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The study of poly(styrene-*co*-*p*-(hexafluoro-2-hydroxylisopropyl)-α-methyl-styrene)/poly(propylene carbonate) blends by ESR spin probe and Raman

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Abstract

Different hydroxyl content poly(styrene-*co*-*p*-(hexafluoro-2-hydroxyisopropyl)-α-methylstyene) [PS(OH)] copolymers were synthesized and blends [noted for PP-X] with poly(propylene carbonate) [PPC] were prepared by casting from chloroform solution. The miscibility, micro heterogeneity and hydrogen bonding interaction of the component polymers were investigated by Differential Scanning Calorimetry (DSC), Electron Spin Resonance (ESR) spin probe method and Micro Raman spectroscopy. DSC results showed that the PP-2, PP-5, PP-8, PP-12 blends exhibited two distinct T_gs, indicating immiscibility, while the PP-20 and PP-27 blends were miscible with the existence of a single T_g. ESR results indicated that the probe molecule: Tempo couldn't give clear micro phase separation or miscibility information and thus was not sensitive to the investigated polymer blends system. On the contrary for all the blends spin probed with the probe molecules: Tempol and Tamine, two spectral components with different rates of motion: 'fast' and 'slow' motion were observed in different temperature range, which indicated the existence of micro heterogeneity on the molecular level; the more mobile PPC-rich micro phase and the more rigid PS(OH) rich micro phase. In addition, the scale of miscibility was progressively enhanced due to the increasing hydrogen bonding interaction between the hydroxyl in PS(OH) and the oxygen atoms in PPC. Meanwhile it was found that the degree of the probe molecule rotation detectable in the ESR spectrum was dependent on the polymer matrix rigidity and the strength of the hydrogen bonding between the probe molecule and the polymer matrix. Micro Raman substantiated the existence of the PS(OH)-rich micro phase and the PPC-rich micro phase. The hydrogen bonding strength between PS(OH) and PPC and the mixing level of the component polymers were increased gradually with the increase of hydroxyl content in the PS(OH) copolymer.

Keywords: Miscibility; Micro heterogeneity; Hydrogen bonding interaction

1. Introduction

Polymer blends are combinations of two or more constituent components that can either mix on the molecular scale or are immiscible and hence form discrete phases in matrix. The blending of polymers is a simple and economical method to produce new technically important material from different polymers. The properties of the polymer blend depend on the morphology and the miscibility of component polymers since only the miscible polymer blends are thermodynamically stable. The micro heterogeneity, chain motion and specific interaction of the polymer blend are of major importance for desired property combinations of the polymer components. The miscibility between polymer components can be enhanced by chemical modification or copolymerization, which incorporates some chemical groups capable of creating hydrogen-bonding interaction into one or both of the immiscible component polymers [1–3]. Various techniques have been adopted to investigate the miscibility and phase behavior of polymer blends: e.g. thermal and mechanical analyses, microscopy, lighting scattering etc. And spectroscopy methods are frequently utilized [4,5]. The sensitivity of various experimental probes to dimensional scale of the homogeneity spans many orders of magnitude [6,7].

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The spin probe and spin label methods based on Electron Spin Resonance (ESR) spectroscopy have proven to be powerful for investigating the intermolecular specific interactions and the phase behavior of polymer blends [8–14]. Nitroxyl radicals dispersed (spin probe) in polymer matrix or covalently bonded to polymer chains (spin label) are sensitive to the environment. If the probe molecules are embedded in a two-phase system with different rates of motion, the spin probe method can be applied to investigate the structural and motional heterogeneity and phase separation on a nanoscale length (<5 nm) [15,16]. Thus it can probe intermolecular specific interaction at the segmental scale and extent of miscibility on the molecular scale.

Raman spectroscopy can provide information about the specific interactions in polymer blends and one major advantage of Raman spectroscopy is the ease of sample preparation [17]. It can be applied to polymers as received or in film, powder, solution and bulk form so that little or no sample preparation is needed [18]. The relative intensity change and the shift of Raman band have been proven to be excellent clues to the detection of the intermolecular interaction by Micro Raman spectroscopy.

In this paper, we are mainly concerned with PS(OH)-X/PPC blends. PS(OH) is the proton-donating polymer whose hydroxyl proton was easily accessible in the 4-position on the aromatic ring. It can interact with proton-accepting polymers through hydrogen bonding, which was the major driving force in inducing miscibility. Poly (propylene carbonate) [PPC] is a new kind of hydroxyl-terminated aliphatic polycarbonate composed of carbon dioxide and propylene epoxide [19] that can be used as adhesives, solid electrolytes, polyols, photoresists, barrier materials, flexibilizers and plasticizers [20,21]. However, such materials are generally easy to decompose under the influence of heat and catalysts, which means that their mechanical properties need to be improved by blending with other polymers to form polymer blends. PPC possesses two possible proton-accepting sites in carbonate groups: oxygen atoms of carbon–oxygen single bonds (ether oxygen) and carbon–oxygen double bonds (carbonyl group). In the investigated blend system, the successively controllable hydrogen bonding between the carbonyl/ether oxygen group in PPC and hydroxyl group in PS(OH) was expected to increase the miscibility of the two component polymers progressively. The main objective of this work was to adopt four different methods: Differential Scanning Calorimetry (DSC), ESR spin probe and Micro Raman to investigate the miscibility, micro heterogeneity, intermolecular specific interaction and morphology of the PS(OH)/PPC blends. In addition the two aspects, which influenced the spin probe molecule mobility: the polymer matrix rigidity and the strength of hydrogen bonding between polymer matrix and spin probe have also been studied.

