ELSEVIER

Polymer 40 (1999) 2231–2237

polymer

Composition dependence of phase instability and cloud point in solution-blended mixtures of polystyrene with poly(cyclohexyl methacrylate)

Fan Hwei Jang, Eamor M. Woo*

Department of Chemical Engineering, National Cheng Kung University, Tainan 701-01, Taiwan

Received 1 April 1998; accepted 4 June 1998

Abstract

Composition dependence of phase behavior in the mixture system of polystyrene (PS) with poly(cyclohexthyl methacrylate) (PCHMA) was examined in details using differential scanning calorimetry, optical and scanning electron microscopy, and infrared spectroscopy. This study shows that the 'transparent' blends of PS/PCHMA with an apparent single T_g, having been thought to be miscible in earlier reports, actually displayed micro-heterogeneity domains of about 100–300 Å. It is thus not appropriate to assess miscibility to the optically clear blends of PS/PCHMA; however, partial miscibility does exist. The PCHMA-rich (PCHMA >70 wt%) compositions are indeed miscible but the PS-rich compositions are only partially miscible with sub-micron discrete phase domains beyond detection limit of optical microscopy. The proximity of the T_gs also prevented that the thermal transition of the micro phase domains in the PS-rich blends being resolved. The criterion of single T_g commonly employed in in assessing phase behavior should be used with extra precaution in cases where micro-heterogeneity exists, whose ambiguity is even compounded in cases where the T_gs of the constituent polymers are close. The FT-ir result indicates that intermolecular interactions are weak or non-specific for the PCHMA-PS pair.

Keywords: PS; PCHMA; Partial miscibility; Morphology

1. Introduction

Lacking any special functional groups in its chain structure, polystyrene (PS) is immiscible with most long-chain thermoplastic polymers. But two well-known exceptions of blends comprising PS are known to be miscible. One is the blend system of PS with poly(1,4-dimethyl-*p*-phenylene oxide) (PPO), which is one of the most studied polyblend, and its miscibility has been demonstrated since early time [1][2][3]. Being one of the most useful commercial resins, miscible blends of PS with PPO of various compositions, known as Noryl, have attracted years of attention and research interests. Another notable example of miscible blends comprising PS is given by the classical PS/poly(vinyl methyl ether) (PVME) system. PS blends with PVME have attracted interests and curiosity since long time ago in the polymer community owing to their interesting but complex phase behavior. Since early time, the PS/PVME blends have been determined to be miscible [4,5,6], but many other studies have yielded results leading to conditional miscibility. Molecular chain aggregation in various scales depending on compositions have been mentioned as a factor responsible for the single T_g, but with significant broadening. In investigation of effects of tacticity on blend phase behavior, a recent study revealed that the blends of semi-crystalline syndiotactic sPS with PVME behave in similar phase structures as the amorphous aPS/PVME blends [7]. Another unique feature in PS/PVME blends is that relatively low 'lower critical solution temperature' (LCST) exists in the PS/PVME blends upon heating to temperatures just above the blend's T_g. The LCST phenomenon in PS/PVME, however, is reversible upon slow cooling back to low temperatures.

Both polymers that have been found to be miscible with PS are ether-containing polymers: i.e. PVME and PPO, respectively. Blends of PS with ester-containing (carbonyl groups) polymers or acrylic polymers are mostly immiscible. Blends of PS with poly(methyl methacrylate) (PMMA) are known to be immiscible and non compatible. However, Shultz and Young [8] reported that single-T_g homogeneous blends of PMMA/PS could be obtained by a rapid freezing of their co-solution in naphthalene followed by room-temperature evaporation of naphthalene. This demonstrates that the phase stability in certain mixtures of PS can be unstable or kinetically dependent.

---

* Corresponding author. Tel.: +886-6-275-7575, ext. 62670; Fax: +886-6-234-4496; E-mail: emwoo@mail.ncku.edu.tw

