Blends of High-Density Polyethylene with Solid Silicone Additive

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ABSTRACT: Silicone masterbatch (SMB) is a pelletized formulation containing 50% of an ultrahigh molecular-weight polydimethylsiloxane dispersed in polyethylene. This SMB is designed to be used as an additive in polyethylene-compatible systems to impart benefits such as processing improvement and modification of surface characteristics. In this work, binary blends of high-density polyethylene (HDPE) and SMB were prepared by melt-mixing technique to study the influence of this masterbatch on the processing and mechanical properties of HDPE. Ternary blends were also prepared by the addition of silane-grafted polyethylene (HDPE-VTES) as compatibilizer. The blends were analyzed by melting flow rate (MFR), differential scanning calorimetry (DSC), scanning electron microscopy (SEM), and tensile tests. Data of final torque and MFR showed that SMB improved the processability of pure HDPE. DSC results showed differences in crystalline behavior between binary and ternary blends. In the former, the degree of crystallinity increased up to 10 wt % of SMB content; beyond this concentration, it decreased. In ternary blends, a reverse behavior was observed. The morphologic study showed silicone particles uniformly distributed in HDPE matrix. With high SMB concentration, the addition of HDPE-VTES significantly reduced the size of silicone particles. In the range of SMB composition studied, the mechanical properties of blends lower slightly compared to pure HDPE. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 2347–2354, 2002

Key words: high-density polyethylene; polydimethylsiloxane; blends; compatibilizer; silicones; vinyltriethoxysilane; thermal properties; scanning microscopy; tensile properties; crystallinity

INTRODUCTION

In the last two decades, the study of the technique of blending of two or more polymers to produce a balanced combination of properties for specific end-use requirements has been a very active area in the field of polymer processing. Polymer blends can be prepared by a variety of techniques, which include solution, latex, mechanical, and mechano-chemical blending.[1] From these techniques, the melt mixing is the most widely used. Although blending looks very attractive, most of the polymer blends are immiscible and incompatible. Reasons for incompatibility are high interfacial tension and poor interface adhesion.[2] However, the phenomenon of compatibility can be induced into

an immiscible binary system by introducing a third component that will either interact chemically with both phases or will have specific interaction with one phase and physical interaction with the other. The addition of a block or graft copolymer reduces the interfacial tension between the two phases, increases the surface area of the dispersed phase, promotes adhesion between the phase components, and stabilizes the dispersed phase morphology.[2]

Polyethylene is one of the most important thermoplastic in terms of commercial production and technological application. It has excellent electrical and mechanical properties, good resistance to cold flow, ease of processing, and notably excellent cost-performance relation.[3] These characteristics of polyethylene have generated great interest in the development of blends with other polymeric materials, to improve some specific property or to enlarge its temperature range of use. In this way, blends of polyethylene with polyorganosiloxanes (or silicones) are of particular interest.

Among poly(organosiloxanes), polydimethylsiloxane (PDMS) is the most widely used in a variety of industrial areas because of its well-known surface-modifying properties.[4] Its structure is composed of highly flexible —Si—O— bonds in the main chain with methyl groups attached to a silicon atom[4]; thus, their physical and chemical properties combine both inorganic and organic characteristics. The surface properties of PDMS are very attractive for modification of other surfaces and interfaces. However, its low solubility parameter makes it highly immiscible with a variety of organic polymers. This immiscibility leads to PDMS rejection from the matrix, causing fast deterioration of blend properties because of phase separation, diffusion of the polymer chains, and so forth. Kole et al.[5] showed that the incompatible nature of 50/50 silicone–ethylene propylene diene monomer rubber (EPDM) blends was overcome by the introduction of silane-grafted ethylene–propylene copolymer (EPR), which interacts with both components. The modification of the blend components [acrylamide grafted silicone (AM-*g*-Si) and sulfonated EPDM (S-EPDM)] was used to induce dipole–dipole interactions.[6] The influence of the chemical interaction in the 50/50 blends of AM-*g*-Si with EPDM modified by maleic anhydride, MA-*g*-EP, on the physicomechanical properties was also reported.[5]

Although polyethylene/PDMS blends can lead to advantages in the processing and improve-ments in the surface property, with low adverse effect on tensile polyethylene properties,[8] few studies related to polyethylene/PDMS blends have been published.[7–10]

