

Blends of Poly(ethylene terephthalate) and Poly(butylene terephthalate)

G. Aravinthan, D. D. Kale

Polymer Engineering and Technology Department, University of Mumbai, Institute of Chemical Technology, Matunga, Mumbai 400 019, India

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ABSTRACT: Commercial grade poly(ethylene terephthalate), (PET, intrinsic viscosity = 0.80 dL/g) and poly(butylene terephthalate), (PBT, intrinsic viscosity = 1.00 dL/g) were melt blended over the entire composition range using a counterrotating twin-screw extruder. The mechanical, thermal, electrical, and rheological properties of the blends were studied. All of the blends showed higher impact properties than that of PET or PBT. The 50:50 blend composition exhibited the highest impact value. Other mechanical properties also showed similar trends for blends of this compo-

sition. The addition of PBT increased the processability of PET. Differential scanning calorimetry data showed the presence of both phases. For all blends, only a single glass-transition temperature was observed. The melting characteristics of one phase were influenced by the presence of the other. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 75–82, 2005

Key words: blends; poly(ethylene terephthalate); poly(butylene terephthalate); rheology

INTRODUCTION

Poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) are both very important commercial aromatic–aliphatic polyester resins. PET is widely used for the fabrication of molded articles, fibers, and films. PBT is mainly used for injection molding and related applications. PET resins are utilized where higher a heat-deflection temperature, greater rigidity, and economy are desired. However, the processing of PET is difficult because of its low melt strength and slow rate of crystallization. PBT resins have the advantages of rapid crystallization rate and good moldability. In general, the mechanical properties as well as chemical resistance characteristics are comparable for both PET and PBT. A major drawback of PET and PBT resins is their brittleness.^{1–3}

Mishra and Deopura⁴ predicted the theoretical compatibility of PET and PBT blends through thermodynamic considerations. In another study,⁵ they argued that, although PET is compatible with PBT in the amorphous phase, it forms separate crystals rather than cocrystals. Therefore, these blends can give significantly different properties than PET or PBT, depending upon the composition and processing conditions. Stein and coworkers⁶ studied the miscibility and morphology of PET/PBT blends using differential

scanning calorimetry (DSC), IR spectroscopy, and wide-angle X-ray diffraction (WAXD) techniques. DSC studies showed that PBT and PET crystallized separately in the melt blends and one phase enhanced the crystallization process of the other. IR spectroscopy indicated a separate crystallization rate for each component in the blends by showing the change in intensity of the 917 and 848 cm^{-1} bands. WAXD studies of PET/PBT melt blends showed diffraction characteristics of the virgin homopolymers. No appreciable shifts in peak positions or new diffractions were observed. Avramova⁷ reported a single glass-transition temperature (T_g), indicating the miscibility of PET and PBT segments in the amorphous phase. PET/PBT blends exhibited only one crystallization peak but separate melting points for the two crystalline species. Some depression of the melting point of one component associated with the presence of the other component indicated compatibility in the amorphous phase. Avramova⁷ also reported the presence of spherulite crystallization of both species in PET/PBT blends with microscopic observation. He concluded that the minor component is excluded within the spherulites of the major component and may subsequently crystallize in this location. Jin and Tao⁸ reported the rheological properties of PET/PBT blends at a temperature of 275°C and a shear rate up to 10^3 s^{-1} . They observed well-defined zero shear viscosity for all blends and shear thinning behavior in the high shear rate region and a network type of morphology for a lower concentration of PBT. They argued that the blend containing 50% PBT was not suitable for fiber spinning be-

Correspondence to: D. D. Kale (ddkale@udct.org).

cause of a sudden loss of elastic effect. This suggests miscibility of PET and PBT over the entire composition range. A fascinating feature for blends in the polyester family is the potential for transreaction, which is also called rereaction or transesterification. Porter and Wang⁹ suggested that miscibility in PET/PBT blends is not a consequence of transesterification, when mixing times are short as in extrusion. It is known that melt mixing over a long period of time at high temperature can lead to a transesterified random copolymer.

Several patents¹⁰⁻¹² mention good properties of PET/PBT blend compositions. However, they do not disclose actual values for these properties. There are no data in the literature on the systematic variation of properties with composition for the important PET/PBT blends. Therefore, the present study is useful.