0032-3861/99/$ - see front matter
PII: S0032-3861(98)00452-2

Lately, Friedrich et al. reported that PS and poly (cyclohexyl methacrylate) (PCHMA) are miscible judging from the results of thermal analysis and rheological studies [9]. It must be pointed out that the T_g of PS and PCHMA are so close (95°C and 110°C) to each other that the single-T_g criterion may not be unambiguous and must be used with extreme precaution. LCST (or cloud point) of about 245°C for the intermediate compositions of PS/PCHMA blend has been observed and used as a supportive evidence of miscibility. However, it must be cautioned that existence of ‘cloud points’ may not be an absolute necessary condition for proving thermodynamic miscibility. An example is given by the issue of binary blends of bisphenol-A polycarbonate (PC) with poly(methyl methacrylate) (PMMA), whose phase behavior has been extensively investigated [10][11][12][13][14], but their equilibrium phase behavior remained controversial for a long time. Most claimed that miscibility exists in PC/PMMA with a then regarded ‘lower critical solution temperature’ (LCST) phenomenon (around 160–190°C depending on compositions). Different newer theories have also been proposed to revised earlier explanations. Nishimoto et al. [15] have reported that solution-cast PC/PMMA blends were actually not thermodynamically miscible and that the previously reported ‘miscibility’ and ‘LCST’ in solution-cast PC/PMMA blend was just an artifact of preparation methods. This view was further reinforced by a few more studies performed in this laboratory [16].

In this study, focus was placed on resolving the equilibrium phase behavior of PS/PCHMA mixtures. The PS/PCHMA blend system was examined by performing thermal analysis and microscopic observation on samples prepared using several methods with proper solvents as well as casting temperatures. Further, experimental schemes were designed to observe detailed morphology of the PS/PCHMA. The true phase behavior of PS/PCHMA is discussed using the experimental results.

2. Experimental

2.1. Materials and sample preparation

Poly(cyclohexyl methacrylate) (PCHMA) was purchased from Scientific Polymers Product, with an approximate $M_w = 65\,000$ g/mol (Gel Permeation Chromatograph), and a T_g of 110°C. Atactic polystyrene (a-PS) was purchased from Polysciences Inc., with $M_w = 125\,000–250\,000$ g/mol. T_g of this grade of PS was only 90°C. PS of relatively lower T_g was chosen as the purpose was to distinguish as much as possible form the T_g of the other component in the blend. They were used without further purification.

Melt-blending (175°C) was first attempted, but it was given up owing to requirement of high temperatures above the cloud points. The blend film samples in this study were prepared by solvent-casting at two temperatures (20 and 45°C, respectively). The solvent of tetrahydrofuran (THF) were used. Another solvent, methylene chloride, yielded total phase separation after blending at any temperatures. PCHMA and PS were first weighed respectively and dissolved into THF with continuous stirring in one of the two chosen solvents. Subsequently, the resulting polymer solution was then poured into an aluminum mold kept at one of the two chosen temperatures (20°C or 45°C). It was found that while casting at 20°C or below yielded apparently phase-separated films, THF casting at 45°C yielded the best-quality clear film samples. The blend films so cast were crystal-clear completely free of any haziness. Note that the casting temperature was limited to a maximum of 45–50°C, and could not be raised further as this is the boiling temperature of THF. The solvent in the cast film samples was first vaporized under a hood at controlled temperature, followed by residual solvent removal in a vacuum oven for 48 h at 50–60°C. Especially for the tenacious THF solvent, subsequent vacuum degassing at an even higher temperature of 80°C was performed on the THF-cast samples for 2 more days.

2.2. Apparatus

2.2.1. Differential scanning calorimetry

The glass transition temperatures were measured with a differential scanning calorimeter (Perkin-Elmer DSC-7) equipped an intracooler and a computer for data acquisition/analysis. All T_g measurements were made at a scan rate of 20°C/min within the range of 25°C–250°C, and the T_g values were taken as the onset of the transition (the change of the specific heat) in the d.s.c thermograms.

2.2.2. Optical microscopy

A polarized-light microscope (Nikon Optiphot-2, POL) was used. The as-cast blends were spread as thin films on glass slides, dried properly in a temperature-controlled oven before they were examined using the optical microscope. For comparison, samples for optical examination were prepared using the same solvents and casting temperature as those in thermal analysis samples. Cloud point measurement of the blends was performed by placing the samples on a microscope heating stage (temperature-programmed), with a programmed heating rate of approximately 2°C/min. from room temperature up to 300°C. Cloud point was registered as the temperature at which separated domains were visible in samples using the maximum magnification of the optical microscope.

