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Improving the heat-resistance and toughness performance of phenolic resins by adding a rigid aromatic hyperbranched polyester

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ABSTRACT: An aromatic hyperbranched polyester (AHBP) was synthesized by melt polycondensation from diphenolic acid and characterized by Fourier transform infrared spectrum (FTIR) spectra. The degree of branching (DB) value of AHBP calculated from the ^{13}C-NMR spectroscopy was 0.67. The number-average molecular weight (M_n) and weight-average molecular weight (M_w) of AHBP were 1792 and 4480 g/mol, respectively. Novel phenolic resins modified with AHBP (PR/AHBP) were then prepared, in which AHBP was used as toughener of phenolic resins. The effect of AHBP on the thermal properties of phenolic resins was studied by means of differential scanning calorimetry (DSC), thermal gravimetric analyses (TGA), and heat deformation temperature tests. The modified resins presented higher glass transition temperature (T_g) than the unmodified system due to that the rigid backbone structure of AHBP with a great deal of the benzene ring groups restricted the mobility of the chain segments of macromolecules. The DSC, scanning electron microscopy (SEM) analyses showed that AHBP had good compatibility with phenolic resin, and the modified resins showed ductile fracture. The results of mechanical performance measurements exhibited that the impact strength of PR/AHBP containing 15 wt % AHBP was about 130% higher than that of the neat phenolic resin, suggesting that the toughness of PR/AHBP was significantly improved by the addition of AHBP. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 42734.

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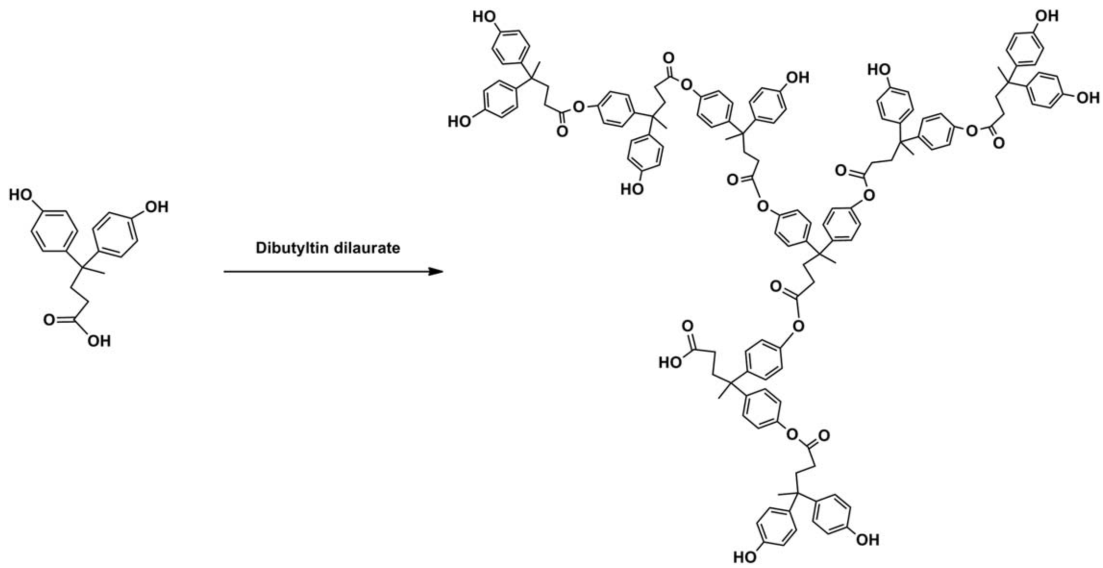
INTRODUCTION

Thermoset resins, especially phenolic resins are widely used in adhesives, coatings, electrical and electronic materials, and molding compounds, owing to their superior performances, such as thermomechanical properties, processability, excellent chemical stability, and electrical properties.[1–6] However, the inherent brittleness as one major disadvantage, limit their application as high performance materials.[7–9] In order to solve this problem, some materials such as rubber, thermoplastic, glass or ceramic particles are used to enhance toughness of thermosetting resins. However, their poor compatibility with phenolic resin matrix negatively affect the processability and thermal properties, thus seriously affected their modification effects.[10–16]

