Thermal, Mechanical, and Morphological Characterization Studies of Poly(2,6-dimethyl-1,4-phenylene oxide) Blends with Polystyrene and Brominated Polystyrene

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ABSTRACT: The miscibility of the binary and ternary blends of poly(2,6-dimethyl-1,4-phenylene oxide), brominated polystyrene, and polystyrene was investigated using a differential scanning calorimeter. The morphology of these blends was characterized by scanning electron microscopy. These studies revealed a close relation between the blend structure and its mechanical properties. The compatibilizing effect of poly(2,6-dimethyl-1,4-phenylene oxide) on the miscibility of the polystyrene/brominated polystyrene blends was examined. It was found that poly(2,6-dimethyl-1,4-phenylene oxide), which was miscible with polystyrene and partially miscible with brominated polystyrene, compatibilizes these two immiscible polymers if its contention exceeds 33 wt %. Upon the addition of poly(2,6-dimethyl-1,4-phenylene oxide) to the immiscible blends of polystyrene/brominated polystyrene, we observed a change in the morphology of the mixtures. An improvement in the mechanical properties was noticed. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 225–231, 2000

Key words: blends; poly(phenylene oxide); brominated polystyrene

INTRODUCTION

It is well known that poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is miscible in all proportions with polystyrene (PS),[1–6] due to the favorable specific interactions of the repeat units of these polymers.[7,8] Mixtures of PPO and PS give amorphous segmentally miscible blends of significant commercial importance.[9] Limited compatibility was observed for the blends of PPO and halogen-substituted PSs.[9] The phase behavior of PS, PPO, and brominated derivatives of these polymers was studied.[7] The mean-field theory of phase behavior was used to discuss, in detail, the interactions and compatibility in polymer/copolymer systems of these blends.[8,10,11]

In this work, first, we studied the miscibility of the two binary polymeric systems: PS/brominated PS, and PPO/brominated PS. Only limited miscibility was observed for a binary PPO/brominated

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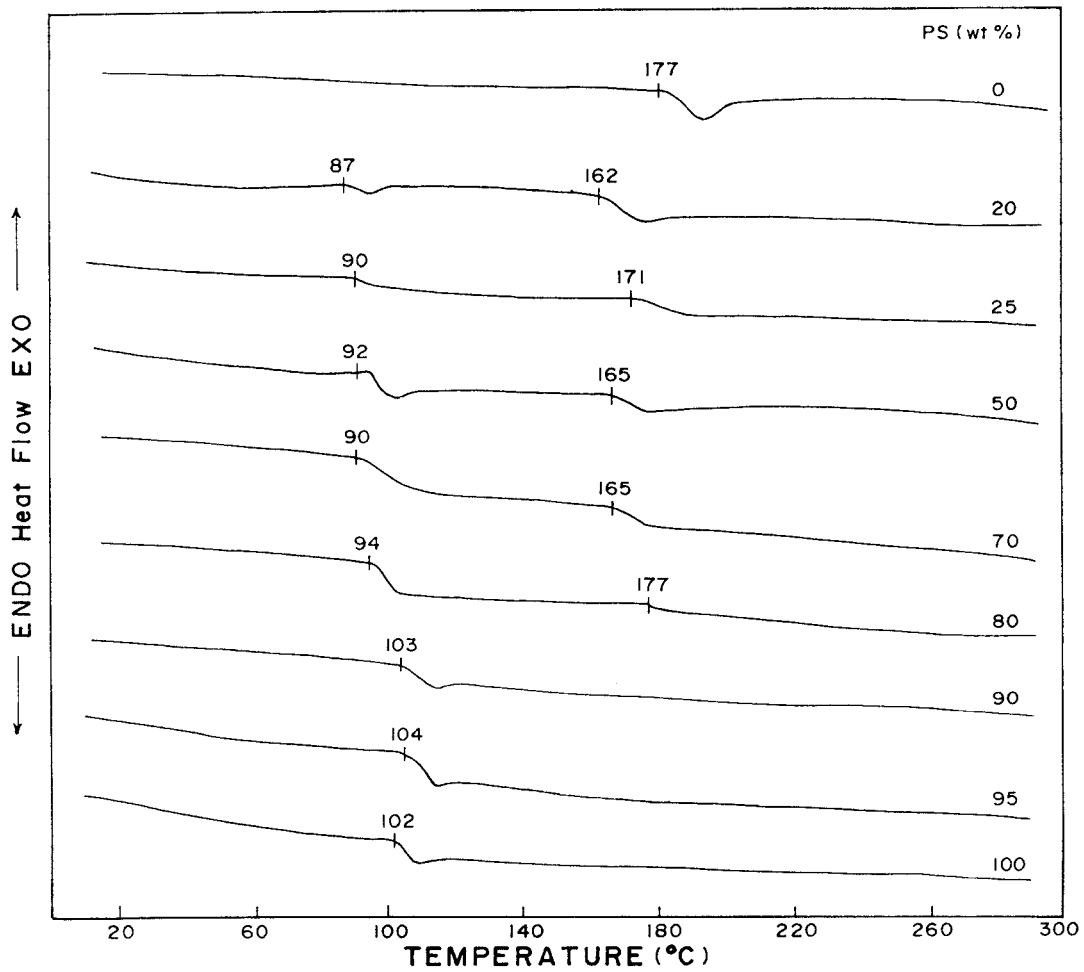