EXPERIMENTAL

Materials

Commercial grades of PET (RELPE, grade G5801, intrinsic viscosity = 0.80 dL/g) and PBT (LUPOX, GP-1000, intrinsic viscosity = 1.00 dL/g) were procured from Reliance Industries Ltd. (Mumbai, India) and LG Polymers India Pvt Ltd., respectively.

Blending

PET and PBT chips were manually mixed and dried at 120°C for 8 h in an air circulating oven. The blend compositions were 80:20, 70:30, 60:40, 50:50, 40:60, and 20:80 in which the numbers represent the weight percentages of PET and PBT, respectively. A blend was also prepared by blending 60 parts PET with 40 parts PET/PBT (50:50), so that the final composition was 80 parts PET and 20 parts PBT. This blend is designated as 80:20 A. The mixture was melt blended using a counterrotating twin-screw extruder (Haake Rheocord 9000, TW100). The screw speed was maintained at 40 rpm and the temperature profiles for blending were 150°C for zone 1, 220°C for zone 2, 240°C for zone 3, and 260°C for the die zone. The extrudates were water cooled and pelletized. The extruded pellets were dried and molded into standard ASTM test specimens by using a microprocessor-based injection-molding machine (Boolani Industries Ltd., Mumbai, India). The temperature profiles were 220°C for zone 1, 250°C for zone 2, and 280°C for the nozzle zone.

Mechanical properties

Tensile strength, flexural strength, and flexural modulus were measured at ambient conditions using a universal tensile testing machine (LR-50K, Lloyds Instrument), according to ASTM procedures. The cross-

head speeds were 50 and 2.8 mm/min for tensile tests (ASTM 638M-91) and flexural tests (ASTM 790M-92), respectively.

The notch for impact testing was cut using a motorized notch-cutting machine (Polytest model 1, Ray Ran). The notched Izod impact strength was measured at ambient conditions according to the ASTM D 256 method using an impact tester (Avery Dension) with a striking velocity of 3.46 m/s and employing a 2.7-J striker.

Electrical properties

The breakdown voltage for PET/PBT blends was measured using an AC High Voltage Tester (Zaran, Mumbai, India).

Thermal properties

Heat distortion temperature (HDT)

Specimens similar to those used for measuring the flexural strength were used to determine the HDT according to ASTM D 648. An HDT Vicat softening point apparatus (Davenport) was employed for measurements.

DSC

The melting and crystallization behavior of PET/PBT blends was studied using a DSC-7 (Perkin-Elmer). Temperature calibration was performed using indium as a reference (melting temperature = 156.60°C, heat flow = 28.5 J/g). The heating rate of the samples was 20°C/min with a sample size between 7 and 13 mg using a standard aluminum sample pan. The sample was maintained under a nitrogen atmosphere.

Rheological properties

The melt rheology of the individual polymers and their blends was studied using a rotational rheometer (Haake RT 10), employing a parallel plate sensor with a diameter of 35 mm at 260°C. The shear rate range was varied from 1 to 10 s⁻¹. For higher shear rates, rheological measurements at 260°C were carried out using a twin-bore capillary rheometer (Rosand Precision). The shear rate range was 100–1000 s⁻¹. The capillary rheological data were subjected to Bagley and Rabinowitch corrections.

Microscopy

The morphological characteristics of PET/PBT blends were examined by scanning electron microscopy with a Shimadzu SS-550 Superscan.

TABLE I
Mechanical and Electrical Properties of PET/PBT Blends

Compositions (wt %)	Tensile strength (MPa)	Flexural strength (MPa)	Flexural modulus (MPa)	Impact strength (J/m)	HDT (°C)	Breakdown voltage (kV)
PET	56	76	2105	25	78	27
PET/PBT						
80:20	53	75	2305	38	72	22
80:20 A	54	67	2872	41	75	22
70:30	51	70	2151	36	68	20
60:40	58	78	2287	44	67	24
50:50	62	73	2457	52	65	26
40:60	59	76	2321	42	60	20
20:80	57	73	2345	40	59	16
PBT	55	75	2127	27	56	14

