Tuning the mechanical properties of glass fiber-reinforced bismaleimide–triazine resin composites by constructing a flexible bridge at the interface

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Abstract

We demonstrate a new method that can simultaneously improve the strength and toughness of the glass fiber-reinforced bismaleimide–triazine (BT) resin composites by using polyethylene glycol (PEG) to construct a flexible bridge at the interface. The mechanical properties, including the elongation, ultimate tensile stress, Young’s modulus, toughness and dynamical mechanical properties were studied as a function of the length of PEG molecular chain. It was found that the PEG molecule acts as a bridge to link BT resin and glass fiber through covalent and non-covalent bondings, respectively, resulting in improved interfacial bonding. The incorporation of PEG produces an increase in elongation, ultimate tensile stress and toughness. The Young’s modulus and \(T_g\) were slightly reduced when the length of the PEG molecular chain was high. The elongation of the PEG-modified glass fiber-reinforced composites containing 5 wt% PEG-8000 increased by 67.1%, the ultimate tensile stress by 17.9% and the toughness by 78.2% compared to the unmodified one. This approach provides an efficient way to develop substrate material with improved strength and toughness for integrated circuit packaging applications.

Keywords: bismaleimide–triazine resin, glass fiber, polyethylene glycol, strength, toughness, interface

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1. Introduction

Thermosets, for example epoxy resins, polyimide and bismaleimide–triazine (BT) resins are widely used in integrated circuit (IC) packaging technology, owing to their excellent mechanical, thermal and dielectric properties. The major problem of thermosets is their brittle fracture behavior, which limits their application.

Traditionally, improving the toughness will lead to sacrifices in strength and vice versa. Therefore, to improve the strength and toughness of the thermosets simultaneously is a challenging and active field of research. Much effort
was made in the past decade [1–3]. For example, An et al [1] developed an approach to prepare polyimide nanocomposite by incorporating rod-like silicaates with covalently grafted polymer chains. The increased interfacial bonding density led to prominent improvements in strength and toughness. Inspired by biomimetic studies, Chen and Liu [2] constructed sacrificial bonds and hidden lengths at the interface of graphene/polyurethane elastomers, resulting in improved strength and toughness. Another representative example comes from the epoxy/single-walled carbon nanotube (SWNT) composites. The non-covalent wrapping of nitric acid-SWNTs with a polyethylene oxide-based block copolymer leads to a highly dispersed filler in the epoxy resin, leading to a 276 and 193% improvement in toughness and impact strength, respectively [3]. The general strengthening and toughening mechanism of the composites involves the interface interaction and effective stress transfer between fillers and the polymer matrix. It is believed that the interfacial structure is important for the mechanical properties of the composites because it could control the load transfer between matrix and filler [4–8]. Although improvements have been achieved in the above reports, the high electrical conductivity of carbon materials, such as carbon nanotube and graphene, prevent them from practical implementation in IC packaging. In contrast, glass fibers are non-conductive and inexpensive and have been extensively employed to reinforce organic substrate materials. Meanwhile, BT resin has become the standard substrate material in the IC packaging industry, owing to their high glass transition temperature ($T_g$), and excellent electrical and mechanical properties [9]. Some researchers have focused on the thermal and dielectric properties of BT resin [10, 11]. However, the mechanical properties of the glass fiber-reinforced BT resins (GBFTs) lack systematic study, and the creation of such strong interfacial interaction between glass fibers and BT resin remains a challenge.

Here, we demonstrate a new method of constructing a flexible bridge at the interface to create a strong interfacial interaction which consequently improves the strength and toughness of the BT resin used as IC packaging substrates. Considering that polyethylene glycol (PEG) is flexible and thermally stable, and used as a surface modifier for the inorganic fillers and a toughener for brittle polymers as previously reported [12–14], we chose PEG as the interfacial modifier to improve the mechanical properties of GFBT composites. The results showed that the PEG molecule acts as a bridge to link the BT resin and glass fiber through covalent bonding and non-covalent bonding, respectively. Owing to this specific interfacial structure, 67.1, 17.9 and 78.2% increases in elongation, ultimate tensile stress (UTS) and toughness were achieved, with little detrimental effect on Young’s modules and $T_g$. The effect of the molecular chain length of PEG on the mechanical and thermal properties of GFBT was investigated systematically.

