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ORIGINAL CONTRIBUTION

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Ternary upper-critical-solution-temperature behavior in a blend system comprising poly(2,6-dimethyl-1,4-phenylene oxide), poly(4-methyl styrene), and polystyrene

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Abstract Upper-critical-solution-temperature (UCST) behavior in a ternary blend of poly(2,6-dimethyl-1,4-phenylene oxide), poly(4-methyl styrene), and polystyrene is reported. The as-cast ternary blend is immiscible at ambient conditions and comprises two different phases, and, however, turns into a miscible system above the "clarity point" ranging from 160 to 300 °C for different ternary compositions. The maximum clarity point is labeled as the UCST for the ternary system, which is about 295 °C. Above the clarity point, the originally immiscible ternary blend turned into one miscible phase. Owing to the thermodynamic UCST behavior and kinetic hindrance, the immiscible ternary polymer blend can be locked into a pseudo-miscible state if it is heated to a temperature above the clarity point followed by a rapid-cooling processing scheme. The quenched ternary blend can remain in a pseudo-miscible state as long as the service temperature does not exceed the glass-transition temperature of the blend.

Keywords Poly(2,6-dimethyl 1,4-phenylene oxide) · Poly(4-methyl styrene) · Polystyrene · Ternary blend · Upper critical solution temperature

Introduction

The most widely studied blends involving polystyrene (PS) are probably those with some ether-containing polymers. The blend system of PS with poly(2,6-dimethyl-*p*-phenylene oxide) (PPO) is one of the most studied polyblends in this class, and its miscibility has been long demonstrated [1, 2]. The PS/PPO blend system is known to be fully miscible with no observable lower-critical-solution-temperature (LCST) behavior (within the experimentally accessible temperatures). Following the discovery of interesting miscibility in a PPO/PS blend in 1970, other blend systems of PPO with different styrenic polymers (such as modified PS) have also been investigated [3, 4, 5]. Attempts have also been made to understand the phase behavior in blends of PPO with a specific styrenic polymer, poly(4-methyl styrene) (P4MS or P*x*MS), which differs from PS by an extra methyl group at the para position (or *x* position) of the pendant phenyl group [6, 7, 8]. The complexity of the phase behavior in the PPO/P4MS system has led to conflicting results and perhaps occasional misinterpretations in the past. Some investigators concluded miscibility occurred, while others found immiscibility in the binary PPO/P4MS system. With the recent reporting of an upper critical solution temperature (UCST) in the binary PPO/P4MS blend system, a settlement was found for the conflicting arguments that had gone on for quite a long time in determination of the thermodynamic phase behavior of the binary PPO/P4MS blend system. UCST behavior in the blend of PPO/P4MS indicates that it is immiscible at ambient temperature but can exhibit miscibility at elevated temperatures. In addition, the phase behavior of blends comprising PS and P4MS was found to be an UCST binary blend [9]. This is interestingly comparable to the more widely studied blend system of PS and PαMS, which is also found to be an UCST system [10, 11, 12, 13]. It is generally known that upon heating to higher temperatures, an originally miscible blend may undergo a process going from original phase homogeneity to phase separation, which is a phenomenon known as the cloud-point transition with the critical point termed as the LCST. The temperature at which the blend turns to a cloudy (phase separation) appearance upon heating is termed the "cloud point". The opposite behavior can be observed in an originally immiscible blend, and is termed the UCST phenomenon. The temperature at which the blend becomes clear, homogeneous and transparent upon heating is hereby termed the "clarity point".

UCST or LCST behavior in ternary blends has not been widely reported. The objectives of this study were to examine the phase behavior and morphology evolution during the UCST demixing/mixing transition in PPO/P4MS/PS mixtures.

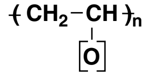
Experimental

Materials

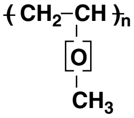
Amorphous PPO was purchased from a specialty polymers supplier (Polysciences, USA), with an approximate $M_w = 50,000$ g/mol (gel permeation chromatograph, GPC) and $T_g = 207$ °C. P4MS was obtained from Scientific Polymers Product (SP2), USA, with an approximate $M_w = 70,000$ g/mol (GPC) with a polydispersity index of about 3.3 and $T_g = 106$–110 °C (onset). PS was purchased from Polysciences, USA, with $M_w = 250,000$ g/mol (GPC). The T_g of this grade of PS was 90 °C. The polymer materials were free of additives and were used without further purification.

