

B. S. Huang
E. M. Woo

Blends of a novel high-temperature poly(oxy-1,4'-diphenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene) with poly(ether imide): structure, interaction, and miscibility

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B. S. Huang · E. M. Woo (✉)
Department of Chemical Engineering
National Cheng Kung University
Tainan 701-01, Taiwan
e-mail: emwoo@mail.ncku.edu.tw
Tel.: +886-6-2757575 ext. 62670
Fax: +886-6-2344496

Abstract Polymer miscibility has been discovered in a blend system comprising poly(ether imide) (PEI) and a new poly(ether diphenyl ether ketone) (PEDEK). The miscibility of the PEDEK/PEI polymer system (quenched from the molten state) was investigated in this study using differential scanning calorimetry and Fourier transform (FT-IR) spectroscopy. A composition-dependent single glass-transition temperature (T_g) in the PEDEK/PEI blends over a full composition range was observed; the sharp transition width and the T_g -composition relationship both suggest that the scale of mixing is fine and uniform. Evidence based

on observation of the cold-crystallization peak and suppression of the blend crystallinity and melting peak also indicated intimate intermolecular mixing. The FT-IR result yielded further evidence that the physical interactions leading to miscibility were weak, with no apparent specific interactions between the constituent polymers. Relationships between structures and interactions responsible for the miscibility in PEI and several ether-ketone-type polymers are briefly discussed.

Key words Miscibility · Poly(ether imide) · Poly(ether diphenyl ether ketone) · Interaction

Introduction

Poly(ether imide) (PEI), which contains imide rings and phenyl ether groups, is known to be miscible with a few polyarylates containing a carbonyl ($-\text{CO}_2$) group in the main chains. As an example, blends of PEI and poly(ethylene terephthalate) (PET) are miscible [1, 2]. A recent study revealed that PEI was also miscible with poly(butylene terephthalate) (PBT) [3, 4]. However, other than the demonstrated miscibility in the blends of PEI/PBT and PEI/PET, the PEI polymer has not been shown to be miscible with any other polyarylates. Additionally, miscibility in blends of PEI with aryl-ether-ketone-type polymers, whose main chains contain a carbonyl and an ether linkage between the phenyls, has been an interesting subject of extensive study. Poly(aryl ether ketones) are an interesting class of engineering polymers with high-temperature applications, while PEI

is an amorphous, high-glass-transition-temperature (T_g) polymer. It has long been established that PEI is miscible with poly(ether ether ketone) (PEEK) [5]. The miscibility in PEEK/PEI is probably the most well known and most extensively studied in all miscible blend systems involving PEI and poly(aryl ether ketone)s. This blend system is particularly interesting because of potential advantages of exploiting the synergistic properties of amorphous PEI and semicrystalline poly(aryl ether ketone)s, which have attracted much recent research [6–9]. Generally, PEI offers toughness, a high T_g , and thermal stability, while the aryl-ether-ketone polymers usually offer crystallinity, solvent resistance, and easy flow at the processing temperature.

Since the discovery of PEEK in late 1970, many other poly(aryl ether ketone) variants with modifications of chemical structures of PEEK have also been synthesized in order to exploit structure-property optimization. Interestingly, PEI has been shown to be miscible with

a few different poly(aryl ether ketone)s of various chemical repeat units. For example, in addition to the demonstrated miscible PEI/PEEK, miscibility of PEI with poly(ether ketone) (PEK) has also been demonstrated [5]. More recently, miscibility in the blend of PEI with a new member of the aryl-ether-ketone polymers, whose structure contains meta-phenyl and biphenyl groups (also called PK99), was recently discovered [10]. Our concurrent study has found the interaction parameter (χ) between PEI and PK99 to be -0.35 [11]. In comparison, the interaction parameter of the PEI/PEEK system based on melting-point depression is -0.4 [12]. The result for the PK99-PEI system and the literature value of χ for the PEEK-PEI system both indicate that the specific interactions between the aryl-ether-ketone polymers and PEI are comparable and are only relatively weak.

