

# Blends of Poly(propylene) and Polyacetal Compatibilized by Ethylene Vinyl Alcohol Copolymers

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**ABSTRACT:** Polymer blends of poly(propylene) (PP) and polyacetal (polyoxymethylene, POM) with ethylene vinyl alcohol (EVOH) copolymers were investigated by differential scanning calorimetry (DSC), rheological, tensile, and impact measurements, Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM). The PP-POM-EVOH blends were extruded with a co-rotating twin-screw extruder. The ethylene group in the EVOH is partially miscible with PP, whereas the hydroxyl group in the EVOH can form hydrogen bonding with POM. The EVOH tends to reside along the interface, acting as a sur-

factant to reduce the interfacial tension and to increase the interfacial adhesion between the blends. Results from SEM and mechanical tests indicate that a small quantity of the EVOH copolymer or a smaller vinyl alcohol content in the EVOH copolymer results in a better compatibilized blend in terms of finer phase domains and better mechanical properties. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1471–1477, 2003

**Key words:** blends; compatibilization; poly(propylene) (PP); copolymerization; morphology

## INTRODUCTION

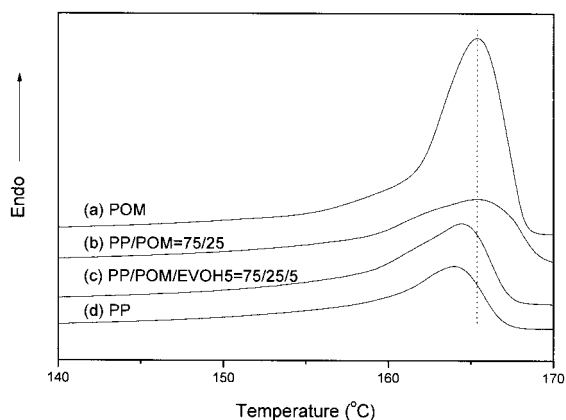
Over the past few decades, polymer blends have been a subject of intensive research because of their potential applications in engineering materials with desirable properties.<sup>1–5</sup> Polyacetal (polyoxymethylene, POM) is one of the major engineering thermoplastics that has very good mechanical properties, such as tensile strength, flexural modulus, and deflection temperature. Furthermore, POM possesses high creep, fatigue, and corrosive resistance that leads to a number of commercial applications, such as bearings, gears, blower wheels, pump impellers, and carburetor bodies.<sup>6</sup> However, like many unmodified polymer matrices, POM is extremely brittle in notched impact. Therefore, many studies have reported the toughening of POM by blending POM with an amorphous polymer.<sup>7–14</sup> For example, Cherdon et al.<sup>7</sup> disclosed improving the impact strength of the POM by blending with various copolymers. Chiang et al.<sup>8, 9</sup> studied the addition of a polyurethane or ethylene-propylenediene terpolymer (EPDM) to the rigid POM matrix to increase its toughness. Kumar et al.<sup>10</sup> reported the effect of thermoplastic polyurethane (TPU) on the melting point and the percentage crystallinity of POM. They found that the crystalline structure of POM remains unchanged even after the addition of amor-

phous TPU. Our earlier studies also reported the toughening of POM by blending with polycarbonate (PC)<sup>11</sup> and TPU.<sup>12</sup>

Although a number of POM blends have been reported, a blend of POM with semicrystalline poly(propylene) (PP) is very rare. PP possesses better flexibility and higher impact strength, but has relatively lower tensile strength and deflection temperature. Moreover, PP and POM have similar melting points, melt viscosities, and processing temperatures. Therefore, blends of PP and POM may provide better impact resistance for POM and better flexural modulus for PP, combined with lower cost, compared with POM alone.<sup>15</sup> Soundararajan and Shit reported that the impact (5% POM) and flexural modulus (20% POM) of PP-POM blends are higher than that of the pure PP.<sup>16</sup> Hence, they concluded that the PP-POM blends may be at least partially compatible. In this work, we studied the properties of PP and POM blends containing ethylene vinyl alcohol (EVOH) copolymers. Based on the similar chemical structure between PP and poly(ethylene) segments in EVOH copolymers, it is expected that PP and EVOH are partially compatible. The hydroxyl groups in EVOH can form intermolecular hydrogen bonding with POM. Therefore, it is expected that EVOH copolymers may be suitable compatibilizers for blends of PP and POM. The objective of the present work was to study the effect of the addition of EVOH copolymers on the morphology, rheological, and mechanical properties of the PP-POM blends.