RESULTS AND DISCUSSION

Mechanical properties

Table I shows the variation of the mechanical properties, electrical properties, and HDT for PET/PBT blends. The tensile strength and flexural strength of PET and PBT are comparable. Therefore, it is not surprising that both of these properties for all blends are relatively comparable, although the 50:50 PET/PBT blend tends to show slightly higher tensile

strength. The impact strength as well as the flexural modulus for the 50:50 PET/PBT blend are appreciably higher than the virgin polymers. It is interesting to note that the impact strength of all the blends is higher than that of virgin polymers. Because a blend of composition 50:50 PET/PBT exhibited the highest impact strength, a blend was prepared by blending 60 parts PET with 40 parts 50:50 PET/PBT blends so that the final composition of the blend was 80 parts PET and 20 parts PBT. The mechanical properties of this blend are

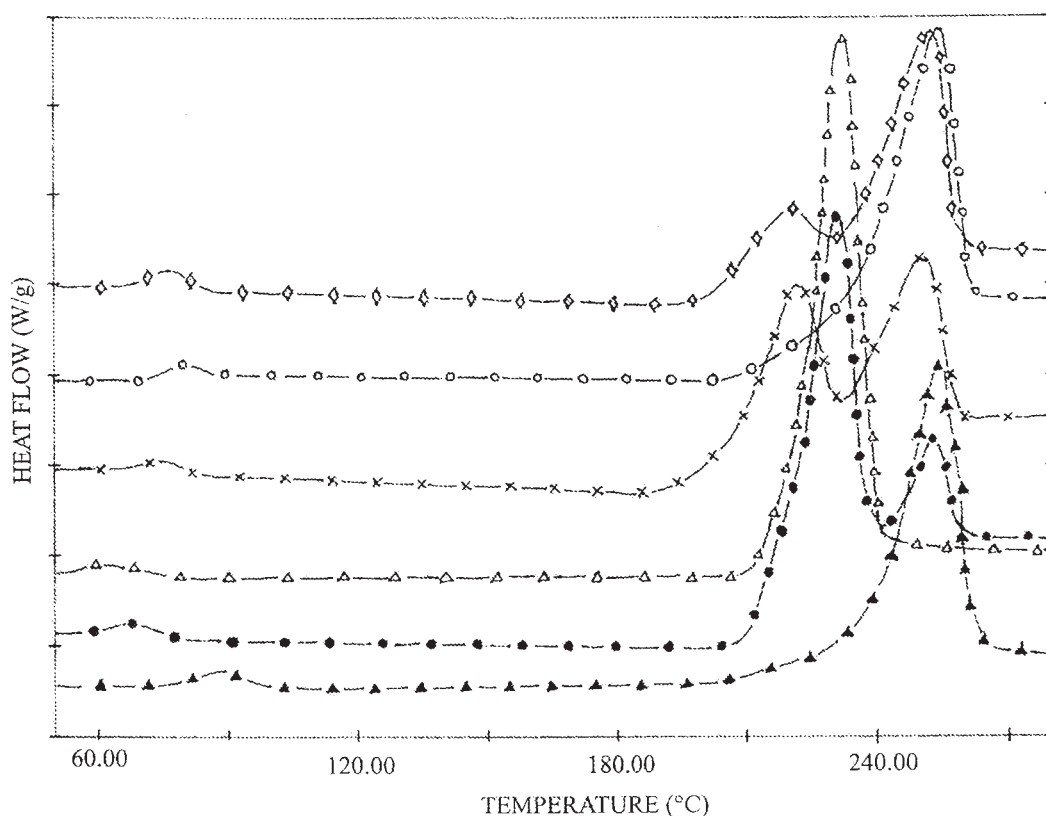


Figure 1 DSC thermograms of PET/PBT blends in the heating cycle: (▲) PET, (○) PET 80, (◇) PET 60, (×) PET 50, (●) PET 20, and (△) PBT.