2. Experimental section

2.1. Materials

2, 2'-Bis (4-cyanatophenyl) propane (BCE, Heijang Kinlyuan Pharmaceutical Co., Ltd, China), 4,4'-bismaleimido-diphenylethahene (BMI, Honghu Bismaleimide Resin Factory, China) and 2, 2'diallyl bisphenol A (DBA, Wuxi Resin Factory, China) were used as starting materials to prepare the BT resin. Borosilicate electrical grade glass fiber commonly known as E-glass fiber (glass style: E-106, plain weave, count: 56 × 56 ends per inches, thickness: 0.0015 inches) was purchased from Shenzhen Sailong Fiberglass Co., Ltd, China. PEGs with different molecular chain length (PEG-4000, PEG-6000 and PEG-8000) were purchased from Alfa Aesar. Other materials and reagents were used as received and purchased from Sinopharm Chemical Reagent Co., Ltd, China. The corresponding chemical structures of BMI, BCE, DBA and PEG are shown in figure S1 (see the supplementary material, available from stacks.iop.org/STAM/14/065001/mmedia).

2.2. Preparation of PEG/GFBT composites (PEG/GFBT)

The BT resin was prepared by a melt method, as reported in our previous work [15]. Then, BT resins and 5 wt% PEG were dissolved in an organic solvent (methyl ethyl ketone) to form a homogeneous solution. The glass fabric was attached to a sheet of polyethylene terephthalate (PET) release film to ensure that the fabric remains flat to minimize thickness variations (figure S2(a), see the supplementary material, available at stacks.iop.org/STAM/14/065001/mmedia). Following that, the resin solution prepared above was coated on the fabric using a bar coating (RK, K202 Control Coater) method. The composites were dried at 100°C for 20 min to remove the solvent, and referred to as a B-stage material (prepreg, figure S2(c)), which will become liquid with a viscosity under controlled temperature and pressure. The PET film was peeled off after drying. Two sheets of prepreg were laminated between sheets of PET release films under a pressure of 0.5 MPa at 150°C for 4 h, resulting in PEG/GFBT composites (figure S2(d)), which are highly cross-linked, or cured. The weight content of glass fiber for different composite laminates was 60%. PEG/GFBT composites containing 5 wt% PEG-4000, PEG-6000 and PEG-8000 were used for further analysis and characterization.

2.3. Characterization

The microstructures of the composites were examined using a scanning electron microscope (SEM, FEI Nova NanoSEM 450), operated in the secondary-electron mode at a voltage of 5 kV and a distance of 5 mm. Cured samples were fractured and the edges were sputtered with a 10 nm gold layer prior to examination.

Fourier transform infrared (FTIR) spectra were obtained using a Bruker Vertex 70 spectrometer. The samples were
FTIR was used to determine the intensity of the characteristic infrared bands that are generated as a function of PEG segment bonding to the BT resin and glass fiber, respectively. The bonding mechanism between BT resin and PEG chain segments is illustrated in figure 2(a). With the reactive bismaleimide groups containing two terminal C=C bonds, BMI can react with an active hydrogen atom-containing molecule through the Michael addition reaction mechanism [16–19]. According to the assignment of bands reported by Wu [19] and Hulubei [20], characterized bands at 3105 and 690 cm$^{-1}$ are associated with the stretching vibration and out-of-plane bending vibration of $\nu_{\text{C–C–H}}$ of the maleimide ring, respectively (figure 2(b), curve B). After the reaction with PEG, these two bands disappeared (figure 2(b), curve C) and other characteristic bands of BMI remained (the characteristic bands of PEG merged with characterized bands of BMI). Moreover, a weak broad band at 2881 cm$^{-1}$ corresponding to the C–H– stretching vibration is observed. The results indicate that the PEG molecule was grafted on BMI by the Michael addition reactions.