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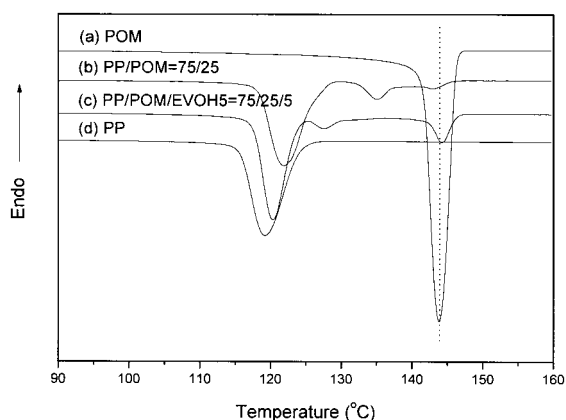


**Figure 2** DSC heating traces of PP, POM, and PP-POM blends: (a) POM, (b) 75/25 PP-POM blend, (c) 75/25/5PP-POM-EVOH5 blend, and (d) PP alone.

## RESULTS AND DISCUSSION

### Hydrogen bonding between POM and EVOH

Infrared spectroscopy is a powerful tool to study polymer blend miscibility. If the blend is immiscible, the absorption spectrum of the blend will be the sum of those for the components. If the blend is miscible or partially miscible, specific interactions between the two components perturb the bonding between atoms, resulting in differences in the spectrum of the blend compared with that of the components. The hydroxyl stretching range in a FTIR spectrum is sensitive to the hydrogen bonding formation. The FTIR spectra of EVOH5 and the 100/5 POM-EVOH5 blend in the range  $3000\text{--}4000\text{ cm}^{-1}$  are shown in Figure 1. The pure EVOH5 shows a major band at  $3447.6\text{ cm}^{-1}$  and a minor absorption at  $3258.6\text{ cm}^{-1}$ . The band of the hydroxyl group shifts to a lower wavenumber ( $3420.5\text{ cm}^{-1}$ ) for the POM-EVOH5 blend, which is an indication of hydrogen bonding formation between the ether group of POM and the hydroxyl group of



**Figure 3** DSC cooling scans of PP, POM, and PP-POM blends: (a) POM, (b) 75/25 PP-POM blend, (c) 75/25/5PP-POM-EVOH5 blend, and (d) PP alone.

**TABLE II**  
Melt Flow Rates of the PP-POM-EVOH Blends<sup>a</sup>

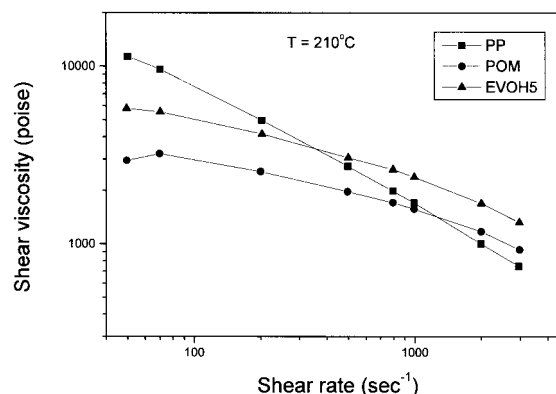
Composition	MFR (g/10 min)
POM	36
POM-EVOH5 = 100/5	12
PP-POM = 25/75	20
PP-POM-EVOH5 = 25/75/5	11
PP-POM = 50/50	12
PP-POM-EVOH1 = 50/50/2.5	6
PP-POM-EVOH2 = 50/50/2.5	7
PP-POM-EVOH5 = 50/50/1	7
PP-POM-EVOH5 = 50/50/2.5	8
PP-POM-EVOH5 = 50/50/5	9
PP-POM-EVOH5 = 50/50/10	10
PP-POM = 75/25	5
PP-POM-EVOH5 = 75/25/5	4
PP	2