As a continuation of previous studies, we report here the result of a miscibility study using PEI and a new high-melting-point poly(ether diphenyl ether ketone) (PEDEK). In addition, structural windows of aryl-ether-ketone-type polymers that are capable of forming miscible blends with PEI are briefly discussed. The miscibility of PEDEK with PEI and the effects chemical structural factors of general aryl-ether-ketone polymers on miscibility are discussed.

Experimental

Materials and preparation

The PEI polymer, with IUPAC name of poly(2,2'-bis(3,4-dicarboxyphenoxy) phenylpropane-2-phenylene bisimide), was obtained from Polysciences. The M_w of PEI is 30,000 g/mol with no additives. PEI is fully amorphous and is not crystallizable, but due to the highly aromatic structure and imide ring in the main chain it has a high T_g of 215 °C. The novel high- T_g PEDEK, with IUPAC name of poly(oxy-1,4'-diphenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene), was synthesized in this laboratory. Although the synthesis of PEDEK was briefly mentioned in recent reports [13, 14], detailed procedures have not been described or disclosed. In this study, we performed synthesis of PEDEK by slightly modifying the established routes for polymerization of other similar types of aryl-ether-ketone polymers, whose procedures were documented in the literature earlier [10, 15].

Synthesis of PEDEK

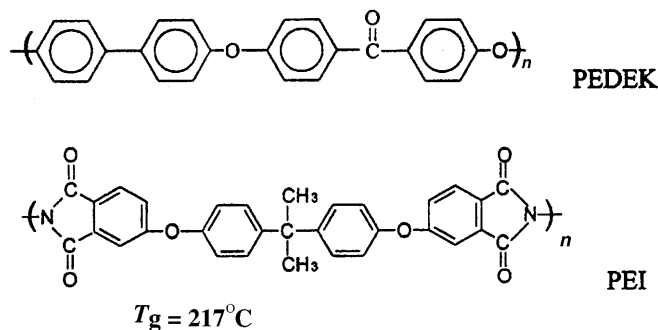
Monomers and materials

4,4'-Difluorobenzophenone (TCI, Japan), 4,4'-dihydroxybiphenyl (Lancaster, UK), diphenylsulphone (Lancaster, UK), K_2CO_3 , and Na_2CO_3 (Showa Chemicals, Japan) were used as received.

Procedures

4,4'-Difluorobenzophenone (2.182 g, 0.01 mol), 4,4'-dihydroxybiphenyl (1.862 g, 0.01 mol), and diphenylsulphone (8.0 g), used as a solvent for solution polymerization, were simultaneously added to a 250-ml three-necked round-bottomed flask fitted with

an overhead stirrer, a nitrogen inlet, thermocouple, and a receiver. The mixture in flask was firstly heated in a sand bath to 175 °C. At this temperature, the contents were in a liquid state. Then, Na_2CO_3 (1.06 g, 0.01 mol) and K_2CO_3 (0.028 g, 0.002 mol) were added to the reaction mixture. The temperature was gradually raised at 1 °C/min until the temperature of the mixture reached 320 °C. After 60-min reaction, an additional quantity of 4,4'-difluorobenzophenone (0.02 g) was added to the flask. After 5 min, the product was poured onto an aluminum sheet, allowed to cool, and then ground to a fine powder. The high-boiling-point diphenylsulphone and residual inorganic salts were removed by leaching several times with acetone (25 °C) followed by water (80 °C). Finally, the polymer was dried at 120 °C under vacuum for 24 h. Preliminary differential scanning calorimetry (DSC) characterization showed $T_g = \sim 156$ °C and a melting point of 396 °C. The chemical structures of PEDEK and PEI are as follows:



