Characterization of Polypropylene and Ethylene–Propylene Copolymer Blends for Industrial Applications

ELINOR L. BEDIA,[1] NURI ASTRINI,[2] ARIS SUDARISMAN,[2] FLORENTINO SUMERA,[3] YASHIKAZU KASHIRO[2]

[1] Industrial Technology Development Institute, Bicutan, Taguig, Metro-Manila, Philippines

[2] Research and Development Centers for Applied Chemistry/Physics, Indonesian Institute of Sciences (LIPI), Bandung, Indonesia

[3] Institute of Chemistry, College of Science, University of the Philippines, Diliman, Quezon City, Philippines

ABSTRACT: The crystalline structure and physico-mechanical properties of polypropylene (PP) blended with ethylene–propylene copolymer (EPM) were investigated. WAXS diffractograms showed that the addition of EPM did not affect the crystalline structure of PP. DSC curves revealed the presence of two T_g peaks indicating the amorphous phases of EPM and PP. As EPM increased, the elastomeric domains cavitated from PP matrix increased while the tensile stress and modulus of elasticity decreased. Impact strength, on the other hand, increased, and showed a remarkable effect at 30% EPM/PP. The properties of the blended polymers were compared with the commercial PP impact copolymer, and it was found that polyblends containing 30% EPM was suited for applications on products requiring very high impact strength. Further addition of EPM from 40 to 50% produced very high impact strength, but the tensile stress and modulus of elasticity were very low. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 1200–1208, 2000

Key words: crystalline structure; physico-mechanical properties; morphology; thermal behavior; commercial PP impact copolymer

INTRODUCTION

Polypropylene (PP) is a widely used thermoplastic because of its outstanding mechanical properties and low cost.[1] However, PP has the disadvantage of becoming brittle at low temperatures because of its high transition temperature and high crystallinity. The impact strength of PP could be improved by blending with an elastomer, usually ethylene pro-pylene rubbers. This could be done by mechanical blending of the homopolymer with an elastomer and ethylene–propylene copolymerization.[2,3]

Numerous investigations have been undertaken on the mechanical blends of ethylene propylene random copolymer (EPM) and PP. The effect of adding EPM on the properties of PP such as mechanical behavior, morphology, rheology, and crystallinity has been evaluated.[4–7] Studies were also conducted on the use of several types of EPM and PP and the blending of the binary blends (EPM/PP) with another polymer such as polyethylene (PE).[8] Most of these studies were conducted with EPM ratio ranging from 5 to 40%. Formulations of the blends can be utilized over a full range, depending on application.
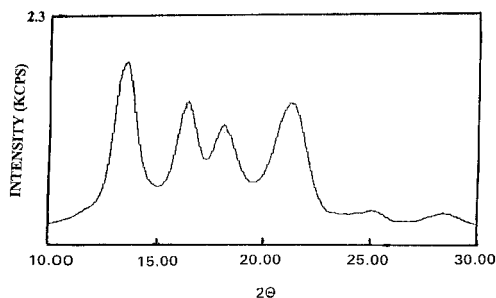
Figure 1 WAXS diffractogram of virgin PP.

On the other hand, ethylene–propylene copolymerization or the *in situ* synthesis of the elastomeric fraction is commercially available as a PP impact copolymer.[9, 10] The ethylene content or the comonomer is usually up to 30%.[11] In this process, the important properties can be precisely tailored by choosing the appropriate catalyst components and reactor conditions that determine base-resin crystallinity, composition, and quantity of the rubber fraction and overall molecular weight distribution.[12]

Both EPM/PP blends and the PP impact copolymer have gained considerable industrial and commercial importance[13, 14] due to their extended applications. The former can be produced by using plastic processing equipment, while the latter necessitates the establishment of a polymerization plant. It is noted, however, that the differences in their properties have not yet been reported.

