

Influence of reactive compatibilization on the mechanical, thermal and rheological properties of highly filled PBT/Al₂O₃ composites

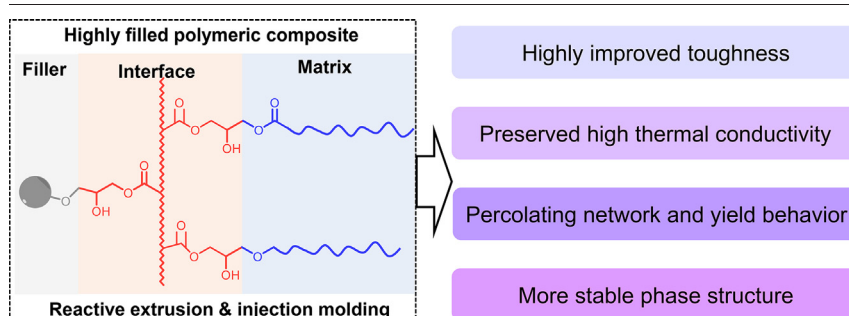
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HIGHLIGHTS

- Highly filled PBT/alumina composites were toughened via reactive processing.
- Excellent thermal conductivity and strength were preserved after modification.
- Percolating network and yield behavior were determined by three rheological criteria.
- More stable phase structure was confirmed via creep-recovery test after reactive compatibilization.
- Improved toughness was attributed to interfacial interaction and stress transfer.

GRAPHICAL ABSTRACT



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ABSTRACT

High filler content is the prerequisite for imparting specific properties to polymeric composite. However, serious mechanical properties degradation happened in this kind of material due to the inevitable reduction of material cohesion. In this work, highly filled poly(butylene terephthalate)/alumina (PBT/Al₂O₃) composites were modified by directly melt mixing with a reactive compatibilizer ethylene-methyl acrylate-glycidyl methacrylate terpolymer (E-MA-GMA). The modified samples presented greatly enhanced elongation at break and impact response, simultaneously preserved their tensile strength and high thermal conductivity. The reactive compatibilization between PBT and Al₂O₃ spheres was confirmed by SEM, FTIR, and rheology characterizations. Three rheology criteria plots demonstrated that the filler percolating network and apparent yield behavior occurred in the ternary PBT/Al₂O₃/E-MA-GMA composites melt. It is believed that enhanced particle-matrix interfacial interaction and stress transfer caused by E-MA-GMA endowed this highly filled composite improved toughness. This study suggests the potential application of E-MA-GMA elastomer to resolve the mechanical properties degradation in highly filled polymeric composites.

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1. Introduction

The rapid development of miniaturized electronic devices requires high-performance materials for protective packaging. The major

challenges confronting such materials are preparing materials with high thermal conductivity, low dielectrical constants, and high electrical resistivity [1]. In this context, polymeric composites consisting of thermally conductive while electrically insulating fillers have attracted extensive attention to solving these problems [2].

As one of the most important engineering plastics, poly(butylene terephthalate) (PBT) possesses excellent chemical resistance, good dimensional stability, and processing advantages, which make it highly

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suitable for electronic devices [3]. Ceramic fillers, including metal oxide fillers [4], nitride fillers [5], and silicon carbide [6], are often used to endow their high thermal conductivity to the polymer matrix. Among these fillers, Al_2O_3 is widely used due to its high electrical resistivity, high elastic modulus, relatively low dielectric constant, and low cost [7,8]. Thus, mixing PBT with Al_2O_3 could obtain a novel material with desirable properties in the application of electronic devices. However, it is generally realized that a high concentration of solid fillers (usually above 40 wt%) must be introduced to impart acceptable thermal conductivity to the polymeric material [9,10]. Such a high loading will deteriorate the mechanical properties because of the inevitable reduction of material cohesion [11]. Additionally, introducing a large quantity of fillers into the molten polymer will also drastically change the rheology behavior and challenge the following processing [12].

In recent years, efforts have been made to enhance the mechanical performance of highly filled composites. External stress field, including extension flow [13], oscillation shear [14], and high shear forces [15], have been developed to improve the dispersion and distribution of fillers, and subsequently obtain high-quality polymer composites. However, additional expensive equipment is required in these processes. Furthermore, this method could not effectively increase the interfacial cohesion strength between fillers and polymer matrix. By contrast, adding interfacial compatibilizer is a simple and effective method [16–18], which could not only strengthen the filler–polymer interfacial interaction, but also improve the matrix property. Recently, Chen et al. [19] prepared highly filled high-density polyethylene (HDPE)/ Al_2O_3 composite, finding that the tensile strength was improved and the good thermal conductivity was preserved with the incorporation of an amphiphilic block copolymer. However, the elongation at break reduced evidently after introducing compatibilizer. Hence, finding an effective and suitable compatibilizer for composites to obtain optimum performance is still a challenging problem for the highly filled composites.

Moreover, rheological behavior is vital to the highly filled composites, which are very sensitive to the filler dispersion and would benefit our understanding of the processing and microstructure of multicomponent composites [20]. Compared with single-phase polymer and relatively low filled polymeric composites, highly filled polymer melts exhibit more complex rheological behavior, which are mainly influenced by the filler–filler interactions [21]. At a high filling level, fillers are closely packed together, making filler–filler interactions predominate over matrix–filler interactions [22]. The friction between fillers results in energy dissipation and a greater viscosity mixture [23]. Many recent studies have specifically targeted to study the rheology of filled polymeric systems; however, few studies have been conducted concerning highly filled compatibilizing polymers.

As outlined above, the ultimate goal of this work is to understand the effect of reactive compatibilization on the mechanical performance and rheological behavior of highly filled PBT/ Al_2O_3 composite. To achieve this objective, ethylene–methyl acrylate–glycidyl methacrylate terpolymer (E-MA-GMA), a flexible compatibilizer with a large quantity of epoxy groups and high reactivity [24,25], was chosen to improve the interfacial interaction between PBT matrix and Al_2O_3 spheres. In the present study, different concentrations of E-MA-GMA were used to modify PBT/ Al_2O_3 composites. The tensile properties, impact property, and thermal conductivity were characterized to evaluate the compatibilization effect of the PBT/ Al_2O_3 /E-MA-GMA composite. SEM, FTIR, and DSC tests were successively conducted to analyze the morphology and interfacial compatibilization behavior. Detailed dynamic rheological measurements were applied to thoroughly study the rheological properties of the ternary composite. The improvement in the mechanical properties of the composites was explained, and the corresponding mechanism was proposed based on these experimental observations.

