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Enhancing the mechanical strength and toughness of epoxy resins with linear POSS nano-modifiers†

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Glass transition temperature (T_g) always deteriorates while improving the strength of epoxy resins which inherently suffer from brittleness. Herein, novel linear polyhedral oligomeric silsesquioxane (POSS)-epoxy nano-modifiers are synthesized with variable contents of POSS. The thermomechanical properties and chemical structure study of the POSS-epoxy indicates significant differences of the rigid POSS content in the linear nano-modifiers. By taking advantage of the synergistic effect of nanofillers and linear polymers, the modifiers disperse at the molecular level when POSS-epoxy is utilized as a co-curing agent for epoxy resins, allowing the applied force to be transferred into the polymer matrix. A good balance of T_g, stiffness, and fracture toughness can be obtained. At 5 wt% of the nano-modifier, the resultant epoxy resins showed 27% enhancement in the Young's modulus relative to the neat epoxy. In addition, the T_g and strength of epoxy thermosets are improved due to the increased cross-linking density, rough surface and tortuous path that resulted in good dispersion of energy during crack propagation.

1. Introduction

Epoxy resin is one of the most important thermosetting polymers. Because of its good mechanical and thermal properties and high chemical resistance, it is widely used as a composite matrix for adhesives and structural materials in the aerospace and electronics industries.[1] However, epoxy resins are inherently brittle and notch sensitive due to their highly cross-linked structure. Various materials have been utilized to improve the toughness of epoxy resins, including inorganic nanoparticles,[2] carbon based nanomaterials,[3,4] synthetic rubber,[5] dendrimers,[6] block copolymers[7] and natural macromolecules.[8] At present, the influence of inorganic nanoparticles and heterogeneous polymers on the modification of epoxy resins is being extensively studied. However, it is difficult for inorganic nanoparticles to be uniformly dispersed in the polymer matrix. Therefore, in addition to the optimization ratio and facile preparation method, the more crucial thing is to consider whether the compatibility between materials and glass transition temperature is reduced at a cost.

In order to improve the compatibility of materials without sacrificing thermodynamic and mechanical properties, the structure of nanofillers must be rationally designed. In our previous study, azobenzene modified graphene oxide and rigid star-shaped cyclophosphazene have been reported to show good compatibility and reinforcement effect toward polyurethane.[9,10] Due to their unique nanoscale structure and excellent mechanical and thermal properties, polyhedral oligomeric silsesquioxanes (POSS) have been suggested to be an ideal reinforcing reagent. If we combine rigid nanoscale POSS and flexible polymer chains, it would be able to toughen epoxy resin without deteriorating the physical properties. POSS is a cage-like structure composed of inorganic $SiO_{1.5}$ units and organic functional groups.[11] The terminal functional groups of POSS can be modulated by various strategies, thus, the interaction and compatibility between POSS and epoxy resins can be improved through physical or chemical mixing.[12–14]

Herein, we report the synthesis of a new series of linear nano-modifiers that can act effectively as molecular modifiers and co-curing agents with a large aspect ratio for high performance epoxy resins. As shown in Fig. 1, the POSS-epoxy modifiers were designed with the purpose of increasing the miscibility with the epoxy resins. The highly aromatic backbone containing phenylfluorene units was chosen to offer good thermal stability, mechanical properties and chemical resistance. Most importantly, dual-substituted POSS was linearly incorporated into the polymer backbones at higher ratios to achieve the purpose of combining nanoparticle reinforcement and linear polymer toughening together. We found that the curing performance of POSS-epoxy conforms to the

