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Elastomer/thermoplastic modified epoxy nanocomposites: The hybrid effect of 'micro' and 'nano' scale

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ABSTRACT

The approach of simultaneously exploit the use of microscale elastomers/thermoplastics and nanoscale fillers for the modification of epoxy systems is presently an active research topic. Such hybrid modification of epoxy primarily helps to tailor multiple mechanical properties, without compromising other required properties. The current review reports about the development and properties of multicomponent epoxy systems modified with both elastomers/thermoplastics and nanofillers, on the basis of an updated literature survey. For a better understanding and comparison, the review initially provides a short discussion on key findings in binary blends of epoxy and elastomers/thermoplastic and binary epoxy nanocomposites. Successful studies dealing with multicomponent epoxy systems are also reported, where it is demonstrated that microscale modification individually, sometimes synergistically, enhances the fracture toughness of epoxy without affecting the properties optimized by nanoscale modification. The mutual role of microscale elastomer/thermoplastic and nanoscale filler on morphology, cure reaction, mechanical and thermal properties of epoxy multicomponent system is discussed. The complex interaction between the micro- and nano-phases determines phase separated morphologies in the multicomponent system, essentially related to the function of microscale modifiers in dispersion/intercalation/distribution of nanofillers and to the role of nanofillers in phase separation kinetics and mechanisms. The specific effect of nanofillers in phase separation mechanisms for epoxy blends, that place via nucleation and growth (NG) and spinodal decomposition, is analysed looking at the final morphology and hence performance of multicomponent system. Moreover, the fracture mechanism that operates in such multicomponent epoxy systems is discussed.

Abbreviations: ABS, poly(acrylonitrile-co-butadiene-co-styrene); ATBN, amine-terminated poly(butadiene-co-acrylonitrile); BCPs, block copolymers; BF3.EA, boron trifluoride monoethylamine; CFRP, carbon-fibre reinforced-plastic; CNF, carbon nanofibers; CNT, carbon nanotubes; CRGO, chemically reduced graphene oxide; CRBN, carboxyl-randomized liquid butadiene–acrylonitrile rubber; CSR, core-shell rubbers; CTBN, carboxyl terminated poly(butadiene-co-acrylonitrile); CTPB, carboxyl-terminated polybutadiene; DDA, Dicyanodiamide; DDM, 4, 4′-diaminodiphenylmethane; DDS, 4, 4′-diaminodiphenyl sulfone; Epoxy/SiC/CTBN_M2, Epoxy hybrid by mixing CTBN in sonicated epoxy/SiC mixture; Epoxy/SiC/CTBN_M1, Epoxy hybrid by sonicating SiC nanofibers in epoxy/CTBN mixture; fCNT, *N*-octyl-functionalized CNT; ETBN, epoxy terminated poly(butadiene-co-acrylonitrile); FRP, fibre reinforced-plastic; GFRP, glass fibre reinforced plastic; GO, graphene oxide; GnP, graphene nanoplatelets; HBPs, hyperbranched polymers; HLNR, hydroxyl terminated liquid natural rubber; HNT, halloysite nanotube; HPEEK, hydroxylated poly (ether ether ketone); HPMM, high pressure mixing method; HTBN, hydroxyl-terminated poly(butadiene-co-acrylonitrile); HTPB, hydroxyl terminated polybutadiene; MA, maleic anhydride; MBS, methacrylated butadiene-styrene copolymer; M-NCDSUs, micro-nano constrained damping structure units; MMT, montmorillonite organoclays; MWCNTs, multiwalled carbon nanotubes; MWCNT–COOHs, carboxylic acid functionalised multi-walled carbon nanotubes; MWCNT-NH2s, amino-functionalized multiwalled carbon nanotubes; PA, polyamides; PCL, poly(ε-caprolactone); PEEKMOH, poly ether ether ketone with pendant methyl groups; PEI, poly(ether imide); PEO, poly(ethylene oxide); PEO–PBO, poly(ethylene oxide)-b-poly-(butylene oxide); PEO–PEE, poly(ethylene oxide)-b-poly(ethyl ethylene); PEO–PEP, (ethylene oxide)-b-poly(ethylene-alt-propylene); PEO–PPO, poly(ethyleneoxide)-b-poly(propylene oxide); PEO–PPO–PEO, poly(ethyleneoxide)-b-poly(propylene oxide)-b-poly(ethylene oxide); PES, poly(ether sulfone); PMMA, poly(methyl-methacrylate); PMMA–PS, poly(methyl methacrylate)-b-polystyrene; PR, powdered rubber; PS–PB, polystyrene-b-polybutadiene; PS-PB-PS, poly(styrene-b-butadiene-b-styrene); PS-PEO, poly(styrene-b-ethylene oxide); RIFT, Resin Infusion under Flexible Tooling; RTM, Resin Transfer Moulding; S-CSR, polysiloxane coreshell rubber; SD, spinodal decomposition; SiC NWs, silicon carbide nanowires; VARTM, vacuum assisted resin transfer moulding.

