

Thermomechanical and Morphological Properties of Epoxy Blends with Hyperbranched Polyester: Effect of the Pseudo-Generation Number

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ABSTRACT: The thermomechanical and morphological properties of some epoxy blends modified with hyperbranched polymers are reported. The effects of pseudo-generation numbers, from the second to the fourth, were studied. All the hyperbranched polymers used had —OH end groups. The blends were thoroughly characterized in both the unreacted and cured states. The unreacted blends, characterized by parallel plate rheometry and hot stage microscopy, revealed that pseudo-generation number can have a profound effect both on the reactivity and the phase separation behavior. Analysis of the cured samples

was carried out through scanning electron microscopy, dynamic mechanical tests, and fracture mechanics. The results supported some findings obtained from the analysis of the unreacted blends; and dynamic mechanical analysis helped shed more light on the phase separation behavior. Pseudo-generation number also influenced the glass transitions of the blends. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 1395–1406, 2010

Key words: hyperbranched; epoxy; blends; morphology; thermomechanical properties

INTRODUCTION

Dendritic polymers^{1,2} are an interesting class of polymeric materials characterized by a tree-like structure. Dendritic covers both dendrimers and hyperbranched concepts. The dendrimer's synthesis requires accurate control of the reaction and several purification steps; on the contrary, the hyperbranched polymers are prepared at a reduced cost. Because of their compact structures, dendrimers and hyperbranched polymers are characterized by lower melt and solution viscosities^{3–5} compared with their analogous linear counterparts. However, unlike dendrimers, hyperbranched polymers are not perfectly branched structures. In addition to dendritic and terminal repeat units, hyperbranched polymers can also contain high fractions of linear units.

The term “generation” is often used to describe the size of this class of polymers. Each generation represents one repetitive step when building a hyperbranched structure of a certain size. Consequently, hyperbranched polymers with many generations have higher molecular weights and a large number of reactive end-groups at their peripheral surface. The high density of functional end groups is

an advantage over the linear analogs because the end groups can be used to tailor both the properties of the hyperbranched macromolecules and of their blends with other polymers.

Among hyperbranched polymers a well-studied type is represented by the hyperbranched aliphatic polyesters. The synthesis of such polymers was first described by Baker et al.^{6,7} and investigated by Hult and coworkers.⁸ Hult et al. used a portionwise monomer addition strategy, adding 2,2-bis(dihydroxymethyl)propionic acid in “pseudo-generation” equivalent portions to a 1,1,1-tris(hydroxymethyl)propane core molecule under acidic catalysis. The term “pseudo-generation” was coined instead of generation to account for the randomly branched structure obtained in these syntheses. The term pseudo-generation will then be used in the rest of this article. In 1995, this work resulted in the commercially available hyperbranched polyols (Perstorp, BoltornTM). The use of these polymers as toughening agents for epoxy resins is a field of active research. Some studies have been conducted for these applications, mainly by Månson and coworkers^{9–18} and Ratna et al.^{19–23}

Månson et al. focused mainly on an epoxy system based on diglycidyl ether of bisphenol A (DGEBA) cured by isophoronediamine (IPD). They modified their systems by the addition of epoxy-terminated hyperbranched polyesters produced by Perstorp. Månson and coworkers^{9,14} showed the effectiveness of hyperbranched polymers in toughening the brittle

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epoxy matrix without introducing negative effects on properties such as the thermal and water resistance. The addition of hyperbranched modifier gave rise to a phase-separated morphology via controlled phase separation inversion (CIPS).^{10,11} The phase separation mechanism was proven to be nucleation and growth.¹³ In most of their studies, Månson et al. used third pseudo-generation hyperbranched polymers with different epoxy equivalent weights (EEWs). This last parameter was shown to have a profound effect on the resulting morphology. In particular, the decreasing EEWs, which corresponds to an increasing number of epoxy groups on the hyperbranched shell for a fixed total molecular mass, was found to increase the initial solubility of the modifier in the epoxy resin and to shift the cloud point to higher conversion, thus resulting in finer morphologies.

Ratna et al. studied several blends using a wide range of epoxy monomers that included: DGEBA,^{19,21,23} triglycidyl *p*-amino phenol (TGAP),^{19,21,22} and tetraglycidyl diaminodiphenyl methane (TGDMM).²³ All the blends were cured by diethyltoluene diamine (DETDA). The hyperbranched polymers analyzed were epoxy-functionalized hyperbranched polymers of the third pseudo-generation or, in other cases, OH-ended hyperbranched polymers of the fourth or fifth pseudo-generation. All the blends showed particulate morphologies on curing except for those based on TGAP/DETDA and modified with a fifth pseudo-generation hyperbranched polymer.²⁰ The studies by Ratna et al. confirmed the efficiency of the hyperbranched polymers in toughening the epoxy systems with different functionality in agreement with the findings of Månson et al. However, they also evidenced some residual miscibility of the hyperbranched polymer, which led to decreasing glass transition temperatures for the blends.

We have recently reported some studies^{24,25} on the effects of the addition of hyperbranched polymers on different epoxy systems. In one study,²⁴ we analyzed two epoxy systems based on DGEBA and TGAP, both of which were cured by 3,3'-diamino diphenyl sulphone and modified with either a third- or a fourth pseudo-generation OH-ended hyperbranched polymer. The study revealed that the third pseudo-generation polymer was unable to undergo phase separation when added to the epoxy blend at low percentages (~15 wt %). The TGAP-based blends showed finer morphologies compared with those observed in blends based on DGEBA. These results confirmed that TGAP is a good solvent for the hyperbranched polymers studied. Analogous results were found when DETDA was used instead of diamino diphenyl sulfone (DDS).²⁵ In the latter article, morphological results were further supported by rheological analyses.

The objective of the present article is to study in further detail the effect of the pseudo-generation number on the morphological and thermal properties of some epoxy/hyperbranched blends. The selected hyperbranched polymers had different pseudo-generation numbers varying from two to four. The epoxy system selected was based on a difunctional diglycidyl ether of bisphenol F (DGEBF) cured by DETDA. The cure cycle was chosen for practical aspects. In fact, it is known that lower cure cycle temperatures are advantageous in terms of reduction of autoclave and tooling costs, so we decided to study a cure cycle divided into two steps:

- i. A precure at medium temperatures (135°C and 155°C) for the processes in an autoclave or in a closed, matched mould;
- ii. A curing at higher temperature (180°C), which can be carried out inexpensively in a standard oven.

After the precure step, it was important to verify the attainment of elastic properties that could allow the precured blend to be easily demolded. The elastic properties of both precured and postcured samples were studied by dynamic mechanical analysis (DMA).

