CHARACTERIZATION OF RUBBER-MODIFIED POLYPROPYLENE

Nuri Astrini[*], **E.L. Bedia**[**], **and A. Sudarisman**[***]

[*]R&D Centre for Applied Chemistry-LIPI, Jalan Cisitu-Bandung 40135
[**]Industrial Technology Development Institute, Philippines
[***]R&D Centre for Applied Physics-LIPI, Jalan Cisitu-Bandung 40135

ABSTRACT

Blending of 10, 20, 30, 40, and 50% ethylene-propylene random copolymer known as EPM with polypropylene (PP) was conducted and the blends were characterized using wide-angle x-ray scattering (WAXS), differential scanning calorimetry (DSC), scanning electron microscope (SEM), Tensile and Impact tester. As shown in WAXS diffractograms, PP retains its crystalline structure when blended with EPM. DSC analysis suggests that the polymer blend consists of two phase systems, one crystalline and one amorphous. Morphological observation of the polymer blend using SEM shows that the EPM globular structure cavitates the PP matrix which further indicates that the polymer blend is only partially compatible. As EPM increases, the tensile yield stress, stress-strain curve and modulus of elasticity decrease. Impact strength on the other hand, increases and showed remarkable effect at 30% EPM - 70% PP.

INTISARI

Telah dilakukan pencampuran polimer 10, 20, 30, 40 dan 50% etilena-propilena random kopolimer yang biasa dikenal sebagai EPM dengan polipropilena (PP) dan karakterisasinya dengan menggunakan wide-angle-x-ray scattering (WAXS), differential scanning calorimetry (DSC), scanning electron mi-crosope (SEM),tes kekuatan tarik dan bentur. Seperti terlihat dalam difraktogram WAXS, PP mempertahankan struktur kristalinnya apabila dicampur dengan EPM. Analisa DSC menunjukkan bahwa campuran polimer terdiri dari sis-tim dua fasa yaitu kristal dan nirbentuk (amorf). Dari pengamatan morfologi campuran polimer dengan menggunakan SEM, terlihat bahwa struktur globular berongga adalah EPM pada matrik PP, yang lebih jauh menunjukkan bahwa campuran polimer hanya kompatibel secara parsial. Dengan bertambahnya jumlah EPM, maka tensile yield stress, stress-strain curve dan modulus elastisitas menurun. Sebaliknya kekuatan bentur bertambah dan pengaruh yang luar biasa terlihat pada campuran polimer 30% EPM - 70% PP.

INTRODUCTION

Polymer blending is a process of combining two or more polymeric material to improve its performance, processibility and lower its production cost. Intensive studies had already been undertaken on polymer blending, some of which are now in commercial production (1,2). But still, there are many works under active developments producing a more sophisticated polymer blends with tailored physical properties (2,3).

One of the polymer blends which had been of increasing industrial importance is the ethylene-propylene copolymer (EPM) and polypropylene (PP). Polypropylene, a widely used thermoplastics, has the property of being brittle at low temperature. On the other hand, addition of EPM improve its impact strength, toughness and reduce its rigidity through absorption of energy dissipated (1, 4-10).

In this research, an attempt was made to produce homogeneous PP-EPM blend and then characterized using wide-angle x-ray scattering (WAXS), differential thermal analysis (DSC), scanning electron microscope (SEM), tensile and impact tests, which play major role in this study.

EXPERIMENTAL

Materials

Polypropylene (PP) used in this research was isotactic PP J150-C, an injection grade with a melt flow index of 8 g/10 min. The elastomeric impact modifier, ethylene-propylene random copolymer (EPM)-JSR was used. Both materials were imported from Japan.

Blending

Blending EPM with PP at 0, 10, 20, 30, 40 and 50% were undertaken using Toyoseiki Labo Plastomill model 30R150. The equipment was set at a temperature of 200°C, screw speed at 30 rpm and a residence time of 10 minutes in an inert atmosphere.

The blended polymers were collected and pressed using Sangyo Hot Press Tester which was set at 200°C and applied pressure of 10 kgf/cm^2 for 5 minutes. The slab test specimen was then quenched in water and cut to the desired size of test specimen. Blending was conducted four times to prepare one slab test specimen per formulation.

