

# Study of Blends of Nylon 6 with EVOH and Carboxyl-Modified EVOH and a Preliminary Approach to Films for Packaging Applications

S. DE PETRIS,<sup>1</sup> P. LAURIENZO,<sup>2</sup> M. MALINCONICO,<sup>2</sup> M. PRACELLA,<sup>1</sup> M. ZENDRON<sup>3</sup>

<sup>1</sup> Centro Studi sui Materiali Macromolecolari Polifasici e Biocompatibili, C.N.R., Via Diotisalvi, 2, 56100 Pisa, Italy

<sup>2</sup> Istituto di Ricerca e Tecnologia delle Materie Plastiche, C.N.R., Via Toiano, 6, 80072 Arco Felice (Naples), Italy

<sup>3</sup> SNIARICERCHE, Via Pomarico, 75010 Pisticci Scalo (MT), Italy

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**ABSTRACT:** Blends of nylon 6 (Ny6) with ethylene-*co*-vinyl alcohol (EVOH) and EVOH modified with the introduction of carboxyl groups (EVOH-COOH) have been studied by Fourier transform infrared spectroscopy, scanning electron microscopy, differential scanning calorimetry, and dynamic-mechanical thermal analysis. The thermal and thermomechanical analyses of the blends show that the melting, crystallization, and relaxational behavior are affected by the blend composition and the presence of carboxyl groups on the EVOH chains. Nevertheless, microscopic and thermal investigations demonstrate the biphasic nature of the two-blend systems. Selective solvent extraction of the EVOH or EVOH-COOH phase in their blends and Fourier transform infrared analysis of the residual products indicates the occurrence of ionic linkages between the amino groups of the polyamide and the carboxyl groups of the modified EVOH, whereas specific interactions are evidenced for Ny6/EVOH blends. Tests performed on extruded Ny6/EVOH films show that the addition of EVOH effectively reduces the gas permeability of Nylon, whereas the addition of small amounts of EVOH-COOH helps to control and stabilize melt rheology. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 637–648, 1998

**Key words:** polymer blends; nylon 6; ethylene-*co*-vinyl alcohol; chemical modification; phase interactions

## INTRODUCTION

Growing interest is witnessed in the development of new materials for packaging applications. One of the most attractive approaches is the use of polymer blends able to substitute multilayer films in rigid and flexible packaging. Advantages are expected both from the viewpoint of the processing and recycling of these materials. In fact,

multilayer films that are generally produced by means of coextrusion processes of chemically different polymer components require good adhesion between the layers, and the presence of a third component (tie layer)<sup>1</sup> is frequently necessary for improving adhesion and the other fundamental properties (barrier, mechanical, etc.).

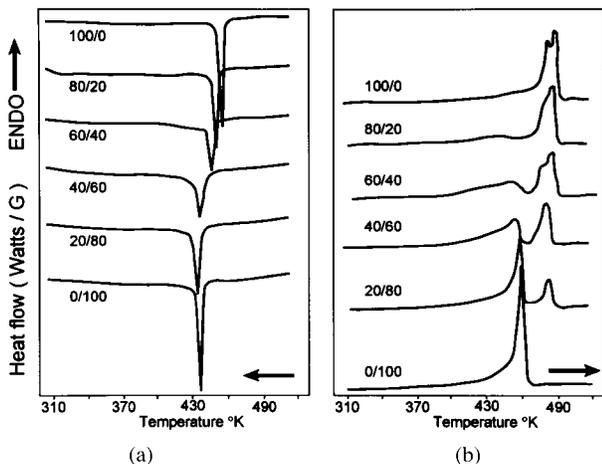
Recycling of these products is a very important issue due to the large amount of scraps generated during the production and use. However, reprocessing of the coextruded materials produces heterogeneous blends as a consequence of the presence of incompatible polymeric layers. This,

Correspondence to: P. Laurienzo (secre@mail.irtemp.na.cnr.it).

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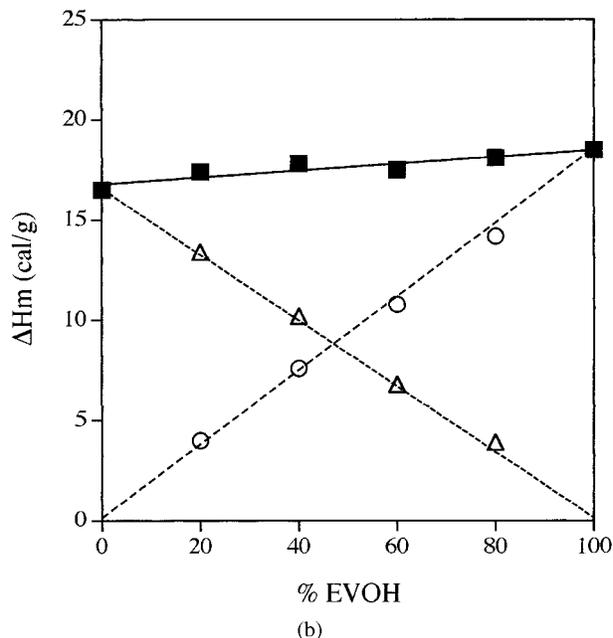
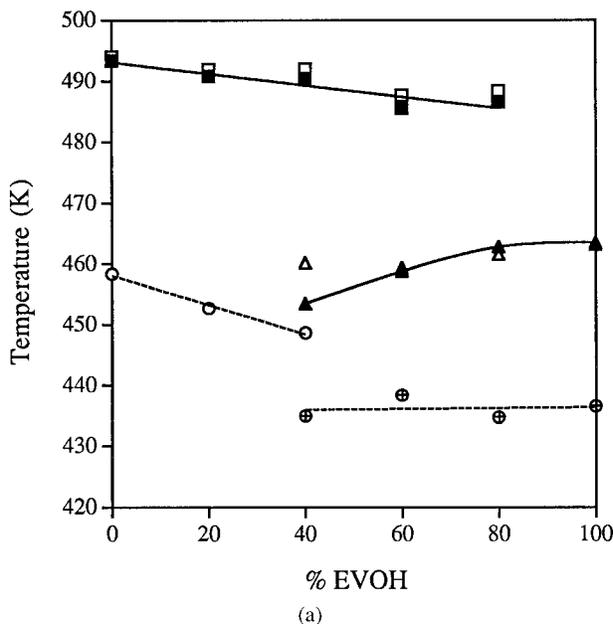
**Figure 1** DSC thermograms (normalized to 1 mg sample) of Ny6/EVOH blends at different compositions: (a) cooling run ( $-10^{\circ}/\text{min}$ ); and (b) second heating run ( $10^{\circ}/\text{min}$ ).

in turn, requires further compatibilization processes to make economically profitable the recovery of the scraps. In this respect, the use of monolayer films obtained by extrusion from blends should be much more promising both for economical and environmental reasons. They, in fact, can be recycled either during the production (primary recycling) or after use (secondary and tertiary recycling); moreover, a reduction in thickness and, hence in cost, is expected.