Dendritic polymers are a class of three-dimensional macromolecules. They exhibit low melt points and solution viscosities due to lack of restrictive interchain entanglements.[17] Besides, they express high chemical reactivity due to a large number of functional terminal groups. All these advantages make them excellent modifiers in polymer materials.[18–20] Dendritic polymers mainly include dendrimers and hyperbranched polymers. Dendrimers have perfectly branched structures, but their synthesis often involves multiple reaction steps, altogether with complicated separation and purification processes. Hyperbranched polymers possess similar excellent properties to dendrimers, and can be easily synthesized through one-step polymerization reaction.[21–24] Hence, hyperbranched polymers as modifiers of thermoset resins have drawn much attention, and many related reports on hyperbranched polymers modification epoxy resins have been reported in the literatures. These hyperbranched polymers included hyperbranched polyester,[25–29] hyperbranched polyether,[30,31] hyperbranched polyimide,[32] and so on. They have already been applied for modification of epoxy resins in order to improve toughness. Among them, hyperbranched polyesters are the most widely used hyperbranched polymers. The researches have shown that hyperbranched polymers could obviously enhance the toughness of epoxy resins without affecting the processability and thermal properties, verifying that hyperbranched polymers are a kind of desirable tougheners for epoxy resins.[33,34]



Scheme 1. The synthesis route of AHBP.

However, as mentioned above, most of former researches focused on epoxy resin/hyperbranched polymers, and less attention was paid on phenolic resin (PR)/hyperbranched polymer systems. In fact, phenolic resin is one of the most important thermoset resins, and thus, the study on toughening modification of phenolic resins is necessary and important in the development of high performance phenolic resins. Until recently, Liu and Xu *et al.* have done some work on the modification of phenolic resins with hyperbranched polyborates (HB).[35–37] They prepared a series of hyperbranched polyborates (HB) terminated with phenol hydroxyl (HBp) and boric acid hydroxyl (HBb) functional groups, and then blended HB with phenolic resins to obtain a type of HB/phenolic resin blends. Their studies suggested that the blends are homogeneous, and the thermal properties of the blends were improved by addition of HB. However, the toughness of these HB/phenolic resin blends were not mentioned in their studies.

To our best knowledge, so far, no work has been reported on phenolic resin/hyperbranched polyester and their toughening performances. In this article, an aromatic hyperbranched polyester (AHBP) was synthesized by melt polycondensation reaction from diphenolic acid. Then, using AHBP as toughening modifier for phenolic resin, a series of new phenolic resins modified with hyperbranched polyester (PR/AHBP) with different AHBP contents were prepared. The thermal properties and toughening performances of PR/AHBP were studied and discussed.

EXPERIMENTAL

Measurements

Fourier transform infrared spectrum (FTIR) was recorded on a Nicolet Magna-IR 550 FTIR spectrophotometer in the 4000–400 cm^{-1} region using KBr pellets. Gel permeation chromatography (GPC) analysis was conducted with a Waters 1515 gel permeation chromatograph (GPC) using polystyrene (PS) as standard and tetrahydrofuran (THF) as the eluent.

Thermal gravimetric analyses (TGA) were run on SHIMADZU TG-40 in the 50–800°C region in nitrogen atmosphere and conducted with a heating rate of 10°C min^{-1}. Differential scanning calorimetry (DSC) were carried out on NETZSCH DSC200 at the temperature of 40–140°C region at a heating rate of 10°C min^{-1} in nitrogen atmosphere. The thermal deformation temperatures were determined by a XRW-300 HDT and VICAT softening point temperature test machine.

The morphologies of the surfaces and fracture surfaces of phenolic resin and PR/AHBP samples were examined with a Hitachi SEM S-520 Scanning electron microscopy (SEM). The SEM images included both surface and fracture section.

The bending strength and toughness of samples were tested on a WDW-20 computer controlled universal testing machine (cross head speed: 2.0 mm/min, gauge length: 80 mm). Izod impact test was carried out with rectangular notched specimens (size: 120×15×10 mm^3, notched thickness: 7 mm) at XJJ-5 impact testing machine (impact velocity: 2.9 m s^{-1}).