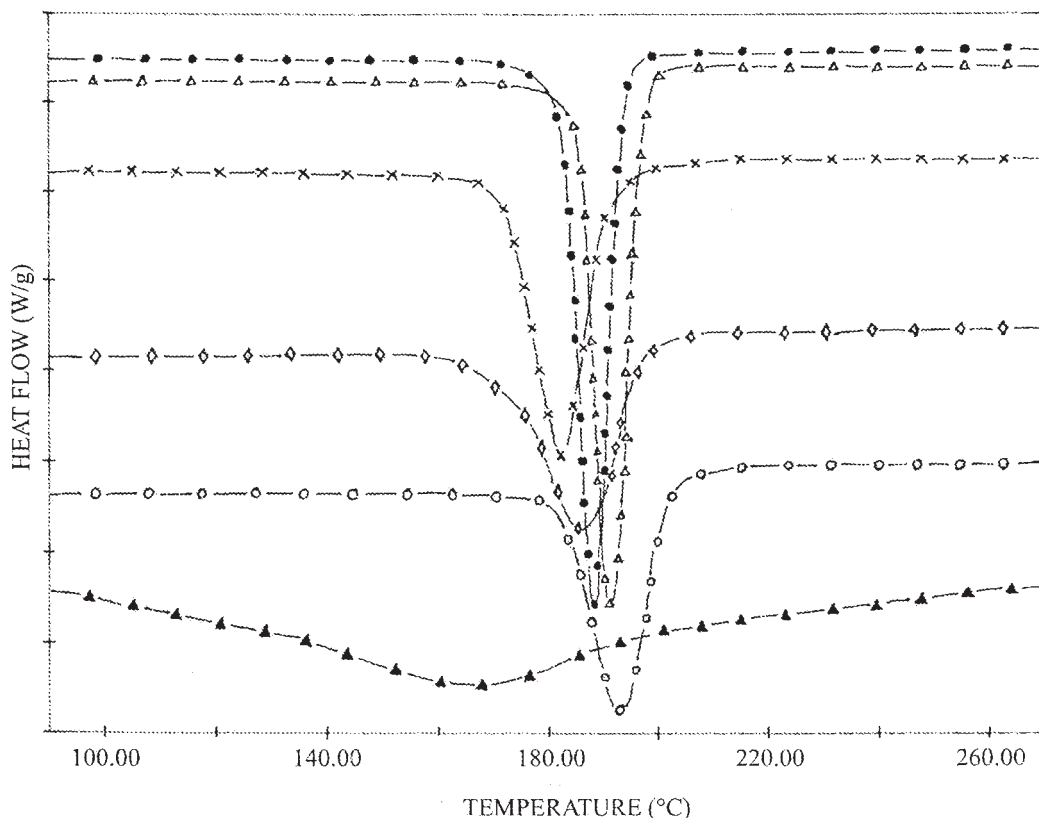


Figure 2 DSC thermograms of PET/PBT blends in the cooling cycle: (▲) PET, (○) PET 80, (◇) PET 60, (×) PET 50, (●) PET 20, and (△) PBT.

also reported in Table I. Note that the impact strength and flexural modulus of these blends increased slightly compared to the blends prepared by blending 80 parts PET and 20 parts PBT. Thus, it is clear that the 50:50 PET/PBT blend composition shows better properties than virgin PET and PBT. The “interesting” properties of 50:50 PET/PBT blends are mentioned in the patent literature.¹⁰ The positive deviation of the impact values may be correlated with the processing

conditions and miscibility, as suggested by Mishra and Deopura.⁵

HDT analysis

The HDT of PET is much higher than that of PBT. As the amount of PET in the PET/PBT blends increased, the HDT steadily increased. Thus, the addition of PET into PBT helps enhance the HDT of PBT. The blend

TABLE II
Thermal Characterization Data for PET/PBT Blends

Compositions (wt %)	Melting temperature (°C)		Heat of fusion (J/g)		Crystallization temperature (°C)	Heat of crystallization (J/g)	T_g (°C)
	PET	PBT	PET	PBT			
PET	256	—	34	—	166	21	81
PET/PBT							
80:20	255	—	35 (27)	— (10)	193	33	75
80:20 A	251	—	47	—	189	38	71
70:30	253	221	26 (24)	4 (16)	187	34	73
60:40	253	222	24 (20)	15 (21)	186	36	72
50:50	252	225	17 (17)	13 (13)	183	40	69
40:60	253	227	15 (14)	21 (31)	185	40	67
20:80	254	233	7 (7)	36 (42)	188	43	64
PBT	—	233	—	52	192	51	58

