

Interfacial Adhesion Through Maleic Anhydride Grafting of EPDM in PP/EPDM Blend

D. Purnima, S. N. Maiti, A. K. Gupta

Centre for Polymer Science and Engineering, Indian Institute of Technology, New Delhi 110016, India

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ABSTRACT: This paper presents a study of interface modification effect through the use of maleic anhydride (MAH) grafting on one of the component polymers of the binary blend. The system used is binary blend of polypropylene (PP) and the elastomer EPDM (copolymer of ethylene-propylene-diene monomer). Two sets of the blend (i) PP/EPDM binary blend and (ii) PP/EPDM-g-MAH binary blend at constant degree of grafting (i.e., EPDM : MAH ratio) and at varying blending ratios were studied and compared for the properties and structure development. Results are discussed to illustrate the effect of interfacial

modification due to presence of MAH by comparing the data of mechanical properties and crystallization behavior for the two sets of the binary blend at identical blending ratios, as well as to study the trends of variation of properties with blending ratio for each individual set of the blend. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 5528–5532, 2006

Key words: poly(propylene) (PP); crystallization; mechanical properties; differential scanning calorimetry (DSC); interfaces

INTRODUCTION

PP/EPDM is an immiscible blend. Commercial success of immiscible blends requires improvement of interfacial adhesion between the components of the blend, necessary to achieve stability of morphology and improvement in mechanical properties. Incorporation of third component as a compatibilizer^{1–9} or grafting of the PP or EPDM with suitable monomer^{10–13} has been widely reported in literature to improve the interfacial adhesion. Melt grafting of EPDM with maleic anhydride (MAH) was reported by Grigoryeva and Kocsis.¹⁴ The use of EPDM-g-MAH as compatibilizer^{15,16} or in dispersed phase¹⁷ in polymer blends has been reported to be successful in improving the properties of the blends. Enhancement of impact strength of PP/EPDM blend upon grafting the EPDM used with 1.5 wt % MAH was reported by Zhao and Dai.¹² Montiel et al.¹³ have reported the effect of level of MAH grafting in Nylon 6/EPR blend to result in improved mechanical properties and morphology of the blend.

In this paper we report a study of the effect of maleic anhydride grafting of EPDM on mechanical properties and crystallization behavior of PP in the PP/EPDM blend. Two sets of the binary blend (i) PP/EPDM and (ii) PP/EPDM-g-MAH were prepared

under identical blending conditions at identical blending ratios. Studies carried out include mechanical properties (tensile and impact) and crystallization behavior. Crystallization behavior is explored through the analysis of changes observed in crystallization exotherms recorded by differential scanning calorimetry (DSC).

EXPERIMENTAL

Materials

Isotactic polypropylene (PP), produced by Reliance Industries Ltd, India, (grade H030SG) having MFI 3 g/10 min was used. EPDM produced by Dupont/Dow Elastomer (Wilmington, DE) (Nordel grade 4770R) having Mooney viscosity, (ML1 + 4125°C) 70, ethylene content 70%, ENB content 5%, was used. Maleated EPDM, produced by Manas Polymers, India, (grade OPTIM P-635) with MAH content 0.3%, MFI 3.4 g/10 min, was used.

Preparation of blends

The blends were prepared by extrusion in a twin screw extruder Berstoff- Model ZE 25, with L/D ratio 48, screw dia 25 mm and channel depth 4 mm, at a screw speed 100 rpm. Temperatures were 433, 453, 473, 483, 493, 498, and 503 K in the zones 2, 3, 4, 5, 6, 7, and 8, respectively. Thick strands emerging from the extruder were cooled by quenching in water and subsequently granulated. The PP sample

Correspondence to: A. K. Gupta (akgncute@hotmail.com).

