



Synergic effects of poly(vinyl butyral) on toughening epoxies by nanostructured rubbers



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ABSTRACT

Synergic effects of poly(vinyl butyral) (PVB) on rubber toughening of epoxies have been examined in detail using two different liquid rubbers. The PVB is seen to be miscible with the epoxy used. Incorporation of the PVB into liquid rubber/epoxy blends lowers the rubber particle size from 0.76 μm to 28 nm, leading to a tremendous increase in fracture toughness, represented by the critical strain energy release rate, G_{IC} , from 100 J/m^2 for the neat epoxy to 2015 J/m^2 for the ternary blend of PVB/liquid rubber/epoxy (14/14/72 by weight). Such an enormous improvement in toughness is largely ascribed to the unique nanostructure of the rubber phase and enhanced deformability of the epoxy. Rubber particle cavitation and shear yielding of the matrix are found to be the main toughening mechanisms. This study provides a novel approach to achieving nano-dispersion of a typical liquid rubber in toughening epoxies which conventional routes fail to deliver. Such an approach serves as first direct evidence about that nano-sized rubber particles other than block copolymers considerably toughen epoxies by over 20 fold.

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1. Introduction

The epoxy resin has been widely used as a structural and encapsulation material in aerospace and electronics industries due to its outstanding mechanical properties (e.g., modulus and strength), adhesion, and heat and solvent resistance [1]. However, the poor ductility and low fracture toughness of the epoxy resin significantly limit its applications [2,3]. Therefore, toughening brittle epoxies is highly desired.

There has been a significant body of literature available for toughening epoxies [2–13]. Incorporation of a reactive liquid rubber into an epoxy resin was long recognized as an effective strategy in enhancing the toughness [2–6,14], though doing so would reduce to some extent the modulus and lower the glass transition temperature (T_g) of epoxies. Another strategy was to blend an epoxy resin with a hard, yet relatively ductile thermoplastic, such as poly(ether sulphone) [15,16], polysulphone [17,18], poly(ether imide) [19–21] and poly(ether ether ketone) [22,23]. This strategy, however, was less effective in toughness enhancement than addition of liquid rubbers. To mitigate the embrittlement of epoxies,

particulate particles were occasionally employed [24–37]. Compared to incorporation of a liquid rubber for toughening, such a strategy typically would not offer a competitive improvement in toughness, and involved different deformation mechanisms such as debonding. Combination of core–shell particles (i.e., hard shell and soft core) with epoxies served as an additional strategy [7,8,11,38–44] for toughening in order to overcome the drawback of uncontrollable rubber particle sizes which the conventional rubber toughening of epoxies had. With this strategy, the sizes of the core–shell particles remained nearly unaltered before and after the curing of epoxy resins, thus allowing one to extensively examine the role of rubber particle sizes in toughening. Generally, the core–shell particles were required to be over at least 50 nm in size to achieve effective toughening [11]. Simultaneous incorporation of both a rubber and filler into epoxies, sometimes called hybrid composites, has recently been reported to be a useful strategy in achievement of considerable toughening without greatly reducing the stiffness, strength, and glass transition temperature of the matrix epoxy [45–57]. Often, a liquid rubber or core–shell rubber particles were employed as the rubber phase, and a variety of fillers were reported, primarily including micrometer-sized glass beads, nano-sized silica, carbon nanotubes, carbon and glass fibers, boron nitride, aluminum silicate, POSS, ZrO_2 particles, and Al_2O_3 fibers [45–57]. Though this strategy appears to be ideal for toughening

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epoxies, special cautions need to be paid to the complex interactions between the epoxy matrix, the rubber phase, and the fillers, such as fillers' structure, geometry, orientation, and surface chemistry. Multiplicative, synergic toughening effects were sometimes (but not always) achieved when the filler concentration was not too high for agglomeration, but the reasons for the synergic effects are still not confirmative [57]. Generally, when the filler was randomly dispersed in the epoxy, the presence of the filler would not alter the nature of toughening mechanisms. This strategy is still under further development for better understanding the relationships between the structure, morphology, and properties of the filler/rubber/epoxy systems so that it becomes essential to industrial applications [57].

A more recent strategy focused on the use of diblock or triblock copolymers in improving the toughness of epoxies [58–83]. Hillmyer and coworkers [84] firstly reported amphiphilic block copolymers of poly(ethylene oxide)-poly(ethyl ethylene) and poly(ethylene oxide)-poly(ethylene-*alt*-propylene) with well-defined, ordered nanostructures as useful tougheners for epoxies. After the pioneer work of Hillmyer et al., numerous efforts have been made to explore the effects of block copolymers on toughening epoxy resins from various facets [8,10,58–75,77,85–87]. Generally, these amphiphilic block copolymers were designed to comprise an epoxy-miscible block and an epoxy-immiscible one; during mixing with uncured epoxy resins, these blocks self-assembled into a variety of nanodomains such as spherical and wormlike micelles and vesicles, depending on the molecular weight, block length, and composition of the block copolymers. The nanodomains were able to preserve themselves after the curing of epoxy resins. It has been shown that a low (typically < 5 wt%) concentration of the block copolymers could increase the fracture toughness of epoxies by 10–20 fold [88]. While significant progress has been made in toughening epoxy resins using block copolymers, detailed toughening mechanisms with the exception of nanocavitation still remain elusive [10].

