

Superiority of Nanosized Over Microsized Hyperbranched Polymer Second Phase in Modifying Brittle Epoxy Resin

Jiao-Ping Yang, Qing-Ping Feng, Zhen-Kun Chen, Shao-Yun Fu

Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China

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ABSTRACT: A hydroxyl-functionalized hyperbranched polymer (HBP, H30) is used to modify 4,4'-diaminodiphenylsulfone-cured bisphenol-A type epoxy resin and a separate phase structure of modified epoxy resins is observed. The effects of the H30 second phase size on the mechanical properties of modified epoxy systems are investigated systematically. The dependence of the toughening mechanisms on the HBP particle size is reported for the first time. It is shown that the nanosized H30 second phase is superior over microsized counterparts in modifying brittle epoxy resin. The tensile strength is slightly enhanced by the introduction of nanosized H30 second phase, whereas the strength is significantly reduced by the addition of microsized H30 phase. The failure strain and impact

strength are obviously enhanced by the introduction of nanosized H30 second phase at low contents, whereas these properties are reduced by the addition of microsized H30 second phase at high contents. Finally, differential scanning calorimetric and thermogravimetric analyses are conducted to examine the effects of the HBP content on the glass transition temperature and the thermal stability, respectively. The glass transition temperature is slightly reduced while the thermal stability is not obviously influenced by the introduction of H30 second phase. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 863–870, 2011

Key words: epoxy resin; hyperbranched polymer; modification; mechanical properties

INTRODUCTION

Thermosetting epoxy resins have wide applications in coatings, adhesives, electrical laminates, and structural components. However, utilization of epoxy resins is often limited by its intrinsic brittleness. Soft modifiers are often used to toughen thermosetting epoxy resins. For example, rubber particles,¹ high-performance engineering thermoplastics, such as polysulfone,^{2,3} poly(ether sulfone),⁴ and poly(ether imide),⁵ and so on, as toughening agents have been employed to enhance the fracture toughness of brittle epoxy resins. It appears that the fracture toughness can be relatively easily improved by introducing soft second phases into brittle epoxy resins. On the contrary, the tensile strength might be relatively easily reduced by introduction of soft second phases into brittle epoxy resins.^{6,7} The mechanical properties

including toughness and strength of the modified epoxy systems depend on the type, volume fraction, and nature of modifiers. Therefore, usage of new toughening agents for modifying brittle epoxy resins is always of great interest.

Hyperbranched polymers (HBPs) are a relatively new group of polymers called dendrimers that are a novel and intriguing new class of modifiers for brittle epoxy resins.^{8–24} The chemical structure of a HBP (H30) is shown in Figure 1. Because of their unique structure, HBPs show properties that are in some cases very different from those of linear polymers. For example, HBPs are known to exhibit a very low degree of chain entanglement and typically have relatively low-melt viscosities even with high molecular weights compared with linear polymers, which gives HBPs a great potential as modifiers for brittle epoxy resins. Therefore, there has been a great research work done on HBPs as modifiers for brittle epoxy resins.^{8–24} The curing evolution and the curing kinetics were investigated for the HBP-modified diglycidylether of bisphenol A resin system.¹⁶ In the epoxy systems modified by hyperbranched polyesters, the cured epoxy/hyperbranched polyester blends generally exhibit separate particulate phase morphology.^{8,12,15–17,21} The mechanism of phase separation was postulated to be nucleation and growth.¹⁸ Moreover, the decrease in the glass transition temperature T_g has often been observed to some degree by the addition of HBPs.^{10,12,14,17,21}

Correspondence to: S.-Y. Fu (syfu@mail.ipc.ac.cn).

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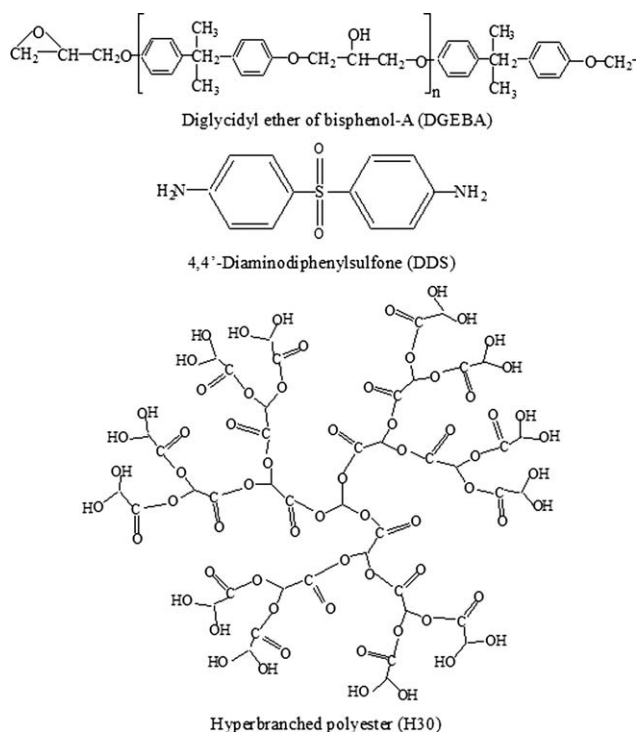