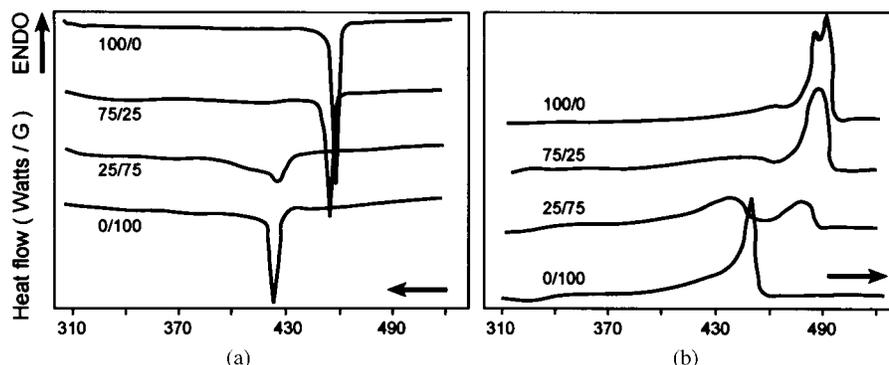
Low permeation to gases is, among others, one of the fundamental properties of films for packaging. Literature reports have shown that, by a proper combination of chemical physical properties and technology of processing, it is possible to realize monolayer films made by polymer blends with a multilayer-type internal structure.<sup>2-4</sup> This can be achieved by stretching the dispersed phase during processing (film blowing) or by varying the geometry of the extrusion die so that it will assume a laminar structure inside the matrix polymer. In some cases, as reported for extruded polypropylene/ethylene-co-vinyl alcohol (PP/EVOH) blends, the oxygen permeability can approach those obtained with a multilayer coextruded film when a laminar morphology of the dispersed barrier phase (EVOH) is formed in the core of the extrudate.<sup>3</sup> Similar results were reported for poly(ethylene terephthalate) blends.<sup>4</sup>

Herein, we focused the attention on the processing structure-property relationships of blends of nylon 6 (Ny6) with EVOH copolymers, both pure and modified with the insertion of acid groups

(EVOH-COOH) by reacting with succinic anhydride. The aim is that of assessing the potential of these systems for film packaging applications. The



**Figure 2** (a) Phase transition temperatures of Ny6/EVOH blends as a function of EVOH content. Melting temperature,  $T_m$  of Ny6 ( $\square$ ,  $\blacksquare$ ) and EVOH ( $\triangle$ ,  $\blacktriangle$ ) on the first and second heating runs, respectively; crystallization temperature,  $T_c$  of Ny6 ( $\circ$ ) and EVOH ( $\oplus$ ). (b) Enthalpy of melting,  $\Delta H_m$  (per gram of blend) of Ny6/EVOH blends on second heating run as a function of EVOH content. ( $\blacksquare$ ) Total  $\Delta H_m$ ; ( $\triangle$ )  $\Delta H_m$  of Ny6 phase; ( $\circ$ )  $\Delta H_m$  of EVOH phase.



**Figure 3** DSC thermograms (normalized to 1 mg sample) of Ny6/EVOH-COOH blends at different compositions: (a) cooling run ( $-10^{\circ}/\text{min}$ ); and (b) second heating run ( $10^{\circ}/\text{min}$ ).

presence of a small amount of carboxyl groups on the EVOH chains was expected to favor specific and/or chemical interactions with the polyamide components contributing to enhance the blend compatibility and, thus, melt stability and processability. Moreover, positive effects on the film properties—such as transparency, gas permeability, and mechanical resistance—can be obtained for the functionalized blends, due to the possibility of controlling the phase morphology and crystallinity. In the present work, preliminary results on extruded monolayer films are also reported.

## EXPERIMENTAL

### Materials

Commercial samples of Ny6 (ADS 40, SNIA) with an  $\eta_{\text{inh}}$  of  $2.9 \text{ dL g}^{-1}$  ( $c = 0.5 \text{ g dL}^{-1}$  in  $\text{H}_2\text{SO}_4$ ) and ethylene-vinyl alcohol copolymer (EVOH) containing 29 mol % ethylene (Soarnol D29) were used.

A carboxyl-modified EVOH (EVOH-COOH), containing about 2 wt % of grafted acid groups, was obtained through partial esterification of the hydroxyl groups of EVOH with succinic anhydride, according to a previously reported procedure.<sup>6</sup> Before mixing, all polymer samples were dried for 12–24 h at  $100^{\circ}\text{C}$  under vacuum to minimize hydrolytic degradation during processing.

### Blend and Film Preparation

Blends of Ny6 and EVOH were prepared at various compositions (20, 40, 60, and 80% by weight EVOH) by melt mixing in a Brabender internal mixer at  $245^{\circ}\text{C}$  and 30 rpm for 10 min under nitro-

gen flow. Blends of Ny6 and EVOH-COOH containing 25 and 75% by weight of EVOH-COOH, respectively, were prepared in Brabender under the same mixing conditions.

Films of Ny6/EVOH 75/25 binary blend and Ny6/EVOH/EVOH-COOH 73.2/24.4/2.4 ternary blend, with an EVOH-COOH to EVOH ratio of 1/10, were prepared by means of a pilot-scale monoextruder at SNIARICERCHE Labs (Pisticci, Italy).

Components were all mixed together in the chosen ratio and fed into the extruder (89.5 rpm), with a melt temperature of  $265^{\circ}\text{C}$ . A flat die allowed to get a cast film ( $30 \mu\text{m}$  thickness) onto a chill roll (uptake speed =  $7.0 \text{ m min}^{-1}$ ).

