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Polymer 43 (2002) 921–927

polymer

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Studies on the miscibility and phase structure in blends of poly(epichlorohydrin) and poly(vinyl acetate)

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Received 24 April 2001; received in revised form 11 June 2001; accepted 30 July 2001

Abstract

The miscibility of atactic poly(epichlorohydrin) (aPECH) with poly(vinyl acetate) (PVAc) was examined under two different conditions: (i) in dilute solution, using vicometeric measurements and (ii) as cast films, using differential scanning calorimetric (DSC) and FT-infrared spectroscopy. Phase separation on heating, i.e. lower critical solution temperature (LCST) behavior of the aPECH/PVAc blends was examined by the measurement of transmitted light intensity against temperature. From viscosity measurements, the Krigbaum–Wall polymer–polymer interaction (ΔB) was evaluated. The DSC results show that the aPECH/PVAc blends are miscible as evidenced by the observation of a single composition-dependent glass-transition temperature (T_g) which is well described by the Couchman and Gordon Taylor models. The Flory–Huggins interaction parameter (χ_{12}) calculated from the T_g-method was negative and equal to -0.01, indicating a relatively low interaction strength. The FT-IR results match very well with those of DSC. The cloud point phenomenon is thermodynamically driven but phase separation, once taken place, is diffusion controlled in normal accessible time. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Atactic poly(epichlorohydrin); Poly(vinyl acetate); Miscibility

1. Introduction

Considerable effort was made to study the miscibility and phase behavior of two polymers [1,2]. Polymer pairs with specific interactions, such as dipole–dipole and hydrogen bonding, are often miscible. Intermolecular interactions are usually considered to be the deriving forces for miscibility and their important role in the miscibility of polymer blends has been clearly demonstrated [3].

Poly(epichlorhydrin), PECH, is an important amorphous elastomer, exhibiting a glass-transition temperature at −23°C. PECH has been used in various branches of technology, such as automotive industry, in fuel, lubricating fluids, in air and vacuum houses and others [4]. There are few published papers on PECH and the majorities were about properties, characterization and chemical modification [5–7]. PECH, because of its α-hydrogen atoms, it may interact through hydrogen bonding with proton acceptor polymers. It has been found that PECH exhibit miscibility with many aliphatic polyester [8,9] polyacrylates [10], polymethacrylates [11], and poly(ethylene oxide) [12].

In an earlier report, Gou has offered experimental evidence to indicate that the blends of atactic PECH and poly(vinyl acetate) (PVAc) are miscible and showed lower critical solution temperature (LCST) behavior. The miscibility between PECH and PVAc was previously presumed to be due to hydrogen bonding between α-hydrogen of PECH and carbonyl of PVAc [13].

In this communication, we wish to report our results about the miscibility and phase behavior for the binary blend aPECH/PVAc. The miscibility was examined under two different conditions: (1) in dilute solution, using viscometry determination and (2) in cast films, using differential scanning calorimeter (DSC) and infrared spectroscopy. It will be shown that the phase structure of this system contains microheterogeneous domains with an apparent single T_g, and the intermolecular interactions between the pairs are relatively weak and mainly of dipole–dipole type. The LCST curve was determined by measurements of transmitted light intensity against temperature. It will be demonstrated that the LCST phenomenon in this system exhibits an apparent irreversibility which is diffusion controlled.

2. Experimental

2.1. Materials and preparation of blends

Atactic poly(epichlorohydrin) and PVAc were both

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PII: S0032-3861(01)00556-0

Table 1
Molecular characteristics of the polymers

Polymer	Code	Source	M_n (g mol^{-1})	M_w/M_n	ρ (g cm^{-3})[a]
Atactic poly(epichlorohydrin)	APECH	Aldrich	1.6×10^5	4.1	1.36
Poly(vinyl acetate)	PVAc	Aldrich	2.2×10^4	4.4	1.19

[a] Values specified by the manufacturer.

purchased from Aldrich and were used without further purification. Molecular weight characterization of the polymers was performed by gel permeation chromatography (GPC) in chloroform, using standard polystyrene samples for calibration. The results are presented in Table 1.