Figure 1 DSC thermograms of PS/brominated PS binary blends.

PS system. On the other hand, the blends of PS/brominated PS are immiscible in all compositions. However, compatible compositions of ternary blends of PPO/brominated PS/PS were obtained due to the compatibilizing effect of PPO in this system.

EXPERIMENTAL

The PPO used to prepare the binary and ternary blends was purchased from Polysciences, Inc. (Warrington, PA; $M_w = 50 \times 10^3$ g mol^{-1}; $M_n = 20 \times 10^3$ g mol^{-1}; high softening point, 90°C). PS was a Koppers Co. Inc. (Linden, NJ) product ($M_w = 4.9 \times 10^4$ g mol^{-1}; $M_n = 4.1 \times 10^4$ g mol^{-1}).

Brominated PS was purchased from Polysciences, Inc. The structural characterization of this polymer was performed using IR, NMR, and chemical analysis. We found that pendant phenyl groups of the PS backbone chain contain, on average, 2.66 Br atoms. (i.e., two of each three pendant phenyl groups were *ortho-para*–tribromo, whereas the remaining one was dibromo-substituted). Gel permeation results were $M_w = 63 \times 10^3$ g mol^{-1} and $M_n = 19 \times 10^3$ g mol^{-1}.

Pure polymers and their binary blends of PS/brominated PS and PPO/PS were cast from the 5 wt % chloroform solution on a mercury surface at room temperature. The resulting films were dried under reduced pressure at 100°C until the films reached a constant weight. Chlorobenzene used