<sup>a</sup> Tested at 210°C, with a load of 2.16 kg

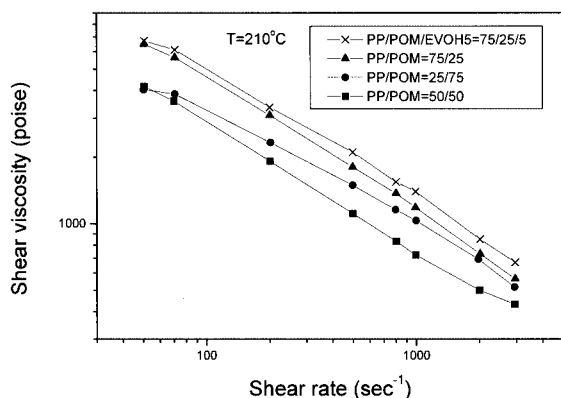
EVOH5. Partial miscibility of POM and EVOH5 due to hydrogen bonding formation is thus assumed.

### Thermal analyses

The compatibility of a polymer blend can be probed by its thermal and crystallization behaviors based on DSC measurements. The thermal properties of the materials tested are summarized in Table I and shown in Figures 2 and 3. The DSC heating scans of PP, POM, and PP-POM blends, at a heating rate of  $10\text{ °C/min}$ , are shown in Figure 2. Both PP and POM are semicrystalline polymers, with melting temperatures of  $163.9$  and  $165.4\text{ °C}$ , respectively. The melting temperature of the uncompatibilized 75/25 PP-POM blend is identical to that of POM (i.e.,  $165.4\text{ °C}$ ), and the heat of fusion is the sum of mass fraction of PP and POM. However, compared with the uncompatibilized blend, the melting temperature of the compatibilized 75/25/5 PP-POM-EVOH5 blend decreases slightly (i.e.,  $164.4\text{ °C}$ ) and the heat of fusion decreases significantly. This result indicates that the presence of EVOH5 in the



**Figure 4** Shear viscosity versus shear rate curves of the neat PP, POM, and EVOH5.



**Figure 5** Shear viscosity versus shear rate curves of the uncompatibilized and compatibilized PP-POM blends.

blend disturbs the crystallization of PP and POM and results in a decrease in the crystallinity of the blend.

The DSC cooling scans of PP, POM, and PP-POM blends from the melt to room temperature at a cooling rate of 10°C/min are shown in Figure 3. POM and PP each exhibit one crystallization peak, at 143.8 and 119.3°C, respectively. There are three crystallization peaks in the DSC cooling curves for the 75/25 compatibilized and uncompatibilized PP-POM blends. Furthermore, the first crystallization temperature for the EVOH5 compatibilized blend appears at 144.2°C, which is slightly higher than that of POM. This result means that the addition of EVOH5 in the blend may act as a nucleating agent to increase the crystallization rate of the POM component. However, the presence of intermolecular interaction tends to hinder the POM and PP crystallization, resulting in lower crystallinity in the compatibilized blend than in the uncompatibilized blend. This tendency can be further proved from the heat of crystallization, as listed in Table I.

