Synthesis and Processing of the (Ethylene-Vinyl Acetate-Vinyl Alcohol) Terpolymer and Its Blends with a Polyamide and Styrene Copolymers

M. FLORES,[1] G. HERNANDEZ,[1] A. ESCOBAR,[2] J. CARDOSO,[1] A. PALMA,[3] A. MACIEL,[3] E. SANCHEZ,[3] O. MANERO[3]

[1] Departamento de Física, Universidad Autónoma Metropolitana-Iztapalapa, A.P. 55-534, México, D.F. 09340, Mexico

[2] Departamento de Ingeniería de Procesos e Hidráulica, Universidad Autónoma Metropolitana-Iztapalapa, A.P. 55-534, Mexico, D.F. 09340, Mexico

[3] Instituto de Investigaciones en Materiales, UNAM, A.P. 70-360, México, D.F. 04510, Mexico

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ABSTRACT: In this article, the synthesis and properties of the (ethylene-vinyl acetate-vinyl alcohol) terpolymer are studied in detail. A transesterification reaction with alcohols was conducted on poly(ethylene-vinyl acetate) to obtain terpolymers with varying hydroxide contents through three different routes: in solution, in a mixing chamber, and in a twin-screw extruder. The kinetics of the reaction in the mixing chamber are compared with those of the twin-screw extruder. Mechanical and rheological properties of the terpolymer are examined as a function of conversion. Blends of the terpolymer with polyamide (Nylon-6) were prepared for various compositions. They show a steep reduction in the equilibrium torque with respect to that of the polyamide. A region of compatibility at high polyamide contents gives rise to an increase of some mechanical properties above the simple mixing rule (Young's modulus). On the other hand, blends with poly(styrene-acrylonitrile) and poly(styrene maleic anhydride) show a region of compatibility at equal proportions of the styrene copolymers and with 10% terpolymer content, induced by the reaction of the hydroxide and maleic anhydride groups. This reaction is inhibited at high styrene-acrylonitrile concentrations due to interference presented by the effect of interactions between the maleic anhydride and acrylonitrile groups. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 1071–1083, 1998

Key words: ethylene-vinyl acetate-vinyl alcohol terpolymer; polymer blends; polyamide blends; styrene acrylonitrile-styrene maleic anhydride copolymer blends; rheological and mechanical properties

INTRODUCTION

Ethylene vinyl acetate (EVA) and ethylene vinyl alcohol (EVOH) copolymers are thermoplastic materials of great commercial interest. These polymers have been used to induce compatibility of blends, because they contain reactive acetate or hydroxide groups that may interact with reactive groups of other polymers. In this regard, it is desirable to obtain polymers that contain both reactive groups in the same macromolecule and, in this case, it is possible to transform a proportion of acetate into hydroxide groups. The transformation of vinyl acetate groups into vinyl alcohol is a kind of acetate–hydroxide exchange known as transesterification reaction[1] producing the terpolymer ethylene vinyl alcohol-vinyl acetate (EVA-OH). This terpolymer has been used as a

Correspondence to: O. Manero.

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starting step in the synthesis of biocompatible materials.[2]

EVOH copolymers have been used in binary blends with Nylons[3] and polypropylene.[4] It combines a superior gas barrier property and high oil resistance with good processability. The blending of EVOH with polypropylene in a multilayer coextrusion results in structures that exhibit mechanical strength, light weight, and also excellent barrier properties. On the other hand, EVA copolymers have been used in blends with ethylene-propylene copolymers. The addition of maleic anhydride-grafted polypropylene in the blend improves the dispersion of the rubber phase in the plastic matrix, producing good impact resistance and low-temperature brittleness.[5] Studies on EVA copolymer blends also include those with natural rubber,[6] polyethylene,[7] poly(vinyl chloride)/polyethylene,[8] poly(ethylene oxide),[9] and poly(vinylidene fluoride-*co*-hexafluoro acetone).[10] EVA copolymers are also good compatibilizers in blends of high-density polyethylene and poly(ethylene terephtalate).[11] In addition, studies on the substitution of polybutadiene for EVA in acrylonitrile butadiene styrene (ABS) polymers, due to the excellent weatherability of EVA, have been performed.[12]

The transesterification reaction to transform the acetate groups of the EVA copolymer into vinyl alcohol groups has been studied in solution and in the bulk.[13,14] High conversions, of the order of 60–70%, have been obtained by reactive extrusion using various alcohols and catalysts. A kinetic study shows that the rate constants in solution and in bulk are the same, regardless of the reactant concentrations and viscosity of the reactant mixture. Because the reaction rate is relatively slow, compared with the rate of diffusion, mechanical mixing effects are unimportant.

Although various studies have been made on the use of EVOH and EVA copolymers in blends, the analysis of the properties and use of the terpolymer (EVA-OH) in blends is still scarce. In this work, the synthesis of the terpolymer is performed through different routes, and its properties and those of some of its blends are studied. To produce the terpolymer with various vinyl alcohol proportions, a transesterification reaction is conducted on the EVA copolymers (that contain $\sim$ 30 wt % vinyl acetate groups) in solution and in the melt, using a mixing chamber and a double-screw extruder. Characterization of the resulting products obtained for various compositions was performed, and mechanical and rheological studies were also performed as a function of concentration of hydroxide groups. Thereafter, blends of the terpolymer with polyamide (Nylon 6) and with copolymers of styrene-acrylonitrile (SAN) and styrene-maleic anhydride (SMA) were processed. Use of the EVA-OH terpolymer allows investigation of the influence of hydroxide and acetate groups on blend compatibility and their properties and processing.

EXPERIMENTAL

EVA (Atochem, France) had approximately a 30 wt % of vinyl acetate content and was used as received. Characterization of the functionalized polymers was performed by differential scanning calorimetry (DSC), thermogravimetry (TGA), Fourier-transform infrared (FTIR) spectroscopy, and proton NMR. TGA (Du Pont 951 controlled by a TA 2100 thermal analyzer, under nitrogen atmosphere at a heating rate of 10°C/min) was used to obtain information on the decomposition temperatures and also to quantify the vinyl acetate content in the EVA copolymer, according to the technique reported by Chiu.[15,16] This technique is based on the thermal decomposition of vinyl acetate to produce acetic acid using a TGA device. DSC (Du Pont 910 under nitrogen atmosphere with a heating rate of 20°C/min) determined the glass transition and the fusion temperatures. FTIR (Perkin-Elmer 1600, with polystyrene standards) was performed on film samples. Finally, proton-NMR (Varian VXR-300S, 300 mHz, with tetramethyl silane as standard) determined the presence of esters in acetate groups of EVA and that of alcohol groups in the functionalized products.