2. Experimental section

2.1. Materials

PS(OH) was the copolymer of styrene and *p*-(hexafluoro-2-hydroxyisopropyl)-α-methylstyene (HFMS). In PS(OH)-X, X was the mole content of hydroxyl group in the copolymer. Hydroxyl-containing monomer HFMS was prepared as previously described [22]. PS(OH) with different content of hydroxyl-containing units was copolymerized by styrene and HFMS as discussed previously [23,24]. The molar content of HFMS in the various PS(OH) copolymers was calculated from fluorine measurements, which were found to be slightly lower than the feed compositions. The characterization data for the PS(OH) copolymers were listed in Table 1. The weight-average molecular weight M_w and the number-average molecular weight M_n and the molecular weight distribution index M_w/M_n were determined by gel permeation chromatography based on a universal calibration with PS standards.

Poly(propylene carbonate) PPC prepared as published [25] was offered by the Department of Macromolecular Science, Fudan University China. The viscosity average weight M_η is 40,000.

The chemical structures of PS(OH) and PPC were listed in Fig. 1.

The spin probes 2,2,6,6-tetramethylpiperidine-1-oxyl (Tempo), 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (Tempol) and 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl (Tamine) were purchased commercially from Aldrich and used as received. The chemical structures of the three nitroxide spin probes were shown in Fig. 2.

2.2. Preparation of the spin probed blends

3% (w/v) $CHCl_3$ chloroform solutions of PS(OH)-X were prepared respectively. Then they were mixed 1:1 by weight with 3% (w/v) $CHCl_3$ solutions of PPC not containing spin probe or containing 0.5 wt% of spin probes under agitation. After evaporation of the solvent at ambient temperature in Teflon container, a thin film was formed. Then the film was further dried under vacuum at 323 K for 72 h to remove the residual solvent. The dried blends were

Table 1
Characterization data for PS(OH)-X copolymers

Polymer[a]	$M_n \times 10^{-4}$	M_w/M_n	OH content (mol%)
PS(OH)-2	2.0	1.60	1.67
PS(OH)-5	2.4	1.73	4.88
PS(OH)-8	1.6	1.65	8.22
PS(OH)-12	1.9	1.50	11.66
PS(OH)-20	1.8	1.68	19.41
PS(OH)-27	1.4	1.74	27.28

[a] The number following PS(OH) represented the approximate integer value of the molar content of HFMS in the copolymer.

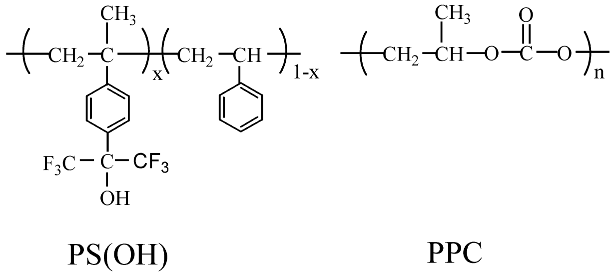


Fig. 1. Chemical structures of PS(OH) and PPC.

stored in a desiccator before use. Three spin probes with different probe sizes and hydrogen bonding strengths were used in the study. Among them, Tempo was chosen because it contained no functional groups, which could be attached to neither PS(OH) nor PPC via hydrogen bonding. The PS(OH)-X/PPC blends samples not containing spin probe or containing Tempo, Tempol and Tamine were noted as PP-X, PP I-X, PP II-X and PP III-X, respectively, where X was the hydroxyl mole content in PS(OH) copolymer.

2.3. ESR measurements

ESR spectra were measured at the X band with a Bruker 200D-SRC spectrometer operating at 9.67 GHz and 100 KHz modulation. An Aspect 3000 computer with the software Epr3002 controlled data acquisition. Spectra as a function of temperature were measured with the Bruker variable temperature unit ER4111VT. All the blend samples were allowed to equilibrate for at least 3 min after approaching the corresponding temperature. The attenuation microwave power (2 mW) and modulation amplitude (0.1 mT) were adjusted well below saturation and distortion of the spectra.