EXPERIMENTAL

Materials

DGEBF, supplied by Hutsman/Vantico under the trade name PY306, was used as the epoxy monomer. The curing agent was a mixture of the two DETDA isomers (74–80% 2,4 isomer and 18–24% 2,6 isomer; LonzaCure DETDA80 supplied by LONZA). The curing agent was always added with a stoichiometric percentage of 100%.

Perstorp Specialty Chemicals kindly provided the hyperbranched polyesters, which are commercialized as BoltornTM. Three polymers were selected for this study; their pseudo-generation number varied from two to four. The code and the characteristics of these polymers are reported in Table I in which the molecular masses are obtained from Žagar et al.²⁶ Our denotations for the hyperbranched polymers are H20, H30, and H40, respectively. The structures of all the reagents are reported in Figure 1.

Boltorn polymers were added at two percentages by weight (10 wt % and 20 wt %). The different formulations used in the study are summarized in Table II.

Preparation of the blends

The blends were prepared by mixing the hyperbranched polymer with the epoxy monomer at 135°C

TABLE I
Properties of the Hyperbranched Used in the Study

Code	Pseudo-generation number	End group	Hydroxyl number ^a (mg KOH/g)	Molecular weight, M_w^b (g/mol)	T_g^c (°C)
H20	2	OH	490–530	2100	7.00
H30	3	OH	480–510	3500	20.02
H40	4	OH	470–500	5100	25.01

^a Data from Perstorp datasheet.

^b Data obtained from Ref. 26.

^c Data obtained from supported DMA.

until a homogeneous solution was obtained (~ 15 min). The temperature was lowered to 90°C and the curing agent added. The mixture was stirred for another 15 min to obtain a homogeneous solution.

For the thermomechanical and morphological investigations, the cured samples were prepared by pouring the unreacted blend in a preheated (135°C) mould. The resin was degassed under high vacuum for 30 min and the panel was cured for 3 h at 135°C. The temperature was then increased to 180°C (2°C/min) and held at this value for 3 h. From this point, the samples termed “pre-cured” are those cured at 135°C for 3 h; the “post-cured” samples are those that, after the pre-curing at 135°C, were cured at 180°C for 3 h.

Characterization of the blends

SEM (scanning electron microscopy) micrographs were obtained with a Cambridge 90. The cured sam-

ples were fractured in liquid nitrogen. The fractured surfaces were sputter-coated with gold before the SEM micrograph was taken. Some cryofractured surfaces were etched with a mixture of sulphuric acid/distilled water (3 : 2) before sputter-coating. The role of the acid mixture was to etch the thermoplastic phase and then to increase the contrast between the phases. After the etching, the samples were washed with water and gold-coated. The comparison of acid-treated samples with nontreated ones is reported.

Optical hot-stage microscopy was used to analyze the morphological behavior of the unreacted blends in the first stages of the curing reaction.

Rheological analyses were performed on a rotational rheometer (ARES by TA instruments) equipped with parallel plates. The unreacted samples were subject to a ramp test (at 2°C/min) experiment to determine the viscosity behavior over a wide temperature spectrum. For ramp testing, parallel plates 40 mm in diameter were used. In addition, isothermal experiments were carried out at several temperatures to determine the gel point of the blends. An isothermal, multiple waveform, dynamic test (also termed “multiwave” rheological measurement) was used to determine the gel point accurately. The test consists of performing simultaneous time sweeps at different frequencies, within the linear viscoelastic regime, for a given temperature. Actually, with this technique, the multiwave strain generation is based on the Boltzmann superposition principle. The total linear strain, γ , applied on the sample is the sum of

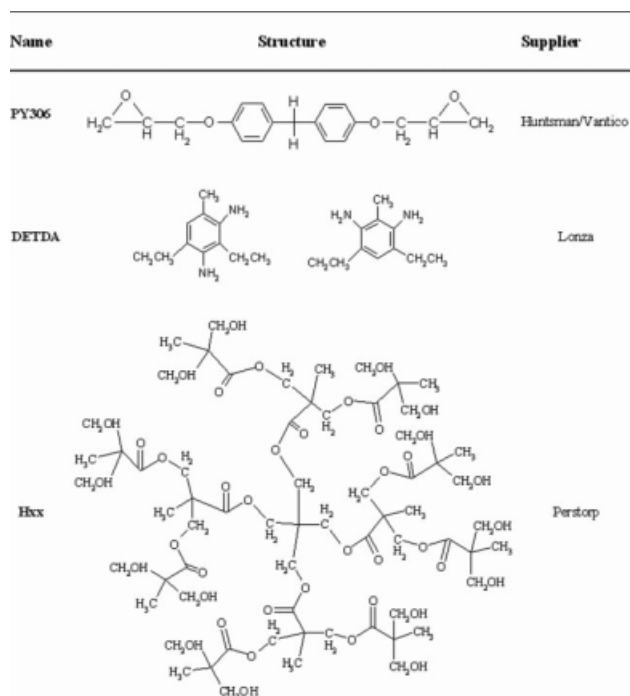


Figure 1 Chemical structures of the reactants used in the study.

TABLE II
Composition in Percent by Weight of the Systems Studied

Component/code	P00	P10	P20
DGEBF	78.68	70.81	62.95
DETDA	21.32	19.19	17.05
Boltorn HPB ^a	0	10	20

^a The abbreviation H20, H30, and H40 will be used in the text to indicate which Boltorn Hxx was added to the system. For example, P10H30 will be used to indicate the system containing 10 wt % of Boltorn H30.

several independent strains, each described by its corresponding Fourier series:

$$y = \sum_{i=1}^n \gamma_i \sin(\omega_i t) \quad (1)$$

$$\sum_{i=1}^n \gamma_i \leq \gamma_c \quad (2)$$

The frequencies ω_i chosen are harmonics of a fundamental frequency ω_f . The strain relation [eq. (1)] expresses the requirement that the sum of the individual strain amplitudes stay below a critical amplitude, γ_c , corresponding to the linear viscoelastic limit [eq. (2)]. From the stress response to this compound strain, the individual stresses at each discrete frequency can be obtained by means of a discrete Fourier transform. With a single experiment, then, this procedure allows the determination of the $\tan \delta$ -versus-time curve at different frequencies for each temperature. The crossover of the $\tan \delta$ curves represents the gel point, according to the Winter criterion. The parallel plates used for the multiwave test were 25 mm in diameter.

DMA on the cured samples was carried out on a dynamic mechanical thermal analyzer (TRITEC by Triton Technology) by single cantilever geometry and using samples of size 30 mm \times 10 mm \times 3 mm. The tests were carried out at 1 Hz, with a 2°C/min heating rate using liquid nitrogen for subambient scans.