Figure 1 Chemical structures of epoxy resin (DGEBA), curing agent (DDS), and hyperbranched polyester (H30).

On the other hand, some research work has also been done on the mechanical behaviors of modified epoxy systems using HPBs as modifiers. The improvements in the fracture toughness^{10–12,19,22} and the impact strength^{20,23,24} were observed with adding HBP to epoxy resins. However, as HBP concentration increases to some certain value, no further increase in fracture toughness could be observed¹¹ or a small decrease in impact strength was observed at high HBP concentrations.²³ On the contrary, the tensile strength was significantly reduced by the addition of HBPs.^{10,20,23} As mentioned above, the HBP-modified epoxy systems would generally show a separate phase morphology. The second HBP phase size depends on the HBP content in the epoxy/HBP blends, and thus, both HBP content and phase size would influence the mechanical behaviors of the modified epoxy systems. However, the effects of the HBP particle size on the mechanical properties of modified epoxy systems have not been investigated systematically. Especially, when the second HBP phase is nanosized, the mechanical behaviors

and the toughening mechanisms have not been reported yet for HBP-modified epoxy systems.

In this work, the hyperbranched polyester (H30) is used to modify the 4,4'-diaminodiphenylsulfone (DDS)-cured bisphenol-A type epoxy resin system. The HBP size decreases with the increase in HBP content in the modified epoxy systems. Then, the effects of HBP particle size especially at nanoscale on the mechanical properties were studied. Especially, the effect of HBP particle size on the toughening mechanisms is reported for the first time for HBP modified epoxy resin systems. It is observed that the nanosized H30 soft second phase are superior over microsized counterparts in modifying epoxy resins. The most likely application of HBPs would be for high-performance epoxy resins and the as-prepared HBP modified epoxy systems are promising for practical applications as matrices for glass and carbon fiber reinforced epoxy composites.²⁵ Moreover, the glass transition temperature and thermal stability are also examined by differential scanning calorimetric (DSC) and thermogravimetric (TG) analyses.

EXPERIMENTAL

Materials

A bisphenol-A diglycidyl ether (DGEBA, CYD-128) with an epoxide value of 0.48–0.51 was purchased from Yueyang Refinery Plant, China. The chemical structure of DGEBA is shown in Figure 1. The curing agent DDS was purchased from Guangzhou Wei Yang Sci. & Technol. Development, China (Fig. 1). HBP used in this work was polyester Boltorn H30, which has been kindly donated by Perstorp Speciality Chemicals. Boltorn H30 is a third-generation hyperbranched polyester with 32 primary hydroxyl groups on the shell (Fig. 1) and it is an amorphous solid at room temperature (RT) with a reported glass transition of 35°C.²

Preparation of samples

The H30 content in the mixture of DGEBA and H30 varied from 0.0 to 15.0 wt % as shown in Table I. Stoichiometric amounts of DGEBA and DDS together with various amounts of H30 were first dissolved in acetone and the resulting mixture was

TABLE I
Formulations and Glass Transition Temperature (T_g) of Pure and Modified Epoxy Resins

H30 content (wt %)	0	2.5	5.0	7.5	10.0	15.0
DGEBA (g)	100.00	97.50	95.00	92.50	90.00	85.00
DDS (g)	35.00	34.12	33.25	32.38	31.50	29.75
T_g (°C)	192.4	185.2	184.2	186.8	187.3	185.8

