

Compatibilization of Poly(ethylene-*co*-vinyl alcohol) (EVOH) and EVOH–HDPE Blends: Structure and Properties

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ABSTRACT: Hydrogenated and maleated S-B-S block copolymer (SEBS-*g*-MA) was applied as a compatibilizer in melt-mixed binary blends with poly(ethylene-*co*-vinyl alcohol) (EVOH) and in ternaries containing high-density polyethylene (HDPE) as the major component. The techniques applied were dynamic, mechanical, and tensile testing; differential thermal analysis; Fourier transform infrared spectroscopy; and optical and electron microscopy (SEM). Small and large deformation behavior under dynamic and static mode, coupled with other physical characterization data, as well as morphological evidence, demonstrated that SEBS-*g*-MA is an efficient compatibilizer in the binary and ternary blends. In the latter, its function is the coupling of EVOH with the HDPE matrix, thus reducing the moisture sensitivity of the former and the improvement of performance-to-cost ratio of the final product. After leaching out EVOH from the ternaries, morphology examination of the cross section of films, showed a laminar EVOH phase distribution, a feature desirable in barrier materials applications. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 589–596, 1998

Key words: EVOH–polyolefin blends; polyolefin blends; compatibilization of polymer alloys

INTRODUCTION

Poly(ethylene-*co*-vinyl alcohol) (EVOH) has been applied extensively in the packaging industry due to its good processability and gas barrier properties.^{1,2} To minimize moisture absorption, it is usually combined with polyolefins (PO) in the form of coextruded films, at the same time improving the property-to-cost ratio. To attain a satisfactory level of mechanical integrity, these structured polymer alloys should provide for a satisfactory level of adhesion between the main components if a suitable compatibilizer is used. However, the degree of compatibilization and processing conditions should be controlled so that dispersive mixing is avoided and EVOH retains its laminar distribution, hence, its low permeability function, in the film.

In the recent past, several articles dealt with EVOH blends either as stratified alloys or as compatibilized binaries. In the former class belongs the work of Gohil, Schultz, and coworkers,³ who studied the rheology and transport properties of EVOH–poly(ethylene terephthalate) (PET) blends with and without a compatibilizer; the latter was a maleic anhydride modified hydrogenated S-B-S block copolymer (SEBS-*g*-MA). The same group reported⁴ also on the morphology and barrier properties of EVOH in blends with PET and with poly(ethylene 2,6-naphthalate).

The phase morphology, as determined by processing conditions, was reported by Kamal and coworkers^{5,6} on EVOH–PP blends with or without the use of PP-*g*-MA as a compatibilizer.

Nonstratified blends of EVOH with varying ethylene contents, in combination with various aliphatic nylons, were characterized by Ahn et al.⁷ and Akiba and Akiyama,⁸ who investigated the miscibility behavior of EVOH–nylon 6–12 blends. Solution-mixed blends of EVOH–nylon

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4–6 were characterized using mainly spectroscopic techniques by Ha et al.⁹

Prasad and Jackson¹⁰ examined the compatibilization of EVOH–HDPE using PE-*g*-MA as a compatibilizer.

In a previous report,¹¹ we examined the compatibilization of EVOH–HDPE using the Zn²⁺ ionomer of ethylene–methacrylic acid–isobutyl acrylate terpolymer. It was expected that because of its polyolefinic nature, the ionomer would be compatible with HDPE while the Zn²⁺ would interact by complexation with the OH groups of EVOH in analogy with the HDPE–ionomer–poly(vinyl alcohol) system studied before.¹²

In the present work, the compatibilizer used in the EVOH–HDPE blend is the SEBS-*g*-MA. SEBS is known to give good mechanical properties with HDPE.¹³ In addition, the MA group during melt mixing is expected to react with the OH groups of EVOH so as to attach it into the PO matrix. In the major part of this report, the compatibility behavior of the EVOH–SEBS-*g*-MA binary is investigated using mechanical, thermal, spectroscopic, and morphology techniques since it determines, to a large extent, the properties of the ternary EVOH–SEBS-*g*-MA–HDPE alloy.