All blend samples were prepared by solution-casting method. Cyclohexanone was used as a solvent. Five precent (w/v) solutions of the blends were prepared. For each blend system, weight fraction of one of the polymers was kept at 0, 0.1, 0.3, 0.5, 0.7, 0.9, and 1, keeping the total blend concentration constant. The polymers were added slowly with stirring to avoid the formation of lumps. This blend solution was then poured on the Teflon-coated aluminum plate, which was placed, on a leveled mercury surface to obtain films of uniform thickness. The solvent was evaporated slowly at room temperature. The residual solvent in the blend films was removed under vacuum at 60°C for three weeks.

2.2. Dilute solution viscometry measurements

The intrinsic viscosity measurements of the homopolymers and each blend compositions were performed at 30 ± 0.1°C using a Ubbelohde glass capillary viscometer with a capillary of bore 0.5 mm. The intrinsic viscosity, $[\eta]$ was obtained using the Huggins equation [14]:

$$\eta_{sp}/C = [\eta] + bC \tag{1}$$

where η_{sp} is specific viscosity and $b = k[\eta]^2$ where k is the Huggins constant.

2.3. Differential scanning calorimetry

The glass-transition temperatures were measured with a Polymer Laboratories differential scanning calorimeter (PL-DSC). The instrument was calibrated for temperature and heat flow using high-purity standard. The mid-point of the slope change of the heat capacity plot of the second scan was taken as the glass-transition temperature. A heating rate of 20°C min^{-1} was adopted and an inert nitrogen atmosphere was maintained throughout the DSC run.

2.4. Infrared spectroscopy

Fourier-transform infrared spectroscopy (FT-IR, Nicolet Magna 560) was used for investigating possible molecular interactions between the constituents. Spectra were obtained at 4 cm^{-1} resolution and averages of spectra at least 36 scans in the standard wave number range 400–4000 cm^{-1}. All the FT-IR samples were cast as thin films of proper thickness directly on KBr pellet and dried as described above.

2.5. Cloud-point determination

Cloud points were determined using a method analogous to that of Schmidt et al. [15]. The temperature of an initially homogeneous blend, in film form, was increased at a rate of 2°C min $^{-1}$, using a Linkam hot stage, while the transmitted light intensity of a 1 mW He–Ne laser across the film was detected by a photodiode. The inflexion of the curve of relative transmitted light intensity, I/I_o, as a function of temperature, T, was considered as the cloud point.

3. Results and discussion

3.1. Viscometry measurements

Many groups have investigated the miscibility of polymer blends by carrying out viscosity measurements of the corresponding ternary polymer–polymer–solvent systems [16–18]. Most of these methods based on the assumption that repulsive interaction may cause shrinkage of the macromolecular coils giving rise to a negative deviation of viscosity from additivity. If there is attractive interaction, associates composed of both kinds of macromolecules are formed resulting in an increase in viscosity and a positive deviation from additivity.

The intrinsic viscosity $[\eta]$ data and the parameter b for the homopolymers and their blends are presented in Table 2. The Krigbaum and Wall interaction parameter, ΔB, of the blend [19] can be obtained from the difference between the experimental and theoretical values of the interaction parameters b_{12} and b_{12}^*. ΔB can be evaluated as follows:

$$\frac{[\eta_{sp}]_{blend}}{C} = [\eta]_{blend} + b_m C \tag{2}$$

where C is the total concentration of polymers ($= C_1 + C_2$), $[\eta]_{blend}$ is the intrinsic viscosity of the blend, and b_m defines the global interaction between all polymeric species. $[\eta]_{blend}$ for non-interacting system can be theoretically written as

$$[\eta]_{blend} = w_1[\eta]_{p1} + w_2[\eta]_{p2} \tag{3}$$

Here, $w_1 = C_1/C$ and $w_2 = C_2/C$ where w_2 and w_3 are the weight fractions of the two polymers. The interaction

Table 2
Viscosity measurement data and interaction parameter of aPECH/PVAc blends