Blending procedures

Melt mixing was not feasible as PEDEK melts at a quite high temperature (400 °C) and thermal degradation was a concern. Common solvents for dissolving both components had to be found. Although PEI is amorphous and easily soluble, the semicrystalline high- T_g PEDEK is not easily soluble in solvents. A common solvent, diphenylsulphone, was found to be suitable for dissolving (at elevated temperatures) both PEI and PEDEK. This solvent has a high boiling point, and care must be taken to remove the solvent after blending. The neat polymers (0.35 g total), weighed in proper weight ratios, were pulverized to a fine powder and codissolved into diphenylsulphone (15 g) at 260 °C with continuous stirring for 120 min. The well-mixed polymer solution was then poured into iced water and the precipitate was ground to powder. Purification was performed by washing with acetone (20 °C), which was followed by final separation with centrifugation. Pure water (80 °C) was then used to wash the solid. The washed solid was then placed in a vacuum oven at 140 °C for 24 h.

Apparatus

The T_g , crystallization temperatures, and melting points of the blend samples were measured using a differential scanning calorimeter (Perkin-Elmer DSC-7) equipped with an intracooler and a computer for data acquisition/analysis. All T_g and/or crystallinity measurements were made at a scan rate of 20 °C/min within the range 25–420 °C, unless otherwise indicated. For a uniform comparison, the T_g values were taken as the onset in the DSC thermograms. The calorimetric measurements were performed immediately after the polymer samples had been quenched in the calorimeter cells from temperatures above their melt state.

A polarized-light optical microscope (Nikon Optiphot-2 POL) with a microscope heating stage (Linkam THMS-600 with TP-92 temperature programmer) was used to examine and confirm the phase structure of the polymer mixtures. Further, the morphology of the samples was examined using a scanning electron microscope (SEM, JEOL JXA-840). The samples were fractured across the

thickness and coated with gold by vapor deposition using a vacuum sputterer prior to SEM characterization.

Fourier-transform IR spectroscopy (FT-IR, Nicolet Magna-560) was used for investigating possible molecular interactions between the constituent polymers. Spectra were obtained at 2-cm^{-1} resolution and averages of spectra were obtained from at least 64 scans in the standard wavenumber range of $400\text{--}4000\text{ cm}^{-1}$. All the blend samples for FT-IR analysis were melt-molded as thin films sandwiched between two KBr pellets at $410\text{--}420\text{ }^{\circ}\text{C}$. Quenching of the samples was performed by quickly dipping them into liquid nitrogen while the KBr-sandwiched polymer was still in a molten state.

Results and discussion

Thermal and morphological evidence

The optical clarity and phase homogeneity of the PEDEK/PEI blend samples of all compositions were preliminarily examined using an optical microscope. The optical microscopy results showed that there was no discernible phase heterogeneity (micrographs not shown). Furthermore, possible temperature-induced changes in the optical clarity of the blends were also inspected at elevated temperatures (up to degradation) in order to monitor the phase transition. In this blend system, no cloud-point transition was observed. No lower critical solution temperature (LCST) phenomenon was found in the PEI/PEDEK system up to the degradation temperature ($450\text{ }^{\circ}\text{C}$ or beyond). Note that the transition associated with melting of the crystalline phase in PEDEK was excluded for discussion of the amorphous phase morphology. The crystal melting

upon heating should not be confused with the thermodynamic phase transition at the upper critical solution temperature (UCST). Neither an UCST nor a LCST was observed in this blend.