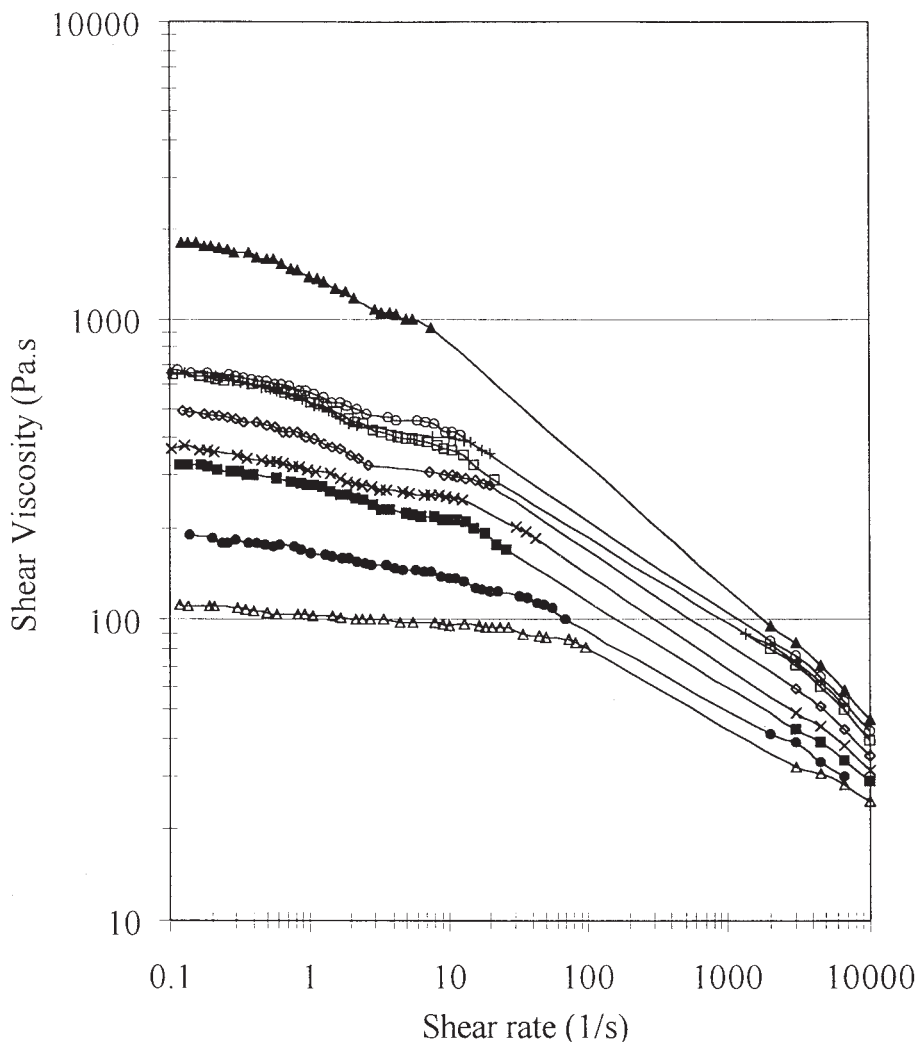


Figure 3 The shear viscosity behavior of PET/PBT blends at 260°C: (▲) PET, (○) PET 80, (+) 80:20 A PET/PBT, (□) PET 70, (◇) PET 60, (×) PET 50, (■) PET 40, (●) PET 20, and (△) PBT.

prepared by mixing 60 parts PET with 40 parts 50:50 PET/PBT blends seems to show slightly higher HDT compared to a normal blend of 80 parts PET and 20 parts PBT.

Electrical properties

Table I also shows the variation of the breakdown voltage for PET/PBT blends. Virgin PET has a higher breakdown voltage than virgin PBT. The addition of PBT into PET in the PET/PBT blend compositions decreased the breakdown voltage. However, 50:50 PET/PBT blends showed appreciably higher values than other compositions.