Falender et al.[9] studied blends of polydimethylsiloxane–polyethylene copolymers with polyethylene resin containing vinyl acetate comonomer, under shearing and high temperature conditions. When compared to pure polyethylene, these blends showed lower modulus over −150 to +65°C and lower mixing energies. The electrical properties showed superior or intermediate values in comparison to values observed in the pure components. Santra et al.[10] demonstrated that blends of ethylene–methylacrylate (EMA) copolymer and PDMS rubber are miscible throughout the composition range via chemical reaction between α–H of the ester group of the EMA copolymer and the vinyl group of the PDMS rubber. Santra et al.[11] studied the effect of the EMA copolymer as a chemical compatibilizer in a 50/50 blend of low-density polyethylene (LDPE) and PDMS rubber. Studies,[12] developed in blends of EMA copolymer and PDMS by rheological measurements, at various temperatures and different shear rates, showed that melt viscosities of the blends were higher than that calculated by the additivity rule. The positive deviation suggested the presence of synergism in the blends.

New additives for thermoplastics, silicone masterbatch (MB50), was commercialized by Dow Chemical Co.[13] These additives are formulated as pellets or powder containing 50% of an ultrahigh molecular weight PDMS, dispersed in the thermoplastic polymer, which allow faster mixing and eliminate the problem of the incorporation of liquid silicones into thermoplastic melts. According to the manufacturer, MB50-002 (Silicone masterbatch containing 50% of ultrahigh molecular-weight PDMS dispersed in LDPE) can be added to high-density polyethylene (HDPE) to improve flow and mold filling, reduce cycle times, lower extruder torque, and improve surface properties.[13]

In the present study, blends of HDPE and silicone masterbatch (MB50-002) were prepared by melt mixing to analyze the influence of the silicone masterbatch on the processing and the mechanical properties of HDPE. The influence of the silane-grafted polyethylene compatibilizer on the morphology and properties of the blends was also analyzed.

EXPERIMENTAL

Materials

HDPE, with and without additives, with densities of 0.955 and 0.951 g/cm^3, respectively, was supplied by Ipiranga Petroquímica S.A. (Brazil). MB50-002 silicone masterbatch [silicone masterbatch containing 50% of ultrahigh molecular weight PDMS dispersed in low-density polyethylene (LDPE), henceforth simply referred to as SMB] was obtained from Dow Corning Co. Vinyltriethoxysilane (VTES) (silan GF56-Wacker-Chemie, Germany), dicumyl peroxide (DCP) 98% (Aldrich Chemical Co.), tetrahydrofuran (THF) (Merck Chemical Co., Germany), and commercial argon were used directly.

Functionalization of HDPE

Silane-grafted polyethylene (HDPE-VTES) was prepared by melt mixing using HDPE (45 g), without additives, VTES (5 wt %), and DCP (0.5 wt %). The functionalization reaction was carried out in a Haake Rheomix 600 internal mixer at 180°C and rotor speed of 60 rpm for 10 min. The modified material was removed from the mixer and cut into small pieces, and the unreacted monomer was removed under reduced pressure in a vacuum oven for 48 h.

Preparation of the Blends

Mixtures of HDPE (with additives), HDPE-VTES, and SMB polymers (all predried overnight) in different compositions defined in Table I, were melt mixed at 180°C in a Haake Rheomix internal mixer 600 with a rotor speed of 60 rpm for 10 min. After removing the blends from the mixer chamber, they were immediately pressed at 180°C for 20 s to obtain thin sheets and, finally, cut into small pieces for tests.

Analyses

The HDPE-VTES was characterized by infrared spectra in a BOMEN BM-102 FTIR spectrometer by using thin films (50–100 μm) molded at 180°C, 5 ton/cm^2 for 2 min. The stretching Si—O absorption, from Si—OCH$_2$CH$_3$, at 1080 and 1108 cm^{-1},[14] was used to confirm the VTES grafting in the HDPE chain.

The melt flow rates (MFR) of pure HDPE, HDPE/SMB, and HDPE/HDPE–VTES/SMB blends were measured by using a plastometer, under a load of 5.0 kg at 190°C (ASTM D1238).

