

The Totally Miscible in Ternary Hydrogen-Bonded Polymer Blend of Poly(vinyl phenol)/Phenoxy/Phenolic

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ABSTRACT: The individual binary polymer blends of phenolic/phenoxy, phenolic/poly(vinyl phenol) (PVPh), and phenoxy/PVPh have specific interaction through intermolecular hydrogen bonding of hydroxyl-hydroxyl group to form homogeneous miscible phase. In addition, the miscibility and hydrogen bonding behaviors of ternary hydrogen bond blends of phenolic/phenoxy/PVPh were investigated by using differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy, and optical microscopy. According to the DSC analysis, every composition of the ternary blend shows single glass transition temperature (T_g), indicating that this ternary hydrogen-bonded blend is totally miscible. The interassociation equi-

librium constant between each binary blend was calculated from the appropriate model compounds. The interassociation equilibrium constant (K_A) of each individually binary blend is higher than any self-association equilibrium constant (K_B), resulting in the hydroxyl group tending to form interassociation hydrogen bond. Photographs of optical microscopy show this ternary blend possess lower critical solution temperature (LCST) phase diagram. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 116–124, 2009

Key words: ternary blend; hydrogen bonding; phase behavior; lower critical solution temperature

INTRODUCTION

During the past 20 years, comprehensive experimental studies were executed that the miscibility and phase behavior of binary polymer blends.^{1,2} Many well-known binary pairs of polymers have been found to obtain miscible blend. In general, these binary polymer blends have been investigated with specific interaction including intermolecular hydrogen bonding, ionic interaction, charge transfer complex, and the like.^{3,4} On the contrary, ternary polymer blends have received much less attention due to complexity of calculating phase diagram and problems of experimental accuracy. Although an increase on the number of polymer components is a complication, there are several good reasons to study the phase behavior of ternary polymer blends in polymer science resulting from the industrial importance. For example, the Scott and Tompa^{5,6} worked on the ternary polymer blends that Polymer B, which is miscible with each of Polymer A and C, can com-

patibilize the immiscible binary pair A and C. Polymer B acts as a “compatibilizer” to reduce the size domain of heterogeneous phase separation structure. Classical examples are the ternary blends of poly(vinylidene fluoride) (PVDF)/poly(methyl methacrylate) (PMMA)/poly(ethyl methacrylate) (PEMA),⁶ poly(vinyl phenol) (PVPh)/PMMA/PEMA,⁷ and SAN/PMMA/PEMA.⁸ Although PMMA and PEMA are immiscible with each other, the addition of a large amount of PVDF, PVPh, and SAN leads to a miscible ternary polymer blend. On the other hand, when all three binary pairs (B-A, B-C, and A-C) are individually miscible, a completely homogeneous or a closed immiscibility loop phase diagram has been observed.^{9–11} The phase separation is caused by the difference in the interaction energy of the binary system, the so-called “ $\Delta\chi$ ” and “ ΔK ” effects in ternary polymer blends such as PVPh/PAS/poly(ethylene oxide) (PEO),¹² PVPh/PVAc/PEO,¹¹ PVPh/PMMA/PEO,¹³ and phenolic/PEO/PCL¹⁴ blend systems. If $\chi_{AB} \neq \chi_{BC}$ or $K_A \neq K_C$, we have the situation where the interaction between the segment of Polymer B with Polymer A and Polymer C are different and this tends to induce phase separation. For our knowledge, only a very few ternary polymer blends have been reported to be homogeneous over the entire compositions. These totally miscible ternary blends include poly(epichlorohydrin) (PECH)/PMMA/PEO,¹⁵

