

Miscibility, Crystallization, and Morphology Studies of Thermosetting Polyimide PMR-15/PEK-C Blends

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SYNOPSIS

Miscibility, crystallization, and mechanical properties of blends of thermosetting polyimide PMR-15 and phenolphthalein poly(ether ketone) (PEK-C) were examined. With the exception of the 90/10 blend, which has two glass transition peaks, all the blends with PMR-15 less than 90 wt % are miscible in the amorphous state according to DMA results. Addition of PEK-C hindered significantly the crystallization of PMR-15, indicating that there must exist some kind of interaction between molecular chains of PMR-15 and those of PEK-C. The semi-IPN system of PMR-15/PEK-C blends exhibits good toughness. Two distinct microphases, interweaving at the phase boundaries, were found in the PMR-15/PEK-C 60/40 blend. The toughness effect of the blends is discussed in terms of the interface adhesion between the two distinct phases and the domain sizes of the phases. The relation between miscibility and toughness of the blends was investigated. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The purpose of blending a thermosetting polyimide with a thermoplastic polymer is to overcome the brittleness of the former and to improve the processibility and to retain the thermal stability as a whole for the blend. In this case, the thermoplastic polymer is linear while the thermosetting polyimide is crosslinked, and a semi-interpenetrating network (semi-IPN) results after blending and curing. Many works have been done on this type of polymer blends in order to obtain synergistic qualities by the combination of the two polymers.¹⁻⁷

About a decade ago, Yamamoto and co-workers³ studied a series of thermoplastic PI2080/thermosetting BMI blends, which were found to possess T_g 's higher than 300°C and show retention of mechanical strength up to 260°C.

One of the leading materials, LARC-RP40, was prepared by *in situ* polymerization of thermosetting PMR-15 imide prepolymer and thermoplastic NR-150B2 monomer reactants.⁴ LARC-RP40 shows

significantly improved properties over PMR-15 in toughness, microcracking resistance, and glass transition temperature. These property improvements were achieved without significantly compromising the easy processing, outstanding mechanical performance at elevated temperature, and cost of PMR-15.

The results of our previous work on the blends of thermosetting PMR-15 with thermoplastic polyimides show that the length of the dianhydride of the thermoplastic component has a significant effect on the compatibility, crystallization, and morphology of the blends. The impact strength and the morphology of the fractured surfaces indicate that among these semi-IPNs the toughening effect of the partially compatible one is the best.^{2,8}

In this article, we present the results of our investigation on the blends of thermosetting polyimide PMR-15 and phenolphthalein poly(ether ketone) (PEK-C). The miscibility and crystallization behavior of the blends were studied by using DMA and DSC methods. The semi-IPN system of PMR-15/PEK-C exhibits good toughness owing to the partial miscibility and phase separation of the blends.

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EXPERIMENTAL

Thermosetting polyimide PMR-15 and thermoplastic PEK-C were prepared in our laboratory. PMR-15 was prepared by esterification of dianhydride in refluxing methanol followed by addition of diamine and a terminating agent with stirring until all dissolved. The mol ratio of the dianhydride : diamine : terminating agent was 2.087 : 3.087 : 2. The preparation of PEK-C is described elsewhere.⁹

Solution blending of the powders of PMR-15 not imidized and the thermoplastic PEK-C was used, i.e., the two components were dissolved in cresol-mixed isomers and then coprecipitated into alcohol. To remove the residual solvent, the blends were dried in a vacuum oven at 80°C for 2 weeks and then at 200°C for 2 h. The blends so obtained were pressed into sheets about 2 mm thick, under 7.0×10^6 Pa at 320°C for 20 min.

Dynamic mechanical analysis (DMA) was carried out with a DuPont 982 DMA with a heating rate of 5°C/min from room temperature to 450°C. The differential enthalpy of the samples was determined with a Perkin-Elmer DSC-2C differential scanning calorimeter with a heating rate of 20°C/min. The Izod impact test was carried out at room temperature (20°C) and the specimens were $30.0 \times 12.0 \times 2.0$ mm. The characteristics of the fractured surfaces and the etched surfaces (in trichloromethane for 10 h at room temperature) were examined by a JEOL-JXA-840 scanning electron microscope.