TABLE I
Variation of Tensile Properties with EPDM Content in PP/EPDM Blend Without Interface Modification and with Interface Modification

Elastomer content (wt %)	Blend without interface modification (PP/EPDM)		Blend with interface modification (PP/EPDM-g-MAH)	
	Yield strength (MPa)	Modulus (MPa)	Yield strength (MPa)	Modulus (MPa)
0	31.4	488.2	31.4	488.2
4.8	29.3	454.2	29.1	476.4
9.1	26.3	409.4	27.4	455.9
16.7	22.6	368.4	24.0	405.0
25.9	17.7	279.0	20.3	330.6
33.3	16.6	252.4	17.5	276.6

to be used as reference was also passed through the extruder under similar conditions as the blend, to give it identical processing history. Five compositions of both the blends (i) PP/EPDM and (ii) PP/EPDM-g-MAH were prepared with weight fraction of the elastomer (EPDM or EPDM-g-MAH) 4.8, 9.1, 16.7, 25.9, and 33.3, identical for both sets of the blends.

Injection molding

Test specimens were prepared by injection molding of vacuum-dried granules (dried at 353 K for 2 h in vacuum oven) on injection molding machine, LT Demag (Model PFY 40-LNC4P), at temperature from 483 to 498 K from the compression zone to the injection nozzle. The cycle time, cooling time, and injection pressure were 100 s, 40 s, and 1000 bars, respectively.

Mechanical properties measurements

Tensile tests on dumb-bell shaped specimens were performed according to ASTM D638 test method at crosshead speed 50 mm/min and crosshead separation of 70 mm on a Zwick Z010 machine. Impact tests on notched rectangular bar samples were carried out following ASTM D256 test method on a pendulum-type tester ATS Faar (Model 16.10,000). Five samples for each composition of the blend were tested and the average values are reported. All the tests were conducted at ambient temperature 303 ± 2 K.

Thermal analysis measurements

Differential Scanning Calorimetry (DSC) measurements were done on a TA 2100 Thermal Analyzer having 910 DSC module using small pieces of injection-molded specimens of about 5 mg weight, dried in vacuum for 2 h at 353 K. To record the crystallization curve during the cooling cycle the samples were first heated from room temperature to above the melting temperature of PP and held there for 2 min to eliminate all previous history of the crystalliza-

tion, and then cooled at 5 K/min to record the thermogram. At this slow speed of cooling, prominent crystallization exotherm for PP appeared in the thermogram. The exotherm was recorded under identical instrumental settings and experimental conditions for all samples for reliable comparison and analysis of the exotherm parameters.

RESULTS AND DISCUSSION

Tensile properties

Results of tensile tests are presented in Table I for both the sets of the blends to illustrate the effect of interface modification on tensile properties. These results can be seen for

- trend of variation of any property with blending ratio (i.e., elastomer content) for each set of the blend,
- effect of interface modification by comparing these trends of variation for the two sets of the blend, and
- comparison of absolute values of any property at identical blending ratio (i.e., elastomer content) in the two sets of the blend.

Trends of variation of tensile properties with elastomer content are in line with the generally believed behavior of PP/elastomer blends, viz. decrease of tensile strength and modulus with increasing elastomer content. The overall decrease of tensile strength and modulus in the studied range of elastomer content is less in case of the blend with EPDM-g-MAH than the blend with ungrafted EPDM, which confirms the effect of increased interface adhesion in the former set of the blend. The greater the interfacial adhesion between the components the higher the tensile strength or the modulus. The interface modification by using maleated EPDM (i.e., EPDM-g-MAH) produces distinct improvement in tensile yield strength and modulus at each composition (i.e., blending ratio) in the entire range of the blending ratios studied, as illustrated in Figure 1.