Materials

Diphenolic acid was purchased from Jiangsu Nantong Jiang Xinsha Chemical Factory. Dibutyltin dilaurate was obtained from Tianjin Damao chemical reagent factory. Phenolic resins were provided by Zhejiang Jiamin plastic and rubber company. All the chemicals were used as received.

Synthesis of Hyperbranched Polyester (AHBP)

The hyperbranched polyester (AHBP) was synthesized by a modified procedure reported in the literature.[17] 1.15 g dibutyltin dilaurate was added into 229.00 g diphenolic acid, and the mixture was heated to 190°C and stir for 4 h under nitrogen atmosphere. Then the temperature was raised to 225°C and stirred for another 3 h to obtain the crude product. The product was dissolved in 1 L of THF, and poured into large amounts of deionized water (about 2 L) to obtain the AHBP precipitate. The precipitate was filtered off, washed with deionized water,

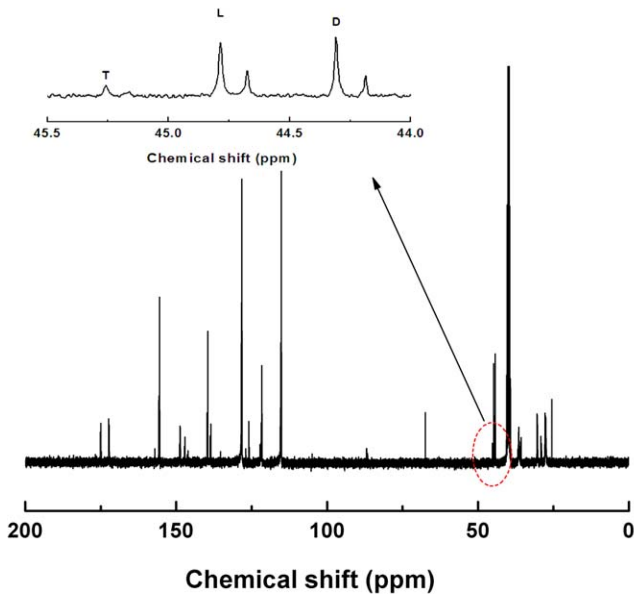


Figure 1. ^{13}C-NMR spectrum of AHBP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and then dried under vacuum at 80°C for 12 h until constant weight was achieved.

Preparation of Phenolic Resins Modified with AHBP (PR/AHBP)

The mixture of AHBP and phenolic resin (1/9: w/w) was heated to 140°C in nitrogen atmosphere and stirred for 2 h to obtain PR/AHBP with AHBP content of 10 wt %. Using the above preparation method, a series of PR/AHBP with AHBP content of 0 wt %, 5 wt %, 15 wt %, and 20 wt % were obtained.

RESULTS AND DISCUSSION

Structure Analysis of AHBP

AHBP was prepared from diphenolic acid by melt polycondensation reaction using dibutyltin dilaurate as catalyst. The synthesis procedure of AHBP is given in Scheme 1. The number-average molecular weight (M_n), weight-average molecular weight (M_w), and molecular weight distribution of AHBP were determined by GPC measurement. The results showed that the M_n and M_w of AHBP were 1792 and 4480 g/mol, respectively, and the polydispersity index (PDI) value of AHBP was 2.5.

As previously mentioned, hyperbranched polymers are a most important kind of dendritic polymers, which have highly branched structures. The degree of branching (DB) is a measurement on the content of branches in the molecular structure and is considered to be a main structural feature for branched polymer. The DB value of branched polymer is commonly determined by ^{13}C-NMR spectroscopy and commonly calculated according to the following equation:[38]

$$DB=(D+T)/(D+L+T)$$

where D, L, and T are the integral intensities of the signals of dendritic units, the linear units, and the terminal units in the ^{13}C-NMR spectrum of the branched polymer, respectively. The DB is 100% for dendrimers and less than 100% for hyperbranched polymers.[39] Figure 1 presents the ^{13}C-NMR spectrum of AHBP. The DB value of AHBP calculated from Figure 1 was 0.67.[40]