All samples were heated and quenched from the molten state prior to T_g measurement. Prior to scanning in the DSC up to the temperature where the single T_g was identified, the quenched PEDEK/PEI blends were initially amorphous glasses with virtually no crystallinity. The DSC thermograms, with clearly a single T_g in each of the quenched PEDEK/PEI blends of various compositions are shown in Fig. 1. All DSC thermograms show a distinct single T_g . For the PEDEK-rich compositions (PEDEK $> 50\text{ wt}\%$), cold-crystallization and melting associated with the PEDEK component in the blends are also evident. In addition to the evidence of the single T_g for miscibility, these thermograms show additional thermal features that provide evidence of mixing of PEI and PEDEK on molecular scales. Firstly, the PEDEK crystallization is quickly suppressed by blending PEDEK with increasing amounts of PEI; this is expected in typical miscible blends where intimate interaction between the miscible chain segments is usually expected to exert such an influence. The noncrystallizing (fully amorphous) PEI chains, capable of intimately mixing with the PEDEK segments, become a disruptive factor in the crystallization of PEDEK. Secondly, upon increasing the PEI content in the blend, the cold-crystallization of PEDEK occurs at increasingly higher temperatures. For blends containing more than $50\text{ wt}\%$ PEI, DSC scanning on quenched PEDEK/PEI blends revealed no cold-crystallization or melting of PEDEK. Again this suggests that the intimate segmental mixing between PEI and PEDEK leads to chain-stiffening of PEDEK ($T_g = 156\text{ }^{\circ}\text{C}$) by the higher- T_g PEI chain ($T_g = 217\text{ }^{\circ}\text{C}$). This chain-stiffening is obviously proportionally enhanced by the increasing content of high- T_g PEI. Thirdly, the thermograms show a sharp DSC transition for each blend composition, and the DSC transition of the blends does not seem to be broadened. For close inspection, the T_g transition widths for all blend compositions are listed in Table 1. As a matter of fact, the transition width remains fairly

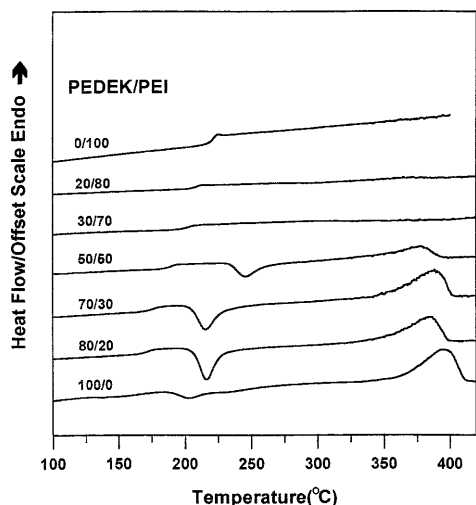


Fig. 1 Differential scanning calorimetry thermograms ($10\text{ }^{\circ}\text{C}/\text{min}$) showing single glass-transition-temperature (T_g), cold-crystallization-temperature, and melting-point peaks in the quenched poly(ether diphenyl ether ketone) (PEDEK) poly(ether imide) (PEI) blends of various compositions

Table 1 Thermal transition characteristics of poly(ether diphenyl ether ketone) (PEDEK)/poly(ether imide) (PEI) blends: glass-transition temperature (T_g), transition width of T_g (Δ), cold-crystallization temperature (T_{cc}), melting point (T_m)

PEDEK/PEI	T_g ($^{\circ}\text{C}$)	Δ ($^{\circ}\text{C}$)	T_{cc} ($^{\circ}\text{C}$)	T_m ($^{\circ}\text{C}$)
100/0	155.8	12.9	202.4	394.8
80/20	166.7	10.1	216.1	384.5
70/30	169.5	10.9	215.8	388.2
50/50	184.3	9.7	245.7	377.8
30/70	196.2	11.9	—	—
20/80	204.0	7.2	—	—
0/100	216.7	7.2	—	—