The functionalization of EVA was performed through a transesterification reaction resulting in a partial conversion of the acetate groups. It was performed through three different stages: in solution, in two Banbury chambers of 60-ml capacity (Haake Rheocord 254 and Brabender), and in a twin-screw extruder (Haake Rheomix TW-100), according to the technique described elsewhere.[13,14]

Synthesis of EVA-OH in Solution

Transesterification of poly-EVA was conducted using a 1*N* solution of KOH in diethylene glycol at 80°C. EVA was dissolved in toluene in 1 g EVA : 12 mL toluene ratio at the same temperature with stirring in a reflux system. The transesterification agent was added according to the values shown

Table I Reaction in Solution: Variation of Conversion with Reaction Time and Amount of Transesterification Agent

KOH/EVA (g/g)	Reaction Time (min)	Conversion (%)
0.012	30	5.7
0.023	30	11.3
0.058	30	19.0
0.100	30	33.3
0.112	30	40.0
0.120	30	59.0
0.112	60	44.0
0.112	90	46.0

in Table I at 100°C for 30 min. Thereafter, the synthesized terpolymer was precipitated and washed with ethanol, filtered, and dried in an vacuum oven at 30°C for 72 hr.

Synthesis of EVA-OH in the Mixing Chamber

This process was performed in two stages. In the first one, the reaction agent used was 1-octanol with sodium methoxide as catalyst. EVA, 1-octanol, and sodium methoxide were mixed in several proportions. The variables of the mixing process included temperature of mixing, time, and velocity of rollers. Table II shows the operating conditions for several molar ratios. Once the mixing time is completed, extraction of the products in an ethanol solution by a Soxhelt fixture for 2.5 h and drying at 30°C under vacuum for 24 h were conducted. In the second stage, the catalyst proportion was kept at 2.4 wt % and besides octanol, ethanol was also used. Alcohol content was fixed in an equal molar ratio to the vinyl acetate content. The reaction was performed at 180°C at a roller speed of 32 rpm. Table III shows the reaction times and the corresponding conversions achieved for both alcohols. With these data, the reaction kinetics are worked out.

Synthesis of EVA-OH in the Twin-Screw Extruder

This process was conducted using octanol and ethanol in separate experiments: at 180°C and 32 rpm. The process *via* octanol was performed with several proportions of catalyst and octanol in the reacting mixture (as shown in Table IV). For a particular sample, a second extrusion was performed at the same conditions. The reactant composition in the process *via* ethanol is also given in Table IV.

The functionalized products were characterized by DSC at a heating rate of 10°C/min. An initial heating from −50°C to 150°C was followed by a constant temperature plateau at the peak temperature and a subsequent decrease from 150°C to −30°C. Thereafter, a further increase to the peak temperature was conducted. TGA provided the material composition. FTIR identified the hydroxide (OH) vibration at 3300–3600 cm^{-1} of a primary alcohol, C—OH band at 1150 cm^{-1} of a secondary alcohol, C═O band at 1735 cm^{-1} of aliphatic esters, C—O band at 1240 cm^{-1} of ethoxy groups (acetates), and the symmetric and asymmetric bands of C—O at 1300–1050 cm^{-1} of the ethoxy group for esters. Elemental analysis (Desert Analytics, Tucson, AZ) was also used to determine the percentage of the atomic species in the products. Proton-NMR determined the coupling of hydrogen atoms in alkane chains at 1.1–1.8 ppm, the corresponding features of

Table II Mixing Chamber Results: First Stage

Sample	T (°C)	t (min)	V (rpm)	Composition (%)[a]	Conversion (%)	T_g (°C)	T_m (°C)	T_d (°C)
EVA-1	170	8	50	100/21.2/3	50	53.9	88.7	312
EVA-2	150	8	50	100/21.2/3	58	61.6	89.5	312
EVA-3	150	5	50	100/21.2/3	38	40.7	87.1	313
EVA-4	150	8	40	100/21.2/3	54	60.1	89.2	312
EVA-5	150	8	30	100/21.2/3	48	52.8	88.5	313
EVA-6	150	8	50	100/10.6/3	16	−23.1	70.3	312
EVA-7	150	9	50	100/21.2/3	59	66.5	89.4	312
EVA-8	150	10	50	100/21.2/3	60	67.2	90.1	313
EVA-9	130	8	50	100/21.2/3	36	33.4	87.7	313

T, t, and V are the temperature, time, and roller speed. T_m and T_d are the melting and decomposition temperatures, respectively.
[a] Percentage of octanol/catalyst/100 g of EVA.

Table III Mixing Chamber Results: Second Stage

rpm = 32 T = 180°C				
Ethanol Composition (%)[a]	Ethanol Conversion (%)	Octanol Composition (%)*	Octanol Conversion (%)	t (min)
100/16/2.4	7.5	100/45.4/2.4	10.3	1
100/16/2.4	17.0	100/45.4/2.4	21.2	2
100/16/2.4	24.0	100/45.4/2.4	32.1	4
100/16/2.4	29.0	100/45.4/2.4	43.2	6
100/16/2.4	33.3	100/45.4/2.4	45.3	8

[a] Percentage of alcohol/catalyst/100 g of EVA.

esters in acetate groups, and the alcohol group at 4.0–5.5 ppm.

Finally, a rheological study and mechanical tests of the resulting products were conducted. These included viscosity measurements performed in a capillary rheometer (Instron Corp., Canton, MA) using three capillaries with length to diameter ratios of 20, 50, and 60, and torque measurements conducted in the twin-screw extruder.

Blends were made with polyamide (Nylon-6, Celanese, Mexico), poly-SAN (Resistol, Mexico), and poly-SMA (Cadon, Monsanto, Mexico). The polyamide had a fusion peak at 225°C, a density of 1.14 g/mL, and a melt flow index of 12. The poly-SAN had a 25 wt % of acrylonitrile groups and poly-SMA had a 25 wt % of maleic anhydride groups. These blends were prepared in the twin-screw extruder for three different proportions (30, 50, and 80% of PA-6 content). The blending process was conducted by maintaining a temperature profile in the extruder of 250, 240, 240, 240, and 235 (°C) for the different heated zones. The samples were fed with negligible humidity content. The screw was of the barrier type, with a 2.5 : 1 compression ratio. In the case of the SAN/SMA/EVA-OH blends, the ingredients were mixed at 200°C, 32 rpm, and with a residence time of 10 min. The proportion of functionalized EVA in the blends was in all cases 10 wt %. The resulting blends were characterized by DSC, TGA, and FTIR. DSC was performed twice from −100°C to 250°C, and the heating rate in the TGA test was fixed at 10°C/min.

