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CRYSTALLISATION BEHAVIOUR AND MECHANICAL PROPERTIES OF HDPE/EPDM BLENDS

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The crystallisation behaviour of binary blends of high density polyethylene (HDPE) and ethylene-propylene-diene tercopolymer (EPDM) was investigated using differential scanning calorimetry (DSC) and wide angle X-ray diffraction studies (WAXS). The rate of crystallization and nucleation of HDPE was influenced by the addition of EPDM. The % crystallinity (WAXS) increased up to 25% (w/w) addition of EPDM to HDPE. A significant improvement in tensile and impact properties was observed upon addition of EPDM to HDPE.

Ethylene-propylene-diene tercopolymer (EPDM) and ethylene-propylene copolymer (EPR) have been used as toughening agents for polyolefins such as isotactic polypropylene. The blends of HDPE with EPR or EPDM, however, have received little attention. Some studies on the effect of rubber composition on the crystallization behaviour of HDPE and LDPE have been reported earlier [1, 2]. It has been suggested that during blend mixing low molecular weight HDPE could dissolve in the rubber phase giving rise to a system with lower crystallinity and higher HDPE perfection. No co-crystallization between HDPE and EPR copolymers was observed [2]. In LDPE/EPDM blends, on the other hand, partial co-crystallization has been indicated when a rubber having higher ethylene/propylene ratio was used [2]. No studies on the effect of concentration of EPDM on the crystallization behaviour and mechanical properties of HDPE have been reported.

It was therefore considered of interest to investigate the influence of various concentrations of EPDM rubber of a fixed composition on the crystallization behaviour and mechanical properties of HDPE. The crystallization behaviour was investigated using differential scanning calorimetry (DSC) and wide angle X-ray scattering (WAXS) techniques.

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Experimental

Materials

High density polyethylene (HDPE) Hostalene, GD–7250 (MFI 6.5 g/10 min) from Polyolefin Industries Limited and EPDM rubber, NORDEL–2760 (abbreviated as rubber in subsequent discussion) of DuPont company was used for the preparation of binary HDPE/EPDM blends. The ethylene content of rubber as determined by FTIR technique (ASTM D 3900) was found to be approximately 80%. Nine binary blends containing 5, 10, 15, 20, 25, 30, 40, 50 and 60% (w/w) of rubber were prepared. These HDPE/rubber blends have been designated as EB blends with a subscript indicating the rubber content. For example, blends containing 10% and 25% (w/w) of rubber have been designated as EB_{10} and EB_{25}, respectively.

Preparation of blends

A Betol single screw extruder (L/D $\simeq$ 20) with the temperature profile of 190°, 200°, 210° and 210° in the feedzone, compression zone, metering zone and die zone, respectively, was used for the preparation of binary HDPE/EPDM blends. The pellets of these two polymers were hand mixed in appropriate ratios prior to their feeding into the extruder hopper. The EPDM content was varied from 5 to 60% (w/w) in these blends. The filament obtained upon extrusion was immediately quenched in water and later on chopped into small granules. The unblended HDPE was also subjected to the same process of extrusion. The granules of polymers were dried before injection molding to prepare specimens for mechanical testing using SPI Windsor injection molding machine at an injection temperature of 200° and pressure of 100–120 kg/cm^2.

Instrumental techniques

DSC scans of 10 ± 1 mg powdered samples were recorded in static air atmosphere using a DuPont 1090 thermal analyser with a 910 DSC module. The crystallization behaviour was evaluated by heating the polymer sample in the DSC pan at 180° for 5 min to allow all the crystallites to melt and then cooling at a rate of 10 deg/min from 180° to 30°. The sample was kept at 30° for 10 min and then the fusion behaviour was recorded by heating the sample to 180° at a rate of 10 deg/min.

The X-ray diffraction measurements on the various blend samples were performed with Philips X-ray generator equipped with microprocessor controlled recorder unit. Radial scans of intensity I *vs.* diffraction angle 2θ were recorded in the range 10° to 50° of 2θ under identical settings of the instrument using nickel filtered CuK$_\alpha$ radiation of wavelength 1.5418 Å. An operating voltage of 40 kV and filament current of 30 mA were used.