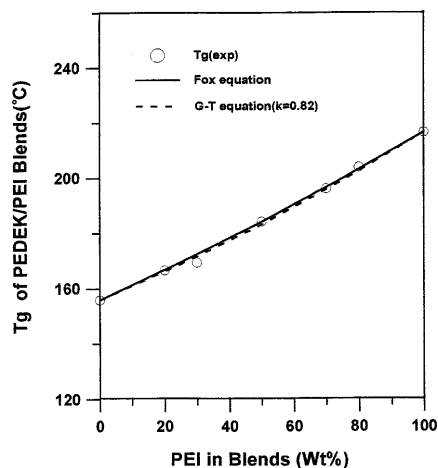


Fig. 2 Composition dependence of T_g of the PEDEK/PEI blend. The agreement of the T_g data with the Fox and Gordon–Taylor equation, respectively, is also shown

constant with the composition of the blends. This observation can be interpreted to state that the interactions between the PEI and PEDEK components may be such that the scale of homogeneity is fine and uniform.

The relationship between T_g and composition provides additional information on the phase behavior of the blend. The composition dependence of the experimental T_g data of the blends is shown in Fig. 2. The T_g data were compared to several established models for miscible blends or copolymer systems. The composition dependence relationship for this system is seen to be well predicted by the classical Fox equation [16]:

$$1/T_g = \omega_1/T_{g1} + \omega_2/T_{g2} ,$$

which is generally valid for two components chemically linked such as those in copolymers. Polymer blends with a fine segmental scale of mixing may also be expected to follow this rule. The fitting between the experimental data and the model was examined. Apparently, the Fox equation describes the data with excellent agreement, suggesting the state of segmental mixing in PEDEK and PEI approaches those expected in chemically bonded copolymers systems.

Another model is also commonly used for describing the T_g –composition relationship of miscible systems with an additional parameter [17]. The Gordon–Taylor equation is

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

where ω_i is the mass fraction of component i , and $k = \Delta C_{p2} / \Delta C_{p1}$, i.e., the ratio of the heat capacity change of PEDEK ($i = 1$ for the low- T_g component, PEDEK) to PEI ($i = 2$ for high- T_g PEI, $T_{g2} = 217^\circ\text{C}$) at T_g . Best-fitting was performed by testing the Gordon–Taylor equation with the T_g data, and the best-fitted value of $k = 0.82$ was obtained, indicating good

interactions that are typically seen in copolymer systems. This value compares well with those for blends of PEI with other poly(arylene ether ketones) reported in the literature, for example, $k = 0.80$ for PK99/PEI [10] and $k = 0.79$ – 0.84 for PEEK/PEI [19, 20]. Note that the case of $k = 1$ suggests linear additivity of T_g of the mixtures, which is an extreme case of segmental mixing that approaches the scale of random copolymers. The value of k of 0.82 for the PEDEK/PEI blend suggests reasonably good segmental intimacy between the molecules of these two components. Thus, the glass-transition evidence clearly shows that the PEDEK/PEI blend is miscible over the whole composition range. Although the extra parameter (k) in the Gordon–Taylor equation has been occasionally suggested by some investigators to be correlated with the “interaction forces” between the constituent molecules [18], it should not be confused with the interaction parameters obtained from melting-point depressions. Rather, it may be viewed as a parameter representing the “wellness” of intermolecular mixing, which is not necessarily a state assured by specific intermolecular interactions.

Estimation of the interaction parameter (χ) by the melting-point-depression technique was not performed experimentally in this study. PEDEK is a high-melting-point polymer (400°C). The measurement of χ would require that the equilibrium melting points of several blend compositions be measured; however, the samples had to be subjected to thermal annealing at high temperatures for long times before the melting point could be measured; degradation of both polymers (PEI, PEDEK) would occur and measurements of the melting point would be inaccurate. As a result, estimation of χ was not feasible experimentally for the PEI/PEDEK blend.

SEM was performed on the fracture surfaces of the samples (quenched to amorphous glass) of several blend compositions. SEM micrographs for as-quenched PEDEK/PEI blend samples (amorphous glasses) are shown in Fig. 3 (results for other compositions are not shown). All the blend samples exhibited a similarly homogeneous morphology free of any discernible separated domains. Although this cannot be readily used as direct evidence of polymer miscibility owing to the resolution limit of the SEM technique, it does provide a supporting view by revealing a homogeneous structure free of any separated phase domains at the SEM magnification that is achievable.