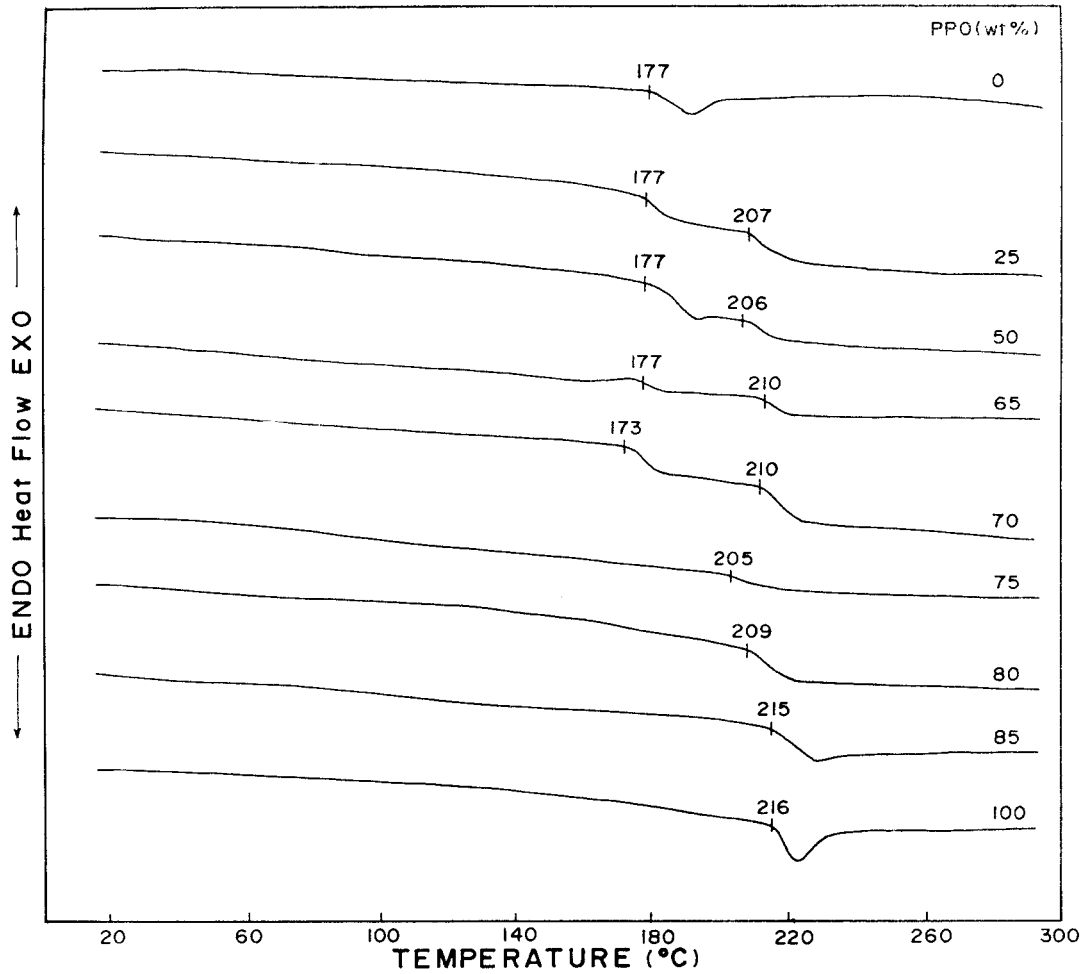

Figure 2 DSC thermograms of PPO/brominated PS binary blends.

as a solvent to cast ternary blends of PPO/brominated PS/PS.

Glass transition temperatures (T_g) of the blends were determined using a DuPont Instrument 90 differential scanning calorimeter and a DuPont Instruments series 99 thermal analyzer at a heating rate 10°C/min under a stream of nitrogen from 20 to 300°C. The reported T_g values were based on the second run. The glass transition temperature was taken as the initial onset of the change of slope in the DSC curve.

Mechanical properties of the polymeric and blended samples were determined by standard tensile stress–strain tests to measure the modulus (E), ultimate strength (σ), and elongation at break (ε). Standard tensile stress–strain experiments were performed at room temperature on an Instron tensile tester (Instron Model TM-S Table Model 1102). All the results were reported as an average of at least three measurements.

Scanning electron micrographs were taken on a JEOL-JXA 840A scanning electron microscope (SEM). The specimens were prepared for SEM by freeze-fracturing in liquid nitrogen and applying a gold coating of approximately 300 Å on an Edwards S 150 B sputter coater.