2.4. DSC measurements

Perkin–Elmer Pyris 1 was used for the measurement in an atmosphere of nitrogen. The typically 10 mg blend sample was heated from −80 to 200 °C at a rate of 10 °C/min in the first scan and then was rapidly quenched to −80 °C, after that the second heating scan was performed in the same way as the first. T_g was taken from midpoint of the heat capacity change with temperature of the second scan curve.

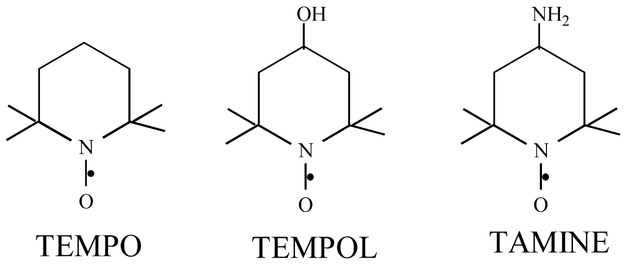


Fig. 2. Chemical structures of the three nitroxide spin probes used in this study.

2.5. Micro Raman measurements

The Raman spectra were obtained from a Dilor LabRam-1B Raman spectrometer coupled with an OLYMPUS BH2 optical microscope. An exciting wavelength of 632.8 nm was provided by a 5.5 mW He–Ne laser source. The laser was focused to a 1 μm diameter spot on the sample using a 100 × objective lens. The Raman spectra were collected and recorded using a Peltier cooled charge-coupled device (CCD) detector with an exposure time of about 200 s.

3. Results and discussion

3.1. DSC and ESR

T_g determined by DSC is the method most commonly used to observe polymer miscibility. The presence of one glass transition implies homogeneous miscible phase, whereas two glass transitions correspond to two immiscible phases differing in segmental environments. And a single T_g indicated phase sizes of about 20–40 nm [26]. However if the size of a phase is smaller than 20 nm, the method is not sensitive enough to display two glass transitions values. The gap between domain size on the order of 40 nm and truly intimate mixing on the molecular scale is quite large. ESR spectroscopy is the technique with which this gap can be bridged. For some polymer blends known to be miscible and showing one single T_g, ESR has detected differences in miscibility on a molecular scale. All the PP-X blends were subjected to DSC measurements and DSC thermograms for these blends with different hydroxyl content in PS(OH) were presented in Fig. 3.

The PP-2, PP-5, PP-8, PP-12 blends curves exhibited two distinct T_gs, indicating immiscibility. On the other hand, PP-20 and PP-27 blends were miscible as shown by the existence of a single T_g, which varied with the blend composition. To explore nanophase separation/microheterogeneity, we applied ESR spin probe technique, which was sensitive to polymer segments. Selected temperature dependent ESR spectra for PP I-X, PP II-X and PP III-X blends were shown in Fig. 4. From DSC data, we knew PP-2–PP-12 blends were immiscible phase separation

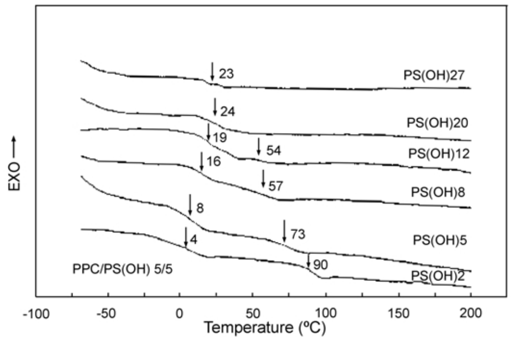


Fig. 3. DSC thermograms for PP-X blends.