EXPERIMENTAL

Materials and Preparations

EVOH from Kuraray Co. Ltd. (Osaka, Japan) had a 32 mol % ethylene content, a melt flow index (MFI) of 1.3 g/10 min (190°C, 2160 g) and density 1.19 g cm⁻³. HDPE (Finathene 58070), a blow-molding grade, was obtained from Petrofina S.A. (Feluy, Belgium; MFI = 10 g/10 min; *d* = 0.955 g cm⁻³). SEBS (Kraton G 1652) was obtained from Shell Chemical Co. (Houston, TX). It contained 29 wt % styrene, and the MW of the styrene block was 7000, and that of ethylene butylene block 37,500. SEBS-*g*-MA (Kraton FG-1901X) was a Shell Chemical Co product with the same styrene content and a MA content of 1.84 wt %.¹⁴

Materials were dried in dynamic *vacuo* at 60°C for 24 h. Blends were prepared by melt mixing in a homemade stainless steel bob-and-cup type of mixer previously described.¹¹ Based on tensile property optimization, the mixing time employed was 15 min at 240°C for both binary and ternary blends.

EVOH–SEBS-*g*-MA compositions prepared and characterized were 90/10, 75/25, 50/50, 25/75, and 10/90. Films were obtained by compres-

sion molding between Teflon sheets at 210°C and 10 MPa, followed by quenching to 0°C. To examine the effect of humidity on properties, tests were made on dry films and on specimens conditioned for 1 week at ambient conditions (approximately 60% RH).

To leach out EVOH for morphology studies, specimens were treated at room temperature with 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) for 1 h. To obtain the interphasial material, boiling toluene was used (2 h) to remove unreacted SEBS-*g*-MA, followed by overnight treatment with HFIP to remove excess EVOH.

Apparatus and Procedures

Tensile tests were performed at a crosshead speed of 10 cm min⁻¹ and at 23°C according to ASTM D882 using a J.J. Tensile Tester type 5001 and rectangular strips measuring 6.0 × 0.65 × 0.25 cm³.

Dynamic mechanical analysis (DMA) data storage modulus *E'*, loss modulus *E''*, and loss angle tan δ were obtained at 10 Hz with the RSA II mechanical spectrometer of Rheometric Scientific Ltd. Specimen dimensions were 2.3 × 0.5 × 0.015 cm³.

Differential scanning calorimetry (DSC) measurements were carried out using the DSC (SP) equipped with the AutoCool accessory from Rheometric Scientific Ltd. Nominal weight was 10 mg, and the heating/cooling rate was 10°C min⁻¹. The thermal cycling applied was 25°C quench → -50°C → 200°C quench → -50°C → 200°C.

Fourier transform infrared (FTIR) spectra were obtained using a Perkin–Elmer 1600 spectrometer.

Optical micrographs with phase contrast and crossed polars arrangement were obtained with a Olympus BH-2 microscope.

Scanning electron microscopy (SEM) was carried out on a JEOL model JSM-500 instrument. Cryofractured or etched surfaces were examined at a tilt angle of 30°.

RESULTS AND DISCUSSION

Binary EVOH–SEBS-*g*-MA Blends

Tensile Properties

The results are summarized in terms of the ultimate properties, strength σ_b , elongation at break ϵ_b , and energy to tensile failure E_b in Table I. The effect of moisture plasticizing EVOH is noticeable