RESULTS AND DISCUSSION

Thermal Properties

Figure 1 shows the DSC thermograms of PS/brominated PS binary blends having various

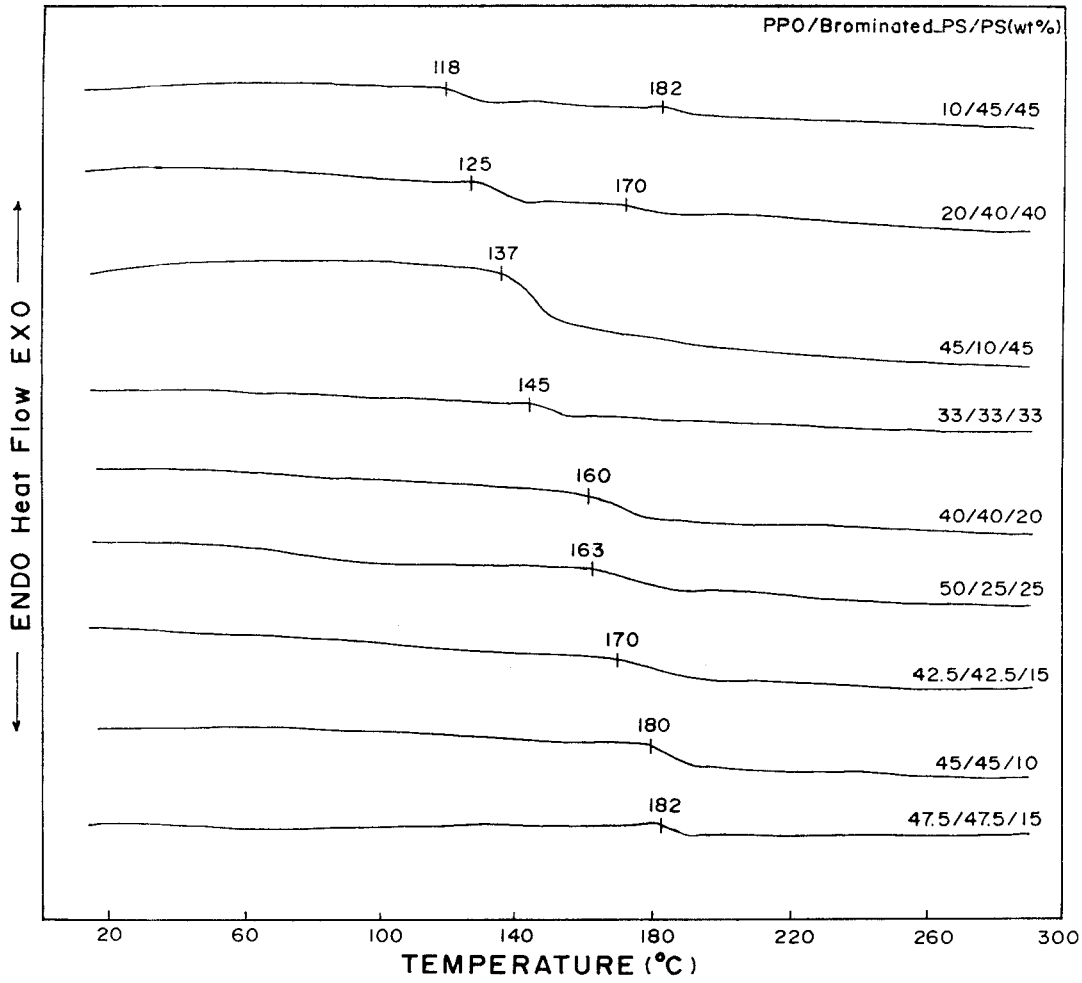

Figure 3 DSC thermograms of PPO/brominated PS/PS ternary blends.

compositions. The glass transition temperatures of PS and brominated PS were 102 and 177°C, respectively. It is known that bromosubstitution is effective to induce incompatibility in PS blends.[8,9] Binary blends of PS and brominated PS, cast from chloroform, seem to be opaque, indicating phase separation. The existence of two glass transitions shows the immiscible nature of this system.