Wide- Angle X-ray Scattering (WAXS)

WAXS was performed using Rigaku WAXS diffractometer which was set at 40 kV and 30 mA with Ni-filtered CuK radiation.

Differential Scanning Calorimetry (DSC)

DSC thermograms of blended polymers were obtained using Seiko DSC-100.

The blended polymer was first subjected to a heating environment from 25° to 220°C to remove its prehistory effects. This was then subsequently cooled down using liquid Nitrogen to (-130°C) to obtain crystallization peak (Tc). Both heating and cooling were undertaken at a rate of 20°C/minute. To obtain transition (Tg) and melting points (Tm) the sample was reheated to 250°C at 10°C/minute.

Scanning Electron Microscopy (SEM)

Test specimen were prepared by cutting the slab test specimen to 4mm width and breaking it in liquid nitrogen. One of the broken surfaces, was etched with xylene in an ultrasonic bath at 25°C for 9 minutes (7). The other broken surface was treated as it is. The etched and the unetched samples were coated with 200 um gold.

Morphological structure of etched and unetched PP/EPM were observed using JEOL-T330A Scanning Electron Microscope.

Tensile Test

Test specimens of dumbbell shape were prepared using Orientec Test Piece making machine model I DT-1.

Tests were conducted using Shimadzu A 6-5000 B at a constant cross head speed of 50 mm/min (JIS K 7113) (11). Tensile yield strength, stress-strain and modulus of elasticity curves were calculated manually from the graph.

Izod Impact Test

Izod impact strength of test specimen were obtained following the ASTM D256-81 (12). The slab test specimen was cut to the desired shape notched and conditioned. Izod Impact Toyoseiki 612 was used in the analysis, and testing was done at room temperature.

RESULTS AND DISCUSSION

Wide-angle X-Ray Diffractometer (WAXS)

WAXS diffractograms are shown in Figure 1. Isotactic PP virgin exhibited reflection at 6.55 A°, 5.41 A°, 4.89 A° and 4.18 A° EPM showed only a broad spectrum indicating its amorphous structure. Hence, as the quantity of EPM increases, as expected the intensity part of crystallinity decreases. Only the peak at 4.89 A° increased, because this was the center of amorphous material (Gaussian of PP and EPM). WAXS diffractograms then suggest that PP retains its crystal structure when blended with EPM.

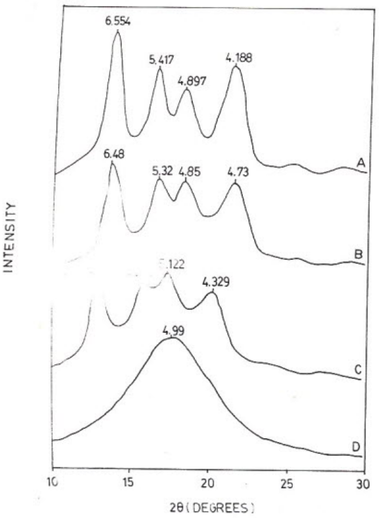

Figure 1. WAXS diffractograms of (A) PP, (B) PP/EPM = 70/30, (C) PP/EPM = 50/50 and (D) EPM

Differential Scanning Calorimetry

As shown in Figure 2 the transition point (Tg) of EPM is lower than PP. For EPM, the Tg point is at -60.6°C whereas for PP, it is -12.6°C. Blending of PP with EPM at 20-30% exhibited both of its Tg points indicating that the blend consists of two amorphous phases partially compatible with each other. Phase diagram of the binary mixture as shown in Figure 3, clearly shows the correlation of these Tg points.

Likewise, the Tm and Tc decrease as EPM increases as shown in Table 1. It should be noted that EPM has no Tc and Tm peaks. In this case EPM acts as a diluent.