2.2.3. Scanning electron microscopy

Furthermore, the morphology (fracture surface) of blends of various preparation methods and/or heating treatments was examined using a scanning electron microscope (s.e.m) (Model JEOL JXA-840). The blend film samples for scanning electron microscopy were thick enough so that fracture surface of the thickness (cross-section) could

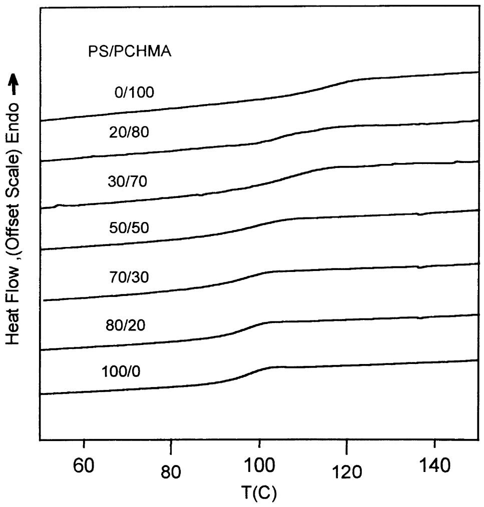

Fig. 1. DSC thermograms showing one apparent single T_g in each of the PS/PCHMA blends of various compositions.

be conveniently examined. The fractured blend samples were coated with gold by vapor deposition using a vacuum sputterer.

2.2.4. Infrared spectroscopy

Fourier-transform infrared spectroscopy (FTi.r., 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 were obtained from at least 64 scans in the standard wavenumber range of 400–4000 cm^{-1}. All the FT-i.r. samples were cast as thin films of proper thickness directly on KBr pellets kept at 45°C.

3. Results and discussion

3.1. Optical clarity and phase stability

The THF solution-cast samples, prepared at room temperature (i.e. 20°C) and 45°C, respectively, were preliminarily examined using optical microscopy. The THF-cast blend films prepared at 20°C were visibly cloudy or opaque, and the optical microscopy revealed easily discernible phase domains of several μm in 20°C-cast blends. Thus, THF-cast blend samples at room temperature (20°C) were judged to be phase-separated and disregarded for further studies. Focus of this study was placed on the samples prepared using the best blending method of THF casting at 45°C. The THF-cast blend samples at 45°C of all compositions were visually clear/transparent and they were judged to be optically homogeneous according to the maximum available magnification of 1000 × . As the optical microscopy could not identify any discernible domains in the 45°C-cast blend films, the results are not shown for brevity. In this study, the samples after preliminary optical microscopy characterization were to be further examined using d.s.c, Ft-i.r., and scanning electron microscopy.

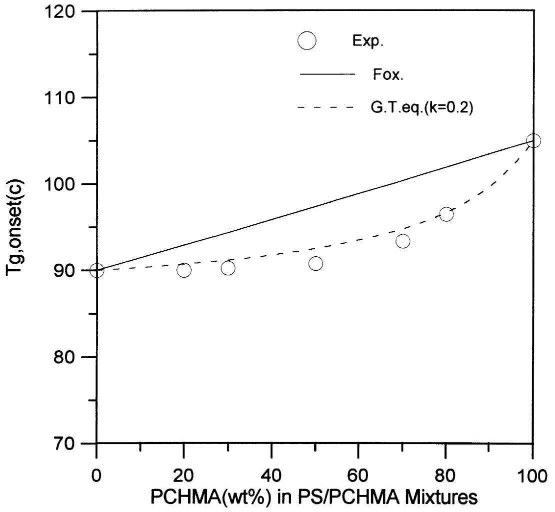

Fig. 2. Composition dependence of the experimental T_g data of PS/PCHMA blends THF-cast at 45°C.

3.2. Glass transition behavior of cast blends

The THF 45°C-cast blend samples were visually clear and free of visible phase-separated domains according to optical microscopy results. D.s.c analysis was performed on these samples to reveal their thermal transition behavior. For the purpose of unifomizing thermal treatment before T_g measurement, all samples were heated to 175°C and quenched to 50°C before the second DSC run was started at a scanning rate of 20°C/min. Fig. 1a–f displays the DSC thermograms showing one apparent single T_g in each of the PS/PCHMA blends of various compositions, as indicated in the curves. The reported thermograms are the results of second run after quenching from above T_g. Note that the T_gs of the neat components were quite close (90°C for PS and 110°C for PCHMA); thus the experimental results of single T_g should be analyzed with care. The transition breadth was also examined and compared. It was found that the thermal transitions for all blend compositions are reasonably sharp and not broadened. However, as the T_gs of two neat components (PS and PCHMA) do not differ much, the lack of broadening may not be used to suggest possible scales of molecular intermixing.