Figure 2 shows the DSC thermograms of a series of binary blends composed of varying weight ratios of PPO and brominated PS. The glass transition of PPO was 216°C. Blends containing less than 25% brominated PS cast either from chloroform or chlorobenzene were transparent. However, binary blends of these mixtures containing more than 25 wt % brominated PS became cloudy and exhibited two glass transition temperatures.

Figure 3 shows the DSC thermograms of ternary blends of PPO/brominated PS/PS. The weight compositions of ternary blends are indicated above each thermal curve. The percentage of one of the components is variable. For each blend, the weight percents of the other two components are identical. It will be seen that the ternary blends containing 33 wt % or more PPO display a single glass transition temperature.

Mechanical Properties

Tensile properties of PS, PPO, brominated PS, and their binary and ternary blends were determined on cast film specimens. The results are given in Table I. The films prepared from brominated PS were too brittle for tensile measurements. The observed modulus values of pure PS and PPO were rather low compared to the lit-

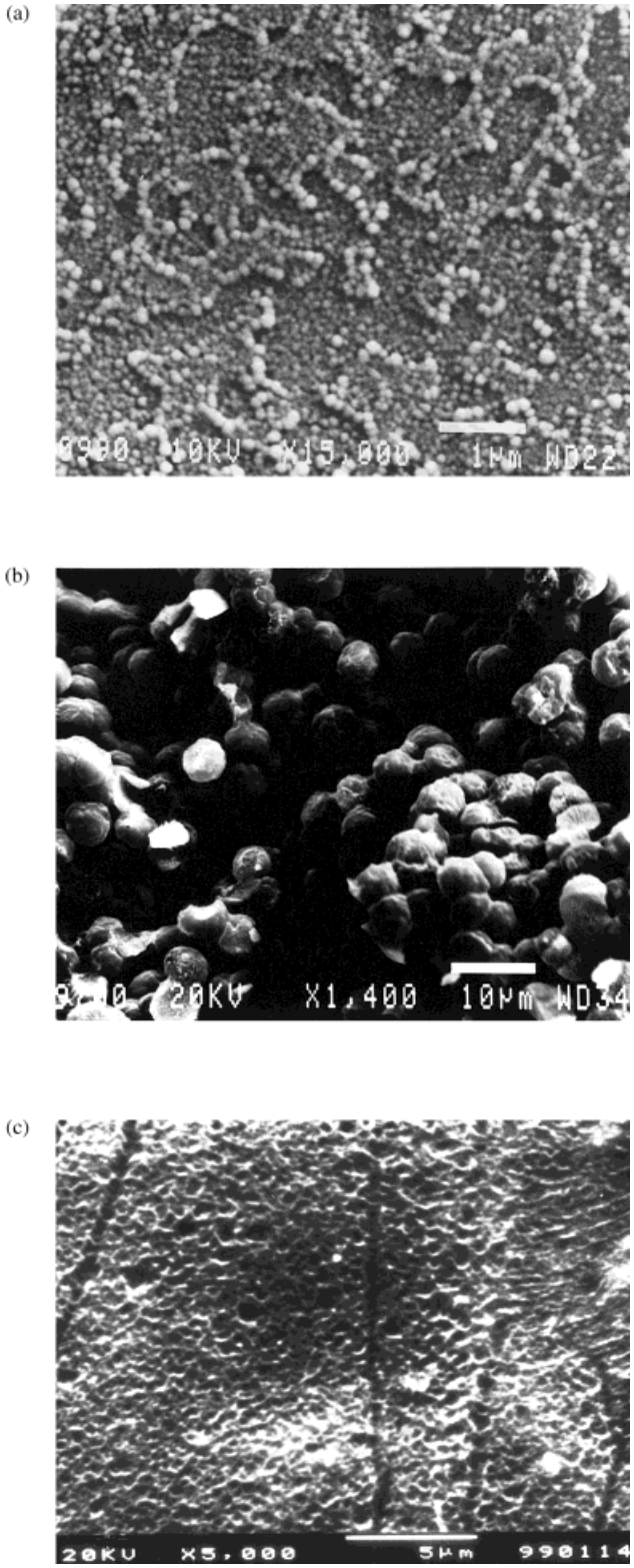

Figure 4 (a) SEM micrograph of pure PS. (b) SEM micrograph of pure PPO. (c) SEM micrograph of pure brominated PS.