2. Materials and methods

2.1. Materials

Poly (butylene terephthalate) (PBT, 1100–211 M) pellets with a density of 1.31 g/cm^3 were purchased from Taiwan Chang Chun Plastics Co., Ltd., China. Spherical Al_2O_3 powders with a mean diameter of $3 \mu\text{m}$ were obtained from Zhengzhou Sanhe New Materials Co., Ltd., China. A commercial compatibilizer ethylene–methyl acrylate–glycidyl methacrylate terpolymer (E-MA-GMA, A2703) was supplied by Shanghai Kunzhen Materials Co., Ltd., China. It had a melt flow rate of 1.5 g/10 min at 190°C ; the graft ratio of GMA is more than 5%. All the materials were used as received without further purification.

2.2. Composite preparation

Prior to the blending, PBT and Al_2O_3 were dried at 100°C in vacuum for 6 h. The PBT/ Al_2O_3 /E-MA-GMA composites were prepared by a corotating twin-screw extruder with an L/D ratio of 44 (CTE20, Coperion Keya Machinery Co. Ltd., Nanjing, China), operated at $220\text{--}270^\circ\text{C}$ with a screw speed of 150 rpm. The temperature profile of the twin screw extruder is shown in Table 1. Afterwards, the extrudates were cooled down and cut into pellets. The tensile (GB/T 1040.2) and impact (GB/T 1843) specimens were injection molded on a Qien (Wuhan) injection molding machine (M1200). The detailed composition of the prepared samples is listed in Table 1, Table 2. The contents of compatibilizer E-MA-GMA were varied (2–8 wt%) in the composites with a fixed Al_2O_3 spheres concentration (40 wt%).

2.3. Characterization methods

2.3.1. Mechanical measurements

Tensile properties were investigated using a universal tensile machine AG-IC (Shimadzu, Japan) according to ASTM D638. The composites samples were characterized under a crosshead speed of 10 mm/min . The slope of the linear portion of the stress–strain curve was calculated as the elastic modulus. The notched Izod impact strength was tested using an XJU-22 impact tester (Chengde, China) according to ASTM D 256-04. The depth and mean radius of the notches were 2 mm and 0.25 mm, respectively, which were machined after injection molding. All the mechanical tests were conducted at room temperature. For each kind of sample, all measurements were repeated at least five times. The average values and standard deviations of the mechanical properties were reported.

2.3.2. Thermal conductivity

A Netzsch Laser Flash Analysis (LFA 427) was used to determine the thermal conductivity of the samples. The thermal conductivity was tested according to ASTM E1461, using the measured thermal diffusivity and heat capacity, with entered density data. The square samples with 10 mm side length and 2 mm thickness were used for the measurements.

2.3.3. Morphological characterization (SEM)

The cyro-fractured and impact fracture surface morphologies of the samples were observed by scanning electron microscopy (SEM) (JEOL, JSM-7600F, Japan) with an accelerating voltage of 5 kV. Samples were coated with a thin layer of gold for 60 s before imaging.

Table 1
Temperature set of the twin-screw extruder.

Zone	1	2	3	4	5	6	7	Die
Temperature ($^\circ\text{C}$)	240	260	270	250	240	230	220	230

Table 2

Sample compositions and the corresponding symbols (all values are in weight proportion %).

Sample	PBT	E-MA-GMA	Al ₂ O ₃
PBT/Al ₂ O ₃	60	0	40
2% E-MA-GMA	58	2	40
5% E-MA-GMA	55	5	40
8% E-MA-GMA	52	8	40

2.3.4. Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared (FTIR) spectra of the samples were obtained using a Bruker Tensor 27 FTIR instrument. All of the samples were measured in transmittance mode in the range of 4000 to 600 cm⁻¹ with a resolution of 4 cm⁻¹.

2.3.5. Differential scanning calorimetry (DSC)

The thermal properties and crystalline behavior of the PBT/Al₂O₃/E-MA-GMA samples were determined using a differential scanning calorimeter (DSC) (Diamond, Perkin-Elmer, USA). Pre-weighted samples (around 8 mg) were sealed in aluminum pans and heated from 30 °C to 280 °C at 10 °C/min, maintained at 280 °C for 3 min to erase any thermomechanical history. Then the sample was cooled down to -20 °C at 10 °C/min, following by reheating to 280 °C at a rate of 10 °C/min. The measurements were all carried out in the nitrogen atmosphere.

2.3.6. Dynamic mechanical analysis (DMA)

The glass transition temperature of the PBT/Al₂O₃/E-MA-GMA samples were determined using a dynamic mechanical analyzer (Diamond, Perkin-Elmer, USA) in the single cantilever mode. The temperature was

increased from -50 °C to 180 °C at a heating rate of 3 °C/min. During the measurements, a fixed frequency of 1 Hz was used.

2.3.7. Rheological characterizations

The rheological behavior was carried out on a stress-controlled rotational rheometer (DHR-2, TA Instruments) equipped with a 25 mm parallel-plate geometry and a gap size of 1000 μm at 270 °C. Dynamic frequency sweep tests varied from 0.01 to 100 rad/s were performed under a fixed strain amplitude of 0.5%, which were measured within the linear viscoelastic region.

3. Results and discussion

3.1. Mechanical properties and thermal conductivity

The tensile mechanical properties were firstly investigated. Fig. 1(a) shows the typical engineering stress-strain curves of all the composites samples, and the corresponding tensile properties dependencies on the compatibilizer content, including tensile strength and elongation at break are illustrated in Fig. 1(b) and Table 3. We can clearly see from Fig. 1(a) that the ternary PBT/Al₂O₃/E-MA-GMA composites showed a typical ductile stress-strain behavior with an extensive elongation before failure. As the content of elastomer increasing, the tensile strength of PBT/Al₂O₃/E-MA-GMA composites decreased due to the elastomeric characteristics of E-MA-GMA [26]. These results were similar to previous works, which indicated that the improved compatibility did not have a significant influence on the low-strain tensile properties [27]. In the case of elongation at break, it exhibits higher values as the content of E-MA-GMA increased. The increment was approximately 83.2% for 2 wt% elastomer filled, 121.5% for 5 wt% elastomer filled, and 200.7% for 8 wt% elastomer filled composites. These results show that adding E-MA-GMA facilitates the improvement of the tensile fracture toughness of the ternary PBT/Al₂O₃/E-MA-GMA composites.