Table I Ultimate Tensile Properties of Binary Blends

EVOH-SEBS- <i>g</i> -MA	Dry Films			Films with Moisture		
	σ_b (MPa)	ϵ_b (%)	E_b (J/cm ³)	σ_b (MPa)	ϵ_b (%)	E_b (J/cm ³)
100/0	75 ± 1	21 ± 2	11 ± 2	38 ± 2	217 ± 81	77 ± 4
90/10	49 ± 9	23 ± 3	4 ± 2	34 ± 4	38 ± 9	13 ± 1
90/10 ^a	—	—	—	36 ± 10	24 ± 11	7 ± 3
75/25	31 ± 3	31 ± 6	6 ± 2	30 ± 6	61 ± 17	19 ± 4
50/50	30 ± 3	355 ± 91	95 ± 28	28 ± 2	328 ± 21	68 ± 9
50/50 ^b	18 ± 3	36 ± 16	3 ± 1	—	—	—
25/75	17 ± 1	521 ± 58	58 ± 6	14 ± 1	471 ± 40	36 ± 2
10/90	24 ± 3	947 ± 143	98 ± 13	15 ± 2	1041 ± 58	95 ± 2
0/100	23 ± 2	1068 ± 38	90 ± 1	26 ± 2	1042 ± 19	80 ± 4

Blends were quenched at 0°C.

^a Mixing time = 10 min.

^b EVOH-SEBS blend.

only in the rich compositions for this component. The data indicate that SEBS-*g*-MA at contents higher than approximately 20 wt %, moisture proofs and flexibilizes EVOH because of its olefinic and elastomeric nature. Also addition of up to 50 wt % does not impair strength of EVOH for films equilibrated at ambient conditions. Table I shows that E_b , often related to impact strength, improves significantly with SEBS-*g*-MA. Of interest is the mechanical behavior of EVOH-SEBS blend at the 50/50 composition. Its poor mechanical performance, especially ϵ_b , underlines the decisive role of MA group in affecting compatibilization of the binary alloy.

Dynamic Mechanical Properties

DMA data, in terms of the temperature dependence of the loss and storage modulus E'' and E' , respectively, at isochronous conditions are given in Figures 1 and 2 and Table II. Main component relaxations at 54°C for EVOH and -49°C for SEBS-*g*-MA persist at all compositions, though shifting to lower temperatures, particularly for EVOH. A secondary relaxation of EVOH attributed to pendant groups of the polyolefin segments is also detected at approximately -12°C. Moisture absorption due to condensation during testing may shift $T_{g,EVOH}$ to lower temperatures. This is of little consequence to the present study in which a relative change with composition is of interest. The drift of $T_{g,EVOH}$ with composition may be attributed to interfacial mixing and has been observed after reactive blending of hydroxyl-terminated poly-(ethylene terephthalate) with SEBS-*g*-MA.¹⁵

Of interest is the significant increase of the $T_{g,EVOH}$ at the 90/10 composition. This causes an increase of modulus E' (stiffness) over that of pure EVOH at ambient temperature (see Fig. 2), and is caused by a chemical and/or physical interaction of MA with the hydroxyl groups (see last section). This effect is further enhanced in the presence of moisture and was observed¹¹ for the EVOH-ionomer blend at this composition. Further addition of SEBS-*g*-MA leads to a $T_{g,EVOH}$ shift to lower temperatures because of the attachment in increasing amounts of the flexible component into EVOH.

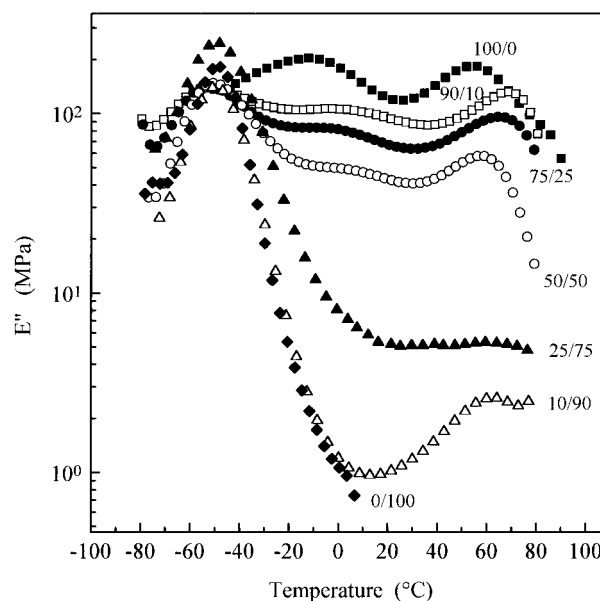


Figure 1 Temperature dependence of loss modulus E'' of dry EVOH-SEBS-*g*-MA blends.