RESULTS AND DISCUSSION

Miscibility of the Blends

In Figure 1 are the dynamic mechanical analysis (DMA) curves of PMR-15/PEK-C blends, from which it is clearly seen that there are two transitions (α and β) above room temperature in the blends as well as in the component PMR-15. With the exception of PMR-15/PEK-C 90/10, the blends with other compositions exhibit only a single glass transition, which means that PMR-15/PEK-C blends are miscible over a rather wide range of compositions.

For PMR-15/PEK-C 90/10, two T_g 's indicate that there are two distinct phases in the blend. The lower T_g at 246°C may be ascribed to the PEK-C phase, while the higher one at 346°C corresponds to the PMR-15 phase. The α relaxation is associated with the excitation of segmental mobility, which is based on the rotation of separate segments of the

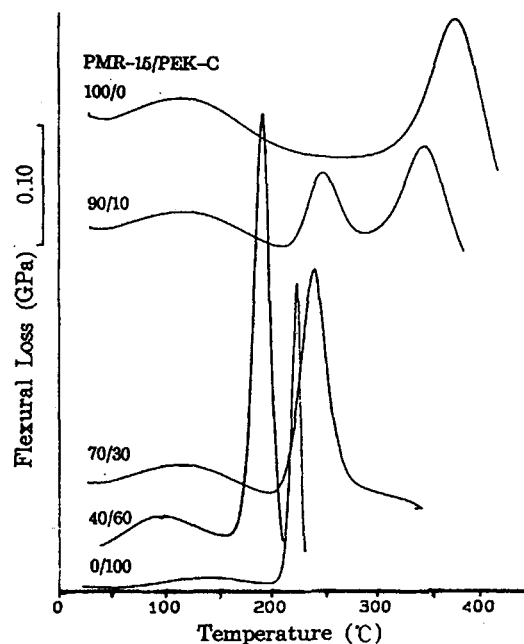


Figure 1 DMA curves of PMR-15/PEK-C blends. Compositions given are weight ratios.

polymeric chains around internal atomic hindrance. The values of T_g 's are relevant to the extent of physical and chemical crosslinkings in the network structure.

Pater and Whitley,¹⁰ gave a simple relation between crosslinking density (ν) and glass transition temperature (T_g):

$$T_g = T_{g_0} + k\nu$$

where T_g and T_{g_0} are the T_g 's of the crosslinked and uncrosslinked materials, respectively, and k is an empirical constant. Therefore, further crosslinking of PMR-15 will cause an increase in T_g of the PMR-15/PEK-C blend. Figure 2 shows the experimental results of heat treatment, from which it is seen that with the increase in time of heat treatment the T_g of the PMR-15 phase increases, while its intensity, i.e., its height, decreases, implying that the crosslinking density of PMR-15 increases and the freedom of movement of PMR-15 chain segments decreases with time of heat treatment, respectively. However, the increase in the T_g of PEK-C means increase in the restriction of its chain segment movement with the density of PMR-15 crosslinking networks.

Crystallization of the Blends

As known, the majority of polyimides are noncrystalline, either inherently or because of a limited

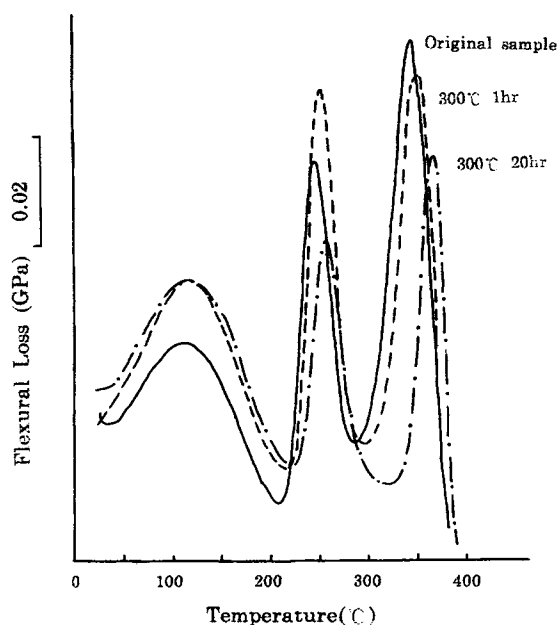


Figure 2 DMA curves of PMR-15/PEK-C 90/10 blend with heat treatment at 300°C for different times.