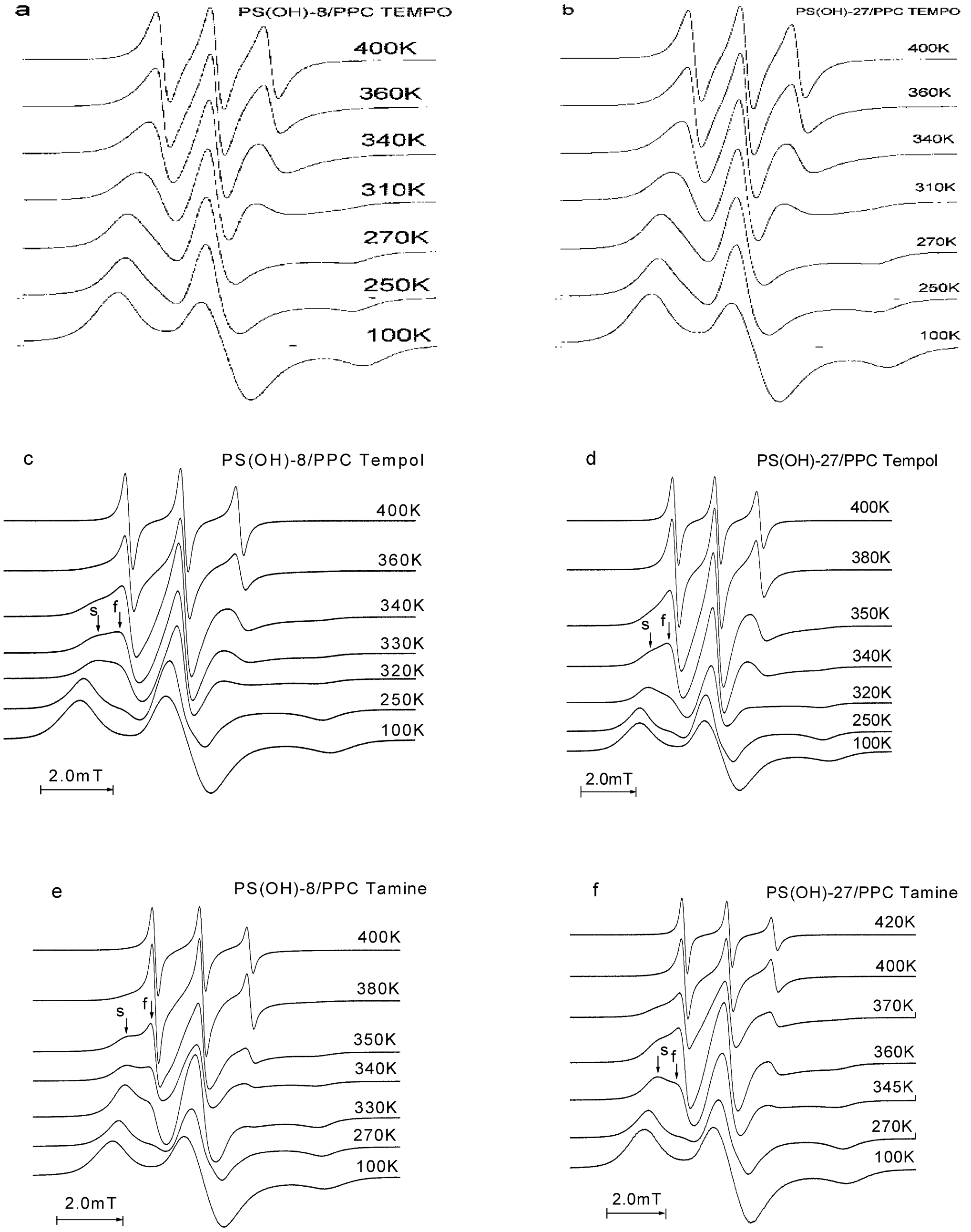


Fig. 4. ESR spectra of nitroxide. (a) Tempo in PP I-8 (b) Tempo in PP I-27 (c) Tempol in PP II-8 (d) Tempol in PP II-27 (e) Tamine in PP III-8 (f) Tamine in PP III-27.

blends, while PP-20 and PP-27 blends were miscible homogenous blends. Here we suppose that the spin probe method should rely on two conditions in order to exhibit microheterogeneity on molecule length scale. (1) Spin probe molecules are partitioned between the two phases in a measurable degree. (2) The ESR lineshape of the spin probe elicits different responses from each phase with the variation of temperature. The spectra of spin probe Tempo for PP-X blends were characteristic of the probe molecule in one type of environment. At 100 K (slow-motion regime), the ESR spectrum approached the rigid limit spectrum, with a characteristic separation between the outer peaks (extreme separation or $2A_{zz}$) of about 70 G. As the temperature increases, the spectral lines narrowed and the outer peaks shift inwards. Eventually the spectrum became similar narrowed form, with $2A_{zz}$ about 30 G at 400 K. That is to say, at any specific temperature, the spectrum was composed of only one spectral component: either slow-motion component or fast motion component. And this indicated the spin probe Tempo was in a ‘homogenous’ polymer matrix phase. Similar to Fig. 4(a) and (b) for all the other Tempo probed PP I-X blends, the ESR spectra were all composed of one spectral component, whether the blends were immiscible or miscible detected by DSC. So the spin probe Tempo can't give clear phase structure information (phase separation or miscibility) on the blends and was not sensitive to the investigated polymer systems. For this reason the Tempo probe results will not be considered further, and all the conclusions presented in this paper were based on the Tempol and Tamine probe results.

In contrast to Fig. 4(a) and (b) with only one spectral component in the entire experimental temperature range, Fig. 4(c)–(f) had one significant difference in some temperature range. Namely, above a specific temperature a second spectral component appeared and two clear spectral components were simultaneously visible, indicating a partition of the spin probe Tempol or Tamine into two environments with different mobilities. In Fig. 4(c)–(f), the two spectral components at low field were indicated by 's' (slow) and 'f' (fast). According to the change of spectral shape with temperature, we focused on three temperature parameters: T_a was the temperature when the fast motion component appeared, while T_d was the temperature when the slow motion component disappeared and ΔT was the span between T_a and T_d. The T_a, T_d and ΔT values for all PP II-X and PP III-X blends with different hydroxyl content were listed in Tables 2 and 3.