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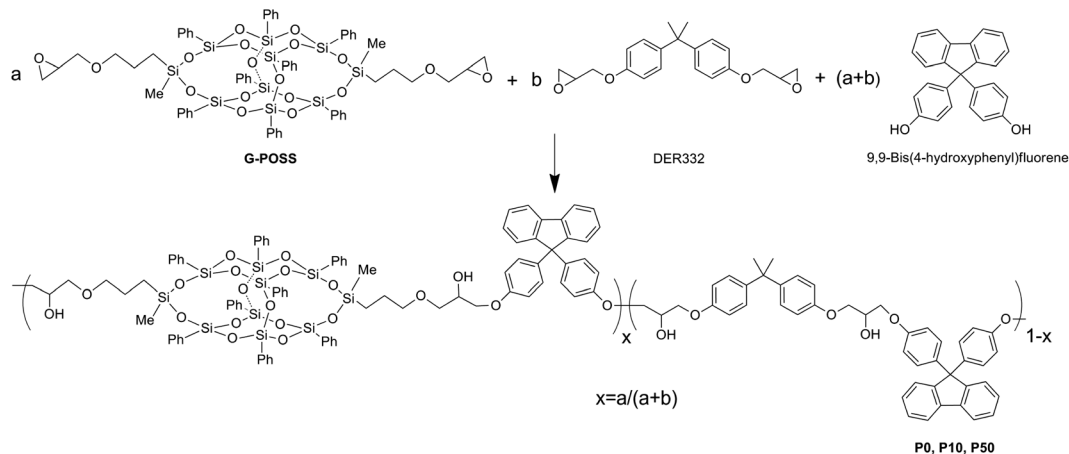
Fig. 1   The synthesis of thermoplastic modifiers G-POSS, P0, P10, and P50 (n in Pn denotes the weight percent of G-POSS used in the feed).

autocatalytic Sestak–Berggren (SB) model,[15] which enhances the interfacial interaction between the POSS-epoxy filler and epoxy resin matrix, resulting in high thermal stability and improved mechanical properties compared with neat epoxy resins.

2.   Experiments and methods

2.1   Synthesis of thermoplastic modifiers

All thermoplastic modifiers were synthesized *via* step polymerization between diglycidyl ether resin (DER332) and G-POSS (ESI†) with 9,9-bis(4-hydroxyphenyl)fluorine by varing the ratio of G-POSS. Different nano-modifiers P*n* (*n* denotes the weight percent of G-POSS) were obtained by adjusting the feeding ratio of DER332 and G-POSS. In a typical synthesis of P10, G-POSS (0.11 g, 0.08 mmol), 9,9-bis(4-hydroxyphenyl)fluorene (1.0 g, 2.86 mmol), DER332 (0.95 g, 2.78 mmol), 0.3 wt% tetrabuty-lammoniumbromide (TBAB) and 1,4-dioxane (6.0 mL) were added into a flask. The mixture was allowed to react at 120 °C for 5 h. After that, 1,4-dioxane was removed by distillation. The reaction was further continued for an additional 16 h at 150 °C. A pale solid was obtained after washing 3 times with methanol. After drying at 60 °C in a vacuum oven for 24 h, 1.65 g product was obtained with a yield of ~80%.

2.2   Preparation of epoxy resins with the modifiers

A series of epoxy resins labeled ER-X (where X = P0, P10, P50 or POSS) were prepared by adding 5 wt% of various modifiers X. Thus, 0.75 g of the modifier was mixed with 2.96 g of LC100, 11.29 g of DER332, and 10 mL of THF. The mixture was stirred at room temperature for 2 hours. After removal of the solvent *via* evaporation, the mixture was poured carefully into a glass mold and cured using the temperature program: 130 °C for 1 hour, 160 °C for 2 hours and 230 °C for 4 hours.

3.   Results and discussion

3.1   Synthesis and properties of the nano-modifiers

The bifunctional G-POSS was synthesized *via* a hydrosilylation reaction between ally glycidyl ether and 3,13-dihydrooctaphenyl POSS following a previously reported method with a minor modification.[16] Fig. S1† shows the ¹H-NMR spectrum of G-POSS and the other modifiers prepared. The resonance peak of Si–H at 4.98 ppm disappeared, suggesting the complete hydrosilylation reaction. New peaks that appeared at 0.75, 1.68, 2.43, 2.65, 2.97, 3.17, 3.47 and 3.34 ppm were assigned to the glycidyloxypropyl groups of G-POSS. ¹³C-NMR was used to further confirm the chemical structure of G-POSS (see the ESI, Fig. S2†). The MALDI-TOF MS spectrum of the sample showed peaks at $m/z = 1381.4$ (1404.45 − 22.99), which is in agreement with the calculated value at 1380.2 (see the ESI, Fig. S3†).

