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The permeation resistance of polyethylene, polyethylene/polyamide and polyethylene/modified polyamide blown tubes against unleaded gasoline

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The barrier resistance of polyethylene (PE), polyethylene/polyamide (PE/PA) and polyethylene/modified polyamide (PE/MPA) blown tubes against gasoline permeation is reported. The blown tubes prepared from pure PE exhibited much poorer gasoline permeation resistance than PE/PA and PE/MPA blown tubes. About 93% of the filled gasoline permeated out of PE blown tubes in 14 days at 40°C. In contrast, the gasoline permeation resistance of the blown tubes improved significantly by blending MPA (or PA) before tube blowing. PE/MPA blown tubes exhibited significantly better gasoline permeation resistance than PE/PA blown tubes of the same PE contents. The order of gasoline permeation resistance of PE/MPA blown tubes is the same as the order of the barrier resistance of MPA resins against gasoline permeation before blending with PE. In fact, by using proper compositions and carefully controlling the MPA morphology, the gasoline permeation resistance of the PE/MPA blown tubes can reach about 360 times better than that of pure PE blown tubes at 25°C. These interesting phenomena were investigated in terms of the morphology, thermal and rheological properties of the base resins and/or blown tubes of PE/PA and PE/MPA blends.

1. Introduction

Containers made out of high density polyethylene (HDPE) are probably the most prevailing and suitable materials for packaging various liquids, however, it is notorious for having poor permeation resistance to hydrocarbon solvents, such as, agricultural chemicals, paint thinner and gasoline. To try to improve this poor permeation resistance of PE, alternative technologies have been applied [1–15]. These technologies include surface treatment of PE by fluorination or sulfonation [1, 2], multi-layer coextrusion of PE, compatibilizer precursor (CP) and polyamide (PA) [1, 2], laminar-blend blow molding of PE, CP and PA blends [3–5] or laminar-blend blow molding of PE and modified polyamide (MPA) [6–15]. Among these improved technologies, the "laminar-blend-blow-molding process" forms a layered structure containing numerous discontinuous, overlapping platelets of barrier resins such as PA or MPA in a PE matrix, which is a well proven barrier technology to enhance the resistance of PE containers to hydrocarbon permeation [3–5]. These heterogeneous laminar blends exhibit significantly better hydrocarbon permeation resistance than the conventional homogeneous blends associated with uniform dispersed PA within the PE matrix [6–19].

By focussing on these few investigations [3–19], the majority of the works reported the improved agricultural chemical permeation resistance of the laminar-blends of PE/CP/PA and PE/MPA compared to that of the pure PE. In fact, PE/CP/PA and PE/MPA laminar-blend containers are being widely used for packaging agricultural chemicals around the world. Somewhat surprisingly, in contrast to the agricultural chemicals, almost no investigation has ever been reported on the permeation resistance of pure PE, PE/PA or PE/MPA laminar blends against gasoline and paint thinner, which have been widely stored by using HDPE as the packaging materials in the industry.

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In this study, the gasoline permeation resistance of PE/MPA blown tubes was investigated in terms of the contents and compositions of MPA resins present in PE/MPA laminar blends. For purposes of comparison, the gasoline permeation resistance of PE and PE/PA blown tubes were also investigated. The contents and compositions of MPA resins were found to have a significant influence on the gasoline permeation resistance, morphology and thermal properties of PE/MPA laminar blends. Possible mechanisms accounting for these interesting phenomena are proposed in this study.

2. Experimental

2.1. Materials and sample preparation

Commercial polyamide (PA) resins were modified by compatibilizer precursor (CP) through the reactive extrusion process. The compatibilizer precursor used in this study is a zinc-neutralized ethylene/acrylic acid copolymer. The type of PA used is nylon 6, which was obtained from Formosa Chemicals and Fiber Corporation with a trade name of Sunylon 6 N. The polyethylene (Taisox 9003) and antioxidant (Irganox B225) used in this study were obtained from Formosa Plastic and Ciba-Geigy Corporation, respectively. Before melt blending, PA and CP were dried at 80°C for 16 hrs and 60°C for 8 hrs, respectively. The dried components of PA, CP and 1500 ppm antioxidant were first dry blended thoroughly, and then fed into a twin screw extruder to prepare MPA resins. Table I summarizes the compositions of MPA resins prepared in this study.

The extruder was operated at 215°C in the feeding zone, 240°C toward the extrusion die and at a screw speed of 100 rpm. The base PA and MPA resins prepared above were then dried and dry-blended with various amounts of PE before tube blowing. PE/PA and PE/MPA blends were then tube-blown at an extrusion temperature of 227°C, a screw speed of 300 rpm and a blow-up ratio of 2.0. Table II summarizes the compositions of PE/PA and PE/MPA blown tubes prepared in this study. For purposes of comparison, blown tubes were also prepared from base PE by using the same screw and blown-tube machine at an extrusion temperature of 190°C, a screw speed of 300 rpm and a blow-up ratio of 2.0. The blown tubes prepared in this study had a diameter of 60 mm and a wall thickness of 0.2 mm.

2.2. Permeation test

The barrier resistance of the blown tubes against gasoline permeation was evaluated by measuring the weight losses of the gasoline after placing the filled tubes at 25°C and 40°C for 14 days, respectively. The PE, PE/PA, and PE/MPA blown tubes were initially filled with 180 g of unleaded gasoline, sealed at both ends by a hot-sealed machine. These sealed blown tubes had a fixed surface area of 0.0329 m^2. On the other hand, the barrier properties of the base PE, PA and MPA resins were determined based on their hot-pressed films with a thickness of 0.2 mm, because pure PA and MPA resins are difficult to process by the tube-blowing process due to their poor melt strengths. The hot-pressed films were cut into circles of 140 mm diameter, which were then sealed as lids on the top of a test flask filled with 180 g of unleaded gasoline. The weight losses of the gasoline were measured every day until the fourteenth day. The barrier improvement of a composition is defined as the weight loss of the pure PE sample over that for the composition.