The tensile and impact properties of various injection molded samples were determined using Instron tensile tester (Model 1121) and Izod impact tester (Model IT–0.42 of Fuel Instruments and Engineers Pvt. Ltd.) respectively. The dimensions of the dumb-bell shaped specimens for tensile testing (ASTM D–638) were: length 165 mm, width of the narrow section 12.5 mm and thickness 3.8 mm. The conditions used for tensile testing were: crosshead speed 20 mm/min, chart drive 20 mm/min, fullscale load 200 kg and jaw separation of 50 mm. Izod impact testing (ASTM D–256) was performed on notched specimens having dimensions: depth 11.5 mm, width 6.0 mm, length 62.5 mm and depth of notch cut on the narrow side (width) 2.5 mm (at an angle of 45 ± 1°). At least five specimens were tested for each property measurement and the results were averaged.

Results and discussion

DSC studies

The crystallization exotherms obtained from cooling curves of DSC scans were characterized (Fig. 1) and the results for various polymer blends are summarized in Table 1.

The T_c for HDPE and rubber were found to be ~112.6° and 30.7°, respectively. An increase of ~2.3 deg in T_c was observed on addition of 5% (w/w) of rubber.

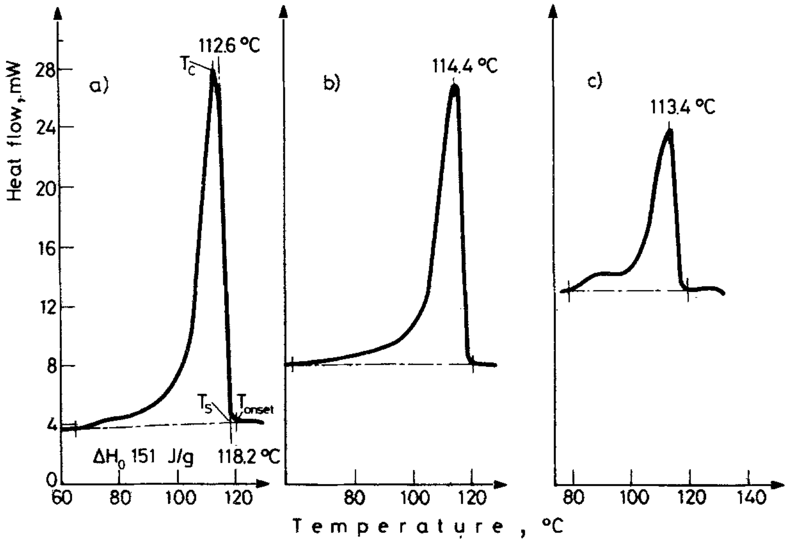

Fig. 1 Crystallization exotherms of (a) HDPE and binary blends, (b) EB_{25}, (c) EB_{60}

Table 1 Evaluation of the crystallisation behaviour of blends of HDPE/EPDM by DSC

Sample designation	wt% of EPDM in blends	T_c, °C	ΔH_0, J/g	$T_s - T_c$, °C
HDPE	0	112.6	151.0	5.6
EB_5	5	114.9	155.0 (143.4)	5.0
EB_{15}	15	113.5	146.0 (128.3)	5.4
EB_{25}	25	114.4	126.0 (113.2)	4.5
EB_{40}	40	114.8	88.5 (90.6)	3.8
EB_{60}	60	113.4	66.5 (60.4)	4.4
EPDM	100	30.7	28.4	9.1

Figures in parentheses indicate the calculated values of heats of crystallisation.

Further addition of rubber to PE resulted in a decrease in T_c but still the T_c values were higher than for HDPE. The observed increase in T_c of HDPE by EPDM addition may be due to an increase in the rate of nucleation [3]. The heat of crystallization showed a maximum at EB_5 followed by a decrease (Fig. 2). The heats of crystallization (ΔH_0) were also calculated by the rule of mixture on the basis of the weight fractions of HDPE in the binary EB blends. The observed values were higher than the calculated ΔH_0 values up to 25% (w/w) of rubber (EB_{25}).

The heating curves obtained in DSC scans were characterized (Fig. 3) and the results are summarised in Table 2. Addition of 5% (w/w) of rubber to HDPE resulted in an increase of ~2.7 deg in T_m. Further increase in rubber concentration from 15 to 60% (w/w) resulted in a decrease in T_m. However, the T_m values of all the EB blends were higher than that of HDPE. The heat of fusion decreased on addition of rubber to HDPE. However, in case of these blends the calculated heats of fusion assuming no contribution from rubber were found to be lower than the experimental ΔH_f values for samples EB_5, EB_{15} and EB_{25} as is obvious from Fig. 2. In samples EB_{40} and EB_{60}, on the other hand, the calculated values were higher than the observed values. The width at half height of the fusion peak increased marginally on addition of rubber up to 25% (w/w).