DMA was also used to characterize the Boltorn polymers. In particular, supported DMA was used. The polymers obtained were finely micronized in powder with an average dimension of 30 μ m and vacuum dried at 40°C for 24 h. Then 0.35 g of polymer powder was weighted in a standard material pocket purchased from Triton and melt pressed at room temperature in a Carver press to obtain a uniform film within the pocket, and finally allowed to cool slowly at room temperature. The test was carried out accordingly to the following protocol. The sample was cooled down to -100°C and then heated to 150°C at 2°C/min to erase previous thermal history. After 150°C was reached, the sample was cooled quickly to -100°C and then heat again to 150°C at 2°C/min. The peak in $\tan \delta$ of the second ramp was used for T_g calculation.

Three-point bending specimens 65 \times 12 \times 4 mm³ were used to perform fracture tests at low strain rate. The measurements were carried out at room temperature with an Instron apparatus Mod. 4301 using a cross-head speed of 1 mm/min. Before testing, the samples were sharply notched with the aid of a notch-vis apparatus by CEAST. The crack was then introduced in the sample by tapping a fresh razor blade. Fracture data were analyzed according to

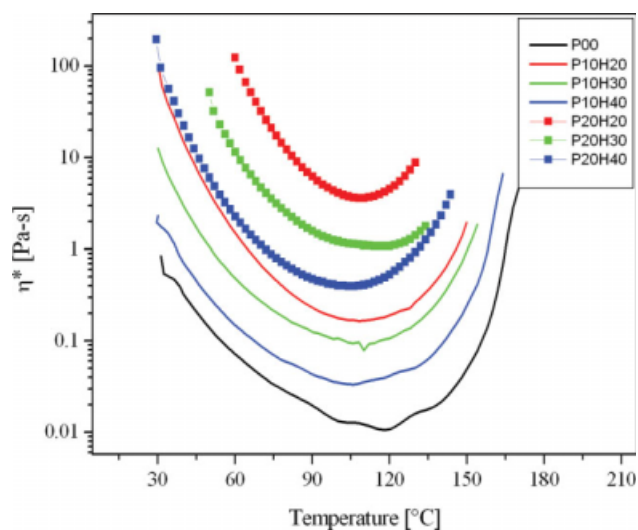


Figure 2 Viscosity (η^*) vs. temperature profiles for ramp test (2°C/min) of formulations with different modifier. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the concepts of linear elastic fracture mechanics (LEFM).

Results and discussion

To verify the behavior of the systems over a wide range of temperatures, dynamic rheological measurements were first carried out at 2°C/min. The results, for various hyperbranched modifiers, are reported in Figure 2. The unmodified resin (P00) shows, as expected, that the minimum viscosity is reached at 120°C. After this minimum, the viscosity starts to rise because of the crosslinking reaction. Hyperbranched polymers with increasing generation number show decreasing minimum viscosity. This behavior confirms the previously reported trend for analogous systems, in which only third- and fourth pseudo-generation polymers were analyzed.²⁵ This behavior is a consequence of the molar mass and structural characteristics of the hyperbranched modifier. Two important studies have been reported on the melt behavior of hyperbranched polymers of this class that can be helpful to explain our findings. The first study by Simon and coworkers²⁷ evidenced shear-thinning behavior for polymers of the second and third pseudo-generation whereas Newtonian behavior was found for higher pseudo-generation numbers. The difference was explained as a consequence of the folding back phenomena. The latter effect was related to the increased flexibility of the branch arms for increasing generation numbers. This increased flexibility leads to the exposure of less polar end groups on the surface of the hyperbranched polymers. The presence of less polar end groups influences the melt behavior. The folding back

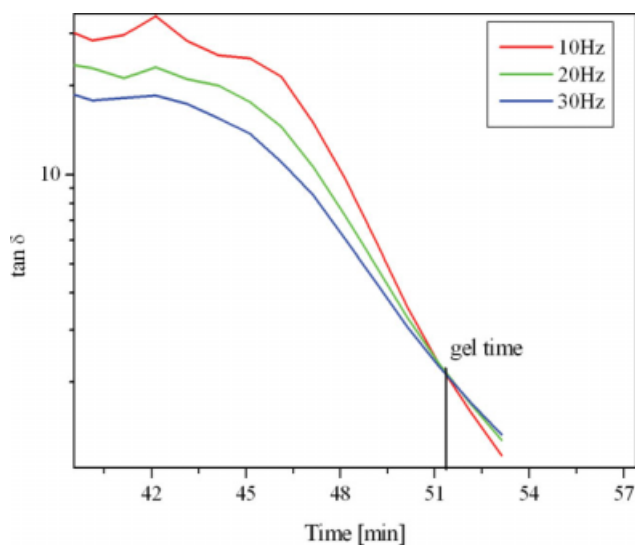


Figure 3 Multiwave isothermal test at 120°C for P10H30 system. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

phenomena has been reported by other authors for the same polymers^{28–30} and for other types of dendritic polymers.^{31,32} The folding back phenomena was first postulated with the Lescanec-Muthukumar model.³³ The second study by Žagar et al.³⁴ presented a detailed analysis of the structure to properties relationship of aliphatic hyperbranched polyester of second and fourth pseudo-generation. In their study, they found that the low molar mass H20 shows stronger H-bond interactions in the melt, at the annealing temperatures, rather than high molar mass H40 not only due to a higher fraction of hydroxyl groups in terminal repeat units, as was explained by Simon and coworkers,²⁷ but also due to the higher mobility and easier accessibility of hydroxyl groups for H-bonding in the linear repeat units. To summarize, for polymers of lower pseudo-generation numbers the higher presence of hydroxyl groups available for interactions can be supposed. These findings support the conclusion that for higher pseudo-generation it reduces the possibility of interactions of the hyperbranched modifier with the epoxy/amine system by means of their hydroxyl groups. Because of minor interaction by hydroxyl groups, the higher pseudo-generation modifiers causes minor increments in the blend's viscosity.

Gel point is another important parameter that can be used to discern the processability of a thermoset system. Thermosets can be easily shaped or processed only before the gel point, in which they can still flow and can be formed without any problems. To determine appropriately the gel point of the studied systems, the well-known Winter criterion was used, along with a multiwave procedure that has

been thoroughly described in the experimental section. In Figure 3 is represented a typical result obtained at 120°C for a modified system, in this case the formulation containing 10 wt % of H30 (P10H30). The gel point is defined as the intersection point of the $\tan \delta$ curves for different frequencies. The tests were conducted at four different temperatures: 110°C, 120°C, 130°C, and 140°C. The gel times obtained are reported in Table III. Hyperbranched polymers with lower generation number strongly reduced the gel time of the blends, thus confirming in low generation polymers the higher presence of hydroxyl groups which are available to interact with the epoxy/amine system during the curing reaction, as they are not on folded-back chains. It is known that hydroxyl groups can catalyze the epoxy curing reaction on the basis of intermolecular transition states. According to this mechanism,³⁵ strong hydrogen-bonding species, such as acids and alcohols, stabilize the transition state, and encourage the nucleophilic attack of the amine.