Recently, the success of amphiphilic block copolymers in toughening epoxies has inspired us to re-consider conventional liquid rubbers, which were firstly used in the field. Compared with core-shell particles and amphiphilic block copolymers, liquid rubbers have advantages such as a lower cost and broader availability; however, they typically phase separate on the micrometer (not nanometer) scale during the curing of epoxies, and generally the rubber particle size is difficult to predict as various factors contribute to the development of rubber particles [2,3,5,6,8,11,88]. In addition, reactive liquid rubbers are known not to form nanodomains as small as amphiphilic block copolymers do. Furthermore, it is unclear whether or not rubber particles smaller than 50 nm, if available by incorporation of liquid rubbers, can still cause effective toughening of epoxies. Thus, although rubber toughening of epoxy resins is well documented [2–5,7,8,11,17,20,41,43,63,65,71–73,80,85–93], the optimal range of rubber particle sizes for effective toughening of epoxies (which is the case for rubber toughening of polyamides [94–96]) is still lacking, preventing one from profoundly understanding the role of rubber particles particularly when they are at the nanoscale, e.g., 10–30 nm, if available. To explore the possibility of nanodispersion of liquid rubbers and its potential effects on toughening epoxy resins, we have recently developed a novel approach in which an epoxy resin was mixed with both a reactive liquid rubber and poly(vinyl butyrate) (PVB) to form a ternary blend with a tunable size of the rubber phase. This approach enables us to achieve nanostructured (e.g., 28 nm in the rubber particle size) rubber-toughened epoxies for the first time which sole incorporation of liquid rubbers fails to attain. The purpose of this study is to examine the roles of nano-sized rubber particles, coupled with the PVB, in

determining the level of toughness of epoxies. Here we report the morphological development of nanostructured rubber particles revealed by electron microscopy; we also describe the miscibility of the PVB with the epoxy resin, and discuss the effects of the rubber concentration and particle size on (both quasi-static and dynamic) mechanical properties and fracture toughness of the ternary blends. In addition, we report possible toughening mechanisms responsible for enhanced fracture toughness of blends.

2. Experimental

2.1. Materials

The diglycidyl ether of bisphenol A epoxy resin (CYD-128) with an epoxide number of 0.51 and methyl tetrahydrophthalic anhydride as a curing agent were purchased from Yueyang Chemical Company (China). *N,N*-dimethylbenzylamine as a curing accelerator was bought from Huihai Instrument Technology Co., Ltd., China. Two liquid rubbers, i.e., a carboxyl-terminated and a hydroxyl-terminated (polypropylene glycol) polyether, were kindly provided by Beijing Jindao Qishi Materials Technology Co., Ltd., denoted as LR1 and LR2, respectively. The saturation solubility of these two reactive liquid rubbers in the epoxy resin at different temperatures is shown in Table 1. The difference in the saturation solubility was primarily believed to stem from both the more polar nature of LR1 than LR2 and the different molecular weights between them. PVB was synthesized in our laboratory, and has a polymerization degree of 500 and the content of butyral group of about 74%. The chemical structures of these materials are given in Table 2.

2.2. Specimen preparation

The basic formulation of the cured epoxy resin consisted of 100 parts of the uncured epoxy resin, 85 phr of the curing agent, and 0.5 phr of the accelerator. Both binary PVB/epoxy and ternary PVB/liquid rubber/epoxy blends were prepared by a hot-melting, one-step method. The liquid rubber was entirely dissolved in the epoxy resin without the curing agent and accelerator at 85 °C under stirring at 300 rpm in a three-necked reaction flask. However, the mixing of the uncured epoxy resin with the PVB was performed at 150 °C under stirring at 300 rpm so that the PVB was dissolved completely in the epoxy resin. The mixture remained transparent during cooling to 85 °C.

To form ternary blends of PVB/liquid rubber/epoxy without the curing agent and accelerator, the PVB was firstly added into the epoxy resin at 150 °C under stirring at 300 rpm at the three-necked reaction flask, and the stirring lasted for 1 h. After the mixture was cooled down to 85 °C, to the mixture was added the liquid rubber under stirring at 300 rpm. The mixing was maintained for 30 min under the same stirring at 85 °C to form a uniform, transparent solution.

To cure and post-cure the premixed solution, the curing agent and accelerator were added in the stoichiometric ratios to the above uniform, transparent solution at the three-necked reaction flask at 85 °C under stirring at 300 rpm. The mixing was maintained

Table 1

The saturation solubility of the liquid rubbers in 100 parts uncured epoxy resin at different temperatures.

Modifier	45 °C/phr	55 °C/phr	65 °C/phr	75 °C/phr
LR1	24	62	100	200
LR2	6	14	30	100

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