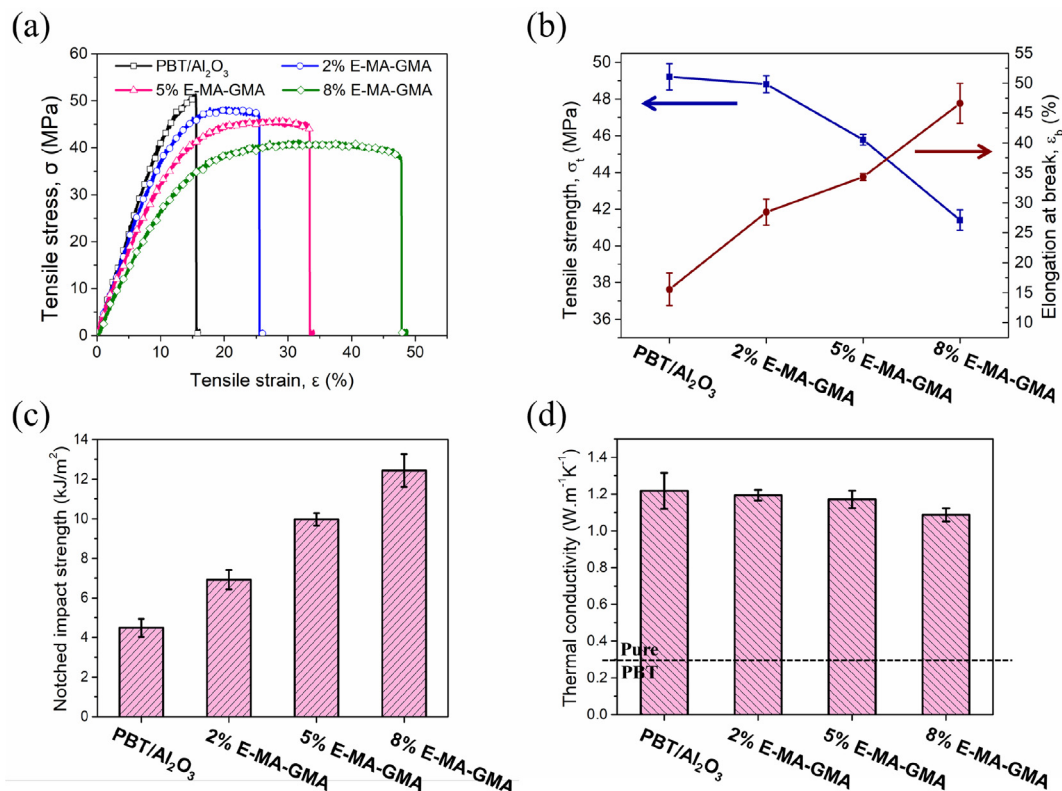


Fig. 1. Mechanical and thermal conductivity properties of PBT/Al₂O₃/E-MA-GMA composites: (a) the tensile stress-tensile strain curve, (b) tensile strength and elongation at break curves, (c) Notched impact strength and (d) thermal conductivity.

Table 3
Mechanical properties and thermal conductivity of the PBT/Al₂O₃ composites.

Sample	Tensile strength (MPa)	Elongation at break (%)	Impact strength (MPa)	Thermal conductivity (W. m ⁻¹ K ⁻¹)
PBT/Al ₂ O ₃	49.2 ± 0.7	15.5 ± 2.7	4.4 ± 0.4	1.21 ± 0.09
2% E-MA-GMA	48.8 ± 0.5	28.4 ± 2.2	6.9 ± 0.5	1.19 ± 0.03
5% E-MA-GMA	45.7 ± 0.3	34.3 ± 0.6	9.9 ± 0.3	1.17 ± 0.05
8% E-MA-GMA	41.4 ± 0.5	46.6 ± 3.3	12.4 ± 0.8	1.09 ± 0.03

The notched Izod impact measurement was used to further confirmed the toughening effect of E-MA-GMA in the PBT/Al₂O₃ specimens. As shown in Fig. 1(c) and Table 3, the binary PBT/Al₂O₃ composites show the lowest impact strength, only about 4.4 kJ/m². Improved impact strength is obtained by simply adding 2 wt% E-MA-GMA to the composite and the value is increased up to 6.9 kJ/m², which is about 54% higher than that of the binary composite. This apparently indicates the toughening effect of E-MA-GMA on the PBT/Al₂O₃ composite. Further increased impact strength is achieved for the ternary composites. Specifically, the impact strength is enhanced up to 12.4 kJ/m² at E-MA-GMA content of 8 wt%, which is about 177% higher than that of binary PBT/Al₂O₃ sample.

The influence of the E-MA-GMA content on the thermal conductivity κ of the PBT/Al₂O₃/E-MA-GMA composites is shown in Fig. 1(d) and Table 3. Neat PBT exhibited a low κ , i.e., around 0.28 W/(m·K) [28], due to the poor phonon transportability of polymers. Well dispersed Al₂O₃ spheres in the PBT matrix could establish percolated pathways at a 40 wt% loading, which induced an evident enhancement of the κ to approximately 1.21 W/(m·K). Subsequent incorporation of E-MA-GMA into PBT/Al₂O₃ composite slightly reduced thermal conductivity. The variation of thermal conductivity was the synthetic result of two factors. On the one hand, the addition of E-MA-GMA enhanced the

interfacial interaction between the PBT matrix and Al₂O₃ spheres by the reactive compatibilization. This could increase the compactness of the composites and thereby increase the thermal conductivity [29]. On the other hand, E-MA-GMA has a relatively low thermal conductivity compared to the PBT matrix [30]. It formed an interface-modified layer on the Al₂O₃ spheres, which could decrease the interfacial thermal conductivity [19]. On the whole, the κ value of the PBT/Al₂O₃/E-MA-GMA composites still kept within a small range nearing that of PBT/Al₂O₃ composites even the E-MA-GMA content is 8 wt%.