Linear thermoplastic epoxies can be obtained *via* an epoxy–phenol reaction, catalyzed by quaternary ammonium salts as the Lewis base.[17] In this work, polymerization between DER332, G-POSS epoxy groups and 9,9-bis(4-hydroxyphenyl)fluorene was used to produce linear thermoplastic modifiers, labelled P0, P10 and P50. The viscosity of the reaction system increased during the reaction, and the resulting thermoplastics were transparent and homogeneous. All these thermoplastics could be readily dissolved in chloroform, THF and dioxane. Typical ¹H-NMR spectra of P0 and P50 are displayed in Fig. S1.† Resonance peaks of benzene rings in G-POSS, DER332 and 9,9-bis(4-hydroxyphenyl)fluorene appeared at 6.75–7.75. New peaks of methylene groups appeared at 4.1 and 4.3 ppm. Ethyloxy groups were found to shift from 3.35 ppm to 3.75 ppm and methyl silicate groups shifted from 0.36 ppm to 0.30 ppm after polymerization. ¹H-NMR spectra confirmed the formation of G-POSS and the linear thermoplastic polymers. The molecular weight and polydispersity of the resultant polymers as presented in Table S1† indicated that higher ratios of DER332 lead to higher molecular weights. This observation can be attributed to the large steric hindrance of POSS, which greatly decreases the coupling possibility and reaction kinetics in P10 and P50 samples.

The thermal stability of the nano-modifiers was evaluated by TGA (Fig. 2a). All samples exhibited similar decomposition temperature (T_d) at ~400 °C, indicating that the thermal stability is mainly determined by the chemical structure of the polymer backbones rather than the POSS content. It has been
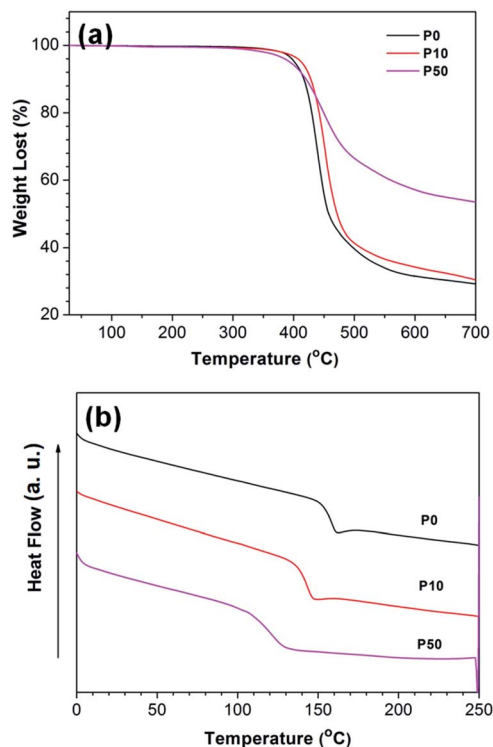
Fig. 2 (a) TGA and (b) DSC curves of the modifiers.

proposed that polymer chain scission is sensitive to the molecular weight and its distribution during the mass loss in TGA.[18] Comparing the trend in the TGA curves, P50 degraded much slower than P0, suggesting that the G-POSS moiety has prohibited the random-chain scissions. A higher percentage of residue was detected in the P50 sample as expected from the higher inorganic content present. The percentage of residue from P10 was rather similar to that of P0 due to the low feed amount of G-POSS incorporated.

DSC analysis (Fig. 2b) confirmed that all the modifiers displayed composition-dependent glass transition temperature. The T_g of P0 was found to be ~159 °C. It decreased to ~130 °C in P10 and further decreased to ~121 °C in P50. It has been suggested that the introduction of nano-POSS into the main chain will increase the free volume between polymer chains, thereby reducing the bulk density of glassy thermoplastics. As a result, the polymer chain rotates more freely, resulting in a lower T_g value.

3.2 Properties of the thermosetting epoxy resins

3.2.1 Morphology of the cross-section. To fabricate the modified epoxy resins, P0, P10 and P50 obtained above were dissolved in THF to give a clear solution. The solution was then mixed with DER332 and a hardener (LC100), respectively, and was cured as described in the experimental section. For comparison, G-POSS itself was also used as a modifier and the resultant resin prepared in the same way was labelled ER-POSS. All the neat epoxy resin (ER) and modified epoxy resins (ER-POSS, ER-P0, ER-P10 and ER-P50) appeared homogeneous and

transparent, indicating good miscibility between the modifiers and the resins.

Fig. 3 presents the TEM images of the epoxy resins added without (Fig. 3a) or with 5 wt% of the modifiers (Fig. 3b–d). The dark lines in each image are cutting marks made by the ultra-microtome. TEM observation indicated a smooth surface and a homogeneous phase throughout the ER, ER-P0 and ER-P10 samples. Aggregation was noticed to a small extent, however, when the POSS content was increased further in ER-P50 as shown in Fig. 3c. The aggregation or phase separation became even more obvious when 100% POSS was used in the sample ER-POSS (Fig. 3d). This phase separation induced by the high POSS content may be attributed to the hydrophobic nature of POSS, which may lead to aggregation of the thermoplastics during curing.