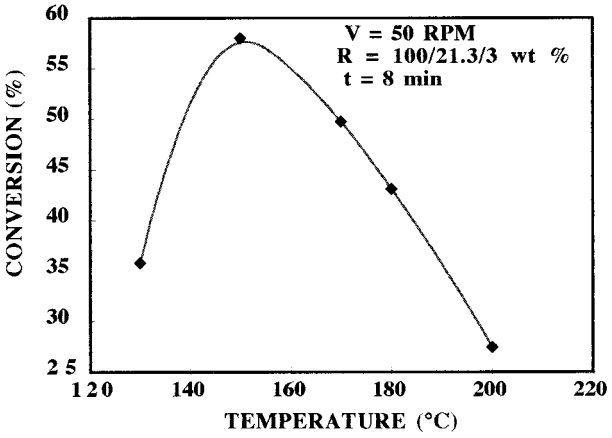
RESULTS AND DISCUSSION

For EVA, glass transition, fusion, and degradation temperatures are −26.8, 69.9, and 301.3°C, respectively. For the solution process, results of conversion as a function of the reaction time and KOH to EVA ratio are given in Table I. Determination of the OH content by TGA and elemental analysis rendered similar results. NMR spectra identified the band at 5.5 ppm of the alcohol group. Similarly, FTIR determined the presence

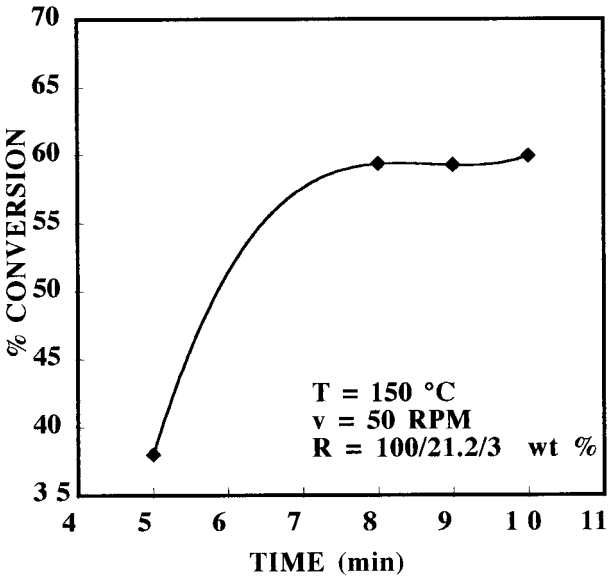
Table IV Twin-Screw Extruder Results

rpm = 32 (t = 8 min)		Variable Residence Time		
Octanol Composition (%)	Octanol Conversion (%)	Ethanol Composition (%)	Ethanol Conversion (%)	t (min)
100/45.4/2.5	54	100/8/2.5	42.5	19.0
100/42.3/2.7	54	100/8/2.5	38	16.7
100/33.3/2.5	42.5 (54.4[a])	100/8/2.5	27	12.5
100/33.3/2.0	42.5	100/8/2.5	21	10.0
100/33.3/1.85	42.1	100/8/2.5	17	8.4
100/33.3/1.6	37	100/8/2.5	14	7.2
100/26.6/1.5	14.8 (24.7[a])			

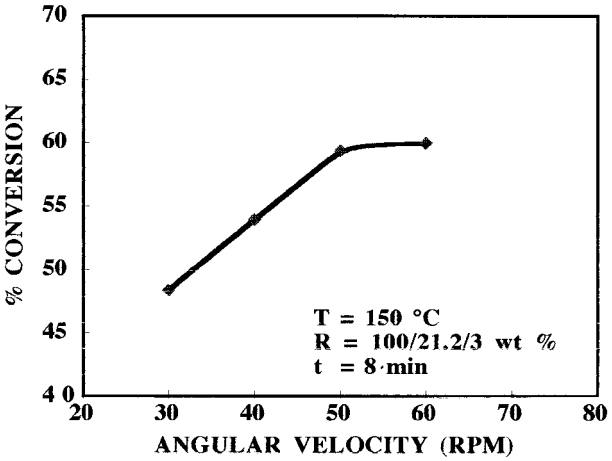
[a] After a second extrusion.



(a)



(b)



(c)

of the OH group at 3425 cm^{-1} and the corresponding band of the C—OH group at 1126 cm^{-1}.

In the mixing chamber, the resulting OH content of the functionalized products depends on the composition of EVA, octanol, and catalyst concentrations in the reactive mixture; roller speed; reaction time; and temperature of the chamber. Table II shows the resulting conversion expressed as a percentage of acetate groups transformed into OH groups, for several processing conditions. (Because EVA contains 30% of acetate groups, the resulting OH content in EVA-OH is 30% of the conversion percentage.) If the composition (100/21.3/3), roller speed (50 rpm), and reaction time (8 min) are maintained fixed, conversion grows with temperature and attains a maximum (58%) at 150°C. Above this temperature, final conversion drops linearly, as indicated in Figure 1(a). At the peak temperature, for the same composition and roller speed, conversion increases as a function of reaction time and attains the 60% conversion at 10 min [as shown in Fig. 1(b)]. A reaction time of $>$ 10 min results in polymer degradation.

The observed decrease in conversion for temperatures higher than 150°C is attributed to octanol vaporization, producing a lower alcohol proportion in the reactive mixture. This observation is similar to results presented by Lambla and colleagues[13] in a twin-screw extruder.

Percentage of OH content is also a function of the roller speed. Figure 1(c) shows that the functionalization degree attains a maximum at $\sim$ 50 rpm, keeping the temperature, ingredients proportion, and reaction time constant.

As observed in Table II, a drastic change in the resulting vinyl alcohol proportion takes place when the reactants concentration (alcohol and catalyst) is modified. A 50% decrease in the alcohol content leads to a 75% drop in OH group production. From Figure 1(a–c), it is apparent that the optimum reaction conditions are achieved at 150°C, with a roller speed of 50 rpm, and with a reaction time of 10 min for the 100/21.3/3.0 reactants content. Reproducibility is quite acceptable, to within 1%.

Glass transition temperatures (T_g's) of functionalized EVA depend on the conversion degree

Figure 1 Percentage of conversion of acetate groups into OH groups in the mixing chamber (first stage) as a function of: (a) temperature (T), (b) reaction time (t), and (c) roller speed (V). Composition (R) is given as 100 g EVA/octanol (wt %)/catalyst (wt %).

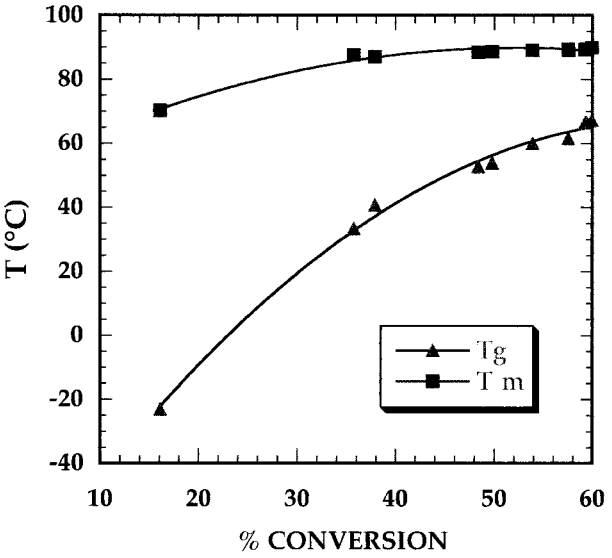


Figure 2 Behavior of T_g and melting temperature (Tm) as a function of the percentage of conversion of acetate groups into OH groups.

and are located between the T_g of pure EVA (−26.8°C) and that of the polyvinyl alcohol (84.8°C). This relationship is logarithmic, and between 33 and 60% T_g increases from 36 to 66°C (Fig. 2). Melting temperatures vary little with conversion, being close to 90°C for conversions larger than 33%. Besides the resulting conversion, Table II shows the glass transition, melting, and decomposition temperatures for the samples considered.