3.2. Morphology and interfacial compatibilization

The cyro-fractured surface morphologies of the PBT/Al₂O₃/E-MA-GMA composites were investigated by SEM, as presented in Fig. 2. For the fractured surface of the PBT/Al₂O₃ composites (Fig. 2 (a) and (a')), it can be seen that many Al₂O₃ spheres are partially embedded in the PBT matrix and surrounded by some well-shaped circular craters due to the Al₂O₃ spheres being pulled out. The relatively clean surface is an obvious evidence of the poor interfacial adhesion. There were fewer Al₂O₃ spheres exposed with the addition of E-MA-GMA, and the Al₂O₃ spheres were wrapped by the PBT matrix due to the enhancement of interface interaction. As the E-MA-GMA content increases to 8 wt% (Fig. 2

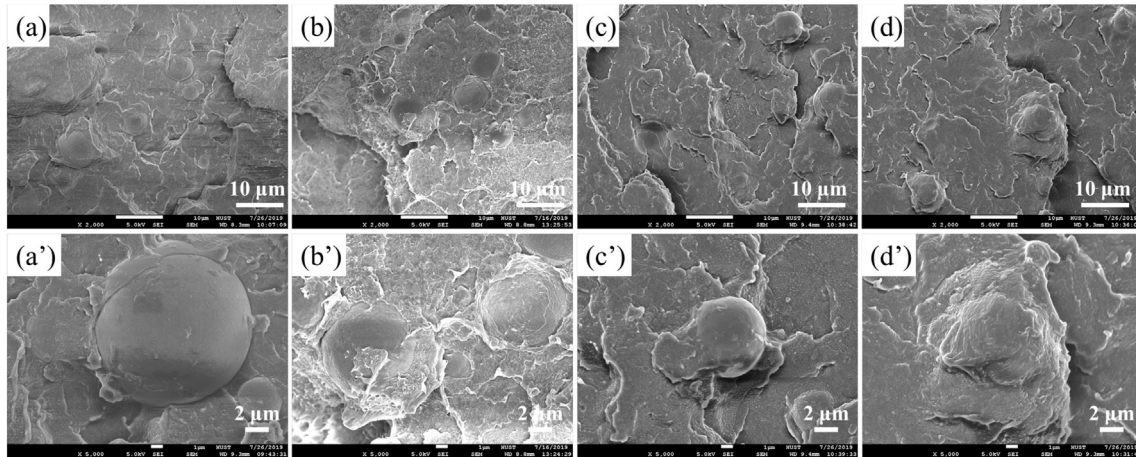


Fig. 2. SEM images of the fractured surface of PBT/Al₂O₃/E-MA-GMA composites: (a) and (a') PBT/Al₂O₃, (b) and (b') PBT/Al₂O₃/2 wt% E-MA-GMA, (c) and (c') PBT/Al₂O₃/5 wt% E-MA-GMA, (d) and (d') PBT/Al₂O₃/8 wt% E-MA-GMA.

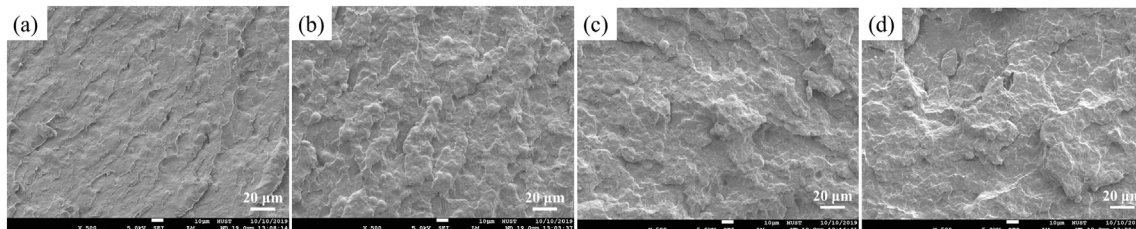


Fig. 3. SEM images of impact fractured surface of PBT/Al₂O₃/E-MA-GMA composites: (a) PBT/Al₂O₃, (b) PBT/Al₂O₃/2 wt% E-MA-GMA, (c) PBT/Al₂O₃/5 wt% E-MA-GMA, and (d) PBT/Al₂O₃/8 wt% E-MA-GMA.

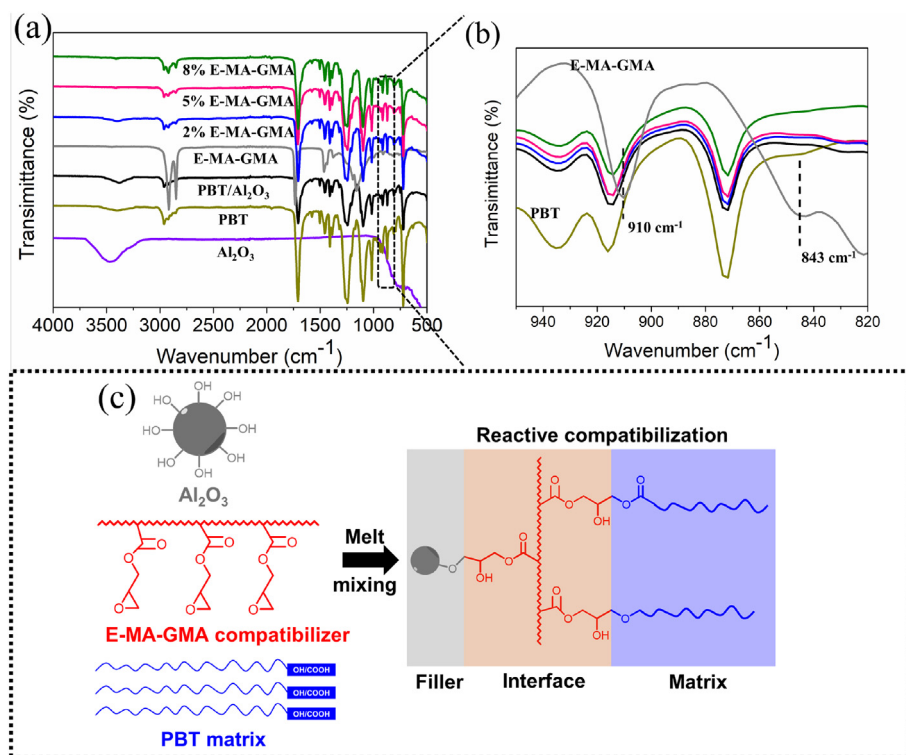


Fig. 4. FTIR spectra of PBT/Al₂O₃/E-MA-GMA composites (a) from 4000 cm⁻¹ to 500 cm⁻¹, (b) from 950 cm⁻¹ to 820 cm⁻¹, and (c) Schematic representation of possible reaction between the ternary components Al₂O₃, E-MA-GMA, PBT.

(d) and (d')), the Al₂O₃ spheres are almost entirely embedded in the PBT matrix. The observed Al₂O₃ spheres surface adhesion indicates improved interfacial adhesion and compatibilization after the introduction of the E-MA-GMA elastomer into the PBT/Al₂O₃ composite system.