TABLE I Compositions of MPA resins

Wt %	MPA_{10}	MPA_{15}	MPA_{20}	MPA_{30}
PA	90	85	80	70
CP	10	15	20	30

TABLE II Compositions of PE/PA and PE/MPA blown tubes

Wt %	PE	PA	MPA_{10}	MPA_{15}	MPA_{20}	MPA_{30}
PE_{90}/PA	90	10				
PE_{85}/PA	85	15				
PE_{80}/PA	80	20				
PE_{90}/MPA_{10}	90		10			
PE_{85}/MPA_{10}	85		15			
PE_{80}/MPA_{10}	80		20			
PE_{70}/MPA_{10}	70		30			
PE_{90}/MPA_{15}	90			10		
PE_{85}/MPA_{15}	85			15		
PE_{80}/MPA_{15}	80			20		
PE_{70}/MPA_{15}	70			30		
PE_{90}/MPA_{20}	90				10	
PE_{85}/MPA_{20}	85				15	
PE_{80}/MPA_{20}	80				20	
PE_{70}/MPA_{20}	70				30	
PE_{90}/MPA_{30}	90					10
PE_{85}/MPA_{30}	85					15
PE_{80}/MPA_{30}	80					20
PE_{70}/MPA_{30}	70					30

2.3. Rheological properties

The melt shear viscosities (η_s) of PE, PA, and MPA resins were determined using a Rosand Precision Advanced Capillary Extrusion Rheometer equipped with a capillary of 1 mm diameter. All η_s were measured at 230°C and shear rates up to about 120 s^{-1}, because the shear rates of polymer melts during extrusion and film-blowing are generally less than 100 s^{-1}.

2.4. Morphology and thermal properties

In order to observe the deformation structures of MPA (or PA) in PE/MPA (or PE/PA) blown tubes, all tubes were fractured in liquid nitrogen and then etched with formic acid. The etched samples were then gold-coated and examined using a Scanning Electron Microscope (SEM) model Jeol JSM-5200. On the other hand, the melting temperatures and crystallinity values of PE, PA, CP, and MPA resins were determined using a Dupont 2000 differential scanning calorimeter (DSC). All DSC experiments were performed at a heating rate of 10°C/min and a N_2 flowing rate of 25×10^3 mm^3/min. The perfect heat of fusion cited for PE [18] and PA [19] are 293 J/g and 191 J/g, respectively, which were utilized to calculate the crystallinity values of PE and PA resins.

3. Results and discussion

3.1. Barrier and thermal properties of hot-pressed PE, PA and MPA sheets

Table III summarizes the barrier properties of hot-pressed PE, PA and MPA sheets. The gasoline permeation rates of hot-pressed PE sheets at 25 and 40°C are 47 and 79 g·mm/m^2· day, respectively. In contrast, the gasoline permeation rates of PA sheet at 25 and 40°C are 4.2 and 7.3 g·mm/m^2· day, respectively. In other word, the gasoline permeation resistance of PA resin is 11.2 and 10.8 times better than that of the base PE resin at 25 and 40°C, respectively. These results clearly indicate that PA is a better barrier resin against gasoline permeation than PE resin. It is further worth noting that the gasoline permeation resistance of the hot-pressed MPA sheets prepared in this study is significantly better than that of the pure PA resin. As shown in Table III, the barrier improvement values of the hot-pressed MPA sheets at 25 and 40°C range from 77 to 313 and from 40 to 207, respectively, which are much better than the corresponding barrier improvement values of the hot-pressed PA sheet. In fact, the barrier improvement values of MPA sheets approach a maximum as the CP content contained in MPA resins (C_{cp}) reaches an optimum value of about 15 wt%. The gasoline permeation resistance of MPA sheets then reduces significantly as C_{cp} deviates from the optimum value (see Table III).

The percentage crystallinity values (W_c) and melting temperatures (T_ms) of PE, CP, PA and MPA resins are summarized in Table IV. Typical DSC thermograms of these resins are shown in Fig. 1. The melting temperatures and percentage crystallinity values of MPA resins are much lower than those of the base PA resin. In fact, T_ms and W_c of the MPA resins reduce consistently with increasing C_{cp}. As shown in Table IV, the theoretical percentage crystallinity values of MPA resins caculated using a simple mixing rule also reduce significantly with increasing C_{cp}. This decrease in W_c can be mainly due to the reduced W_c caused by reducing the amounts of PA in the MPA as the content of less crystallizable CP increases. Somewhat interestingly, the measured percentage crystallinity values are even lower than the theoretical percentage crystallinity values. As indicated in our previous investigations [6–9], formation of CP-grafted-PA copolymers through the reaction of carboxyl groups of CP with the amine groups of PA during the preparation of MPA was found. Moreover, each CP molecule may be grafted with several different PA molecules, since each CP molecule is associated with more than one carboxyl group. Presumably, the possible formation of "crosslinked" CP-grafted-PA copolymers during reaction extrusion of MPA can further reduce the W_c of MPA, because the "complex" and "irregular" CP-grafted-PA copolymers can prohibit the incorporation of PA molecules into the crystal lattice during crystallization process.

It is not completely clear why PA restricts the mobility of permeant gasoline molecules more efficiently than PE, and MPA shows even better gasoline permeation resistance than pure PA. However, it is generally recognized that permeant molecules diffuse through the polymers mostly by penetrating through the amorphous regions, and can hardly diffuse through the ordered crystalline regions of polymers. Moreover, it is suggested that the molecular composition and configuration in the amorphous phase of the polymer can greatly affect its barrier properties. The presence of polar amide, terminal amine groups and intermolecular hydrogen bonding in PA can barely allow the nonpolar gasoline molecules to enter and permeate through the amorphous regions of PA as compared to nonpolar PE molecules, although W_c of PE is higher than that of PA. On the other hand, the "crosslinked structures" of CP-grafted-PA copolymers can significantly reduce the free volume of MPA and further prohibit the nonpolar gasoline molecules from entering into and permeating through the amorphous regions of MPA resins. It is, therefore, the MPA resins prepared in this study which showed significantly more improvement in permeation resistance than pure PA resin. However, the reduction in W_c of MPA resins with increasing C_{cp} can significantly shorten the permeation path of nonpolar gasoline molecules as C_{cp} increases and compromises the beneficial effect of "crosslinked" CP-grafted-PA molecules on the barrier properties of MPA resins. As a consequence, the MPA_{15} resin exhibits better gasoline