In the case of BCE, it has been reported that the highly reactive terminal cyano groups (–C≡N) can react with the hydrogen group via an addition reaction at a low temperature (80°C), and then can be triggered by a hydrogen group to form an iminocarbonate group at a high temperature, by a known mechanism [21]. Here, the hydroxyl-terminated PEG also reacts with BCE through the addition reaction, as depicted in figure 2(a). The characteristic absorption bands of the –C≡N groups in cyanate ester were generally observed between 2233 and 2381 cm$^{-1}$ in the infrared spectrum (figure 2(b), curve D). In the blend of PEG and BCE (figure 2(b), curve E), the occurrence of a possible addition reaction between hydroxyl groups and cyanate moiety at a lower temperature (120°C) is indicated by the appearance of the –C≡N band at 1370 cm$^{-1}$ and a broad O–H stretching band at 3350 cm$^{-1}$. The fact that all the cyanate groups are not consumed in this temperature regime, suggests that this reaction occurs only in part. It is also possible that the cyclotrimerization of cyanate groups can be further triggered by the OH groups, as proved by the previous reports [21–23]. The modification of cyanate ester resin by hydroxyl-terminated liquid butadiene acrylonitrile rubber has been reported which also shows the existence of an addition reaction between hydroxyl groups and cyanate groups [24].

On the other hand, it has been reported that a considerable number of reactive silanol groups (Si–OH) situated at the edges of the glass fiber structure (figure 3(a)), provide sites to form bonds with some functional groups on polymer chains, silane coupling agents [25–28] and poly(methylmethacrylates) [29, 30], etc, improving the adhesion between glass fibers and the polymer matrix. Different from the chemical reaction between glass fibers and silane coupling agents, PEGs are adsorbed on the surface of glass fibers through a combination of electrostatic interaction, van der Waals or hydrogen bonding, all of which are non-covalent. FTIR spectra of the bare glass fibers, free PEG-4000 and glass fiber-PEG-4000 are shown in figure 3(b). The unmodified glass fibers show a broad

Figure 1. Cross-section SEM images of the GFBT composite and PEGs/GFBT composites: (a) GFBT composite, (b) PEG-4000/GFBT composite, (c) PEG-6000/GFBT composite and (d) PEG-8000/GFBT composite.

milled with potassium bromide (KBr) and then compressed into a thin pellet for measuring.

Dynamical mechanical analysis (DMA) tests were carried out using a dynamic mechanical analyzer (TA Q800), in tensile mode at a fixed frequency of 1 Hz and amplitude of 10 µm. The specimen dimensions were ~20 × 10 × 0.007 mm$^3$. Measurements were performed from 30 to 300°C, at a heating rate of 3°C min$^{-1}$.

Tensile tests were performed using a universal testing machine (RGM-4000, REGER, China) at room temperature according to the American Society for Testing and Materials (ASTM) standard D822-09. The crosshead speed was set at 12.5 mm min$^{-1}$. All samples were cut into (120 × 10 × 0.007 mm$^3$) blocks, and at least five samples were tested. The images of the composites before and after tensile test are presented in figure S3 (see the supplementary material, available from stacks.iop.org/STAM/14/065001/mmedia).

3. Results and discussions

3.1. Structural analysis

Figure 1 shows the SEM micrographs of the cross-section of the GFBT composite and PEG/GFBT composites using PEG with varied molecular chain length. The single glass fiber in the unmodified specimen (figure 1(a)) protruded under load, with only a little polymer remaining on its surface (the inset of figure 1(a)), indicating poor adhesion of glass fiber to the matrix. In contrast, when PEGs are used as the toughener, some of the glass fibers were exposed with more polymers remaining on their surface compared with the unmodified specimen. The results indicate that PEG-modified BT resin is more adhesive to glass fiber surface than the unmodified one, indicating that a strong interfacial interaction was constructed.
Figure 2. (a) The reaction mechanism of PEG with BMI and BCE. (b) FTIR spectra of PEG, BMI, PEG–BMI, BCE and PEG–BCE.

