

Compatibility and Morphology Studies of PPO Multicomponent Blends

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SYNOPSIS

The compatibility and phase morphology of poly(phenylene oxide) (PPO) multicomponent blends with poly(ethylene terephthalate) (PET) and polystyrene (PS) were studied using differential-scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and scanning electron microscopy (SEM) methods. The effect of glycidyl methacrylate-styrene copolymer (GMS), as a compatibilizer, on the morphology of the PPO blends has also been studied in detail. The influence of the molecular weight of PET and the synergetic effect of the compatibilizers of GMS and phenoxy (PN) on the morphology were examined. The DSC and DMA results show that two distinct glass transitions corresponding to PET and PPO existed; however, the T_g of PPO shifts toward lower temperature region due to the addition of GMS and PS. The SEM results reveal that PET component exists as dispersed phases in the PPO matrix, while PS is miscible in the PPO matrix. A significant improvement of the compatibility was achieved for the PPO multicomponent blends because of the synergetic effect of GMS and phenoxy. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The compatibility of multicomponent blends has been a basic problem to be investigated in the development of new polymeric alloys because it dominates their phase morphologies and closely correlates with the ultimate mechanical properties of the polymer blends. For many incompatible polymer blend systems of interest, they often possess high interfacial tension and weak adhesion at the interfaces between the dispersed phases and matrix, forming very coarse morphologies with, as a result, inferior mechanical properties. A general route to enhance the adhesion at the interfaces of two incompatible polymeric components is by adding a third one having affinity with both of them, namely, the compatibilizer. Much attention has recently been focused on seeking the efficient compatibilizers for the incompatible blend systems.¹

The phase morphology of PPO blend with PS has been well-documented in the literature,² which is a miscible blend and is used as a promising engineering plastic with higher heat distortion temperature. The compatibility of PPO binary blends or modified PPO with PS and other polymeric components has also been studied extensively over the past years.³⁻⁷ For further improving the processibility, oil-resistance, and impact-resistance of PPO blend materials, there were many recent patents involved in the PPO multicomponent blends containing some incompatible components, such as nylon 6,6,⁸ nylon 6,⁹ poly(butylene terephthalate),¹⁰ and PET,¹¹ as well as a small amount of compatibilizer. However, there were only a few fundamental studies about PPO multicomponent blends with the addition of a small amount of block copolymer as a compatibilizer.^{12,13}

In this article, the compatibility and phase morphology of PPO binary and multicomponent blends have been studied in detail. The effect of the composition, the molecular weight of PET, and the compatibilizers on the morphology of the blends has been addressed.

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EXPERIMENTAL

Materials

The polymers used in this study were poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), poly(ethylene terephthalate) (PET), a random copolymer of glycidyl methacrylate-styrene (15 : 85 mol), high-impact polystyrene (PS) under the trade name Denka Styrol MW-1, and phenoxy (PN), a polyhydroxyether from the condensation of bisphenol A and epichlorohydrin. PPO had an intrinsic viscosity (int. vis.) of 0.58 (measured at 30°C in chloroform). PET had an int. vis. of 0.6 and 1.0. All the materials used were kindly supplied from Toyobo Co.

Blending

The melt blending of PPO multicomponent blends with various compositions was carried out on a Brabender ZSK30M9/II twin screw extruder at 290°C and pelletized. The composition of the blends is listed in Table I.

Characterization

The DSC measurement was carried out on a DuPont 910 differential-scanning calorimeter at heating rate of 20°C/min under nitrogen stream. The dynamic mechanical properties of the blends were measured using a DDV-II-EA viscoelastometer at a heating rate of 2°C/min and frequency 11 Hz in a temperature range from -80°C to 240°C. The film samples were prepared by a hot press at 290°C.

The phase morphology of the blend extrudates from twin-extruder were examined with a Camscan-4 high-resolution scanning electron microscope. The fracture surfaces of the blend samples were prepared in liquid nitrogen and then sputter-coated with a gold-palladium alloy to prevent charging in the electron beam.

RESULTS AND DISCUSSION

Compatibility Analysis

The compatibility of the polymer blends can be sensitively probed by their thermal and crystallization behaviors based on the DSC and DMA measurements. For an incompatible blend system, the glass transition corresponding to the individual components will be detected, while for a miscible blend system only one glass transition exhibited a temperature between them. Moreover, the crystallization characteristic of the crystallizable component in the incompatible blends usually remains.