3.2.2 Thermal properties of the epoxy resins. The thermal stability of the neat and modified epoxy resins was tested using TGA and DSC. As shown in Fig. 4, all the modified resins showed higher T_d (~390 °C) compared to the neat ER at 377 °C. The enhanced thermal stability may have arisen from the good miscibility of the thermoplastics and their strong interactions with the epoxy resins. Furthermore, the enhancement in thermal stability can also be attributed to the high thermal stability of POSS since POSS units can form heat resistant layers as thermal barriers during degradation.[19]

From Fig. 4a, all the samples showed closer decomposition rates which is in agreement with the small amount of modifiers added (5 wt%), the intrinsic properties of the epoxy resin are not altered. The DSC thermographs of all the samples are presented in Fig. 4b. A single glass transition was detected, suggesting completely cured structures and uniform dispersion of the modifiers in the epoxy resins. An increment in T_g may be attributed to the reduction of matrix chain mobility in the presence of the modifiers.[20] During the fabrication of the epoxy resins, we believe that the thermoplastics bridged into the matrix with their dangling hydroxyl groups and thus a strong interfacial interaction was produced. This strong interaction confined the mobility of the chains and contributed to the increased T_g.
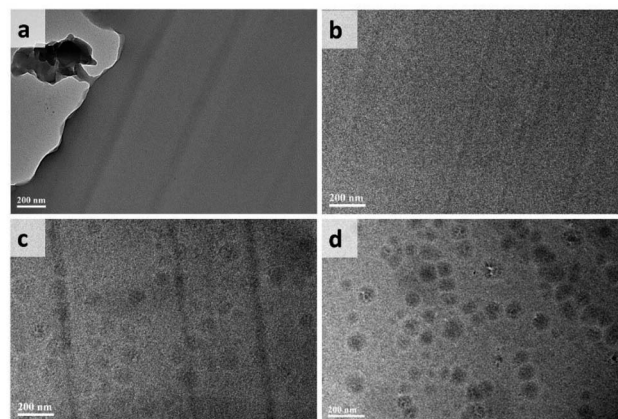

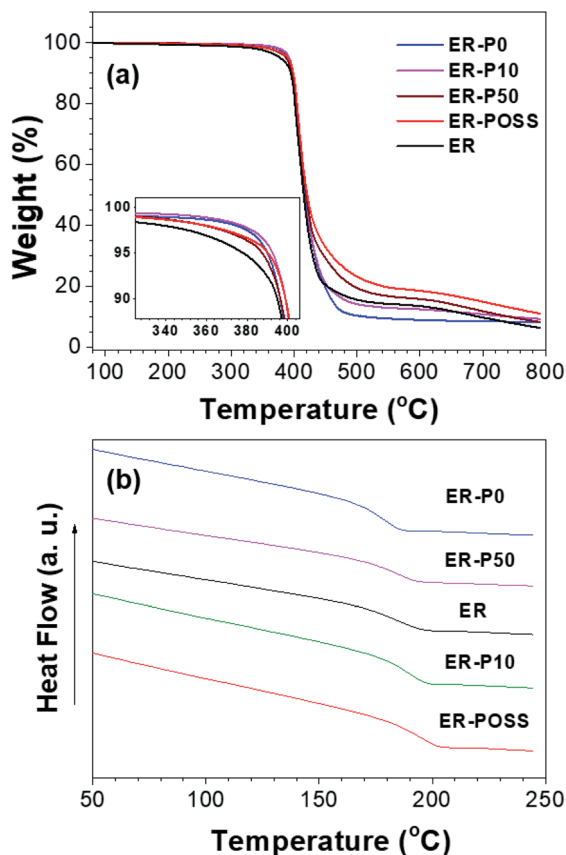Fig. 3 TEM images of the epoxy resins prepared with: (a) neat, (b) P10, (c) P50 and (d) POSS modifiers.

Fig. 4 (a) TGA and (b) DSC curves of the neat and modified epoxy resins.