### Morphology

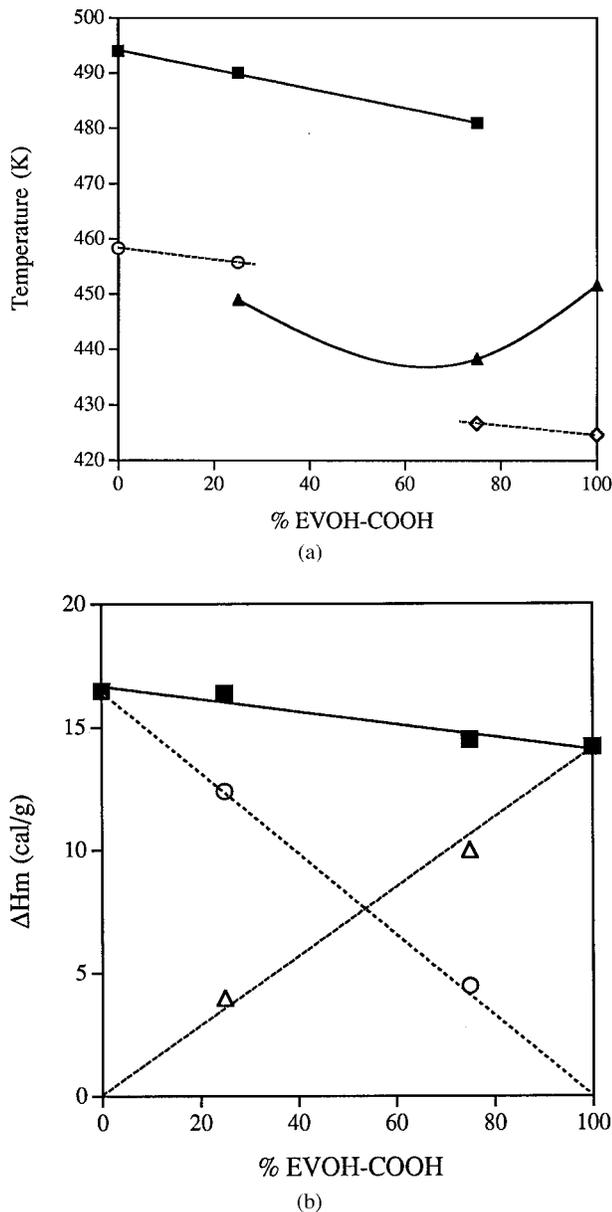
Scanning electron microscopic (SEM) analyses were conducted on all blends by a Philips model XL20, both on cryogenically fractured surfaces of melt-quenched samples and on films surfaces of nylon-matrix blends etched with boiling dioxane/water (1/1, v/v) mixture for 24 h. Such treatment allows for a selective dissolution of EVOH and EVOH-COOH phases.

### Infrared Spectroscopic Analysis

Fourier transform infrared (FTIR) spectra were performed by a Perkin-Elmer spectrometer model PARAGON 500 on compression-molded films, at a resolution of  $4 \text{ cm}^{-1}$  (10 scans collected).

### Thermal Analysis

Differential scanning calorimetry (DSC) measurements were conducted by a Perkin-Elmer DSC 2C



**Figure 4** (a) Phase transition temperatures of Ny6/EVOH-COOH blends as a function of EVOH-COOH content. Melting temperature,  $T_m$  of Ny6 (■) and EVOH-COOH (▲) on the second heating run; crystallization temperature,  $T_c$  of Ny6 (○) and EVOH-COOH (◇). (b) Enthalpy of melting,  $\Delta H_m$  (per gram of blend) of Ny6/EVOH-COOH blends on second heating run as a function of EVOH-COOH content. (■) Total  $\Delta H_m$ ; (△)  $\Delta H_m$  of Ny6 phase; (⊕)  $\Delta H_m$  of EVOH-COOH phase.

interfaced with Data Station 3600. The samples (5–7 mg) were first scanned from 30° to 250°C at a heating rate of 10°/min (first run) under nitrogen flow, then after cooling to 30°C (–10°/min) were

reheated through the melting range in the same conditions (second run). Blends isothermally crystallized from the melt and samples annealed at temperatures below the melting point of EVOH were also analyzed by DSC. The phase transition temperatures and enthalpies of the polymer components were determined from the maxima and the areas of the peaks after calibration with standard substances.

### Dynamic-Mechanical Analysis

A Polymer Labs DMTA was used for dynamical mechanical measurements. Samples were compression-molded into a bar and rapidly cooled at room temperature. Analysis was performed at a 1-Hz frequency in the range from –100° to 250°C at a heating rate of 4°C/min.

### Mechanical Testing

The tensile mechanical properties of films of Ny6, Ny6/EVOH and Ny6/EVOH/EVOH-COOH blends were studied by an Instron machine under controlled humidity and temperature conditions, according to the ASTM D882 testing method (testing rate: 50 mm min<sup>-1</sup>). Several specimens (an average at least six) of each film were tested to determine the mechanical parameters.

### Gas Permeability

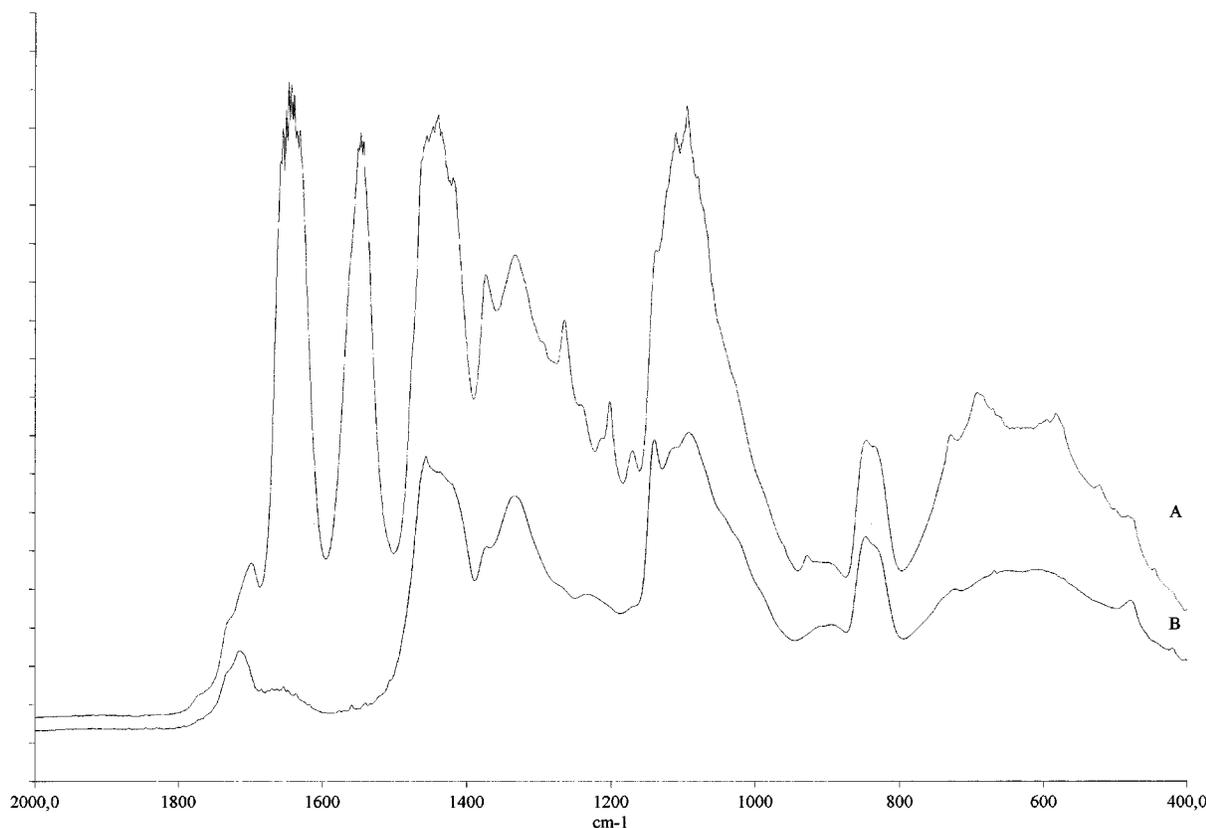
Permeability to oxygen was tested on films of Ny6 and blends by means of a MOCON apparatus model Oxtran 2/20 operating at controlled humidity and temperature conditions, according to the ASTM D3985 testing method.