In Figures 1 and 2, the DSC and DMA results of the PPO/PET binary and multicomponent blends are presented. The transitions of these blends are compared in Table II. Figure 1(a): PET shows T_g at 79°C, T_c at 187°C, and T_m at 256°C. PPO only shows a T_g at 218°C, manifesting its amorphous nature. In 20 PPO/80 PET and 40 PPO/60 PET compositions, there is a distinct transition at 78°C corresponding to the T_g of PET, but no transition of PPO was detected, which possibly associated with the

Table I Composition of PPO Binary and Multicomponent Blends

Sample Code	PPO (wt %)	PET ^a (wt %)	PET (1.0) (wt %)	GMS (wt %)	PS (wt %)	Phenoxy (wt %)
80 PPO/20 PET	80	20				
60 PPO/40 PET	60	40				
50 PPO/50 PET	50	50				
40 PPO/60 PET	40	60				
20 PPO/80 PET	20	80				
80 PPO/20 PET (1.0)	80		20			
50 PPO/47 PET/3 GMS	50	47		3		
50 PPO/45 PET/5 GMS	50	45		5		
50 PPO/40 PET/10 GMS	50	40		10		
45 PPO/40 PET/5 GMS/10 PS	45	40		5	10	
45 PPO/30 PET/5 GMS/20 PS	45	30		5	20	
50 PPO/40 PET/10 PN	50	40				10
50 PPO/40 PET/5 GMS/5 PN	50	40		5		5
50 PPO/35 PET/5 GMS/10 PN	50	35		5		10

^a The intrinsic viscosity of PET is 0.6.