Observation of slow and fast motion in the composite ESR spectrum indicated that spin probe molecular existed in two dynamically different environments due to the local heterogeneity in the blends [16,27]: a PPC-rich micro domain and a PS(OH)-rich micro domain. Meanwhile the existence of two micro domains showed that the all the PP II-X and PP III-X blends were not miscible on the molecular level and the spin probe molecular located in the micro heterogeneous polymer matrix. Although the relative fast or slow motion component intensity is not an absolute measure for the number of immobilized or freely rotating spin probes located in the more rigid micro domain or the more flexible micro domain, due to the simplicity of quantitative analysis, the fast motion component fraction noted by $F\%$ can be estimated from the ratio of the intensity of the fast motion in the composite spectrum to that of the fast motion in the wholly single spectrum [15,28]. The fast component fraction obtained by this method was presented in Fig. 5(a) for selected PP II-X and Fig. 5(b) for selected PP III-X blends. Fig. 5(a) and (b) showed that as the temperature was raised, the fast motion component increased at the expense of the slow motion component. The number of segregation of the probe molecules in flexible and rigid micro domains can also be obtained from $F\%$ and $(1 - F)\%$ in Fig. 5(a) and (b) quantitatively.

Table 2
T_a, T_d, ΔT values for PP II-X blends

	PP II-2	PP II-5	PP II-8	PP II-12	PP II-20	PP II-27
T_a (K)	250	250	250	250	250	250
T_d (K)	350	360	360	370	370	380
ΔT (K)	100	110	110	120	120	130

Table 3
T_a, T_d, ΔT values for PP III-X blends

	PP III-2	PP III-5	PP III-8	PP III-12	PP III-20	PP III-27
T_a (K)	270	270	270	270	270	270
T_d (K)	370	380	380	390	390	400
ΔT (K)	100	110	110	120	120	130

In PPC-rich domain the polymer matrix was more flexible and the polymer segment motion was faster, while in PS(OH)-rich domain the polymer matrix was more rigid and accordingly the polymer segment motion was slower. The composite ESR spectra of all PP II-X and PP III-X blends that evolved in a certain temperature range appeared to be the most valuable contribution of the spin probe method to differentiating more than one phase: phase heterogeneity on molecular level. PP II-X and PP III-X blends were partially miscible (micro phase separation) and the two kinds of polymer chains penetrated each other due to the hydrogen bonding interaction between the hydroxyl in PS(OH) and the carbonyl/ether oxygen in PPC. The miscibility extent between the two polymer components has been progressively enhanced by controllable increasing hydrogen bonding interaction from PP II-2 to PP II-27 blends. And this miscibility enhancement can be deduced from the above mentioned T_a, T_d and ΔT values. Table 2 showed that T_a was the same for all the PP II-X blends while T_d and ΔT increased with increasing hydroxyl content in PS(OH)-X copolymer. The same T_a values in different

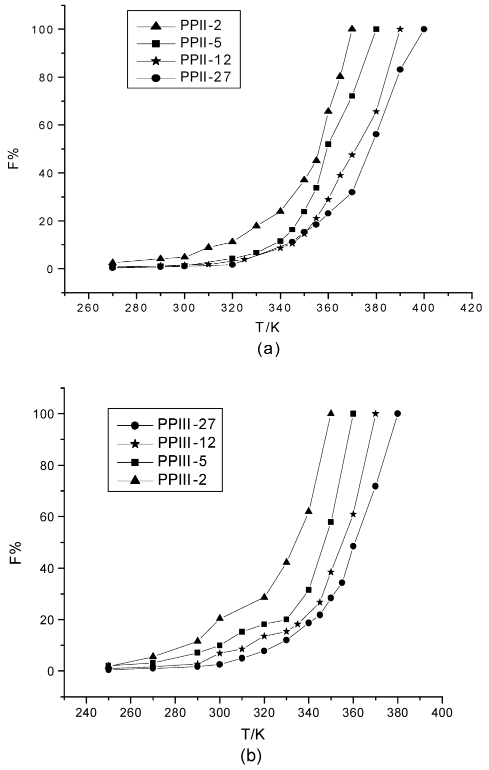


Fig. 5. Change of fast motion fraction ($F\%$) with temperature. (a) The PP II blends (b) The PP III blends.

hydroxyl content PS(OH) copolymer blends indicated that the appearance of fast motion was not sensitive to polymer matrix rigidity. It was assumed that at low temperatures (<250 K) the motion of spin probes was not much influenced by the surrounding polymer matrix. Below 250 K, for PP II-X blends both PPC and PS(OH) chains were in the glass state. The spin probe molecules rotated in the 'holes' of dimensions comparable to those of a probe in the polymer matrix and were almost independent of the molecular motion of the polymer [29]. When the temperature was raised, both polymer chains were activated. The spin probe motion was perturbed by molecular motion of the polymer chain and segment. That is to say, with the progressively increasing hydrogen-bonding interaction, the penetration of one kind of polymer chain into the other polymer domain became more and more profound and accordingly the mesh size of the physical network induced by hydrogen bonding crossing linking progressively decreased. So a higher temperature and a broader temperature range were needed to obtain the completely narrowed ESR spectra. Meanwhile the progressively enhanced net-like interconnection would also contribute to the motional restriction of polymer segments, which could be characterized by rotational correlation time τ_c [30]. τ_c can quantitatively characterize the changes in the rotational rate of the nitroxide spin probe. The natural logarithm of τ_c in the fast motion range ($10^{-9}\text{ s} < \tau_c < 10^{-11}\text{ s}$) as a function of the reciprocal temperature was shown in Fig. 6.