Comparison of the torque curves of both EVA and EVA-OH as a function of the mixing time (Fig. 3) indicates that the lowest torque at short mixing times is achieved in the sample with the highest proportion of OH groups. The equilibrium torque (i.e., the torque at long times) is attained sooner as the OH content is larger. Eventually, for times longer than 5 min, the torque value is the same for the three polymers shown in Figure 3.

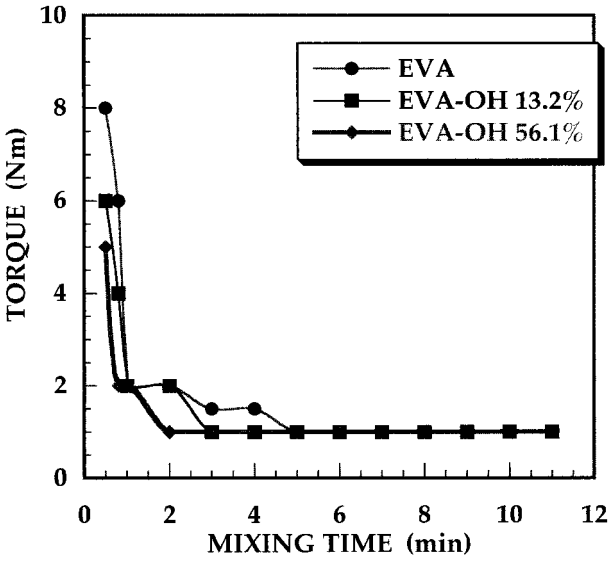


Figure 3 Torque as a function of mixing time for EVA and EVA-OH with 13.2 and 56.1% conversion.

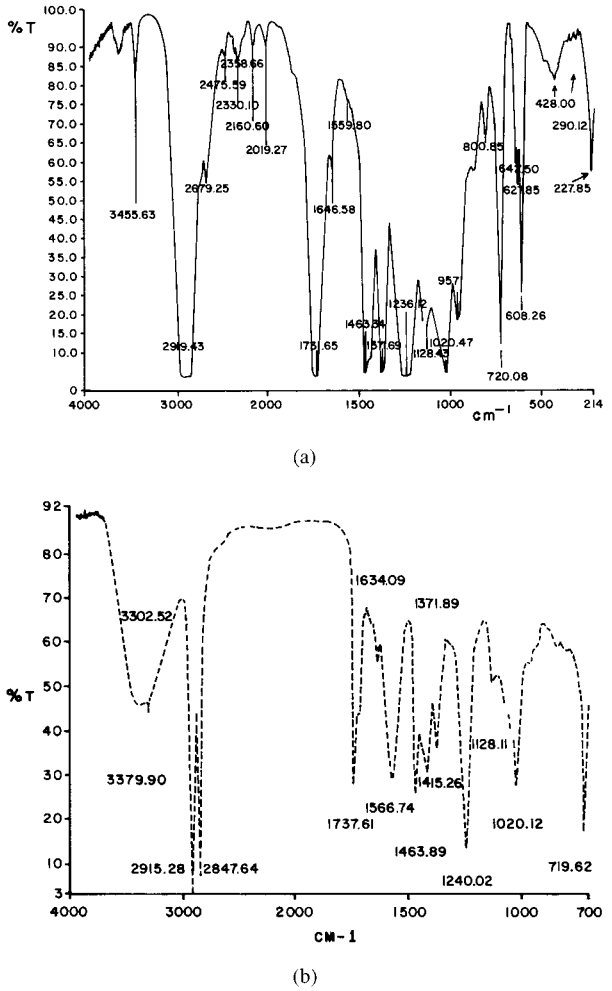


Figure 4 FTIR spectra of EVA (a) and EVA-OH with 56.1% (b) conversion degree.

Finally, for increasing OH groups content, the FTIR spectra show changes in the width of the 3380 cm^{-1} band corresponding to alcohol groups, and the band at 1100–1200 of the group C—O of secondary alcohols [Fig. 4(a,b)] is also noticeable.

In the second stage, the evolution of the conversion (x) as a function of time (t), together with the predictions of the reaction kinetics, are given in Fig. 5(a,b) for both octanol and ethanol processes. After the expressions used in ref. 13, the continuous lines are predicted by the equation:

$$\frac{1}{X_1 - X_2} \ln[X_2(X_1 - x)/X_1(X_2 - x)] = (k_1 - k_2)t \quad (1)$$

X_1, X_2 are the roots of the equation

$$x^2 - (a + b)mx + mab = 0 \quad (2)$$

k_1, k_2 are the reaction constants for the reversible reaction

$$A + B \underset{k_2}{\overset{k_1}{\rightleftarrows}} C + D \quad (3)$$

where a and b are the initial concentrations of EVA and alcohol, respectively, and

$$m = k_1/(k_1 - k_2) \quad (4)$$

$$K = k_1/k_2 \quad \text{is the equilibrium constant.} \quad (5)$$

The resulting values of k_1, k_2, and K at 180°C for octanol are 0.072 L/mol-min, 0.0213 L/mol-min and 3.38, respectively. For ethanol, these are 0.0692, 0.0267, and 2.59, respectively. The maximum equilibrium conversions are 0.65 for octanol and 0.62 for ethanol.

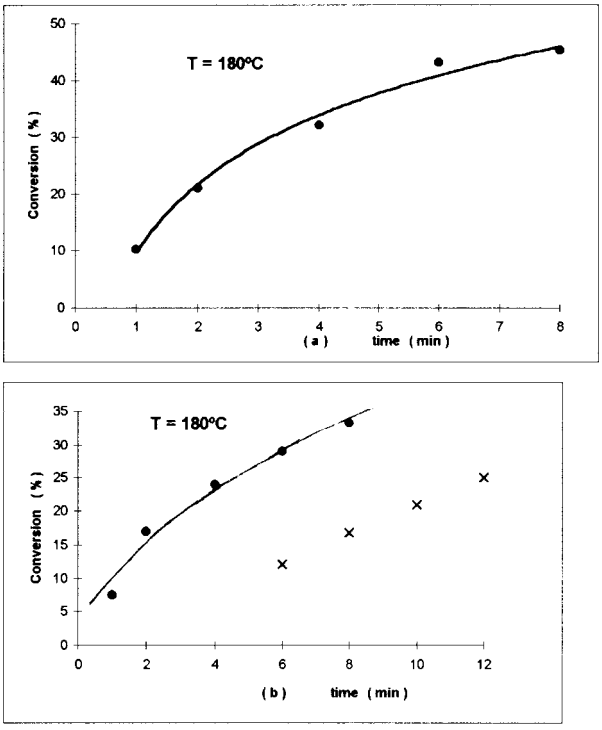


Figure 5 Conversion *versus* time plots of experimental data and theoretical predictions of the transesterification reaction [eq. (1)]. Mixing chamber results (rpm = 32) of the reaction *via* (a) octanol and *via* (b) ethanol (circles), together with the twin-screw extruder results (×).