Blend composition APECH/PVAc	Intrinsic viscosity $[\eta]$		Slop of reduced viscosity vs. conc. curves	Experimental b_{12}	Theoretical b_{12}	ΔB	μ
	Experimental (dl g^{-1})	Theoretical (dl g^{-1})					
0/100	0.17	0.170	0.088				
10/90	0.21	0.190	0.1004	0.156	0.096	0.060	1.66
30/70	0.23	0.227	0.12439	0.171	0.096	0.075	2.08
50/50	0.28	0.265	0.12125	0.146	0.096	0.050	1.39
70/30	0.32	0.303	0.11649	0.136	0.096	0.040	1.11
90/10	0.34	0.341	0.10843	0.125	0.096	0.029	2.49
100/0	0.36	0.360	0.105				

parameter b_{12} is defined by the equation:

$$b_m = w_1^2 b_{11} + w_2^2 b_{22} + 2 w_1 w_2 b_{12} \tag{4}$$

The Krigbaum and Wall interaction parameter, ΔB, is given by

$$\Delta B = (b_{12} - b_{12}^*) \tag{5}$$

where b_{12} may be obtained experimentally by Eq. (4) and b_{12}^* is the theoretical value given by

$$B_{12}^* = (b_{11} b_{22})^{1/2} \tag{6}$$

Accordingly, $\Delta B \geq 0$ signifies miscibility and $\Delta B < 0$ indicates phase separation. However, if $[\eta]_1$ and $[\eta]_2$ are dissimilar, more effective parameter μ can be used to predict the miscibility:

$$\mu = \frac{\Delta B}{(|\eta|_2 - |\eta|_1)^2} \tag{7}$$

Plot of ΔB and μ vs weight fraction of one of the blend components is shown in Fig. 1. For all the compositions study, the values of ΔB and μ are positive, indicating that the blend exhibits miscibility in cyclohexanone at 30°C. This suggested that in cyclohexanone, there are attractive forces that induce miscible behavior.

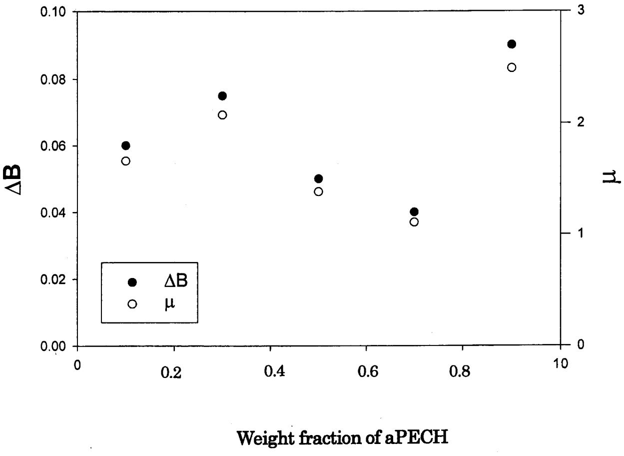

Fig. 1. Plot of Krigbaum factors ΔB and μ vs. composition for aPECH/PVAc blends.

3.2. *Differential scanning calorimetry*

DSC analysis was performed on the cyclohexanone-cast blend samples to reveal their glass-transition behavior and the T_g data of PVAc/aPECH blends are summarized in Fig. 2 as a function of composition. In accordance with previous result [13], the blends were miscible over the entire composition range as shown by the presence of the single glass-transition temperatures that were intermediate between those of the pure components and regularly varied with blend composition.

A quantitative evaluation of the T_g–composition relationship of a miscible blend may provide some clue about the of the scale of blend homogeneity. Accordingly, fitting of the T_g data with several common models for miscible polymer systems was examined and compared in Fig. 2. Fitting the T_g