Figure 2 gives the FTIR spectra of diphenolic acid and AHBP. In the spectrum of diphenolic acid, the wide and strong band at about 3308 cm^{-1} was the overlapping band corresponding to the O–H stretching vibration of hydroxyl group and carboxyl group of diphenolic acid. The peak at 1703 cm^{-1} was attributed to the C=O stretching vibration of carboxyl group. The peaks at 1610 cm^{-1} and 1513 cm^{-1} were ascribed to C=C stretching vibration of the benzene ring backbone. The characteristic absorption peak of carboxyl group of diphenolic acid at 1703 cm^{-1} was absent in the FTIR spectrum of AHBP, but a new peak at 1743 cm^{-1} appeared, which was associated to C=O stretching vibration of ester group of AHBP. Meanwhile, the peak intensities at 1175 and 1015 cm^{-1} were obviously enhanced, which could be assigned to the asymmetric and symmetric stretching vibrations of C–O–C bond of ester group, respectively. These analyses indicated that the hydroxyl groups and the carboxyl groups on the diphenolic acid molecule indeed reacted to form ester groups. On the other hand, the overlapping band corresponding to the O–H stretching vibration of hydroxyl group and carboxyl group appeared at about 3420 cm^{-1}, and became narrow compared with the corresponding band of diphenolic acid, which provided further evidence for the fact that part of hydroxyl groups on the diphenolic acid reacted with the carboxyl groups.

Effect of AHBP on the Thermal properties of Phenolic Resins

The thermal stability of PR/AHBP with different AHBP contents were studied by means of TGA. The TGA curves for neat phenolic resin, AHBP, and PR/AHBP containing 5 wt % AHBP are shown in Figure 3. The related data obtained are listed in Table I. It could be seen that the temperatures of 5%, 10%, and 30% weight loss of the neat phenolic resin were 343°C, 438°C, and 598°C, respectively. Compared to neat phenolic resin, the thermal decomposing temperatures of PR/AHBP were obviously low. The temperatures of 5%, 10%, and 30% weight loss of PR/AHBP containing 5 wt % AHBP were 249°C, 282°C, and 380°C, respectively. Consequently,

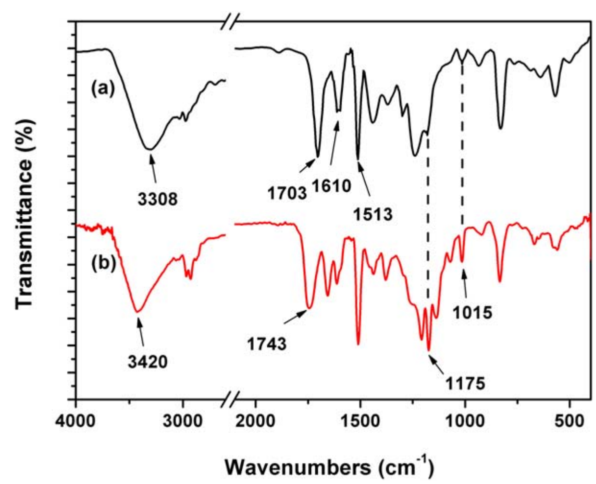


Figure 2. FTIR spectra of (a) diphenolic acid and (b) AHBP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

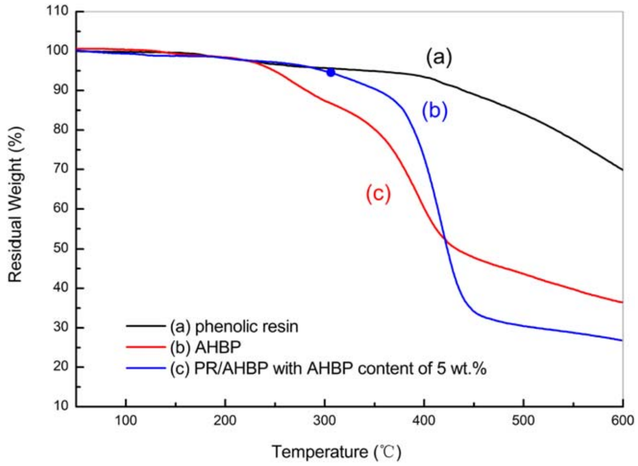


Figure 3. TGA curves of (a) phenolic resin (b) AHBP, and (c) PR/AHBP with AHBP content of 5 wt %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