Table I Total Results of Pure Components and Blends

Sample Code	SMB (wt %)	HDPE-VTES (wt %)	Final Torque (Nm)	MFR (g/10 min)	T_m (°C)	ΔH_f^a (Cal/g)	T_c (°C)	Crystallinity (%)	Young's Modulus (MPa)	Yield Stress (MPa)	Elongation at Yield (%)
HDPE	—	—	10.5	2.0	134	42.8	117	66.3	908	24.5	9.1
HDPE-VTES	—	100	17.4	—	130	40.2	115	62.3	—	—	—
SMB	100	—	—	—	−42/113	2.3/11.5	−77/101	3.5/17.8	—	—	—
B$_2$	2	—	10.2	2.2	134	42.7	115	66.2	892	25.0	9.1
B$_5$	5	—	9.0	2.3	134	44.8	117	69.5	901	25.0	8.0
B$_{10}$	10	—	8.7	2.4	−38/134	45.3	116	70.2	778	22.1	8.4
B$_{20}$	20	—	7.4	3.6	−39/133	35.8	118	55.5	690	19.1	8.4
B$_{2C}$	2	5	11.1	1.1	134	43.7	118	67.7	766	24.1	10.0
B$_{5C}$	5	5	10.2	1.8	135	40.2	115	62.3	728	22.8	9.7
B$_{10C}$	10	5	9.2	1.8	−38/133	36.6	118	56.7	679	21.4	9.9
B$_{20C}$	20	5	8.0	2.6	−39/133	44.5	118	68.9	627	18.8	10.0

^{a} ΔH_f, heat of fusion.

Differential scanning calorimetry (DSC) was used to analyze the melting and crystallization behavior of pure components and the HDPE/SMB, HDPE/HDPE–VTES/SMB blends. DSC-PL-POLYMER LAB and normal calibration procedures involving standard materials were used. DSC measurements were performed on 5- to 10-mg samples, at a heating or cooling rate of 10°C/min under nitrogen. Before any measurement, each sample was heated up to 200°C and maintained at this temperature for 5 min to erase its thermal history. The degree of crystallinity of the blends was evaluated by the ratio between the enthalpy of fusion of the blend and the enthalpy of fusion of the perfectly crystalline HDPE ($\Delta H_f^0 = 64.5$ cal/g).[15]

The morphology of pure HDPE, HDPE/SMB, and HDPE/HDPE–VTES/SMB blends was studied by using a scanning electron microscope (SEM, JEOL JSM 5800) after sputter coating the samples with gold. The surface analysis was carried out by using cryogenically fractured samples. To facilitate identification of the phases and morphological features, the silicone phase was extracted by using THF.

The tensile properties of pure HDPE, HDPE/SMB, and HDPE/HDPE–VTES/SMB blends were measured at room temperature [25°C and relative humidity (RH) 55%] on an ISTRON Tester Model 4200, according to ASTM D882, at a crosshead speed of 50 mm/min.

RESULTS AND DISCUSSION

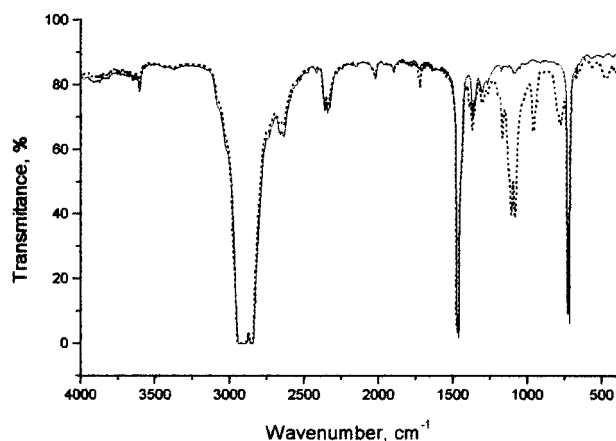Figure 1 shows spectra of pure HDPE before and after the functionalization reaction with VTES
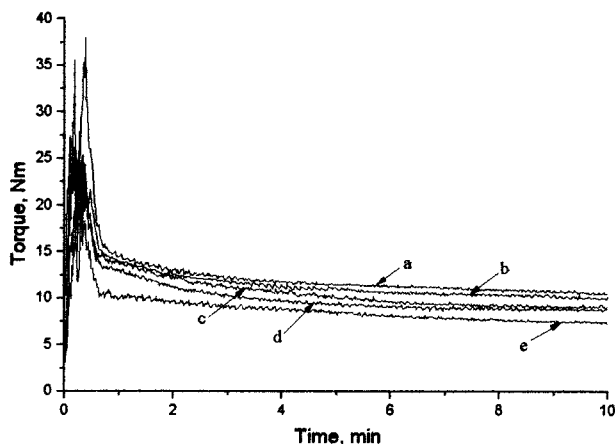