The chemical structures of PS, P4MS, and PPO are as follows:

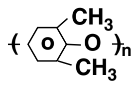
PS:



P4MS:



PPO:



The blend samples in this study were prepared by solvent-mixing and solution-casting from chloroform at a constant temperature slightly higher than ambient (45 °C). For labeling purposes, PPO is labeled as component 1, P4MS as component 2, and PS as component 3. The ternary blend compositions are designated as weight ratios of $x/y/z$, where $x+y+z=100$ and x, y, and z represent the contents (0–100) of components 1, 2, and 3 in the ternary blend. As there are numerous combinations of ternary blend compositions, it was impossible to cover the full range in small increments. For a balance of convenience and detail, the ternary blend compositions were covered in four systematic variations. First, P4MS was kept constant at 10 wt% while the relative ratios of PPO/PS in the ternary PPO/P4MS/PS were systematically changed from low to high; this is designated as the ($x/10/z$) series. A second series of ternary compositions was chosen in a way that the relative PPO/PS contents were kept constant at equal proportions (1/1) but the content of P4MS was varied from low to high (10–80 wt%); this is termed the ($x/y/x$) series, where $2x+y=100$. A third series of ternary compositions was chosen in such a way that the relative PPO/P4MS contents were kept constant at equal proportions (1/1) but the content of PS was varied from low to high (10–80 wt%);this is termed the ($x/x/z$) series. A fourth series of ternary compositions was chosen in a way that the relative P4MS/PS content was kept constant at equal proportions (1/1) but the content of PPO was varied from low to high (10–80 wt%); this is termed the ($x/y/y$) series. These four series of samples cover most of all the possible ternary compositions in the full range.

Apparatus

A polarized-light microscope (Nikon Optiphot-2 Pol) was used for observation of optical phase behavior. The blend cast films were placed on the microscope heating stage (Linkam THMS-600 with TP-92 temperature programmer) for observation at temperatures higher than ambient. Most of the as-cast ternary blend samples were optically cloudy when examined using optical microscopy (1,000×). The ternary blend samples were heated slowly in a microscope heating stage (2 °C/min) and the temperatures at which the sample turned from a cloudy (phase-separated domains) to clear (one phase) appearance were examined using the optical microscope and the temperatures of the apparent phase transitions were carefully recorded.

The glass-transition temperatures and other thermal transitions of the ternary blend samples were measured with a differential scanning calorimeter (DSC) (PerkinElmer DSC-7) equipped with a mechanical intracooler (down to −60 °C) and a computer for data acquisition/analysis. Additional subambient DSC runs (temperatures down to −80 °C) were cooled with a liquid nitrogen tank and helium gas purge. Unless otherwise specified, all the T_g measurements were made at a scan rate of 20 °C/min on second scanning after quenching from above the estimated T_g. The T_g was taken as the onset of the transition (the change of the specific heat) in the DSC thermograms.

Results and discussion

DSC thermograms revealing two T_g for most of the representative as-cast ternary PPO/P4MS/PS blend samples are shown in Fig. 1. A small number of samples exhibited an apparent single T_g (possibly overlapping T_g), which, however, displayed distinctly phase separated morphology. The DSC thermal evidence clearly demonstrates immiscibility in the as-cast ternary blend system. The results suggest that there are at least two phases in the as-cast ternary blend system. These two phases might be associated with PPO/PS in one phase and with P4MS in another, respectively. DSC traces for other ternary blend compositions are too numerous for all of them to be shown here. For reasons of brevity, only the results for some representative samples are shown in Fig. 1.

T_g versus composition for a series of as-cast ternary PPO/P4MS/PS ($x/y/y$ I series) blend samples is shown in Fig. 2. The DSC results revealed two distinct T_g for several ternary compositions. For other samples examined using DSC, two T_g were not evident, but the microscopy result showed apparent immiscibility in the as-cast ternary blend system. It must be emphasized that thermal analysis does not always reveal multiple T_g in a phase-separated blend system owing to masking, broadening, or overlapping effects. The plots shows the trend of T_g variation and suggest that the upper T_g of the