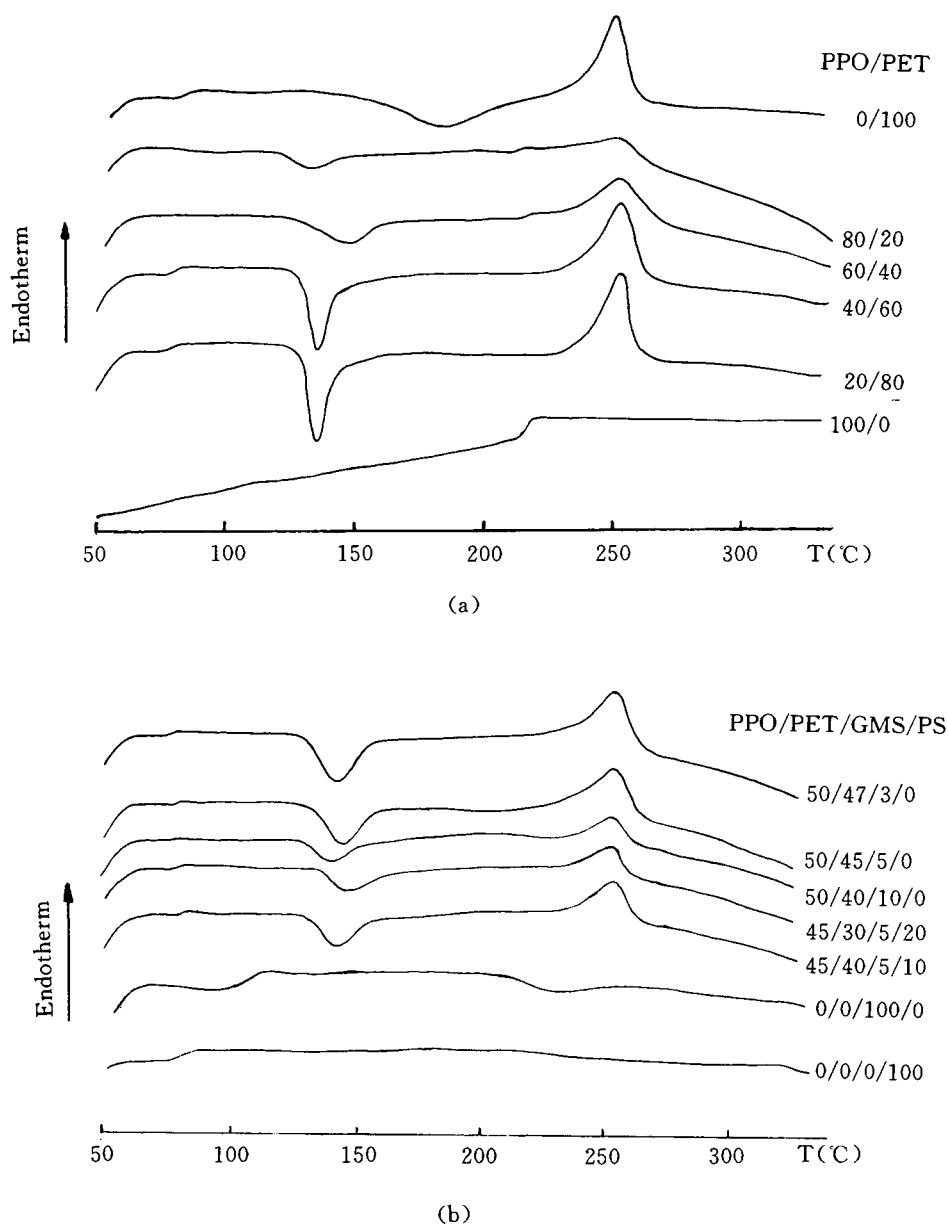


Figure 1 DSC curves of the PPO blends: (a) PPO/PET binary blends; (b) PPO multicomponent blends.

crystallization of PET component during heating and the sensibility of the DSC method. However, the T_g of PPO could be detected for the compositions of 60 PPO/40 PET and 80 PPO/20 PET, which perhaps has lower crystallinity of PET. The T_c of PET in the blends is markedly lower than that of the virgin PET, indicating that PPO may partly act as nucleating agent to promote the nucleation of the PET component. The addition of GMS is expected to somewhat improve the compatibility between PPO and PET; however, PET still exhibit a distinct

T_g in the ternary blends of PPO/PET/GMS with various content of GMS [Fig. 1(b)]. It is also true for the addition of PS in the PPO/PET/GMS/PS multicomponent blends.

The DMA results are more sensitive to reveal the compatibility of the multicomponent blend system. In 20 PPO/80 PET, there are two distinct transitions at 90°C and 234°C corresponding to the T_{g1} of PET and T_{g2} of PPO viewed on the dynamic mechanical spectrum, indicating they actually existed in two separate phases (see Fig. 2). It is clear that