characteristic band over 900–1200 cm\(^{-1}\) which are related to the Si–O–Si vibrations and the one near 3431 cm\(^{-1}\) corresponds to the O–H stretching from silanol groups. A sharp –C–H– stretch around 2881 cm\(^{-1}\) and a sharp –C–O stretch around 1110 cm\(^{-1}\) are observed in both PEG and the PEG-modified glass fibers, revealing the presence of PEG residue in the final product. These results clearly show that PEGs have been absorbed on the surface of glass fibers. Other researchers have also reported the preparation of modified inorganic fillers using PEG as the surface modifier via polymer adsorption \cite{12,31–34}. Overall, the results provided by FTIR show that the flexible PEG bridge at the interface was constructed as shown in figure 4, which will facilitate mechanical improvement.

3.2. Analysis of mechanical properties

In a typical tensile experiment, the obtained stress–strain (\(\sigma–\varepsilon\)) curves for the BT resin with PEG modification are shown in figure 5. The elongation (\(\varepsilon_{\text{max}}\)) and UTS are extracted from the curves just before the failure. The Young’s modulus (\(E\)) is obtained from the slope of the linear fit in the initial section of the curve. Finally, the toughness (\(G\)) is estimated by calculating the area under the curve using

\[
G = \sum_{0}^{\varepsilon_{\text{max}}} \sigma \Delta \varepsilon. \tag{1}
\]

The mechanical parameters drawn from \(\sigma–\varepsilon\) curves for the different samples are presented in figure 6, and the error bars are also marked. The unmodified composite possesses a low \(\varepsilon_{\text{max}}\) (1.6\%) and \(G\) (1.6 MJ m\(^{-3}\)) as expected for the inherently brittle material. As PEG-4000 (5.0 wt\%) was added, the \(\varepsilon_{\text{max}}\) and toughness increased by 36.7 and 55.7\%, respectively, and \(E\) was found to be moderately decreased by 15.3\%. The flexible segments of PEG molecule can open up the BT resin segments, and the resulting high free volume or loose network is advantageous for segmental mobility, reflected in the increased toughness and decreased \(E\). It is interesting to note that an addition of PEG leads to the increased UTS from 183.1 MPa for neat BT resin to 201.8 MPa for 5\% PEG-4000. This result is different from previous work, in which the classical methods to toughen polymers usually sacrifice other mechanical properties \cite{24}.

The effect of varying the molecular chain length of PEG on the mechanical properties of PEG/GRBT composites was further examined. The \(\varepsilon_{\text{max}}\) and toughness increase with the molecular chain length, indicating that a higher molecular chain length facilitates the improvement of toughness. Meanwhile, the values of UTS increase from 201.5 MPa for PEG-4000 to 215.8 MPa for PEG-8000, indicating that the higher molecular weight leads to more prominent strength improvement. The addition of PEG resulted in a slight decrease of \(E\), which is attributed to the nature of the soft segment of PEG. Under the elastic deformation load region, the PEG molecule firstly deforms due to the easy segmental (\(-\text{O}–\text{CH}_2\text{–CH}_2\text{–}\)) motion.
3.3. Possible toughening and reinforcement mechanism

For the PEG/GFBT composites, the enhancements of the elongation at break as high as 67.1% and toughness enhancement of 78.2% are both quite attractive, which may benefit from the specific interface structure constructed by the flexible PEG. Given the fact that all the composites were synthesized with the same PEG loading, it is speculated that the differences of mechanical performance are induced by the variations in the strength of interfacial interaction among the glass fiber, the BT matrix and the flexible chain of PEG. Different from GFBT composites, PEG links BT resin and glass fiber through covalent bonding and non-covalent bonding (H-bonding), respectively. Figure 7 further presents the schematic illustration of the toughening mechanism of PEG/GFBT composites. In the case of no load, the PEG chain is entangled on the surface of glass fiber and acts as a bridge between glass fiber and BT resins. When PEG/GFBT composites are stretched under tensile loading, the alignment forces the orientation of PEG/GFBT composites to occur along the loading direction, which was also observed in other polymer composites [2, 35]. At the same time, the hidden length of PEG is released and the energy can be absorbed during deformation before fracture occurs, resulting in high toughness. With the increase of the molecular chain length of PEG, the degree of stretch is enhanced due to the increased molecular length and chain flexibility, leading to the improved toughness of PEG/GFBT composites. Kim et al [36] also believed that PEG of the proper molecular weight is located mainly at the interface between the starch and poly (ε-caprolactone) phases and interact with both, which facilitates the enhancement of the toughness of poly (ε-caprolactone). However, the addition of PEG cannot simultaneously improve the strength of the composites in their study.