Thermal properties

DSC

Figures 1 and 2 show DSC heating and cooling scans for PET/PBT blends. All of the blends, except the 80:20

PET/PBT blend composition, show two melting peaks corresponding PBT and PET phases. The melting peak temperature for PET is lower in the blends in comparison to virgin PET. The peak melting temperature for 50:50 PET/PBT blends is the lowest. Similarly, the peak melting temperature of PBT is also lower in blends compared to virgin PBT. The lowering of this temperature for PBT appears to be related to the systematic variation in the compositions.

The heat of fusion (δH_m) values show very interesting behavior. The δH_m value for PET-rich blends is higher than the value expected from its amount present in the blends based upon the linear additivity rule. The values in the parentheses in Table II correspond to the additivity rule. Similarly, the δH_m values for PBT are also shown in parentheses. It is clearly seen that the δH_m values for PBT are lower than the values expected on the basis of additivity. One of the reasons for this could be the miscibility of PET and PBT, which depends upon the composition. Therefore,

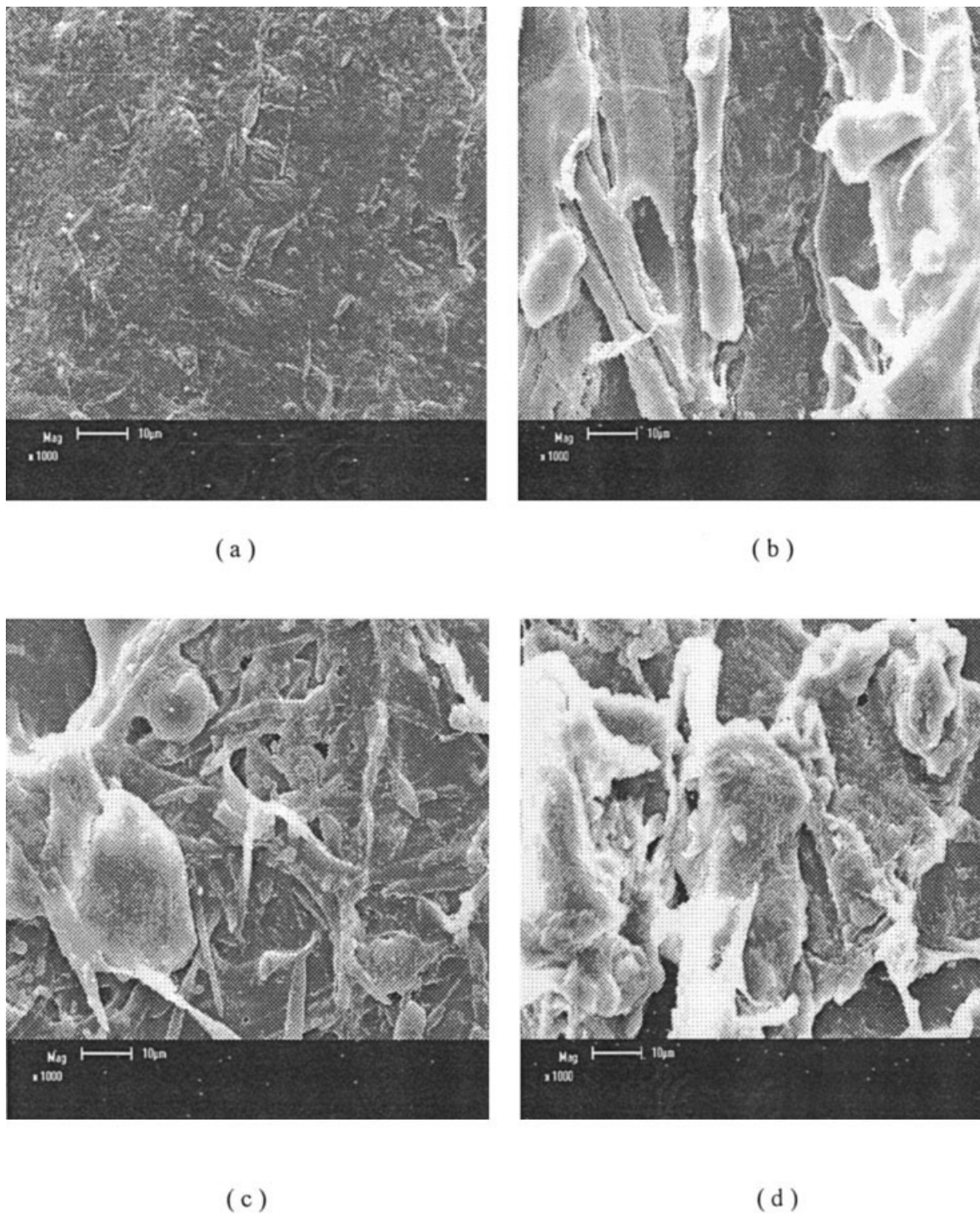


Figure 4 Scanning electron microscopy photomicrographs of PET/PBT blends (original magnification $\times 1000$): (a) 20:80, (b) 40:60, (c) 50:50, (d) 60:40, (e) 70:30, (f) 80:20, and (g) 80:20 A.

PET-rich blends show different behavior than PBT-rich blends.

Only a single T_g value is observed for all blends. These values are also listed in Table II. The variation of the T_g seems to be linearly proportional to the change in composition. This also indicates good miscibility of the two polymers in the amorphous

phase. DSC studies reported by Avramova⁷ also show similar results.

The cooling curves show very interesting behavior. Only one peak is observed for all of the blends. The peak crystallization temperatures are 166°C for PET and 192°C for PBT. The peak crystallization temperature for all blends is higher than PET and lower than