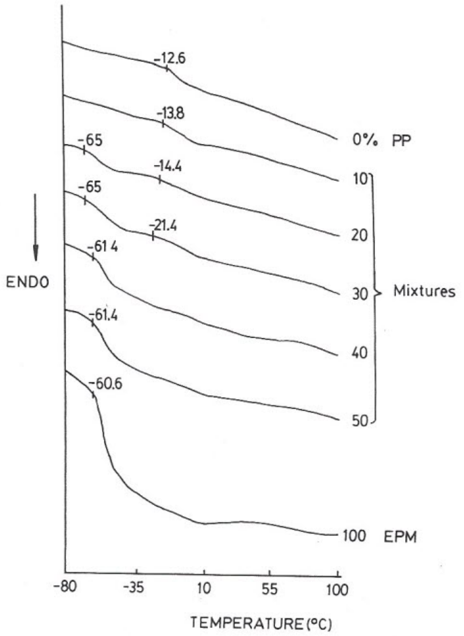

Figure 2. DSC thermograms indicating the glass transition temperatures (Tg) of PP, EPM and its binary mixtures percentage composition of EPM is as indicated.

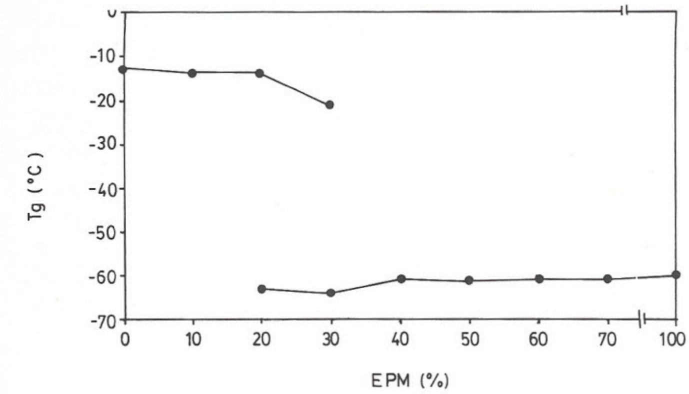

Figure 3. Phase diagrams of the binary mixtures of PP and EPM.

Tabel 1. DSC, Modulus of Elasticity, Impact Strength and Tensile yield Strength of PP, EPM and the blends.

No.	PP/EPM	Tg	Tm	ΔHm	Tc	ΔHc	E	I.S.	T.Y.S
1.	100/0	-12.6	163.1	136.3	110.1	129.1	85.98	2.06	336.34
2.	90/10	-13.8	162.9	120.8	110.0	117.8	68.13	4.78	271.61
3.	80/20	-14.0 -65.0	162.3	109.8	109.3	102.7	55.04	8.50	213.13
4.	70.30	-21.4 -65.0	161.6	94.9	109.5	90.3	47.09	50.83	117.13
5.	60/40	-61.4	161.6	70.4	109.4	77.2	37.06	53.56	120.28
6.	50/50	-61.4	160.3	65.4	109.9	61.4	30.97	51.73	74.37
7.	30/70	-60.6	160.0	39.3	107.1	33.2	-	-	-
8.	0/100	-60.6	-	-	-	-	-	-	-

Legend:

Tg : glass transition peak °C
Tm : melting peak °C
Tc : crystallization peak °C
ΔHm : heat melting capacity J/g
ΔHc : heat crystallization capacity J/g
E : modulus of elasticity kg/cm^2. 10^{-3}
I.S : impact strength kg cm/cm
T.Y.S : tensile yield strength kg/cm^2