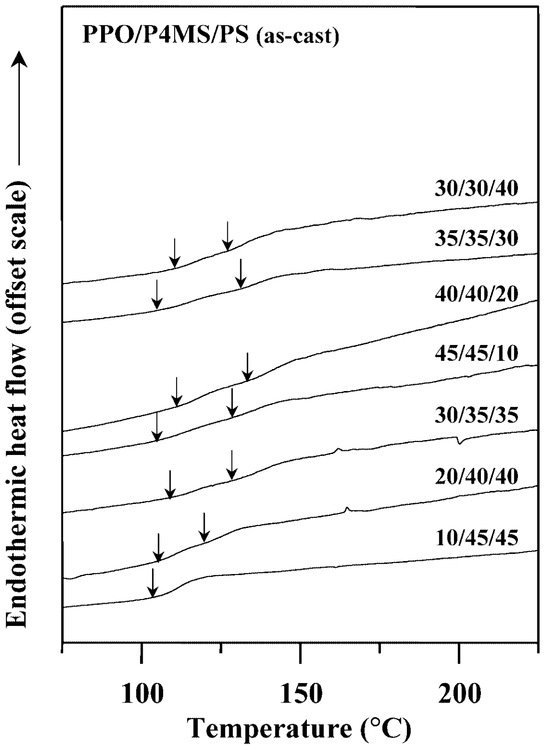


Fig. 1 Differential scanning calorimetry (*DSC*) thermograms for as-cast ternary poly(2,6-dimethyl-1,4-phenylene oxide) (*PPO*)/poly(4-methyl styrene) (*P4MS*)/polystyrene (*PS*) blends

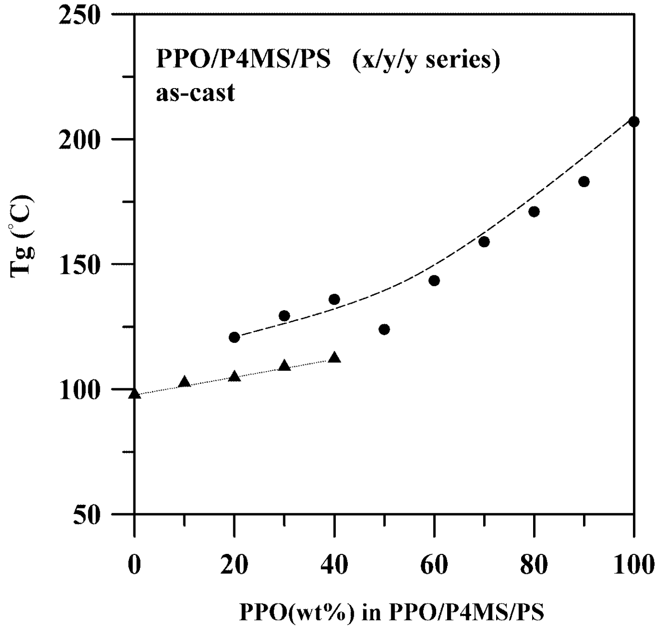


Fig. 2 T_g versus composition for a specified series of as-cast ternary PPO/P4MS/PS blends (*x*/*y*/*y* series)

ternary blend system might be associated with the PPO/PS domain, while the other T_g (the lower one) may be associated with the P4MS domain. Plots of T_g versus composition for the other three series of as-cast ternary PPO/P4MS/PS (II, III, and IV series samples) are similar, and for reasons of brevity are not shown here.

"Clarity point" and UCST in the ternary blends

The as-cast PPO/P4MS/PS blends of all compositions were heated and examined using polarized-light optical microscopy (POM) to reveal the "clarity point". The clear-point temperatures for the ternary PPO/P4MS/PS blend are summarized in Tables 1 and 2. The results for the clarity points, T_g, and the phase behavior for the $x/y/y$ series (I), the $x/x/z$ series (II), and the $x/y/x$ series (III) are listed in Table 1. The result for the $x/10/z$ series, where $x+10+z=100$, is listed in Table 2. x, y, and z represent the contents (0–100) of the PPO, P4MS, and PS components, respectively, in the ternary blend.

It would be interesting to compare the experimental cloud points for the ternary system to those of the binary

Table 1 Summary of phase behavior of ternary poly(2,6-dimethyl-1,4-phenylene oxide) (*PPO*)/poly(4-methyl styrene) (*P4MS*)/polystyrene (*PS*) blend systems. *x*: phase separation, *o*: no phase domains; clarity point: the temperature of phase change from two phases (cloudy) to one phase (clear)