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PVDF/PVAc/PMMA,¹⁶ PECH/PVAc/PMMA,¹⁷ and poly(3-hydroxybutyrate)/PEO/PECH¹⁸ because they do not lead to a $\Delta\chi$ effect. Here, we need to emphasize that these totally miscible ternary blends do not have hydrogen-bonding interaction between their polymer segments. As a result, they are easy to obtain totally miscible ternary blend due to omitting the ΔK effect in ternary polymer blend. In a previous study by Coleman and coworkers,¹¹ they considered that it would be difficult to find totally miscible ternary blend over a wide composition range due to significant $\Delta\chi$ and ΔK effect in ternary hydrogen-bonded polymer blend. Only in very rare cases such as ternary blend of PVPh/PVAc/poly(methyl acrylate) (PMA)¹¹ give a completely miscible ternary polymer blend because the $\Delta\chi$ and ΔK interaction are finely balanced. Taking into account the both structures of PVAc and PMA, the repeat units of two polymers are isomorphous. Of course, this ternary polymer blend shows completely homogeneous amorphous phase. In our previous study,¹⁰ we found that a completely miscible ternary polymer blend of phenolic/phenoxy/PCL because the intermolecular hydrogen bonds that exist within the individual binary blends create a network-like structure beside to two isomers of polymers. In this study, we will extend this ternary blend of phenolic/phenoxy/PCL to phenolic/phenoxy/PVPh and characterize their phase behaviors. The phenolic, PVPh, and phenoxy are the well-known hydrogen-bonded donor polymers that can interact with polyacrylate, polyester, polyether, and polyvinylpyridine.^{20–29} However, based on our knowledge, few studies pay attention on the binary polymer blends of both self-association polymers.^{30–32} The phenolic/phenoxy^{32–35} and PVPh/phenoxy³⁵ blends are totally miscible in the amorphous phase due to interassociation hydrogen bonding existing between their hydroxyl groups of polymer segments. In addition, an unusual totally miscible hydrogen-bonded ternary blend of phenolic/phenoxy/PCL was first observed in our previous study.³⁴ We confirm that the complicated intermolecular hydrogen-bonding interactions existing in this ternary polymer blend system behaves like a network. Even though the different hydrogen bonding strength in each binary blend was found that still exists a completely miscible ternary blend. As a result, if the intermolecular hydrogen bonding exists between each binary component in the ternary blend, it may obtain a completely miscible ternary blend. It is a clue that if the ternary blend components are all hydrogen-bonded donor polymer, we would have the totally miscible ternary blend system. Therefore, the ternary hydrogen-bonded polymer blends of phenolic/PVPh/phenoxy is reported in this present study. Interestingly, this ternary polymer blend actually gives a completely miscible amorphous phase over the entire compositions range based on differential scanning cal-

orimetry (DSC) analyses. In this article, we propose another result on completely miscible ternary hydrogen-bonded polymer blend except for the isomer of two polymers.

EXPERIMENTAL

Materials

Polymers used in this study were phenolic, poly(hydroxyether of bisphenol A) (phenoxy), and PVPh. The phenolic was synthesized with sulfuric acid via a condensation reaction and average molecular weights are $M_n = 500$ g/mole and $M_w = 1200$ g/mole. The PVPh with a $M_w = 9,000$ – $10,000$ g/mole were purchased from Polyscience, USA. The phenoxy was obtained from the Union Carbide with $M_n = 23,000$ g/mole and $M_w = 48,000$ g/mole. These molecular characteristics of these polymers and their corresponding model compounds are listed in Table I.

Preparation of blend samples

The ternary polymer blends of phenolic/phenoxy/PVPh with various compositions were prepared by solution blend. Tetrahydrofuran solution containing 5 wt % polymer mixture was stirred for 6–8 h and then allowed to evaporate slowly at room temperature for 1 day. The film of the blend was then dried at 50°C for 2 days to ensure no any residual solvent.

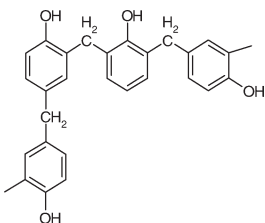
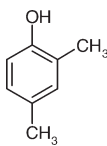
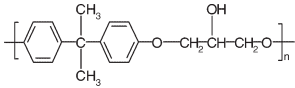
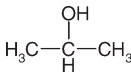
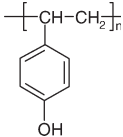
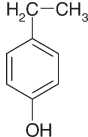
Differential scanning calorimetry

The glass transition temperature (T_g) of a polymer blend was determined by using a DSC (Du-Pont, DSC model 2900). The scan rate was 20°C/min ranging from 0 to 170°C with 5–10 mg sample on a DSC sample cell, and the specimen was quickly cooled to 0°C after the first scan. The T_g value was obtained at the midpoint of the transition point of the heat capacity (C_p) change with scan rate of 20°C/min and temperature range of 0 to 200°C.

Infrared spectra

The infrared spectra were recorded by a Nicolet Avatar 320 Fourier transform infrared (FTIR) spectrometer. In all cases, at least 32 scans with an accuracy of 1 cm^{-1} were signal averaged. Infrared spectra of polymer blend films were determined by using the conventional NaCl disk method. The THF solution containing the blend (5% w/v) was cast onto NaCl disk and dried under condition similar to that used in the bulk preparation. The film used in this study was sufficiently thin to obey the Beer-Lambert law. For the solution samples, an adequate permanently sealed cell with NaCl windows of 0.2 mm path length was used. A single optical path was used for studying the interassociation between 4-ethyl

TABLE I
Summary Molecular Structure, Characteristic, T_g , and Model Compound of Polymers Used in this Study

Material	Molecular structure	Molecular weight	T_g ($^{\circ}\text{C}$)	Model compound
Novolak type phenolic resin		$M_n = 500$ $M_w = 1200$	66 ± 2	 2,4-xyleneol
Phenoxy		$M_n = 23,000$ $M_w = 48,000$	95 ± 2	 2-propanol
Poly(vinylphenol)		$M_w = 9,000-10,000$	150 ± 2	 4-ethyl phenol

phenol (EPH) and 2,4-xyleneol. All model compound solutions in the absorption range obey Beer-Lambert law. Cyclohexane was selected as the solvent because the specific conformation of the cyclohexane is favorable in this study.