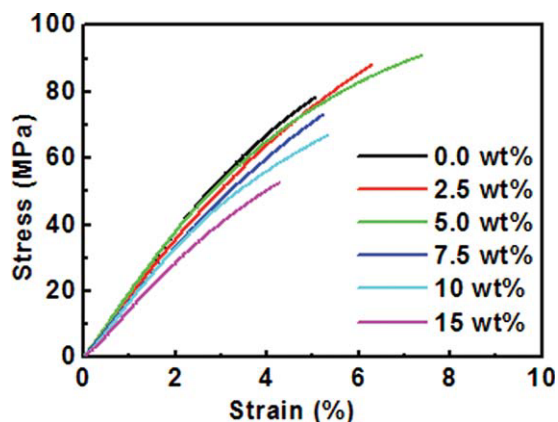


Figure 2 Typical stress–strain curves of the unmodified and modified epoxy systems. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

mixed until a homogeneous and clear solution was obtained. Then, the acetone was eliminated from the mixture. The mixtures of H30, DDS, and DGEBA were degassed under vacuum for 40 min at 100°C and cast in a preheated mold with a temperature of 100°C, which was cured at 140°C for 6 h and then postcured at 170°C for 3 h. The tensile samples were prepared according to the recommendation of ASTM D-638-96. The geometries of the impact samples are 4 mm × 10 mm × 80 mm according to the ASTM D-256. The notched depth is 0.2 times of its width for the notched impact samples.

Characterization

The tensile properties of the cured samples at RT were measured by a RGT-20A Reger Mechanical Tester using a 10 kN load cell with a crosshead speed of 2 mm/min. The unnotched and notched impact strength of the cured samples was measured with a REGER Impact Tester. At least five samples were tested for each composition. The data for the tensile strength, tensile modulus, and failure strain of the epoxy resins are obtained from these stress–strain curves via the REGER testing software.

The fracture surfaces of the samples after impact testing were observed by scanning electron microscopy (SEM) using a HITACHI S-4300 microscope (Japan). Before examination, the fracture surfaces

were cleaned with alcohol and coated with a thin layer of evaporated gold to improve conductivity. As the size of soft second phase dispersed in the epoxy matrix for the 2.5 wt % H30 content case is too small to be clearly observed from the SEM micrograph via the HITACHI S-4300 microscope, the dispersion of the H30 particles in the epoxy matrix was observed using transmission electron microscopy (TEM) (JEM-100CX). TEM specimens were cut from the sample blocks using an ultramicrotome (LKB III) equipped with a diamond knife. Thin specimens of 50–60 nm thick were cut from a mesh of about 1 × 1 mm². Then, they were collected and placed on 200 mesh copper grids for taking TEM micrographs. SEM and TEM photographs were used for measurement of second phase particle sizes by the SemAfore 4.0 software. Over 50 measurements were made to get the average values of the second phase particle sizes.

The glass transition temperature (T_g) and thermal stability of the cured samples were measured via DSC and TG analyses in nitrogen environment at a heating rate of 10°C/min using a NETZSCH STA 409PC. The heating temperature ranged from 30°C to 350°C and from 30°C to 650°C for T_g and TG analyses, respectively.

RESULTS AND DISCUSSION

Tensile properties

The stress–strain curves of the unmodified and H30 modified epoxy resins are shown in Figure 2. And the results are summarized in Table II. It can be seen from Figure 2 and Table II that the tensile strength and failure strain are enhanced by the introduction of low H30 contents, whereas they are reduced by the addition of high H30 contents. The tensile modulus tends to decrease with increasing the H30 content. This can be mainly attributed to the low modulus of HBP (H30) particles.²⁶ Similar results have also been observed in modified epoxy systems by other soft matters.^{27–29}

From the TEM image of the sample with the 2.5 wt % H30 content in Figure 3 and the SEM images of the samples with the 5.0–15.0 wt% H30 contents in Figure 4, it can be observed that the HBP has formed spherical particles in the epoxy matrix. The results

TABLE II
Effects of H30 Content on Tensile Properties of Epoxy Resins^a

H30 content (wt %)	0	2.5	5.0	7.5	10.0	15.0
Tensile strength (MPa)	84.91 (±5.92)	87.89 (±6.99)	90.57 (±6.09)	73.55 (±2.86)	60.98 (±5.64)	44.37 (±5.53)
Tensile modulus (GPa)	1.91 (±0.11)	1.83 (±0.18)	1.84 (±0.08)	1.71 (±0.13)	1.72 (±0.15)	1.43 (±0.16)
Failure strain (%)	5.04 (±0.73)	6.29 (±0.86)	7.37 (±0.40)	5.22 (±0.33)	5.31 (±0.36)	4.26 (±0.16)

^a The data in the brackets are standard errors.