## RESULTS AND DISCUSSION

### Characterization of Blends

#### DSC Analysis

Figure 1(a,b) shows the DSC traces of neat polymers and Ny6/EVOH blends at various compositions recorded on cooling from the melt and on the second heating run from 30° to 250°C, respectively. Melting traces of the blends as obtained from the Brabender mixer (first run) do not show any significant differences in the peak position, compared with the second heating run. It can be seen [Fig. 1(b)] that all blends display separated



**Figure 5** FTIR spectra in the range 2000 to 400  $\text{cm}^{-1}$  of: Ny6/EVOH-COOH 75/25 blend (A) and plain EVOH-COOH (B).

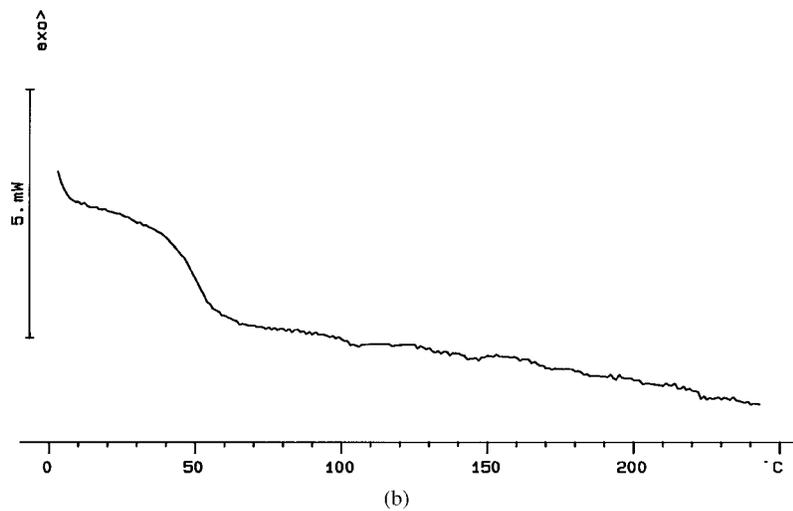
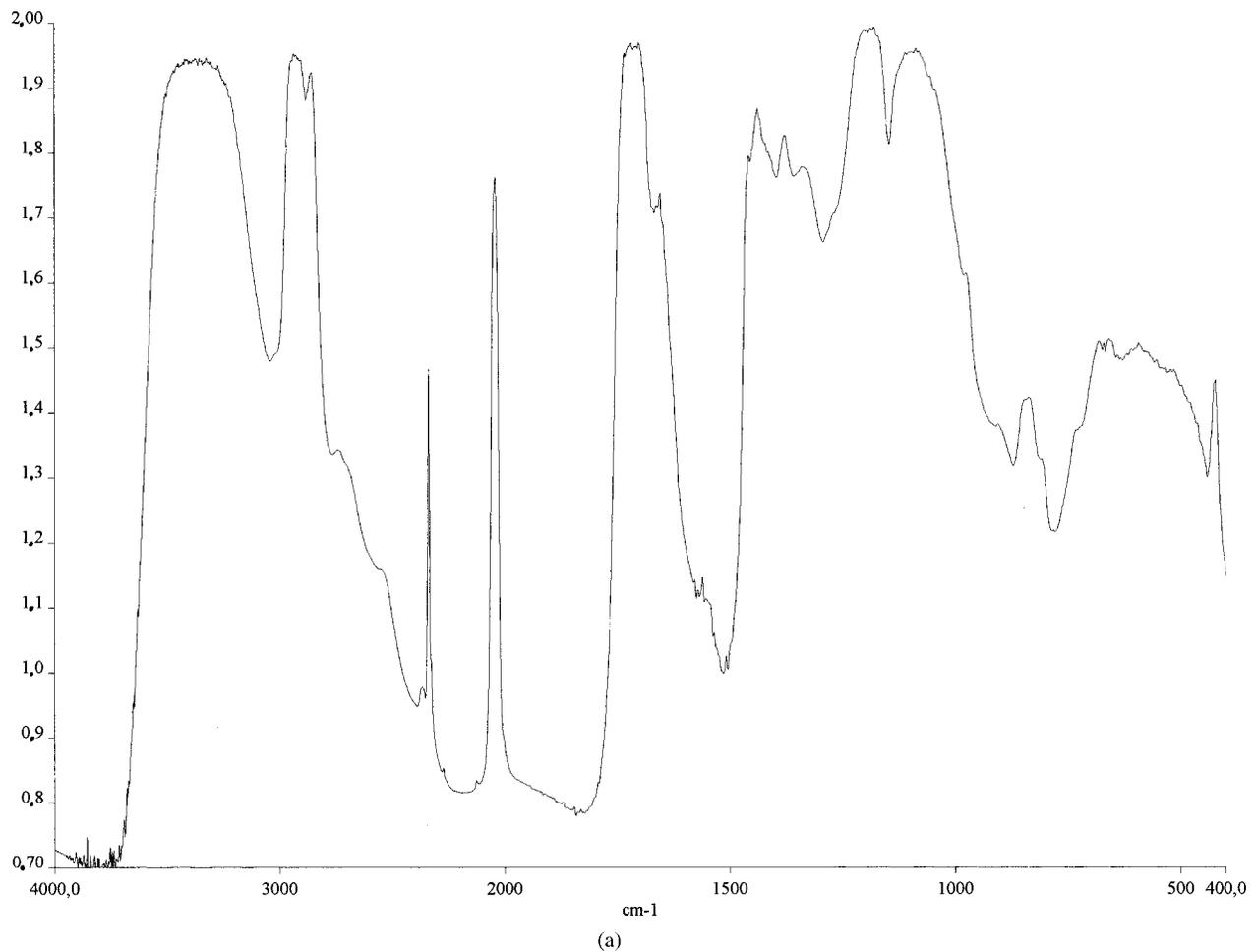
melting peaks of Ny6 and EVOH phases, as expected for a heterogeneous two-component system. On the contrary, a single exothermal transition is generally observed in the cooling thermograms of the blends from the melt [Fig. 1(a)] accompanied by a peak broadening in the intermediate composition range. Values of the melting ( $T_m$ ) and crystallization ( $T_c$ ) peak temperature are plotted in Figure 2(a) as a function of percentage of EVOH.