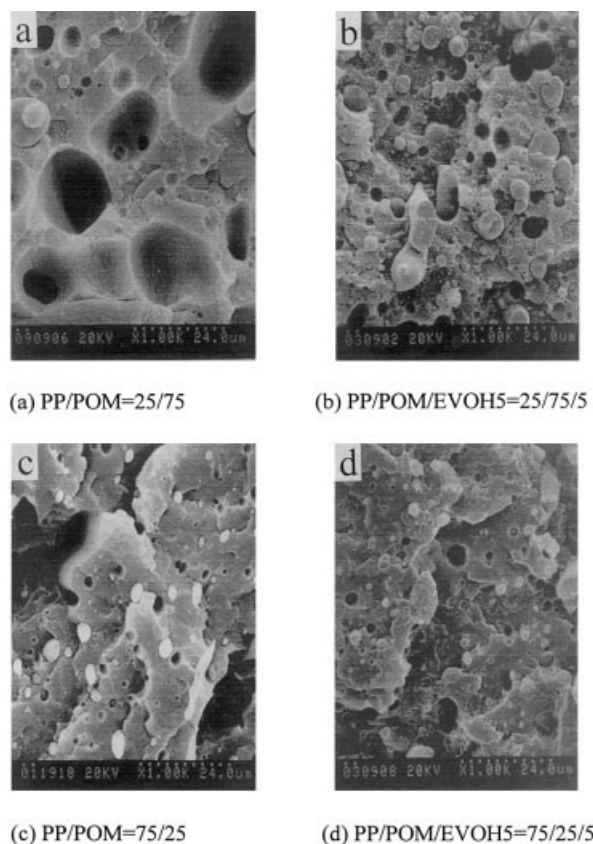
### Melt flow rates (MFRs)

MFR is an inverse function of viscosity and can be used to assess the interaction between phases. The MFRs of the matrices and blends, measured at 210°C and 2.16 kg, are summarized in Table II. Pure PP exhibits the lowest MFR in all the specimens, indicating that pure PP possesses the highest viscosity under the testing conditions. Furthermore, the uncompatibilized blend with higher POM content (e.g., 25/75 PP-POM) exhibits higher MFR (lower viscosity). Comparing pure POM with the 100/5 POM-EVOH5 blend, it is clearly that only 5 wt % EVOH5 blended with POM results in a significant reduction in MFR values from 36 to 12 g/10 min. Without the presence of the compatibilizer, the PP-POM blends show higher MFR, as would be expected. In Table II, the trend clearly shows the decrease in MFR after compatibilization for all the compositions. It is well known that the hydroxy group

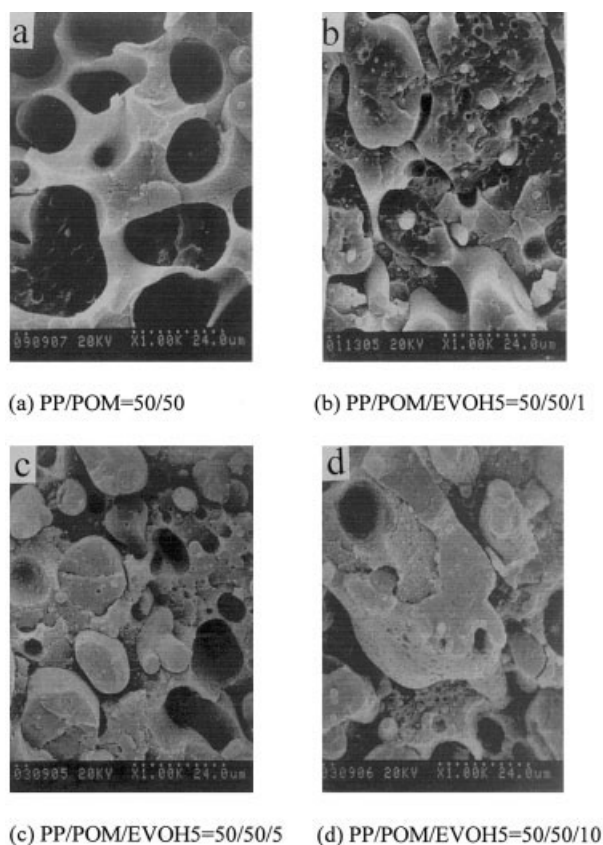
in the EVOH5 copolymer is able to interact with POM to form intermolecular hydrogen bonding, which tends to anchor along the PP-POM interface. The increase of the interfacial friction of the compatibilized blend compared with that of the corresponding uncompatibilized blend is believed to be the major contributor for the increase in viscosity of the blends. However, the increase in EVOH5 content leads to a decrease in viscosity for the PP-POM-EVOH5 (50/50/x) blend (Table II). Because the EVOH5 contains a higher weight percent of vinyl alcohol, it can form its own phase when a higher content of the EVOH5 is used during melt processing and thereby cause a decrease in viscosity.