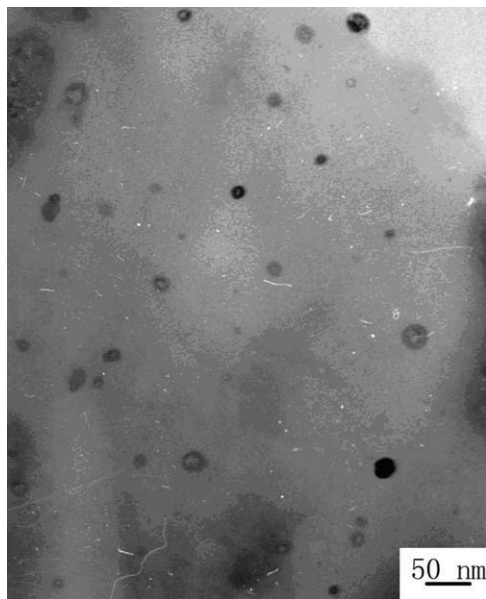


Figure 3 TEM micrograph of the sample with the 2.5 wt % H30 content.

for the average diameter of H30 particles are summarized in Figure 5(a). It can be seen from Figure 5(a) that the average diameter of H30 particles is about 21, 114, and 439 nm, respectively, for the samples with 2.5, 5, and 7.5 wt % H30 contents. Afterwards, the average second phase diameter increases dramatically when the H30 content increases further over 5.0 wt %, and is 2.952 and 3.167 μm for the samples with the 10.0 and 15.0 wt % H30 contents, respectively. Furthermore, one can see from the optical photograph shown in Figure 5(b) that the samples become less transparent as the H30 content increases. This is because the H30 particle size increases with the increase in the H30 content as shown in Figures 3, 4, and 5(a) and both the increases in the H30 content and size would lead to a lower transparency due to the fact that higher H30 contents and larger second phase particles scatter light to a higher degree in terms of the relationship of the transmittance with the filling particle content and size.³⁰