$$\tau_c = 8.7\times 10^{-10}\left[\left(\frac{h_0}{h_{-1}}\right)^{1/2} - \left(\frac{h_0}{h_{+1}}\right)^{1/2}\right]\Delta H_{PP} \qquad (1)$$

Where h_{-1}, h_0 and h_{+1} were the measured low, central and high field peak-to-peak amplitudes of the nitroxide radical spectrum; ΔH_{PP} was the width of the central peak in Gauss. The change of τ_c showed the enhanced hydrogen bonding interaction in the blends restricted the motion of the spin probe progressively. τ_c decreased with increasing temperature for any PP II-X blend, while increased with the increasing hydroxyl content in the PS(OH)-X at any temperature.

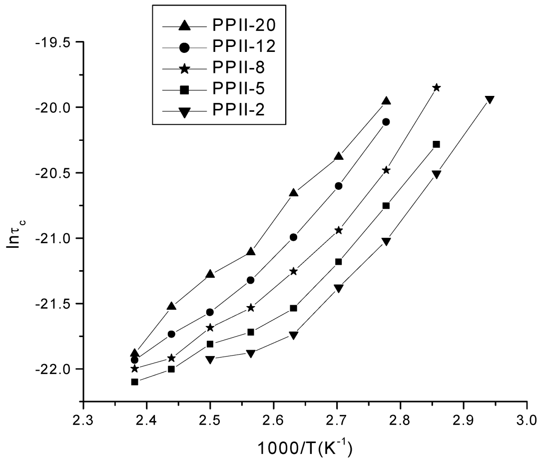


Fig. 6. Variation of τ_c with the reciprocal temperature.

It is well known that the macroscopic properties of a polymer such as glass transition temperature and phase morphology are correlated with polymer segment mobility. However, the ESR experiment only reports information originating from the spin probe, and the correlation with macroscopic properties rests on the assumption that the probe mobility is correlated with polymer mobility. This correlation of mobility depends on a coupling or connectivity between the spin center and polymer matrix. For spin probes dispersed in the polymer matrix, this coupling occurs by a combination of dense molecular packing and seconding bonding forces such as hydrogen bonding which is sufficient to immobilize the probe in the matrix [31]. The temperature dependence of ESR spectra is due to changes in the rotational rate of spin probe. The degree of probe rotation detectable in the ESR spectrum is dependent on probe size, polymer matrix rigidity and strength of the hydrogen bonding between probe and polymer matrix [31]. In PP II-X and PP III-X blends, the matrix rigidity was the same for the same hydroxyl content but different probed blends. And the probe size for Tempol (177 Å^3) and Tamine (182 Å^3) were nearly constant in size [31]. So the strength of hydrogen bonding between the polymer matrix and the probe was the main factor that determined the molecular motion of the probe. From Tables 2 and 3, it was known that the T_a and T_d results for Tempol and Tamine probes dispersed in PP II-X and PP III-X blends displayed increasing temperature variations with hydrogen bonding capabilities between the probe and the polymer matrix. But the span between T_a and T_d were all the same for the corresponding same hydroxyl content PP II-X and PP III-X blends. The hydroxyl and amine functional groups in Tempol and Tamine served as sites for hydrogen bonding between the probe and the polymer matrix. The carbonyl group and ether oxygen in PPC also had strong hydrogen bond acceptor strength. Substitution of amine group for hydroxyl group caused almost 20 °C increase in T_a and T_d for the same hydroxyl content but different probed PP II-X and PP III-X blends. Hydrogen bond donor and acceptor strength parameters for amine and hydroxyl functional group sites in spin probe can be characterized by respective solvatochromic hydrogen bond acidity (α) scales and hydrogen bond basicity (β) scales which range from 0 (very weak) to 1 (very strong) [32]. Representative values based on analogues with the respective alcohol, and amine functionalities (2-propanol for Tempol, cyclohexyl amine for Tamine) were as followings: α (Tempol) = 0.30, β (Tempol) = 0.51, α (Tamine) = 0.00, β (Tamine) = 0.72 [31]. For Tempol and Tamine, there was a correlation between hydrogen donor strength (β-scale parameter) and the T_a, T_d values. The stronger the hydrogen bond between the probe and the polymer matrix, the higher the temperature necessary for thermally activated probe rapid motion [29]. Tempol had smaller β value than Tamine, so