Hot-stage microscopy was used to investigate the morphological behavior of the blend in the early stages of the precuring reaction. Figure 4 shows the sequences of video captures for the blends with 10 wt % of H20, H30, and H40, respectively. Clear second phase domains cannot be distinguished in the sequence of the P10H20 and P10H30 systems, respectively, even though some small darker zones are present in the pictures. This result could be due to the absence of phase separation or to phase domains too small to be observed by optical microscopy. The system modified with 10 wt % of H40 shows instead the clear formation of second phase domains. Increasing the content of the modifier allows clear visualization of the phase separation, even for the system containing the third-generation hyperbranched polymer H30 (Fig. 5) but not for the systems containing the H20 modifier. The hot-stage microscopy analysis seems to sustain the finding that lowering the pseudo-generation number leads to homogenous blends without a clear phase separation. This trend can be explained by the fact that, due to molecular features mentioned above, H20 has

TABLE III
Gel Points^a Determined for the Different Formulations

Formulation/temperature	110°C	120°C	130°C	140°C
P00	131.2	81.5	55.0	36.6
P10H20	62.1	45.5	28.0	18.3
P10H30	73.2	51.1	36.1	28.4
P10H40	82.3	60.2	40.5	34.1
P20H20	48.1	31.1	21.5	10.3
P20H30	54.3	43.5	35.1	21.7
P20H40	65.2	57.6	41.1	32.0

^a All data are given in minutes.

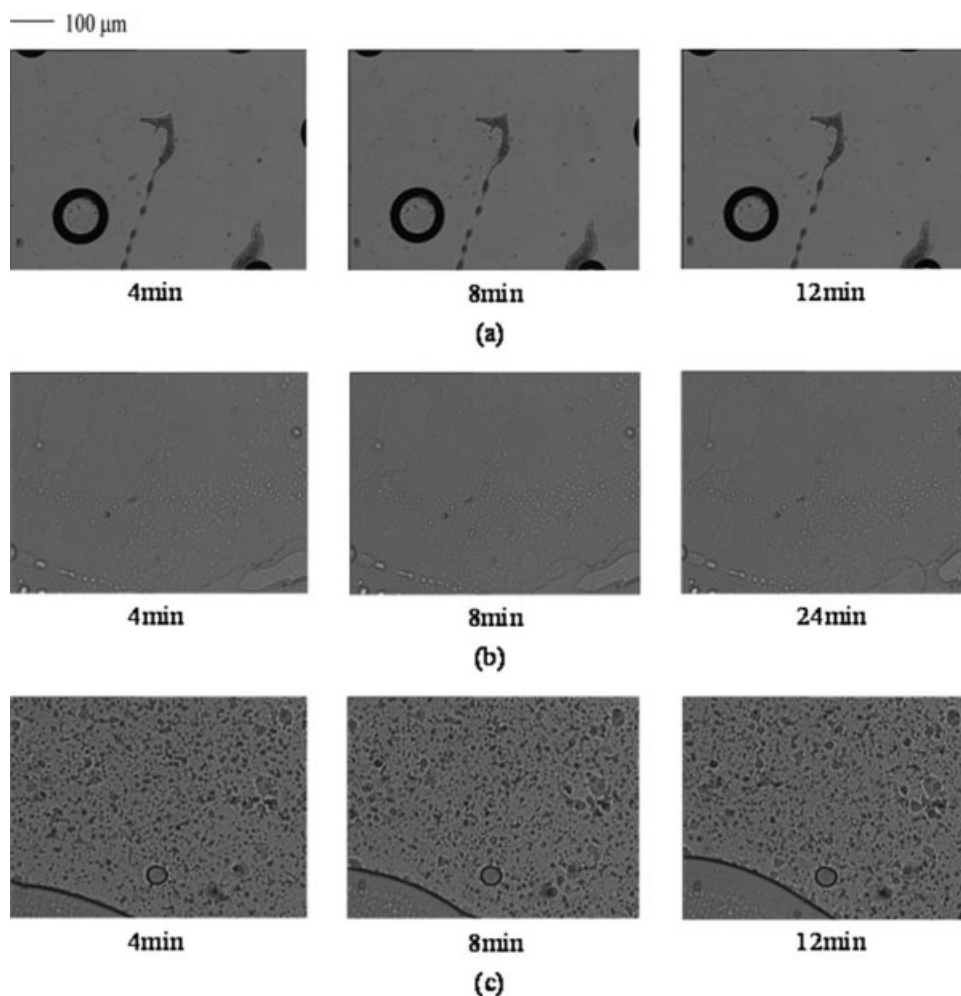


Figure 4 Hot stage micrographs for P10H20 (a), P10H30 (b), and P10H40 (c) systems at test temperature of 135°C.

more hydroxyl groups which can interact with the growing network and thus it has higher solubility with the epoxy matrix.

Scanning electron microscopy was used to further assess the blend morphology after the curing step. All the microscopic investigations were conducted on cryofractured samples. To enhance the phase contrast, one-half of the cryofractured sample was treated with a mixture of acids and one-half without, to have a better interpretation of the blend morphology. Figure 6 shows the micrographs

obtained for the P10H20 blend. The surface is homogeneous and after the acid treatment only very small darker spots (less than 1 μm) can be seen with the higher magnification view (1000 \times). These results confirm the findings of the hot-stage microscopy. Similar results were found for the E20H20 system.

Figures 7 and 8 show the SEM micrographs for the formulations containing 10 wt % of H30 and H40, respectively. The untreated fracture surface of the samples is rough and some hyperbranched rich particles can scarcely be distinguished. The acid

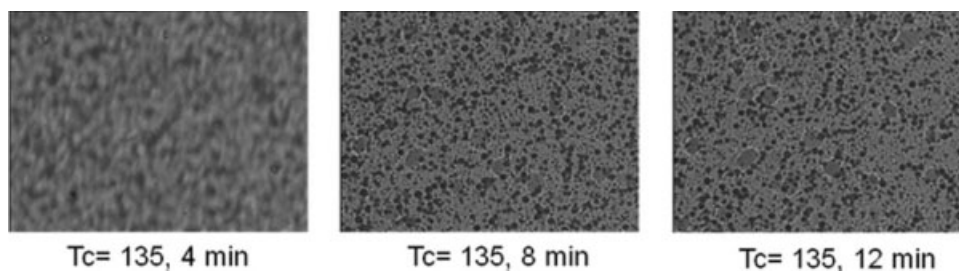


Figure 5 Hot stage micrographs for the P20H30 system at test temperature of 135°C.