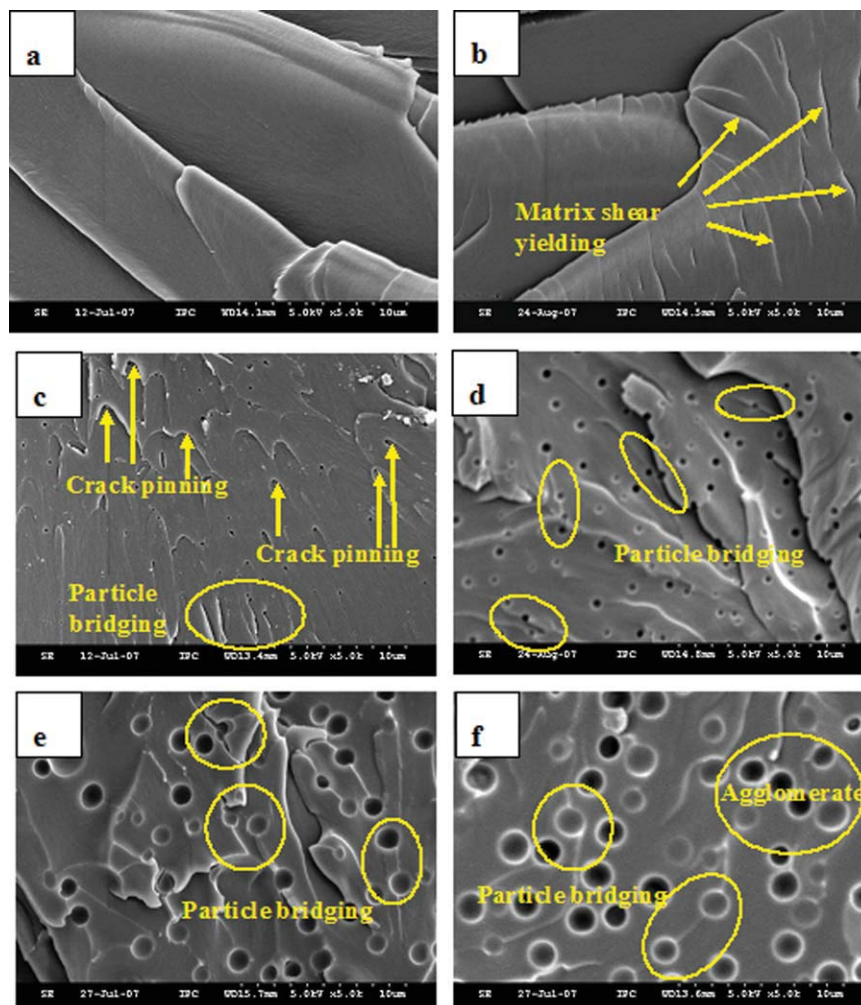


Figure 4 SEM micrographs of the fracture surfaces of the samples after impact testing with different H30 contents of (a) 0.0 wt %, (b) 2.5 wt %, (c) 5.0 wt %, (d) 7.5 wt %, (e) 10 wt %, and (f) 15 wt %. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

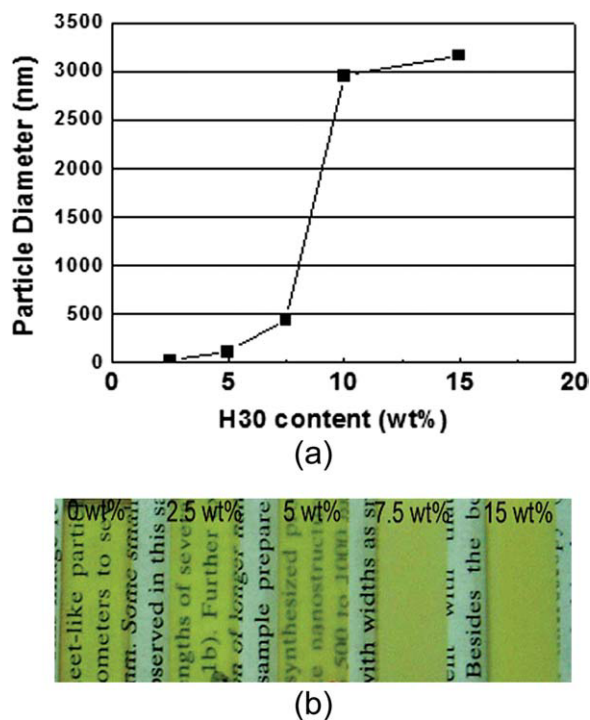


Figure 5 (a) Second phase diameter versus H30 content and (b) optical photograph of the cured samples with different H30 contents. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

The effect of the H30 content is shown in Table II on the tensile strength of the cured modified epoxy systems. It is often observed that soft second phases with fine sizes are beneficial to enhancement of the tensile strength of epoxy resins.^{4,31,32} It can be seen from Table II that the tensile strength is slightly enhanced on an average by the addition of H30 at the low H30 contents of 2.5 and 5.0 wt % followed by a rapid decrease with the further increase in the H30 content. In general, the addition of soft matters like rubber and polyurethane to epoxy resins results in the reduction of tensile strength.^{6,7,33} And the enhancement in the tensile strength by adding the low amounts of H30 can be explained in terms of the effect of second particle size on the tensile strength as follows.

It is well known that the curing reaction of thermosetting epoxy resins will lead to volume shrinkage of the epoxy system.^{34,35} Meanwhile, epoxy resins are cured at high temperatures in a geometrically constrained environment (such as steel mold) and bulk shrinkage occurs during the cooling process from the curing temperature to RT.³⁴⁻³⁶ Finally, the internal stress in the final epoxy samples can be divided into two parts.³¹ One is the shrinkage internal stress σ_1 caused by bulk shrinkage during the curing period; the other is the thermal stress σ_2 induced by the difference of thermal expansion coefficient between the epoxy resin and the steel mold. σ_1 is given by:³⁷

$$\sigma = k_1 E \gamma \quad (1)$$

where k_1 is a constant, E the elastic modulus of the cured resin, and γ the bulk shrinkage fraction of the cured resin during the curing processing. σ_2 can be expressed as due to the temperature change (T_1 - T_2):

$$\sigma_2 = k_2 \int_{T_1}^{T_2} E(\beta_1 - \beta_2) dT \quad (2)$$

where k_2 is also a constant, β_1 and β_2 are the linear thermal expansion coefficients of the epoxy resin and steel mold, respectively.