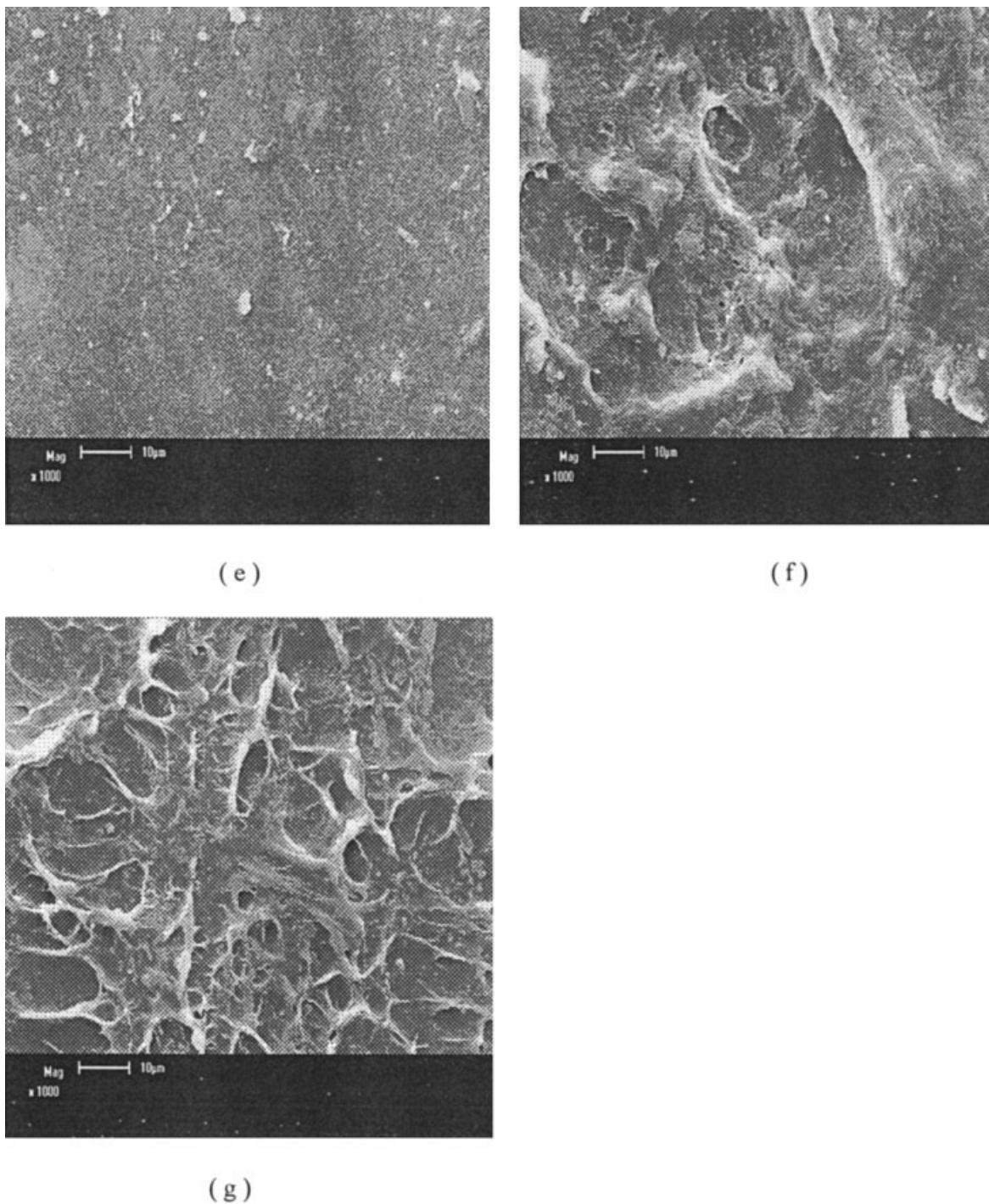


Figure 4 (Continued from previous page)

PBT. The miscible PBT phase could have a nucleating effect on PET, which can alter these temperatures. Tao et al.'s¹³ results also support the miscibility of PET and PBT and the nucleating effects.

Rheological properties

Figure 3 shows the variation of the melt viscosity of PET, PBT, and different PET/PBT blends over a wide

range of shear rates. It is clear that the viscosity of PET is higher than PBT. All blends show Newtonian behavior at a low shear rate and non-Newtonian behavior at a high shear rate. The viscosity of all of the blends changes systematically with the composition. This may indicate compatibility between PET and PBT. Mishra and Deopura¹⁴ studied the rheological behavior of PET and PBT blends. They found that blends containing up to 4% PBT showed higher vis-

cosity than PET. They attributed this affect to increased entanglement. However, when the concentration of PBT was more than 4%, the viscosity of the blends was less than PET. They suggested phase segregation as the possible reason.

The difference in the viscosity of PET and PBT in the present study at a high shear rate is less than that in the low shear rate region. Because a lower viscosity ratio of the blend components provides better dispersion in a given blend, blending of PET and PBT at a high shear rate gives better uniformity and properties.

The results reported by Jin and Tao⁸ showed that the viscosity of the blend was less than that of PET and PBT. Lower viscosity values of blends could be due to slip between the two phases because the intrinsic viscosities of PET and PBT in their study were 0.65 and 1.05 dL/g, respectively. Their processing conditions were also different.