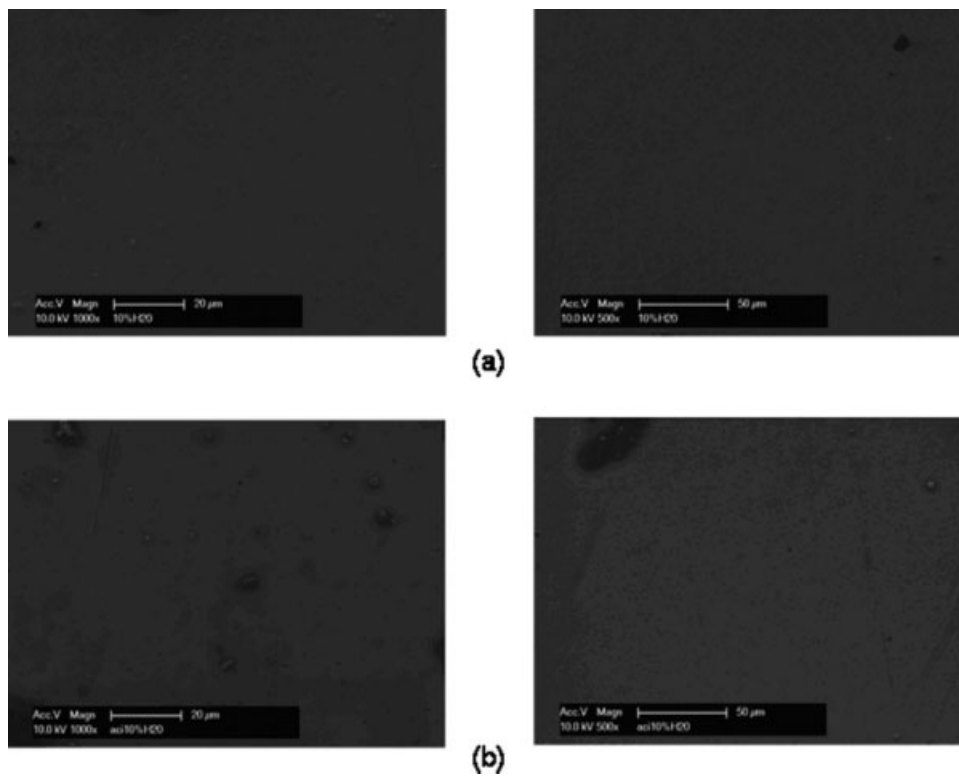


Figure 6 SEM micrographs without acid treatment (a) and with acid treatment (b) of P10H20 samples.

treatment reveals clearly the particulate morphology for each formulation. The system modified with H30 (P10H30) has an uneven distribution of the hyper-

branched-rich particles, whereas the formulation containing H40 (P10H40) has a uniform distribution of particles larger than those observed for the

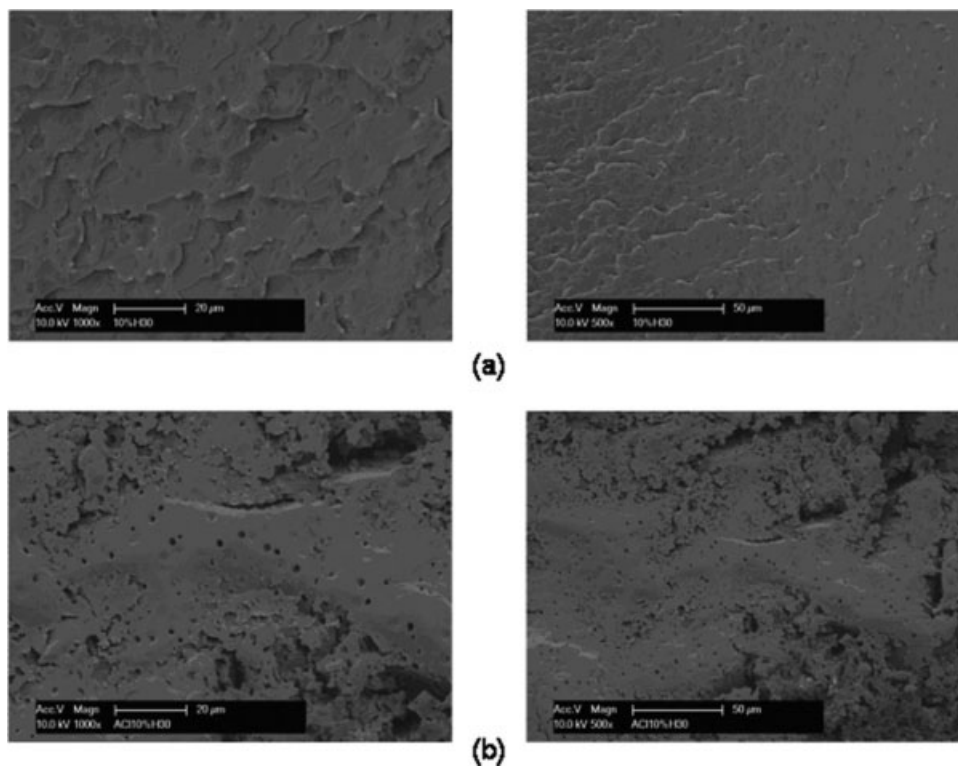


Figure 7 SEM micrographs without acid treatment (a) and with acid treatment (b) of P10H30 samples.

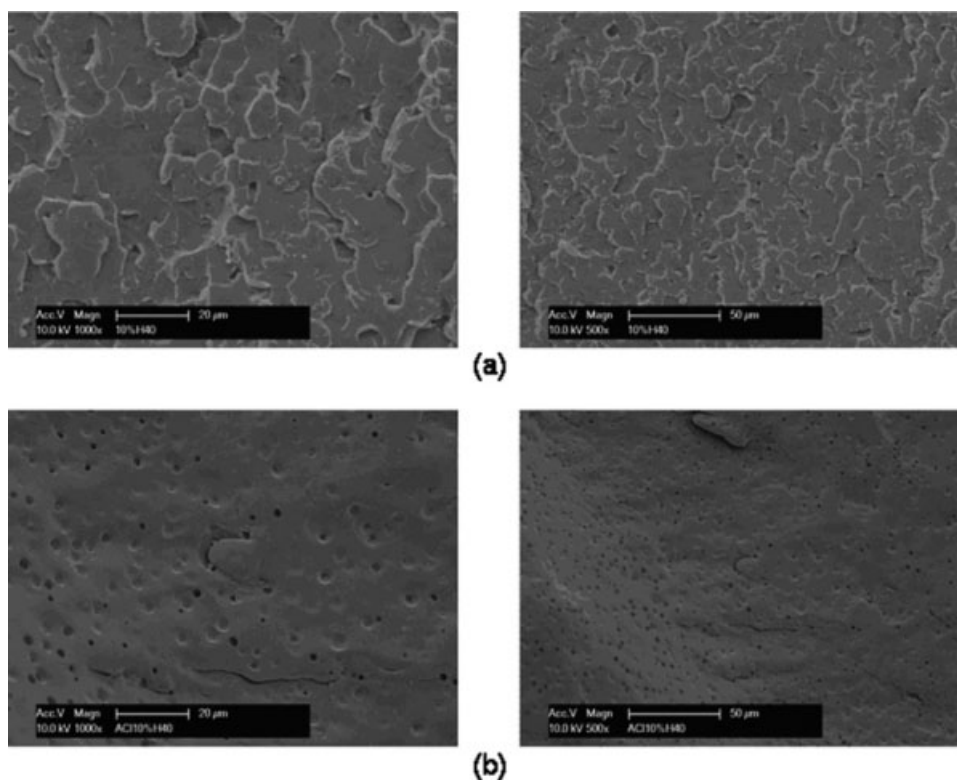


Figure 8 SEM micrographs without acid treatment (a) and with acid treatment (b) of P10H40 samples.