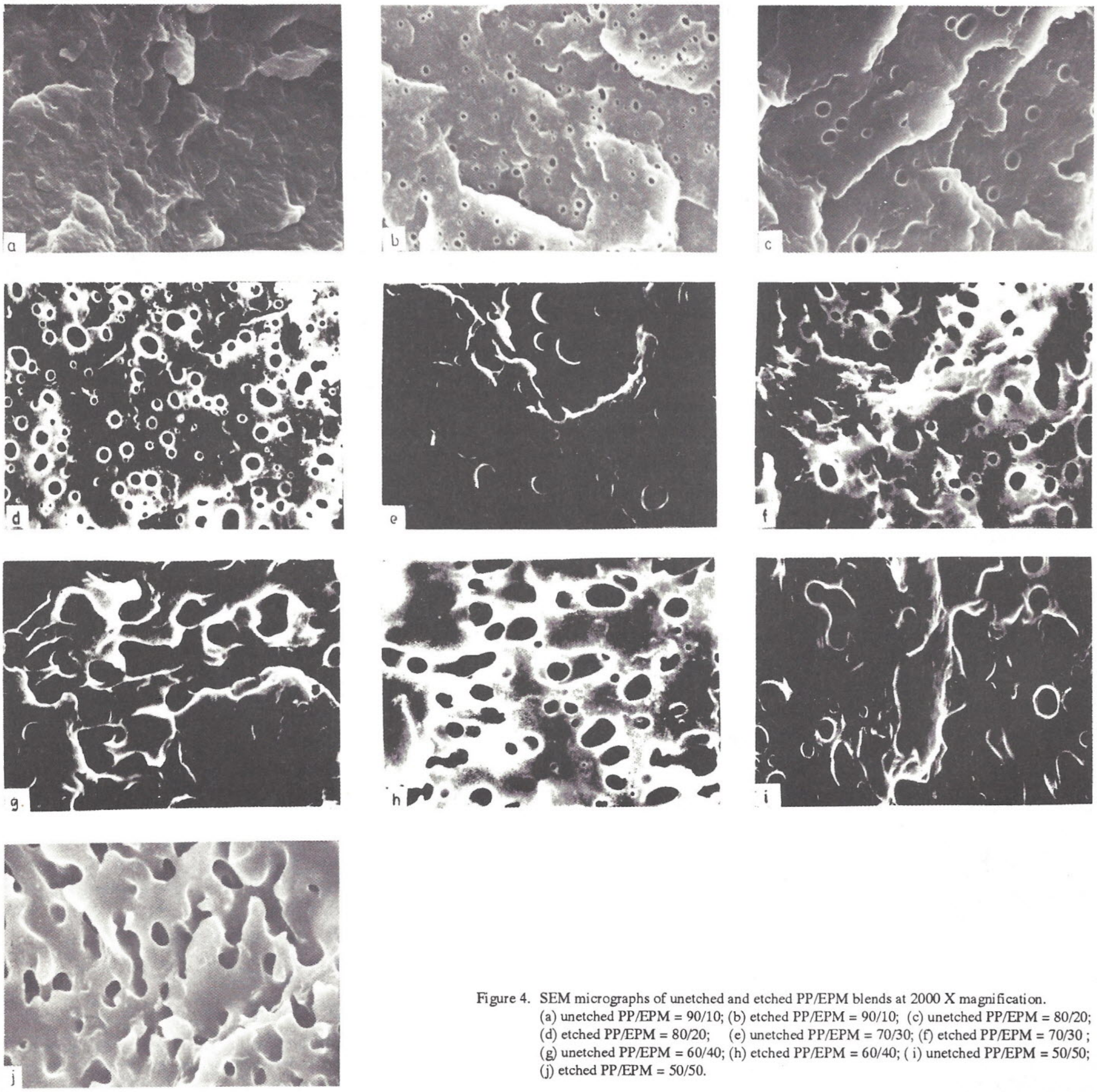

Figure 4. SEM micrographs of unetched and etched PP/EPM blends at 2000 X magnification.
(a) unetched PP/EPM = 90/10; (b) etched PP/EPM = 90/10; (c) unetched PP/EPM = 80/20; (d) etched PP/EPM = 80/20; (e) unetched PP/EPM = 70/30; (f) etched PP/EPM = 70/30 ; (g) unetched PP/EPM = 60/40; (h) etched PP/EPM = 60/40; (i) unetched PP/EPM = 50/50; (j) etched PP/EPM = 50/50.

Scanning Electron Microscopy

SEM micrographs are shown in Figure 4. The unetched broken surface of polymer blend showes that EPM has been impaired from the PP matrix. However, there are still some EPM adhering to the PP matrix, hence its distribution is rather difficult to observe.

By chemical etching, the EPM globular structure becomes discernible. In this technique, several methods had been employed before a good result was obtained. This was done by etching the surface of the sample which was broken under liquid Nitrogen temperature with xylene in ultrasonic bath for 9 minutes. The homogeneous distribution of EPM globular structure can now be seen clearly. Furthermore, as EPM increases, the globular structure also increases.

Dynamic Mechanical Properties

The effect of the enhancement of EPM on the mechanical properties of polymer blend such as the tensile yield stress, stress-strain and modulus of elasticity is shown in Figure 5, Figure 6, and Figure 7. From the graph, an increase of EPM fraction decreases linearly its mechanical property. Hence, the rigidity of PP decreases.