TABLE III Barrier properties of hot-pressed PE, PA and MPA sheets

Type of resin Barrier properties		PE	PA	MPA_{10}	MPA_{15}	MPA_{20}	MPA_{30}
Gasoline permeation rates of hot-pressed sheets (g·mm/m^2·day)	40°C	79	7.3	2.0	0.38	0.88	9.0
	25°C	47	4.2	0.61	0.15	0.3	0.38
Barrier improvement	40°C	1	10.8	40	207	90	88
	25°C	1	11.2	77	313	157	124

TABLE IV Thermal properties of PE, CP, PA and MPA resins

Type of resin Properties	PE	CP	PA	MPA_{10}	MPA_{15}	MPA_{20}	MPA_{30}
Measured crystallinity value (%)	71.0	17.0	37.8	31.4	28.7	26.3	24.5
Theoretical crystallinity value (%)	—	—	—	35.7	34.7	33.6	31.6
Melting temperature T_m (°C)	130.1	95.0	223.0	222.4	221.3	219.7	218.5

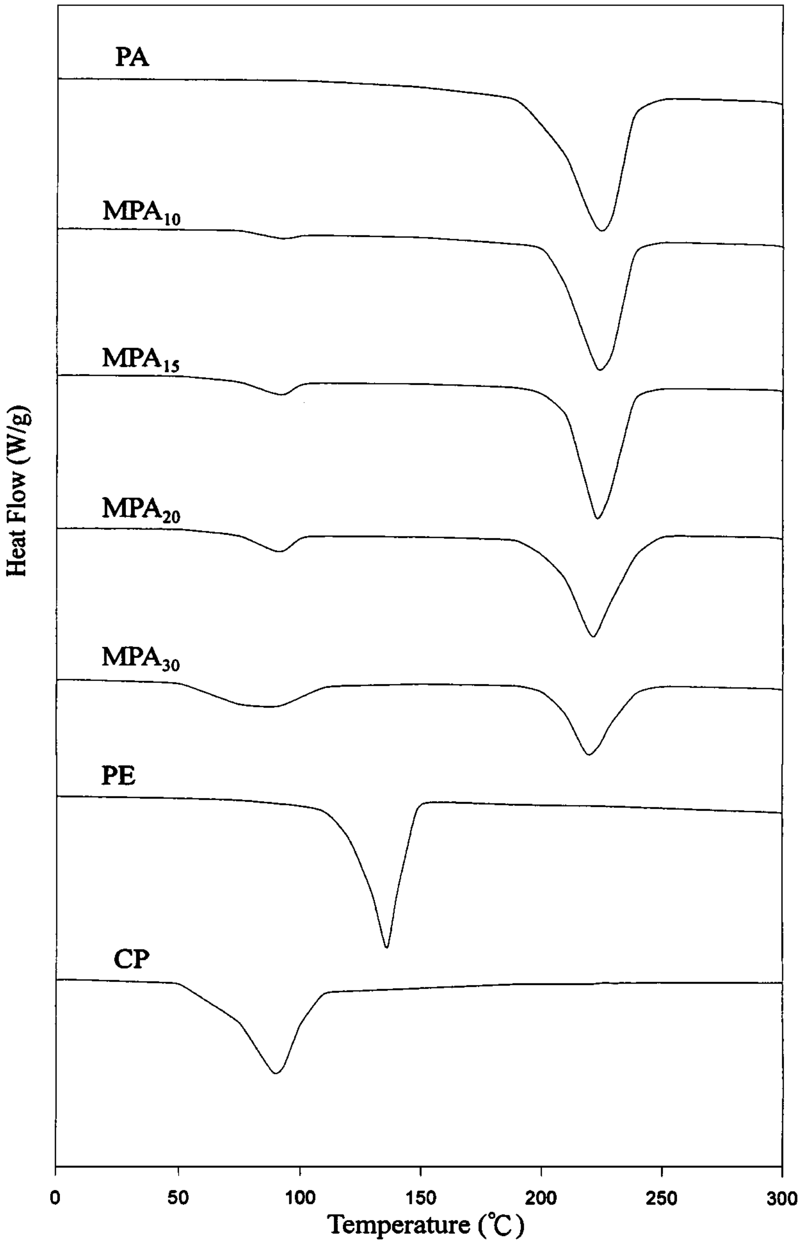

Figure 1 DSC thermograms of CP, PE, PA and MPA resins.

permeation resistance than other MPA resins prepared in this study.

3.2. Barrier properties of PE, PE/PA and PE/MPA blown tubes

After 14 days of permeation testing at 25 and 40°C, the residual weights of the unleaded gasoline inside the PE, PE/PA and PE/MPA blown tubes are summarized in Table V and Figs 2 to 9. Similar to those found in the previous section, the PE blown tubes exhibited worse gasoline permeation resistance than that of PE/PA and PE/MPA blown tubes. About 31 and 93% of the filled gasoline permeated out of PE blown tubes in 14 days at 25 and 40°C, respectively. By blending PE with varying amounts of PA, PE/PA blown tubes exhibited slightly better permeation resistance than the base PE blown tubes, and the permeation resistance of the PE/PA blown tubes improved consistently with the PA content contained in PE/PA blends (see Figs 2 and 6). As shown in Table V, by addition of 20% PA in PE matrix, the barrier improvement of PE_{80}/PA blown tube is only about 2.6 and 2.2 times better than that of the PE blown tubes at 25 and 40°C, respectively. In contrast, by adding the same amount of MPA in PE matrix, PE/MPA blown tubes showed significantly better gasoline permeation resistance than the corresponding PE/PA blown tubes at 25 and 40°C, respectively (see Figs 2 to 9). In fact, the order of gasoline permeation resistance of PE/MPA blown tubes is the same as the order of the barrier resistance of MPA resins before blending with PE. In other words, at the same MPA content, PE/MPA_{15} blown tubes exhibit better gasoline permeation resistance than other PE/MPA blown tubes associated with MPA rather than MPA_{15} resin. Furthermore, the barrier improvements of PE/MPA blown tubes increase consistently with the MPA contents. For instance, the barrier improvement values of PE_{90}/MPA_{15} blown tubes increase from 1.7 to 44 and to 193 times at 40°C, when MPA_{15} contents contained in PE/MPA blown tubes increase

TABLE V Gasoline permeation barrier properties of PE, PE/PA and PE/MPA blown tubes