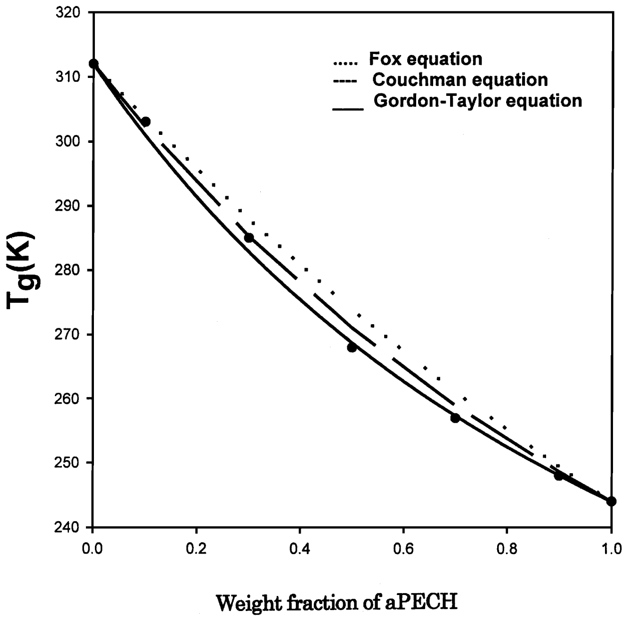

Fig. 2. Composition dependence of the DSC glass transition of aPECH/PVAc blends.

data to the classical Fox equation [20], ($1/T_g = w_1/T_{g1} + w_2/T_{g2}$), which describes volume additivity, indicates a large negative deviation, suggesting that the intermolecular homogeneity between PVAc and aPECH may be far from those expected in covalent-bonded copolymers. The evident deviation from Fox model may, to a major degree, due to significant T_g broadening for the blend samples. Broadening phenomena have been observed in many literature-reported miscible blend systems whose miscibility occurs in the absence of any strong specific interaction or whose constituent's polymers only possess weak polar interactions ([21] and references cited therein). The T_g broadening suggests that the scale of mixing might have a limit and that various scales of molecular aggregation might exist. Aggregation here means microheterogeneity resulted from the same polymer chain segments aggregating in large domains or in greater probability than that of chains of different kinds. Table 3 lists the composition dependence of the transition breadth of the T_g (ΔT). The breadth of the T_g ranges from 7°C for neat polymers to about 24°C for a 50/50 blend composition. Most other compositions exhibited a breadth of about 10–20°C. The T_g broadening for the blend samples of compositions near 50/50 suggests various scales of molecular microheterogeneity.

Another two models that describe the composition dependence of the T_g in miscible polymer blends are the Gordon–Taylor model [22] and Couchman [23] models. The Gordon–Taylor equation is written as

$$T_g = \frac{w_1 T_{g1} + K w_2 T_{g2}}{w_1 + K w_2} \tag{8}$$

where w is weight fraction and 1 and 2 refer to lower and higher T_g components, respectively. In the Gordon–Taylor equation, $K = (\rho_1/\rho_2)/(T_{g1}/T_{g2})$ where ρ is the density. If $\rho_1/\rho_2 = 1$, then Eq. (8) reduces to the well-known Fox model. The Couchman version of Eq. (8) puts $K = \Delta c_{p2}/\Delta c_{p2}$ where Δc_p is the change in specific heat capacity at T_g.

The curves in Fig. 2 are the theoretical T_g–composition curves calculated with $K = 0.57$ (Gordon–Taylor equation) and $K = 0.66$ (Couchman equation), where these parameters are calculated using glass-transition temperature and specific heat capacity data from DSC measurements on aPECH and PVAc homopolymers. A similar analysis of an earlier study gave a value of K, as a fitting parameter, of 0.62 [13].

Table 3
Glass-transition temperatures and transition breadth of aPECH/PVAC

Blend composition aPECH/PVAc	T_g^{DSC} (°C)	ΔT (°C)
00/100	39	7
10/90	30	11
30/70	14	15
50/50	0	24
70/30	−12	21
90/10	−24	14
100/00	−29	6

Recently, an equation developed by Lu and Weiss [24] puts

$$K = k + \frac{A}{(T_{g2} - 1)} \tag{9}$$

with

$$A = \frac{\chi_{12} R (T_{g1} - T_{g2})(\rho_1 - \rho_2)}{M_1 \Delta c_{p1}} \tag{10}$$

and

$$k = \frac{\Delta c_{p1}}{\Delta c_{p2}} \left[1 + w_1 \frac{\delta c_p^l}{\Delta c_{p2}} + \frac{\delta c_p^g}{\Delta c_{p1}} \right] \tag{11}$$

where ΔC_p is the change in specific heat capacity at the glass transition; δC_p is change in specific heat capacity, in the liquid and glassy states, due to mixing. M_1 is the molecular weight of the repeating units in polymer 1 and χ_{12} is a binary interaction parameter. As δC_p is usually small compared with ΔC_p, the right-hand side of Eq. (11) can be replaced by $\Delta c_{p1}/\Delta c_{p2}$.