The internal stresses can greatly affect the performance of the finished products³⁴⁻³⁶ often reducing the yield strength.^{4,34} By introducing uniformly distributed soft H30 particles, the internal stresses within the samples would be released and thus reduced,^{4,32,38} which then contributes to the enhancement of the tensile strength of the modified epoxy systems. The enhancement in the tensile strength by reducing internal stresses can be expressed by ΔS_1 . Moreover, the strength of H30/epoxy blend systems is contributed by both H30 and epoxy phases. The soft matter H30 has a lower strength than the epoxy resin and the reduction in the strength of modified epoxy by the introduction of lower strength H30 can be expressed by ΔS_2 with a negative value. The dependence of the tensile strength of modified epoxy resins on the H30 content as exhibited in Table II is determined by the two competing effects of reduced internal stress and lowered strength by the introduction of soft H30 phase. When the H30 contents are low (2.5 and 5.0 wt%), the H30 phase sizes are small as shown in Figures 3 and 4 and the stress reducing effect of H30 is superior, thus preserving the mechanical properties of the epoxy resin.³⁶ As a result, the strength is not reduced but is enhanced by a few percentage by the addition of nanosized H30 phase at low contents. However, when further increasing the H30 content, the H30 particles become larger. Because of its relatively low strength the large H30 particles cannot bear a high load as the epoxy matrix does, leading to the significant reduction of the tensile strength of the modified epoxy system after the addition of H30. Consequently, the two competing effects from the release of internal stresses and the decrease of load bearing capacity lead to the reduction in the tensile strength at high H30 contents.

Moreover, the internal stresses within the bulk material are also responsible for the early failure of the materials since they can greatly affect the performance of the finished products by creating defects.³⁴⁻³⁶ The release of the internal stresses by the introduction of H30 leads to an enhancement in the failure strain as shown in Table II. The

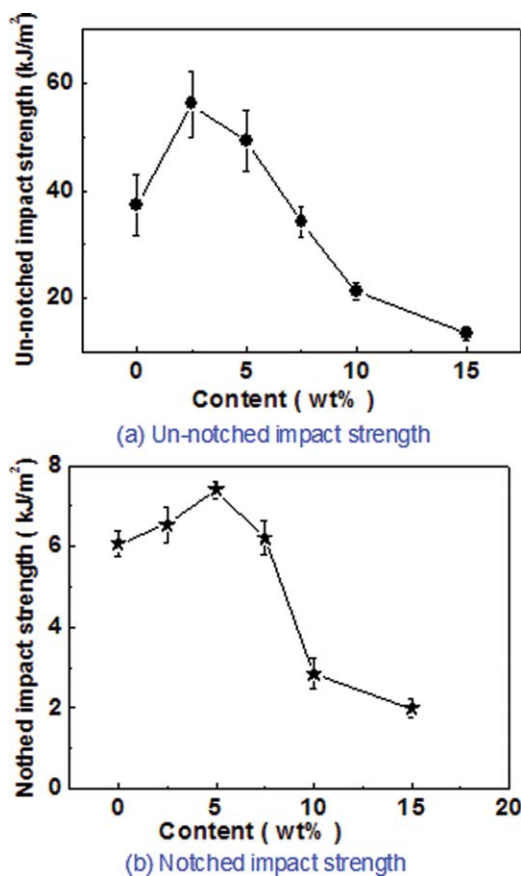


Figure 6 Effects of H30 content on (a) the un-notched impact strength and (b) the notched impact strength of H30-modified epoxy systems.

enhancement of the failure strain at low H30 contents can be attributed to the plasticization of the brittle epoxy resin by the soft H30 particles.³² However, the H30 particle size increases dramatically as the H30 content increases. The large H30 particles reduce the load bearing capacity of the modified epoxy systems and thus bring about the earlier failure of the samples. Therefore, the failure strain reaches the maximum at the 5.0 wt % and then decreases with further increasing the H30 content as shown in Table II. Nevertheless, the failure strain for the 7.5 and 10.0 wt % cases is still higher than that for the pure epoxy resin.

Impact strength

The effects of H30 content on the un-notched and notched impact strength of modified systems are exhibited in Figure 6. It is clear from Figure 6 that both the un-notched and notched impact strength of the modified epoxy samples increases initially to a maximum and then decreases as the H30 concentration increases further. The maximum of the un-notched and notched impact strength occurs at the H30 content of 2.5 wt % and 5 wt %, respectively. The

maximum un-notched impact strength with a value of 56.1 kJ/m² occurs at the 2.5 wt % H30 content with an improvement of about 50.4% compared with that of the pure epoxy sample. The maximum notched impact strength occurs at the 5.0 wt % H30 content and is equal to 7.4 kJ/m² with an improvement of 22.3% compared with the pure epoxy sample.