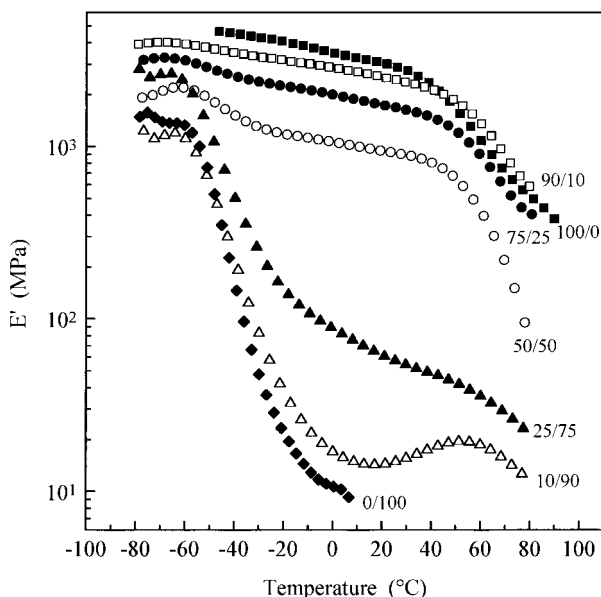


Figure 2 Temperature dependence of storage modulus E' of dry EVOH-SEBS-*g*-MA blends.

Thermal Properties

Melting point T_{mb} , crystallization temperature T_c , bulk EVOH crystallinity in the blend X_c , and crystallization exotherm width at half-height $W_{1/2}$, are reported in Table II. The significant T_{mb} , T_c , and X_c depression with changing composition is characteristic of strong component interaction.¹⁶ This also causes a considerable broadening of the $W_{1/2}$ at increased levels of the elastomeric component, which interferes with the crystallization of EVOH, leading to a progressively wider crystallite size distribution.¹⁷

Optical Microscopy

Phase-contrast micrographs in Figure 3(a–d) show a finely dispersed polymeric alloy, the degree of homogeneity increasing with SEBS-*g*-MA, which, at positive phase contrast, is represented by the dark domains. Analogous findings were reported in previous work.^{11,12} Observation with crossed polars show gross crystalline domain formation at the intermediate blend compositions [see micrographs in Figure 3(e–h)].

Ternary HDPE-EVOH-SEBS-*g*-MA Blends

Tensile Properties

Table III summarizes the results on ultimate properties of dry blends and after conditioning at ambient humidity levels. The data indicate that the presence of polyolefin renders the alloy moisture-proof since tensile properties become independent of moisture. The binary EVOH-HDPE is incompatible, but the addition of 5 wt % compatibilizer is sufficient to bring about compatibilization. At the particular HDPE-EVOH ratio, strength remains essentially constant at up to 15 wt % SEBS-*g*-MA, while ductility and energy to tensile failure continuously increase. In Table III, data on the ultimate properties of blends using the unmodified SEBS are also included. As in the case of the 50/50 binary blend quoted in Table I, these data confirm the all-important role of MA in bringing about compatibilization.

Dynamic Mechanical Properties

Table IV summarizes DMA and thermal data. The T_g of the reactive components remain essentially

Table II Main Viscoelastic and Thermal Data of EVOH-SEBS-*g*-MA Blends

EVOH-SEBS- <i>g</i> -MA	T_g		SEBS- <i>g</i> -MA (°C)	T_{mb} EVOH (°C)	T_c EVOH (°C)	X_c EVOH ^b (%)	$W_{1/2}$ EVOH (°C)
	EVOH (°C)						
	α	β					
100/0	54	-12	—	183	163	75	5
90/10	66	-5	-51	182	162	69	5
75/25	63	-3	-51	181	160	65	7
50/50	60	1	-49	176	156	60	6
25/75	— ^a	—	-49	173	151	49	10
10/90	60	—	-49	169	151	41	12
0/100	—	—	-49	—	—	—	—

Blends were quenched to 0°C.