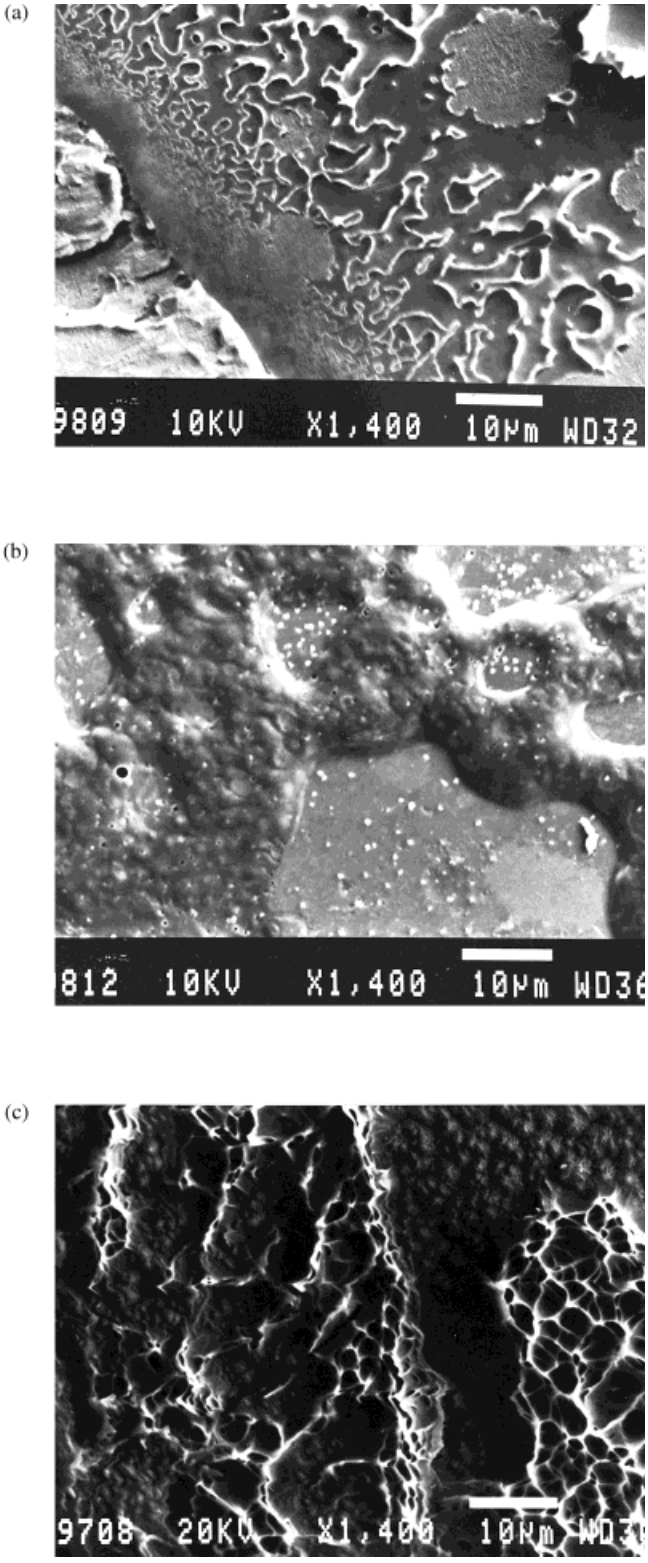

Figure 5 (a) SEM micrograph of pure PS/PPO (50/50) binary blend (T_g = 143°C). (b) SEM micrograph of pure PS/brominated PS (85/15) binary blend (T_{g_1} = 97°C; T_{g_2} = 173°C). (c) SEM micrograph of PPO/brominated Ps (75/25) binary blend (T_{g_1} = 205°C).