Fig. 4(a) shows the smooth glassy fractured surface with cracking in different planes. This indicates the brittle fracture characteristics of pure epoxy resin. Uniform distribution of the H30 particles in the matrix has been observed as shown in Figures 3 and 4(c–f). This is very important for toughening as it allows toughening mechanisms to operate throughout the matrix. The fracture surfaces of modified epoxy resins evidence various toughening mechanisms including matrix shear yielding, crack pinning and particle bridging for toughened epoxy resins as shown in Figure 4(b,f).

Argon³⁹ proposed that shear yielding occurs in rubber-modified epoxy resins. Kim and Brown⁴⁰ showed that shear yielding also exists in thermoplastic particle modified epoxy systems. Crack pinning was proposed by Lange et al.^{41–43} In the crack pinning theory, the crack front bows out between the filler particles but remains pinned at the particles. In the particle bridging mechanism,⁴⁴ a rigid or ductile particle plays two roles: (1) it acts as a bridging particle that applies compressive traction in the crack plane, (2) the ductile particle deforms plastically in the material surrounding the crack tip, providing additional crack shielding but the shielding is negligible in contributing to toughness. In contrast to the crack pinning mechanism, the particle-bridging mechanism favors large particles. This is probably why the particle bridging mechanism dominates for the cases of high H30 contents. Thus, it appears that matrix shear yielding would be the major toughening mechanism in the HBP-modified epoxy system at the 2.5 wt % H30 [Fig. 4(b)], contributing to a high impact strength of 56.1 kJ/m². Both crack pinning and particle bridging mechanisms contribute to the impact strength at the 5.0 wt % H30 content [Fig. 4(c)], leading to a relatively high impact strength of 49.3 kJ/m². Only particle bridging mechanism makes contribution to the impact strength for the high H30 content cases, finally leading to a relatively low impact strength.

It can be noticed that for the systems with 2.5 wt % and 5 wt % H30 content, the second H30 phases are nanoscale sized in diameter. The large specific surface areas can be provided by small H30 particles in these cases, which will help stress transfer between H30 particles and epoxy matrix. Nanosized H30 particles have very high surface areas and thus relatively more energy will be consumed for the cases of smaller H30 particles to prevent the production of microcracks and propagation of the flaws

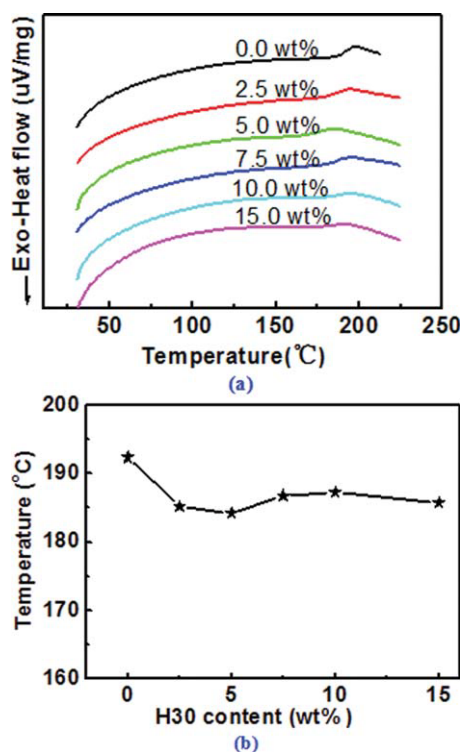


Figure 7 (a) DSC curves and (b) glass transition temperature T_g of the H30 modified cured epoxy systems with various H30 contents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

when the samples suffer impact testing, and hence contributing to the improvements in the impact resistance. On the other hand, when the H30 particles are microscale-sized, only particle bridging mechanism works for toughening epoxy resins as shown in Figure 4(d–f). Meanwhile, the large-sized H30 particles are combined with each other to form agglomerates as the H30 content increases. These would result in a relatively low impact strength for the high H30 content cases.

Moreover, it is observed that the un-notched impact strength is much higher than the notched impact strength. For the un-notched samples, energy is dissipated in two stages of crack initiation and crack propagation.⁴⁵ However, notched samples only dissipate the crack propagation energy as notches have been made in advance. Thus, the un-notched impact strength of the samples is higher than the notched impact strength at the same H30 content. The above results suggest that the initiation of cracks in soft second H30 phase toughened epoxy system could consume a hugely larger quantity of energy compared to the unmodified system. This is because nanoscale sized soft phases have a high surface area and could effectively resist crack initiation even at a low content and thus consume a huge energy.