The percentage crystallinity of samples was also calculated by taking ΔH_f^0 of 290 J/g for 100% crystalline linear polyethylene [4, 5] and was found to be 53%. It decreased on addition of rubber. Here again up to 25% (w/w) of rubber, the calculated values of % crystallinity were lower than the experimental values. These results thus indicate that addition of EPDM up to 25% (w/w) causes an increased

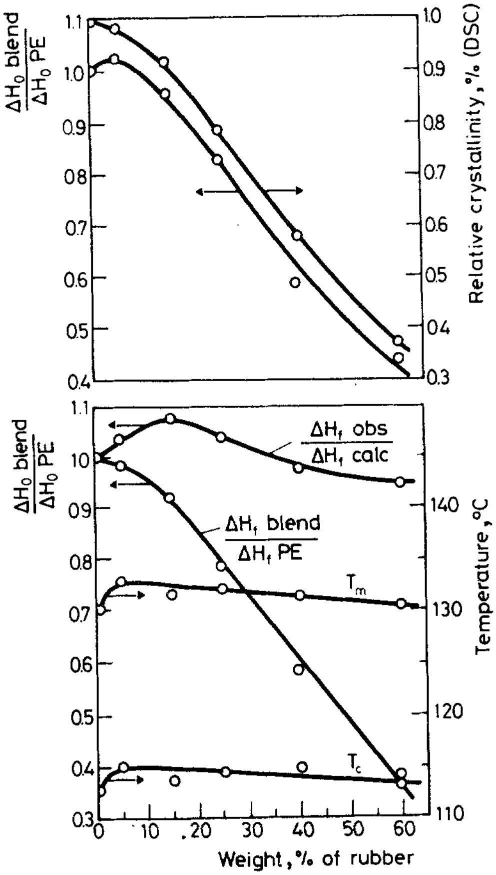

Fig. 2 Effect of rubber content on the phase transitions of HDPE

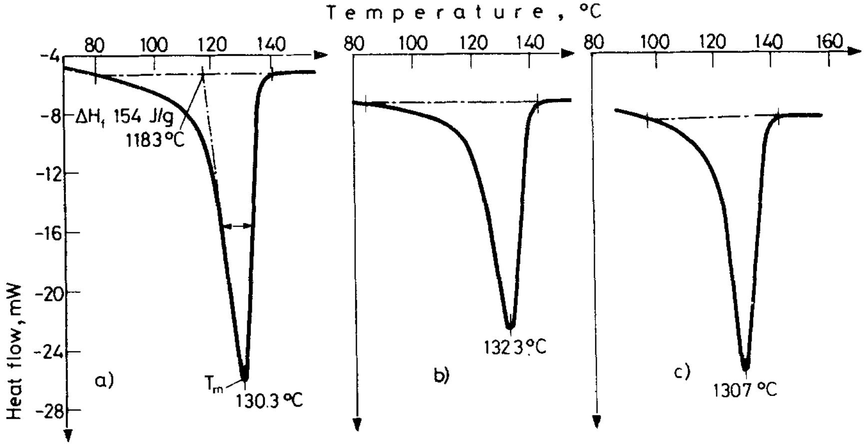

Fig. 3 Melting endotherms of (a) HDPE and binary blends, (b) EB_{25}, (c) EB_{60}

Table 2 Results of DSC scans of binary blends of HDPE/EPDM

Sample designation	T_m, °C	ΔH_f, J/g	Width at half height Arb. units	% crystallinity
HDPE	130.3	154.0	10.0	53
EB_5	133.0	152.0	11.5	52
		(146.3)		(50)
EB_{15}	131.7	142.0	12.5	49
		(130.9)		(45)
EB_{25}	132.3	121.0	11.5	42
		(115.5)		(40)
EB_{40}	131.6	90.7	10.0	31
		(92.4)		(32)
EB_{60}	130.7	58.8	10.0	20
		(61.6)		(21)
EPDM	45.6	23.7	—	—

Figures in parentheses indicate the calculated values of heats of fusion and % crystallinity.