Table V Mechanical Properties: Process *Via* Ethanol as a Function of Conversion

Conversion (%)	Young's Modulus (MPa)	Strain at Break (%)	Stress at Break (MPa)
0	2.20	938	20.3
7.2	2.35	945	19.7
14.4	3.80	1,160	17.7
22.0	3.50	1,092	18.9
30.0	3.20	1,020	19.2
35.0	2.35	924	20.0
42.5	2.30	874	21.5

A study on transesterification reactions in molten polymers (refs. 13 and 14) yields similar results to those obtained herein for the reaction and equilibrium constants (using octanol in the mixing chamber), except that a different catalyst was used (dibutyl tin dilaureate). Rate constants k_1 and k_2 in the referred article are 0.053 and 0.022 L/mol min at 170°C and 0.13 and 0.031 at 190°C, respectively. Equilibrium constants obtained at those temperatures are 2.4 and 4.2, respectively.

In the twin-screw continuous process, a major factor in the resulting conversion is the alcohol content in the reacting mixture. In Table IV, the effect of varying catalyst concentration is also illustrated, keeping the same EVA/octanol ratio. In this case, a constant conversion is attained for catalyst contents of > 2 wt %. For lower concentrations, conversion is affected. Conversion may be increased by performing a second extrusion under the same processing conditions, as indicated in Table IV.

With data of the evolution of conversion as a function of time for ethanol (Table IV), eq. (1) renders the corresponding results for k_1 and k_2 in the continuous process. These are 0.054 and 0.029 L/mol min at 180°C, respectively, and they are also shown in Figure 5(b) for comparison with the mixing chamber results. Deviations with results obtained from the mixing chamber manifest different thermorheological histories, wherein viscous dissipation and diffusion processes lead to departures in the rate constants.

The mechanical properties of the resulting terpolymers as a function of conversion are shown in Table V for the process *via* ethanol. Herein,

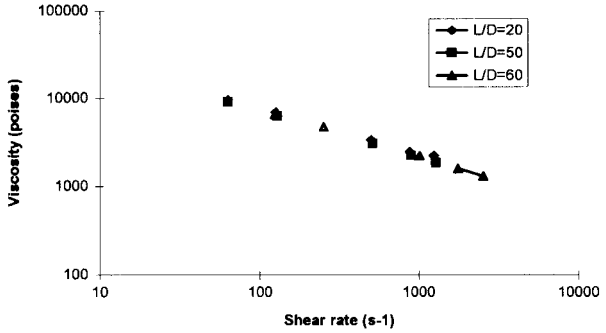


Figure 6 Variation of viscosity with shear rate for the terpolymer with 14.4% conversion. Data were obtained using three capillaries with L/D values of 20, 50, and 60.

Table VI Rheological Properties: Process *Via* Ethanol as a Function of Conversion

Conversion (%)	Power Law Index (n)	Consistency Index (K) (poises)
0	0.49	72,000
7.2	0.47	86,100
14.4	0.47	86,100
22.0	0.46	95,500
30.0	0.47	88,400
35.0	0.40	192,700

results are given for the percentage of strain at break, stress at break, and Young's modulus. As observed, both percentage of strain at break and Young's modulus exhibit a maximum at 14.4% conversion. On the other hand, the stress at break attains larger values for higher conversions, although these changes are not very substantial.

The rheological behavior of the products can be examined analyzing the values of the equilibrium torque and in the results of the viscosity *versus* shear rate curves obtained from capillary data. The process *via* octanol presented a lower equilibrium torque than the one *via* ethanol (8.7 and 11.7 Nm) due to higher alcohol proportion, which diminishes the blend viscosity because an equimolar ratio of alcohol/vinyl acetate is preserved in both cases.

The viscosity variation with shear rate for the terpolymer with 14.4% conversion is shown in Figure 6. Data from the three capillaries coincide along the shear rate range of the measurements. Table VI illustrates in a concise form the results from most of the samples for various conversions, including those of EVA. All curves exhibit a power law behavior, with a consistency index K and a slope n-1. These values present substantial differences as the conversion is increased, showing the larger viscosity for the highest conversion. Simultaneously, the pseudoplasticity of the samples increases as the power law index diminishes with conversion. These results indicate that, for higher conversions, viscosity in general increases, but, at the same time, the samples become more non-Newtonian or more shear rate-dependent.

Blends of EVA-OH with PA-6 (Nylon-6)

Results for this blend are illustrated in Figures 7–9. In Figure 7, the fusion endotherms depict a shift in the fusion peak of Nylon from 222°C to almost 217°C as the concentration of EVA-OH increases. Simultaneously, a decrease in the area of the fusion peak of EVA-OH is observed, becoming similar to the DSC diagram of pure Nylon when the Nylon/EVA-OH content is 80/20 (EVA-OH conversion degree is 33%). This result suggests the incorporation of EVA-OH in the polyamide by reaction that takes place between the reactive COOH groups of the polyamide and those (OH) of the vinyl alcohol in the terpolymer.

The decrease in the melting temperature of PA-6 as the content of EVA-OH increases is similar to that observed in miscible poly-EVOH-Nylon 6 blends[3] with 62% of vinyl alcohol content. This blend presents a pronounced depression in the melting temperature (from 221.2°C with 100% Nylon to 214.6°C with 30% Nylon). A large melting point depression is associated with a small

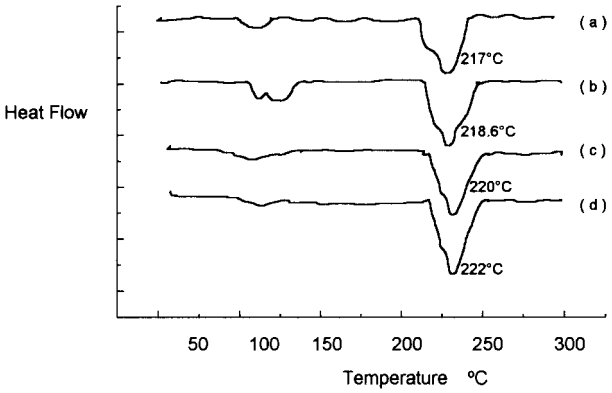


Figure 7 DSC results for the polyamide (PA-6), and blends with different EVA-OH compositions. (a) PA-6/EVA-OH = 30/70%, (b) 50/50%, (c) 80/20%, and (d) 100/0%. EVA-OH had a conversion degree of 33%.