^a shoulder.

^b $\Delta H_f = 25.6$ cal/g.

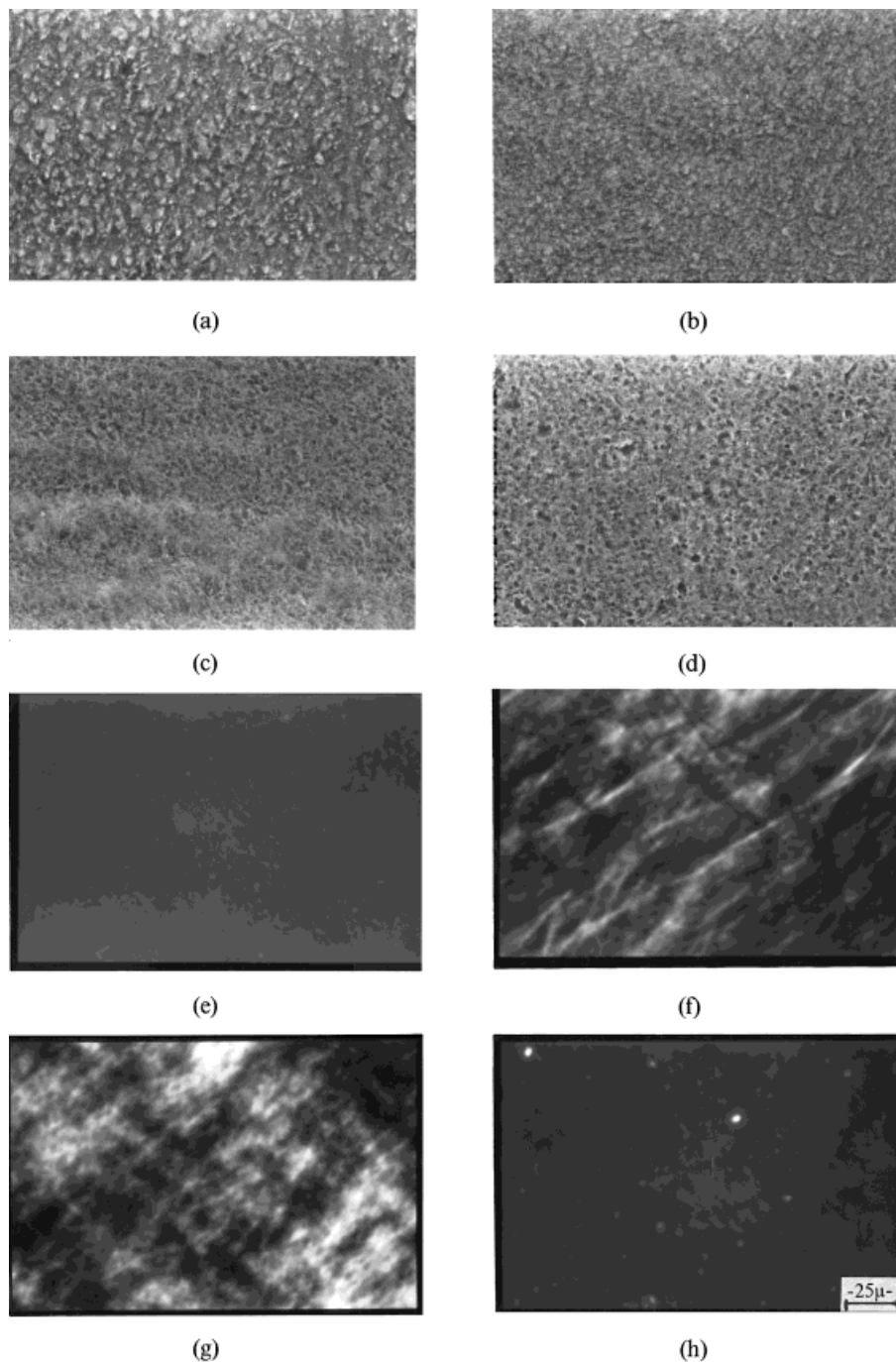


Figure 3 Phase contrast micrographs of EVOH-SEBS-*g*-MA blends: (a) 90/10; (b) 75/25; (c) 25/75; (d) 10/90. With crossed polars: (e) 90/10; (f) 75/25; (g) 50/50; (h) 25/75.