Figure 8 shows the scheme of the reinforcement mechanism of PEG/GFBT composites. As the strain is low (A), the deformation is improved owing to the flexibility of PEG chains, so the E value of PEG/GFBT composite is lower than that of the GFBT composites, as illustrated in figure 6(b). At ultimate strain (B), the weak interaction between BT resin and glass fiber without PEG leads to the low UTS. When PEG is added, the interaction is improved due to the existence of ‘bridges’ between glass fibers, leading to the efficient load transfer. As the molecular chain length of
Figure 6. Mechanical parameters extracted from stress–strain curves: (a) maximum strain, (b) Young’s modulus, (c) ultimate tensile strength and (d) toughness.

Figure 7. Toughening mechanisms involving hidden length release of PEG in mechanical texts of PEG/GFBT composites.

PEG increases, the interaction between PEG and glass fiber is improved because PEG with a long molecular chain possesses more interacting points through H-bonding and an improved ability to entangle the glass fiber. This finding is supported by the previous reports [8, 37], that with longer and more flexible chains, the energetic penalty for the loss of conformational entropy decreases due to the chain confinement on the surface. Therefore, the strong interaction between the polymer and surface outweighs the entropic loss, and the more flexible chains form additional anchoring points with the surface, enabling the absorption of much energy upon fracture [8, 38]. PEG-8000 provides a larger number of anchoring sites for stress transfer compared to the other PEGs with less molecular weight, leading to an enhancement of the UTS as high as 17.9%.

3.4. Dynamical mechanical analysis

DMA over a wide temperature range is very sensitive to the physical and chemical structure of polymer and their composites. A clear understanding of the $G'$ (storage modulus), $G''$ (loss modulus) and $\tan \delta (G''/G')$ temperature curve provides valuable insights into the toughness of a material as well as the molecular relaxation taking place.

The relative change in $G'$ of the PEG/GFBT composites compared to the respective unmodified GFBT composites at 50 °C, are summarized in table 1. The incorporation of 5% PEG resulted in a decrease of $G'$, which is apparently independent of the molecular chain length under study. The $G'$ decreases at higher temperatures, manifesting a rubbery state
Table 1. Summary of DMA results for unfilled PEG composite and composites with PEG.

| Samples                  | $\Delta G'$ (%) | $T^b$ at $G'_{\text{DMA}}$ ($^\circ$C) | $T^c$ at $\delta'_{\text{DMA}}$ ($^\circ$C) | $\rho^d$ (mol cm$^{-3}$) |
|--------------------------|-----------------|----------------------------------------|---------------------------------------------|--------------------------|
| Unfilled PEG composite   | --              | 239.2                                  | 249.8                                      | 0.50                     |
| 5 wt% PEG-4000           | $-13.8$         | 221.7                                  | 229.4                                      | 0.45                     |
| 5 wt% PEG-6000           | $-0.2$          | 216.2                                  | 226.6                                      | 0.44                     |
| 5 wt% PEG-8000           | $-10.4$         | 217.2                                  | 225.1                                      | 0.40                     |

$^a$ $\Delta G'$ is the relative change of storage modulus at 50 $^\circ$C.

$^b$ $T$ at $G'_{\text{DMA}}$ is the temperature at the loss modulus maximum, associated to the apparent $T_g$.

$^c$ $T$ at $\delta_{\text{DMA}}$ is the temperature corresponding to the tan $\delta$ peak maximum, defining the apparent $T_g$.

$^d$ $\rho$ refers to the cross-linking density of the network.

Figure 8. Scheme of the reinforcement mechanism of PEG/GFBT composites.