On the other hand, the impact strength of the notched test specimen increases (Figure 8). This is due to the energy absorbing capacity of the EPM on the polymer blend. A remarkable increase of impact strength was observed when 30% EPM was added. As mentioned by Wu (13), sharp brittle - tough transition will occur if the average thickness of matrix ligament is at critical value. It is also interesting to take note that on the phase diagram (Figure 3) two phase system exists. It could therefore be deduced that although PP and EPM are partially compatible, there

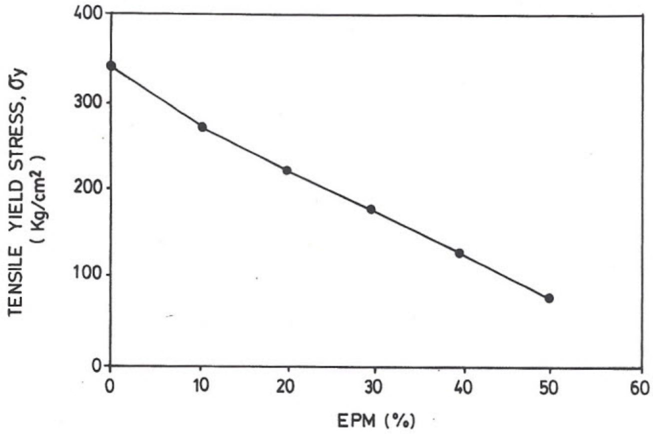

Figure 5. Tensile yield stress of PP and its binary mixtures as a function of composition.

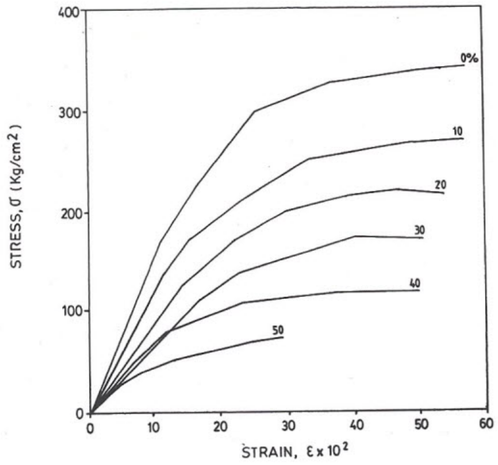

Figure 6. Stress - strain curves of PP and its binary mixtures percentage composition of EPM is as indicated.

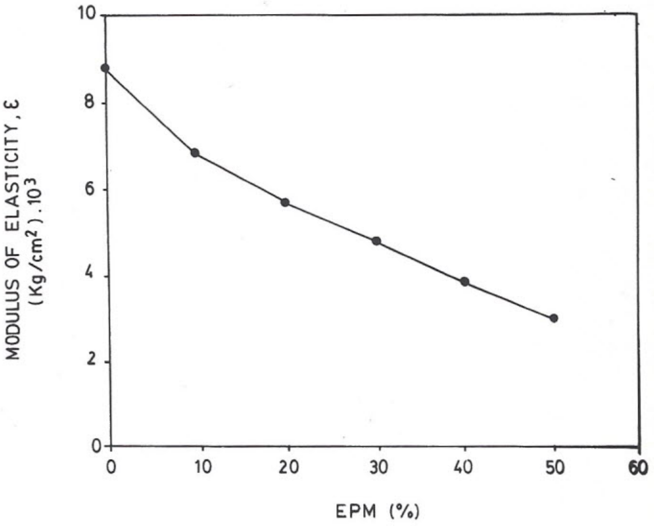

Figure 7. Modulus of elasticity of PP and its binary mixtures as a function of composition.