To further study the interfacial adhesion behavior, the impact fracture surface morphologies of the PBT/Al₂O₃/E-MA-GMA composites were characterized using SEM. Fig. 3 shows the morphologies of the representative samples. As shown in Fig. 3(a), the binary PBT/Al₂O₃ sample exhibits a smooth surface without visible plastic deformation. This is consistent with its relatively low impact strength. The ternary PBT/Al₂O₃/E-MA-GMA composites exhibit different morphologies compared with the binary samples. Firstly, the fracture surface became rougher with the addition of E-MA-GMA elastomer. Secondly, fewer Al₂O₃ spheres exposed to the fractured surface due to the intensive plastic deformation. These results further indicate that the interfacial interaction between the PBT matrix and the Al₂O₃ fillers becomes stronger after adding E-MA-GMA. The improved interfacial adhesion prevents

the initiation and propagation of the cracks at the interface of the composite [31], thereby enhanced toughness was obtained.

As a reactive compatibilizer, the epoxy groups of E-MA-GMA may react with the hydroxyl groups on the surface of Al₂O₃ spheres, the terminal hydroxyl and carboxyl groups of PBT during the melt mixing process. Here, FTIR analysis was conducted to probe these interactions qualitatively. Fig. 4(a) shows the FTIR spectra of Al₂O₃ spheres, PBT, PBT/Al₂O₃, E-MA-GMA, and PBT/Al₂O₃/E-MA-GMA composites. The broad band peak at 3472 cm⁻¹ is assigned to the hydrogen-bonded OH groups on the surface of Al₂O₃ spheres [32]. This indicates the presence of massive hydroxyl groups on the surface of Al₂O₃ spheres. For pure PBT, the peak at 1706 cm⁻¹ is assigned to the stretching vibration of the C=O group, the peaks at 1250 cm⁻¹ and 1101 cm⁻¹ correspond to the stretching of C-O [33]. Compared with the corresponding position of PBT, all the peaks of the PBT/Al₂O₃ spectrum slightly shift to the direction of high wavenumber. This indicates the interactions with the terminal groups of PBT and hydroxyl groups on the surface of

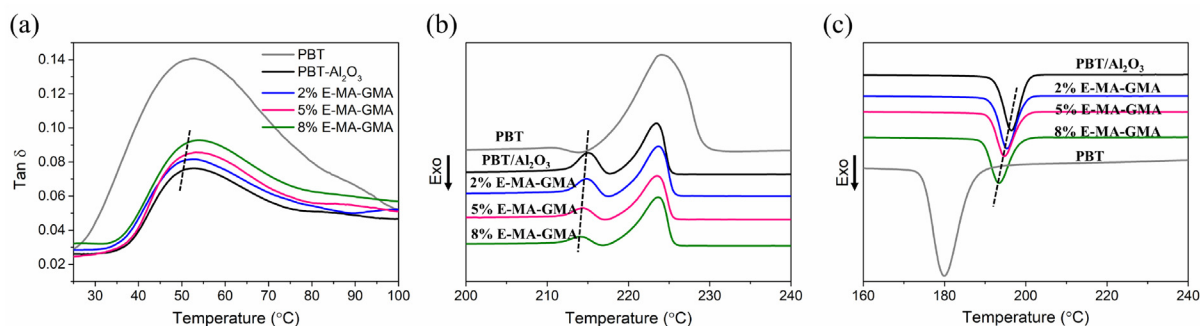


Fig. 5. (a) Tan δ curves, DSC results (b) second heating cycle and (c) cooling cycle of PBT/Al₂O₃/E-MA-GMA composites.

Table 4

Thermal properties of the composites analyzed by DMA and DSC tests.

Sample	T_g (°C)	T_{m1} (°C)	T_{m2} (°C)	T_c (°C)	X_c (%)
PBT	52.8	–	224.2	179.8	50.4
PBT/ Al_2O_3	52.5	215.1	223.4	196.5	31.3
2% E-MA-GMA	52.8	214.8	223.7	195.4	30.9
5% E-MA-GMA	53.2	214.4	223.6	194.7	28.9
8% E-MA-GMA	54.2	214.1	223.6	193.3	29.7

Al_2O_3 spheres, which could increase the electronegativity and lead to the blue shift [34]. For the E-MA-GMA spectrum, the apparent absorption peak at 910 cm^{-1} and 843 cm^{-1} attributed to the C–O stretching vibration peak of the epoxy group. The peak of the hydroxyl groups became weaker distinctly for the PBT/ Al_2O_3 /E-MA-GMA composites spectra, and no similar epoxy group characteristic peaks could be seen (Fig. 4(b)) [25]. These FTIR spectra confirm that the reactive compatibilization was achieved in the PBT/ Al_2O_3 /E-MA-GMA composites. The possible chemical reaction between Al_2O_3 , E-MA-GMA, and PBT is illustrated in Fig. 4(c). The epoxy groups of E-MA-GMA not only reacted with hydroxyl groups on the surface of Al_2O_3 , but also reacted with hydroxyl and carboxyl groups at the end of PBT chains. Hence, the compatibilizer E-MA-GMA reacted with both Al_2O_3 fillers and the PBT matrix during melt processing by in situ grafting reaction. Accordingly, graft copolymers were formed at the interface, which would promote the compatibility between the ternary components.

3.3. Thermal behavior

PBT is a semi-crystalline thermoplastic polymer, whose mechanical and thermal performance are greatly dependent on the phase structure and crystallinity level. Therefore, the relaxation, melting and crystallization behavior of all the samples were investigated by DMA and DSC. The

thermograms are shown in Fig. 5, and the corresponding results are summarized in Table 4. Fig. 5(a) illustrates the variations of loss factor ($\tan \delta$) with increasing temperatures. The glass transition temperatures (T_g) of the composites can be obtained from the maximum relaxation peaks positions. From Fig. 5(a) one can see that their T_g improved from 52.5°C to 54.2°C by introducing compatibilizer E-MA-GMA. This increment in T_g can be considered due to the effect of improved interfacial adhesion between the PBT matrix and Al_2O_3 spheres [31], which demonstrates that the presence of E-MA-GMA restricts the molecular motion of the PBT matrix. It can be seen from Fig. 5(b) that two distinct endotherm peaks were observed for all the composites, which differ from the virgin PBT. This indicates that highly filled Al_2O_3 spheres restricted the mobility of the PBT chains and brought about some imperfect crystals [32]. The imperfect crystals melted firstly at low temperatures due to their poor stability and might recrystallize to more perfect crystals. All the more perfect crystals subsequently melted at high temperatures [35]. The crystallinity for the ternary PBT/ Al_2O_3 /E-MA-GMA composites was around 30%. Also, the melting temperatures T_{m1} and T_{m2} show no visible change. This indicates that the crystallinity of PBT was not significantly influenced by E-MA-GMA. This result agrees well with other PBT/elastomer blends and other semicrystalline polymer matrix/elastomer blends [33,36,37]. Therefore, it can be concluded that the mechanical properties improvement of the composites was not dependent on the variation of the PBT matrix crystallinity.