In this study, polyblends of PP and EPM were prepared and characterized by using WAXS, DSC, SEM, Tensilon, and Izod Impact Tester. The properties of these blends were compared with the data of the commercial PP impact copolymer of Daelim Poly, Korea. Product applications of the EPM/PP blends were also determined.
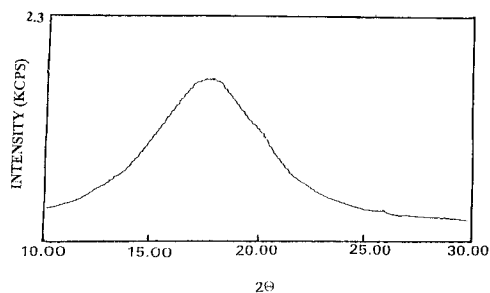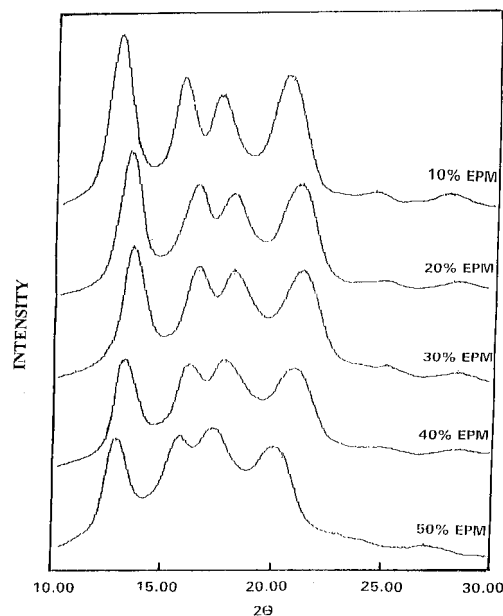

Figure 3 WAXS diffractograms of blended EPM/PP.

EXPERIMENTAL

Materials

Polypropylene (PP) used in this study was Nisseki Polypro J150-C, an injection grade thermoplastic resin with a melt flow index of 8 g/10 min. For an elastomeric impact modifier, ethylene–propylene random copolymer EPM-JSR-11 was used. The ethylene–propylene ratio of the rubber was 51/49 w/w.

Preparation of Blends

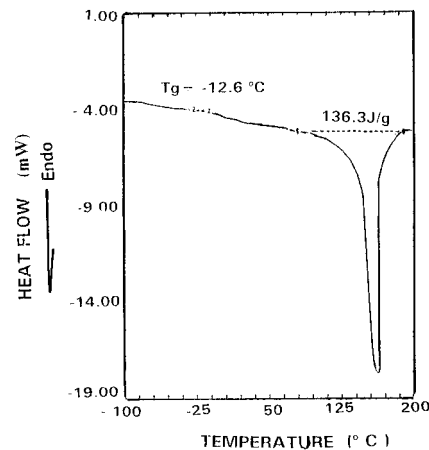Blending of EPM with PP at 10, 20, 30, 40, and 50% was undertaken using a Toyoseiki Labo Plas-

Figure 2 WAXS diffractogram of EPM.

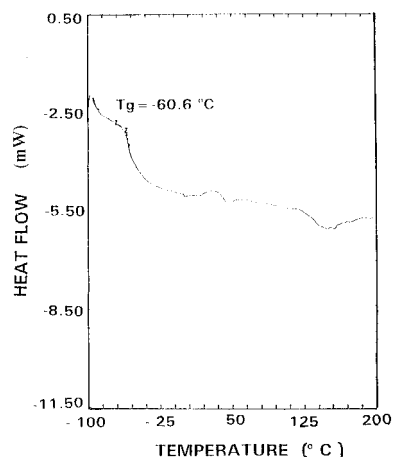**Figure 4** DSC curve of virgin PP (melting process).

Figure 5   DSC curve of EPM (EPM is an amorphous polymer).

tomill model 30 R150. The equipment was set at 200°C, screw speed at 30 rpm, and a residence time of 10 min in an inert atmosphere.

The blended polymers were collected and pressed using a Sangyo Hot Press Tester that was set at 200°C and with an applied pressure of 10 kgf/cm^2 for 5 min. The slab specimen was quenched in water and cut to the desired dimension of the test specimen.