The  $T_c$  of Nylon-rich blends decreases from about 458°K (185°C) to about 449°K (176°C) in the range of 0–40% EVOH, whereas a value of about 436°K (163°C) is found for blends with EVOH content more than 60%, corresponding to the  $T_c$  of pure EVOH. In the latter case, crystallization of the dispersed polyamide results to be shifted to about 20° lower than its usual crystallization temperature and the values of the area of the crystallization peak correspond to the weighted sum of the crystallization enthalpies of the single components, indicating that Ny6 and EVOH crystallize almost coincidentally from the molten blends. Such an effect can be regarded as

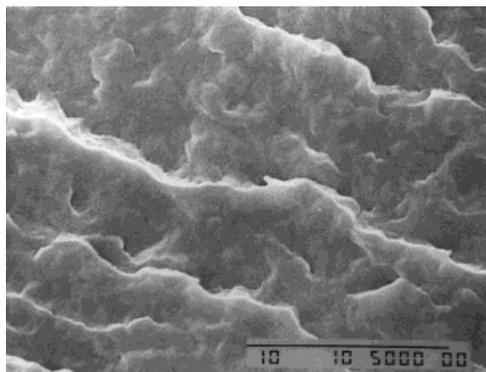
an indication of nucleating interactions between the two polymers.<sup>7</sup>

The melting temperatures of the two components in the blends are also depending to some extent on the composition. A decrease of the maximum peak temperature of Ny6 phase is observed over the whole composition range, from about 493°K (220°C) to about 487°K (214°C). For EVOH, the  $T_m$  (second run) decreases from about 463°K (190°C) to 453°K (180°C) for a content of 40% EVOH.

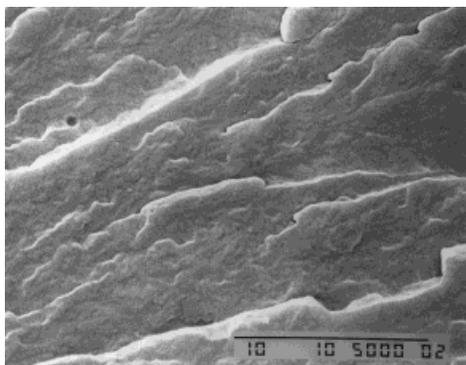
It should be noted from the thermograms in Figure 1(b) that the melting peak of the EVOH phase becomes progressively broader and shallower as the EVOH content decreases. This effect can be associated with the type and stability of the crystals that are formed on cooling from the melt and thus with the phase dispersion of the components in the blends. The same holds for the polyamide component when its content falls below 60 wt %. The appearance of the melting peak of Ny6 at a lower temperature in the blends, as compared with the plain polymer, can be related to kinetic effects due to the retarded or fractionated crystal-



**Figure 6** FTIR spectrum (a) and DSC thermogram (b; heating rate: 20°/min) of the residual fraction from Ny6/EVOH-COOH 25/75 blend after extraction with formic acid. (The poor resolution of FTIR spectrum is due to the difficulty of obtaining a thick film.)



(a)



(b)

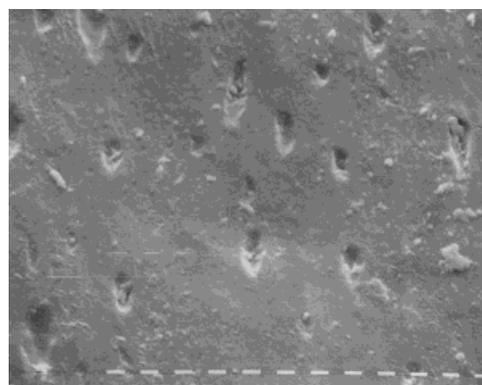
**Figure 7** SEM micrographs of fracture surfaces of Ny6/EVOH 80/20 (a) and Ny6/EVOH-COOH 75/25 (b) blends.

lization phenomena of the polyamide during cooling from the melt. Such phenomena, which are depending on the nucleation process of the dispersed phase, can affect the crystal structure of the polyamide.<sup>8,9</sup> In fact, it has been observed for compatibilized Ny 6/polyolefin blends that, when the polyamide is highly dispersed as small droplets (less than 1  $\mu\text{m}$ ), its crystallization can be shifted to temperatures as low as 403°–413°K (130°–140°C), thus giving rise to crystals of  $\gamma$ -form with a melting point near 488°K (215°C).<sup>10</sup> A similar conclusion was reported for blends of Ny6 with an ethylene-based polymer containing carboxyl or anhydride groups.<sup>11</sup>

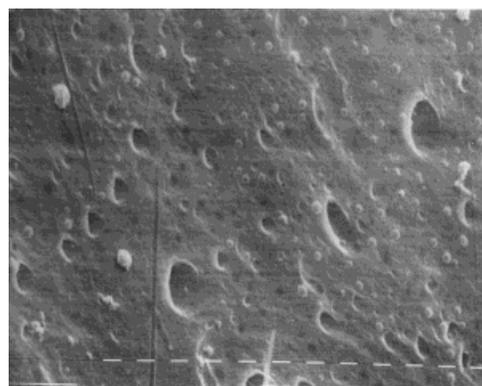
In Figure 2(b), the melting enthalpy,  $\Delta H_m$ , of the polymers in the blends is plotted as a function of the composition. It seems that, for each component, the  $\Delta H_m$  changes proportionally to its content, according to the presence of separated crystalline phases. Földes and Pukanszky<sup>5</sup> observed the occurrence of large variations of both melting temperature and enthalpy, with the composition

for blends of polyamide 6/66 and EVOH (Selar, Du Pont). These effects were ascribed to hydrogen-bonding interactions between the two polymers.