The χ_{12} value that is calculated by Eq. (10) is not the segmental χ_{12} value. The segmental χ_{12} value is defined by the following equation [25]:

$$\Delta H_m = \chi_{12} R T \phi_1 \phi_2 (m_1 n_1 + m_2 n_2) \tag{12}$$

where ϕ_i is the volume fraction of the component i. n_1 and n_2 are the number of moles of PVAc and aPECH in the blend, respectively. m_1 and m_2 are the number of lattice sites of the PVAc and aPECH molecules, respectively. m_1 and m_2 can be obtained with the following relation [25]: $m_1 = V_1/V_0$ and $m_2 = V_2/V_0$, where V_1, V_2 and V_0 are the molar volumes of the PVAc, aPECH, and repeating units of aPECH, respectively.

The magnitude of χ_{12} depends intimately on molecular parameters such as V_1 and V_2. The polydispersity of PVAc and aPECH used in this study is considerably wide, so the choice of V_1 and V_2 may affect the magnitude of χ_{12} evaluated. When both polymers are polydispersed, the number-average molecular weight can be used in the place of monodisperse molecular weights in the modified Flory–Huggins equation with very little effect on the consequent value of χ_{12} [26]. The segmental χ_{12} value of the PVAc/aPECH blend can be obtained by the χ_{12} value calculated from Eq. (10) being divided by the average values of m_1 and m_2 [25]. The values of $m_1 = 255.8$ and $m_2 = 1729.7$ were used for PVAc and aPECH, respectively. A repeating unit of the aPECH was chosen as a site reference volume. The segmental χ_{12} value of the PVAc/aPECH blend obtained by this way is equal to -0.01.

3.3. Molecular interactions

The miscibility of PECH with PVAc was previously

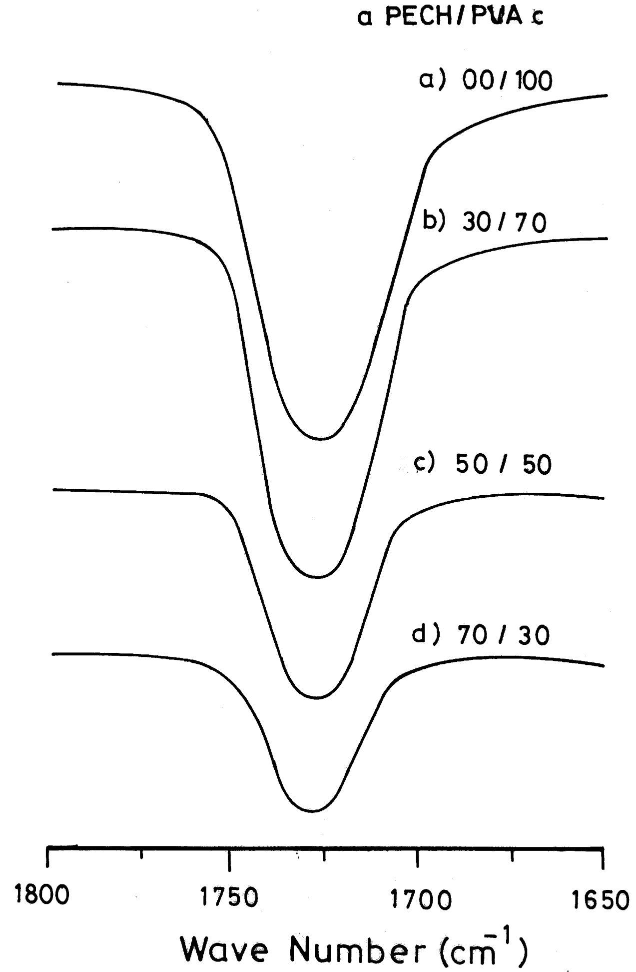

Fig. 3. FT-IR spectra of (a) neat PVAc, and aPECH/PVAc; (b) 30/70; (c) 50/50; (d) 70/30 compositions in the range 1650–1800 cm^{-1}.