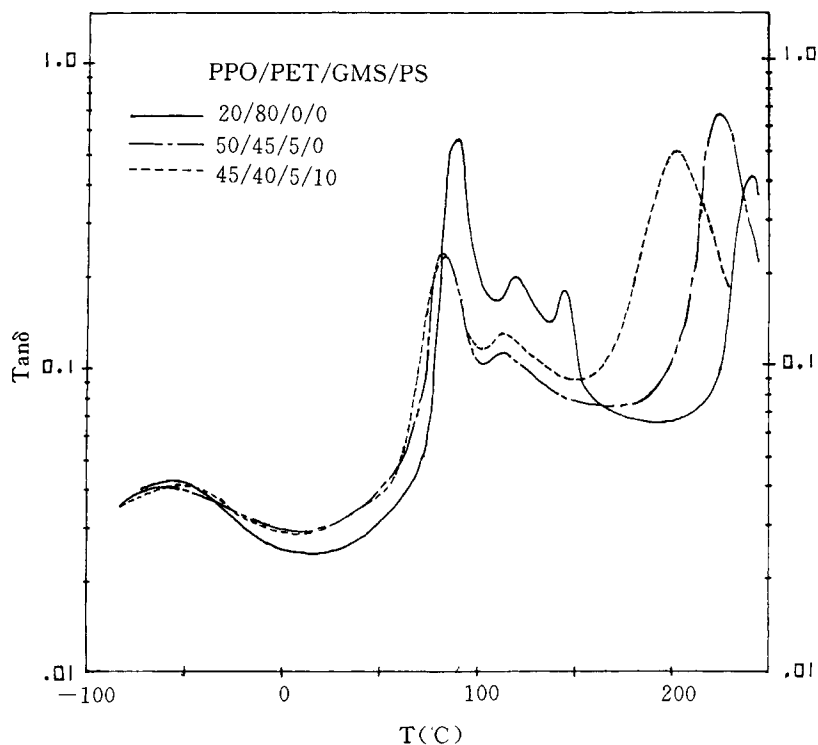


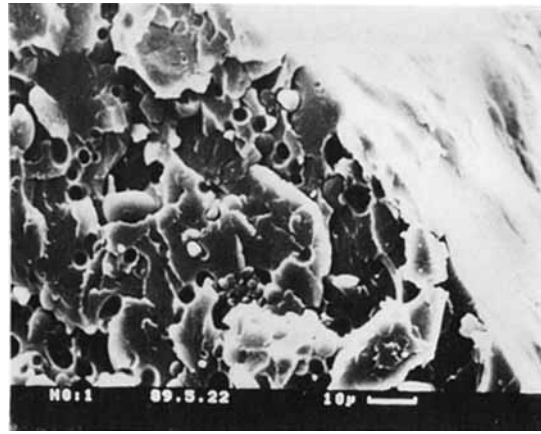
Figure 2 DMA spectra of PPO binary and multicomponent blends.

the peak at -56°C corresponds to T_{β} of PET, whereas both peaks at 120°C and 144°C associate with the segmental motion of PET in the crystalline region with different orders. It is interesting to note from the spectra of 50 PPO/45 PET/5 GMS and 45 PPO/40 PET/5 GMS/10 PS that both the T_{β_1} of PET and the T_{g_2} of PPO shift toward a lower tem-

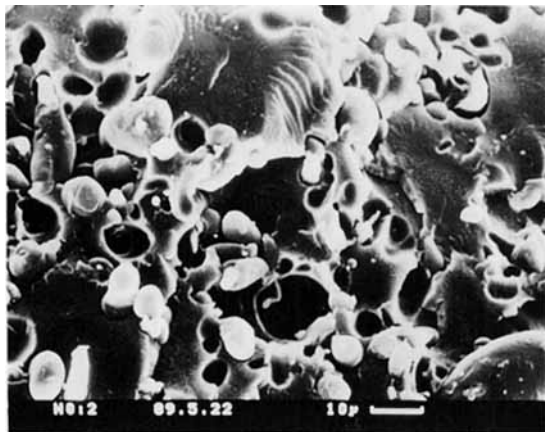
perature region due to the addition of GMS and PS, respectively. However, a significant drop of T_{g_2} in the latter case may be ascribed to the fact that PS is actually miscible with PPO to form a separate matrix phase; the peak at 113°C is due to the T_g of GMS, which is reasonably consistent with the result measured by DSC listed in Table II.

Table II Effect of Composition on the Transition Temperatures

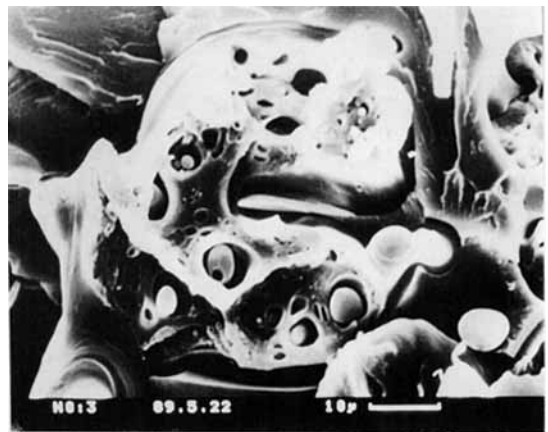
Sample	DSC				DMA					
	Td_{g_1}	T_c	T_{g_2}	T_m	T_{β}	T_{g_1}	T_g	T'_c	T_c	T_{g_2}
PPO/PET/GMS/PS	(°C)				(°C)					
0/100/0/0	79	187		256						
100/0/0/0			218							
0/0/100/0	108									
0/0/0/100	82									
20/80/0/0	79	136		258	-57	90		120	144	234
40/60/0/0	79	135		258						
60/40/0/0		147	216	257						
80/20/0/0		133	217	256						
50/47/3/0	77	141		255						
50/45/5/0	78	146		255	-56	83	113			224
50/40/10/0		140		254						
45/40/5/10	79	142		254	-56	82	113			200
45/30/5/20	78	147		254						