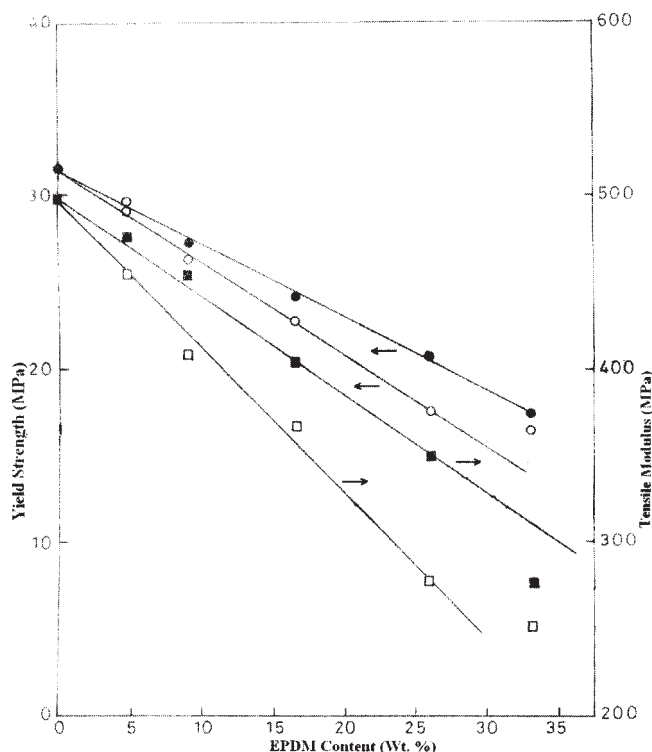


Figure 1 Variation of yield strength (○), and tensile modulus (□) with EPDM content in PP/EPDM blend. (a) Unfilled symbols: PP/EPDM blend; (b) Filled symbols: PP/EPDM-g-MAH blend.

Impact properties

Izod impact strength of PP/EPDM and PP/EPDM-g-MAH blends are shown in Table II. Impact strength increases with increasing elastomer content, which is in line with the well-established effect of rubber toughening of polymers. The increase of impact strength (at each individual elastomer content, as well as the overall increase in the studied full range of blending ratio) is greater in case of PP/EPDM-g-MAH blend than in PP/EPDM blend, which is the effect of improved interfacial adhesion due to the presence of MAH groups. These results indicate that 0.3 wt % grafting of MAH on EPDM produces sufficient improvement of interfacial adhesion required for considerably enhancing rubber-toughening effect of EPDM on PP. Although strength of interfacial bonding between the matrix and the dispersed elastomer domains is crucial in the impact toughening, it is believed that neither too strong nor too weak interfacial bonding is favorable for this effect.^{18,19} Too strong interfacial bonding is detrimental to impact toughening.¹⁸ In the rubber toughening the stress concentration at the interface gives rise to deformation of the elastomer domains, which in turn produces crazing or shear band formation in its neighboring matrix. In this way the stress concentration energy gets dissipated without producing detri-

mental effect of generating a crack leading to fracture. This mechanism of energy dissipation will be affected by interfacial bonding. In the extreme case of perfect adhesion, the elastomer deformation will be restricted by the surrounding matrix, whereas in case of extremely poor adhesion (i.e., no bonding), the stress transfer at the matrix elastomer interface may not take place as desired for deforming of the elastomer domain and consequent generation of crazes or shear bands. In the present work we have studied only a fixed MAH content (i.e., 0.3 wt %). However it may be interesting to investigate the effect of producing optimum impact toughening by varying the MAH content in the EPDM-g-MAH.

Differential scanning calorimetry

Crystallization exotherms of PP obtained in the DSC thermograms recorded during cooling cycle of the PP/EPDM and PP/EPDM-g-MAH blends are shown on identical scales on the axes, in Figures 2 and 3, for comparison. These exotherms, recorded under identical experimental conditions and instrumental settings, are analyzed in terms of following parameters, as described and used previously,²⁰ which are represented in Figure 4

- i. T_{onset} , the onset temperature, is indicative of the start of the process.
- ii. T_p , the peak temperature, which may be referred to as the temperature of the overall process.
- iii. S_i , the initial slope, is indicative of the rate of the initial process of crystallization, viz., the nucleation.
- iv. Δw , the width of the exotherm measured at half height, is indicative of crystal size distribution.
- v. A/m , the ratio of peak area (A) to the mass (m) of the crystallizable component, is related to crystallinity.