Optical microscopy

Morphological observations of the various blending compositions were carried out with the use of the Olympus BX50 microscope. A small amount of sample was sandwiched between two microscope cover glasses and then heated from room temperature to 280°C with heating rate of $10^{\circ}\text{C}/\text{min}$. The hot stage is Mettler Toledo FP90 with temperature accuracy $\pm 0.1^{\circ}\text{C}$.

RESULTS AND DISCUSSION

Binary blend system

Conventionally, the DSC was used to assess the miscibility of polymer blend by measuring the glass transition temperature of the blend composition. Figure 1 shows the DSC traces of the series binary polymer blending compositions of the phenolic/PVPh, phenolic/phenoxy, and phenoxy/PVPh. All these binary compositions exhibit a single T_g , which strongly suggests that all of the compositions are miscible with homogeneous phase. These T_g s of various compositions of each binary blend are summarized in Figure 2, where the negative T_g deviation from additive rule on all compositions is observed, which is similar with the other two self-associating polymer blending system.^{37,38} The phenolic contains

a high density hydroxyl group that possesses the strong self-association hydrogen bonding, which serves as a physical crosslink and results in higher T_g than other polymers with similar molecular weight. The T_g deviation of Figure 2(a) can be interpreted as that self-associations of phenolic and PVPh are partially broken off and the hydroxyl groups are diluted by blending each others. In general, the T_g deviation is a result of entropy change corresponding to the change in the number of hydrogen-bonding interaction.³⁴ The phenoxy molecule with the long repeating unit provides relative less potential hydrogen bonding sites to form less interaction with other blending polymers. The reduction of forming

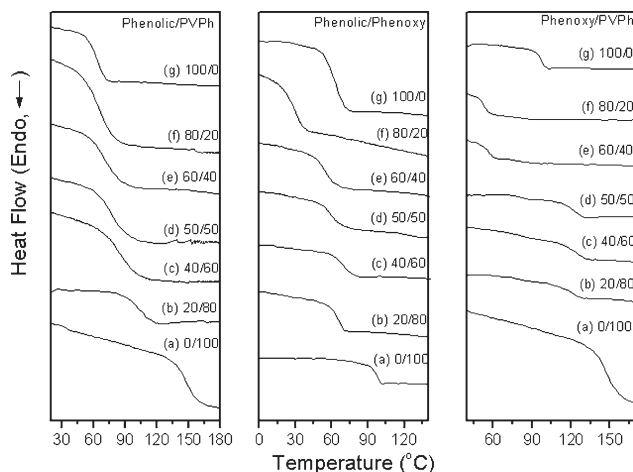


Figure 1 The DSC traces of the individual binary blends (wt/wt %) with various compositions: (a) Phenolic/PVPh, (b) Phenolic/Phenoxy, and (c) Phenoxy/PVPh.

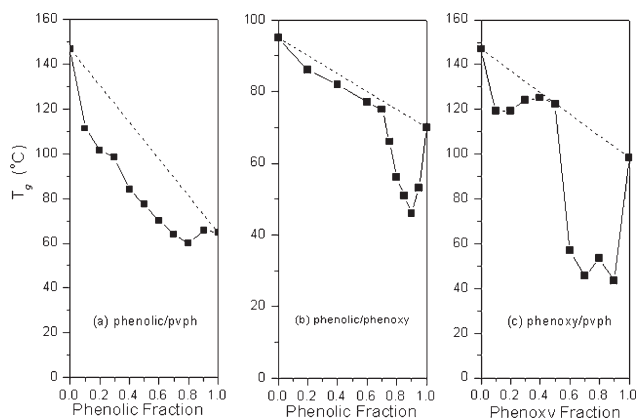


Figure 2 T_g vs. composition curves of the individual binary blend: (a) phenolic/PVPh, (b) phenolic/phenoxy, and (c) phenoxy/PVPh.

interassociation hydrogen bonding is too small to overcome the entropy increase due to remove the self-association hydrogen bonds of each polymer with hydroxyl group. As a result, negative T_g deviations were also obtained in Figure 2(b,c) that has been widely discussed in previous studies.³⁴

Ternary blend system

Thermal analyses

Figure 3 shows selected DSC thermograms of several phenolic/phenoxy/PVPh ternary blends with various compositions, revealing that every ternary blend has only single glass transition temperature. A single T_g strongly suggests that the ternary polymer blend is fully miscible at total compositions. On the basis of these evidences, we suggest that any phenolic/phenoxy/PVPh blend composition is miscible at temperatures in the range of 0–170°C. The phase dia-