constant. This is not unexpected since any copolymer that may form at the interphase would contain segments of EVOH and SEBS-*g*-MA. Examination of the loss modulus spectra not included in this report shows that addition of SEBS-*g*-MA at constant HDPE-EVOH ratio leads to an increase of the relaxation strength of the material because

of its elastomeric nature. DMA data were also obtained from the interphasial material obtained after extraction of SEBS-*g*-MA and EVOH from the ternary. The product obtained is alloyed with the HDPE matrix, thus making possible the preparation of a test piece by melt-pressing. The spectrum obtained show both relaxations though

Table III Ultimate Tensile Properties of Ternary Blends

HDPE-EVOH-SEBS- <i>g</i> -MA	σ_Y^a (MPa)	σ_b (MPa)	ϵ_b (%)	E_b (J/cm ³)
Dry Films				
67/33/0	—	22 ± 1	7 ± 1	
63/32/5	24 ± 1	23 ± 2	20 ± 7	3 ± 2
60/30/10	20 ± 2	19 ± 1	90 ± 19	14 ± 2
57/28/15	18 ± 1	22 ± 1	454 ± 58	81 ± 14
57/28/15 ^b	—	17 ± 2	12 ± 4	0.075 ± 0.006
Films Conditioned at 60% RH				
67/33/0	—	17 ± 3	7 ± 1	
63/32/5	20 ± 2	19 ± 2	26 ± 4	3 ± 2
60/30/10	17 ± 3	16 ± 2	93 ± 7	15 ± 2
57/28/15	18 ± 1	20 ± 1	376 ± 58	72 ± 12
57/28/15 ^b	—	15 ± 1	12 ± 2	0.06 ± 0.005

Blends were quenched at 0°C.

^a Yield stress.

^b HDPE-EVOH-SEBS.

shifted to each other (see Table IV). The HDPE relaxation located at approximately 54°C coincides with the main EVOH relaxation at approximately 54°C. As expected after extraction of the latter, the relaxation strength of the composite peak is reduced.

Thermal Properties

Thermal data of the ternaries are summarized in Table IV. The T_m of the crystalline components are affected little in the compatibilized blends. Similar findings characteristic of weak intermolecular interactions were reported¹⁰ by Prasad and Jackson on the EVOH/PE-*g*-MA blend. The addition of SEBS-*g*-MA seems to facilitate crystallization of EVOH in the ternary, and this, in turn, induces crystallization of HDPE, possibly by heterogeneous nucleation. Thus, the overall crystallinity of both crystalline components increases

with the addition of the compatibilizer. It is of interest to note that in the ternaries, the behavior observed is contrary to that shown by the binary EVOH-SEBS-*g*-MA blends where all corresponding data indicated considerable component interaction (see Table II). It is possible that in the ternary, SEBS-*g*-MA acts mainly as an emulsifier because of its low concentration. At the higher concentrations used in the binary blends, the effects of intermolecular interactions become more evident. The interphasial material showed traces of the thermal transitions and a significant T_m depression (see Table IV).

Morphology

SEM micrographs of cryofractured surfaces of blends containing varying amounts of compatibilizer are shown in Figure 4. The incompatible HDPE-EVOH binary, wherein EVOH is coarsely

Table IV Main Viscoelastic and Thermal Data of Ternary Blends

HDPE-EVOH- SEBS- <i>g</i> -MA	T_g			T_m		T_c		X_c	
	EVOH (°C)		SEBS- <i>g</i> -MA (°C)	HDPE (°C)	EVOH (°C)	HDPE (°C)	EVOH (°C)	HDPE (°C)	EVOH (°C)
	α	β							
67/33/0	54	-13	—	134	183	118	156	35	64
63/32/5	54	—	-44	133	183	120	156	38	65
60/30/10	54	-16	-44	132	180	120	155	46	69
57/28/15	54	-18	-44	133	183	119	158	55	70
57/28/15 ^a	50	—	-37	130	179	119	156	11	83

Blends are quenched, equilibrated at ambient conditions.