chain diffusion rate arising from high T_g . However, some aromatic polyimides exhibit a characteristic crystalline structure in the solid state due to their strong intermolecular forces and structural properties, especially for those polyimides whose dianhydride is short and the molecular chains are rigid. PMR-15, as studied in a previous work,¹¹ shows a characteristic crystalline pattern with several rather distinct peaks on a wide-angle X-ray diffraction curve. Listed in Table I are the differential enthalpies of PMR-15/PEK-C blends (corresponding to PMR-15 content) as determined using differential scanning calorimetry (DSC). Compared with that of PMR-15, the crystallinities of the blends are much lower. Hence, a conclusion may be drawn from this result that there must exist interaction between the PMR-15 and PEK-C molecular chains and the addition of PEK-C hinders effectively the crystallization of PMR-15. Heat treatment at 300°C under ordinary atmospheric conditions has a marginal effect on the crystallinity and melting point of the

Table I ΔH of PMR-15/PEK-C Blends (Corresponding to PMR-15 Content)

	PMR-15/PEK-C				
	100/0	90/10	80/20	70/30	60/40
ΔH (J/g)	32.0	2.8	1.8	0.9	0.5

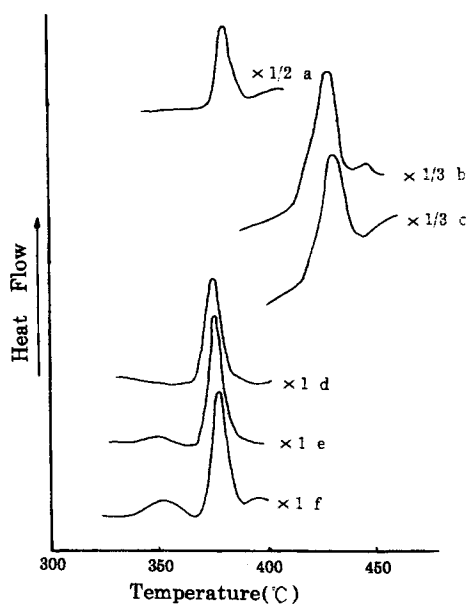


Figure 3 DSC curves of PMR-15/PEK-C 90/10 blend with heat treatment at 300 and 380°C for different times: (a) original sample; (b) 380°C 2 h; (c) 380°C 5 h; (d) 300°C 1 h; (e) 300°C 5 h; (f) 300°C 10 h.

blend. The melting points of the specimens heat-treated at 300°C are all much lower than those of the original specimen, but, strangely, they are in increasing order with time of heat treatment as shown in Figure 3. At present, we do not have enough evidence to explain this phenomenon. When the blend is heat-treated at a higher temperature, phase separation may occur, as its crystallinity and T_m become higher and higher with the time of heat treatment, which might be due to further crystallization of PMR-15. Listed in Table II are the crystallinities and T_m 's of PMR-15/PEK-C 90/10 blends heated at 380°C at different times. It is seen that both the crystallinity and the melting point increase with the time of heat treatment. As well known, the melting point of crystallinity is related to the degree of perfectness of the crystalline structure. Therefore, the

Table II Effect of Heat Treatment at 380°C on the Crystallinity and T_m of PMR-15/PEK-C 90/10 Blend

	Heat-treatment Time (h)				
	0	1.0	2.0	5.0	10.0
ΔH (J/g)	2.8	8.5	15.6	20.3	18.8
Melting point (°C)	377	387	405	427	429

crystalline structure of the PMR-15 component becomes more and more perfect with time for the specimens heat-treated at a higher temperature (380°C), which is most probable due to phase separation at higher temperature, as it can be seen that it is easier to crystallize to a more perfect degree in a purer phase.

Mechanical Properties of the Blends

The semi-IPN system of PMR-15/PEK-C blends is expected to have a higher T_g and good toughness. Since the impact strength of PEK-C is much higher than that of PMR-15, then blending of PMR-15 with PEK-C will increase the impact strength of the blends; this result is shown in Table III. Addition of only 10 wt % of PEK-C increases the impact strength of the blend to twice of that of PMR-15. From the fractographs of the blends shown in Figure 4, the difference in their morphology can be seen, i.e., the fractured surface of the semi-IPN with higher PEK-C content is rougher than that of the one with lower PEK-C fraction. The effect of heat treatment at 300°C at 1 and 20 h, respectively, on the fracture toughness of the PMR-15/PEK-C 90/10 blend is shown in Figure 5, i.e., the toughness of the blend decreases with the time of heat treatment. Because heat treatment causes further crosslinking of PMR-15,¹² which is in good agreement with that the T_g of the PMR-15 phase in the blends increases with the increase in the time of heat treatment (Fig. 2). It may be also due to higher crystallinity and more perfect crystallization in a purer phase resulting from phase separation at high temperature with a longer time.