Product Evaluation

Wide-Angle X-ray Scattering (WAXS)

WAXS was performed using a Rigaku WAXS Diffractometer that was set at 40 kV and 30 mA with Ni-filtered CuK radiation.

Differential Scanning Calorimeter (DSC)

The blended polymers were cut from the molded slab and tested using a SEIKO DSC-100. The equipment was set to a heating environment from 25 to 220°C to remove its prehistory heat effects. After 2 min at 220°C, the temperature was cooled down to -130°C using liquid nitrogen. Both heating and cooling were undertaken at a rate of 20°C/min. The sample was heated again to 250°C at 10°C/min to obtain the transition (T_g) and melting points (T_m) and heat energy on melting (ΔH_m). The test procedure and the calculation of the crystallinity of iPP have been described elsewhere.[8,15,16]

Scanning Electron Microscopy (SEM)

Test specimens were prepared by cutting the slab test specimen to a 4-mm width and breaking it in liquid nitrogen. The fracture surface of the sample was coated with 200-μm gold, and was observed using a scanning electron microscope JEOL-T330 A.

Tensile Test

Dumbbell-shaped test specimens were prepared using an Orientec Test Piece Making Machine Model 1 DT-1. The dimensions of the test specimens were measured and tested using a Shimadzu A 6-5000 B, which was set at a constant cross head speed of 50 mm/min (JIS K 7113) at room temperature. Tensile stress at the yield point, modulus of elasticity, and stress–strain curves were calculated manually from the graph.

Table I   DSC Data of Virgin PP, Blended EPM/PP, and EPM

Composition % EPM	T_m (°C)	ΔH_m (J/g)	T_g (°C)	% Crystallinity of iPP	
				a	b
0	163.1	136.3	-12.6	65.13	65.13
10	162.9	120.8	-13.8	57.72	58.62
20	162.3	109.8	-14.4	52.72	52.10
			-65.2		
30	161.6	94.9	-21.4	45.35	45.59
			-65.0		
40	161.6	76.7	-61.4	33.64	39.08
50	160.3	65.4	-61.4	31.25	32.57
100			-60.6		

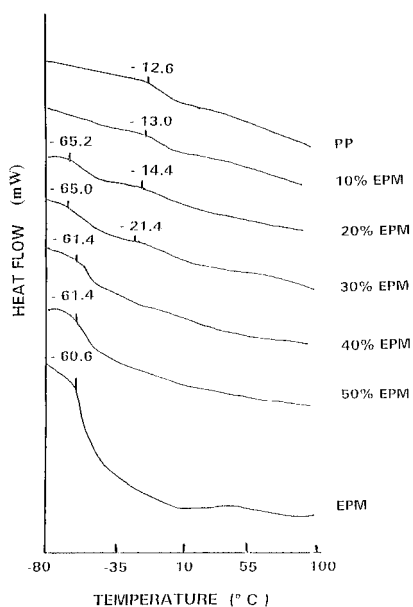[a] Experimental value.
[b] Theoretical value.

Figure 6 Glass transition point of virgin PP, blended EPM, and PP and EPM.

Izod Impact Test

Izod impact strengths of the test specimen were obtained based on ASTM D256-81. The slab test specimen was cut to the desired shape, notched, and conditioned. An Izod Impact Toyoseiki 612-1/1 was used in carrying out the test at room temperature.

RESULTS AND DISCUSSION

Wide-Angle X-ray Scattering (WAXS)

Virgin PP is a semicrystalline polymer. As shown in Figure 1, WAXS diffractogram exhibits reflections at $2\theta = 13.5$, 16.4, 18.1, and 21.2° indicating α-phase monoclinic structure of isotactic polypropylene (iPP).[17] The broadened background scattering area of PP suggests the presence of amorphous structure.

EPM, on the other hand, exhibits only a diffuse gaussian curve with its center at $2\theta = 17.8°$, indicating that the polymer has disordered structure (Fig. 2).