PPO/P4MS/PS	Clarity point (°C)	T_g (°C)	Comments
I: $x/y/y$ series, where $x+2y=100$			
10/45/45	> 300	103.3	x
20/40/40	> 300	105.4, 120.7	x
30/35/35	> 300	109.8, 129.3	x
40/30/30	> 300	113.0, 135.9	x
50/25/25	274	123.9	x
60/20/20	273	143.4	x
70/15/15	266	158.9	x
80/10/10	–	171.0	o
90/5/5	–	183.0	o
II: $x/x/z$ series, where $2x+z=100$			
45/45/10	275	104.7, 129.7	x
40/40/20	282	111.9, 134.5	x
35/35/30	286	104.2, 132.1	x
30/30/40	274	110.7, 127.6	x
25/25/50	265	100.0, 121.4	x
20/20/60	267	106.5	x
15/15/70	252	103.6	x
10/10/80	225	100.0	x
III: $x/y/x$ series, where $2x+y=100$			
40/20/40	276	127.4	x
35/30/35	295	111.3, 135.6	x
30/40/30	275	101.6, 131.3	x
25/50/25	268	106.9, 126.9	x
20/60/20	278	108.3, 131.3	x
15/70/15	285	107.1, 131.5	x
10/80/10	265	106.5	x
5/90/5	166	106.5	x

Table 2 Summary of phase behavior of ternary the PPO/P4MS/PS blend system

PPO/P4MS/PS	Clarity point (°C)	T_g (°C)	Comments
IV: $x/10/z$ series, where $x + 10 + z = 100$			
10/10/80	225	100.0	x
20/10/70	240	107.9	x
30/10/60	262	122.2	x
40/10/50	275	128.4	x
50/10/40	264	135.2, 150.0	x
60/10/30	258	143.2, 161.4	x
70/10/20	260	143.2, 167.0	x

ones. The clarity points for the ternary PPO/P4MS/PS system ($x/y/y$ series) are compared with those for the binary PPO/P4MS or P4MS/PS blends in Fig. 3. Interestingly, the clarity points for the ternary UCST system are comparatively higher than those for the two binary blend systems, which also exhibit UCST behavior (PPO/P4MS and P4MS/PS, respectively). The result suggests that a higher temperature, on average, is needed for the ternary PPO/P4MS/PS blend to undergo an UCST phase transition than the respective binary UCST systems. Plots of the clarity points for the other series of ternary PPO/P4MS/PS blend samples are similar. A consistent trend is seen that the clarity points and UCST for the ternary blend system are always higher than those for the binary PPO/P4MS or P4MS/PS blends.

Scanning electron microscopy (SEM) micrographs of several representative ternary compositions of the as-cast blend are shown in Fig. 4. The SEM morphology reveals interesting phase-in-phase domains, with one domain being interconnected and the other being discrete. The discrete spherical domain, in turn, contains

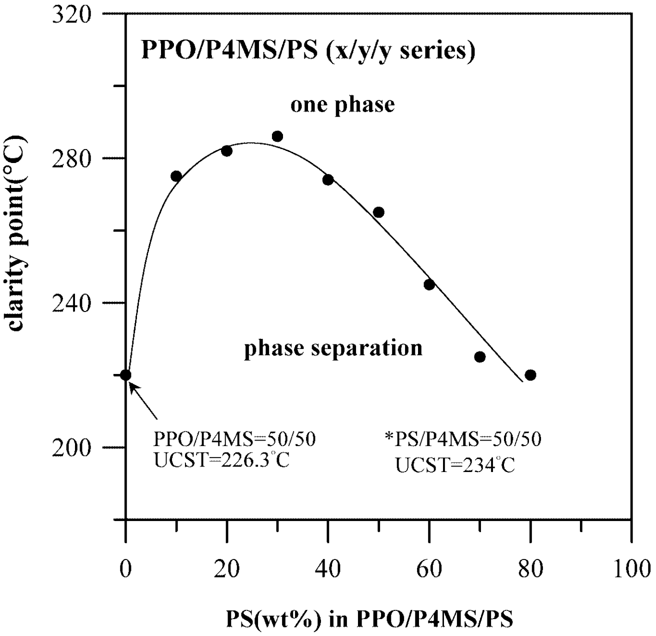


Fig. 3 Clarity points for the ternary PPO/P4MS/PS blend ($x/y/y$ series) compared with those for the binary PPO/P4MS or P4MS/PS blends