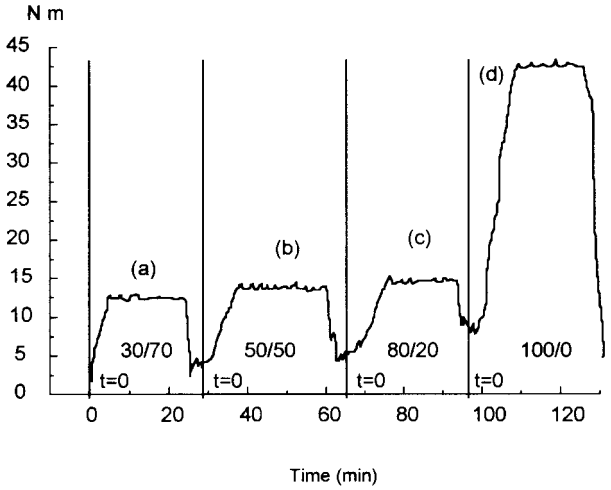


Figure 8 Equilibrium torque results for the same systems presented in Fig. 7. Processing temperature: 248°C.

intermolecular interaction parameter (related to the heat of mixing per unit volume of the components in the blend) and an increasing miscibility. In the system, EVA-OH + PA-6 analyzed herein the melting point depression amounts to 222–217.5°C when the proportion of PA-6 changes from 100% to 30%. In this case, however, the content of OH groups in the blend with 30% PA-6 is 7%, compared with 18.6% in the poly-EVOH blend of ref. 3. Thus, the depression of 4.5°C indicates a substantial degree of compatibility. It is interesting that a common feature of both systems is the similarity between the endotherms of 100% and 70% (or 80%) Nylon [compare Fig. 3(c,d) of ref. 3 with Fig. 7(c) of this article].

Figure 8 shows the equilibrium torque results for the three systems, compared with that of pure Nylon. There is a dramatic decrease in the torque ($\sim$ 300%) for the blends with EVA-OH. It readily illustrates that a small percentage of EVA-OH in the blend (20%) is capable of reducing the energy requirements of the processing of this blend by a large extent.

Finally, Figure 9 shows the variation of the Young's modulus with polyamide content. The most interesting observation is the unusually high value of the modulus for the blend with 80% polyamide content, quite close to that of the pure polyamide. This effect provides blends with high modulus and at the same time with high processability. In addition, it is interesting to observe that the previously described high value of the modulus takes place inside the region of compatibility, also shown by the endotherms for the 20/80 EVA-OH/PA-6 blend.

Blends of SAN/SMA/EVA-OH

The system SAN/SMA forms a miscible blend as long as the proportion of the acrylonitrile groups and that of the maleic anhydride groups in the blend is equal.[17] Blends were prepared inside and outside the miscibility region to elucidate the action of the compatibilizer in the system.

Results of the processing conditions are given in Figure 10(a–c). Herein, it is interesting to observe that the torque is affected drastically by the presence of EVA-OH and its OH content.

Variation of the torque as a function of time for a sample with 10% EVA-OH and equal amounts of SAN and SMA is presented in Figure 10(a). It is observed that the equilibrium torque is attained past 7 min, and its value depends on the OH percentage. It is 20% higher in samples with conversions larger than 7%. Steady-state is attained sooner in samples with the lower conversions and an overshoot is observed at short times. The overshoot shifts to shorter times and grows in magnitude as the concentration of OH groups diminishes. The increase in the torque with time is indicative of reaction between the reactive groups of the polymers.

The peak magnitude of the torque as a function of the SAN content is given in Figure 10(b). The torque diminishes steeply in the presence of EVA-OH in the blend and attains a magnitude considerably smaller than that of the SAN/SMA blend.

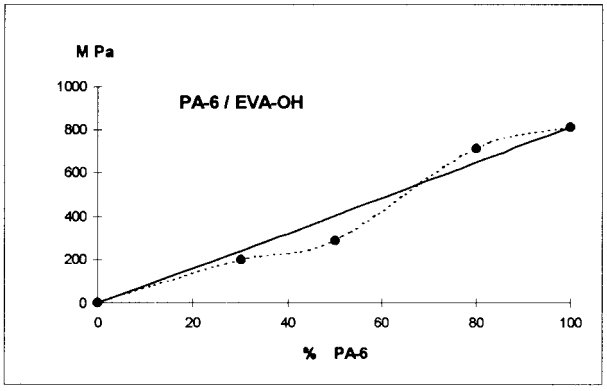
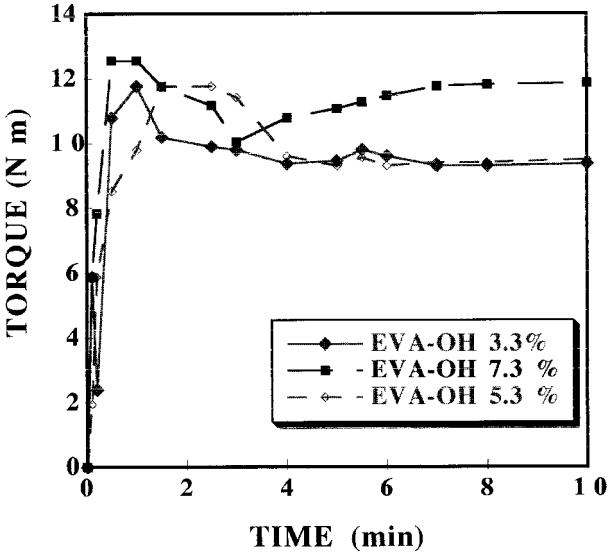
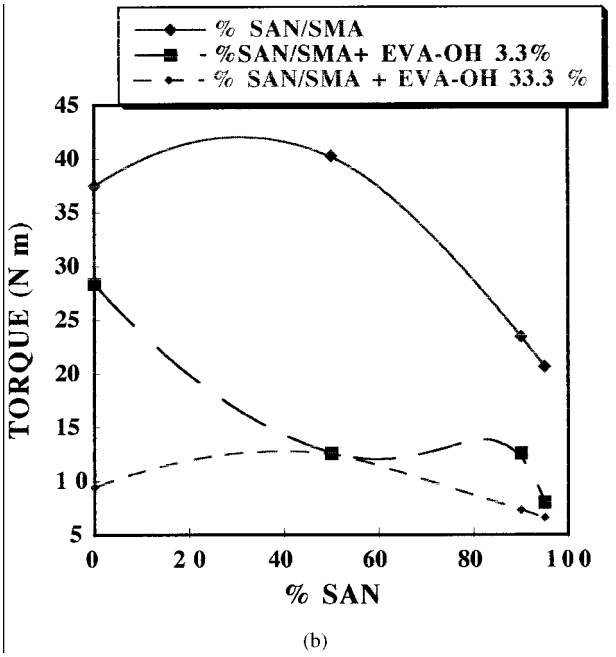