It is known, however, that aggregation or phase separation of the thermoplastics in the system would lead to weakening of interactions at the interfaces and thus a decrease in T_g. This was indeed observed for the ER-P50 sample. It is worthwhile to note here that G-POSS is a macromolecule containing two end functional groups. Thus, comparing with P50, the same amount (weight) of G-POSS can provide more than tenfold functional groups than that in P50. Hence, we propose that the higher T_g in ER-POSS may be attributed to the strong interfacial interaction between G-POSS and the epoxy matrix. On the other hand, the lower T_g in ER-P0 was probably due to the plasticizer effect,[21] which has been reported in similar P0 doped polymers.

3.2.3 Mechanical performance study. As shown in Fig. 5, the storage modulus of all modified epoxy resins increased except the ER-POSS compared with neat ER. This decrease may be due to the increased crosslink density by the nano-size POSS, resulting in an amplified crystalline domain.[19]

DMA also characterizes T_g at the point when there is sufficient vibrational energy for the rearrangement of cross-linked chains. As shown in Fig. 5b, the T_g value obtained from DMA is consistent with the T_g value obtained from DSC. This can be attributed to the nano-sized POSS and the active hydroxyl groups on the modifiers. The multifunctional groups on POSS cages could limit the mobility of polymer chains. Active hydroxyl side groups on the modifier can participate in the curing reaction, leading to the formation of covalent bonds between the POSS-epoxy and the polymer matrix. It was found that the T_g in ER-P10 and ER-POSS samples was 194.5 °C and 195.1 °C, respectively. On the other hand, the bulky POSS could also increase the free volume of the system, resulting in a depression of T_g. Thus, the higher POSS content in ER-P50 provided higher free volume between the chains, leading to a decrease of T_g to 185.4 °C. The maximum loss moduli of the modified epoxy resins are all higher than that of the control. It increased in the sequence from ER to ER-P50, ER-P10, ER-P0 (Fig. 5c), indicating that the mobility of the polymer chains was enhanced during the glass transition process.

The mechanical properties of thermoset blends depend on the morphological type of nanofillers. The toughening effect of rigid particles depends on the functional groups, dispersibility, amount of loading, particle size and shape.[22,23] By direct mixing, POSS molecules with different substituents (methacryloyl, glycidyl, and trisilanol phenyl) were added to the epoxy resin at a loading amount of 0.5 to 8% by weight. The results showed that the addition of POSS increased the fracture toughness of the epoxy resin by 130%, while the elastic modulus and strength did not change significantly. Furthermore, the glass transition temperature decreases with the increase of POSS content due to aggregation.[24] In order to improve the dispersibility of nanofillers, a hyperbranched POSS-NH$_2$ grafted onto the surface of carbon fiber was fabricated for the toughening epoxy resin. The results showed that the number of amino groups, the hydrophilicity of the interface and the number of covalent bonds formed are all related to the toughening effect. The glass transition temperature of the composite material increased to about
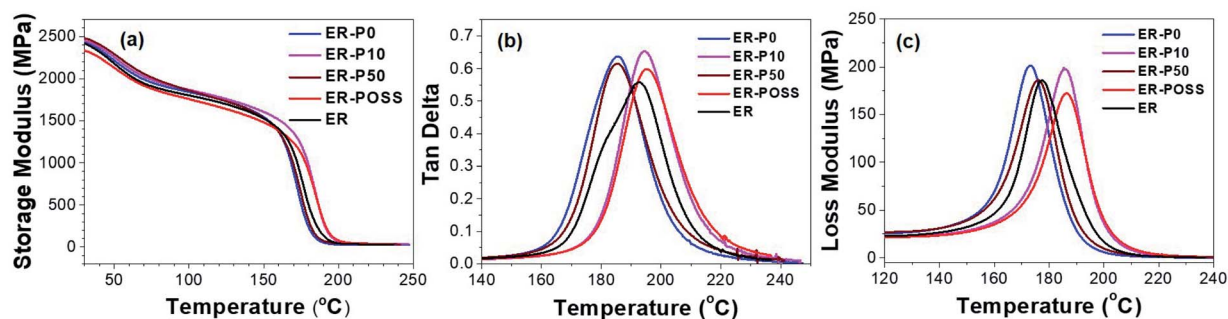

Fig. 5 Temperature plots of (a) storage modulus, (b) loss factor tan δ, and (c) loss modulus of the neat and modified epoxy resins.