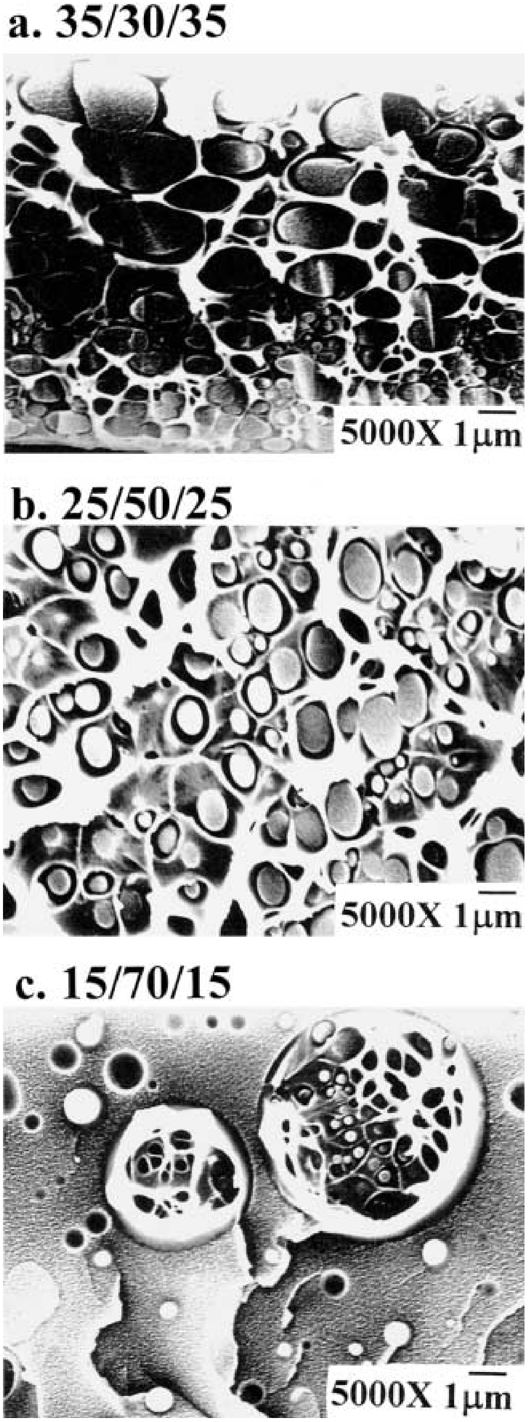


Fig. 4 Scanning electron microscopy micrographs of several representative ternary compositions of the as-cast blend: **a** 35/30/35, **b** 25/50/25, and **c** 15/70/15

an interconnected phase and a discrete phase. Other compositions of as-cast ternary blend samples revealed a similar phase-separated morphology and are not all shown for brevity.

To summarize the phase behavior of the PPO/P4MS/PS system, Fig. 5 shows the result in a triangular diagram for all ternary blend compositions examined in this study. The ternary blend system is apparently immiscible as judged by the thermal evidence of two glass transitions and visible phase domains found in the ternary compositions. Note that only two extreme PPO/P4MS/PS compositions (90/5/5 and 80/10/10) were judged to be miscible according to the T_g and POM criteria; all other compositions of the as-cast ternary blend in the diagram were phase-separated. Apparently, this ternary blend can be classified as an UCST system, whose "clarity points" range from 160 to 300 °C. The maximum clarity point, which is the UCST for the ternary system, is about 295 °C for a composition of PPO/P4MS/PS (35/30/35) that is near the center of the triangle plot.

Pseudo-miscibility

The result has shown that the originally immiscible PPO/P4MS/PS blend can be brought to a miscible state by heating it to a temperature above the "clarity point". Owing to kinetic hindrance, the blend may be locked (i.e., kinetically preserved) into a pseudo single phase by rapid quenching. The blend samples of a few compositions were heated to various temperatures above the UCST, stabilized at intended temperatures, then quickly quenched to ambient to freeze the phase morphology. DSC was then performed to reveal the glass transitions in these samples. The DSC traces for the heated/quenched blend samples are shown in Fig. 6. The as-cast PPO/P4MS/PS blend showed two T_g, as discussed earlier for its two-phase morphology (Fig. 1). By comparison, the heated/quenched PPO/P4MS/PS samples exhibited a single T_g revealing a kinetically preserved pseudo single phase in the quenched ternary blend. The thermodynamic and kinetic nature of the UCST transition in the PPO/P4MS/PS ternary system is evident. Expectedly, after thermal processing above the UCST, the ternary blend can be locked into a miscible state if rapid cooling is imposed. The ternary blend can remain miscible as long as the service temperature does not exceed the glass-transition temperature of the ternary blend.

