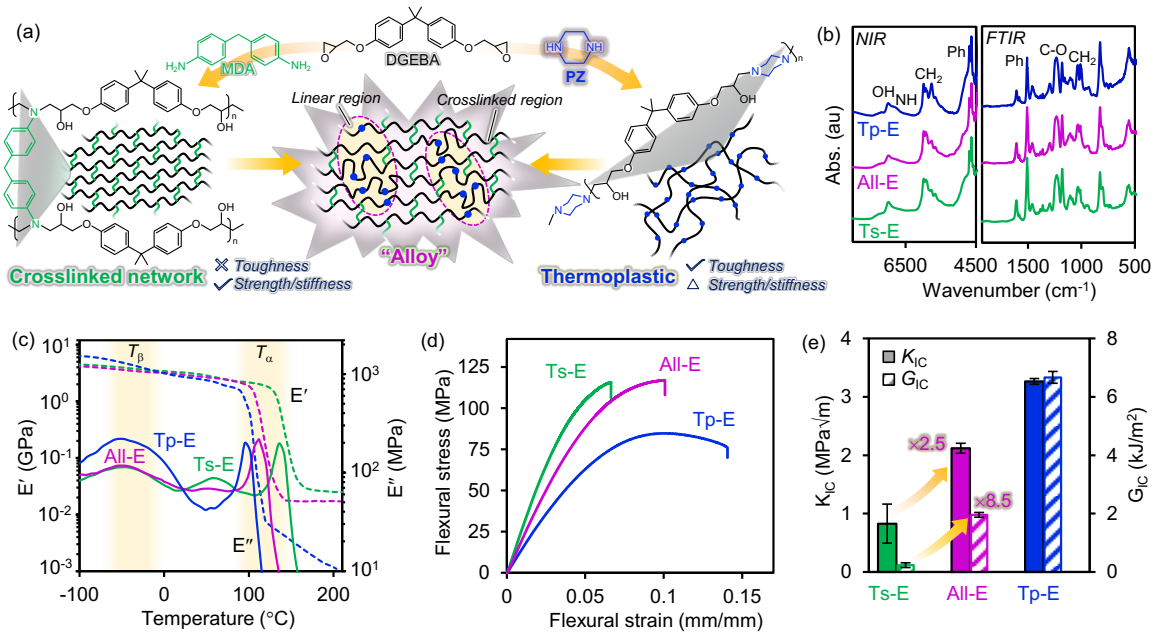

Figure 1. (a) Chemical structure of thermoplastic/thermoset epoxy-based polymers and their in-situ polymerized alloy. (b) FTIR-NIR spectra, (c) storage modulus (E') and loss modulus (E'') curves, (d) flexural properties, and (e) fracture toughness (K_{IC}, G_{IC}).

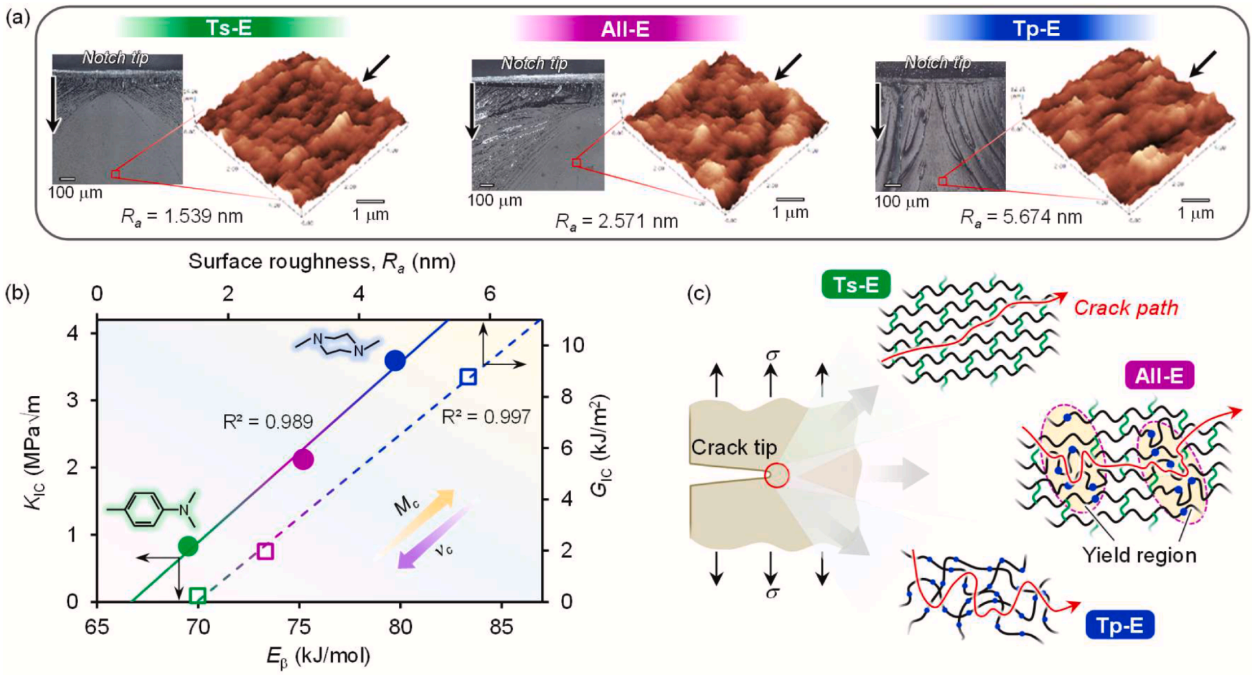

Figure 2. (a) OM images of fracture surfaces near the notch tip and AFM topographical images away from the notch tip (black arrows indicate crack growth direction), (b) relationship between K_{IC} vs E_β and G_{IC} vs R_a, and (c) schematic of the intrinsic toughening mechanism in All-E involving localized shear yielding of the thermoplastic epoxy phases.