Fig. 2 shows the composition dependence of the experimental T_g data of PS/PCHMA blends THF-cast at 45°C. It must be noted that fitting between the experimental data with appropriate models may not tell very much about miscibility owing to the fact that the T_gs of the constituent polymers are too close. However, the trend of T_g-composition relationship can be analyzed by comparing the data with proper models. All T_g data clearly show negative deviation from a linear relationship. This is quite different from what reported earlier by Friedrich et al. [9], who claimed that the blend system shows positive deviation. Positive deviation from linear relationship generally does not exist in physically miscible blends, but only in blends

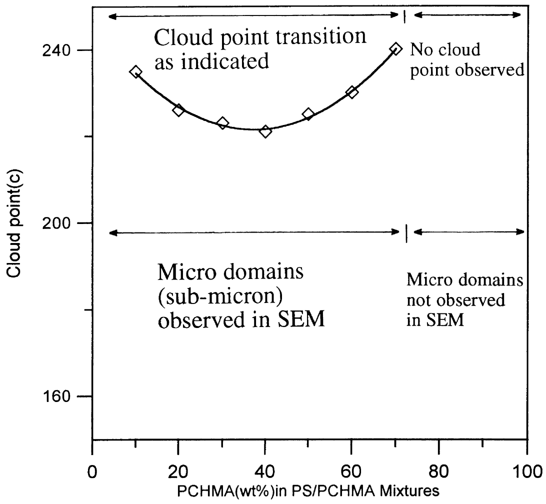

Fig. 3. Cloud point (initiation) of PS/PCHMA blend as a function of composition.

with ionic bondings or other stronger intermolecular interactions. The molecular interactions between the functional groups of PS and PCHMA do not seem to justify a positive deviation. The classical Fox equation obviously does not fit the data. The Gordon–Taylor equation is thus used for describing this system, k: [17]

$$T_g = (\omega_1 T_{g1} + k\omega_2 T_{g2})/(\omega_1 + k\omega_2) \qquad (1)$$

where ω_i is the mass fraction of component i, and $k = \Delta C_{p2}/\Delta C_{p1}$, i.e. ratio of heat capacity change of PS polymer ($i = 1$ for the low-T_g component, $T_{g1} = 90°C$) to the change of PCHMA ($i = 2$ for the high-T_g component, $T_{g2} = 110°C$) at T_g. Best fitting was performed by testing the Gordon–Taylor equation with the T_g data, and the best-fitted value of parametric k was found to be 0.12–0.2, indicating relatively low interactions between polymer segments. Is the interaction strength so low that the miscibility is on the borderline or even partial miscibility? Further evidence had to be pursued by examining the morphology and phase structure of the PS/PCHMA blends, which will be discussed in later sections.

3.3. Cloud point

Furthermore, changes of optical clarity of the blends with respect to temperature were also inspected at step-wise elevating temperatures up to where degradation occurred (300°C) in order to monitor whether or not there existed a cloud-point transition. The result of cloud point (initiation) of blend as a function of composition is shown in Fig. 3. Note that for the blend samples of compositions relatively rich in PCHMA (greater than 70 wt%), cloud point transition was not observed. For those compositions, the cloud point transition either did not exist or was located at temperatures too high above degradation to be recorded. For most other compositions (PS-rich, especially), a concave-shape cloud point curve is observed with a minimum temperature of 220°C for the PS/PCHMA blend of 60/40. Does the existence of the cloud point suggest a thermodynamic phase separation from original miscibility? Can the observed cloud point be called a thermodynamic transition of lower critical solution temperature (LCST)? We will address this issue after examining other related evidence for determining possible molecular segregation that influences the equilibrium phase behavior.

