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**Part II**

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# Contents

# Improving Tenacity Capability and the Heat-resistance of Phenolic Resins by Adding a Rigid Aromatic Hyper Branched Polyester

Anderson L. D., Stem W.Morgan

Polymer chemistry, California Miramar University, California, American

**Abstract:** An aromatic hyper branched polyester (AHBP) was synthesized by melt polycondensation from diphenolic acid and char- cauterized by Fourier transform infrared spectrum (FTIR) spectra. The degree of branching (DB) value of AHBP calculated from the 13C-NMR spectroscopy was 0.67. The number-average molecular weight (Mn) and weight-average molecular weight (Mw) 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 (Tag) 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, scan- nine 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 con- tainting 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. VC  2015 Wiley Periodicals, Inc. J. Appl. Polyp. Sci. 2016, 133, 42734.

**Keywords:** Polyesters; Resins; Thermoses

## 1. Introduction

Thermoses resins, especially phenolic resins are widely used in adhesives, coatings, electrical and electronic materials, and molding compounds, owing to their superior performances, such as thermo mechanical properties, process ability, excellent chemical stability, and electrical properties.[1–6] However, the inherent brittleness as one major disadvantage, limit their apply- action 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 thermoset-mers mainly include dendrites and hyper branched polymers. Dendrites have perfectly branched structures, but their seethe- sis often involves multiple reaction steps, altogether with com- placated separation and purification processes. Hyper branched polymers possess similar excellent properties to dendrites, and can be easily synthesized through one-step polymerization reach- tion.[21–24] Hence, hyper branched polymers as modifiers of theremost resins have drawn much attention, and many related reports on hyper branched polymers modification epoxy resins have been reported in the literatures. These hyper branched poly-25–29ting resins. However, their poor compatibility with phenolicmers included hyper branched polyester, hyper branched resin matrix negatively affect the process ability and thermal polyether,30,31hyperbranched polyimide,32and so on. They have properties, thus seriously affected their modification effects.10–1Dendriteic polymers are a class of three-dimensional macramé- locales. They exhibit low melt points and solution viscosities due to lack of restrictive interchange 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  Dendrite poly-already been applied for modification of epoxy resins in order to improve toughness. Among them, hyper branched polyesters are the most widely used hyper branched polymers. The researches have shown that hyper branched polymers could obviously enhance the toughness of epoxy resins without affecting the process ability and thermal properties, verifying that hyper-branched polymers are a kind of desirable toughness for epoxy resins.

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However, as mentioned above, most of former researches focused on epoxy resin/hyper branched polymers, and less attend- ton was paid on phenolic resin (PR)/hyper branched polymer systems. In fact, phenolic resin is one of the most important thermoses resins, and thus, the study on toughening modification- ton of phenolic resins is necessary and important in the devil- orpiment of high performance phenolic resins. Until recently, Liu and CSU et al. have done some work on the modification of phi- colic resins with hyper branched collaborates (HB).35–37 They prepared a series of hyper branched collaborates (HB) terminated with phenol hydroxyl (Hip) and boric acid hydroxyl (Hob) functional groups, and then blended HB with phenolic resins to

obtain a type of HB/phenolic resin blends. Their studies sag- gusted that the blends are homogeneous, and the thermal prop- reties of the blends were improved by addition of HB. However, the toughness of these HB/phenolic resin blends were not men- tined in their studies
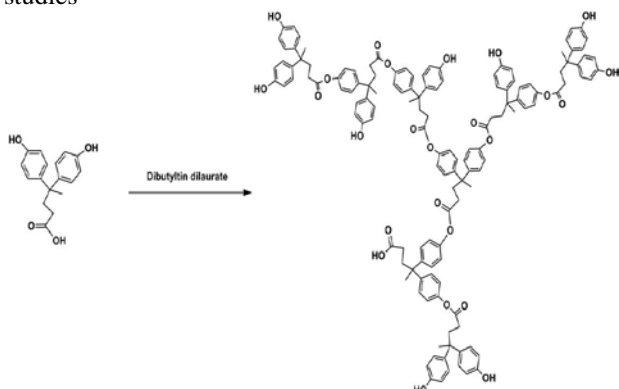


**Figure 1. The synthesis route of AHBP**

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

## 2. Experimental

Fourier transform infrared spectrum (FTIR) was recorded on a Nicolet Magna-IR 550 FTIR spectrophotometer in the 4000– 400 cm21 region using Ker pellets. Gel per- meation chromate- ropy (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 50–8008C region in nitrogen atmosphere and con- ducted with a heating rate of 108C min21. Differential scanning calorimetry (DSC) were carried out on NETZSCH DSC200 at the temperature of 40–1408C region at a heating rate of 108C min21 in nitrogen atmosphere. The thermal defor- mation tem- prelatures were determined by a XRW-300 HDT and VICAT softening point temperature test ma- chine.

The morphologies of the surfaces and fracture surfaces of phi- colic resin and PR/AHBP samples were examined with a Hit- chi SEM S-520 Scanning electron microscopy (SEM). The SEM images included both surface and frac- ture section.