Figure 9. (a) Stress-strain curves of different PEG/GFBT composites; (b) TEM images showing the formation of BT collagen fibers. As can be seen in figures 9(b) and (c), the PEG/GFBT composites display one transition peak in the loss modulus and the tan $\delta$ curves, indicating that phase separation does not occur between BT resin and PEG, and the chemical bonds were formed between the BT resin and PEG. The $T_g$ can be defined as the temperature corresponding to the peak maximum of the loss modulus or of the tan $\delta$. These values are also summarized in table 1 and the tendency of their variation based on the $G''$ peak is similar to that based on the tan $\delta$. The addition of PEG with increased molecular chain length leads to a progressive decrease in $T_g$ of the GFBT composite (initially about 249.8 $^\circ$C). The fact that both $G'$ and $T_g$ decrease with the increased molecular chain length can be explained by the cross-linking density theory that the lower cross-linking density, the lower $T_g$ and $G'$.

According to the polymer elasticity theory, the cross-linking densities ($\rho$) of cross-linked networks are related to the storage modulus in the rubber region, and can be calculated according to [39]

$$\rho = \frac{G'}{3RT},$$  \hspace{1cm} (2)

where $\rho$ is the cross-linking density of the composites, $G'$ and $T$ are the storage modulus at $T_g + 50$ K and the absolute
temperature of $T_g + 50 \text{ K}$, respectively. $R$ is the gas constant, $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$.

The cross-linking density of the composites is also summarized in table 1. Among the four samples, the GFBT composite has the highest cross-linking density, which results in high brittleness and $T_g$. Compared to GFBT composite, the addition of 5 wt% PEG-4000 causes a more apparent reduction of cross-linking density from 0.50 to 0.45 mol cm$^{-3}$. The reason is that the flexible ethylene glycol segments ($-\text{O--CH}_2\text{--CH}_2\text{--O}--$) of PEG molecules produce a high free volume or a loose network which is advantageous for the segmental mobility as reflected in the decreased $T_g$. When PEG with a longer molecular chain was added, the cross-linking densities decreased and both $G'$ and $T_g$ reduced. Because the longer molecular chain benefits the segmental mobility and elongates the average chain length, the cross-linking densities decrease progressively. Although $T_g$ decreases with the molecular chain length, it is still above 210°C which meets the requirement in the IC package industry. Moreover, based on the above results and in consideration of the balance of the mechanical properties and $T_g$, we can conclude that the optimum PEG is PEG-8000 with the molecular weight of 8000 in our study.

4. Conclusions

In this work, a bridging strategy based on PEG has been successfully applied in a high-performance BT resin used in standard substrate materials. The PEG molecule links BT resin and glass fiber through covalent and non-covalent bonds (H-bonding), respectively, resulting in improved interfacial bonding. Both the strength and toughness of the glass fiber-reinforced composites containing PEG were improved with the increase of the PEG molecular chain length, and the Young’s modulus was slightly decreased. The elongation of the PEG modified glass fiber-reinforced composites containing 5 wt% PEG-8000 increased by as much as 67.1%, UTS by 17.9% and toughness by 78.2% compared to the unmodified one. The ‘bridge effect’ of PEG between BT resin and glass fiber was proposed to be responsible for the improved toughness and strength. DMA characterization showed that although $T_g$ decreases with the molecular chain length, it still possesses a sufficiently high $T_g$ above 210°C which meets the need in the IC package industry. The modification approach on the BT resin revealed in this study provides an efficient method to enhance the interfacial bonding as well as to generate substantial improvements in strength and toughness.
4.1. Supporting information

Chemical structures of BMI, BCE, DBA and PEG (figure S1 (see the supplementary material, available from stacks.iop.org/STAM/14/065001/mmedia)). Schematic illustration of the fabrication process of PEG/GFBT composites (figure S2(a)). Macroscopic photograph of the woven glass fabric (E-glass 106, 33 µm thick, figure S2(b)), prepreg (50 µm thick, figure S2(c)), composite substrate (80 µm thick, figure S2(d)). Images of the composite film (figure S2(e)). SEM image of the composite substrate (figure S2(f)). Photograph of samples before and after tensile test (figure S3).

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