### Capillary rheometry

Plots of shear viscosity versus shear rate for pure PP, POM, and EVOH5, measured at 210°C, are shown in Figure 4. At lower shear rates, the viscosity of PP is higher than those of POM and EVOH5. However, PP shows a higher shear thin behavior and gives the lowest viscosity at higher shear rates. The shear viscosity and shear rate for the uncompatibilized and compatibilized PP-POM blends are compared in Fig-



**Figure 6** SEM micrographs of the uncompatibilized and compatibilized PP-POM blends: (a) 25/75 PP-POM blend, (b) 25/75/5 PP-POM-EVOH5 blend, (c) 75/25 PP-POM blend, and (d) 75/25/5 PP-POM-EVOH5 blend.



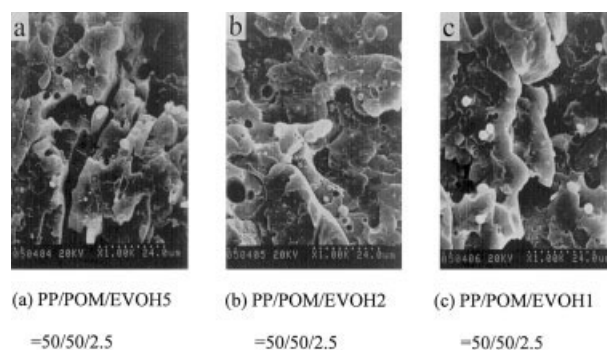
**Figure 7** SEM micrographs of the uncompatibilized and compatibilized PP-POM blends containing different content of EVOH5 in the blends: (a) 50/50 PP-POM blend, (b) 50/50/1 PP-POM-EVOH5 blend, (c) 50/50/5 PP-POM-EVOH5 blend, and (d) 50/50/10 PP-POM-EVOH5 blend.

ure 5. For all the uncompatibilized blends, the 50/50 PP-POM blend has the lowest shear viscosity, whereas the 75/25 PP-POM blend shows the highest viscosity. The observed trend is similar to the MFR data, and the 75/25/5 compatibilized PP-POM-EVOH5 blend exhibits the highest viscosity in all the blends. For the uncompatibilized blend, a “slide” takes place easily between phases of two immiscible homopolymers under shear stress due to higher shear tension and lower interfacial friction. This phenomenon leads to lower viscosity of the uncompatibilized blend. On the contrary, higher interfacial friction of the compatibilized blend is caused by the hydrogen bonding between POM and EVOH5 and results in higher viscosity compared with the corresponding uncompatibilized blend. The flow behaviors of the blends are further supported by the morphological structure of the blends determined by SEM morphology investigations.