145 degrees.[25] At the same time, the crosslink density also has a great influence on the material properties. Within a certain content range, the lower the crosslink density, the stronger the toughening effect. It is reported that the nanoparticles cavitation could induce shear banding of the epoxy resin matrix.[26] The results of fracture toughness and tensile tests showed that all modified epoxy resins exhibit higher elongation at breaks except ER-POSS (Fig. 6a), indicating that the modified resin has higher stress absorption capacity. Under the synergistic effect of the rigid nanocore and rubbery linear chain of the modifiers, the modified resin exhibited high strength and toughness, and Young's modulus (Fig. 6b). The G-POSS modified sample showed a maximum average modulus of 3716 MPa, which was an increase of about 26.9% compared with neat epoxy resin. The Young's modulus and strength of the linear polymer modified resin were both increased. This is because the thermoplastic modifier acts as a stress release center, allowing energy to be dispersed throughout the resin, resulting in higher elongation. Therefore, unlike other nanoparticle toughened epoxy resins,[27] POSS-based linear modifiers can toughen epoxy resins without sacrificing the stiffness and glass transition temperature of the resulting material. The stress–strain curve is integrated to obtain the toughness value as shown in Fig. 6c. All modifiers showed toughening effects on epoxy resins, conforming the synergistic effect of nano-POSS and rubbery linear chains. Among them, samples with a higher proportion of conjugated segments have better toughening effects, which are related to the reactive hydroxyl groups.

Hardness is a measure of how resistant a solid material is when a force is applied. In nanoindentation hardness measurement, the resistance and deformation of the sample towards constant compression from a sharp object were monitored. As an important engineering material, the modified epoxy resins also showed higher hardness and elastic modulus. As shown in Fig. 7d, the addition of G-POSS resulted in high hardness due to increased crosslinking density. Surprisingly, in the modifier, the resin hardness decreases from ER-P0 to ER-P50. This indicates that the hardness is more sensitive to the soft interface surrounding the core of the POSS. Elastic modulus is used to describe the elastic deformation of a substance when a force is applied. It is defined as the slope of the stress *versus* strain curve in the elastic deformation region. So, a stiffer material will have higher elastic modulus. Therefore, harder materials will have a higher modulus of elasticity. This is consistent with our indentation results.

Our indentation results were in agreement with the observation that all the prepared thermoplastics showed the toughening effect compared with the neat ER.

3.2.4 Toughening mechanism. In order to further study the toughening mechanism, the morphology of the tensile test samples at the breakpoint was observed using a scanning electron microscope. Fig. 7a shows that the fracture surface of ER is smooth, indicating that epoxy resin has weak resistance to crack generation and propagation without the presence of modifiers. In contrast, the fracture surface with the 5 wt% modifier is rougher, as shown in Fig. 7b–e. A large area of tortuosity was observed in the modified resin. Many parallel bending microcracks can be observed in ER-POSS, as highlighted by the circles in Fig. 7b. However, these microcracks overlap each other in ER-P50, ER-P10 and ER-P0, and form
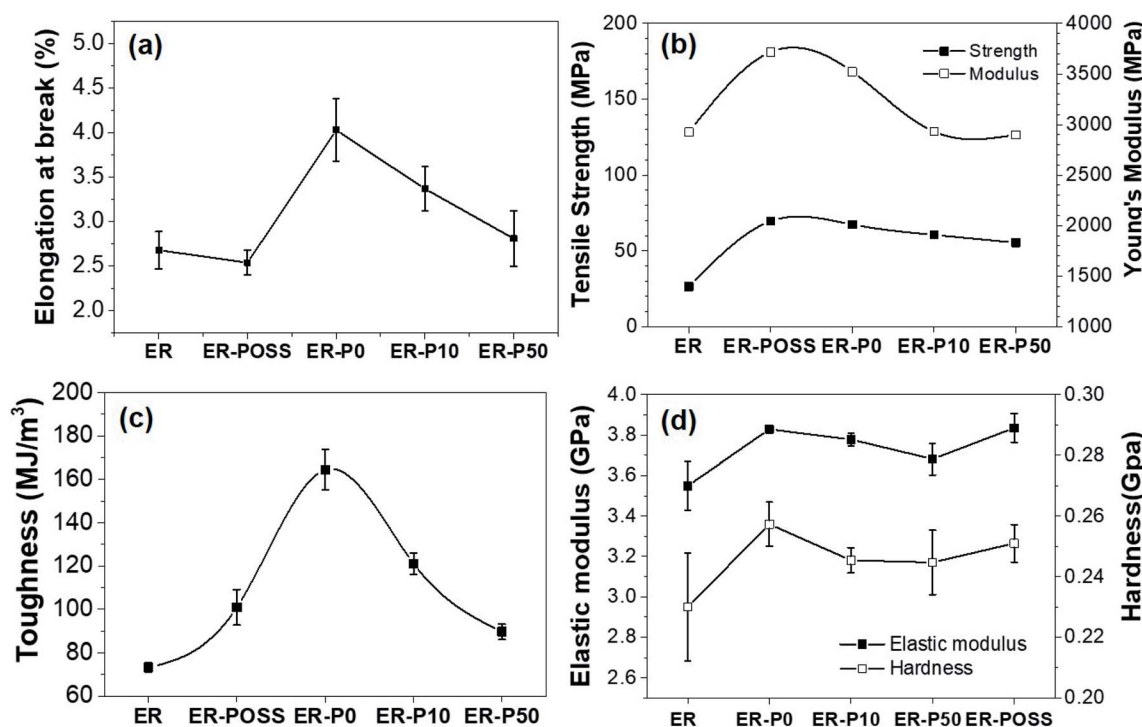