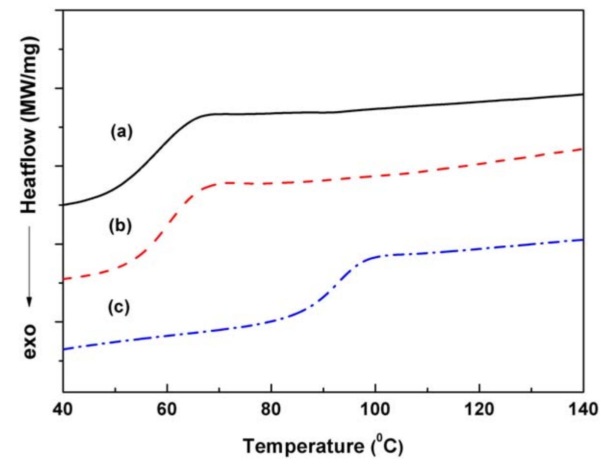


Figure 4. DSC curves of (a) phenolic resin, (b) PR/AHBP with AHBP content of 5 wt %, and (c) AHBP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

PR/AHBP exhibited the decreased thermal stability in comparison with unmodified resin. The thermal stability of the PR/AHBP blends did not change obviously as the AHBP content increased continuously from 5 wt % to 20 wt %.

Figure 4 presents the DSC curves of phenolic resin, AHBP and PR/AHBP with AHBP content of 5 wt %, respectively. It could be seen that, similar to neat phenolic resin, PR/AHBP only exhibited a single glass transition temperature (T_g), showing that PR/AHBP formed a homogeneous phase. The result indicated that AHBP had good compatibility with phenolic resin. On the other hand, it can be obtained from Figure 4 that the T_g of phenolic resin, AHBP and PR/AHBP containing 5 wt % AHBP were 58°C, 92°C, and 60°C. Compared with unmodified resin, the T_g of PR/AHBP was slightly increased. It is well known that T_g mainly depends on the mobility of the macromolecular chain segments in the network structure.[26] In the PR/AHBP system, the introduction of AHBP with the rigid structure restricted the mobility of the chain segments of macromolecules, and as a result, PR/AHBP displayed a higher T_g. At the same time, according to Scheme 1, there is no reactive groups (such as hydroxyl methyl group) in AHBP molecular chain that can react with phenolic resins, thus the crosslink density will decrease with addition of AHBP.

The heat deformation temperature is another important index for heat-resistance property of material. The heat deformation temperatures of the PR/AHBP blend with different AHBP contents were investigated, and the data obtained are listed in Table II. It could be found that the heat deformation temperature of neat phenolic resin was 187°C. When 5 wt % AHBP content was introduced in phenolic resin, the heat deformation temperature was increased to 194°C. This could be mainly attributed to the fact that, the introduction of AHBP with a large number of phenyl groups (Scheme 1) could inhibit the thermal motion of the macromolecular chain segments, resulting in the increase of the heat deformation temperature of PR/AHBP. The result suggested that the heat-resistance of PR/AHBP could be improved by the addition of AHBP, which agreed with the corresponding DSC results. However, as the data shown in Table II, when the AHBP content further increased to 10 wt %, the heat deformation temperatures of PR/AHBP decreased to 180°C from 194°C of PR/AHBP containing 5 wt % AHBP. This result was mainly due to the decrease of crosslink density of phenolic resin with increasing AHBP content.

Table I. Thermal Analysis Data of PR/AHBP Containing 5 wt % AHBP and Phenolic Resin

Sample	T_5[a] (°C)	T_{10}[b] (°C)	T_{30}[c] (°C)	RW[d] (%)
Phenolic resin	343	438	598	58
PR/AHBP	249	282	380	32

[a] T_5 refers to the temperature at 5% weight loss.
[b] T_{10} refers to the temperature at 10% weight loss.
[c] T_{30} refers to the temperature at 30% weight loss.
[d] RW refers to the residual weight percentage at 800°C.