Figure 2   Torque–time curves for pure HDPE (a) and HDPE/SMB blends: 98/2 (b), 95/5 (c), 90/10 (d), 80/20 (e).

and the DCP as initiator. The grafted product was characterized by the presence of the peaks at 1080 and 1108 cm^{-1} in the FTIR spectrum, which correspond to the ν Si—O of the Si—OCH$_2$CH$_3$, from VTES.[14]

The blends were designated B_2, B_5, B_{10}, and B_{20}, where the subscripts indicate the proportion of SMB in the blends. When the blends were prepared with 5 wt % HDPE-VTES, the subscript C was added. Then, for example, B_{5C} indicates a blend with a HDPE/HDPE–VTES/SMB weight composition of 90/5/5.

Figure 2 shows the torque–time curves of pure HDPE and blends B_2, B_5, B_{10}, and B_{20}. This figure shows that the final torque decreased with the increase in the SMB amount in the blends. This figure also shows that after about 4 min all samples reached a nearly constant torque plateau. The torque value in the plateau region was directly related to the blend viscosity. Furthermore, the presence of this plateau indicates that there was no degradation process taking place on the system. Table I shows the final torque values of pure HDPE and blends.

The final torque values increased with the HDPE-VTES addition on the blends. This behavior may be due to some compatibilization effects promoted by HDPE-VTES polymer.[16] MFR values increased with the increase in the SMB content. This result agreed with the final torque values discussed above and indicates that SMB acted as processing aids for HDPE.

DSC studies were carried out to analyze the melting and crystallization behavior of pure polymers and blends in the −150–200°C temperature range. Melting and crystallization temperatures,

Figure 1   Infrared spectra of pure HDPE (—) and HDPE-VTES (· · ·).

melting enthalpy, and degree of crystallinity values for all polymers and blends are reported in Table I. Figure 3 shows the thermograms of these polymers.

DSC thermogram of HDPE-VTES [Fig. (3c)] showed a decrease in the melting temperature of HDPE-VTES with respect to pure HDPE. This decrease was probably due to the silane grafts, which reduced the structural regularity of HDPE.[17] SMB sample [Fig. (3b)] showed crystallization peaks at −42 and 113°C, characteristic of the PDMS and LDPE chains, respectively. The three DSC thermograms showed an inflexion between −110 and −120°C, which was assigned to the glass transitions of HDPE and PDMS chains.

Figure 4 shows DSC thermograms for pure HDPE and B_{20} and B_{20C} blends. There was practically no change in the melting and crystallization temperatures of HDPE matrix when the SMB and HDPE-VTES were added. On the other hand, significant changes were observed in the degree of crystallinity of blends. Blends of HDPE/SMB showed an increase in the degree of crystallinity with the SMB content, up to 10%. Beyond to this concentration, the degree of crystallinity decreased. This behavior can be attributed to the nucleation effect that SMB domain imparts to the system.[1] Above 10 wt % of SMB, because of coalescence phenomenon, SMB domains are too large [Fig. (5e)] to act as nucleation centers.

A different behavior was observed when HDPE-VTES was added to the blends. Initially, the degree of crystallinity of HDPE/HDPE–VTES/SMB blends decreased with the SMB content up to 10 wt % and then, an increase in the crystal-
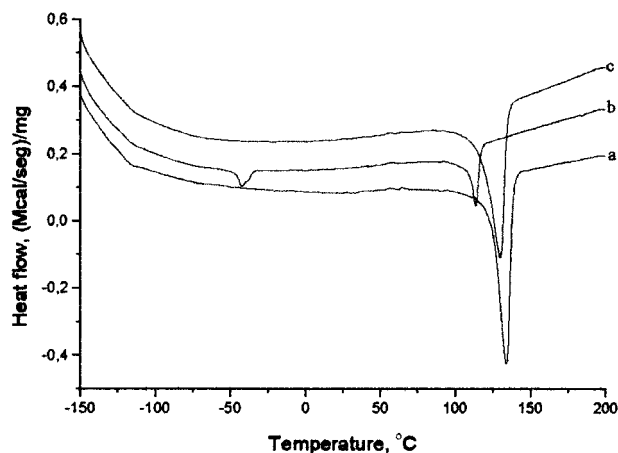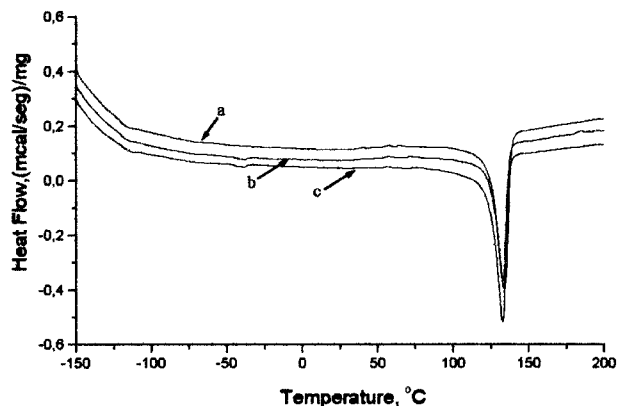