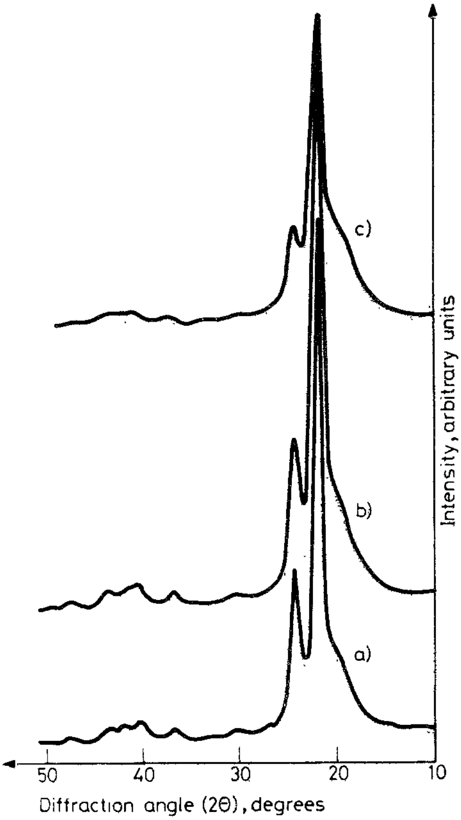

Fig. 4 I vs. 2θ plots of (a) HDPE and binary blends, (b) EB_{25}, (c) EB_{60}

nucleation and higher rate of crystallization of HDPE. The degree of crystallinity of HDPE was also determined from its density value (0.945 g/cm^3) at 25° using the specific volume relationship of Chiang and Flory [6] for amorphous and crystalline polyethylene and was found to be 67.4%.

X-ray diffraction studies

In I *vs.* 2θ plots for various blends and HDPE, prominent diffraction maxima were observed at 21.7° and 24.0° of 2θ (Fig. 4). The intensity of the peak at 21.7° of 2θ increased on increasing the rubber concentration up to 25% (w/w). Further addition of rubber resulted in a decrease in the intensities of the peaks at 21.7° and 24.0° of 2θ. The % apparent degree of crystallinity (X_c) was calculated according to Ruland's method [7, 8]. The degree of crystallinity thus evaluated is denoted as the apparent degree of crystallinity (X_c), which is emphasized for its comparative value alone.

The experimental I *vs.* 2θ curves were converted into IS^2 *vs.* S curves (Fig. 5). The results are summarized in Table 3. A slight increase in % crystallinity was observed

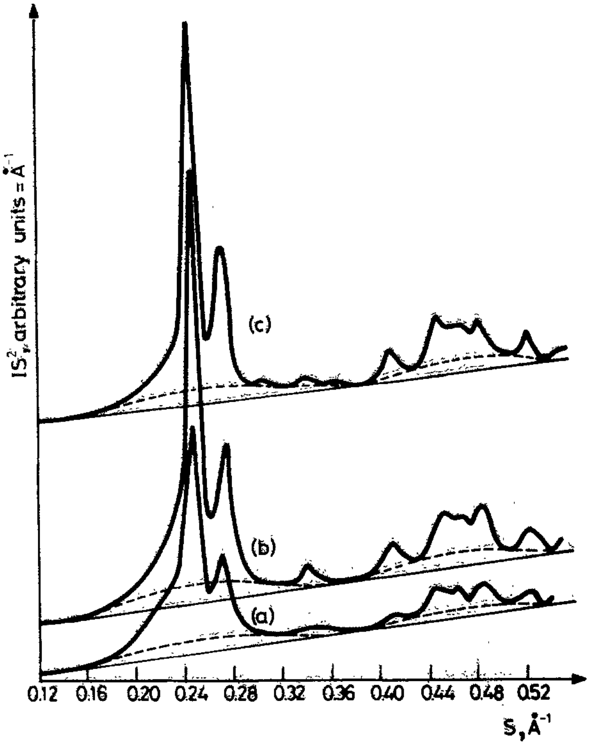

Fig. 5 IS^2 *vs.* S plots of (a) EB_{60}, (b) EB_{25} and (c) HDPE

by addition of rubber to HDPE up to 25% (w/w). Further increase in rubber content resulted in a decrease in overall crystallinity. The values of % X_c as calculated from the rule of mixture were found to be lower than the experimental values at all weight fractions of rubber (Table 3).