3.4. Linear rheological behavior

Dynamic rheological measurements provide not only the processing flowability data of materials but also the information about the microstructure of the composites. Here, the rheological property changes of PBT/ Al_2O_3 composites induced by E-MA-GMA elastomer were investigated, and the effect of E-MA-GMA content on complex viscosity ($|\eta^*|$), storage modulus (G'), loss modulus (G'') and loss factor are

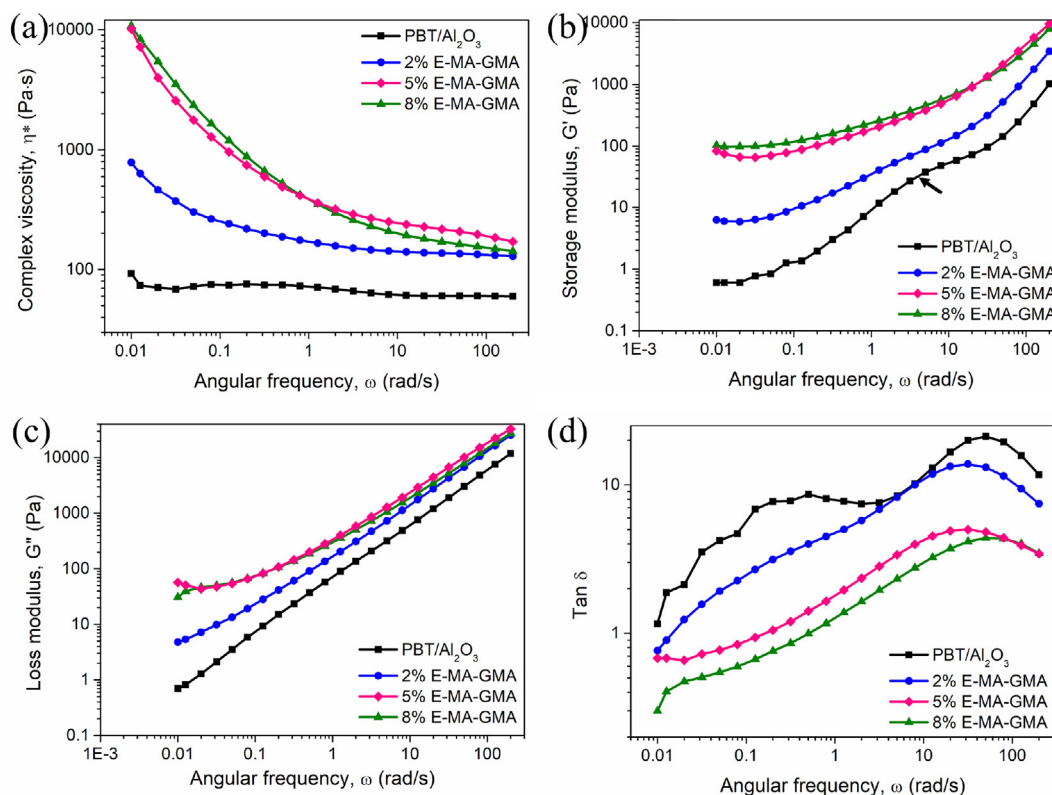


Fig. 6. Rheological properties of the PBT/ Al_2O_3 /E-MA-GMA composites: (a) complex viscosity, (b) storage modulus, (c) loss modulus, and (d) $\tan \delta$.

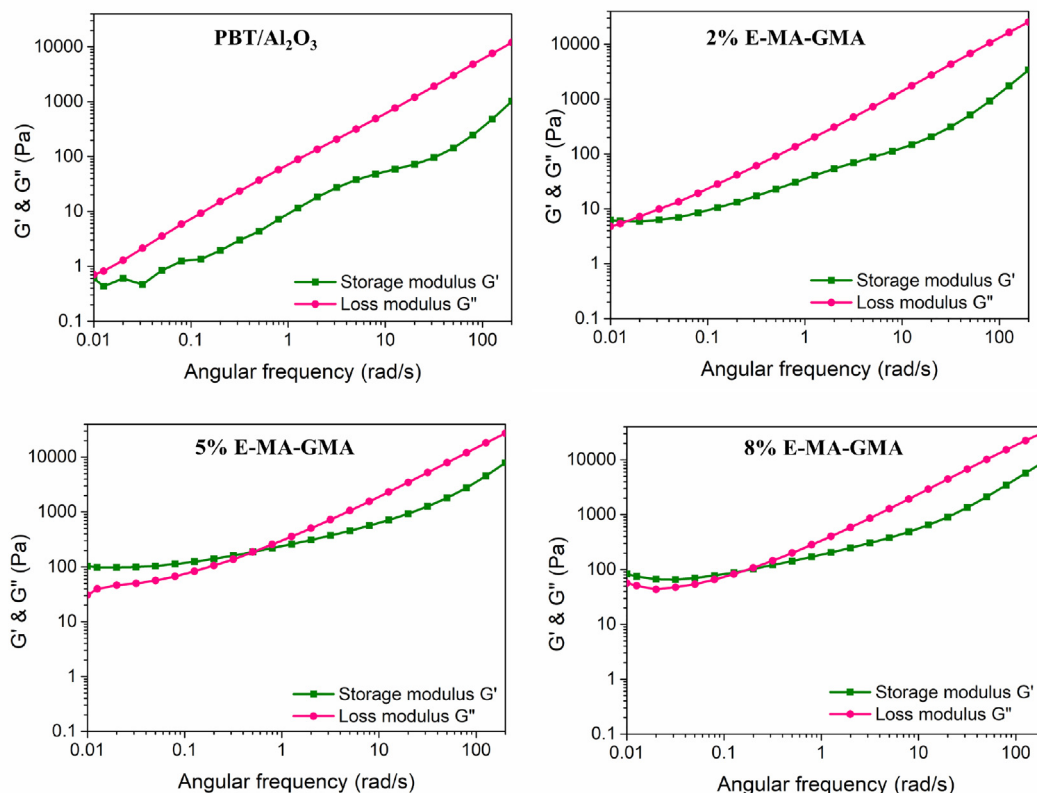


Fig. 7. Variation of storage and loss modulus with frequency at different E-MA-GMA contents based PBT/Al₂O₃ composites.

shown in Fig. 6. As shown in Fig. 6(a), the incorporation of E-MA-GMA could obviously increase the viscosity of PBT/Al₂O₃ composites. This effect became more pronounced with the increase in E-MA-GMA content. In addition, the PBT/Al₂O₃/E-MA-GMA composites shown more pronounced shear thinning behavior and altered the Newtonian behavior of PBT/Al₂O₃ in the medium frequency region. These observations demonstrate that the interfacial interaction and the molecular chain entanglement ability were enhanced due to the introduction of E-MA-GMA elastomer [38].