P10H30 system. The SEM micrographs confirm the findings of the hot-stage microscopy analysis: the lower the pseudo-generation of the hyperbranched polymer, the more likely the epoxy/hyperbranched blend will not have a clear or well-distributed phase separation. This behavior can be explained as the result of two causes: the higher solubility and the catalytic behavior of the lower pseudo-generation polymers. The first cause is a consequence of both the lower molecular mass and the high availability of polar hydroxyl groups for the lower pseudo-generation number hyperbranched polymers. The presence of hydroxyl also influences the catalytic behavior of the epoxy/hyperbranched blends by decreasing the gel time due to the catalyst effect of hydroxyl on the epoxy/amine reaction. When the gel point is reached, the blend has such a high viscosity that polymer chain diffusion is hindered, and thus the phase demixing process is mostly suppressed.

Figures 9 and 10 compare acid-treated and nonacid-treated samples with higher contents of hyperbranched polymers for H30 (P20H30) and H40 (P20H40), respectively. In both cases, the increased percentage of hyperbranched leads to clear particulate morphologies with more and denser particles in comparison with the blends with lower modifier content. These effects result from shifting to conditions closer to the critical concentration when higher

modifier amounts are added. In a recent article, Guo et al.³⁶ showed similar effects and also proved that phase inversion for an epoxy/hyperbranched blend containing H40 is obtained for modifier contents of about 40 wt %.

DMA is widely recognized³⁷ as a useful technique to study phase composition in polymer blends by the analysis of the relaxation processes. The $\tan \delta$ -versus-temperature plots for the precured systems are shown in Figures 11 and 12 for high and subambient temperature ranges, respectively. The damping is low below the glass transition (T_g), as the chain segments in that region are frozen. Below T_g , the deformations are thus primarily elastic and the number of molecular slips resulting in viscous flow is low. Above T_g , the damping is low because the segments are free to move; consequently, there is little resistance to flow. In the transition region, which is associated with T_g occurrence, the damping is high because of both the initiation of micro-Brownian motion of the molecular chain segments and their stress relaxation. Graphically, this results in the presence of $\tan \delta$ peaks when glass transitions occur. Table IV reports the temperatures of the $\tan \delta$ peaks measured in Figures 11 and 12 as the main peak and the lower peak, respectively.

The unmodified system (P00) presents a single glass transition temperature of 120°C when precured. All the other precured systems containing the

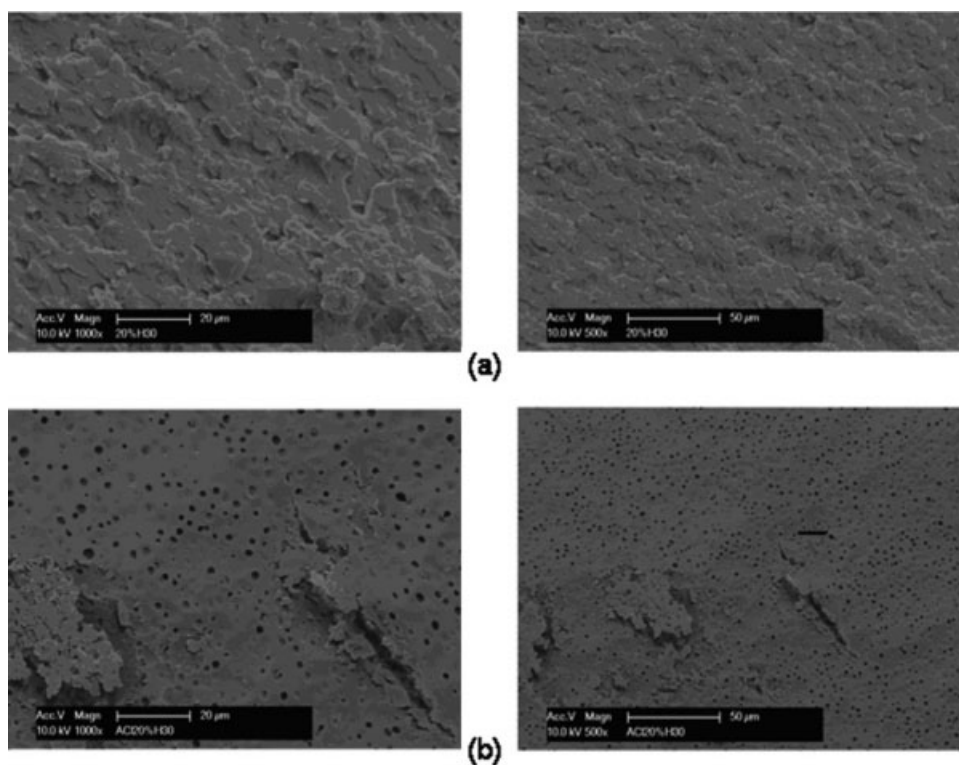


Figure 9 SEM micrographs without acid treatment (a) and with acid treatment (b) of P20H30 samples.

hyperbranched modifiers show two peaks: one main peak in the high temperature range, which is associated with the epoxy-rich phase, and one less-intense peak in the subambient region, which can be attrib-

uted to the hyperbranch-rich phase. For all the formulations containing the hyperbranched modifier, the glass transition of the epoxy-rich phase is lower than the T_g found for the pure epoxy network. This