Samples		PE	PE_{90}/PA	PE_{85}/PA	PE_{80}/PA
Permeation rates	40°C	72	61	35	33
(g·mm/m^2·day)	25°C	33	23	14	12
Barrier improvement	40°C	1	1.2	2.1	2.2
	25°C	1	1.4	2.4	2.6
Samples		PE_{90}/MPA_{10}	PE_{85}/MPA_{10}	PE_{80}/MPA_{10}	PE_{70}/MPA_{10}
Permeation rates	40°C	57	22	20	0.94
(g·mm/m^2·day)	25°C	19	11	4.3	0.38
Barrier improvement	40°C	1.3	3.3	3.7	77
	25°C	1.7	3.3	7.7	86
Samples		PE_{90}/MPA_{15}	PE_{85}/MPA_{15}	PE_{80}/MPA_{15}	PE_{70}/MPA_{15}
Permeation rates	40°C	42	6.1	1.7	0.37
(g·mm/m^2·day)	25°C	15	2.5	0.47	0.09
Barrier improvement	40°C	1.7	12	44	193
	25°C	2.3	13	71	367
Samples		PE_{90}/MPA_{20}	PE_{85}/MPA_{20}	PE_{80}/MPA_{20}	PE_{70}/MPA_{20}
Permeation rates	40°C	53	20	9.7	0.85
(g·mm/m^2·day)	25°C	22	7.0	2.9	0.18
Barrier improvement	40°C	1.4	3.6	7.4	85
	25°C	1.5	4.7	12	181
Samples		PE_{90}/MPA_{30}	PE_{85}/MPA_{30}	PE_{80}/MPA_{30}	PE_{70}/MPA_{30}
Permeation rates	40°C	60	32	24	5.0
(g·mm/m^2·day)	25°C	17	5.7	4.7	0.94
Barrier improvement	40°C	1.2	2.2	3.0	14
	25°C	2.0	5.8	7.0	35

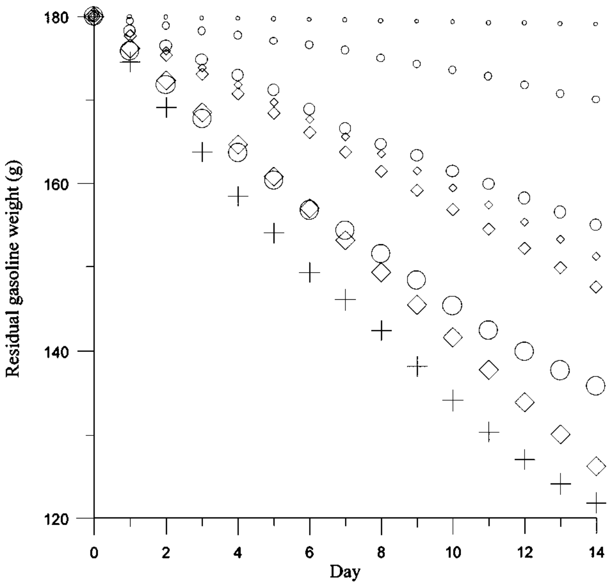

Figure 2 Residual gasoline weights of PE (+), PE_{90}/PA (◇), PE_{85}/PA (◇), PE_{80}/PA (◇), PE_{90}/MPA_{10} (○), PE_{85}/MPA_{10} (○), PE_{80}/MPA_{10} (○) and PE_{70}/MPA_{10} (○) blown tubes at 25°C.

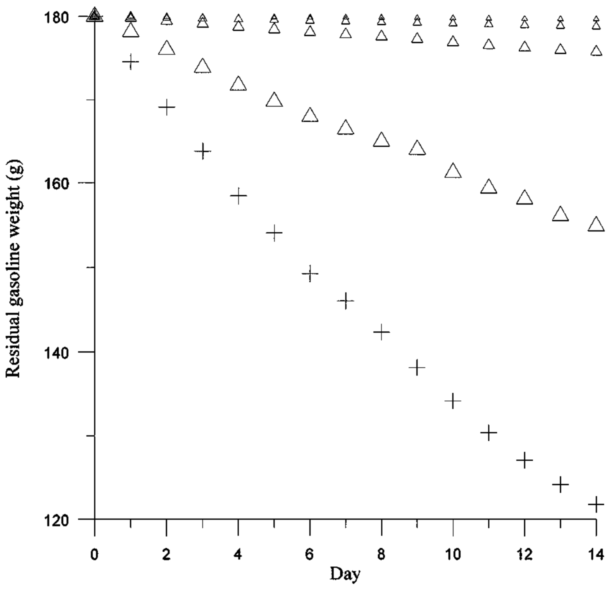

Figure 3 Residual gasoline weights of PE (+), PE_{90}/MPA_{15} (△), PE_{85}/MPA_{15} (△), PE_{80}/MPA_{15} (△) and PE_{70}/MPA_{15} (△) blown tubes at 25°C.

from 10 to 20 and to 30 wt%. These results clearly suggest that the gasoline permeation resistance of PE/MPA and PE/PA blown tubes depends significantly on the barrier properties of the MPA (or PA) itself, and improves consistently as the MPA (or PA) contents increase.

3.3. Rheological properties of the base PE, CP, PA, and MPA resins

As shown in Fig. 10, the melt shear viscosities (η_s) of PE are much higher than those for the other base resins (i.e. CP, PA and MPA) at 230°C and shear rates up to about 120 s^{-1}. On the contrary, at these testing conditions, CP and PA show the lowest and second lowest η_s among these base resins. In contrast, the η_s of the MPA resins are significantly higher than that of PA and improve consistently with increasing the C_{cp}. Presumably, the melt shear viscosities of the CP-grafted-PA copolymers formed during reaction extrusion of MPA can be higher than those of CP and PA, because the structures of CP-grafted-PA copolymers can be quite huge and complex compared to those of CP and PA molecules. For instance, short CP chains may be dispersed into PA matrix and grafted into several long PA molecules and present as huge

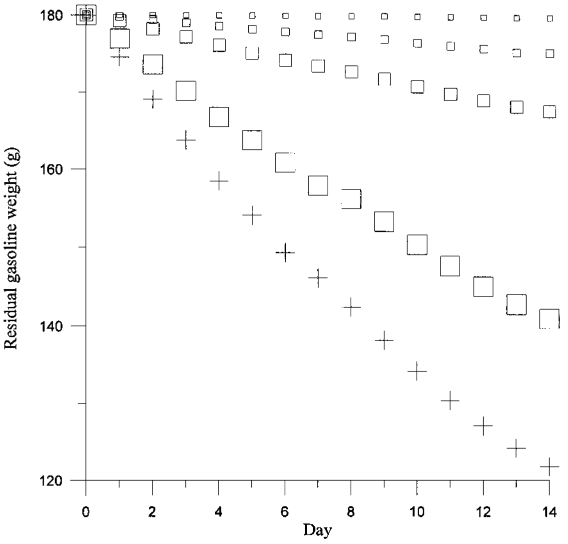

Figure 4 Residual gasoline weights of PE (+), PE$_{90}$/MPA$_{20}$ (□), PE$_{85}$/MPA$_{20}$ (□), PE$_{80}$/MPA$_{20}$ (□) and PE$_{70}$/MPA$_{20}$ (□) blown tubes at 25°C.