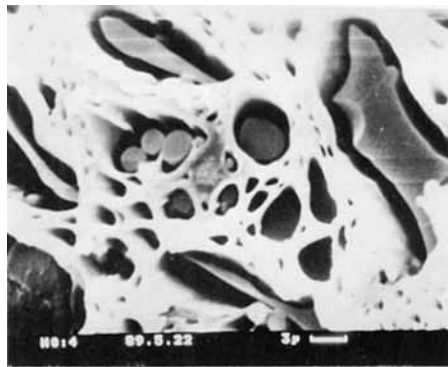
(a)



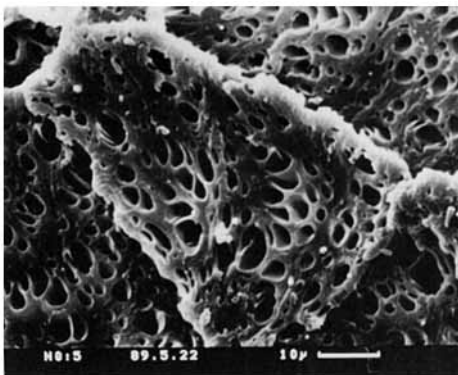
(b)



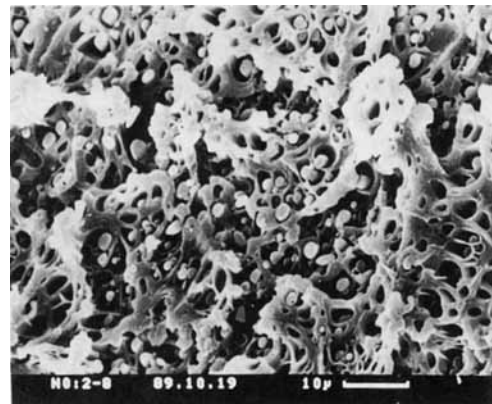
(c)



(d)



(e)



(f)

Figure 3 SEM photomicrographs of PPO/PET binary blends: (a) 20 PPO/80 PET; (b) 40 PPO/60 PET; (c) 50 PPO/50 PET; (d) 60 PPO/40 PET; (e) 80 PPO/20 PET; (f) 80 PPO/20 PET (1.0).