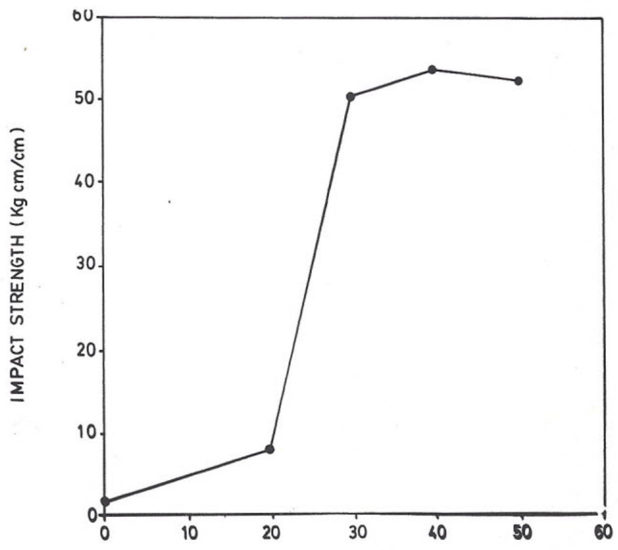

Figure 8. Notched iod impact strength of PP and its binary mixtures as a function of composition.

exist a point by which significant increase of impact strength could be obtained. Further addition of EPM could have a little effect as far as the impact strength is concerned but then, it has the tendency to decrease once the maximum impact strength was obtained.

CONCLUSION

PP and EPM are partially compatible polymer blend as can be seen from the DSC curve exhibiting two Tg peaks and by SEM micrograph wherein EPM globular structure cavitated PP matrix.

Despite this partial compatibility, EPM significantly modifies the impact strength of PP. At 30% EPM the highest increase of impact strength was observed. At this point, two peaks on DSC curve are discernible indicating the occurrence of two amorphous phase. Other mechanical properties such as the tensile yield stress, modulus of elasticity and stress-strain properties suffer. Hence, a certain amount of EPM could only be added to PP depending on the properties of polymer needed to attain.

ACKNOWLEDGEMENT

Most heartfelt thanks are due to JICA through ASEAN - JAPAN Cooperation Programme on Materials Science and Technology, for their initiation and financial support in this project. The authors also wish to thank Drs. Iguchi, Nilyardi and Suparno for their technical advises, and to Dr. Roestamsjah and Mr. Kashiro, for their assistance during the preparation of this manuscript. Special thanks are also due to LIPI, Pertamina and Textile Institute staff members for assisting us in the sample testing.

REFERENCES

1. D.J. Lohse, The melt compatibility of blends of polypropylene and ethylene-propylene copolymer. *Polym. Eng. Sci;* 26 : 1500- 1509, (1986).
2. R.L. Jalbert, Alloys, blends and compounds. *Modern Plastic Encyclopedia;* 60: 1st ed. A.MC Graw-Hill 1983-1984, pp.98-100
3. S. Krause, *Polymer Blends.* Chapter.2, D.R. Paul and S. Newman (editors)., Academic Press, New York, 1978.
4. D. Orazio, L, R. Greco, E. Martucelli and G. Ragosta, Effect of the addition of EPM copolymers on the properties of high density polyethylene/isotactic polypropylene blend : II. Morphology and mechanical properties of extruded samples. *Polym. Eng. Sci;* 23: 489-497,(1983).
5. E. Martucelli, C. Silvestre and G. Abate, Morphology, crystallization and melting behaviour of films of isotactic poly-propylene blended with ethylene-propylene copolymers and polyisobutylene. *Polymer;* 23: 229-237,(1982).
6. Auchter, J and G. Holden, Thermoplastic elastomer. *Modern Plastic Encyclopedia;* 60: First edition. A. Mc. Graw-Hill 1983-1984, pp. 95-97
7. F.C. Stchling, T. Huff, C.S. Speed and G. Wissler, Structure and properties of rubber-modified polypropylene impact blends *J. Appl. Polym. Sci;* 26: 2693-2711,(1981)
8. H.W. Starkweather,JR., Cocrystallization and polymer miscibility. *J. Appl. Polym. Sci;* 25: 139-147,(1980).
9. R. Greco, C. Mancarella, E. Martuscelli, G. Ragosta and Yin Jinghua, Polyolefin blends: 2. Effect of EPR composition on structure, morphology and mechanical properties of iPP/EPR alloys. *Polymer;* 28: no.11, (1987).
10. J.K. Kocsis, A. Kallo, A. Szafner, G. Bodor and Zs. Senyei, Morphologycal study on the effect of elastomeric impact modifiers in polypropylene systems. *Polymer;* 20: 37-43, (1979).
11. Japanese Industrial Standard, K.7113.
12. American Standard Testing Measurement, D 256-81.