Effect of AHBP on the Toughening Performances of Phenolic Resins

Figure 5 displays the effect of AHBP content on impact strength of PR/AHBP. The related data are listed in Table II. It could be found that when the content of AHBP was only 5 wt %, the impact strength of PR/AHBP was greatly improved to 4.5 kJ/m^2 from 2.4 kJ/m^2 for the neat phenolic resin. PR/AHBP containing 15 wt % AHBP showed an impact strength of 5.5 kJ/m^2, which was about near 130% higher than that of the neat PR

Table II. Effect of AHBP Content on Heat Deformation Temperature of PR/AHBP

AHBP content (%)	Heat deformation temperature (°C)	Impact strength (KJ/m^2)	Bend strength (MPa)
0	187	2.4	60.73
5	194	4.5	87.07
10	180	5.3	86.98
15	177	5.5	86.74
20	175	3.8	72.76

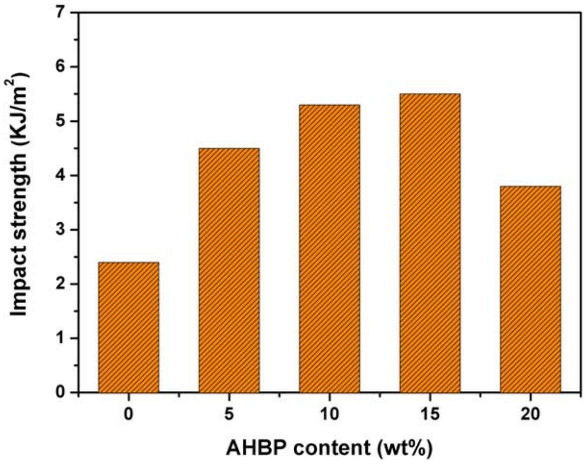


Figure 5. Effect of AHBP content on impact strength of PR/AHBP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

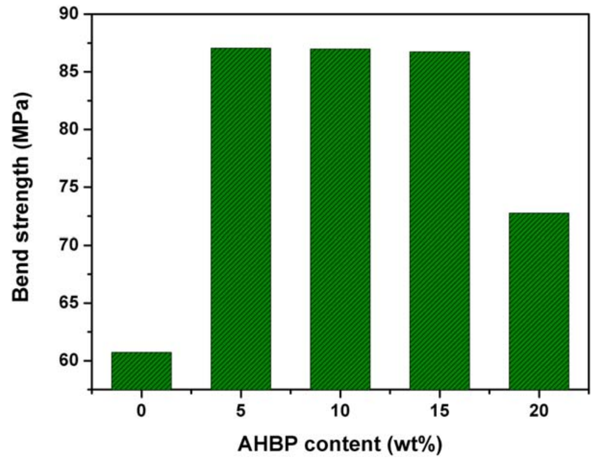


Figure 6. Effect of AHBP content on bend strength of PR/AHBP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

resin. The impact strength of PR/AHBP exhibited a small decrease at the higher content of AHBP (20 wt %), but still was much higher than that of unmodified resin. These results suggested that the impact strength of PR/AHBP could be obviously enhanced by the addition of AHBP. The improvement of impact strength was due to the decrease in the crosslink density and increasing in the unoccupied free volume causing by the introduction of AHBP with rigid phenyl structures.[41] A similar effect of AHBP content on bend strength of PR/AHBP was observed, as shown in Figure 6 and Table II.

The sample surfaces of the neat phenolic resin and PR/AHBP containing 5 wt % AHBP were studies by SEM measurements