Morphological study

Figure 4 shows scanning electron photomicrographs for the PET/PBT blends. The 40:60, 50:50 and 60:40 PET/PBT blend compositions show a cocontinuous morphology [Fig. 4(b–d)]. The 50:50 and 40:60 blends seem to show even a fibrillar nature. The PET-rich 80:20 [Fig. 4(f)] and 70:30 [Fig. 4(e)] blends show slightly higher size of the dispersed phase (PBT) compared to the size of the dispersed PET phase in the PBT-rich 20:80 blend [Fig. 4(a)]. There is also a tendency toward a fibrillar nature in PET-rich blends [Fig. 4(f)]. The morphological behavior of PET-rich blends reported by Jin and Tao⁸ is similar to the present study. The morphology of the 80:20 A blend is very interesting and quite different than the 80:20 blend prepared by normal mixing of the two components. The fibrillar nature and some network formation are clearly visible [Fig. 4(g)]. In the 80:20 A blend, the dispersion of a cocontinuous 50:50 blend into PET produced different morphology in the final blend compared to dispersing 20 parts PBT into 80 parts

PET. Thus, the 50:50 blend seems to show unique properties.

CONCLUSIONS

The impact strength of all PET/PBT blends is higher than that of PET and PBT. The 50:50 blend showed the highest impact strength value. PET and PBT seemed to be miscible over the entire composition range. The miscibility of the amorphous phase of PET and PBT resulted in a single T_g . The rheological behavior suggested mixing of PET and PBT at a high shear rate. PET-rich blends had a fibrillar nature. Cocontinuous behavior was observed for of 40:60, 50:50, and 60:40 blend compositions.

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