Figure 4 DSC thermograms of pure HDPE (a) and blends: HDPE/SMB 80/20 (b), HDPE/HDPE–VTES/SMB 75/5/20 (c).

linity was observed. This behavior can indicate that at low SMB concentrations the dispersion effect of HDPE-VTES is significant, giving rise to a better dispersion of SMB phase in the HDPE matrix and lowering the degree of crystallinity. At highest SMB concentrations, the presence of HDPE-VTES prevents coalescence phenomenon in SMB phase, lowering significantly the SMB domain sizes, promoting a nucleation effect, and increasing the degree of crystallinity.

In the SEMs of the surface fracture of pure HDPE and blends (Fig. 5), the holes indicate that the silicone phase was extracted. In the blends, SMB phase remained as dispersed particles in the continuous HDPE matrix. The domain size of the disperse phase increased with the increase in the SMB amount, because of the coalescence of the disperse particles. The action of compatibilization agent is clearly seen in the blend with 20 wt % of SMB, B_{20C}. In this blend, the domain sizes are considerably lower because of the presence of HDPE-VTES [Fig. 5(i)].

The tensile properties of the HDPE/SMB and HDPE/HDPE–VTES/SMB blends are reported in Table I and illustrated in Figure 6 as a function of SMB content.

The effect of the SMB addition on tensile properties of HDPE matrix is relatively small in the range of SMB contents studied. Furthermore, the modulus and yield stress of HDPE/SMB blends are nearly constant up to 5% of SMB [Figs. (6a,b)] and lightly decrease above this concentration. For HDPE/HDPE–VTES/SMB blends, the small decrease in modulus and yield stress started at lower SMB concentration. This difference in tensile response of binary and ternary systems is in
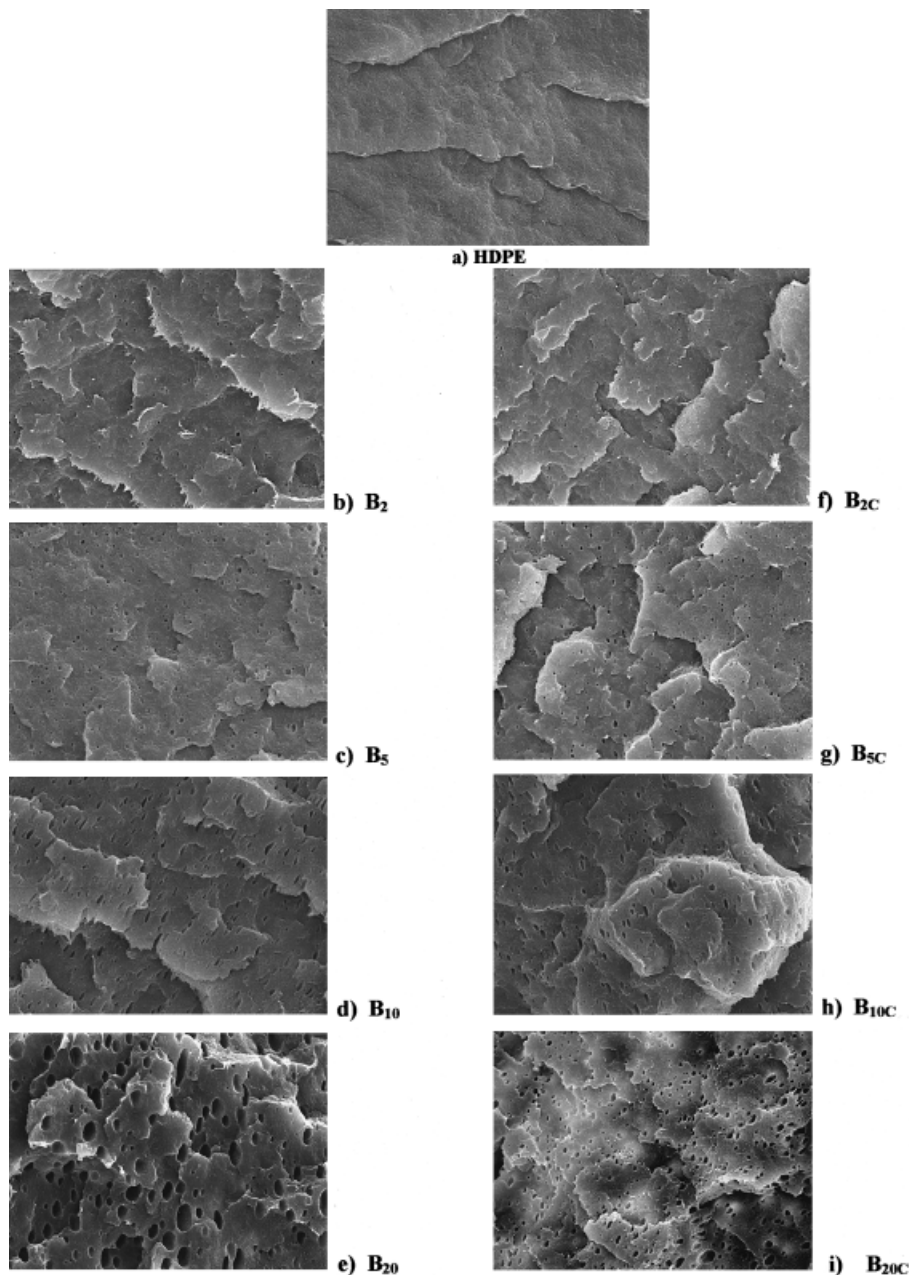