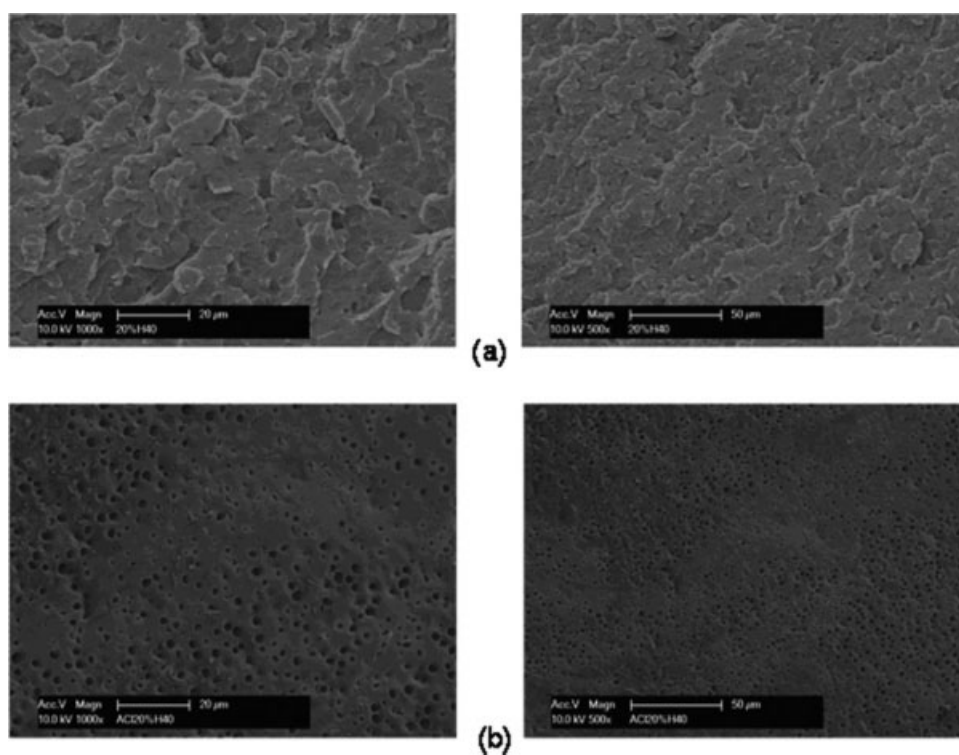


Figure 10 SEM micrographs without acid treatment (a) and with acid treatment (b) of P20H40 samples.

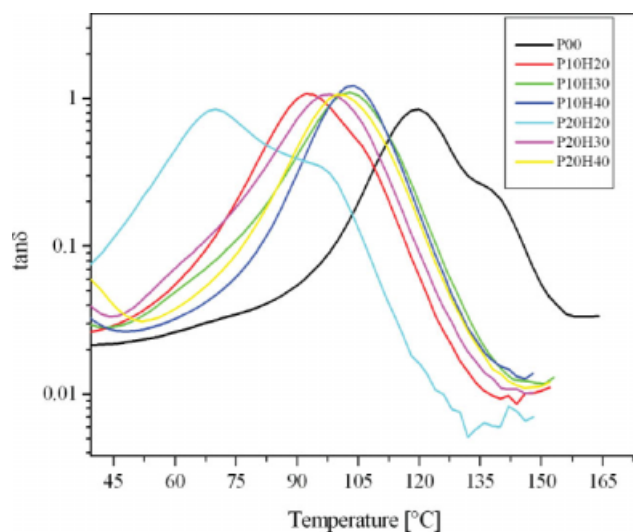


Figure 11 The $\tan \delta$ vs. temperature curves for the precured formulations. High-temperature range. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

finding suggests that some residual miscibility is still present, even for the systems that showed a clear phase separation under the microscope (i.e., those containing H30 and H40). Also, a bigger decrease is found for those formulations containing H20, thus confirming the higher miscibility of second pseudo-generation polymers in the epoxy network. The higher reduction for the formulations containing 20 wt % of modifier can be explained as the impossibility of completing the phase separation process when higher amounts of polymer are added because the higher blend's viscosities reduce polymer diffusivity more. However, in all cases, the blends presented a

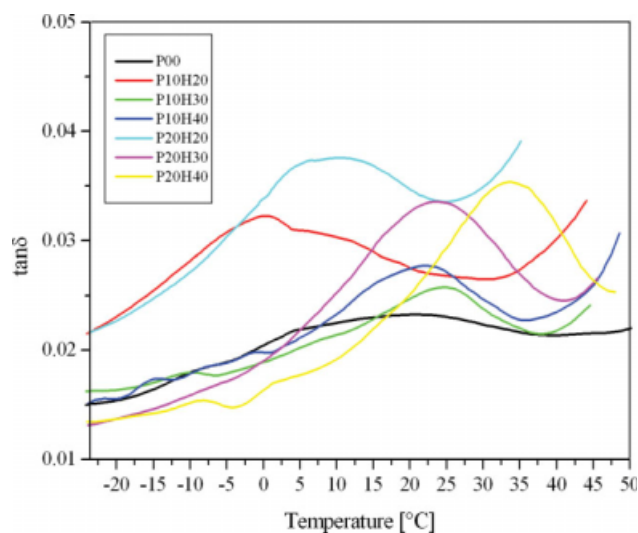


Figure 12 The $\tan \delta$ vs. temperature curves for the precured formulations. Subambient temperature range. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE IV
Glass Transition Temperatures^a for the Different Formulation After Precure and Postcure

Formulation/ cure cycle	Precure		Postcure	
	Main peak ^b	Lower peak ^c	Main peak ^b	Lower peak ^c
P00	120	–	147	–
P10H20	92	0	120	–
P10H30	103	25	138	55
P10H40	104	22	134	50
P20H20	70	7	110	7
P20H30	98	24	128	37
P20H40	100	34	124	28

^a All data are in degree Celsius.

^b The main peak refers to the $\tan \delta$ peaks associated to the relaxation of the matrix phase (epoxy rich).

^c The lower peak refers to the $\tan \delta$ peaks associated to the distributed phase (hyperbranched rich).

T_g higher than room temperature, thus allowing the system enough stiffness to be easily demoulded after the precuring step.

DMA analysis in the subambient region revealed some interesting features. The blends containing H20 (i.e., P10H20 and P20H20) presented small peaks in $\tan \delta$ at 0°C and 7°C, respectively. The other formulations presented peaks which were more intense and closer to the T_g of the pure hyperbranched polymers (see Table I). However, the values of those peaks were always smaller than the pure values, thus leading to the conclusion that some residual epoxy is always present in the hyperbranch-rich phase. The occurrence of $\tan \delta$ peaks in the subambient region for the formulations modified with H20 and the morphological observations (Fig. 6) imply that the small darker spots observed by SEM are particles rich in H20. However, the very low value of those peaks suggests that the phase composition of such small particles is not as rich in hyperbranched modifier as the other systems.