IR interpretation

FT-IR characterization was performed on the blend pair of PEDEK–PEI. The IR absorbance spectra in the wavenumber range covering the vibration of imide ring carbonyl, ketone carbonyl, ether, and phenyl carbon

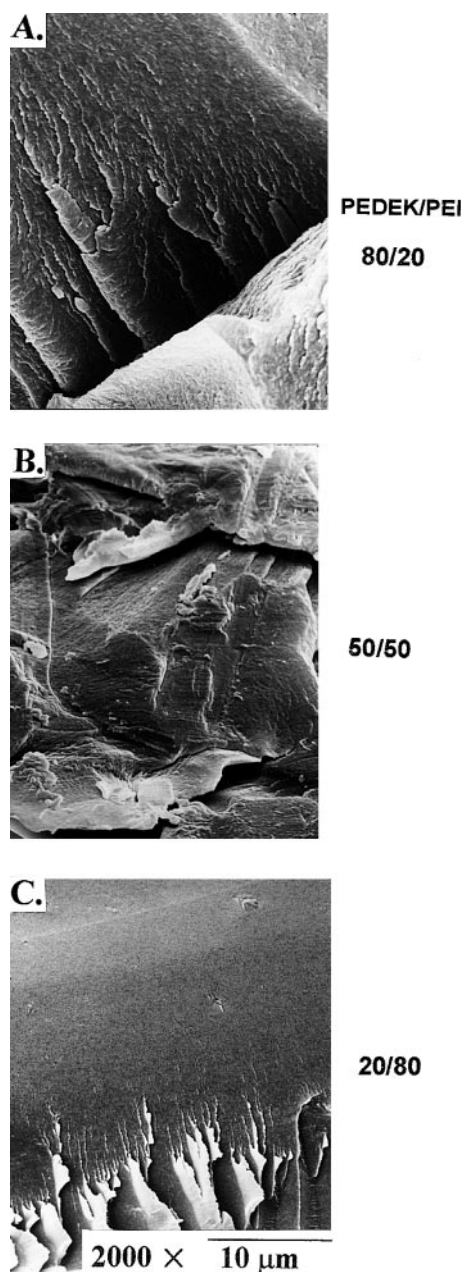


Fig. 3 Scanning electron microscopy micrographs for as-quenched PEDEK/PEI blend samples (amorphous glasses) of compositions **A** 80/20, **B** 50/50, and **C** 20/80

stretching for the PEDEK/PEI samples of various compositions (weight ratios) are shown in Fig. 4. IR characterization was performed on two sets of blend samples: quenched (amorphous) and air-cooled (partially crystallized). The spectroscopic results obtained from both sets were found to be comparable. For a detailed comparison of the peak positions, the values of the absorbance wavenumbers for each of the functional groups are listed in Tables 2–3.

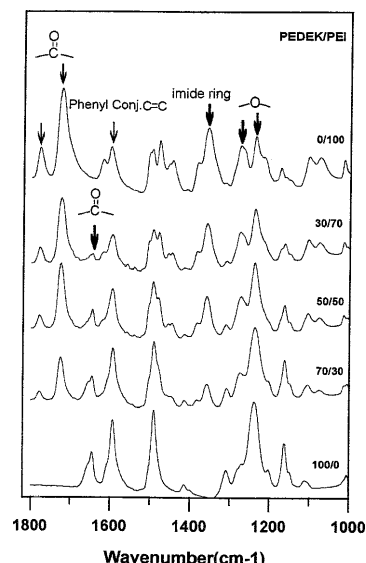


Fig. 4 IR absorbance spectra for the PEDEK/PEI samples of various compositions (weight ratios)