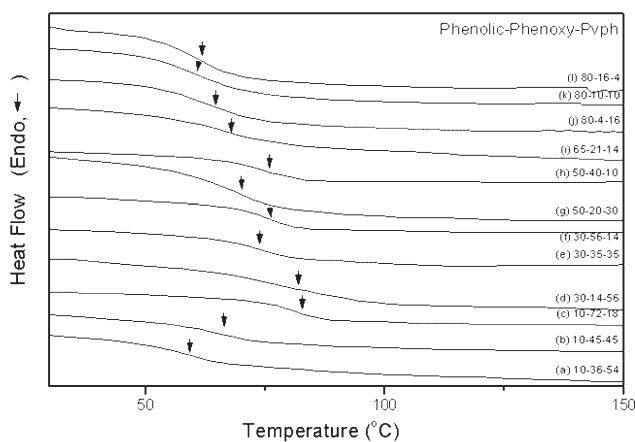


Figure 3 The DSC thermograms of phenolic/phenoxy/PVPh (wt/wt/wt %) blends with difference compositions: (a) 10-36-54, (b) 10-45-45, (c) 10-72-18, (d) 30-14-56, (e) 30-35-35, (f) 30-56-14, (g) 50-20-30, (h) 50-40-10, (i) 65-21-14, (j) 80-4-16, (k) 80-10-10, and (l) 80-16-4.

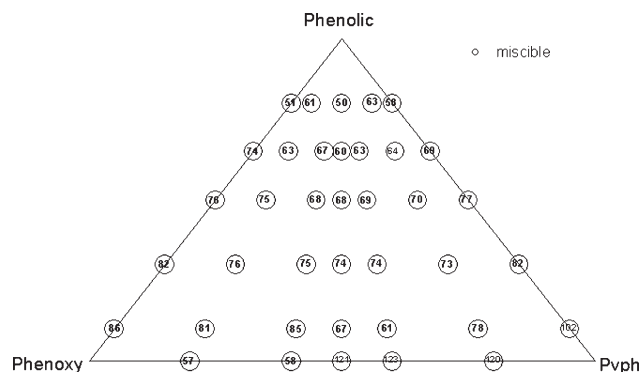


Figure 4 Ternary phase diagram of the phenolic/phenoxy/PVPh system with individual composition T_g showed in each cycle.

gram of this ternary polymer blend is displayed in Figure 4 with T_g of each composition. Therefore, we can confirm that this ternary polymer blend is totally miscible. The well-known Fox equation³⁹ has been proposed to predict the variation of glass transition temperatures of copolymers and blends as a function of composition,

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \quad (1)$$

where T_g is the glass transition temperature of this blend, W is the weight fraction, and the subscripts indicate the Polymers 1 and 2, respectively. This equation is generally applicable to binary blend systems, which are compatible and not too strongly polar. For three miscible components blends, this equation must be extended to the T_g -composition relationship: $\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} + \frac{W_3}{T_{g3}}$. The calculated T_g s and the T_g s measured from DSC analyses from all compositions are plotted in Figure 5. It is obvious to found out that these T_g s calculated from the Fox

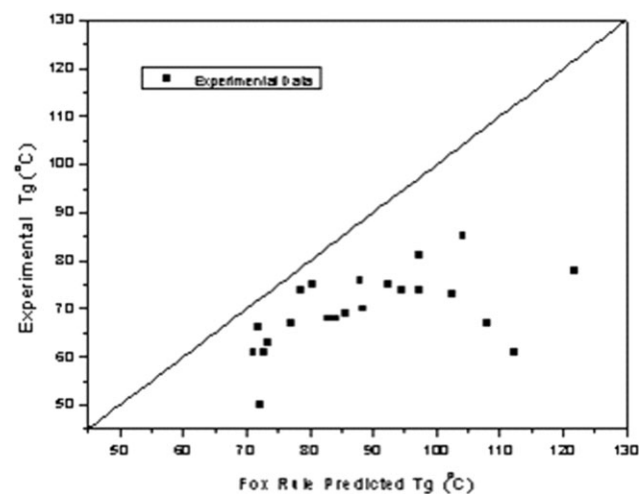


Figure 5 T_g vs. composition scatters based on (●) experimental data and line calculated from the Fox equation.

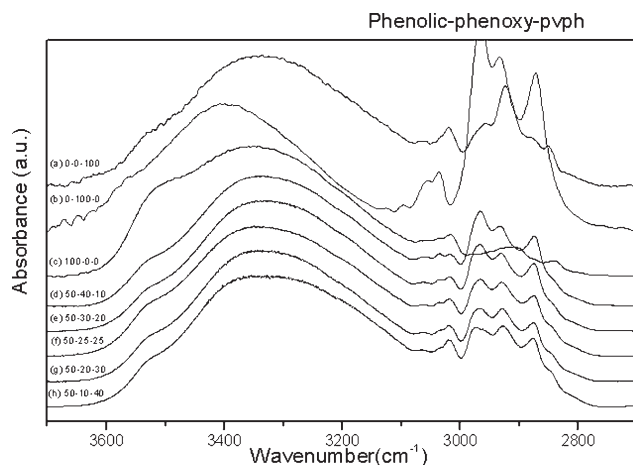


Figure 6 Infrared spectra recorded in the region of 2700–3700 cm^{-1} for the series compositions of phenolic/phenoxy/PVPh (wt/wt/wt %): (a) 0-0-100, (b) 0-100-0, (c) 100-0-0, (d) 50-40-10, (e) 50-30-20, (f) 50-25-25, (g) 50-20-30, (h) 50-10-40.