Figure 3 DSC thermograms of pure HDPE (a), SMB (b), and HDPE-VTES (c).

Figure 5 Photomicrographs of pure HDPE and blends.

accordance with crystallinity data shown in Figure 7. An initial decrease of the degree of crystallinity in ternary blends was observed at low SMB contents. At higher SMB contents, the degree of crystallinity of these blends increased, suggesting an effective interaction of HDPE-VTES with the phases, which leads to a decrease in SMB particle size and higher nucleation effect. The decrease of the modulus and yield stress with an increase of SMB contents, in the range of 5–20 wt %, is more pronounced in binary blends because of higher

incompatibility of components and also because of the increase of SMB domain sizes. These results are in accordance with crystallinity data and micrographs. The presence of HDPE-VTES lead to a lower decrease in modulus and yield stress in ternary blends than binary blends.

CONCLUSION

Functionalization of HDPE with VTES was confirmed by FTIR analysis. Data of final torque and
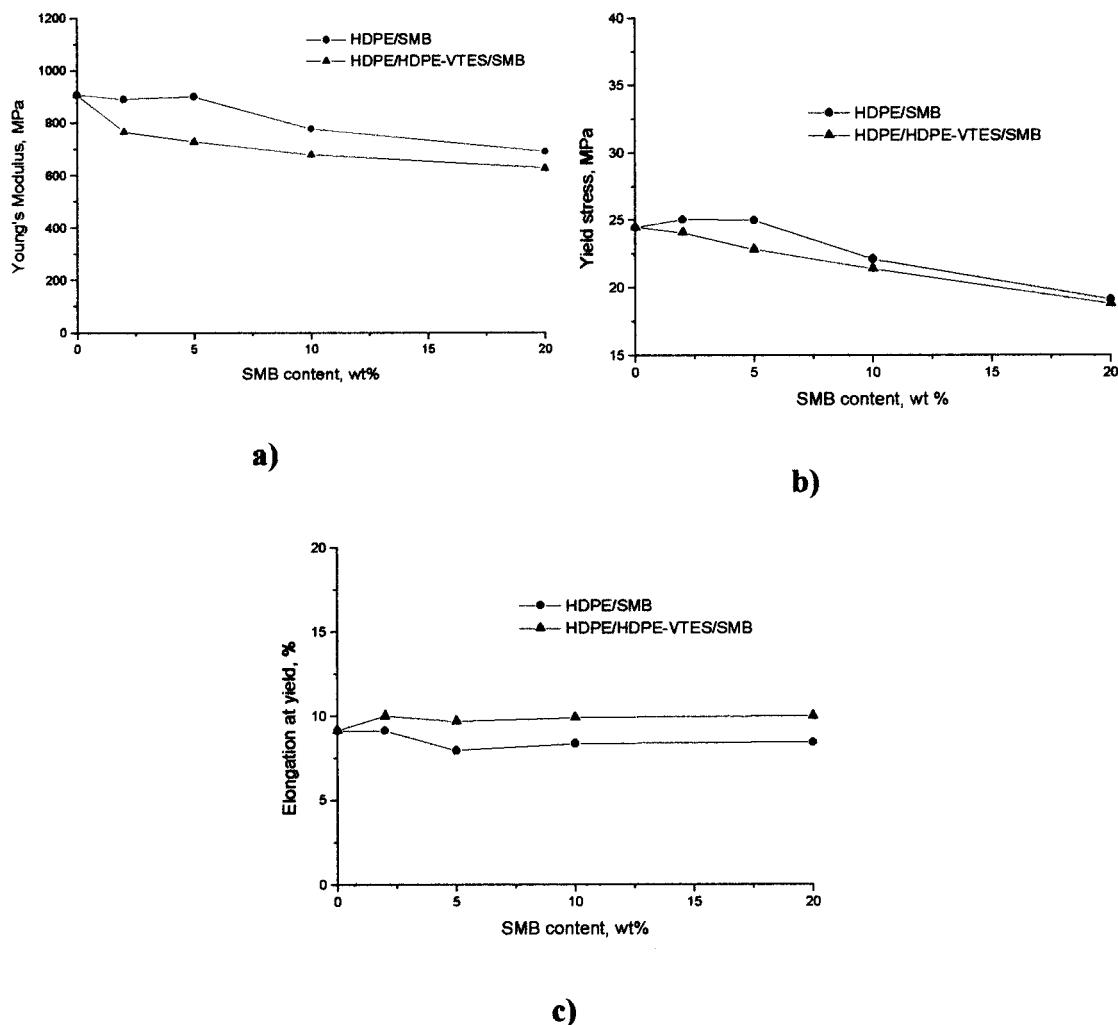
Figure 6 Tensile properties of blends: Young's modulus (a), yield stress (b), and elongation at yield (c) as function of SMB content.