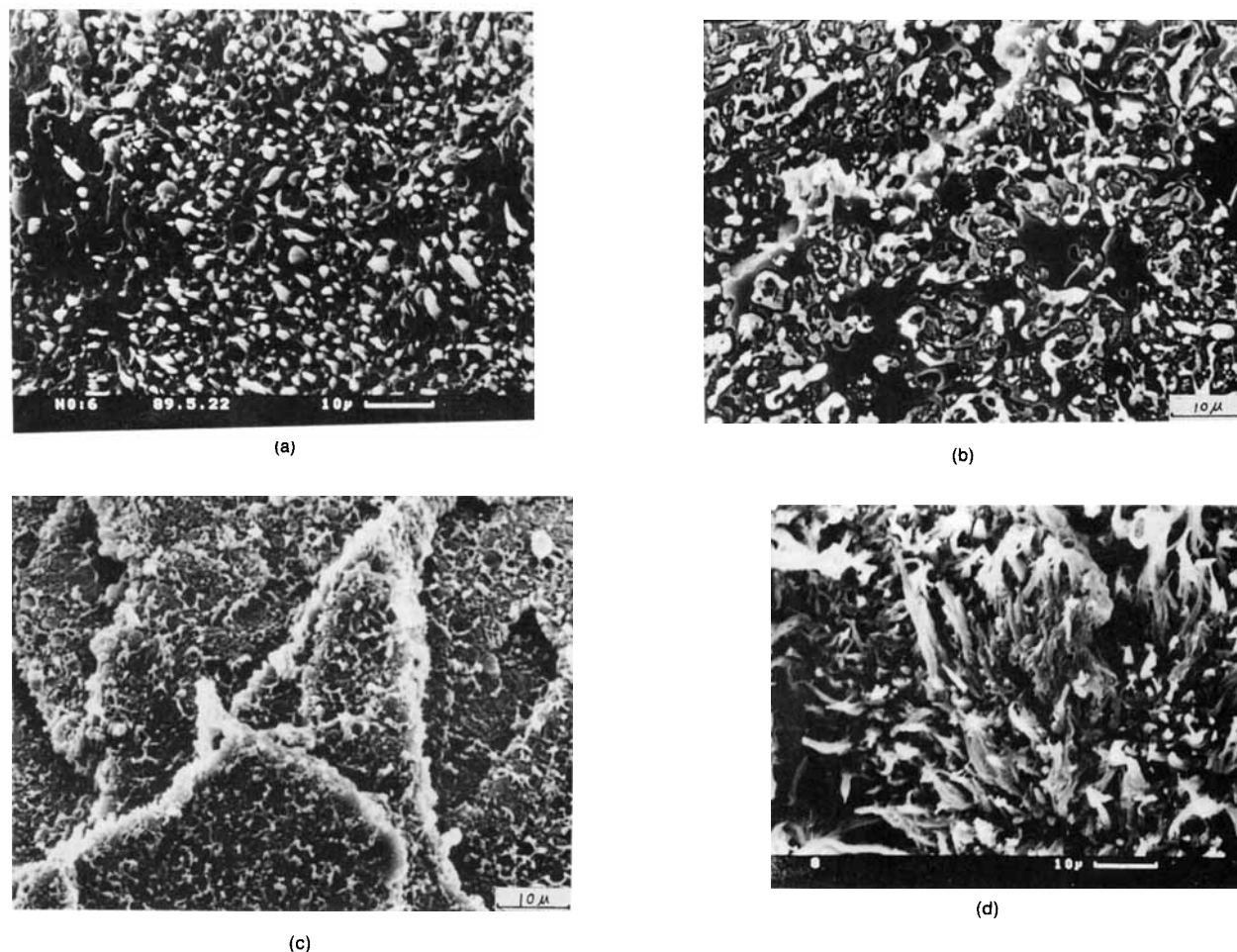


Figure 4 SEM photomicrographs of PPO/PET/GMS ternary blends: (a) 50 PPO/47 PET/3 GMS; (b) 50 PPO/45 PET/5 GMS; (c) 50 PPO/40 PET/10 GMS; (d) 50 PPO/40 PET/10 GMS blend after chemical etching with xylene.

Phase Morphology Analysis

The SEM photomicrographs of PPO/PET binary and multicomponent blends are shown in Figure 3(a–e). PPO is completely incompatible with PET; they virtually existed with a two-phase morphology. However, the shape and size of the dispersed phases and matrix of the blends are highly composition dependent. As shown in Figure 3(a,b), PPO is a dispersed phase in the PET matrix. At 20 PPO/80 PET composition, the PPO component shows a spherical shape, with the average size about $4\ \mu\text{m}$; increasing the PPO amount, the dispersed phases of PPO agglomerated to be larger particles with irregular shape. At 50 PPO/50 PET composition, it seems to form a co-continuous morphology with inclusion of small particles of PPO or PET component in the PET or PPO sea [Fig. 3(c)]. A clear phase-inversion is observed for the 60 PPO/40 PET composition,

which shows a rather irregular shape of the PET dispersed phases and meandering boundaries with PPO matrix. In 80 PPO/20 PET blend, the PET component is uniformly distributed in the PPO matrix, which shows a fine rod-like shape, with a diameter from $0.5\ \mu\text{m}$ to $2\ \mu\text{m}$. In contrast with 20 PPO/80 PET composition, we consider that PET has lower interfacial tension and viscosity than those of PPO; as a result, it is easier deform forming the fine rod-like dispersed phases. Furthermore, the viscosity ratio of PPO/PET is also a predominant factor of controlling the morphology of the blends. The SEM results for the 80 PPO/20 PET composition with different molecular weight (or int. vis.) show that the higher the molecular weight of PET, the coarser the dispersed phases formed [see Fig. 3(e,f)].