Blending of EPM did not affect the crystalline structure of iPP, as shown in Figure 3. However, the intensity of the crystalline peaks of iPP decreases as EPM increases. Similar behavior has been reported by several researchers on PP blended with EPM,[6,8] ethylene propylene diene

(EPDM) terpolymer,[18] and polybutadiene (PBu).[19] They found that the elastomers slightly influence the crystalline structure of iPP, and suggested that the elastomer acts as a nucleant agent for iPP spherulites. For the EPM/PP blend, Orazio et al.[8] observed that the average dimension of iPP spherulites on the EPM/PP blends crystallized isothermally from the melt decreases as EPM increases. Furthermore, Martuscelli et al.[4] noted the nucleation efficiency to be strongly dependent on the chemical structure and molecular mass of the elastomer.

Differential Scanning Calorimeter (DSC)

Virgin PP exhibits an endothermic peak at 163.1°C, indicating the absorption of heat energy during melting process (T_m) (Fig. 4). The amount of heat energy (ΔH_m) measured is 136.3 J/g.

An estimate of the degree of crystallinity of isostatic polypropylene (iPP) can be obtained using the following formula:[6]

$$\% \text{ Crystallinity} = \frac{\Delta H_m}{\Delta H \text{ (100\% crystallized PP)}}$$
$$\times 100$$

where ΔH_m (experimental value) = 136.3 J/g

$$\Delta H \text{ (100\% crystallized PP)} = 209 \text{ J/g}^7$$

$$\frac{136.30 \text{ J/g}}{209.28 \text{ J/g}} \times 100 = 65.13\%$$

EPM shows an ill-defined curve that is attributed to its noncrystalline structure (Fig. 5). Hence, ΔH_m was not observed.
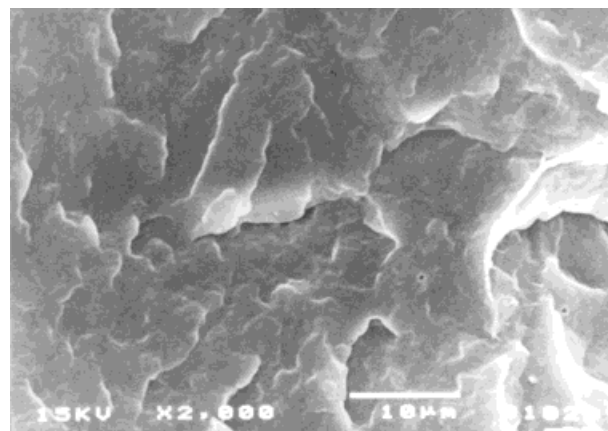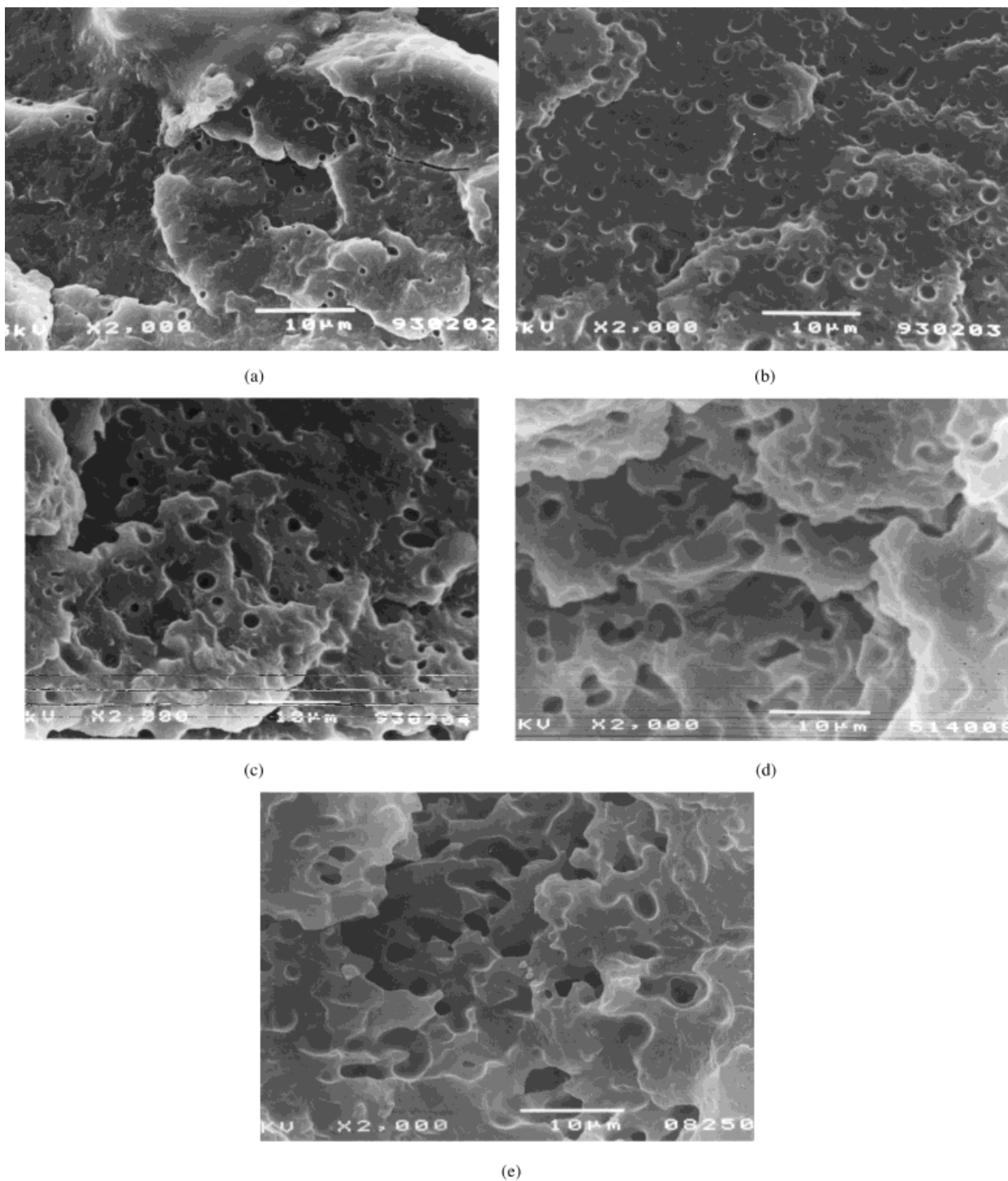