DMA analysis was also carried out on the samples after the postcuring cycle. The results are reported in Figures 13 and 14 for high and subambient temperature ranges, respectively. The data for the $\tan \delta$ peaks are summarized in Table IV. Postcuring is normally used in the industrial practice as a feasible and economical alternative to extend the epoxy conversion in free-standing ovens without the use of expensive cycles in autoclaves. In fact, increasing the cure temperature over the T_g developed in the first precuring step enables the devitrification of the system, thereby leading to further reaction of the unreacted groups. The data reported in Table IV confirms the achievement of higher T_g for the epoxy-rich phase after postcuring for all the studied blends. The modified systems show still lower glass transition temperatures compared with the pure epoxy for the main

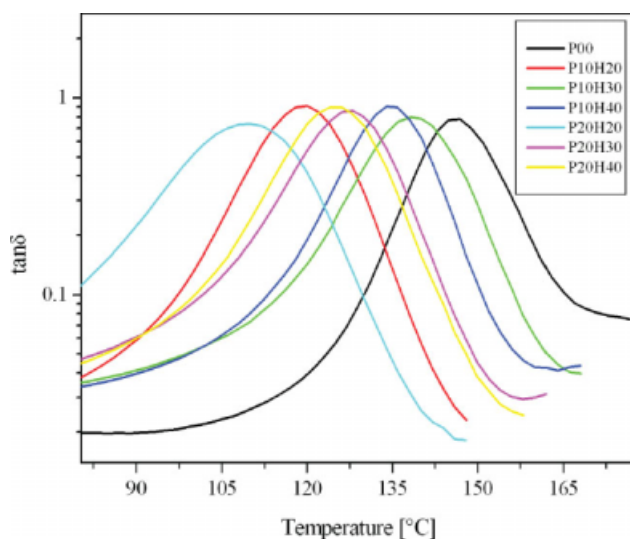


Figure 13 The $\tan \delta$ vs. temperature curves for the post-cured formulations. High-temperature range. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

peaks. An unclear trend is shown for the subambient relaxation. In a previous article,²³ it was shown for similar blends that postcuring not only affects the epoxy network but also the morphology because:

- i. The epoxy/amine reactions proceed further and cause changes in the interaction parameter χ with the generation of new driving forces for the demixing;
- ii. The devitrification of both phases favors the mobility of materials, and thus allows the mass transfer.

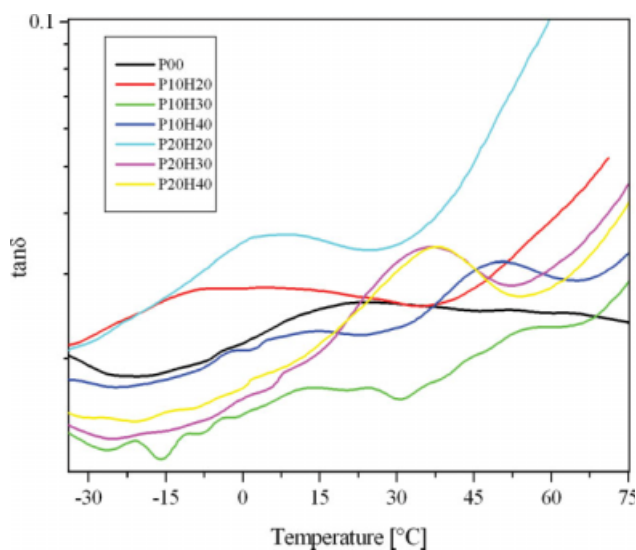


Figure 14 The $\tan \delta$ vs. temperature curves for the post-cured formulations. Subambient temperature range. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE V
Comparison of T_g Values Calculated According to Gordon-Taylor Equation and Experimental T_g Values

Sample	G_c (kJ/m ²)	K_c (MPa m ^{3/2})
P00	0.25	0.83
P10H20	0.35	1.17
P10H30	0.45	1.46
P10H40	0.37	1.25
P20H20	0.52	1.71
P20H30	0.49	1.66
P20H40	0.61	2.05

The postcure step allows the part of the epoxy dissolved in the hyperbranch-rich phase to separate out, thus shifting its transition to higher temperatures. This process is further complicated by the catalytic activity of the hydroxyl groups, which can interfere with further development of the epoxy network and thus can lead to the unclear trend observed for the low-temperature peaks. A further study varying curing temperatures and using multi-frequency techniques could be used to shed more light on this complex processes. However, such a study is beyond the scope of the present article.

The glass transition temperatures of the main phase can be used for the prediction of miscibility of the blend if Gordon-Taylor equation is used for calculation. Table V reports the comparison between the T_g values calculated according to Gordon-Taylor equation and the experimental T_g values. The sample P10H20 displays a negative deviation whereas all the other samples display for the experimental values a positive deviation compared with the values calculated with the Gordon-Taylor equation. The positive deviation is a consequence of the influence of the hydrogen bonding which exist between the hyperbranched and the epoxy molecules. This result confirms the partial miscibility of our systems because it is well known that Gordon-Taylor equation gives good fits only for miscible systems.

Fracture mechanics were performed on postcured samples and the results are summarized in Table VI. The data show an enhancement of fracture resistance for all the samples modified with the hyperbranched polymers. The increase of toughness is higher when

TABLE VI
Fracture Mechanics Results

Sample	T_g (calc) °C	T_g (exp) °C
P00	147.00	147
P10H20	127.00	120
P10H30	129.55	138
P10H40	130.48	134
P20H20	108.82	110
P20H30	113.50	128
P20H40	115.22	124

H40 is used. The driving toughening mechanism for hyperbranched polymers, associated to particulate morphology, has been recognized¹⁶ to be the cavitation process. The fourth pseudo-generation polymer (H40) lead to higher toughness compared with the third pseudo-generation polymer (H30) as already shown for similar blends cured with the aromatic amine 3,3'-diamino diphenyl sulphone.²⁴ This result is largely due to the more homogenous morphology which characterize the blends modified with H40. It is interesting to note that, despite the absence of a clear phase separation, the second pseudo-generation polymer H20 still induces some toughening in the resin. The measured increase in toughness for the blends modified with H20 can be explained as the results of the increased flexibility of the matrix with dissolved hyperbranched.

CONCLUSIONS

The aim of this work was to characterize the thermo-mechanical and morphological properties of some epoxy blends modified with different hyperbranched polymers. The reduction of the pseudo-generation number influenced both the catalytic activity and the miscibility of the hyperbranched polymers; both of these properties are enhanced for lower pseudo-generation modifiers. As a result, the blends containing the second pseudo-generation polymer show a scarcely developed phase separation and the higher reductions in glass transition for the epoxy phase due to the presence of dissolved hyperbranched polymer in this phase. Minor reductions were also observed for the other blends, which showed much clearer particulate morphologies.

Despite the use of a medium temperature (135°C) for the precure step and the reductions due to hyperbranched dissolution in the epoxy phase, the blends presented cured properties after precuring which were still enough to guarantee the possibility of demolding. The postcuring yielded good thermal properties that make this system suitable for most applications in the general adhesives and composites fields.

Fracture mechanics were evaluated for the post-cured systems showing that higher pseudo-generation polymers, leading to a more homogenous particulate morphology, can lead to higher toughness increments.

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