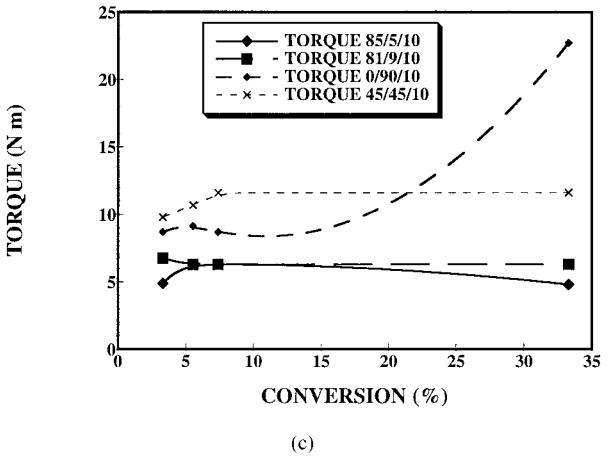
Figure 9 Variation of Young's modulus with composition of the system PA-6/EVA-OH, expressed as a percentage of PA-6 in the blend. EVA-OH has a conversion degree of 33%.



(a)



(b)



(c)

This figure also illustrates that, for the system SMA/EVA-OH (EVA-OH content is 10%), the peak torque is a strong function of the OH content. In this case, it further shows that the reaction between the maleic anydride groups and the OH groups is taking place without interference from the acrylonitrile group. As the concentration of acrylonitrile grows, differences in the peak torque diminish as the reaction described previously is restricted. This hypothesis is based in the strong interaction existing among the acrylonitrile and the maleic anydride groups, and the direct evidence of such is the formation of miscible SMA/SAN blends.

Figure 10(c) shows evidence that reaction between maleic anhydride groups and OH groups in the SMA/EVA-OH blend takes place and its extent increases as the OH content grows. This figure also shows that the systems wherein the torque is independent on the OH content are those where the SMA content is equal or lower than 45%, indicating a restriction in the reaction of the reactive groups due to increasing amounts of SAN in the blend. As observed, the sample with 45/45/10 proportion of SAN/SMA/EVA-OH presents the same asymptotic torque for conversions up to 33%.

Results of the thermal characterization are given in Table VII. Herein the glass transition temperatures of selected blends are given, varying the proportion of the three components and the conversion degree. A single T_g is observed for each compatible blend. In contrast to systems without EVA-OH, the presence of the hydroxylated compound gives rise to a subtle change in T_g ($\sim$ 2°C), with the exception of the 45/45/10 blend with 33% conversion, which shows an increase of 11°C. T_g increases upon increasing the concentration of SMA in the blend. No substantial variation in T_g is observed in the systems located outside the region of miscibility (i.e., that found at equal proportions of SAN and SMA in the blend).

In Table VII, decomposition temperatures indicate that thermal stability is favored in systems with high SAN concentrations, and this dimin-

Figure 10 Torque results for the system SMA/SAN/EVA-OH. (a) Variation of the torque as a function of time with various conversion degrees. Blend composition is 45/45/10%. (b) Variation of the maximum torque as a function of composition, expressed as SAN percentage (EVA-OH content is 10%), for various conversions. (c) Variation of the equilibrium torque with conversion for several compositions.

Table VII SMA/SAN/EVA-OH Blends

System	Conversion (%)[a]	Composition (%)	T_g (°C)	T_d (°C)
SMA	0	100/0	152	292
SMA/EVA-OH	3.3	90/10	152	275
SMA/EVA-OH	33.0	90/10	152	268
SMA/SAN	0	50/50	126	297
SMA/SAN/EVA-OH	3.3	45/45/10	128	318
SMA/SAN/EVA-OH	33.0	45/45/10	137	301
SMA/SAN	0	10/90	109	336
SMA/SAN/EVA-OH	3.3	9/81/10	110	330
SMA/SAN/EVA-OH	33.0	9/80/10	110	315
SMA/SAN	0	5/95	108	347
SMA/SAN/EVA-OH	3.3	4.5/85.5/10	109	334
SMA/SAN/EVA-OH	33.0	4.5/85.5/10	110	328

T_d = decomposition temperature.
[a] Percentage of acetate groups converted into OH groups in EVA-OH.

ishes with the increase in OH groups content. As a conclusion, the blend 45/45/10 content with the highest concentration of OH groups presents an adequate torque for processing with a high T_g, confirming the reaction between reactive groups and the blend compatibility.

Figure 11(a,b) shows results from a FTIR analysis. Schematically, the ratio of the absorbance intensities that is proportional to the ratio of concentration of C—OH groups in secondary alcohols (located at 1156 cm^{-1}) to that of C=O groups in aliphatic esters (1736 cm^{-1}) (produced by the opening of the maleic anhydride ring) is presented. This is shown for two samples with different conversions. Because the reaction that takes place between SMA and EVA-OH involves the anhydride and OH groups of both polymers, this ratio readily indicates the consumption of OH groups in EVA-OH and the increase in C=O groups of the resulting products.

As observed in the results shown in Figure 11, the consumption of OH groups increases as the proportion of SAN in the blend diminishes. The reaction is consequently favored with lower SAN concentrations, in agreement with the torque measurements [Fig. 10(c)] where an increase in the torque due to the reaction is observed for lower SAN concentrations. In the case of samples without SAN with two contents of OH groups, it is interesting to calculate the amount of OH groups that have reacted from the data shown in these figures. It turns out that, in the sample with the lowest proportion of OH groups (conversion = 3.3%), 87% of these groups have reacted, whereas in the blend with EVA-OH, 33% conversion (initial concentration of OH groups is 10 times higher) 78% of OH groups have reacted. Now, for the blend with 45/45/10 composition, the corresponding percentages are 86% and 73%, respectively. This illustrates that, when the amount of OH groups is small, almost the same amount of OH groups react in the SMA/EVA-OH blend and the blend at equal proportions SAN/SMA. On the other hand, when the amount is large, interactions of the reactive groups with SAN restrict the OH-maleic anhidride reaction, and the proportion of OH groups that have reacted changes from 78% (in the SMA/EVA-OH blend) to 73% (in the 45/45/10 composition blend).