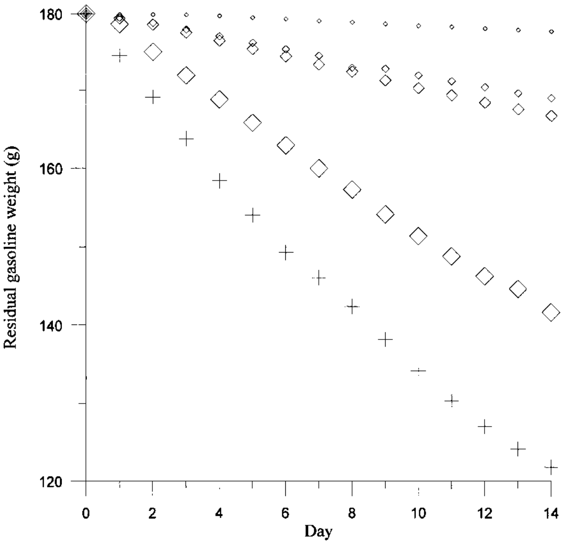

Figure 5 Residual gasoline weights of PE (+), PE$_{90}$/MPA$_{30}$ (◇), PE$_{85}$/MPA$_{30}$ (◇), PE$_{80}$/MPA$_{30}$ (◇) and PE$_{70}$/MPA$_{30}$ (◇) blown tubes at 25°C.

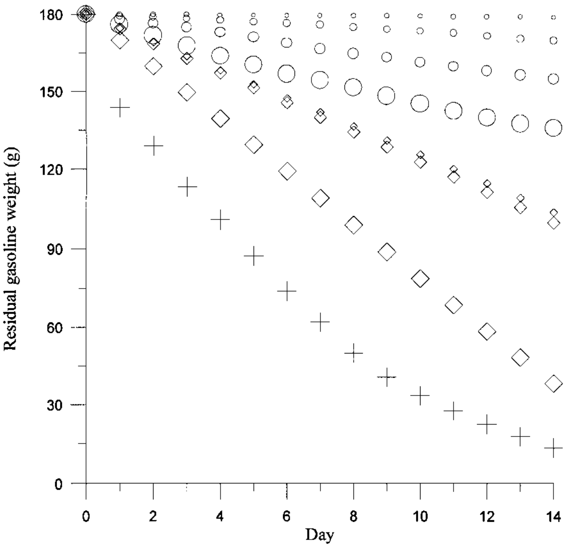

Figure 6 Residual gasoline weights of PE (+), PE$_{90}$/PA (◇), PE$_{85}$/PA (◇), PE$_{80}$/PA (◇), PE$_{90}$/MPA$_{10}$ (○), PE$_{85}$/MPA$_{10}$ (○), PE$_{80}$/MPA$_{10}$ (○) and PE$_{70}$/MPA$_{10}$ (○) blown tubes at 40°C.

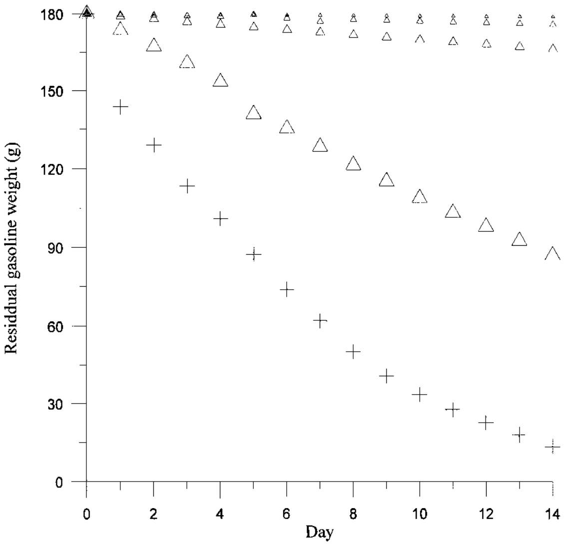

Figure 7 Residual gasoline weights of PE (+), PE$_{90}$/MPA$_{15}$ (△), PE$_{85}$/MPA$_{15}$ (△), PE$_{80}$/MPA$_{15}$ (△) and PE$_{70}$/MPA$_{15}$ (△) blown tubes at 40°C.

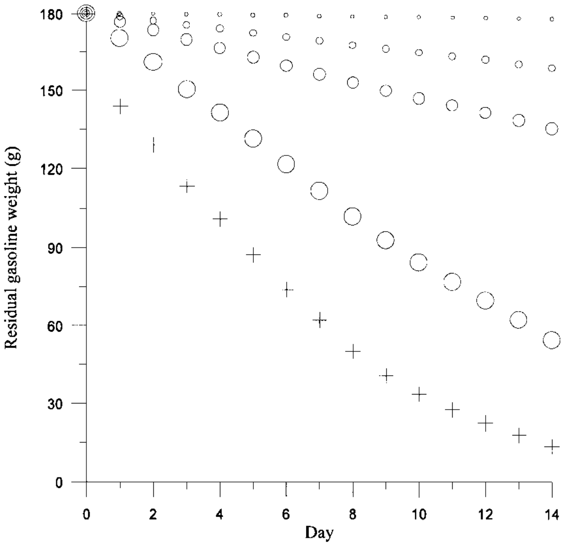

Figure 8 Residual gasoline weights of PE (+), PE$_{90}$/MPA$_{20}$ (○), PE$_{85}$/MPA$_{20}$ (○), PE$_{80}$/MPA$_{20}$ (○) and PE$_{70}$/MPA$_{20}$ (○) blown tubes at 40°C.