Figure 7 SEM of virgin PP.

Figure 8 SEMs of EPM/PP Blends. EPM contents: (a) 10%, (b) 20%, (c) 30%, (d) 40%, and (e) 50%.

Blending of EPM with PP shows the occurrence of an endothermic peak but with decreasing ΔH_m and T_m values from 120.8 J/g and 162.9°C to 65.4 J/g and 160.3°C at 10 and 50% EPM, respectively (Table I). As mentioned by Martuscelli[3] and Karger-Kocsis,[5] the incorporation of an elastomer alters the superstructure of iPP matrix by decreasing the average size of spherulites. In effect,

Table II   Particle Size of EPM in EPM/PP Blends

Composition EPM/PP (%)	Particle Size of EPM in EPM/PP Blends (μm)
10/90	0.5–0.9
20/80	0.8–2.5
30/70	0.8–2.7
40/60	0.9–4.0
50/50	1.0–5.0

the smaller spherulites with lower heat capacity shifted the melting point range of the blends to a lower temperature.

Based on the given formula, the degree of crystallinity of the iPP phase in the blends was determined. The experimental and theoretical data for the blends were calculated from the ΔH_m obtained from the DSC, and computation based on the composition of the blends, respectively. Both sets of data exhibit a gradual decrease of crystallinity as EPM increases. It is noted that values for both are almost similar, which can be ascribed to the even distribution of EPM on the iPP matrix.