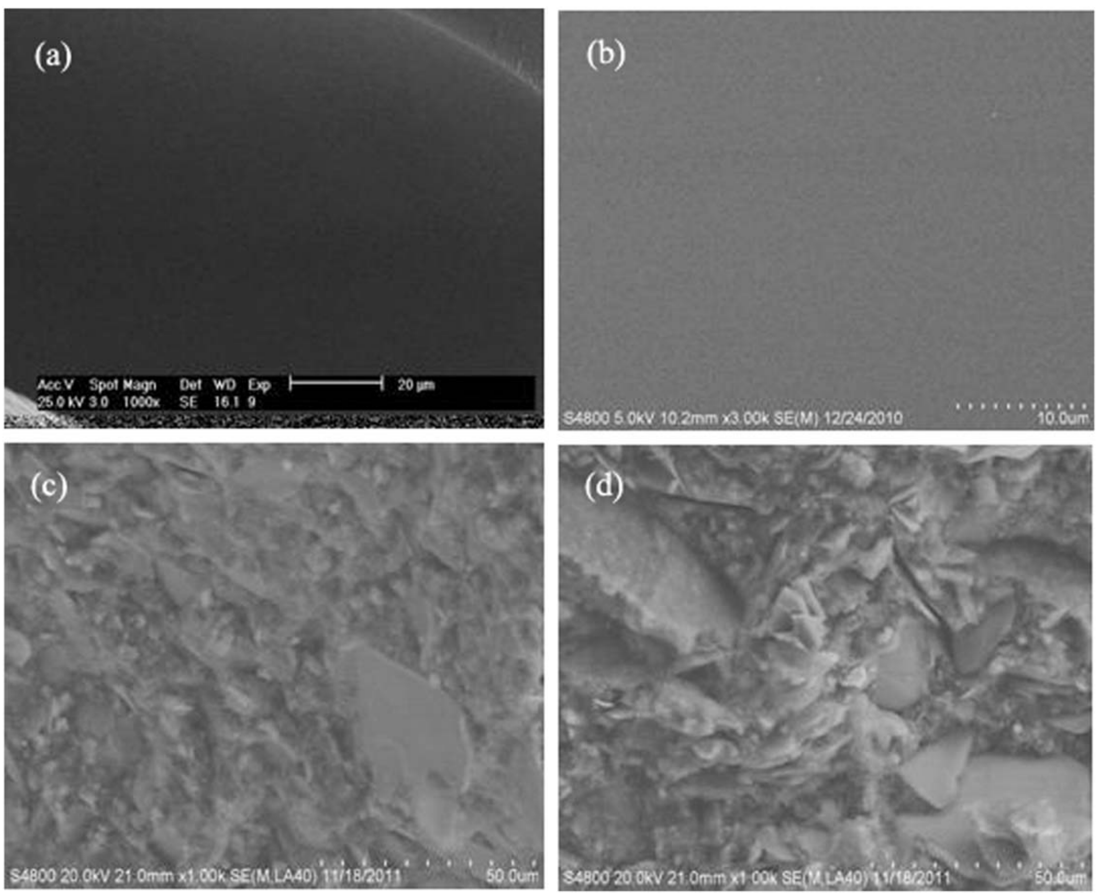


Figure 7. SEM images of the sample surfaces (a) phenolic resin and (b) PR/AHBP containing 5 wt % AHBP and the fracture surfaces of (c) phenolic resin, and (d) PR/AHBP containing 5 wt % AHBP.

as illustrated in Figure 7(a,b), respectively. Similar to neat phenolic resin, the sample surface of PR/AHBP was smooth, showing that there was not phase separation between AHBP and phenolic resin. In order to confirm this point, the fracture surface of the PR/AHBP containing 5 wt % AHBP sample was investigated by SEM as shown in Figure 7(d). For comparison, the fracture surface SEM image of neat phenolic resin was also given in Figure 7(c). As expected, PR/AHBP showed a single phase similar to neat phenolic resin, suggesting the good compatibility between PR and AHBP, which was well consistent with the result of DSC of PR/AHBP.

The careful comparison of the fracture surface SEM images of neat phenolic resin and PR/AHBP containing 5 wt % AHBP revealed that, the fracture surface of neat phenolic resin was smooth and displayed the brittle fracture, while that of PR/AHBP containing 5 wt % AHBP was rougher than that of neat phenolic resin, indicating that PR/AHBP had the ductile nature of the cracks. Therefore, PR/AHBP could absorb much energy than neat phenolic resin when cracks occurred, resulting in the higher impact strength than neat phenolic resin, as shown in Figure 5. The results above confirmed that the toughness of PR/AHBP could be significantly improved by the addition of AHBP.

CONCLUSIONS

A series of novel hyperbranched polyester modified phenolic resins (PR/AHBP) with different AHBP contents were prepared successfully, and their thermal properties and mechanical performances, as well as fracture morphology were studied. The results demonstrated that, the heat-resistance of PR/AHBP could be enhanced by the introduction of AHBP. PR/AHBP displayed the ductile fracture. The impact strength of PR/AHBP with AHBP content of 15 wt % was greatly improved to 5.5 kJ/m^2 from 2.4 kJ/m^2 of the neat phenolic resin. The above results verified that AHBP was a desirable toughening agent for phenolic resin.

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