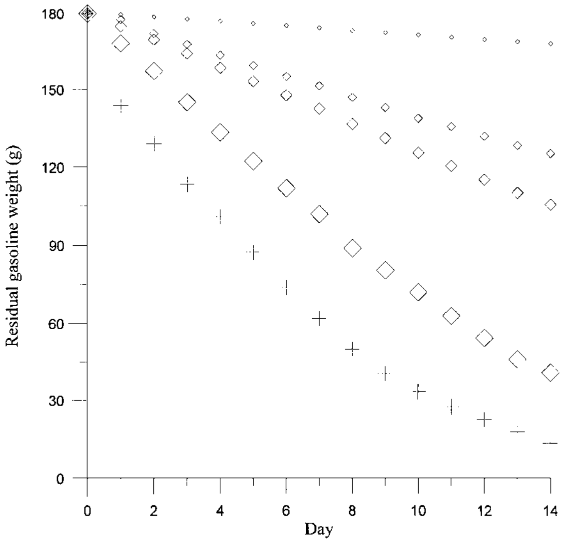

Figure 9 Residual gasoline weights of PE (+), PE$_{90}$/MPA$_{30}$ (◇), PE$_{85}$/MPA$_{30}$ (◇), PE$_{80}$/MPA$_{30}$ (◇) and PE$_{70}$/MPA$_{30}$ (◇) blown tubes at 40°C.

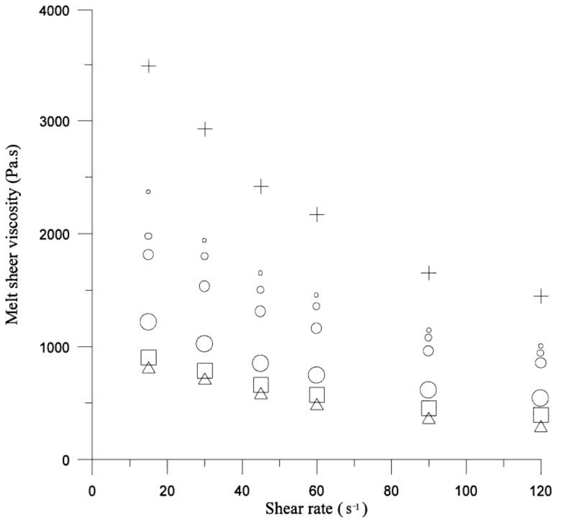

Figure 10 Melt shear viscosities of PE (+), CP (△), PA (□), MPA$_{10}$ (◯), MPA$_{15}$ (○), MPA$_{20}$ (○) and MPA$_{30}$ (∘) measured at 230°C and varying shear rate.

"crosslinked" CP-grafted-PA copolymers. Moreover, the possibility of formation of CP-grafted-PA copolymers can be higher with increasing C_{cp}. As a consequence, the η_{s} of MPA resins are higher than those of CP and/or PA resins, and increase consistently with C_{cp}.

3.4. Morphology of PE/PA and PE/MPA blown tubes

As shown in Fig. 11, regardless of the amounts of PA added in PE/PA blown tubes, the fracture surfaces of the blown tubes exhibit "marbled structures," wherein no demarcated PA laminar structure was found. In contrast, somewhat demarcated MPA lamina layers were found and distributed in PE matrices through the wall thickness direction of the PE/MPA blown tubes. Moreover, the MPA laminar structures became more structured as the MPA contents increased (see Figs 12–15). These more structured MPA laminas are believed to further improve the permeation resistance of PE/MPA

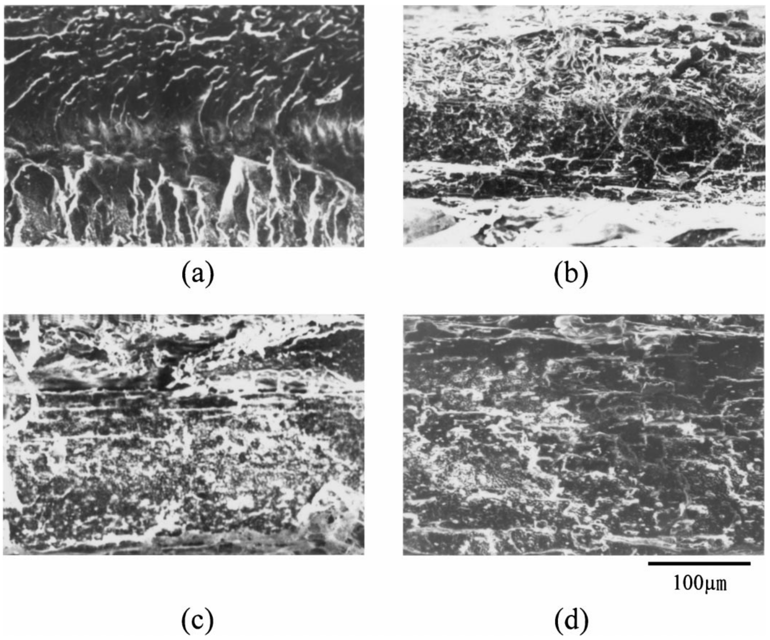

Figure 11 Fracture surfaces of (a) PE, (b) PE$_{90}$/PA, (c) PE$_{85}$/PA and (d) PE$_{80}$/PA blown tubes.

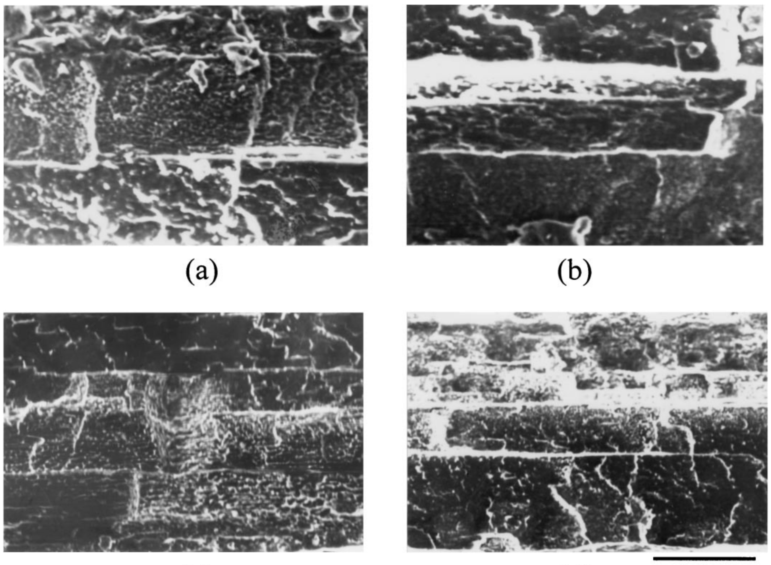

Figure 12 Fracture surfaces of (a) PE$_{90}$/MPA$_{10}$, (b) PE$_{85}$/MPA$_{10}$, (c) PE$_{80}$/MPA$_{10}$ and (d) PE$_{70}$/MPA$_{10}$ blown tubes.