The effects of GMS, as a compatibilizer, on the morphology of PPO/PET blends are shown in Fig-

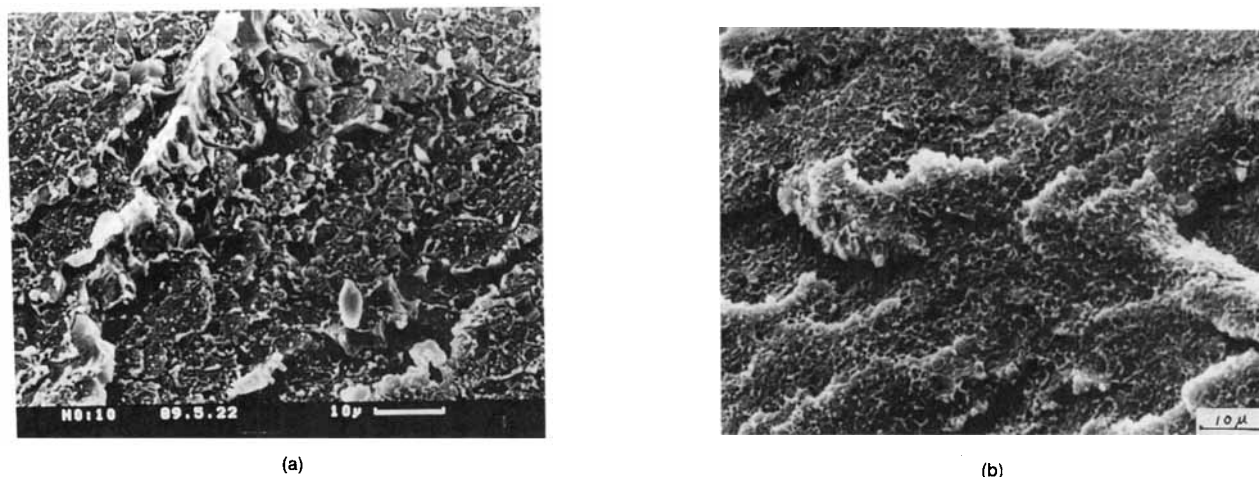


Figure 5 SEM photomicrographs of PPO multicomponent blends: (a) 45 PPO/40 PET/5 GMS/10 PS; (b) 45 PPO/30 PET/5 GMS/20 PS.

ure 4(a–c). Comparing with the 50 PPO/50 PET composition, a much finer dispersed phase of PET was viewed as only 3 wt % of GMS substituted for the PET in the blend. With further substituting PET by 5 and 10 wt % GMS, respectively, the dimensions of the dispersed phases became smaller and smaller; moreover, it showed more irregular shape with good adhesion at the interfaces, indicating GMS is a quite good compatibilizer for the PPO/PET blend system. In addition, Figure 4(d) shows the morphology of 50 PPO/40 PET/10 GMS after chemical etching on the surface of the sample with xylene at room temperature for 30 min. It seems that both the PPO and GMS were dissolved in xylene while a fiber-like dispersed phase of PET was remained; therefore, we may further infer that GMS has stronger interaction with PPO than with PET, although it is believed that the epoxy groups of GMS can react and bind to the PET under certain conditions.

In Figure 5(a,b), the effect of the fourth component PS on the morphology of PPO/PET multicomponent blends has also been checked. At the 45 PPO/40 PET/5 GMS/10 PS composition, it can be concluded that PS is miscible with PPO to form the matrix, while PET formed very fine dispersed phases included in the matrix, which was separated into several domains. With increasing PS content (up to 20 wt % in the blend), the domains became smaller.

Synergetic Effect of the Compatibilizers

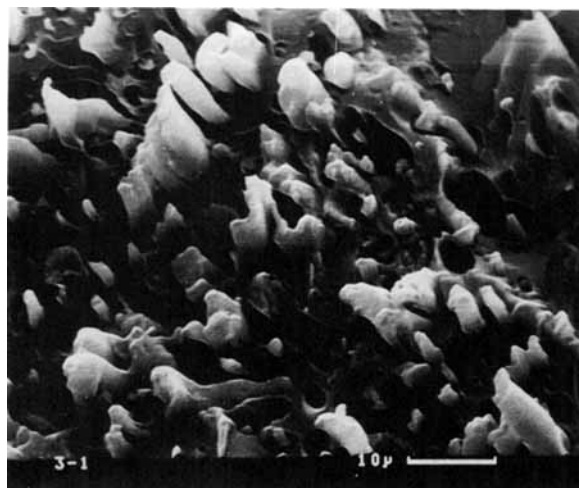
It is well-known that PET is compatible with phenoxy due to the specific interaction between the hy-