Fig. 6 Plots of (a) elongation at breaks, (b) tensile strength, (c) toughness and (d) hardness for the neat and modified epoxy resins.
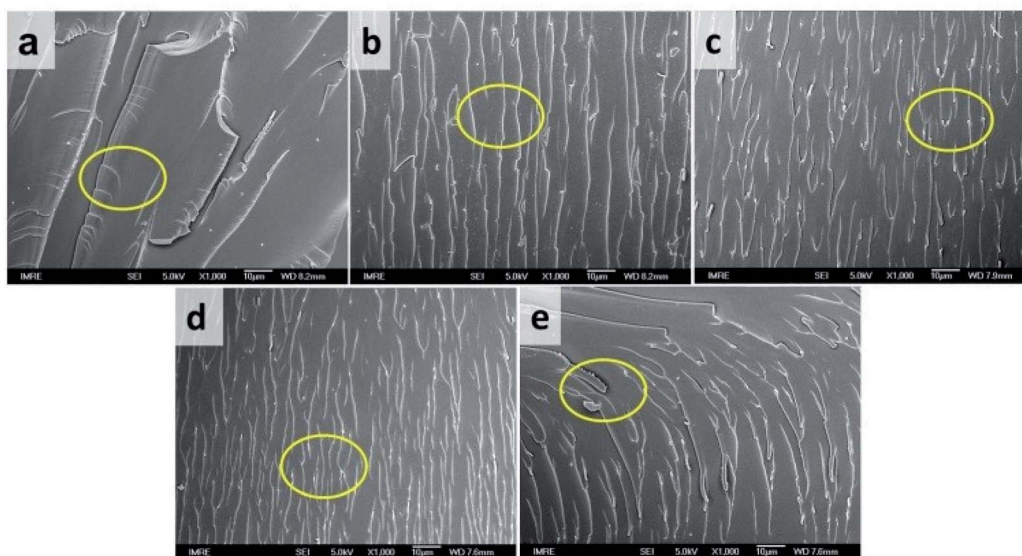
Fig. 7 Fracture surfaces of the tensile test samples: (a) ER, (b) ER–POSS, (c) ER-P50, (d) ER-P10, and (e) ER-P0.

a dendritic pattern. The density and branching of these twists may be related to the ductility and toughness of the resin. The greater the density and interaction of the microcracks, the more tortuous the crack propagation path, and greater the degree of toughness observed, which is consistent with the previous mechanical results. Fracture and plastic deformation are mainly caused by energy absorption.[28] The greatest toughening effect was observed in ER-P0, where crack path deflection may be the main toughening mechanism.[29,30] These differences in the fracture surface further confirm the favorable toughening effect caused by the introduction of these linear reactive modifiers.

4. Conclusions

A new series of linear POSS-containing epoxy thermoplastics were designed and used as reactive modifiers to enhance the toughness and hardness of epoxy resins. With only 5 wt% addition of our thermoplastics, a 27% increment of Young's modulus could be achieved. It was possible to enhance both the toughness and thermal stability at the same time. The results revealed that the toughening effect was owing to the effective increase of crack propagation energy due to the synergistic effect of the rigid POSS core and the flexible polymer chain.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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