As discussed above, PMR-15/PEK-C blends are partially miscible. Although there is only one glass transition for the PMR-15/PEK-C 60/40 blend, the broadness of the glass transition peak indicates that there might exist microphase separation in this blend. Figure 6 shows the scanning electron micrographs of the PMR-15/PEK-C 60/40 blend etched for 10 h with trichloromethane at room temperature, from which the two-phase morphological structure

Table III Impact Strength of PMR-15/PEK-C Blends (kg cm/cm²)

	PMR-15/PEK-C				
	100/0	90/10	80/20	70/30	60/40
kg cm/cm ²	3.2	6.6	7.2	7.6	8.8

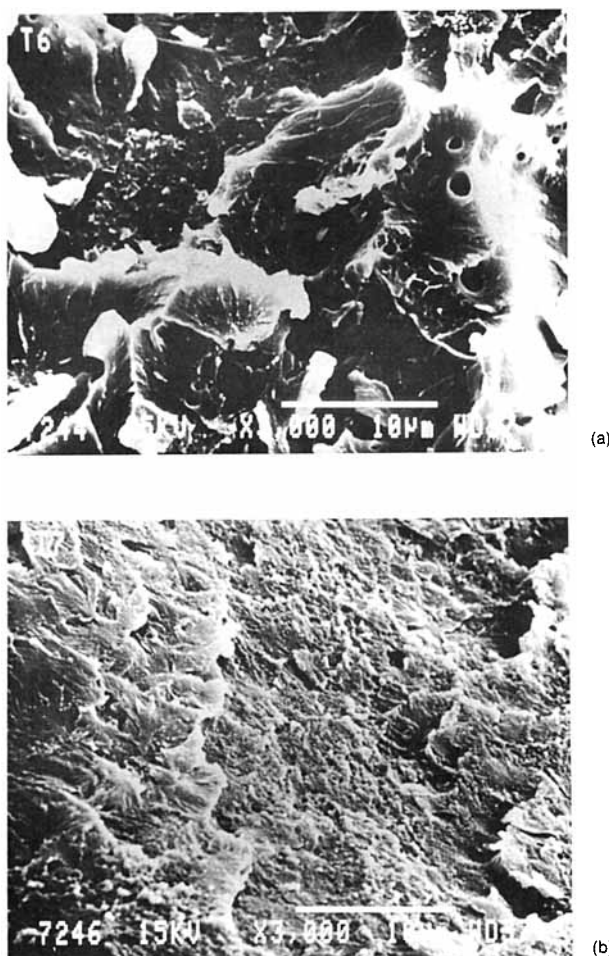


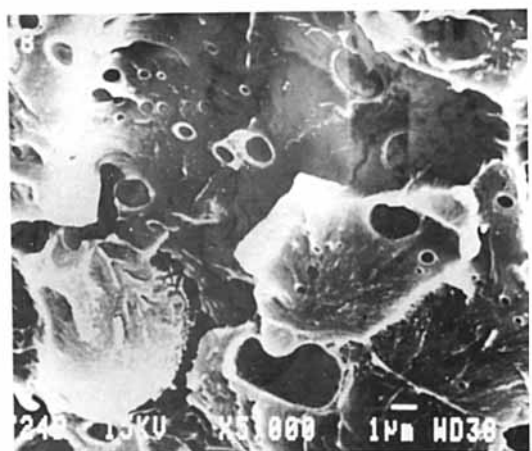
Figure 4 The fractographs of PMR-15/PEK-C blends with different compositions (fractured at room temperature): (a) 90/10; (b) 60/40.

is clearly seen. Both components have almost the same domain size, about 3 μm , while the two phases interweave each other at the boundaries. This interweaved interface and the semi-IPN structure as a whole make the blends have high T_g 's and good toughness.