The cooling and heating (second run) thermograms of the functionalized blends Ny6/EVOH-COOH are shown in Figure 3(a,b). It can be noted that a larger variation of the crystallization and melting ranges are compared with Ny6/EVOH blends. In particular, plain EVOH-COOH displays lower crystallization and melting temperatures than EVOH. Values of the transition temperatures and the melting enthalpy of the polymer components are plotted versus the % EVOH-COOH in Figure 4(a) and Figure 4(b), respectively. It is worth noting that, for the 25/75 blend, both the crystallization and melting temperature of the Ny6 phase are lower than those observed for Ny6/EVOH 20/80 blend, thus suggesting that the presence of the carboxyl groups on EVOH gives rise to

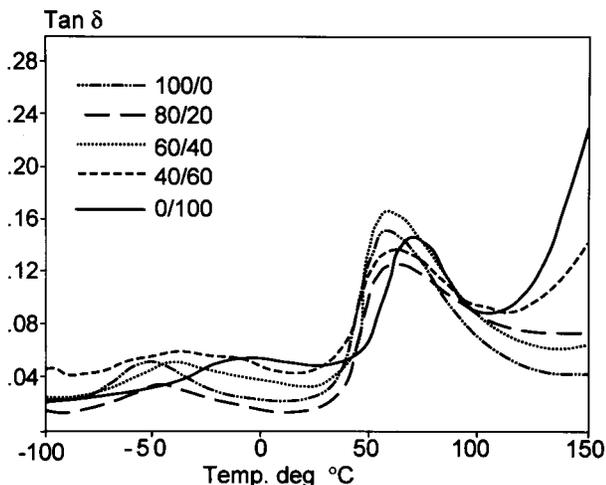


(a)



(b)

**Figure 8** SEM micrographs of smoothed surfaces after etching of Ny6/EVOH 80/20 (a) and Ny6/EVOH-COOH 75/25 (b) blends.



**Figure 9** Tan  $\delta$  curves versus temperature for Ny6/EVOH blends at different compositions.

stronger interfacial interactions with the dispersed polyamide.

#### Infrared Analysis

As the thermal analysis indicates that both  $T_c$  and  $T_m$  of the blend components are a function of composition, the possible occurrence of specific interactions between the polymers was investigated by FTIR analysis. Our studies confirmed the existence of specific interactions between the N—H of Ny6 and the O—H of EVOH, as reported by other authors.<sup>5</sup> Moreover, in the functionalized blends, a shift of about  $15\text{ cm}^{-1}$  of the C=O stretching of the acid group of EVOH—COOH (from  $1715$  to  $1698\text{ cm}^{-1}$ ) was noted (Fig. 5). This significant shift is attributed to very strong physical interactions between the —COOH and the amido and/or the amino-end functionalities of nylon.

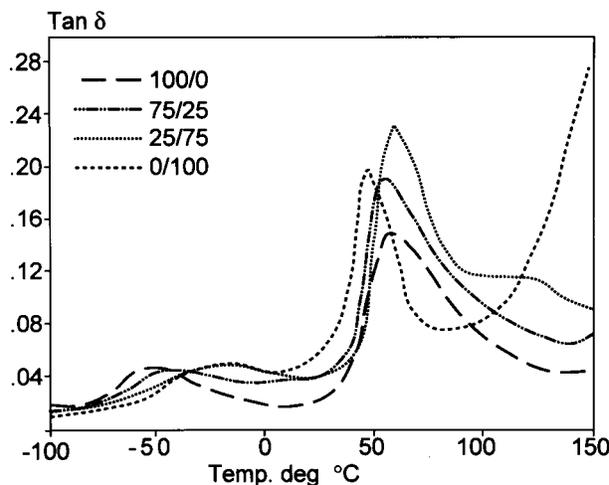
To check the occurrence of a chemical reaction, selective extraction aimed to isolate an intermediate, copolymeric phase has been made on the Ny6/EVOH—COOH 25/75 blend.

#### Chemical Characterization

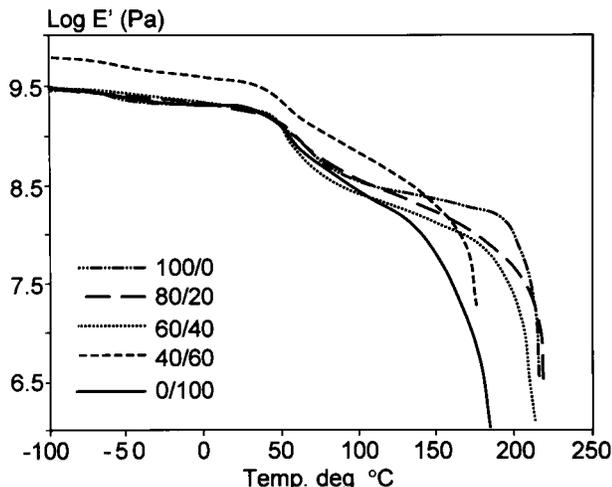
A selective extraction of the EVOH component by a boiling dioxane/water (1/1 v/v) mixture has been done on Ny/EVOH 20/80 and Ny6/EVOH—COOH 25/75 blends. The Ny6/EVOH blend leaves a solid residue of about 60% by weight, which has been analyzed by FTIR and DSC, and consisted of both polymers, whereas the soluble fraction consists of plain EVOH.

This is another evidence of strong interactions between the polymers that are very interassociated. For what concerns the Ny6/EVOH—COOH blend, the dioxane/water mixture extracts only a minor soluble fraction (about 10% by weight) after prolonged heating, which consists of EVOH—COOH.

To investigate on the occurrence of a chemical reaction between the amino groups of the polyamide and the carboxyl groups of the modified EVOH, the Ny6/EVOH—COOH blend has been treated with a nonselective solvent, namely formic acid. For sake of comparison, the Ny6/EVOH blend too has been treated with formic acid. Whereas the Ny6/EVOH blend is totally soluble, the Ny6/EVOH—COOH blend leaves a fraction of about 50% by weight. The soluble and insoluble fractions have been characterized by FTIR. Although the soluble fraction consists of both components with no variation in the spectrum respect to the overall blend, the insoluble one is very rich in EVOH and shows two additional bands at  $2336$  and  $2042\text{ cm}^{-1}$  [Fig. 6(a)]. These bands are very characteristic of an ammonium salt of a primary aliphatic amine ( $-\text{NH}_3^+$  and  $\text{C}-\text{N}^+$  stretching, respectively). This result can be probably explained as the formation of an ionic linkage between the —COOH of modified EVOH and the amine end groups of Ny6. The low intensity of the amidic bands of Ny6 ( $1650$  and  $1550\text{ cm}^{-1}$ ) could be due to the fact that the salification reaction occurs preferentially with the lower molecular weight molecules of Ny6, richer in amino groups. This is also confirmed by the strong carboxylic



**Figure 10** Tan  $\delta$  curves versus temperature for Ny6/EVOH—COOH blends at different compositions.



**Figure 11** Young's moduli,  $E'$ , versus temperature for Ny6/EVOH blends at different compositions.

acid stretching band around  $1710\text{ cm}^{-1}$ , due to the end acid groups of nylon.