Likewise, EPM and PP exhibit glass transition points (T_g) at −60.6 and −12.6°C due to the presence of their amorphous structure (Fig. 6). In a blend, the two T_gs can sometimes be seen. When this occurs, a heterogeneous mixture is obtained. At 20 and 30% EPM, these two peaks can be observed. However, above 40% of EMP, PP's T_g peak is no longer observable in the experimental conditions used. This is because the PP is only 35% amorphous as calculated from its ΔH_m value.
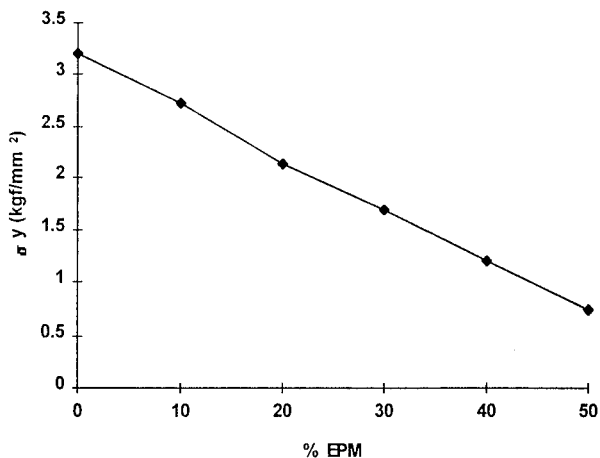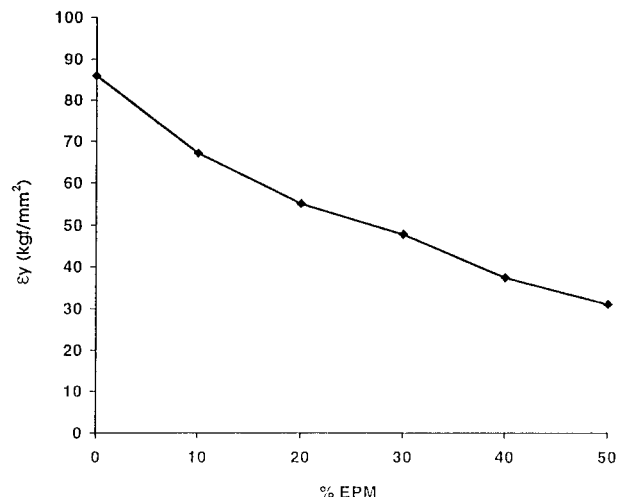
Figure 10   Modulus of elasticity (E) of virgin PP and EPM/PP blends.

Scanning Electron Microscopy

The SEM micrograph of virgin PP exhibits a wavy-like structure that was the result of the breaking of the polymer in liquid nitrogen (Fig. 7).

Figure 8 shows typical SEMs of fractured surfaces of EPM/PP blends. The breaking of the blends in the liquid nitrogen temperature has impaired the adhesion of the EPM and PP. The globular structures are the EPM cavitated from the continuous PP matrix. However, at 40 and 50% of the EPM, some of the globular structures coalesced, resulting in unsymmetrical cavities. Table II shows the range of the size of the rubber domains dispersed in the PP matrix. As the EPM content increases from 10 to 50%, the rubber domains also increase from 0.5 to 5 μm. Furthermore, it can be observed that there seems to be no
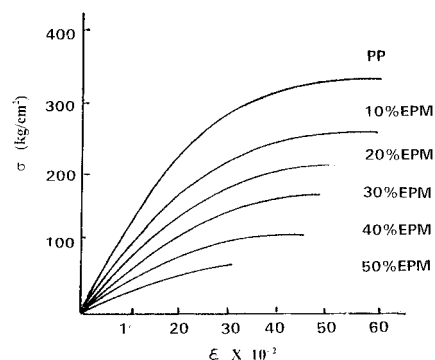
Figure 9   Tensile stress at yield point (σ_y) of virgin PP and EPM/PP blends.

Figure 11   Stress–strain curves of virgin PP and EPM/PP blends.