The bending strength and toughness of samples were tested on a WDW-20 computer controlled universal test- ing machine (cross head speed: 2.0 mm/min, gauge length: 80 mm). IPod impact test was carried out with rectangular notched specimens (size: 120315310 mm3, notched thickness: 7 mm) at XJJ-5 impact testing ma- chine (impact velocity: 2.9 m s21).

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

The hyper branched polyester (AHBP) was synthesized by a modified procedure reported in the literature.17 1.15 g deputy- tin deflagrate was added into 229.00 g diphe- nolic acid, and the mixture was heated to 1908C and stir for 4 h under nitrogen atmosphere. Then the temperature was raised to 2258C and stirred for another 3 h to obtain the crude product. The prod- cut was dissolved in 1 L of THF, and poured into large amounts of deionizer water (about 2 L) to obtain the AHBP precipitate. The precipi- tate was filtered off, washed with deionizer water and then dried under vacuum at 808C for 12 h until con- stant 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 1408C in nitrogen atmosphere and stirred for 2 h to obtain PR/AHBP with AHBP con- tent 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.

## 3. Results and Discussion

AHBP was prepared from diphenolic acid by melt polyc- lone- station reaction using dibutyltin deflagrate as cata- lyst. The sin- thesis procedure of AHBP is given in Scheme 1. The number- average molecular weight (Mn), weight-average molecular weight (Mw), and molecular weight distribution of AHBP were determined by GPC measurement. The results showed that the Mn and Mw

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of AHBP were 1792 and 4480 g/mol, respectively, and the polydispersity index (PDI) value of AHBP was 2.5. As previously mentioned, hyper branched polymers are a most important kind of dendrite polymers, which have highly branched structures. The degree of branching (DB) is a mea- cerement 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 13C-NMR spectroscopy and commonly calculated according to the following equation:38.
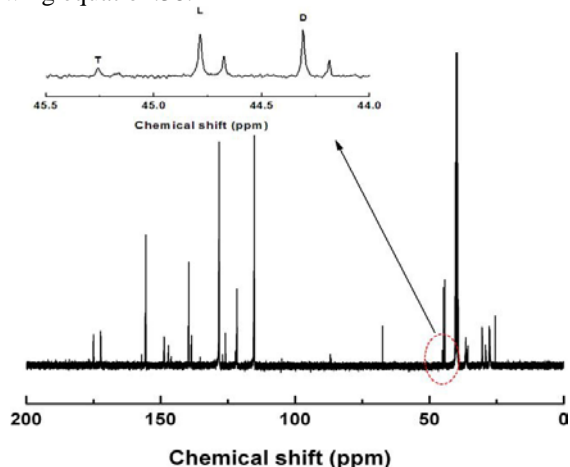


**Figure 2. 13C-NMR spectrum of AHBP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]**

where D, L, and T are the integral intensities of the signals of den- critic units, the linear units, and the terminal units in the 13C- NMR spectrum of the branched polymer, respectively. The DB is 100% for dendrites and less than 100% for hyper branched polymers.39 Figure 1 presents the 13C-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 cm21 was the overlapping band corresponding to the O–H stretching vibration of hydroxyl group and carboxyl group of diphenolic acid. The peak at 1703 cm21 was attributed to the C5O stretching vibration of carboxyl group. The peaks at 1610 cm21 and 1513 cm21 were ascribed to C5C stretching vibration of the benzene ring backbone. The characteristic absorption peak of carboxyl group of diphenolic acid at 1703 cm21 was absent in the FTIR spectrum of AHBP, but a new peak at 1743 cm21 appeared, which was associated to C5O stretching vibration of ester group of AHBP. Meanwhile, the peak intensities at 1175 and 1015 cm21 were obviously enhanced, which could be assigned to the asymmetric and sym- metric 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 overlap- ping band corresponding to the O–H stretching vibration of hydroxyl group and carboxyl group appeared at about 3420 cm21, and became narrow compared with the correspond- in 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 3438C, 4388C, and 5988C, respect- timely. 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 2498C, 2828C, and 3808C, respectively. Consequently, 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 %.
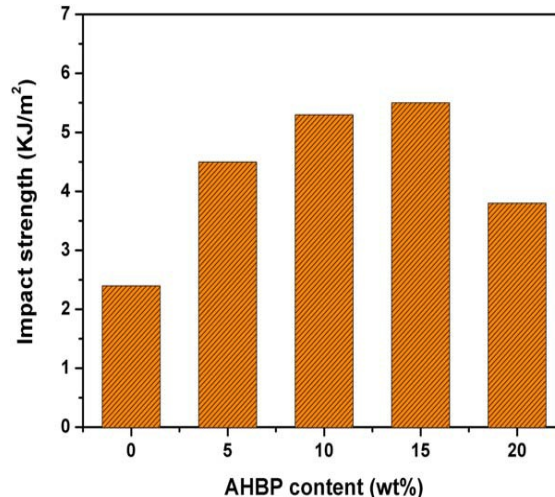


**Figure 3. Effect of AHBP content on impact strength of PR/AHBP. [Color fig- urea can be viewed in the online issue, which is available at wileyonlinelibrary. com.]**