Storage modulus (G') and loss modulus (G'') reflect the energy stored and dissipated during the flow and deformation process, which are highly sensitive to the inter structure of macromolecular at low frequency region [20]. Hence, variation in G' and G'' of composites for different wt% of E-MA-GMA in PBT/Al₂O₃ with angular frequencies is illustrated in Fig. 6 (b) and (c). At lower frequencies, as shown in Fig. 6 (b), the binary PBT/Al₂O₃ blend shows a 'shoulder' on the G' curve (as shown by an arrow). Generally speaking, the existence of the interface with longer relaxation leads to an additional transition 'shoulder' on the G' curve during the oscillatory shear flow process [39]. In other words, the presence of the 'shoulder' is due to the occurrence of a new relaxation process. This indicates the phase separation occurred in the PBT/Al₂O₃ binary composites under the dynamic shear condition, along with the formation of a large number of interfaces. For the ternary composites, several changes are presented in the G' curves that merit attention. Firstly, the 'shoulder' disappears after the introduction of E-MA-GMA. This means that the contribution of the interface on the G' is weakened. The previous SEM analysis also has demonstrated that E-MA-GMA enhanced the interaction between the polymer and Al₂O₃ components, which could lead to the disappearance of the 'shoulder'. Secondly, the ternary composites show an increased G' especially at low frequencies compared to PBT/Al₂O₃ binary sample. This indicates slight crosslink structure and strengthened Al₂O₃ spheres network structure could be observed in the melt [40]. Thirdly, the G' curves are similar between

PBT/Al₂O₃/5% E-MA-GMA and PBT/Al₂O₃/8% E-MA-GMA samples. This could conclude that the interfacial enhancement effect has almost reached its limit after adding 5 wt% E-MA-GMA. Fig. 6(c) shows G'' versus angular frequency for all the composites. It was evident that the G'' of ternary samples was higher than that of binary composites. The G'' enhanced as the E-MA-GMA content increasing.

The loss angle (δ) or tangent δ is also widely used to evaluate the elastic response of composites [38,41]. Fig. 6(d) shows the angular frequency dependence of $\tan \delta$ for the composites. After adding E-MA-GMA in the composites, the slightly crosslinked structure was formed in the ternary system resulted in more molecular entanglement, which was capable of decreasing the $\tan \delta$ at low frequency region. Meanwhile, it could find that the $\tan \delta$ reduced further by incorporating E-MA-GMA elastomer in the system. It can be concluded that the incorporation of E-MA-GMA in the PBT/Al₂O₃ composites works as an interfacial compatibilizer and cross-linked elastomer components.

Dynamic intersection frequency (ω_c) indicates the crossover of G' and G'' curves in the rheological criterion of viscous and elastic behavior [42,43]. The value of crossing frequency relies on the homogeneity of the system. The G' and G'' of the PBT/Al₂O₃/E-MA-GMA composites are plotted against frequency, which is shown in Fig. 7. For PBT/Al₂O₃ sample, the G' and G'' curves do not intersect, and the G'' is higher than G' in the whole investigated frequency range, although the loading level of Al₂O₃ spheres was up to 40 wt%. This implies that the PBT/Al₂O₃ sample exhibits liquid-like behavior, and the Al₂O₃ spheres can move freely and independently in the PBT phase. The reason for this phenomenon may be due to the relatively lower aspect ratio of the spheres [44]. For the ternary composites, the pseudo-solid-like behavior ($G' > G''$) in the lower frequency zone appears, and it gradually turns evident with the further increase of the E-MA-GMA elastomer content. This indicates that the ternary composites behave as more elastic materials due to the presence of E-MA-GMA [45,46]. In other words, the E-MA-GMA elastomer significantly promoted filler-filler and filler-polymer

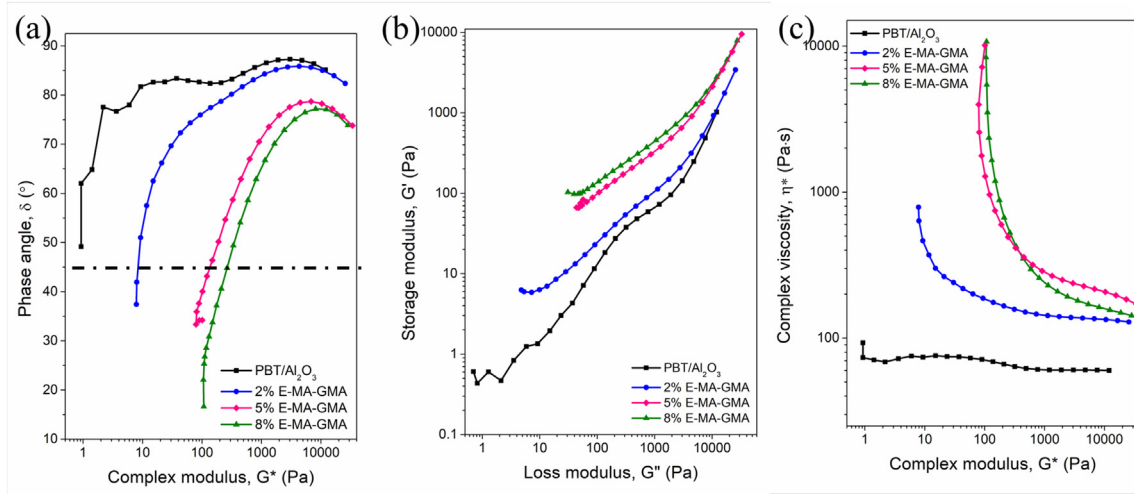


Fig. 8. (a) Van Gurp Palmen plots, (b) Han plots, and (c) complex viscosity versus complex modulus plots of the PBT/Al₂O₃/E-MA-GMA composites.

interaction. An interconnected structure of Al₂O₃ spheres-Al₂O₃ spheres and Al₂O₃ spheres-polymer was formed in the PBT/Al₂O₃/E-MA-GMA composites.