Table 3 Results of wide angle X-ray diffraction studies of various HDPE/EPDM blends

S. No.	Wt. % of EPDM in blend	% Apparent crystallinity	
		observed	calculated
1	0	72.8	—
2	5	73.8	70.0
3	10	73.8	67.2
4	15	74.5	64.4
5	20	73.5	61.5
6	25	75.7	58.8
7	30	70.4	55.9
8	40	72.5	50.3
9	50	68.5	44.7
10	60	69.5	39.1
11	100	16.6	—

Mechanical properties

The tensile and impact properties of HDPE and binary EB blends are reported in Table 4. Addition of rubber to HDPE up to 10% (w/w) resulted in an increase in Young's modulus. About 46 and 11% improvement in the Young's modulus was obtained upon addition of 5 and 10% (w/w) of rubber (Table 4). Blend EB_5 exhibited the maximum tensile strength at yield. Further addition of rubber to

Table 4 Mechanical properties of various HDPE/EPDM blends

Wt. % of EPDM in blends	Young's modulus, kg/cm^2	Tensile yield strength, kg/cm^2	% elongation at break	Impact strength, J/m
0	3100	126.8	722	84.4
5	4550	154.4	> 1057	97.3
10	3450	145.7	915	131.8
15	3050	130.6	870	202.0
20	2650	116.8	803	257.3
25	2150	104.8	800	—
30	1400	85.9	819	—
40	800	69.9	785	—
50	550	51.6	916	—
60	250	43.7	884	—

HDPE resulted in a decrease in the tensile strength (Fig. 6). About 22 and 15% increase in tensile yield strength was observed by addition of 5 and 10% (w/w) of rubber to HDPE, respectively. However no systematic trend in the % elongation at break was observed. About threefold improvement in impact strength was observed on addition of 20% (w/w) of rubber to HDPE (Fig. 6). Addition of more than 20% (w/w) of rubber resulted in samples which did not show a complete break upon izod impact testing.

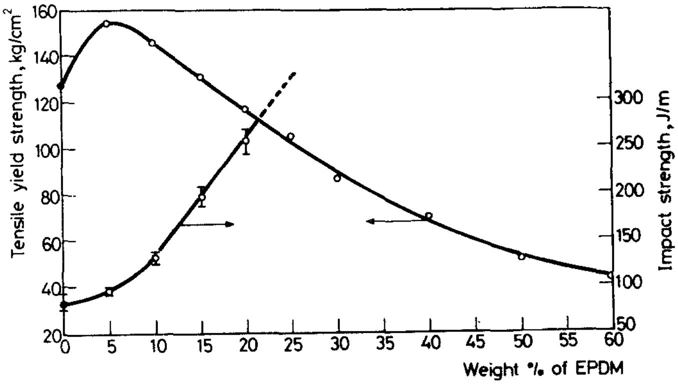

Fig. 6 Effect of EPDM concentration on the mechanical properties of HDPE

These results thus indicate that the rate of crystallization and nucleation of HDPE was influenced by the addition of EPDM.

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Zusammenfassung — Mittels Differential-Scanning-Kalorimetrie (DSC) und Weitwinkelröntgendiffraktion (WAXS) wurde das Kristallisationsverhalten von binären Gemischen aus hochverdichtetem Polyäthylen (HDPE) und Äthylen-Propylen-Dien Trikopolymer (EPDM) untersucht. Die Geschwindigkeit von Kristallisation und Keimbildung von HDPE wird durch Zusatz von EPDM beeinfluß. Die prozentuelle Kristallinität wuchs bis zu einer Zugabe von 25 Gewichtsprozenten EPDM zu HDPE an. Bei Zusatz von EPDM zu HDPE konnte eine eindeutige Verbesserung der Zug- und Stoßfestigkeitseigenschaften festgestellt werden.

Резюме — Методом ДСК и широкоуглового рассеяния рентгеновских лучей изучена кристаллизация двойных смесей полиэтилена высокой плотности (ПЭВП) и этилен-пропилен-диен тройного сополимера (ЭПДМ). Скорость кристаллизации и образование центров кристаллизации ПЭВП затрагивалась прибавлением к нему ЭПДМ. Процент кристалличности смеси увеличивался при добавлении ЭПДМ в количествах до 25 вес.%. Прибавление ЭПДМ к ПЭВП приводило к улучшению противоударных и противорастягивающих свойств полиэтилена.