equation do not fit well with T_g s obtained from DSC analyses and many compositions shows significant negative deviation. Since these three binary blends show negative deviations, it is reasonable that this ternary blend show negative deviation. The large deviation between the experimental data and values calculated from Fox equation is resulting from the ternary blend system containing some kinds of strongly intermolecular interactions.

FTIR analysis

FTIR spectroscopy has been used widely in the study of polymer blends. This method is useful to verify the presence of intermolecular interaction between hydrogen-bonded donor and various hydrogen-bonded acceptor groups due to the sensitive of the hydrogen-bonding formation. Figure 6 shows the scale-expanded infrared spectra of the hydroxyl group stretching absorption of series phenolic/phenoxy/PVPh blends with phenolic content fixed at 50 wt % in the region of 3700–2700 cm^{-1} . All these bands show two distinct bands, the higher wavenumber centered at 3525 cm^{-1} can be assigned as the free hydroxyl group of phenolic and PVPh and 3570 cm^{-1} for the free hydroxyl group of phenoxy. In addition, the lower broad band at 3100–3450 cm^{-1} was contributed from the absorption of the hydroxyl groups that formed hydrogen bonded with other hydroxyl groups, so called the multimer hydrogen-bonded hydroxyl group absorption. Clearly, the intensity of the free hydroxyl group of phenolic was decreased with the increase of phenoxy and PVPh content in the ternary blend system. Meanwhile, this broad hydrogen-bonded hydroxyl band of phenolic shifts into lower frequency with increasing PVPh and

phenoxy content. This observed change come from the switching from the strong intramolecular hydroxyl–hydroxyl bond of phenolic into the intermolecular hydroxyl–hydroxyl bond between phenolic, phenoxy, and PVPh segments. However, it is difficult to dwell further on this hydroxyl stretching region and hard to quantify these bands due to each of three polymer component containing hydroxyl group. Therefore, we should simulate this complicated hydrogen-bonded ternary polymer blend system by using the individual binary blend of model compound. Figure 7 shows the FTIR spectrum of each model compound, the 0.02M of EPH/cyclohexane [Fig. 7(a)] and 2,4-xyleneol/cyclohexane [Fig. 7(b)] display a strongly absorption band of the “free” hydroxyl stretching (3620 cm^{-1}) and the spectrum of 2-propanol also shows the relatively sharp free hydroxyl stretching in 3632 cm^{-1} . After we mixed the three compounds in cyclohexane (each composition contains constant concentration of 0.02M), a broad band envelope stretching from ca. 3150–3550 cm^{-1} became more obvious, illustrated in Figure 7(d). As above results, it indicates that intermolecular hydrogen bond has formed in this mixing solution. Meanwhile, we also can obtain indirect evidence about the intermolecular interaction of the ternary miscible polymer blend.

Interassociation equilibrium constant (K_A)

According to the previous study,³ the self-association of phenolic, phenoxy, and PVPh requires at least two association equilibrium constants, K_2 and K_B , to account for the formation of hydrogen-bonded “dimers” and “multimers,” respectively. The hydroxyl group exhibits various interassociation equilibrium constants with different type proton acceptor (e.g., hydroxyl, ester, ether, and amine

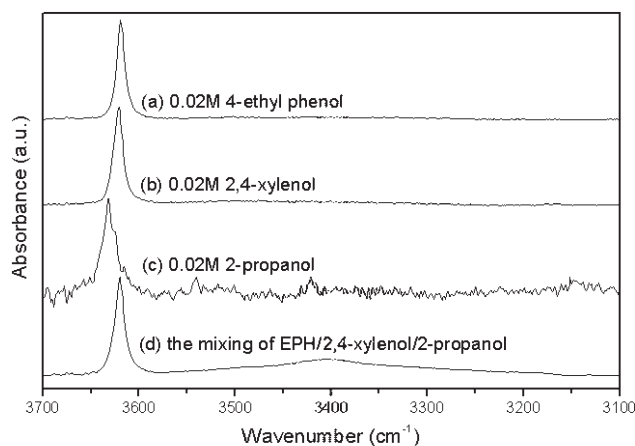


Figure 7 Infrared spectra recorded at room temperature in the region from 3100–3700 cm^{-1} of EPH, xyleneol, propanol, and their mixtures in cyclohexane.