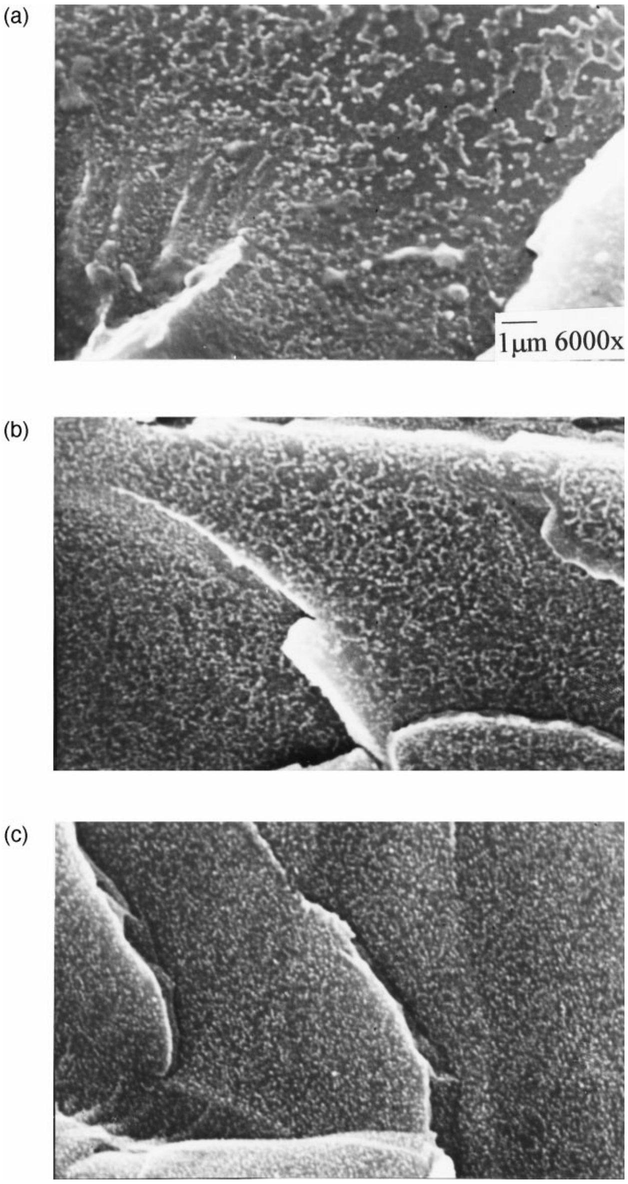

Fig. 4. S.e.m micrographs of the THF-cast PS/PCHMA blend samples: (a) 90/10; (b) 70/30; (c) 50/50.

3.4. Micro heterogeneity in clear cast blend

To probe further, electron microscopy was performed. First, fracture surfaces of the THF-cast (45°C), transparent PS/PCHMA blend with single T_g was examined using s.e.m. S.e.m. was performed on the fracture surfaces of PS/PCHMA samples of various compositions. Fig. 4a–c

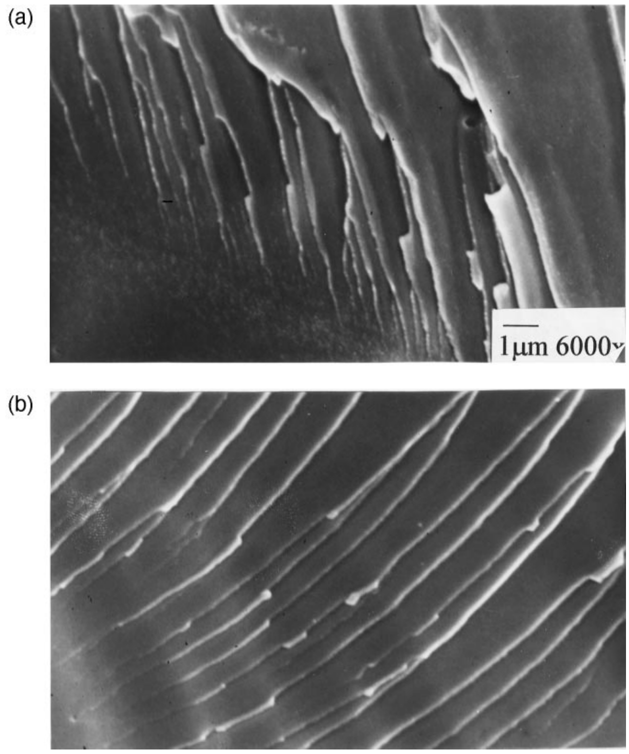

Fig. 5. S.e.m. micrographs of the THF-cast PS/PCHMA blend samples of two PCHMA-rich compositions: (a) 30/70; (b) 10/90.

shows the s.e.m micrographs of the THF-cast PS/PCHMA blend samples of four PS-rich compositions (all THF-cast, 45°C). Especially for the PS-rich compositions of blends (compositions with PS>50 wt% or PCHMA <50 wt%), the micro graphs show that there are tiny (sub-micron) segregated domains (0.3 μm or smaller) scattering across the fracture surface (thickness cross section). Most of the separated domains are partially connected, suggesting a spinodal mechanism. Thus, according to the s.e.m result, these blends were not all completely homogeneous, but exhibited micro phase domains with domain sizes dependent on the composition.