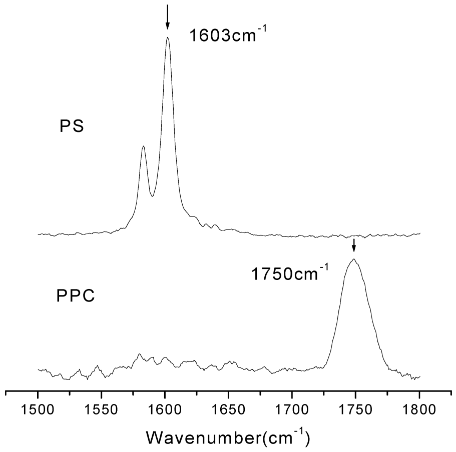


Fig. 7. Raman spectra of PS and PPC in the range of 1500–1800 cm^{-1}.

the T_a and T_d values changed as expected. It is worthy notice that the ΔT were the same for the same hydroxyl content but different probed PP II-X and PP III-X blends. And this indicated that ΔT was mainly dominated by the polymer matrix rigidity and wasn't affected by the property of the spin probe molecules. Actually, whether in PP II-X or PP III-X blends, ΔT increased with the increasing polymer matrix rigidity induced by hydrogen bonding interaction between the two component polymers.

3.2. Micro Raman

It is known that if two polymers form an immiscible blend, there should be no appreciable change in the vibrational spectrum of the blend compared with the coaddition of each component spectrum since each individual polymer does not recognize in spectrum terms, the existence of the other in the blend. On the other hand, if the polymers are miscible, interactions in the blend will result in differences in band shifts, intensity changes and broadening, all of which are sensitive to the strength and extent of hydrogen bonding [17]. The Raman spectra for respective Polystyrene (PS) and PPC components in 1550–1800 cm^{-1} ranges were shown in Fig. 7. PPC showed a Raman band at 1750 cm^{-1}, which was attributed to the stretching mode of the carbonyl groups, while PS showed a Raman band at 1603 cm^{-1}, which was ascribed to the stretching mode of phenyl rings. Only the Raman band at 1750 cm^{-1} appeared in pure PPC while only the Raman band at 1603 cm^{-1} appeared in pure PS.

Meanwhile the thin films of all the blends were observed under an optical microscope in transmission. Fig. 8(a)–(d) presented the optical micrographs of PP-X blends containing 5, 12, 20 and 27% hydroxyl in the PS(OH)-X copolymer. Fig. 8(a) showed typical immiscible/phase separation morphology with a two-phase structure: a darker phase and a brighter phase. The darker phase as large as about 5 μm was dispersed in the brighter phase matrix with distinct phase boundaries. Also Fig. 8(b) presented a two-phase structure with fuzzier phase boundaries between the darker and brighter phases than Fig. 8(a). An obvious morphology change was taken place in Fig. 8(c) and the average size of the dispersed phase diminished dramatically and also the phase boundaries became much fuzzier. In Fig. 8(d) it was nearly impossible to distinguish the relatively bright and dark areas, no clear phase boundaries can be seen.

At the same time the Raman spectra of the darker and brighter phase of the two-phase structures allowed each phase to be identified. The Raman spectra of brighter continuous phase were shown in Fig. 9(a). It was the

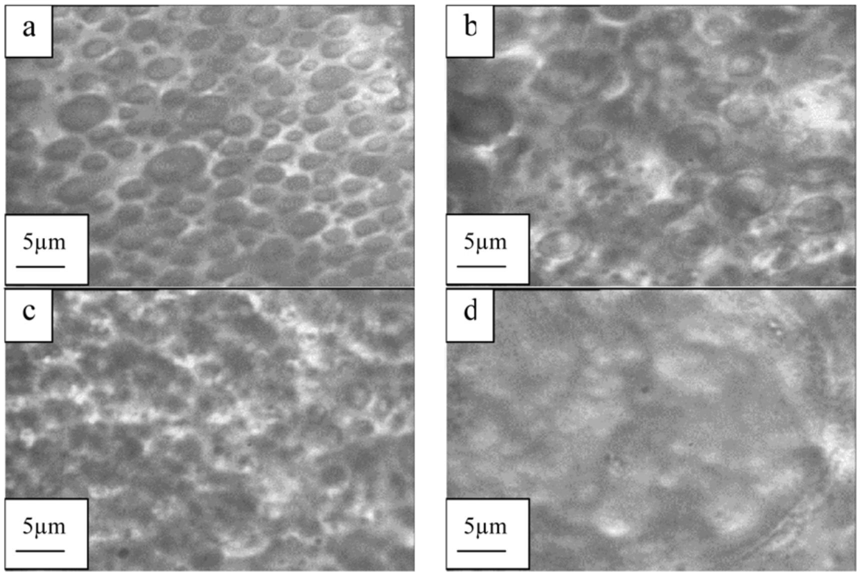
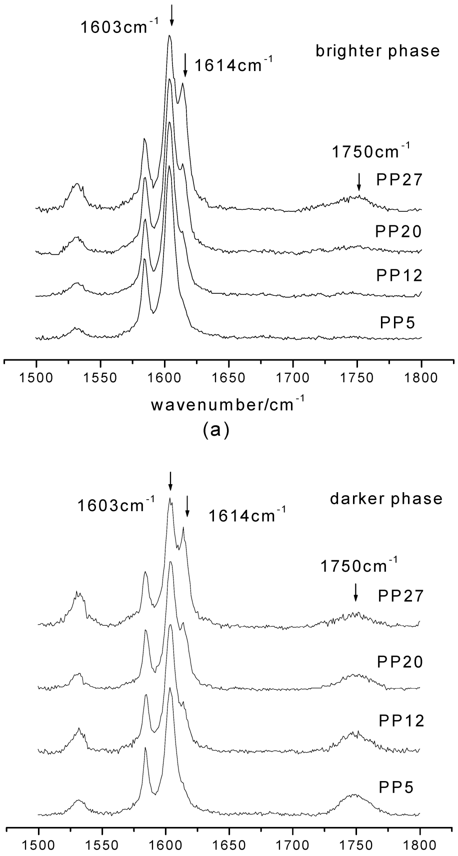