Three rheology criteria plotted in Fig. 8 are utilized to detect the secondary structure differences in the PBT/Al₂O₃/E-MA-GMA composites. Fig. 8(a) shows the plot of the complex modulus $|G^*|$ versus phase angle δ , which is well-known as van Gurp–Palmen plots. This plot is utilized to estimate the liquid-solid transition point and study the internal structural variations of polymer composites [47]. Specifically, if the δ value is above 45° in the low $|G^*|$ region, the heterogeneous composite system has liquid-like behavior. Otherwise, below 45° indicates solid-like behavior [48]. It is observed that for PBT/Al₂O₃ sample, the δ value is close to 50° in the low G^* region indicates the viscous flow is dominant. That is to say, PBT can completely relax at 270 °C with 40 wt% Al₂O₃ spheres incorporation. An apparent decrease in the δ values is observed with the addition of E-MA-GMA elastomer. The 8 wt% E-MA-GMA elastomer addition even makes the δ value reduce to approximately 15°. This is ascribed to the generation of a pseudo-solid network. This is the well-known percolated behavior from the rheological point of view. It is mainly dependent on the concentrations of fillers and their interactions with polymer chains [49]. Here, the concentration of fillers kept the same in all the composite samples, which indicates

that the particle-polymer interaction is dominant in this work. The incorporation of E-MA-GMA elastomer improved Al₂O₃ spheres-PBT affinity, which encourages polymer chain bridging particles and promoting particle percolation. The particle percolation behavior can be further determined by the Han plots, as shown in Fig. 8(b). Two distinct phenomena can be seen in this figure. First, the slope of the curves in the terminal region decreased when the E-MA-GMA was added, which might indicate the distinctive interaction mechanisms of E-MA-GMA and PBT/Al₂O₃ composites [50]. Second, the G' and G'' at the end of the curve increased significantly, which further confirms the enhanced interaction between fillers and polymer. Finally, the plot of $|\eta^*|$ versus $|G^*|$ (Fig. 8(c)) is used to further characterize the rheological behavior of the composites. It has previously been reported that the strong interactions between the components in the composites could lead to apparent yield stress [43,51]. Moreover, this effect is more pronounced in the $|\eta^*|$ versus plot. Here, it is clear from Fig. 8(c) that $|\eta^*|$ is independent of $|G^*|$ for the ternary sample. For the ternary composites, $|\eta^*|$ increase rapidly at low $|G^*|$ region, which indicates the strong melt flow restrictions. Also, an evident yield behavior ($|G^*|_{\eta^* \rightarrow \infty}$) can be observed, especially when the content of E-MA-GMA above 5 wt%. This means the deformation of the percolating network could be suppressed by the strong viscous restriction under the weak shear field [19].

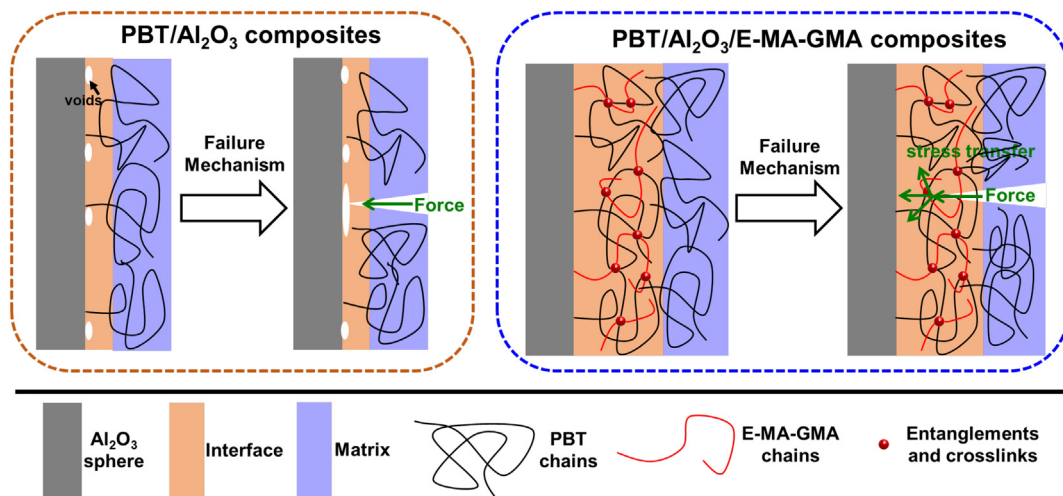


Fig. 9. Schematic of the possible toughening mechanism of PBT/Al₂O₃/E-MA-GMA composites.

3.5. Toughening mechanism

Based on the above experimental results, we propose the possible toughening mechanism of PBT/Al₂O₃/E-MA-GMA shown in (Fig. 9). For binary PBT/Al₂O₃ composites, there are some little gaps between the Al₂O₃ spheres and the PBT matrix due to the weak interactions. Hence, stress concentration preferred to occur in the interphase between the fillers and polymer matrix when the sample was subjected to the external force. On the contrary, when the E-MA-GMA elastomer was added, the elastomer could not only react with the hydroxyl groups of Al₂O₃ spheres, but also entangle and react with the PBT chains, thus leading to a strong interaction between Al₂O₃ spheres and PBT matrix. Under large external force, it is the two reasons that improve the toughness of the composites. First, strong particle-matrix interfacial adhesion can effectively reduce the risk of micro-cavitation and micro-debonding round the Al₂O₃ spheres, thereby preventing the cracks of the composites [52]. Second, the soft E-MA-GMA phase facilitated stress-transferring from the elastomer phase to multiple directions, which could prevent the stress concentration [16,53]. Consequently, the ternary PBT/Al₂O₃/E-MA-GMA composites exhibit superior fracture toughness compared with the binary PBT/Al₂O₃ composite.

4. Conclusion

In summary, the ternary PBT/Al₂O₃/E-MA-GMA composites with varied E-MA-GMA contents have been prepared in this work. The introduction of compatibilizer in the highly filled PBT/Al₂O₃ composite system presented a higher elongation at break and greatly enhanced impact response, simultaneously showing little impact on tensile strength and thermal conductivity. Morphological and FTIR characterizations demonstrated that the interfacial compatibility between PBT and Al₂O₃ spheres could be improved via reactive compatibilization during melt mixing. The crystallinity and melting temperature were not significantly influenced by E-MA-GMA. The enhanced interfacial interaction was further confirmed in the composites melt, leading to the percolation phenomenon and apparent yield behavior in the PBT/Al₂O₃/E-MA-GMA composites melt. Two effects, i.e., the particle-matrix interfacial interaction and stress transfer, were used here to explain the toughening phenomenon. This work provides an alternative way to resolve the challenge of mechanical degradation for highly filled polymeric composites.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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