Table III   Properties of Impact Copolymer[e]

Properties	Melt Index[a]	Yield Strength[b]	Flexural Modulus of Elasticity[c]	Izod Impact Strength[d]	Characteristics	Applications
Injection Grade						
PP-230	1.5	2.80	125	36	High impact strength	
PP-232	1.5	2.80	130	36	High impact strength	
PP-234	3.5	2.80	130	16	High impact strength	Containers, Stadium seating, Automotive industry (steering wheels), Furniture, Closures, Crates and Totes
PP-235	3.5	2.80	130	16	Medium-flow, High impact	
PP-241	7.0	2.80	150	10	High impact strength	
PP-242	7.0	2.80	140	10	High impact strength, Heat stability	
PP-243	8.0	2.10	100	51	Very high impact strength	Automotive bumper
PP-245	13.0	3.00	145	8	High flow, high impact strength	Packaging closures
PP-246	20.0	3.00	140	8	High stiffness, High flow articles	Household Containers Furnitures

ASTM	Unit	ASTM	Unit
[a] D 1238	g/10 min;	[c] D 256	kg · cm/cm
[b] D 638	kg/mm^2	[d] D 790	kg/mm
[e] Source: Ref. 10.			

reaction at the the interface of the blends. Hence, the adhesion between EPM and PP is poor.

Tensile Test

Tensile stress at the yield point of the virgin PP is 3.20 kfg/mm^2 (Fig. 9). The addition of EPM, however, decreases the tensile stress of PP in almost a linear trend. At 50% EPM, the minimum stress of the blend is observed.

The decrease of tensile stress of blended EPM/PP is proportional to the decrease of its modulus of elasticity (Fig. 10). Modulus of elasticity of virgin PP decreases gradually from 85.98 to 30.97 kgf/mm^2 when 50% of EPM was added. In general, polymer blends have large interfacial tension and poor interfacial adhesion, and thus

exhibit poor mechanical properties relative to the composition of their constituents.[20]

A computation of the stress–strain curves of PP and EPM blends reveals the decreasing mechanical properties of PP as EPM quantity increases. Figure 11 shows the decrease of stress and strain as EPM increases.

Table III shows the properties of the commercial PP high impact copolymer[10] of Daelim Poly. PP 241, PP 242, and PP 243 with a melt flow index of 7 and 8 g/10 min, exhibit tensile strength and flexural modulus of elasticity of 2.80, 2.80, and 2.10 kg/mm^2 and 150, 140, and 100 kgf/mm^2, respectively. Similar properties can be obtained for some of the experimental polyblends. At 10 to 20% EPM, the tensile strength and tensile mod-
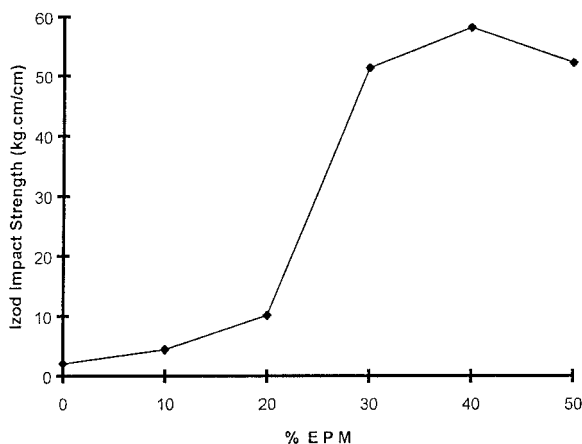
Figure 12 Izod impact strength of PP and PP/EPM blends.

ulus of elasticity of the polyblends are 2.72 and 2.13 kg/mm^2 and 67.03 and 55.03 kgf/mm^2, respectively. It should be noted, however, that the difference in the flexural and tensile modulus of elasticity has always been observed.

Izod Impact Test

Virgin PP has 2.06 kg cm/cm Izod impact strength (Fig. 12). The addition of EPM from 10 to 20% increases its impact strength gradually, and then sharply when 30% of EPM was blended. This remarkable change is not observed in WAXS, DSC, SEM, and the tensile test wherein the change in the test results is a function of the elastomer content. Wu (1988)[21] mentioned that a sharp brittle–tough transition will occur if the average thickness of the matrix ligament is at critical value that is dependent on the rubber volume fraction. The highest impact strength is obtained at 40% EPM, and starts to decrease at 50% EPM. It could also be observed that the increase of impact strength from 30 to 40% is gradual but not significant. From this data, the addition of 30% EPM is the most recommendable blend for balancing the impact strength, tensile, and modulus of elasticity. Stress whitening is also observed, which is attributed to the multicraze formations of the blends.[5]

In Table III, the high-impact strength of the PP copolymers ranges from 9 to 36 kg · cm/cm to the very high impact PP-243 with 51 kg · cm/cm. Blending of 20% EPM with PP produces a high-impact polyblend with 10.12 kg · cm/cm. Furthermore, the 30% EPM has almost similar properties as the PP-243, and is, therefore, suitable for ap-

plications requiring very high-impact strength such as automotive bumpers.