^a Leached sample; $\Delta H_f^\circ = 25.6$ cal/g (EVOH); $\Delta H_f^\circ = 64.8$ cal/g (HDPE).

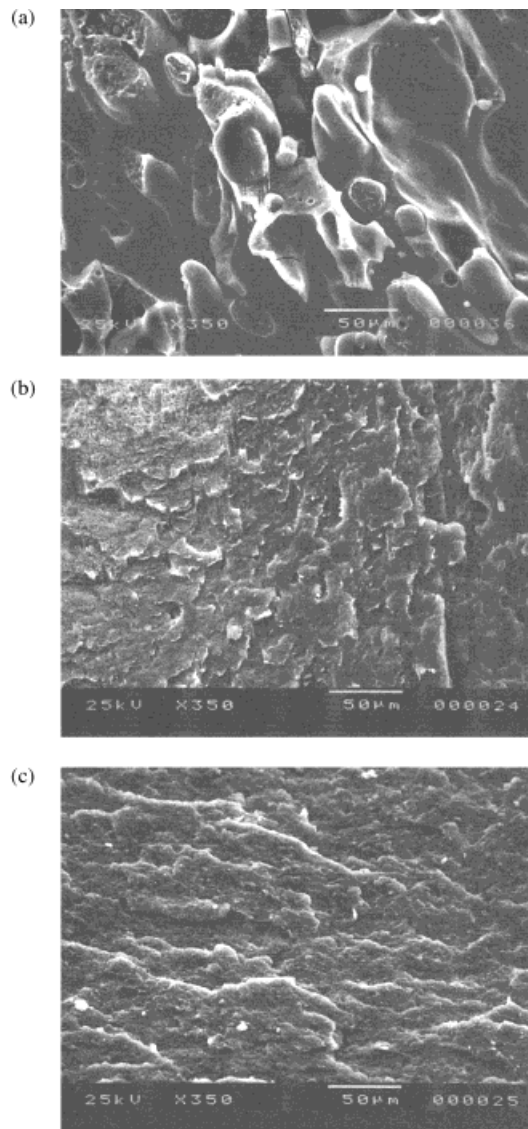


Figure 4 SEM micrographs of cryofractured HDPE-EVOH-SEBS-*g*-MA blends: (a) 50/50/0; (b) 63/32/5; (c) 57/28/15.

distributed as globules in HDPE [Fig. 4(a)], is compatibilized with the addition of SEBS-*g*-MA [Fig. 4(b,c)]; a higher degree of dispersion is obtained at increased amounts of compatibilizer. In the compatibilized alloys, distinct phase boundaries are absent, and features of ductile fracture caused by strong interphase adhesion are evident.

Phase distribution of EVOH of particular importance for barrier applications was also examined in the ternaries. EVOH was leached out from the smooth cross section cut out of films using a surgical blade. The results obtained with SEM are shown in Figure 5(a-c) at low and higher compatibilizer levels. At low compatibilizer contents, these micrographs display a laminar EVOH

morphology within the polyolefin matrix [see Fig. 5(a,b)]. At higher compatibilizer levels, the laminar distribution of EVOH is impaired, supporting the view^{6,18} that a high degree of compatibilization should be avoided if the alloy is intended for use as a barrier material.