It is necessary to point out that the un-notched impact strength of the samples with the 2.5 wt %

H30 content is higher than that of the samples with 5.0 wt %, which are contrary with their notched impact strength. This interesting phenomenon suggests that the H30 particles with a size of 21 nm can effectively prevent the initiation of microcracks when the samples suffer impact testing and the H30 particles with a size of 110 nm within the samples can effectively prevent the propagation of the cracks. The surface area of the nanosized particles with a diameter of 21 nm at a content of 2.5 wt % is about 2.71 times of that of the particles of 114 nm at a content of 5.0 wt % H30. Smaller H30 particles have a much higher surface area and could more effectively resist crack initiation. Thus, when the samples suffer impact testing, more energy will be consumed to initiate cracking for the case of smaller H30 particles, finally leading to the fact that the un-notched impact strength is higher for the 2.5 wt % H30 case than for the 5.0 wt % H30 case.

Thermal properties

The DSC curves of the H30 modified epoxy samples are shown in Figure 7(a). The glass transition temperature (T_g) of the cured systems was obtained as shown in Figure 7(b) from the curves of Figure 7(a). It can be seen that the T_g of the cured systems is slightly reduced by the introduction of H30. H30 is an amorphous solid polymer at RT with a reported glass transition of 35°C.² Therefore, it is easy to understand that T_g is reduced by the introduction of H30 polymer with low glass transition temperature. Similar results have been reported in the literature.^{10,12,14,17,21} On the other hand, the presence of H30 phase would limit the motilities of the epoxy molecules in the cured system, resulting in the insensitivity of T_g to the H30 content when it is

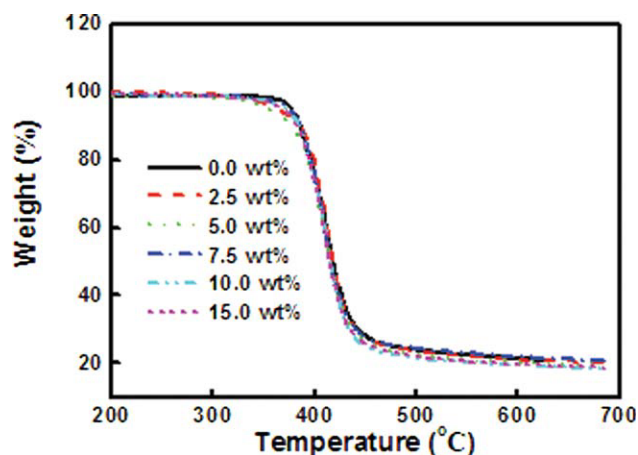


Figure 8 The effect of H30 content on the thermal stability of modified epoxy resin. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

increased from 2.5 to 15.0 wt %. Therefore, as the H30 content increases further, no further in T_g is observed.

Thermal stability of the modified samples was derived from TG traces in Figure 8. The cured neat and H30 modified epoxy samples show weight loss in temperature interval 350–475°C when heated under nitrogen atmosphere. The maximum weight loss rate takes place around 400°C because of the decomposition of epoxy network for all the samples. Moreover, it can be seen from the TG curves that the H30 content shows only an insignificant effect on the decomposition of epoxy networks.

CONCLUSIONS

In this article, a hydroxyl-functionalized HBP (H30) has been used for modifying the DGEBA/DDS epoxy system to enhance the tensile and impact properties. SEM and TEM micrographs of the impact fracture surfaces revealed the uniform distribution of H30 particles as the second phase in the epoxy matrix. The tensile strength, failure strain (ductility) and un-notched/notched impact strength have been simultaneously enhanced by the introduction of the nanosized second soft H30 phase at low contents. This interesting observation is promising for practical application because of its relatively high cost compared with epoxy resins. Different toughening mechanisms have been observed as the size of H30 particles changes from tens of nanometers to a few of micrometers. In particular, the maximum un-notched impact strength of 56.1 kJ/m² with an improvement of 50.0% compared with the unmodified system has been attained at the 2.5 wt % H30 content. DSC and TG analyses showed that the glass transition temperature T_g of the toughened system was decreased by several degrees while the thermal stability was not obviously influenced by the introduction of H30.

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