Table I Tensile Properties of Homopolymers and Their Blends

Run No.	Components	Stress (σ, MPa)	Elongation (ε, %)	Modulus (E, MPa)	T_g (°C)
1	PS	19.1	9	350	102
2	PPO	28.2	4	1550	216
	PS/PPO				
3	(50/50)	49	12	765	143
	PS/BrPS				
4	(75/25)	8	30	203	94; 177
5	(50/50)	7	1	174	92; 165
6	(25/75)	11	1	112	90; 171
	PPO/BrPS				
7	(75/25)	42	5	844	205
8	(65/35)	16	8	392	177; 210
9	(25/75)	9	5	223	177; 207
	PS/BrPS/PPO				
10	(45/10/45)	41	10	427	137
11	(10/45/45)	31	4	470	180
12	(33/33/33)	19	30	643	145
13	(20/40/40)	22	2	630	125; 170
14	(45/45/10)	17	1	340	118; 182

BrPS, brominated polystyrene.

erature values of commercial homopolymers, since the molecular weights of our samples were rather low. The mechanical properties of immiscible blends of PS/brominated PS (runs 4–6) PPO/brominated PS (runs 8, 9) exhibiting two glass transition temperatures show inferior behavior compared to the homopolymers. The binary blends of PS/PPO (run 3) are miscible in all compositions and they exhibit superior performance as engineering thermoplastics. Since the properties of these blends are well documented in the literature, we have not studied their tensile properties in detail. The miscible blends of PPO/brominated PS/PS ternary mixtures (runs 10–12) indicating only a single T_g show superior tensile properties (higher elastic modulus and ultimate strength) compared to PS.

Morphological Studies

Electron micrographs of the homopolymers and the binary and ternary blends of PS, PPO, and brominated PS films cast from the chloroform solution (5 wt %) are shown in Figures 4–6. Secondary electron image (SEI) compositional contrast was applied in the SEM micrographs. Figure 4(a,b) show the rod-sphere structures of rather homogeneous matrices of PS and PPO homopolymers. The micrograph of brominated PS [Fig. 4(c)] shows a heterogeneous and more complex morphology with respect to PS and PPO.

Figure 5(a) shows an SEM micrograph of a miscible binary blend of PS/PPO (50/50 wt %). The binary blend of PS/brominated PS (85/15 wt %) exhibits a heterogeneous immiscible morphology [Fig. 5(b)]. Figure 5(c) shows a partially miscible surface structure of PPO/brominated PS (75/25 wt %). The morphology of the fractured surface of this sample is similar to the surface micrograph.

SEM micrographs of the ternary blends of PPO/brominated PS/PS having different compositions are shown in Figure 6(a–d). A ternary blend of these components of a (10/45/45) mixture exhibits two T_g values at 118 and 182°C. An SEM micrograph of this mixture [Fig. 6(a)] shows a complex morphology. It can be seen in Figure 6(b–d) that the micrographs of the ternary mixtures of PPO/brominated PS/PS exhibiting single T_g values show a rather homogeneous morphology.