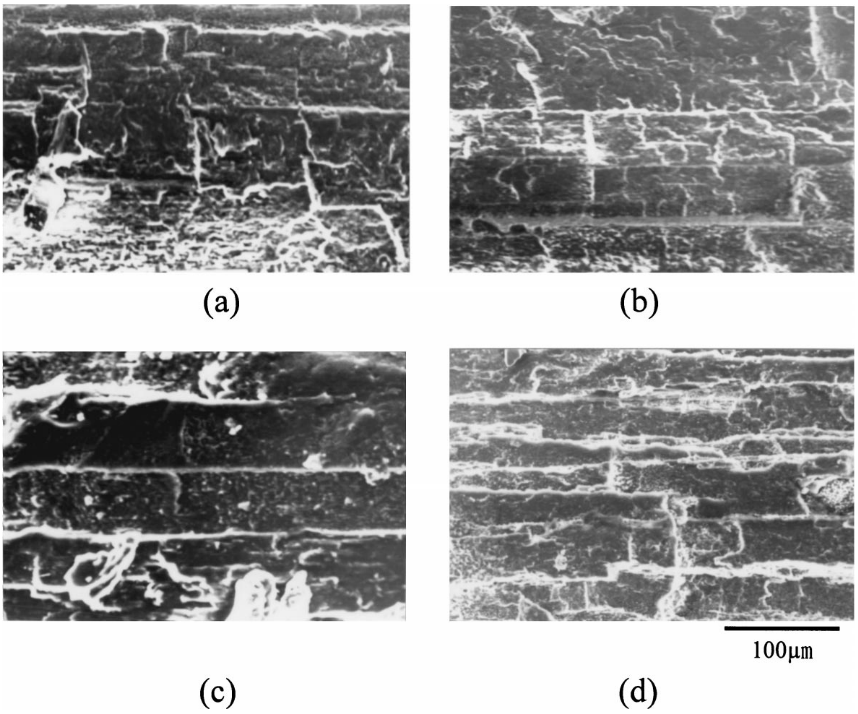

Figure 13 Fracture surfaces of (a) PE_{90}/MPA_{15}, (b) PE_{85}/MPA_{15}, (c) PE_{80}/MPA_{15} and (d) PE_{70}/MPA_{15} blown tubes.

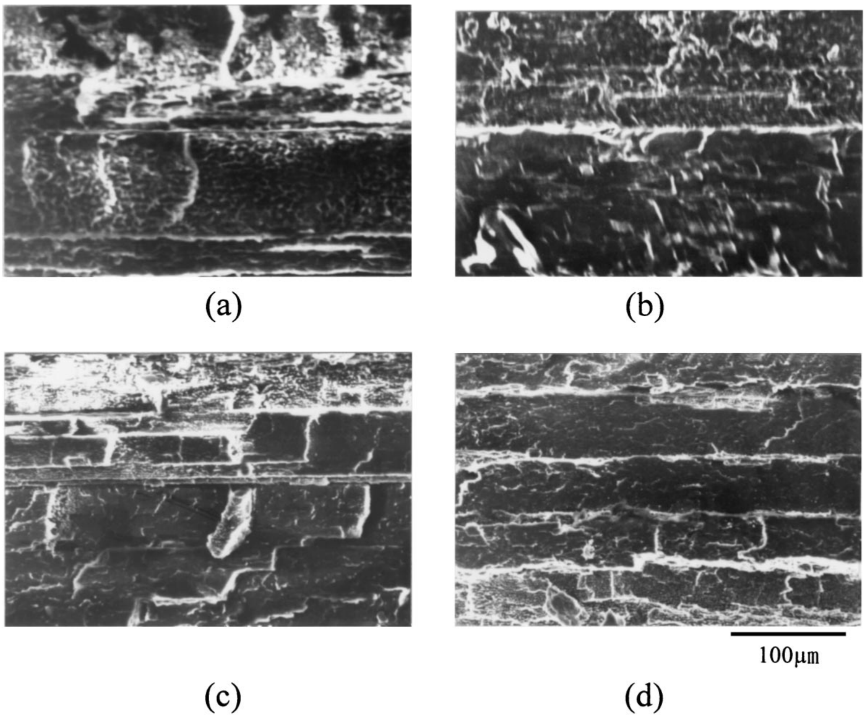

Figure 14 Fracture surfaces of (a) PE_{90}/MPA_{20}, (b) PE_{85}/MPA_{20}, (c) PE_{80}/MPA_{20} and (d) PE_{70}/MPA_{20} blown tubes.

tubes against unleaded gasoline, because the permeation time of the gasoline molecules is prolonged by the structured and prolonged MPA laminas present in the PE matrix. The underlying mechanisms accounting for these interesting phenomena are not clear at this moment. Presumably, a good level of interfacial adhesion between MPA (or PA) and PE matrix is necessary for the formation of laminar structures, because MPA (or PA) cannot be easily stretched by PE with a higher melt shear viscosity when the interfacial adhesion between MPA and PE matrix is poor during the blow-molding process. The CP-grafted-PA copolymers of higher η_s are believed to be more compatible with PE and adhere better to PE than PA resins, because it is well known that PA resins are thermodynamically immiscible with PE and poorly adhered to PE during blow- molding. It is, therefore, reasonable to suggest that MPA can be more easily biaxially stretched by a PE matrix than PA and form demarcated laminar structures in PE/MPA blown tubes.