It is recognized, however, that further work on film processing conditions is needed to optimize morphology along the line suggested in the literature.⁴⁻⁶

Large deformation mechanical behavior, DMA, and the morphology study support the view that SEBS-*g*-MA compatibilizes the EVOH-HDPE alloy. To trace the origin of compatibilization,

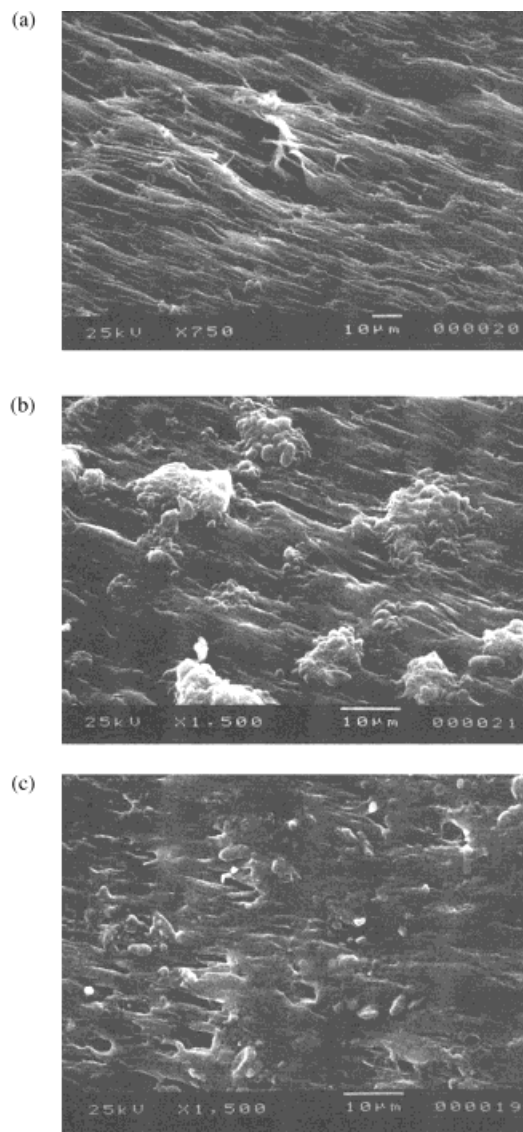
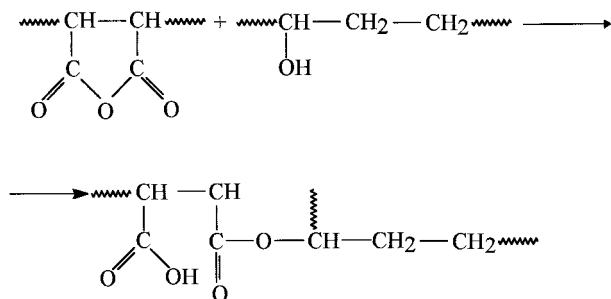


Figure 5 SEM micrographs of blends after extraction of EVOH: (a) 63/32/5, (b) at higher magnification; (c) 57/28/15.

FTIR measurements were carried out on the binary EVOH–SEBS-*g*-MA blends to identify products obtained from a possible reaction of MA with the hydroxyl groups of EVOH according to the scheme.¹⁹



No spectroscopic evidence was obtained to support formation of an ester bond at approximately 1225–1230 cm^{-1} expected from the above reaction path.²⁰ This may be due to the low concentration of the interphasial material formed caused by dilution and the reversibility of the above reaction during melt mixing reported²¹ for model polymers. Failure to obtain spectroscopic evidence for MA functionality reacting with the hydroxyl group was alluded to for the PP–PP-*g*-MA–PVOH²² blend. An alternative route for compatibilization would be of a physicochemical nature, i.e., the hydrogen donor–acceptor interaction²³ involving the carbonyl groups of MA (acceptor) and the EVOH (donor) providing the acidic hydrogen. This type of interaction was also reported¹⁰ to have been detected for the EVOH–PE-*g*-MA blend.

CONCLUSIONS

1. SEBS-*g*-MA compatibilizes EVOH probably by intermolecular interactions, and at concentrations ≥ 5 wt %, it is effective in compatibilizing the HDPE–EVOH blend.
2. The ternary obtained is practically moisture-proof; thus, useful barrier properties of dry EVOH may not be impaired by humidity.
3. At low compatibilizer contents, EVOH obtains a laminar phase distribution within the HDPE matrix. This further enhances the suitability of the ternary as a packaging barrier material.

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