Fig. 8. Optical micrograph of the blends. (a) PSOH-5/PPC (b) PSOH-12/PPC (c) PSOH-20/PPC (d) PSOH-27/PPC.



(a)

(b)

Fig. 9. Raman spectra obtained (a) in the brighter phase (b) in the darker phase corresponding to the optical micrograph.

PS(OH)-rich phase. In all PP-X blends there existed 1603 cm^{-1} band, which could be ascribed to the phenyl ring of PS(OH) [18]. With increasing hydroxyl content in PS(OH)-X copolymer, a new shoulder at 1614 cm^{-1} (ascribed to the hydrogen bonded phenyl ring associated with OH → O=C interaction) was clearly observed (from PP-12 blend in Fig. 9(a)) in higher wavenumber near the normal non-hydrogen bonded phenyl ring of pure PS. And the relative intensity of the hydrogen bonded to the non-bonded phenyl ring band centered at 1614 and 1603 cm^{-1}, respectively, increased gradually in favor of the former as the hydroxyl content in the blend increased. Meanwhile, with the increase of hydroxyl content in PS(OH)-X copolymer, the carbonyl stretching band at 1750 cm^{-1} was also observed (from PP-12 blend in Fig. 9(a)). The simultaneous appearance of all the bands at 1603, 1614 and 1750 cm^{-1} in the PP-X blends indicated a hydrogen bonding induced PS(OH) and PPC mixed phase. And also the relative intensity of the carbonyl group at 1750 cm^{-1} to the non-hydrogen bonded phenyl ring centered at 1603 cm^{-1} increased with the increasing hydroxyl content in the PS(OH)-X copolymer.

On the other hand, in the Raman spectra of the PPC-rich dark phase (Fig. 9(b)), the relative intensity of the hydrogen bonded to the non-bonded phenyl ring band had similar change trend, while the relative intensity of the carbonyl stretching band at 1750 cm^{-1} to the non-hydrogen bonded phenyl ring centered at 1603 cm^{-1} decreased with the increasing hydroxyl content in the PS(OH)-X copolymer.

All the new shoulder band appearance and the relative intensity changes indicated that the strength of the hydrogen bonding between PS(OH) and PPC and the mixing level of the component polymers improved as the amount of hydroxyl in the PS(OH)-X copolymer increased although complete miscibility was not achieved. Thus the Raman results have successfully confirmed the ESR spin probe results in the PS(OH)/PPC system. It was demonstrated that Raman spectroscopy was a very promising and powerful technique for detailed characterization of polymer blends. It can not only detect the phase structure of the blends but also provide information on the existence of specific interactions in the blends.

4. Conclusion

DSC results indicated that by progressively strengthening the intermolecular hydrogen bonding the PS(OH)/PPC blends can achieve immiscibility to miscibility transition successively. The ESR spectra of Tempol and Tamine in all the blends showed composite spectra in a differently specific temperature range, indicating the existence of the micro heterogeneity on the molecular level. The fast motion was attributed to the spin probe molecule in the PPC-rich, more mobile micro domain, while the slow motion corresponded to the spin probe molecule in the PS(OH)-rich, more rigid micro domain. According to the variation of the T_a, T_d, ΔT, τ_c values with hydroxyl content in PS(OH) copolymer, it can be concluded the miscibility of the blends increased with the increase of hydrogen density. Micro Raman results substantiated the existence of the PS(OH)-rich phase and the PPC-rich phase. The relative intensity change of the hydrogen bonded to the non-bonded phenyl ring band and the relative intensity change of the carbonyl group to the non-bonded phenyl ring band proved the increasing hydrogen bonding favored the enhanced miscibility of the blends.

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