CONCLUSIONS

Experimental polyblends of EPM and PP are comparable with the commercial PP impact copolymer. Based on their melt index of 8 g/10min, the 30% EPM/PP blend and PP-243 exhibit similar properties. Both exhibit impact strength of about 50 kg · cm/cm; however, tensile stress and tensile modulus of elasticity of the EPM/PP blends are lower. At this point, the EPM/PP blends attained very high impact strength, which are suitable for automotive bumpers. Blends less than 30% EPM can be used in the production of products that do not require very high impact strength such as household articles, containers, furniture, etc. Further addition of EPM from 40 to 50% produces very high impact strength but the tensile stress and flexural modulus are very low.

The modification of polymers through mechanical blending has catered to the needs of the industry. But it should be noted that the technology of copolymerization, although difficult to process, provides cheaper polyblends.

REFERENCES

1. Harper, C. Handbook of Plastics and Elastomers; McGraw-Hill Inc.: New York, 1975.
2. Starke, J. U.; Michler, G. H.; Grellman, W.; Seidler, S.; Gahleitner, M.; Fiebig, J.; Nezbedova, E. Polymer 1998, 39, 75.
3. Galli, P.; Foshini, G.; Moro, A. In Polymer Blends and Mixtures; Walsh, D. H.; Higgins, J. S.; Maconnachie, Dordecht Martinus Nijhoff Publishers, 461, 1985.
4. Martuscelli, M.; Silvestre, C.; Abate, G. Polymer 1982, 23, 229.
5. Danesi, S.; Porter, R. Polymer 1978, 19, 448.

6. Karger-Kocsis, J.; Kallo, A.; Shaftner, A.; Bodor, G. Polymer 1979, 20, 37.

7. D'Orazio, L.; Greco, R.; Mancarella, C.; Martuscelli, E.; Ragosta, G.; Silvestre, G. Polym Eng Sci 1982, 22, 536.

8. D'Orazio, L.; Greco, R.; Martuscelli, E.; Ragosta, G. Polym Eng Sci 1983, 23, 301.

9. Utracki, L. Polymer Alloys and Blends—Thermodynamics and Rheology; Hanser Publishers: Munich, 1990.

10. Technical Brochure of Daelim Poly, Korea.

11. Moore, E. In Polymeric Materials Encyclopedia; Salamone, H., Ed.; CRC Press, New York, 1996, p. 6583, vol. 9.

12. Vernom, W. In Modern Plastics Encyclopedia; Juran, R., Ed., McGraw-Hill, Inc.: New York, 1990, p. 100.

13. Danesi, S.; Porter, R. Chemical Bibliography # 685.

14. Russo, R.; Vittoria, V. J Appl Polym Sci 1996, 60, 955.

15. Ghijsels, A.; Grossbeek, N.; Yip, C. W. Polymer 1982, 23.

16. Blundell, D. J.; Beckett Willcocks, P. H. Polymer 1981, 22, 704.

17. Cheremisinoff, N. Handbook of Polymer Science and Technology; Marcel Dekker, Inc.: New York, 1989, p. 2.

18. Choudhary, V.; Varma, H. S.; Varma, K. Polymer 1991, 32, 2534.

19. Gupta, A. K.; Ratnam, K. J Appl Polym Sci 1991, 4, 297.

20. Kim, S.; Kim, J. K.; Park, C. E. Polymer 1997, 38, 1809.

21. Wu, S. J Appl Polym Sci 1988, 35, 549.