TABLE II
The Various Association Equilibrium Constants and Thermodynamic Parameters Were Used in this Research

Material	Molar volume (cm ³ /mol)	Solubility parameter (cal/mL) ^{0.5}	Self-association equilibrium constant		Interassociation equilibrium constant
			K_2	K_B	K_A
Phenolic	84 ^a	12.1 ^a	23.3 ^a	52.3 ^a	
Phenoxy	216 ^a	10.2 ^a	14.4 ^a	25.6 ^a	
PVPh	100 ^b	10.6 ^b	21 ^b	66.8 ^b	
Phenolic-Phenoxy					114 ^a
Phenoxy-PVPh					101.7 ^c
Phenolic-PVPh					91.9 ^d

^a Ref. 32.

^b Ref. 3.

^c Ref. 33.

^d Measured in this study.

group) when mixing with other polymer. These three constants are expressed as self-associated dimer equilibrium constant (K_2), self-associated multimer equilibrium constant (K_B), and the interassociation equilibrium constant (K_A). As can be seen, each component of this ternary hydrogen-bonded polymer blend can form self-association by individually hydroxyl group and develop intermolecular hydrogen bond between hydroxyl and hydroxyl groups. These self-association values of phenolic, phenoxy, and PVPh are summarized in Table II, which also contains the interassociation equilibrium constants of each binary blend. Therefore, all self- and intermolecular interaction competitions would be deduced from the relationship of these self- and interassociation equilibrium constants.

A value for the interassociation (K_A), which is described as the ability of the interaction of hydrogen bonding between phenolic and PVPh, was measured in this study based on classical Coggeshall and Saier⁴⁰ methodology, using the hydroxyl stretching region of the infrared spectra of concentrated 2,4-xylenol and EPH mixtures. To obtain the free intensity of free hydroxyl group (means unassociated) (f_F^{OH}) stretching of EPH, we chose the cyclohexane as the mixing solution due to the inertness for hydrogen bonded and exhibiting no any fundamental vibrational frequency in the hydroxyl stretching region (3100 cm⁻¹–3700 cm⁻¹) of the infrared spectra. As we are dealing the hydroxyl stretching region, the overtone and combination bands of cyclohexane make major contribution that must be subtracted first. At Figure 8(a), the typical spectrum of 0.02M EPH in a cyclohexane solution is displayed and the pure cyclohexane stretching recorded in the 3100 cm⁻¹–3700 cm⁻¹ range shows in Figure 8(b). Meanwhile, the spectrum of pure cyclohexane was digitally subtracted as illustrated in Figure 8(c). There is a relative sharp band in 3620 cm⁻¹ present

assigned to the free hydroxyl stretching absorption of EPH.

Now let us turn our attention to the calculation of the interassociation equilibrium constant between the hydroxyl group of EPH and the 2,4-xylenol hydroxyl group. When we introduced the interaction species such as 2,4-xylenol, the hydroxyl–hydroxyl interaction band centered at 3350 cm⁻¹ was increased and then the free hydroxyl band showed lower and lower intensity as illustrated in Figure 9. In Figure 9, all series infrared spectra of EPH/2,4-xylenol/cyclohexane mixtures were displayed, the spectrum of various concentration of 2,4-xylenol/cyclohexane was also digitally subtracted. However, the hydroxyl stretching of EPH was overlaid by the hydroxyl stretching of 2,4-xylenol. When the interaction of two hydroxyl group occurred, the background (the subtracted absorption band of various concentration 2,4-xylenol) would be affected. As

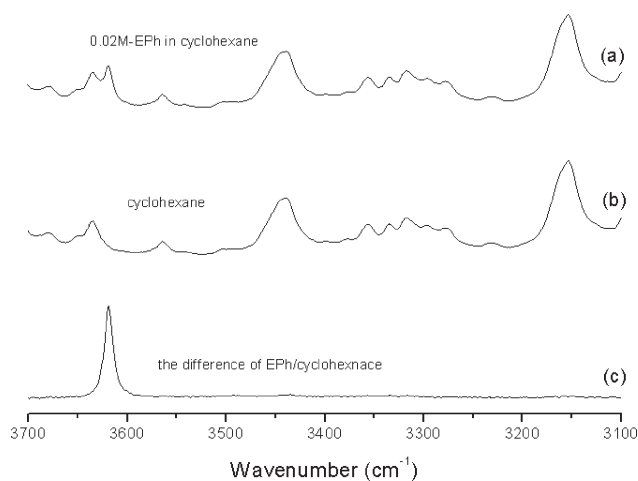


Figure 8 The scale-expanded infrared spectra ranging from 3100–3700 cm⁻¹ of EPH, cyclohexane, and their difference spectrum.