Apparently, the UCST phase transition in the PPO/P4MS/PS ternary blend may be reversible if kinetically accessible time is allowed for the process. Earlier studies have shown that reversibility may be expected in the UCST system. Although heating can turn an originally immiscible polymer blend into a miscible state, the miscibility above the UCST could also be returned back

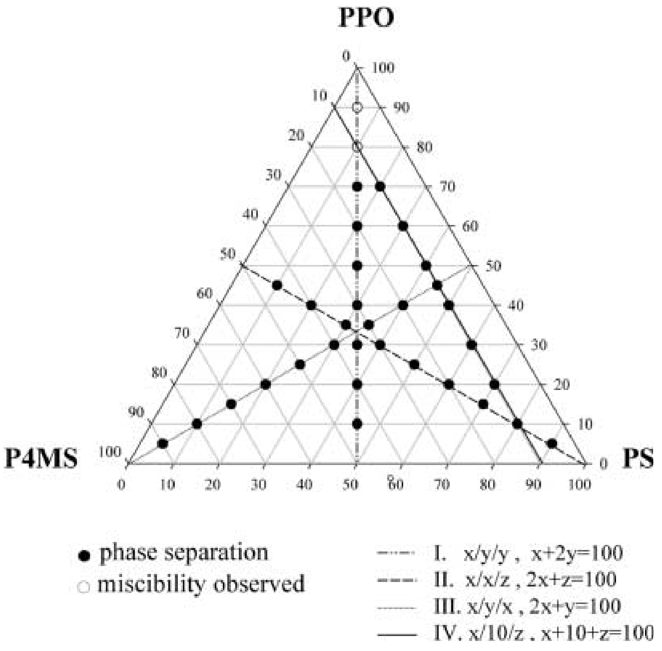


Fig. 5 Triangular diagram for all the ternary blend compositions examined in this study

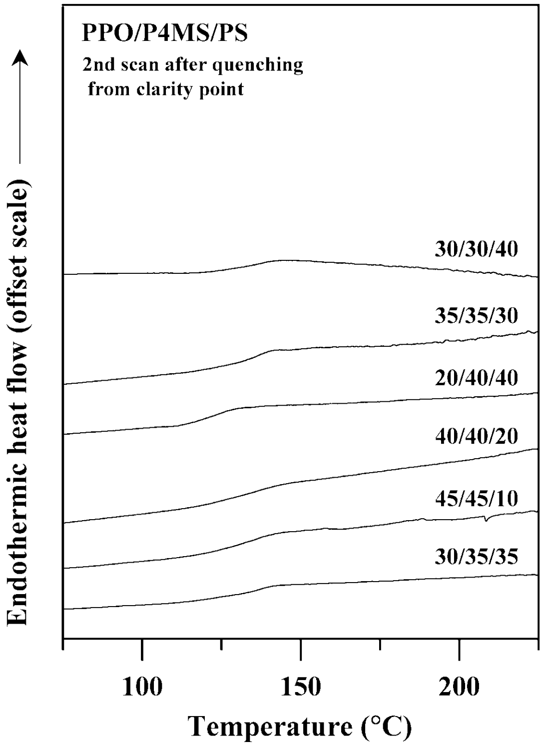


Fig. 6 DSC traces for heated/quenched ternary blends of PPO/P4MS/PS of a few representative compositions

to its original immiscibility below the UCST, if given sufficient time for the polymeric chains to reorganize, for example, by controlled slow cooling rather than rapid quenching.

Conclusion

A ternary UCST blend of PPO/P4MS/PS was reported. The ternary blend system was determined to be immiscible at ambient temperature but could undergo a thermodynamic phase transition into a miscible system above the clarity point ranging from 160–300 °C for different compositions. The maximum clarity point, labeled as the UCST for the ternary blend system, is about 295 °C. The thermal analysis showed that the ternary blend below the clarity points displayed two phases that might be associated with PPO/PS in one phase and P4MS in another. The SEM morphology reveals interesting phase-in-phase domains, with one domain being interconnected and the other being discrete. When kept above the clarity point, however, the ternary blend turned into a single phase, which is evidenced with SEM, POM, and glass-transition temperature data. The ternary blend can be locked into a pseudo-miscibility state if it is subjected to a processing scheme of heating it to a temperature above the clarity point followed by rapid quenching. Thus, although the thermodynamic nature for the ternary blend system involves immiscibility and UCST behavior, the PPO/P4MS/PS can be kinetically processed to exploit useful properties related to ternary pseudo-miscibility.

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