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Contents

1. Introduction

As one of the most widely used thermoset materials, epoxy resins have special characteristics compared with other thermosetting resins, such as low shrinkage during cure, minimum pressure needed for fabrication of products, use of a wide range of temperature by careful selection of curing agent with good control over the degree of crosslinking and availability of the resin ranging from low viscous liquid to tack free solid. Excellent adhesion to many substrates, high mechanical strength, chemical corrosion and electrical resistance possessed by epoxy, make this material suitable for versatile applications like structural adhesives, protective coatings, resin matrices for composites and electronic and electrical components [1]. However, the inherent brittleness of epoxies [2] has limited their application in fields requiring high impact and fracture strengths, such as reinforced plastics, matrix resins for composites and coatings. Modifiers are added to epoxy resins to overcome their limitation [3]. Various microscale modifiers have been used for this purpose, such as low molecular weight liquid rubbers, core-shell rubbers (CSR), engineering thermoplastics [1]. The incorporation of elastomers often resulted in a significant reduction in modulus and strength, which are desirable properties for engineering polymers. This effect induced the researchers to think about a hybrid approach for epoxy modification, in order to achieve a high toughness with sustained or even enhanced modulus achievable by incorporating both particulate filler and elastomers. A combination of elastomer and rigid filler like carboxyl terminated poly (butadiene-co-acrylonitrile) (CTBN) + glass beads [4–6], and CSR + alumina [7] were investigated. It was found that the addition of glass bead compensated for the loss in modulus and significantly contributes to the fracture toughness by providing additional mechanisms for toughening in the epoxy filled with both CTBN and glass beads [8].

With the advancement of nanotechnology in material science research, the development of polymer based nanocomposites has attracted the researchers. Subsequently, many researches on epoxy nanocomposites has been carried out to further improve the mechanical, thermal and barrier properties of epoxy by taking the advantage of fillers distribution at the nano level [9,10]. Thereafter, the concept of 'hybrid' has been extended to systems where the nanofillers were used, instead of macro scale particulate fillers, along with micro-scale elastomers/thermoplastic, for epoxy modification. The significance of such multi-component systems is the attainment of tailored properties by utilizing the advantages of both micro and nano-scale modification. Fig. 1 schematically shows tailored properties in epoxy hybrid systems and their applications. During the last decade, a good number of research articles on processing, characterization and application of elastomer/thermoplastic modified epoxy hybrid nanocomposites has been published. A number of reviews and book chapters were published during the past two decades on rubber/thermoplastic toughened epoxy and epoxy nanocomposites and lack of such an attempt on epoxy hybrid systems need to be filled since the research in this area is now vast enough to generalize the trends.

A concise discussion on the advances in rubber/thermoplastic toughening of epoxy and epoxy nanocomposites are presented in the first part so as to give an idea on the individual role of rubber/thermoplastic modifiers and nanofillers on the cure reaction, phase separation, morphology generation and properties. Thereafter, in the major part of the review, a systematic literature review on the generation and various aspects of epoxy hybrid systems modified with both elastomers/thermoplastics and nanofillers is given. As a complex multi-component polymer system, the mutual effect of micro scale modifiers and nanoscale fillers on morphology generation and hence the properties are discussed with foremost importance.

2. Elastomers/thermoplastic modifiers for epoxy

2.1. Liquid rubbers

Incorporation of an elastomeric second phase component is an efficient way to toughen epoxy matrix. The first attempt to overcome the inherent brittleness of epoxy resins using a low