droxy group of phenoxy (as a proton donor) and the carbonyl group of PET (as a proton acceptor).¹⁴ Phenoxy was also patented as a compatibilizer for the PPO/PBT blend system.¹⁵ We considered that phenoxy has significant interaction with PET, but not with PPO. GMS is more compatible with PPO than PET. It is interesting to investigate the synergetic effect of phenoxy and GMS on the morphology of the PPO/PET blends. The SEM results are compared in Figure 6(a–c).

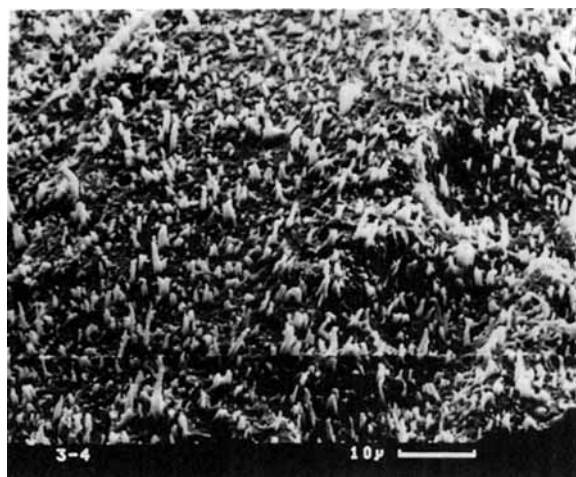
Comparing the morphology of 50 PPO/40 PET/10 PN composition with that of 50 PPO/40 PET/10 GMS, we can conclude that as a compatibilizer for this blend system, GMS is much better than PN, because the latter shows a rather coarse morphology with unscored voids. However, substituting 5 wt % GMS for the PN in this composition, a much finer dispersed phase of PET formed, which are uniformly distributed in the matrix with good adhesion at the interfaces. At the composition of 50 PPO/40 PET/5 GMS/5 PN, we can clearly see an interpenetrating network-like morphology formed which is even better than that of 50 PPO/40 PET/10 GMS composition. Therefore, we can reasonably speculate that there is specific interaction among the hydroxy group of phenoxy and the carbonyl group contributed from both PET and GMS.

CONCLUSIONS

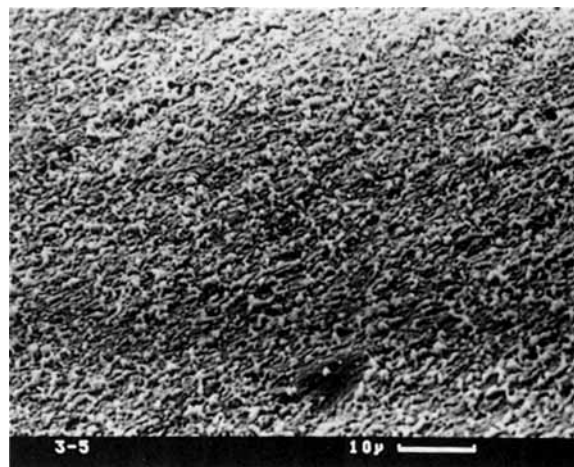
The PPO/PET binary blend system is incompatible because of their large difference in solubility parameters, the morphology of which is markedly depen-



(a)



(b)



(c)

Figure 6 Synergetic effect of GMS and phenoxy on the morphology of PPO/PET blends: (a) 50 PPO/40 PET/10 PN; (b) 50 PPO/40 PET/5 GMS/5 PN; (c) 50 PPO/35 PET/5 GMS/10 PN.

dent on the composition. The molecular weight of PET also affects the shape and the size of the dispersed phases, which are associated with the viscosity ratio of the PPO/PET components. GMS is an effective compatibilizer for the PPO/PET blend system; the synergetic effect of GMS and phenoxy on this blend system further improves its compatibility. The PS in the multicomponent blend system is virtually miscible with PPO to form a separated matrix phase.

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Received January 6, 1994

Accepted June 15, 1994