Fig. 5a,b shows the s.e.m micrographs of the THF-cast PS/PCHMA blend samples of PCHMA-rich compositions (THF-cast, 45°C). For both compositions of PCHMA-rich samples (PCHMA >70 wt%, i.e. PS wt% < 30), microphase domains are not observed in the s.e.m. graphs at a large magnification of 6000 × , and the blend samples appeared to be completely homogeneous. Apparently, although miscibility may be possible for the PS/PCHMA blends of PCHMA-rich compositions, the s.e.m. result demonstrates that it is not proper to assess miscibility to the PS/PCHMA blends of PS-rich compositions exhibiting micro phase domains.

An assessment of microphase separation to the PCHMA-rich compositions, of course, is in conflict with the DSC results of single T_g for the corresponding compositions. This demands detailed explanations. The DSC results earlier indicated that for the THF 45°C-cast PS/PCHMA blends of all compositions exhibited a single T_g. In addition, the optical micrographs at the magnification of approximately 1000 × failed to reveal any discernible phase domain(s) either. However, micro phase domains do exist in certain blend compositions. The s.e.m result (6000 × or larger) revealed micro-heterogeneity of ultra small domains (sub-micron) in these transparent-looking blends of PS-rich compositions showing an apparent single T_g. Apparently, the blends appear to be optically clear as the micro phase domains of sub-micron sizes do not scatter light. Similarly, the single T_g in the THF-cast blends might be a result of that the domain sizes are so small that their thermal transition appear ‘homogeneous’ as far as the resolution limit of thermal analysis is concerned. Normally, borderline miscibility with molecular segregation or phase separation in immiscible blends easily leads to a broadened T_g or even two T_gs. However, for the present case, the proximity of the T_gs of the constituent polymers prevents T_g broadening phenomenon being observed.

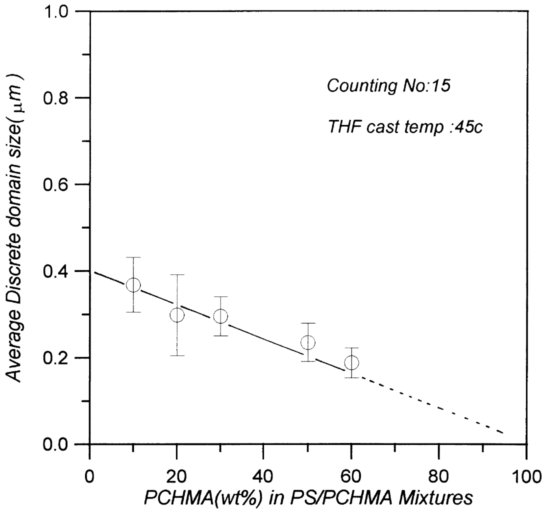

Fig. 6. Micro domain size as a function of PCHMA wt% in the PS/PCHMA blend samples (THF-cast, 45°C).

To show the composition dependence of the micro phase domain, the estimated average size of the discrete phase domains in the PS/PCHMA blends was plotted. Fig. 6 shows the average domain size as a function of PCHMA wt% in the PS/PCHMA blend samples (THF-cast, 45°C). The error bar indicates the size distribution range. The plot shows that the domain size decreases with increasing PCHMA content in the blends. All micro heterogeneous domains are sub-micron, and PS-rich compositions of blends exhibit a relatively larger domain size (0.4 μm). In estimating the average size, the counting number was about 15 and the partial connection between the discrete domains was ignored for simplicity. The domain size is seen to steadily decrease as the PCHMA content increases. For the compositions with PCHMA >70 wt%, micro phase domains were not observed in the s.e.m. graphs, and the domain size is supposedly approaching zero as PS and PCHMA become completely soluble within these compositions.

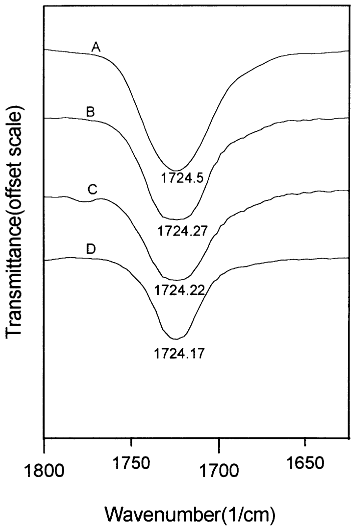

Fig. 7. Carbonyl IR absorbance peaks for the samples: (A) neat PCHMA; and (B) PS/PCHMA blend (30/70); (C) 50/50; and (D) 70/30 blend compositions; and (E) neat PS.