The carbonyl ($\text{C}=\text{O}$) absorbance peaks for the PEDEK/PEI blends with different compositions are shown in Fig. 5. Note that both polymers (PEDEK and PEI) possess the $\text{C}=\text{O}$ group, whose IR absorbance peaks, however, are located at slightly different frequencies. For the carbonyl in the PEI chains, an absorbance doublet is found at 1776 cm^{-1} (symmetric stretching) and at 1722.5 cm^{-1} (asymmetric stretching). The wavenumber of the $\text{C}=\text{O}$ doublet peaks (with PEI) remain unchanged with the compositions of the blends. The $\text{C}=\text{O}$ peak (with PEDEK) is located at approximately 1644 cm^{-1} ; similarly, the $\text{C}=\text{O}$ absorbance apparently does not change with respect to composition. It is likely that the carbonyl groups of the PEDEK and PEI chains

Table 2 IR absorbance peaks (quenched blend samples)

PEDEK/PEI	$\nu(\text{C}=\text{O})$	$\nu(\text{phenyl C}=\text{C})$
0/100	1777.8, 1723.0, –	1599.7
30/70	1778.1, 1724.2, 1644.5	1595.4
50/50	1778.4, 1724.8, 1644.3	1594.8
70/30	1777.4, 1724.6, 1645.2	1593.0
100/0	–, –, 1644.7	1593.0

Table 3 IR absorbance peaks (quenched blend samples)

PEDEK/PEI	Imide ring in PEI	Ether ($-\text{O}-$) doublet
0/100	1355.8	1273.5, 1236.3
30/70	1357.7	1274.0, 1236.8
50/50	1358.2	1271.4, 1273.3
70/30	1357.0	1272.8, 1236.4
100/0	–	1268.7, 1237.4

constituents exhibit apparently specific interactions in forming a homogeneous mixture, a minor alteration of the chemical structure of one of the constituents can lead to a dramatic disruption of interactions and phase separation. This does not seem to be the case for the miscible blends comprising PEI and aryl-ether-ketone polymers.

Several key points of the structures of the aryl-ether-ketone polymers that are miscible with PEI are listed in Table 4. All aryl-ether-ketone polymers possess similar solubility parameters, which are all close to that for PEI. PEI is also miscible with PET and PBT as binary blends [1–3] or collectively as a ternary blend [4]. For additional comparisons, the calculated solubility parameters for PET and PBT are also listed. The solubility parameters for all polymers vary between 10.8 (for PEI) and 11.1 (for others). Closely matched dispersive forces seem to be a major factor. The miscibility of PEI with a number of different poly(arylene ether ketone)s suggests that it is more likely to be a result of van der Waals forces or weakly interacting polarity between the constituents, rather than stronger specific interactions.

Conclusion

Miscibility and phase homogeneity over a wide composition range has been demonstrated in the blend comprising (PEI) and the novel high-melting-point

PEDEK. All blends yielded a single T_g with a narrow transition width, which indicated that the state of intermolecular mixing is uniform and on fine segmental scales. The T_g -composition relationship can be well described by the conventional models for miscible systems. The cold-crystallization behavior of PEDEK in the quenched PEDEK/PEI system is influenced by the content of PEI, in agreement with the typical crystallization behavior expected in miscible crystalline/amorphous pairs. The molecular interpretation of miscibility in the PEDEK/PEI polymer system was also investigated using FT-IR. The FT-IR result yielded evidence that the physical interactions leading to the observed miscibility are weak by nature, with no apparent specific interactions between the constituent polymers. Furthermore, the optical microscopy and SEM characterization of the quenched blends also supported the conclusion of phase homogeneity. In summary, the state of miscibility of PEI and PEDEK was compared to the binary blends of PEI with PK99, PEEK, or PEK, respectively, and it can be concluded that the miscibility of these polymer pairs may be attributed to similarly weak intermolecular polar interactions.

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