MFR of blends indicated that SMB acts as processing aids to HDPE.

DSC study showed no significant change in the melting and crystallization temperatures of HDPE matrix when the SMB and HDPE-VTES were added to blends. On the other hand, a different crystalline behavior of the blends was observed. In binary blends, the degree of crystallinity increased with the SMB contents up to 10%; beyond this concentration, the degree crystallinity decreased. In ternary blends, a reversal behavior was also observed. The former behavior resulted in SMB nucleation effect in the binary blends, and the later behavior could be explained by the compatibilization effect inferred by HDPE-VTES as the third component of the blends.

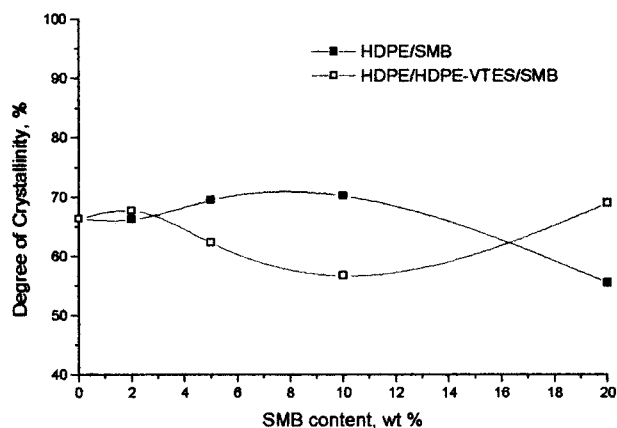The incompatible nature of pure HDPE and SMB defined the blend morphologies. SMB was

Figure 7 Degree of crystallinity of binary and ternary blends as function of SMB content.

found as disperse domains in the HDPE matrix. The SMB domain size was significantly lower in the presence of HDPE-VTES at higher SMB amounts.

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