The above s.e.m results have demonstrated that the as-cast (THF, 45°C) transparent PS/PCHMA blends with a single T_g actually were phase-separated, which are more apparent for the PCHMA-rich compositions. The microphase domains, however, are likely beyond detection limits of optical light techniques or thermal analysis. Earlier reports in the literature [16][18][19] also discussed similar situations where single T_g in the d.s.c thermograms alone does not necessarily indicate thermodynamic phase homogeneity or miscibility in the blends. This phenomenon is frequently encountered in cases where the phase domains are small and beyond the detection sensitivity of d.s.c.

Fig. 7 shows the offset plots of carbonyl i.r. absorbance peaks (located at approximately 1725 cm^{-1}) for the samples: (A) neat PCHMA, and (B) PS/PCHMA blend (30/70); (C) 50/50, and (D) 70/30 blend compositions; and (E) neat PS. These spectra show that the carbonyl absorbance peak shift is negligible, suggesting relatively low level of specific interactions, if any. The carbonyl group of PCHMA does not seem to interact specifically with any cites of the PS molecules. Fig. 8 shows the spectra in the wavenumber range where the absorbance peaks of ether group (1157 cm^{-1}) of PCHMA and aromatic C–H bending (700 cm^{-1}) of PS are compared. The ether (C–O–C) peak of PCHMA does not show significant shifting with respect to blend composition. One likely site of interaction is between the ether or carbonyl of PCHMA and the phenyl ring of PS. The aromatic C–H bending of PS is seen to remain at 700 cm^{-1} regardless of molecular environment change brought about by forming a mixture with PCHMA. The C–H bending absorbance peak stays at the same wavenumber for the neat PS and PS/PCHMA blend samples alike.

Hsu et al. [20] conducted a spectroscopy study on PS-PVME blends in compatible or non compatible state, and concluded that the vibrations most sensitive to change in molecular environment of compatibility are the CH out-of-plane bending (700 cm^{-1}) in PS and C–O–CH_3 stretching (1100 cm^{-1}) of PVME. The change, either in terms of wavenumber for the 700 cm^{-1} peak or intensity for the 1100 cm^{-1} peak, is relatively minor. By contrast, corresponding changes were not observed in the present PS/PCHMA blend system regardless of miscibility state. The experimental i.r. result in this study shows that possible interactions between likely functional groups in PS and PCHMA are relatively low or non-specific. Therefore, the FT-i.r. analysis agrees with the T_g result of blends revealing relatively low intermolecular interaction forces.

4. Conclusion

The blend system of PS with PCHMA has been studied in greater details as some controversy exists regarding the phase structure being miscible or not. The controversy was especially difficult to resolve as a result of proximity of the T_gs of the constituent polymers. Ideally, direct melt-blending should be employed in preparing the blend samples to exclude possible solvent effect on equilibrium phase behavior. However, melt-blending must be performed at 250°C or higher and could not be proceeded without inducing gross phase separation above the cloud point of 220°C or higher. Optimum solution blend methods were searched, and it was found that the THF casting at 45°C led to the best samples with optically clear and homogeneous film samples ideally suitable for electron microscopy characterization as well as thermal analysis and FT-i.r.

We further attempted to clarify the true state of phase structure of this blend by carefully analyzing the s.e.m. micrographs in comparison with the DSC result. The polymer blends with a single T_g are generally expected to exhibit a homogeneous structure, with at least scales corresponding to the molecular segments responsible for thermal transition. Surprisingly not all blends with single T_g and optically homogeneous are really homogeneous in phase structure when observed using the s.e.m. The cloud point phenomenon observed in this blend system may not be confused with thermodynamic behavior of LCST. The 45°C-cast blend may seem to be optically clear using optical microscopy. However, they still may contain submicron phase domains beyond the detection limits of the optical microscopy. Thus, the cloud point transition at which an optically clear/transparent appearance to opaque/cloudy occurs must be carefully assessed. If the mixtures already contained submicron phase domains, then obviously the mixtures were not in a solution state. The observed cloud point may not be appropriately called a thermodynamic transition of lower critical solution temperature (LCST).