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 (Tag), showing that PR/AHBP formed a homogeneous phase. The result Indi- cited that AHBP had good compatibility with phenolic resin. On the other hand, it can be obtained from Figure 4 that the Tag of phenolic resin, AHBP and PR/AHBP containing 5 wt %

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AHBP were 588C, 928C, and 608C. Compared with un-modified resin, the Tag of PR/AHBP was slightly increased. It is well known that Tag mainly depends on the mobility of the macro-molecular chain segments in the network structure.26 In the PR/AHBP system, the introduction of AHBP with the rigid struck- true restricted the mobility of the chain segments of macramé- locales, and as a result, PR/AHBP displayed a higher Tag. 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 con- tents 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 1878C. When 5 wt % AHBP content was introduced in phenolic resin, the heat deformation temper- nature was increased to 1948C. 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 ma-cromolecular chain segments, resulting in the increase of

the heat deformation temperature of PR/AHBP. The re-sult suggested that the heat-resistance of PR/AHBP could be improved by the addition of AHBP, which agreed with the cur- responding 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 1808C from 1948C of PR/AHBP containing 5 wt % AHBP. This result was mainly due to the decrease of crosslink density of phenol-ic resin with increasing AHBP content.

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

from 2.4 kJ/m2 for the neat phenolic resin. PR/AHBP contain- in 15 wt % AHBP showed an impact strength of 5.5 kJ/m2, which was about near 130% higher than that of the neat PR

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 sag- gusted that the impact strength of PR/AHBP could be obviously enhanced by the addition of AHBP.
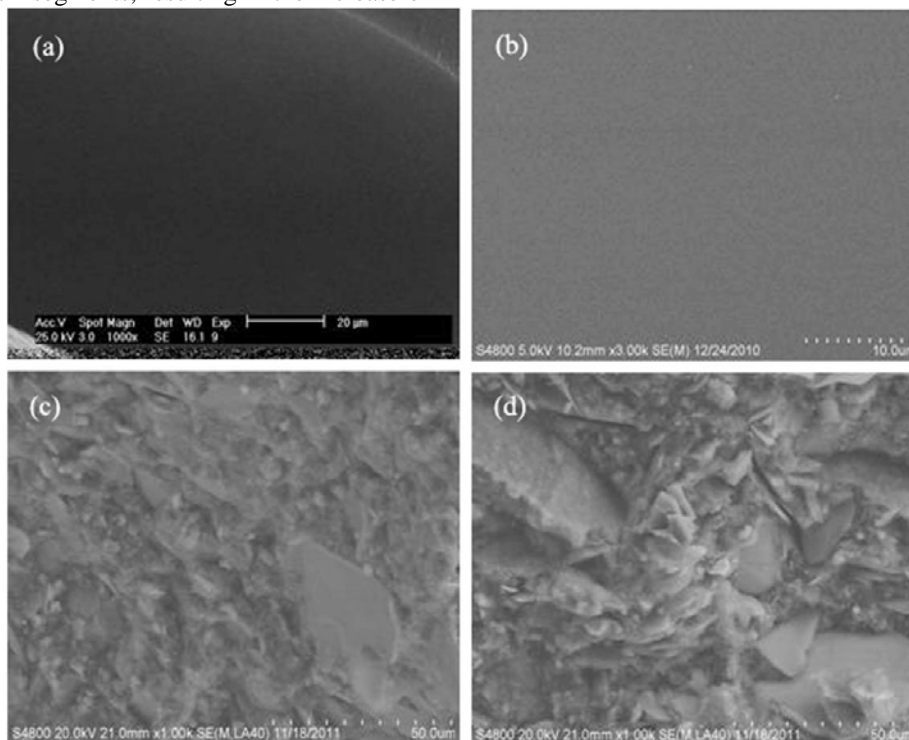


**Figure 4. SEM images of the sample surfaces (a) phenolic resin and (b) PR/AHBP containing 5 wt % AHBP and the fracture surfaces of (c) phenolic resin, and (d) PR/AHBP containing 5 wt % AHBP**

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

SEM measurements as illustrated in Figure 7(alb), re-spectively. Similar to neat phi- colic resin, the sample

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surface of PR/AHBP was smooth, show- in that there was not phase separation between AHBP and phenolic resin. In order to confirm this point, the fracture sure-face 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 ex-pected, PR/AHBP showed a single phase similar to neat phenolic resin, suggesting the good com- ratability be-tween 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 re-sults above confirmed that the toughness of PR/ AHBP could be significantly improved by the addition of AHBP.

## 4. Conclusions

A series of novel hyper branched polyester modified phenolic resins (PR/AHBP) with different AHBP con-tents were prepared successfully, and their thermal prop-erties and mechanical per- dormancies, 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 dies- played the

ductile fracture. The impact strength of PR/AHBP with AHBP content of 15 wt % was greatly improved to 5.5 kJ/m2 from 2.4 kJ/m2 of the neat phenolic resin. The above results verified that AHBP was a desirable tough-ening agent for phenolic resin.

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