The DSC analysis of this product [Fig. 6(b)] shows that it is totally amorphous, with a  $T_g$  of  $49^\circ\text{C}$ . Moreover, successive experiments of slow cooling and reheating demonstrate that the product is not able to crystallize. This result supports the hypothesis of the formation of an ionic complex between the polymers that is stable until  $250^\circ\text{C}$ .

### Morphology

Micrographs of liquid  $\text{N}_2$  fracture surfaces of two selected blends, namely Ny6/EVOH 80/20 and Ny6/EVOH-COOH 75/25, are reported in Figure 7(a,b) as obtained by scanning electron microscopy. It is evident that the blends are featureless, as consequence of the highly entangled morphology. In an attempt to clarify the morphology, smoothed surfaces of nylon-based blends have been exposed to dioxane/water vapors. The results of the extractions of 80/20 Ny6/EVOH blend is reported in Figure 8(a). The etching reveals cavities on the surface whose dimensions are in the range of  $1\text{--}2\ \mu\text{m}$ . Similar etching is conducted on the Ny6/EVOH-COOH 75/25 blend, and the result is reported in Figure 8(b). It is evident that, apart from cavities of  $1\text{--}2\ \mu\text{m}$  size, a large number of spherical domains, about  $0.2\ \mu\text{m}$  diameter, not extracted but protruding from the surface, as if they were swollen by the solvent vapors, appear. In view of the above chemical characterization,

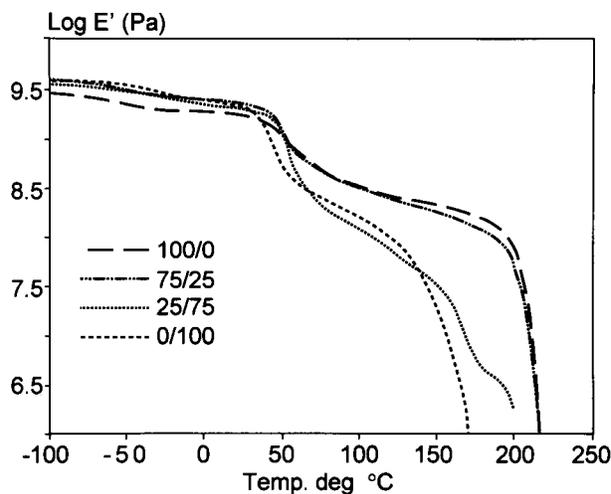
it is likely that such domains are constituted by Ny6/EVOH-COOH ionic interpolymeric complex, no more soluble in the etching solvent.

### Dynamic-Mechanical Analysis

DMTA curves of  $\tan \delta$  performed on samples of Ny6/EVOH and Ny6/EVOH-COOH blends in the range from  $-100^\circ$  to  $250^\circ\text{C}$  are shown in Figures 9 and 10, respectively, as a function of temperature. The corresponding curves for Young's modulus are shown in Figures 11 and 12.

In the investigated temperature range, both the pure polymers show two relaxation peaks centered at about  $60^\circ$  and  $-50^\circ\text{C}$  for Ny6 and at about  $70^\circ$  and  $-8^\circ\text{C}$  for EVOH. The high temperature peaks ( $\alpha$ -peak) are commonly ascribed to the glass transition. The low temperature peak ( $\beta$ -peak) of Ny6 has been interpreted<sup>11</sup> as due to the segmental motions of amide groups not bonded to other amide groups.

More complex is the interpretation of the low temperature peak of EVOH. In fact, due to the presence of  $-\text{OH}$  groups, EVOH is very hygroscopic, and this greatly affects mechanical properties and measurements. As a matter of fact, in EVOH, the  $-\text{OH}$  groups can form intermolecular hydrogen bonds that can be broken by absorbed water molecules. In the interpretation of Takayanagi,<sup>12</sup> the local twisting motion of chain segments around which the intermolecular hydrogen



**Figure 12** Young's moduli,  $E'$ , versus temperature for Ny6/EVOH-COOH blends at different compositions.

**Table I Effect of Composition on Loss Peaks Temperatures ( $T_\alpha$ ,  $T_\beta$ ) and Glass Transition Temperature ( $T_g$ ) of Ny6/EVOH Blends**

Ny6/EVOH	$T_\alpha$ (°C)	$T_\beta$ (°C)	$T_g$ (°C; DSC)
100/0	58	-50	56
80/20	62	-45	54
60/40	60	-40	54
40/60	62	-37	54
20/80	62	-18	59
0/100	70	-8	65

bonds have been broken, could be responsible for the low temperature  $\beta$ -peak of EVOH.

In Tables I and II, the observed transition temperatures ( $T_\alpha$ ,  $T_\beta$ ) of Ny6/EVOH and Ny6/EVOH-COOH blends are reported for the various compositions examined. In Ny6/EVOH blends, a single  $\alpha$ -transition is observed at about 60°C, whereas the  $\beta$ -transition occurs at temperatures intermediate between those of the pure components (-50°C to -8°C). The temperature  $T_\beta$  of Ny6 in the blends is found to increase as the EVOH content increases. In particular, for blends with Ny6 content lower than 60%, the  $\beta$ -peak appears as a very broad transition, including both the  $\beta$ -transitions of the two components (Fig. 9). This shifting of the  $\beta$ -peak can be considered as an indication of the presence of intermolecular interactions between the amide groups of Ny6 and hydroxyl groups of EVOH.

In the blends containing the functionalized EVOH (Fig. 10) the  $\alpha$ -transitions occur at lower temperatures and display higher  $\tan \delta$  peak intensity, with respect to those of Ny6/EVOH blends, thus suggesting a lower degree of order and/or high molecular mobility, compared with nonfunctionalized systems. This is in good agreement with the decrease of the  $\Delta H_m$  values of EVOH-COOH with respect to EVOH, as shown in Figures 2(b) and 4(b).

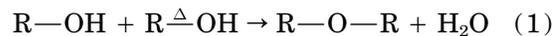
The  $\beta$ -transition is seen again increasing with the EVOH content, although the peak temperature of plain EVOH-COOH is lower than that of plain EVOH (Table II). However, the  $\beta$ -peak of 25/75 blend practically coincides with that of EVOH-COOH. These findings, even taking into account the limited composition ratio of the examined functionalized blends, suggest the occurrence of strong phase interactions between the components mainly in Ny6-rich samples.