TABLE II
Variation of Impact Properties with EPDM Content in PP/EPDM Blend Without Interface Modification and with Interface Modification

Elastomer content (wt %)	Impact strength (kg cm/cm)	
	Blend without interface modification (PP/EPDM)	Blend with interface modification (PP/EPDM-g-MAH)
0	4.0	4.0
4.8	5.5	6.4
9.1	6.0	7.7
16.7	8.7	10.6
25.9	13.5	15.0
33.3	23.0	26.2

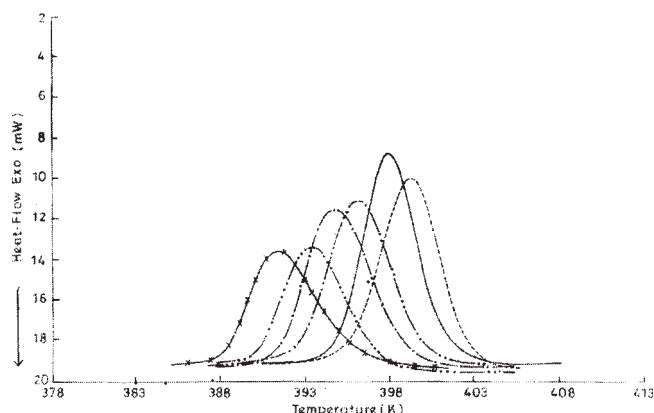


Figure 2 DSC thermograms showing crystallization exotherms with varying EPDM content (wt %) in PP/EPDM blend without interface modification. 0 wt % (—), 4.8 wt % (---), 9.1 wt % (---), 16.7 wt % (---), 25.9 wt % (---), 33.3 wt % (---).

These data, shown in Table III, indicate drastic decrease of T_{onset} of PP on addition of the elastomer EPDM or EPDM-g-MAH at its lowest weight fraction, viz., 4.8 wt %, and thereafter very small decrease with further increase of elastomer content. Unlike T_{onset} , T_p shows very small decrease, which is apparently accounted for by variation of peak width. Decrease in T_{onset} implies slowing down of the initial process, i.e., the nucleation. Slowing down of nucleation would result in wider distribution of crystal size, or broader exotherm peak. Variation of exotherm peak width with elastomer content of the blend causes T_p of PP to show random variation by only 6° .

Slowing down of nucleation rate with increasing elastomer content as indicated by decreased value of S_i shows some noteworthy differences in trends of variation in the cases of the “blend without interface modification (i.e., Set (i))” and “blend with interface

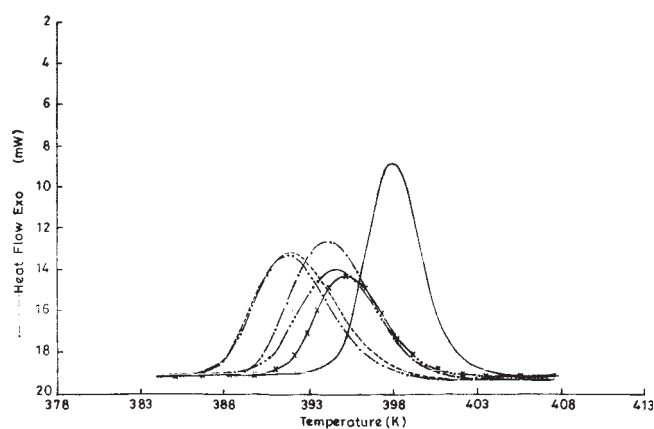


Figure 3 DSC thermograms showing crystallization exotherms with varying EPDM content (wt %) in PP/EPDM-g-MAH blend. 0 wt % (—), 4.8 wt % (---), 9.1 wt % (---), 16.7 wt % (---), 25.9 wt % (---), 33.3 wt % (---).

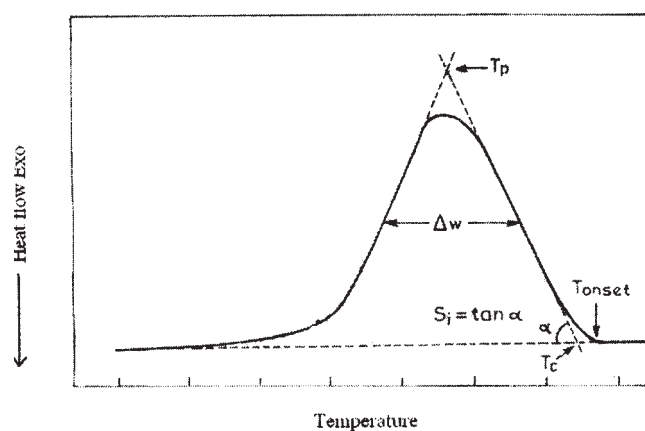


Figure 4 Typical DSC exotherm to illustrate the definition of the characteristic crystallization parameters.