Composition dependence of the phase behavior was observed. For the compositions of PCHMA-rich (PCHMA>70 wt%, i.e. PS wt% $<$ 30), microphase

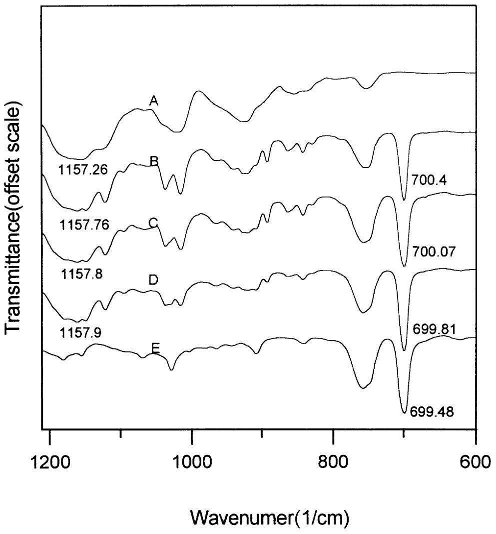

Fig. 8. IR absorbance peaks of the pendant ether group (in PCHMA) and aromatic C-H bending (in PS) for samples: (A) neat PCHMA, PS/PCHMA blend; (B) (30/70); (C) 50/50; (D) 70/30; and (E) neat PS.

domains are not observed and the blends appeared to be homogeneous. For the PS-rich compositions, however, sub-micron phase domain of 0.4 μm or smaller (spinodal decomposition) was observed. The s.e.m. result proved that it is not proper to assess miscibility to the PS/PCHMA blends of all compositions even though an apparently single T_g is observed for the blends. Note that although an apparent single T_g was identified for the PS-rich blend compositions, the change of the blend's T_g was relatively insensitive to the composition. This phenomenon suggests that the PCHMA polymer in the mixtures (PS-rich compositions) may likely be segregated and predominantly in the discrete microphase domains rather in a homogeneous solution state. For the PCHMA-rich (PCHMA wt%>70) blend compositions, the state of phase structure was found to be different from PS-rich ones. No micro phase domains could be observed in the s.e.m. micrographs for the PCHMA-rich compositions. The single T_g for the PCHMA-rich blend compositions obviously changed with composition and followed a relationship described by the Gordon–Taylor model. Thus, partial miscibility does exist, although it is not appropriate to assess miscibility to entire compositions range of the seemingly homogeneous blends of PS/PCHMA. The PCHMA-rich compositions are judged to be miscible but the PS-rich compositions are only partially miscible with micro discrete phase domains beyond detection limit of optical microscopy. The proximity of the T_gs also prevented that the thermal transition of the micro phase domains in the PS-rich blends being resolved.

Acknowledgements

Research grant was provided by National Science Council of Taiwan (# NSC 87-2216-E006-005). Instrument support of scanning electron microscopy by NSC Tainan Regional Instrument Center is acknowledged. The author (EMW) appreciates the competitive university (NCKU) matching fund for acquiring some of the analytical instruments used in this study.

References

[1] Stoelting J, Karasz FE, MacKnight WJ. Polym Engng Sci 1970;10:133.
[2] Shultz AR, Beach BM. Macromolecules 1974;7:902.
[3] Prest WM Jr, Porter RS. J Polym Sci, Part A-2 1972;10:1639.
[4] Kwei TK, Nishi T, Roberts RF. Macromolecules 1974;7:667.
[5] Bank M, Leffingwell J, Thies C. Macromolecules 1971;4:43.
[6] Bank M, Leffingwell J, Thies C. J Polym Sci, Part A-2 1972;10:1097.
[7] Mandal TK, Woo EM. Polymer (in press).
[8] Shultz AR, Young AL. Macromolecules 1980;13:663.
[9] Friedrich C, Schwarzwalder C, Riemann R-E. Polymer 1996;37:2499.
[10] Kim CK, Paul DR. Macromolecules 1992;25:3097.
[11] Kyu T, Saldanha JM. J Polym Sci, Polym Lett 1989;27:421.
[12] Butzbach GD, Wendorff J. Polymer 1991;32:1155.
[13] Landry ChJT, Henrichs PM. Macromolecules 1989;22:2157.
[14] Debier D, Devaus J, Legras R. J Polym Sci, Polym Phys 1994;33:407.
[15] Nishimoto M, Keskkula H, Paul DR. Polymer 1991;32:272.
[16] Woo EM, Su CC. Polymer 1996;37:4111.
[17] Olabishi O, Robeson LM, Shaw MT. In: Polymer–polymer miscibility, chap. 6. New York: Academic Press, 1979:279.
[18] Zhang H, Bhagwagar DE, Graf JF, Painter PC, Coleman MM. Polymer 1994;35:5379.
[19] Cowie JMG, Li G, McEwen IJ. Polymer 1994;35:5518.
[20] Lu FJ, Benedetti E, Hsu SL. Macromolecules 1983;16:1525.