presumed to be due to hydrogen bonding between α-hydrogen of PECH and carbonyl of PVAc [13]. We have performed IR characterization to reveal absorbance peaks of the carbonyl stretching (C=O) of PVAc, and for the aPECH/PVAc blends of several compositions. Fig. 3 shows the FT-IR spectra of the carbonyl stretching for samples: (a) neat PVAC and aPECH/PVAC blend; (b) 30/70; 50/50; and 70/30 blend composition. The absorption peak is seen to be located at approximately 1728 for all blend compositions and the peak shifting is negligible. The lack of peak shifting suggests that the carbonyl groups of PVAc may not involved in a hydrogen-bonding interaction with α-hydrogen of aPECH. aPECH is a weak proton donor via hydrogen bonding and if indeed there exists a hydrogen bonding type of interaction in this blend system, we should also observe shifts in the methylene α C–H stretching mode. However, for this latter mode, there are numerous methylene units in both polymers, and consequently, it was practically impossible to obtain a conclusion concerning the involvement of the α hydrogen in any interactions. Unfortunately, the carbonyl stretching vibration occurs in a range free of underlying absorbances and is reasonably isolated and more intense mode, which does not couple significantly with the backbone vibrations of the polymers. Recently, Cheung et al. [27] performed solid state ^{13}C NMR study on PECH/PVAc blends and observed no downfield shift of the PVAc's carbonyl peak, which is a signature of strong hydrogen bonding with the PECH's α-hydrogen and an indication of molecular mixing. Apparently, weak polar interactions between aPECH and PVAc possibly through a match of polarity may have been the only factor leading to the miscibility.

3.4. Cloud point observation

The cast-film samples of all compositions were visually clear and completely free of any haziness as observed using optical microscope. LCST behavior of polymer blends provides information on the intensity of interaction. An increase in the strength of interaction leads to a higher temperature of phase separation [28,29]. Fig. 4 shows the results of cloud point of blend as a function of composition. The shape of the cloud point curve is not symmetrical, showing a minimum cloud point of 185°C for 60/40 aPECH/PVAc composition. As the phase structure of the blend at below the cloud point was determined to be completely free of any visible heterogeneity domains. The occurrence of a cloud point phenomenon suggested a thermodynamic phase separation from original miscibility. The cloud point transition temperatures observed in this blend system are lower than those obtained previously by Guo [13] for the same system. Guo has used optical observation for phase separation on heating at a rate of 10°C min^{-1}. However, in the present work, the cloud point curve was determined by measuring the relative transmitted light intensity using a heating rate of 2°C min^{-1}. This gives reliable measure of the cloud point. We have repeated our LCST measurements and are, therefore, confident in our results.

In normal accessible time scales, the LCST phenomenon

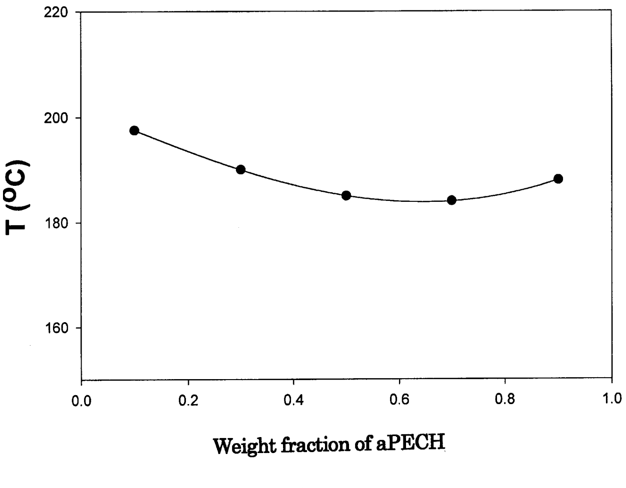

Fig. 4. Cloud point curve for the aPECH/PVAC system.

taking place in the aPECH/PVAc blend upon raising the temperature was found to be irreversible upon lowering the temperature. This means that upon cooling slowly from above the LCST temperatures to ambient, phase-separated structure remained. A true LCST should be thermodynamically reversible.