CONCLUSIONS

Results presented for the transesterification of EVA show that the resulting terpolymer possesses mechanical and rheological behaviors quite different to those exhibited by the EVA copolymer alone. An increase in the Young's modulus with conversion is detected. Similarly, the percentage of strain at break shows an increase over values given by pure EVA, which seems simultaneous to a small reduction of the stress at break, for specific conversions. An increase of pseudoplasticity and viscosity is also observed at high conversions. In addition, the incorporation of OH groups gives

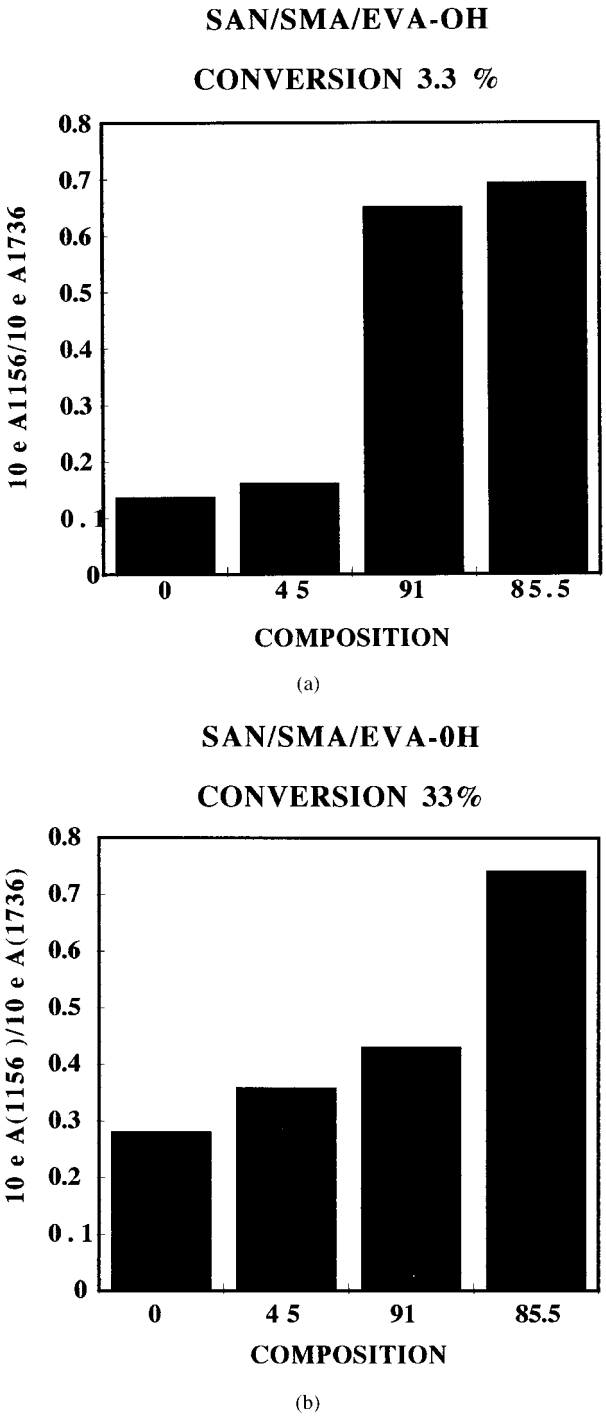


Figure 11 FTIR results for the system SMA/SAN/EVA-OH. Ratio of absorbances of C—OH to C=O groups, illustrating the consumption of OH groups for several blend compositions expressed as a percentage of SAN in the blend. The proportion of EVA-OH is 10%. (a) 3.3% conversion. (b) 33% conversion.

rise to an increase in the degradation temperature of the samples.

The addition of small quantities of EVA-OH to polyamides (Nylon-6) gives rise to an increased processability of the resulting blends, which exhibits a reduction in the torque of the order of 300%. Compatibility is obtained for concentrations lower than 20 wt % of EVA-OH in the blend. This is evidenced by a positive departure observed in Young's modulus for these concentrations, as also shown in the melting endotherms.

In the SAN/SMA/EVA-OH blend, a reduction in the processing torque is obtained when EVA-OH is added to the miscible SAN/SMA system. At high SAN concentrations, evidences of the interference of the acrylonitrile group in the reaction between the maleic anhydride and OH groups were presented, attributed to the high interaction existing among the acrylonitrile and maleic anhydride groups and acrylonitrile-OH groups.

Compatibility of the ternary system was obtained inside the miscibility region of the SAN/SMA blend, when the proportion of EVA-OH is 10% and that of the acrylonitrile and maleic anhydride groups is the same (45%). Evidences of the reaction that leads to compatibility are the strong decrease in the C—O band of a primary alcohol in the FTIR spectra of the ternary blend, the increase in the equilibrium torque that is proportional to the conversion degree of the EVA-OH terpolymer, and the increase in the glass transition (10°C) and degradation temperatures of the blend.

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REFERENCES

1. R. J. Koopmans, R. van der Linden, and E. F. Vansant, *Polym. Eng. Sci.,* **22,** 645 (1982).
2. R. Barbucci, M. Benvenuti, A. Magnani, and F. Tempesti, *Makromol. Chem.,* **193,** 2979 (1992).
3. T. O. Ahn, C. K. Kim, B. K. Kim, H. M. Jeong, and J. D. Huh, *Polym. Eng. Sci.,* **30,** 341 (1990).
4. G. W. Lohfink and M. R. Kamal, *Polym. Eng. Sci.,* **33,** 1404 (1993).
5. I. Hudek, M. M. Sain, and V. Sunova, *J. Appl. Polym. Sci.,* **49,** 425 (1993).
6. A. T. Koshi, B. Kuriakose, S. Thomas, C. K. Premalatha, and S. Varghese, *J. Appl. Polym. Sci.,* **49,** 901 (1993).

7. I. Ray, S. Roy, and D. Khastgir, *Polym. Bull.,* **30,** 685 (1993).
8. P. van Ballegooie and A. Rudin, *J. Appl. Polym. Sci.,* **39,** 2097 (1990).
9. S. Cimmino, E. Martuscelli, M. Saviano, and C. Silvestre, *Polymer,* **32,** 1461 (1991).
10. M. Hasegawa and S. Akiyama, *Polymer J.,* **20,** 471 (1988).
11. C. Chen and F. S. Lai, *Polym. Eng. Sci.,* **34,** 472 (1994).
12. H. Alberts, H. Bartl, L. Morbitzer, K. Riebel, U. Steffen, and G. Weber, *J. Appl. Polym. Sci., Appl. Polym. Symp.,* **36,** 165 (1981).
13. M. Lambla, J. Druz, and A. Bouilloux, *Polym. Eng. Sci.,* **27,** 1221 (1987).
14. G. H. Hu, J. T. Lindt, and M. Lambla, *J. Appl. Polym. Sci.,* **46,** 1039 (1992).
15. J. Chiu, *Appl. Polym. Symp.,* **2,** 25 (1966).
16. J. Chiu, *Anal. Chem.,* **40,** 1516 (1968).
17. D. R. Paul and J. W. Barlow, *Polymer,* **25,** 487 (1984).