### Scanning electron microscopy (SEM) morphologies

SEM micrograph is the most convenient approach to differentiate the morphologies between a compatibi-

lized and an uncompatibilized blend. An immiscible and incompatible blend usually results in coarser morphology than the corresponding compatibilized blend. In general, the coarse morphology can be improved by the addition of a suitable compatibilizer. The cryogenic fracture surfaces parallel to the flow direction of the uncompatibilized and compatibilized PP-POM blends are shown in Figure 6. For the 25/75 uncompatibilized PP-POM blend (Fig. 6a), the large dispersed and spherical PP particles with different dimensions can be easily identified from the blend because of the incompatibility of these two polymers. After compatibilization, the PP domain size is significantly reduced, as shown in Figure 6b. The finer phase domain is an indication of better compatibilization of the blend. Furthermore, the morphology of the 75/25 uncompatibilized PP-POM blend (Fig. 6c) shows a clear phase contrast. For the 75/25/5 compatibilized PP-POM-EVOH5 blend (Fig. 6d), the interface of PP and POM is less clear and the particle size of the dispersed POM phase becomes smaller with the addition of EVOH5 in the blend. The SEM micrographs of the 50/50/x PP-POM-EVOH5 blends, with different contents of EVOH5, are shown in Figure 7. The interface between the PP and POM is quite sharp for the 50/50 PP-POM blend, which is an indication of low interfacial adhesion. Comparison of Figures 7b–d reveals that the surface morphologies of the compatibilized blends become coarser with increasing EVOH5 content in the blend. This result implies that too high a content of EVOH5 in the blend may result in rougher morphology and lead to lower mechanical properties. For further investigation, the 50/50/2.5 PP-POM-EVOHx blends containing different contents of vinyl alcohol in EVOH are shown in Figure 8. Comparing the fractured morphologies, the blend with a lower vinyl alcohol content (EVOH1; Figure 8c) exhibits a smoother interface than the corresponding blends with higher vinyl alcohol contents (EVOH5



**Figure 8** SEM micrographs of 50/50/2.5 PP-POM-EVOHx blends containing different vinyl alcohol content in EVOH: (a) 50/50/2.5 PP-POM-EVOH5 blend, (b) 50/50/2.5 PP-POM-EVOH2 blend, and (c) 50/50/2.5 PP-POM-EVOH1 blend.

TABLE III  
Tensile and Impact Properties of the PP-POM-EVOH Blends

Composition	Tensile strength (MPa)	Tensile modulus (MPa)	Unnotched impact strength (J/m)
POM	46	2676	40
POM-EVOH5 = 100/5	46	2508	54
PP-POM = 25/75	30	2227	22
PP-POM-EVOH5 = 25/75/5	37	2292	44
PP-POM = 50/50	22	2022	37
PP-POM-EVOH1 = 50/50/2.5	32	2129	56
PP-POM-EVOH2 = 50/50/2.5	29	2212	48
PP-POM-EVOH5 = 50/50/1	28	2248	48
PP-POM-EVOH5 = 50/50/2.5	26	2176	46
PP-POM-EVOH5 = 50/50/5	28	2253	41
PP-POM-EVOH5 = 50/50/10	29	2304	38
PP-POM = 75/25	24	1924	44
PP-POM-EVOH5 = 75/25/5	27	2072	48
PP	21	1579	53

and EVOH2 in Figures 8a and 8b, respectively). Therefore, a lower quantity of EVOH or a smaller vinyl alcohol content in the EVOH results in a better-compatible blend with higher mechanical performance. This phenomenon was demonstrated by the Izod impact test results; blends with smaller vinyl alcohol content in the EVOH copolymer exhibited a higher un-notched Izod impact strength.

### Mechanical properties

The interfacial properties of the blends play an important role in determining the dispersion of the minor phase and the resultant mechanical performance. The tensile modulus, strength, and Izod impact strength data for these PP-POM blends are summarized in Table III. Both compatibilized and uncompatibilized PP-POM blends exhibit comparable tensile modulus values. The effects of composition and EVOH5 compatibilizer on the un-notched impact strength of the PP-POM blends are shown in Figure 9. For the uncompatibilized PP-POM blends, impact strength in-