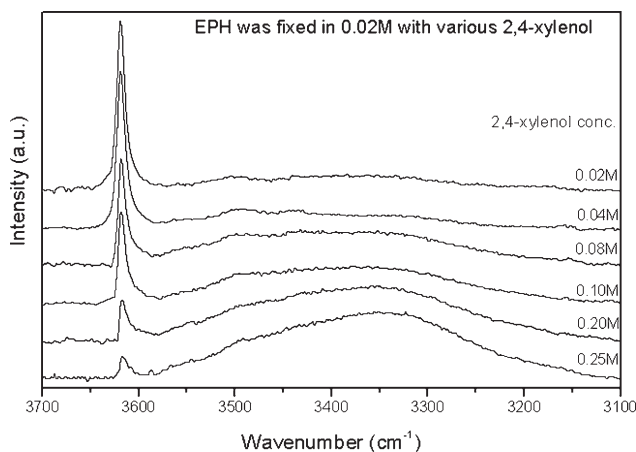


Figure 9 The free hydroxyl absorption band of 4-ethylphenol hold at 0.02 mol/L in EPH/2,4-xyleneol/cyclohexane solutions with various xyleneol concentrations ranging from 3100–3700 cm^{-1} .

previous literature,⁴¹ the intensity of free hydroxyl group stretching in 3620 cm^{-1} must be corrected by considering the intensity change of different background. Measurement of f_F^{OH} from the EPH/2,4-xyleneol/cyclohexane mixtures allow us to calculate the appropriate interassociation equilibrium constant, K_A , from eq. (4) derived by Coggeshall and Saier.⁴⁰ These values were listed in Table III.

$$K_a = \frac{1 - f_F^{\text{OH}}}{f_F^{\text{OH}} [C_A - (1 - f_F^{\text{OH}})C_B]} \quad (2)$$

where C_A and C_B are the concentrations of 2,4-xyleneol and EPH, respectively. In previous view,⁴² the absolute absorptivity of the free hydroxyl group stretching of EPH was determined by the extrapolation process, $a_F^{\text{OH}} = \lim_{c \rightarrow 0} A/bc$. The f_F^{OH} of any given concentration of EPH/2,4-xyleneol/cyclohexane would be obtained, $f_F^{\text{OH}} = A/a_F^{\text{OH}}bc$. However, the K_a value is dependent of concentration. A reliable K_a (9.19 in L/mol) value would calculate form extrapolation of zero 2,4-xyleneol concentration. It is simply to convert K_a value to the dimensionless equilibrium constant K_A by dividing the molar volume of the repeating unit of PVPh ($100 \text{ mol}^3/\text{mol}$). Thus the interassociation equilibrium constant, K_A , of 91.9 was measured.

In our knowledge, the chain stiffness such as intramolecular screening and functional group accessibility effect⁴³ plays an important role to determine the conversion between the model compounds and polymer blend. As far as these researches are concerned, no suitable equation to transform from model compounds to polymer blend. Meanwhile, the K_A value calculated from model compounds would not exactly describe the interaction between two polymers containing hydroxyl group. In this study, we attempt to

compare the relative magnitude of all inter- and self-association equilibrium constants based on the classical Coggeshall and Saier methodology. Therefore, in this ternary hydrogen-bonded blend each K_A constant is significantly higher than any self-association equilibrium constant (K_2 and K_B), which implies the hydroxyl groups of three components favor to form interassociation and then the self-association of individual polymer would be broken off. In general, the phase diagram of ternary blend is affected by so called “ $\Delta\chi$ ” effect, which is the difference of physical interaction between individual binary blend. When the inter-association of the individual binary blend is difference, named “ ΔK ” effect, it is tendency to induce phase separation.¹¹ However, the complicated intermolecular hydrogen-bonding interactions existing in this ternary polymer blend system behaves like a network. Even though the different hydrogen bonding strength in each binary blend (“ ΔK ” effect), it still exists a completely miscible ternary blend. We again confirm here that if the intermolecular hydrogen bonding exists between each binary component in the ternary blend, it may obtain a completely miscible ternary blend such as previous phenolic/phenoxy/PCL.³⁶

Optical micrographs analysis

Figure 10 shows optical micrographs of given compositions taken at different temperature. In these photographs, there is a homogeneous phase are observed at 100°C in the composition of phenolic/phenoxy/PVPh = 30/14/56 (w/w) [Fig. 10(a)]. However, as increase in temperature the hydrogen bond would be broken so that the degree of hydrogen-bonded hydroxyl group also decreases.³ A phase-separated structure has been found at 190°C showed at Figure 10(b). In addition, the same trend which is homogeneous phase at low temperature but heterogeneous phase at higher temperature is also measured in the composition of phenolic/phenoxy/PVPh = 65/17.5/17.5 (w/w) from the Figure 10(c,d). From these results, the ternary hydrogen-bonded blend follows a lower critical solution temperature (LCST) phase transition.