At first glance, demixing upon cooling might imply that the equilibrium LCST could lie at a much lower temperature than indicated by the observed cloud point. To test this idea, we placed some homogeneous blends at some temperatures below the cloud point and observing phase separation microscopically. Optical observation reveals that the 50/50 blend film remains transparent when heated at 175°C for 30 min. This suggests that our LCST curve is almost near equilibrium. We attribute the irreversibility of LCST to kinetic but not thermodynamic factors. To prove this, we performed the following experiment: a heated-induced phase separated 50/50 blend was redissolved into cyclohexanone and cast to prepare regenerated blend and observing its homogeneity using optical microscope (see Fig. 5). The recasted blend was found to be as homogeneous as that of the original sample. This means that if the molecular chains were given enough high mobility, by redissolving the phase-separated blend into a solvent and recasting into a blend sample, the phase separation above LCST can be made reversible by forming a homogeneous phase again. This also suggested that no chemical changes were involved in the phase separation process at above LCST.

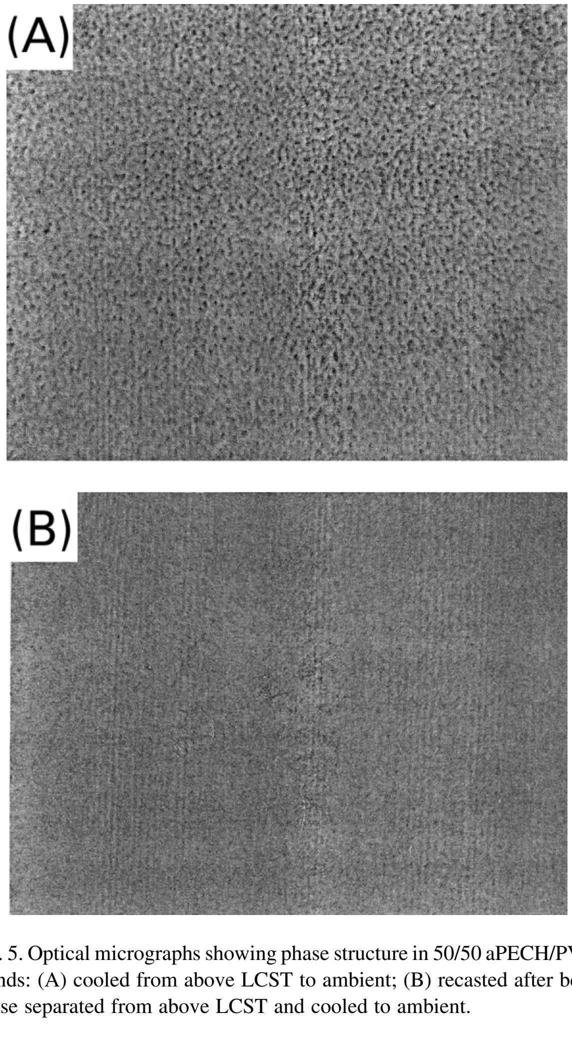

Fig. 5. Optical micrographs showing phase structure in 50/50 aPECH/PVAc blends: (A) cooled from above LCST to ambient; (B) recasted after being phase separated from above LCST and cooled to ambient.

4. Conclusion

In conclusion, based on the results obtained by different techniques in this study, we can say that the aPECH/PVAc blends are miscible in cyclohexanone at 30°C. The as-cast blend films present only one blend-composition dependent T_g, which means that the molecular mobility of the chains of each homopolymer is mutually affected. The Flory–Huggins interaction parameter (χ_{12}) calculated from the T_g-method was negative and equal to -0.01, indicating a relatively low interaction strength. The FT-IR results confirm the above finding. The cloud point phenomenon in this system is thermodynamically driven but phase separation, once taken place, is kinetically irreversible in normal accessible time.

Acknowledgements

The author wishes to thank Mrs Nabela H. Slim, at South Wady Nile University, Aswan, for carrying out the viscosity measurements.

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