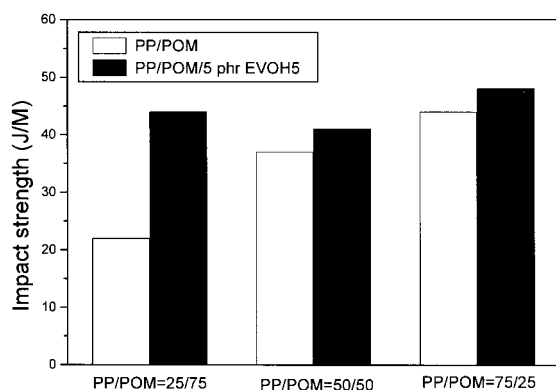


Figure 9 Effect of composition and EVOH5 on the un-notched Izod impact strength of the PP-POM blends.

creases with increasing PP content in the blend. POM is a notched-sensitive material, whereas PP is more ductile than POM. The effects of vinyl alcohol content on both the un-notched impact strength and tensile strength of the 50/50/2.5 PP-POM-EVOH<sub>x</sub> blends are shown in Figure 10. It is evident that the lowest vinyl alcohol content of 15 wt % (EVOH1) possesses the highest impact strength and tensile strength. This result is also proved by the SEM morphology observation as shown in Figure 8, where the 50/50/2.5 PP-POM-EVOH1 blend shows the finest domains. The effects of composition and EVOH5 on the tensile strength of the PP-POM blends are shown in Figure 11. For three uncompatibilized compositions, the 50/50 PP-POM blend shows the lowest tensile strength because the interfacial tensile strength between these two polymers is larger than that between other compositions. The tensile strength of each of the compatibilized blends is higher than that of the corresponding uncompatibilized blend.

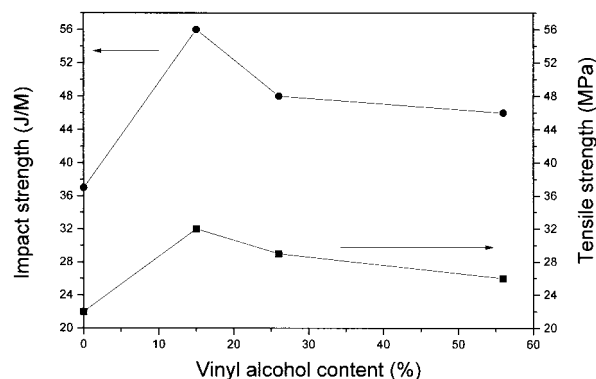
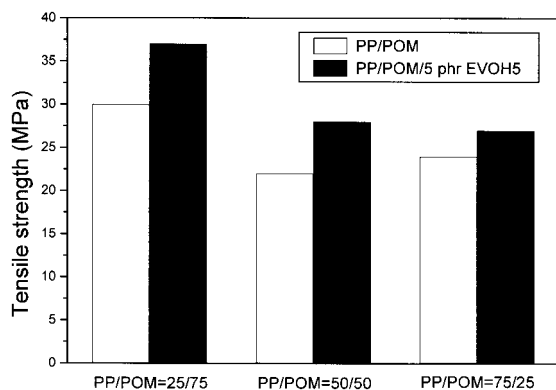


Figure 10 Effect of vinyl alcohol content on the un-notched Izod impact strength and tensile strength of the 50/50/2.5 PP-POM-EVOH<sub>x</sub> blends.



**Figure 11** Effect of composition and EVOH5 on the tensile strength of the PP-POM blends.

### CONCLUSIONS

The EVOH copolymers have been demonstrated to be effective compatibilizers for immiscible and incompatible PP-POM blends. The ethylene segments of EVOH copolymer are partially miscible with PP, and the hydroxyl groups in EVOH can form intermolecular hydrogen bonds with POM to function as an interfacial surfactant for PP and POM. This EVOH copolymer tends to reside along the interface to reduce the interfacial tension in the melt and result in finer phase domains. Additionally, an increased interfacial adhe-

sion is expected, which would result in better mechanical properties. Lower vinyl alcohol content in EVOH implies a higher ethylene segment content and better miscibility between EVOH and PP, which results in a finer phase domain and better mechanical properties.

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