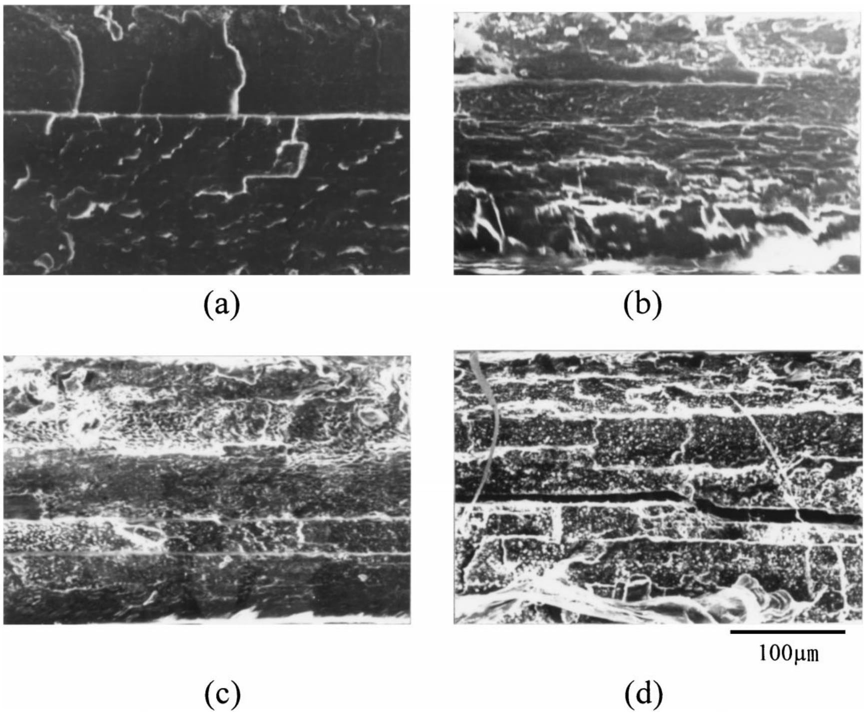

Figure 15 Fracture surfaces of (a) PE_{90}/MPA_{30}, (b) PE_{85}/MPA_{30}, (c) PE_{80}/MPA_{30} and (d) PE_{70}/MPA_{30} blown tubes.

4. Conclusions

Barrier property investigations of the PE, PA and MPA sheets indicate that PA is a much better barrier resin against gasoline permeation than PE resin. Further investigations found that CP can modify and significantly improve the gasoline permeation resistance of PA resin, but the level of barrier improvement depends significantly on the CP contents contained in MPA resins. Differences in crystallinity values and molecular composition in the amorphous phases of these resins are proposed to account for their different gasoline permeation resistance. Similar to those found above, PE blown tubes exhibited much poorer barrier resistance against gasoline permeation than other blown tubes prepared from PE/PA or PE/MPA blends. About 93% of the filled gasoline permeated out of PE blown tubes in 14 days at 40 °C. The barrier resistance of PE/MPA blown tubes against gasoline permeation is significantly better than that of PE/PA blown tubes of the same PE content. In fact, the order of permeation resistance of PE/MPA blown tubes is the same as the order of the barrier resistance of MPA resins before blending with PE. The barrier improvements of PE/PA and PE/MPA blown tubes were found to increase consistently with the PA and MPA contents, respectively. However, regardless of the PA contents, only marbled but no demarcated PA lamina was found on the fracture surfaces of PE/PA blown tubes. In contrast, somewhat demarcated MPA laminar structures were found on the fracture surfaces of PE/MPA blown tubes, and the MPA laminar structures became more structured as the MPA content increased. These results clearly suggested that the gasoline permeation resistance of PE/MPA and PE/PA blown tubes depends significantly on the barrier properties of the MPA (or PA) itself. Moreover, the more structured MPA laminas are believed to further improve the barrier resistance of PE/MPA blown tubes against gasoline permeation, since the permeation time of the gasoline molecules is prolonged by these MPA laminas. Finally, by using proper compositions and carefully controlling the MPA morphology, the gasoline permeation resistance of PE_{70}/MPA_{15} blown tubes is 193 and 367 times better than that of pure PE blown tubes at 40 and 25°C, respectively.

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References

1. J. H. SCHUT, *Plastics Technol.* **5** (1992) 52.
2. K. CHANDRAMOUL and S. A. JABARIN, *Adv. Polym. Technol.* **14** (1995) 35.
3. P. M. SUBRAMANIAN, *US Pat.* No. 4410482 (1983).
4. *Idem., US Pat.* No. 4444817 (1984).
5. ROBERT LEAVERSUCH, in "Proceedings of Modern Plastics International," Lausanne, Switzerland, July 24, 1986 (McGraw-Hill).
6. J. T. YEH, C. C. FAN-CHIANG and M. F. CHO, *Polym. Bull.* **35** (1995) 371.
7. J. T. YEH and C. C. FAN-CHIANG, *J. Polym. Res.* **3** (1996) 211.
8. J. T. YEH, C. C. FAN-CHIANG and S. S. YANG, *J. Appl. Polym. Sci.* **8** (1997) 1531.
9. J. T. YEH and C. C. FAN-CHIANG, *ibid.* **66** (1997) 2517.
10. J. T. YEH, C. F. JYAN and S. CHOU, *SPE Antec* (1998) 3567.
11. J. T. YEH and C. F. JYAN, *Polym. Eng. Sci.* **38** (1998) 1482.
12. J. T. YEH, C. F. JYAN and S. CHOU, *ibid.* accepted for publication.
13. J. T. YEH, W. S. JOU and Y. S. SU, *J. Appl. Polym. Sci.* accepted for publication.
14. W. S. JOU, Y. S. SU and J. T. YEH, *SPE Antec* (1999) 1921.

15. J. T. YEH, C. C. CHAO and C. H. CHEN, *J. Appl. Polym. Sci*. accepted for publication.
16. P. M. SUBRAMANIAN, *Polym. Eng. Sci*. **25** (1985) 483.
17. *Idem*., *ibid*. **27** (1987) 663.
18. *Idem*., in "Conference Proceedings-Technical Association of Pulp and Paper Industry," Laminations and Coating Conference, 1984, p. 341.
19. P. M. SUBRAMANIAN and V. MEHRA, *SPE Antec* (1986) 301.
20. B WUNDERLICH, "Macromolecular Physics," Vol. 1 (Academic Press, New York, 1973) p. 388.
21. Polymer Handbook, Vol. 82, 2nd ed. John Wiley and Sons Inc., New York, 1975.

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