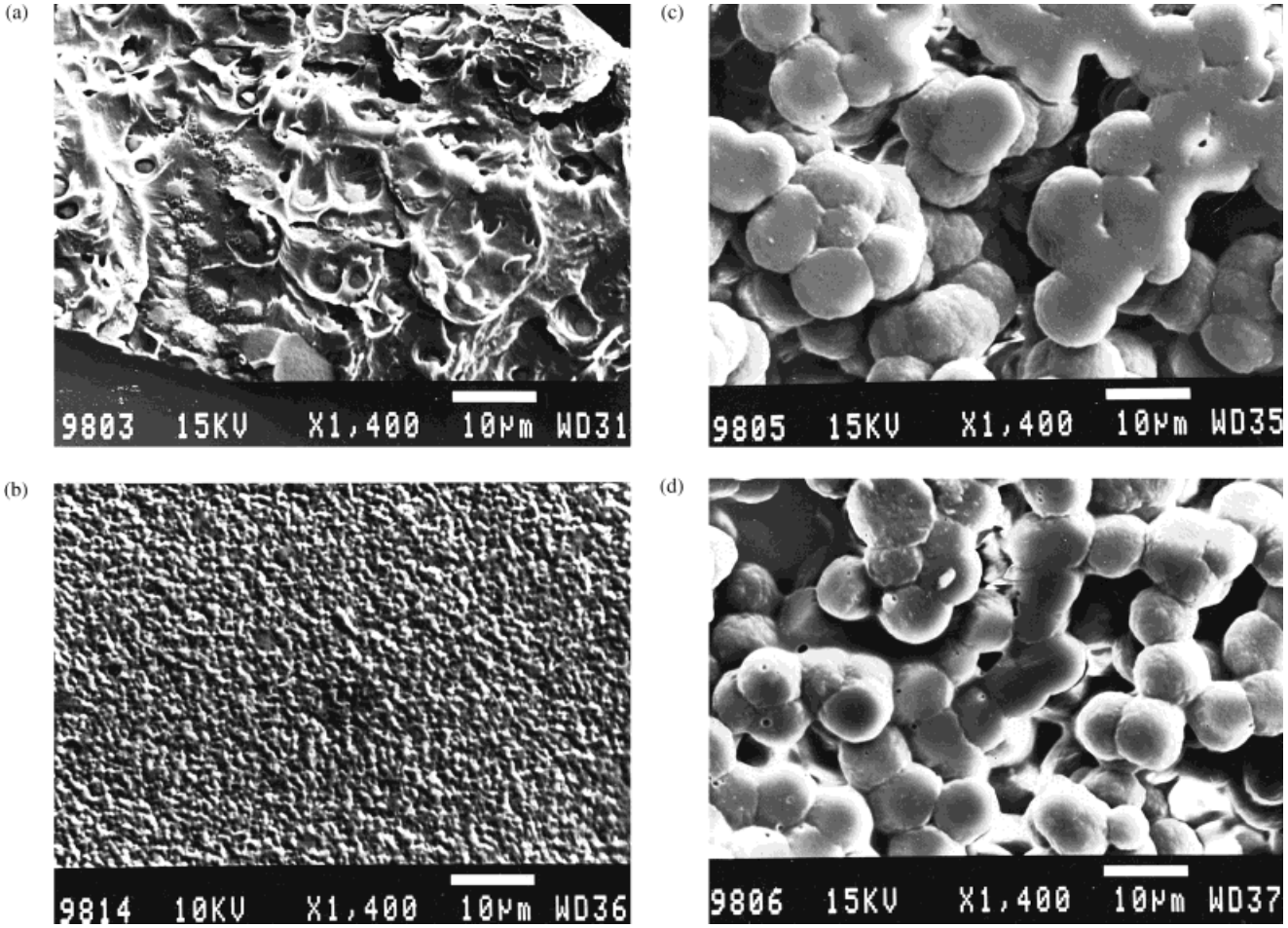

Figure 6 (a) SEM micrograph of PPO/brominated PS/PS (10/45/45) ternary blends (T_{g_1} = 118°C; T_{g_2} = 182°C). (b) SEM micrograph of PPO/brominated PS/PS (33/33/33) ternary blends (T_g = 145°C). (c) SEM micrograph of PPO/brominated PS/PS (45/45/10) ternary blends (T_g = 180°C). (d) SEM micrograph of PPO/brominated PS/PS (45/10/45) ternary blends (T_g = 137°C).

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