TABLE III
The Fraction of Free Hydroxyl Groups of 4-Ethyl Phenol

Concentration of 2,4-xyleneol (M)	Corrected intensity of IR spectra	f_F^{OH}	Interassociation equilibrium constant (K_a) mol/L
0.02	0.1154	0.8435	10.3765
0.04	0.1088	0.7953	7.1673
0.08	0.0984	0.7193	5.2462
0.10	0.0979	0.7156	4.2130
0.20	0.1068	0.7807	1.4359
0.25	0.1213	0.8867	0.5158

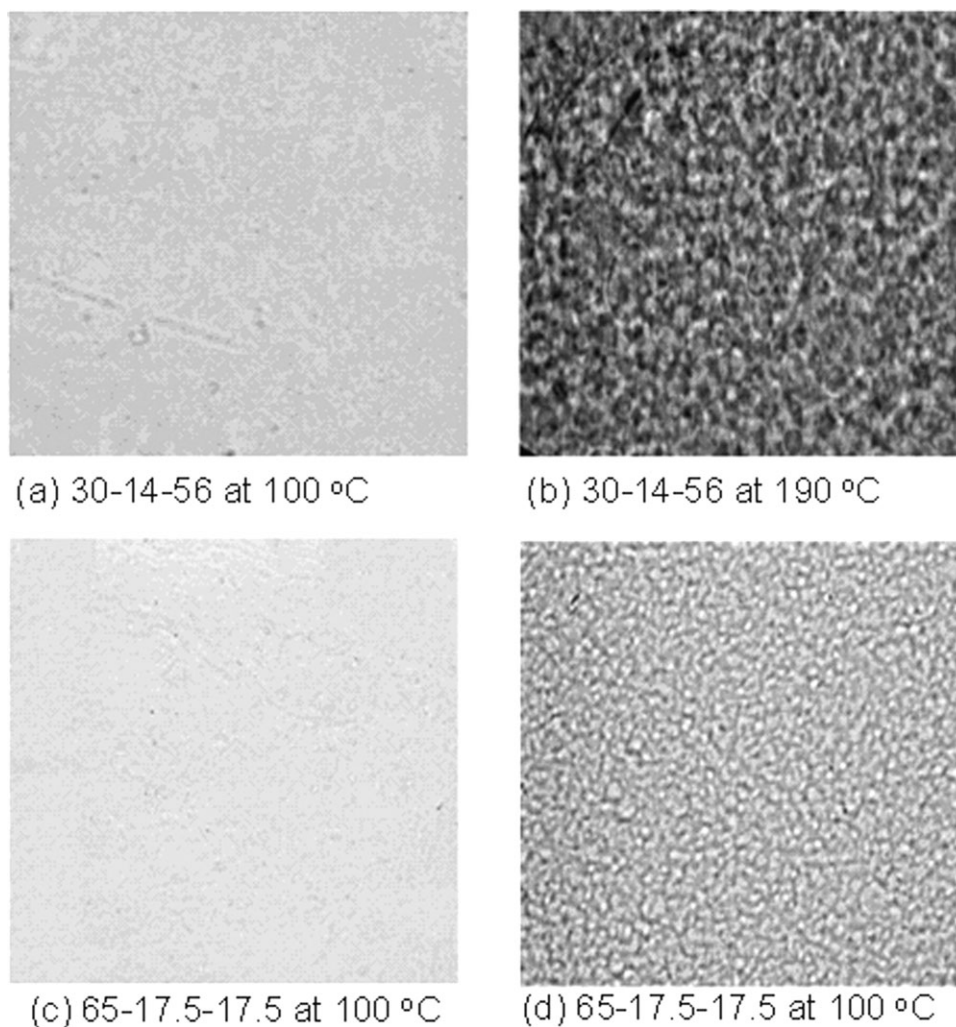


Figure 10 Optical micrographs of phenolic/phenoxy/PVPh blends with various compositions and difference temperature: (a) 30-14-56 at 100°C, (b) 30-14-56 at 190°C, (c) 65-17.5-17.5 at 100°C, (d) 65-17.5-17.5 at 190°C.

CONCLUSIONS

The phase behavior and hydrogen bonding of ternary blend of phenolic/phenoxy/PVPh have been investigated by using DSC, FTIR, and optical microscopy. All three individual binary blends are miscible and then unusually the ternary hydrogen-bonded blend is totally miscible. The magnitude of three kinds of interassociation equilibrium constant (K_A) is higher than any self-association equilibrium constant (K_2 and K_B). At this ternary blend system, there is no significant " ΔK " effect and the " $\Delta\chi$ " effect does not dominate over entire compositions. Meanwhile, the individual three polymers with hydroxyl functional group tend to form more the interassociation hydrogen bond with other two kinds polymer than the self-association of the intramolecular hydrogen bonding of an individual polymer. From the optical microscopy photographs this ternary blend system exhibits LCST behavior, indicating that it is homogeneous at room temperature consistent with DSC

analysis. These results reveal that this ternary hydrogen bonded blend has an entire totally miscible phase diagram.

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