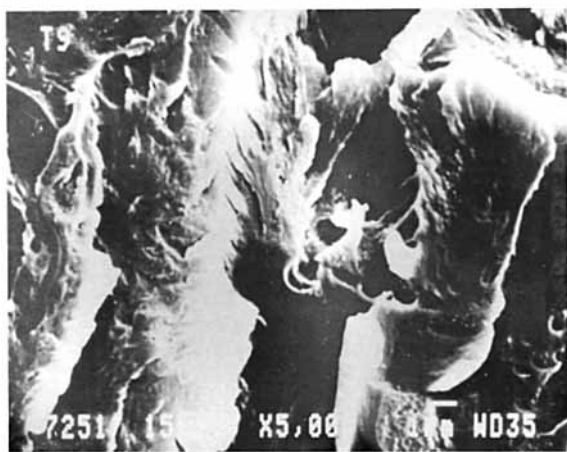
According to Bucknall and Gilbert,¹³ the key for toughness of a resin-plastic blend is good phase separation. In our previous studies of PMR-15/PI blends, more or less the same result was obtained, i.e., when the composition is the same, PMR-15/PI (YS-30) is tougher than is PMR-15/PEI-E, while the DMA result showed that PMR-15/PI (YS-30) is partially miscible and PMR-15/PEI-E is miscible.¹¹ The interface adhesion of the two phases and the phase domain size also have a significant effect on the toughness of the blends; as known, effective toughening requires good interface adhesion and the phase domain size should be appropriate. Mean-



(a)



b)



(c)

Figure 5 The fractographs of PMR-15/PEK-C 90/10 blend with heat treatment at 300°C for different times: (a) original sample; (b) 300°C 1 h; (c) 300°C 20 h.

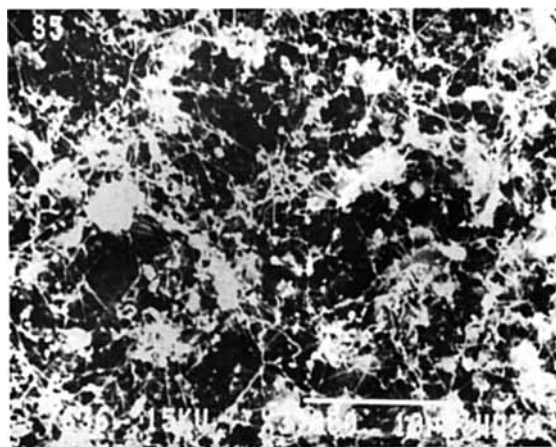
while, interface adhesion will increase with the miscibility of the blend, but the phase domain size will decrease. Therefore, the control of miscibility of the blends is an effective way to improve the toughness

of a blend. The relationship among miscibility, interface adhesion, phase domain size, as well as toughness will be investigated in a further study.

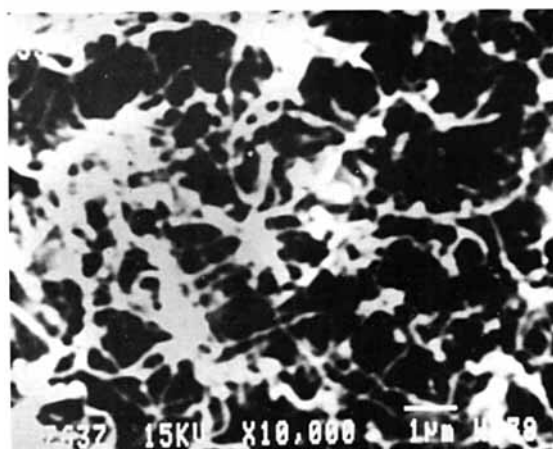
CONCLUSIONS

Miscibility, crystallization, and mechanical properties of the blend of PMR-15/PEK-C have been investigated. The blend is partially miscible, because when the blend composition is 90/10, two T_g 's corresponding to the T_g 's of the two components were observed. Heat-treatment causes further crosslinking of PMR-15, resulting in an increase in the T_g 's of PMR-15/PEK-C blends.

PMR-15 is capable of crystallizing, either in its pure form or in blends with PEK-C. Addition of PEK-C will hinder the crystallization of PMR-15. However, high-temperature (380°C) heat treatment



(1)



(2)

Figure 6 Scanning electron micrographs of PMR-15/PEK-C 60/40 blend etched with trichloromethane at room temperature.

will increase both the crystallinity and the melting point of PMR-15, which may be a result of phase separation of the blends. For heat treatment of the samples at 300°C, its effect on the crystallinity is marginal and PMR-15 begins to crystallize to a less perfect crystalline pattern.

The semi-IPN system of PMR-15/PEK-C blends has a reasonably high T_g and good toughness. The SEM micrograph of the PMR-15/PEK-C 60/40 blend shows that there exist two distinct micro-phases interweaving at the phase boundaries. The good toughness of the blend is ascribed to the strong interface adhesion between the two distinct phases and the appropriate size of the phase domain.

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