modification (i.e., Set (ii)).” The observed decrease of S_i as function of increasing elastomer content is accompanied by increase of peak width Δw (i.e., crystal size distribution) for both sets of the blend. This mutually opposite trend of variation of S_i and Δw is due to the fact that slowing down of rate of nucleation causes nuclei to be created at different instants of time, which in turn grow to different sizes of the crystallites leading to wider crystal size distribution. Whereas for fast nucleation almost all nuclei are created at the same time (or within a narrow interval of time) and thus grow to nearly equal size, and thereby accounting for narrow distribution of crystal size. A/m decreases continuously as the rubber content increases, indicating a decrease in crystallinity on addition of rubber. Effect of interface modification on the trend of variation of S_i (or rate of nucleation) with elastomer content of the blend is quite significant. In the absence of interface modification (i.e., without the use of MAH-grafted EPDM) S_i decreases gradually, while in the case of the blend with interface modification, S_i decreases drastically; the decrease in the former case is from 4.3 to 1.8 in the entire range, while in the latter case decrease of S_i from 4.3 to 1.6 is merely in the first step of addition of the elastomer (i.e., at 4.8 wt % elastomer) followed by very small variation upto the highest elastomer content. This shows distinct effect of interfacial adhesion in the crystallization behavior of PP.

Formation of crystal nuclei is governed by chain mobility along with other factors such as intermolecular forces. Presence of EPDM chain slows down chain mobility of PP in the EPDM in the interfacial region and thereby slowing down nucleation rate. Improved interfacial adhesion increases this effect of slowing down chain mobility of PP further. A/m (i.e., crystallinity) decreases more distinctly in this case than in the case of the blend without interface

TABLE III
Variation of Crystallization Parameters with EPDM Content in PP/EPDM Blend Without Interface Modification and with Interface Modification

Elastomer content (wt %)	Blend without interface modification (PP/EPDM)					Blend with interface modification (PP/EPDM-g-MAH)				
	T_{onset} (K)	T_p (K)	S_i (Arb. units)	Δw (K)	A/m (Arb. units)	T_{onset} (K)	T_p (K)	S_i (Arb. units)	Δw (K)	A/m (Arb. units)
0	421.0	397.6	4.3	2.4	74.0	421.0	397.6	4.30	2.4	74.0
4.8	406.6	399.0	4.27	2.5	73.0	403.0	391.8	1.57	3.6	70.9
9.1	403.0	394.5	2.67	2.8	74.5	403.6	393.9	1.88	3.6	73.3
16.7	404.3	395.0	3.33	2.7	70.3	402.5	391.6	1.74	3.3	69.5
25.9	401.9	393.1	2.30	2.8	66.3	403.6	394.4	1.50	3.7	68.4
33.3	401.1	391.4	1.82	2.9	76.8	404.4	395.1	1.67	2.9	62.7

modification. Decreased chain mobility due to improved interfacial adhesion resulting in slow nucleation rate may have resulted in decreased crystallinity.

CONCLUSIONS

PP/EPDM blend showed a decrease in tensile strength and modulus on increasing the EPDM content, which is a general trend well obeyed by thermoplastics–elastomer blends. Impact strength of the blend increases with increasing EPDM content. However, when EPDM in this blend is replaced by EPDM grafted with MAH, the blend shows higher tensile strength and modulus compared with the corresponding PP/EPDM blend at each identical blending ratio. Impact strength of PP increases on blending with EPDM. Use of EPDM-g-MAH, instead of the ungrafted EPDM, produces greater improvement of impact strength, indicating a clear role of MAH grafting of EPDM in the impact toughening. Effect of interfacial adhesion enhanced because of the use of MAH-grafted EPDM, instead of ungrafted EPDM, produces significant effect on crystallization of PP in this blend. Decrease in nucleation rate and crystallinity are attributed to hindrance to chain mobility due to improved interfacial adhesion. These results thus consistently indicate enhanced interfacial adhesion between PP and EPDM in presence of grafted maleic anhydride.

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