The Young's modulus  $E'$  of both the blend sys-

tems (Figs. 11 and 12) does not seem to be greatly affected by the blend ratio and functionalization, with the exception of Ny6/EVOH 40/60, which shows a slightly higher value than the plain components. The same holds for  $T_g$  values, as confirmed by DSC analysis (Tables I and II), taking into account the small difference between the glass transition temperatures of the pure components.

### Preliminary Characterization of Films

The system Ny6/EVOH has been processed in films on a single screw extruder normally used for Ny6 processing. It has been observed as a serious melt instability, because after a few minutes of running, gel formation became apparent, up to a point that the same formation of the film is hindered. We believe that this is due to a progressive phase separation that occurs in the melt, when hydrogen bonding between polyamide and EVOH are weakened by temperature (260°C). Thus, EVOH tends to phase-separate in larger regions, where EVOH chains spontaneously undergo gelation through etherification with the elimination of water<sup>13</sup>:



Gel formation is strongly reduced when a few percentages of EVOH-COOH are added to the blend. In our opinion, this is more clear evidence of the formation of a stable ionic interaction between Ny6 and EVOH-COOH that is not destroyed during the extrusion process. In fact, due to its presence, the interface between Ny6 and EVOH is stable in the melt, and phase aggregation is prevented or, at least, kinetically delayed so much to overcome all problems of gel formation.

Mechanical analysis has been performed on extruded films of plain nylon, of a binary Ny6/EVOH 75/25 blend, and of a ternary blend of

**Table II Effect of Composition on Loss Peaks Temperatures ( $T_\alpha$ ,  $T_\beta$ ) and Glass Transition Temperature ( $T_g$ ) of Ny6/EVOH-COOH Blends**

Ny6/EVOH-COOH	$T_\alpha$ (°C)	$T_\beta$ (°C)	$T_g$ (°C; DSC)
100/0	58	-50	56
75/25	53	-42	50
25/75	56	-20	57
0/100	45	-20	65

**Table III Mechanical Parameters of Plain Ny6 and Blends Films**

Sample	Tensile Break Strength (MPa)	Tensile Elongation Break (%)	Elastic Modulus (MPa)
Ny6	123	478	640
Nylon/EVOH (75/25)	108	440	590
Nylon/EVOH/EVOH-COOH (73.2/24.4/2.4)	104	429	630

composition: 73.2% nylon, 24.4% EVOH, and 2.4% EVOH-COOH. The films (particularly those of Ny6/EVOH blend) show a diffused presence of gel probably due to degradative phenomena (see above), so the results may be affected by these "defects" that could cause a lower break deformation. Anyway, we can observe from Table III that there are no big differences between the blends for what concerns stress and strain break values, which are lower than for nylon, whereas the elastic modulus is lower only in the binary blend.

An oxygen permeability test has been performed on the ternary blend, because it is the only blend that gives a film with at least a reduced presence of gels. The obtained value [about 10 mL/(m<sup>2</sup> day atm)] is 2 orders of magnitude higher than that of a coextruded film with the same percentage of EVOH. At any rate, this value, is lower than that theoretically expected for the blend with the unmodified EVOH, calculated as the weighted sum of the permeabilities of the single components.

No significant differences have been noted in DSC and FTIR analyses of films respective to the blends.

## CONCLUSIONS

The study of chemical, physical, and mechanical properties of blends of Ny6 with EVOH and carboxyl-modified EVOH clearly evidenced the presence of strong intermolecular interactions between the polymer components and the occurrence of ionic linkages that are formed between the functional groups of Ny6 and EVOH-COOH during the melt blending process. This process is responsible for the formation of new ionic copolymers that can play the role of compatibilizing agents for the systems presented herein.

The results of thermal analysis show that the

crystallization process of the blends is largely affected by the composition and functionalization of the EVOH component. The occurrence of coincident crystallization of both components can be correlated with the low interfacial energies between the phases and the high degree of dispersion of the polyamide, which depends on the interactions in the melt.

The dynamic-mechanical analysis of blends of Ny6 and EVOH gives evidence of phase interactions between the two components, as revealed by the large variations of the tan  $\delta$  peak location on the temperature scale and their intensity.

Preliminary characterization of films processed into monoextruders have shown that the permeability of nylon is effectively modified by the EVOH, whereas the chemical-physical (as well as the mechanical) properties remain only slightly perturbed. Morphological investigation seems to indicate that the EVOH-COOH acts as an interfacial agent.

More work is in progress to understand better and control the rheology of the system and to analyze the influence of processing on the morphology and properties of the blends.

## REFERENCES

1. M. M. Alger, T. J. Stanley, and J. Day, in *Barrier Polymers and Structures*, American Chemical Society Edition, Washington, DC, 1990, p. 203.
2. D. E. Kirckpatrick and D. Ranck, in *Plastic Film Technology*, Vol. 1, K. M. Finlayson, Ed., Technomic Publishers, 1989, p. 173.
3. G. W. Lohfink and M. R. Kamal, *Polym. Eng. Sci.*, **33**, 1404 (1993).
4. K. M. Kit, J. M. Schultz, and R. M. Gohil, *Polym. Eng. Sci.*, **35**, 680 (1995).
5. E. Földes and B. Pukanszky, *4th European Symposium on Polymer Blends*, Capri, Italy, May 24-26, 1993, Abstract, p. 140.

6. M. A. Del Nobile, P. Laurienzo, M. Malinconico, G. Mensitieri, and L. Nicolais, *Packag. Technol. Sci.*, **10**, 95 (1997).
7. H. French and B.-J. Jungnickel, *Third European Symposium on Polymer Blends*, Cambridge, UK, 1990, Abstract D12.
8. B. Wunderlich, in *Macromolecular Physics*, Vol. 3, *Crystal Melting*, Academic Press, New York, 1980, p. 186, and refs. therein.
9. G. Gurato, A. Fichera, F. Grandi, R. Zannetti, and P. Canal, *Makromol. Chem.*, **175**, 953 (1974).
10. M. Pracella, E. Marin, M. Psarski, A. J. Muller, and M. Malinconico, *European Symposium on Polymer Blends*, Maastricht, The Netherlands, 1996, Abstract 216.
11. H.-K. Chuang and C. D. Han, *J. Appl. Polym. Sci.*, **30**, 2431 (1985).
12. M. Takayanagi, in *Anelastic and Dielectric Effects in Polymeric Solids*, N. G. McCrum, B. E. Read, and G. Williams, Eds., Wiley, London, U.K., 1967.
13. H. F. Mark and N. G. Gaylord, Eds., *Encyclopedia of Polymer Science and Technology*, Vol. 14, Wiley, New York, 1971, p. 173.