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Miscibility behavior of Poly(vinyl alcohol)/Nylon 6 blends and their reactive blending with Poly(ethylene-co-ethyl acrylate)

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Melt-mixed blends of Poly(vinyl alcohol) (PVOH) with Nylon 6 were found to have good mechanical properties in the entire composition range. Determination of the glass transition temperature by dynamic mechanical analysis showed one broad T_g for the compositions rich in Nylon 6. In the case of the blends rich in PVOH, two T_g's were obtained, one close to that of the pure PVOH and another one in the region between the T_g's of the pure components. Characterizing blends with differential scanning calorimetry indicated a depression of the equilibrium melting point of Nylon 6. From the melting point data of the high T_m component, a value for the polymer–polymer interaction of $\chi_{12} = -0.05$ was derived using the simplified Nishi–Wang equation. Ternary blends composed of PVOH/Nylon 6/Poly(ethylene-co-ethyl acrylate) (PEEA) were prepared under reactive conditions in order to examine the possibility of using them as oxygen barrier material. The bonding of the ethylenic copolymer through reactive processing to the PVOH/Nylon 6 binary is expected to facilitate dispersion as well as interfacial adhesion in the case of mixing the above ternary in a polyethylene matrix. © 1998 Published by Elsevier Science Ltd. All rights reserved.

(Keywords: nylon 6; polyvinyl alcohol; polyethylene-co-ethylacrylate)

INTRODUCTION

Polymers with high gas barrier properties is one of the fastest growing areas in food packaging products[1]. Examples of polymers that are good barriers against oxygen are poly(vinyl alcohol), ethylene-vinyl alcohol copolymer, polyamide 6 and poly(ethylene terephthalate)[2]. Since these materials must also possess other properties, one polymer cannot always fulfill all the requirements. For this reason, a combination of polymeric materials is employed, mostly by the multilayer coextrusion technology. However, this technology, requires high capital and complex control and also presents recyclability limitations. An alternative approach for achieving desirable properties by using immiscible polymer blends has been proposed[3].

Combination of a thermoplastic barrier material with a lower cost matrix polymer, such as polyethylene, could be achieved in a single-step operation offering process versatility and low product costs[3-5]. In recent years EVOH has received considerable industrial attention due to PVOH processing shortcomings. An alternative proposal to EVOH could be the binary of PVOH with polyethylene, which is indeed incompatible. In order to achieve good adhesion of the PVOH dispersions in the polyethylene matrix, polyethylene copolymers containing reactive groups towards PVOH seemed to be the proper solution. However the strong intramolecular hydrogen bonding in PVOH[6-9] resulted in PVOH/polyethylene copolymer blends having poor mechanical properties for compositions rich in PVOH[10]. Taking into account a previous work on the reactive compatibilization of Nylon 6 with polyethylene copolymers[11,12], the recent findings on the semicompatibility of copolyamides with PVOH[13] and ethylene vinyl alcohol[14], as well as the patent literature referring to mixtures of PVOH/Nylons dispersed in polyolefine matrixes[15,16], addition of Nylon 6 seemed to be the answer to the incompatibility of the previous binary. Nylon 6 can be reactively mixed with polyethylene copolymers and additionally being a polar polymer it may possibly form hydrogen bonds with PVOH, resulting in opening the tight structure of PVOH thus improving the blending of PVOH with the polyethylene copolymer.

This work presents a study on the miscibility behavior of the binary blends of PVOH with Nylon 6 as well as a study on the properties of its ternary with PEEA.

EXPERIMENTAL

Materials and specimen preparation

PVOH (Mowiol 8–88) was supplied by Hoechst A.G. Its $\overline{DP}_n$ was given as 1400, $\bar{M}_n$ as 67 000 gmol^{-1} and the degree of hydrolysis (saponification) 88 mol%. Nylon 6 was obtained from BDH, and was found to have $n = 0.778$ dl/g in formic acid 85% at 25°C and $\bar{M}_n = 20\,600$. Its amount of amine end groups was estimated by titration to be 52.5 equiv/10^6 gr. PEEA with 18% w/w acrylic ethyl ester was obtained from Aldrich (Europe). All materials were dried in a vacuum oven at 60°C for 48 h to remove sorbed water before processing.

Blends were prepared by melt-mixing in a stainless steel home-made batch mixer, consisting of a cylindrical rotor, rotating into a thermostated cylindrical cup at about 100 rpm. The base of the rotor was tapered into a flat cone (ca. 2°). Mixing was carried out under a blanket of inert gas (Ar) and the maximum amount produced per batch was ca. 10 g. Temperature and blending time were varied to

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obtain improved ultimate tensile properties, in particular elongation at break. Optimum mixing condition were determined to be 230°C and a mixing time of 7 min for the binary and 15 min for the ternary. In the case of the ternary blends addition of catalyst, dibutyl tin dilaureate 0.8% w/w, was required. Blending experiments were repeated at least two times to assure that the blending procedure was reproducible.

Compositions prepared under these conditions for the binary PVOH/Nylon 6 were 3/1, 2/1, 1/1, 1/2, 1/3. The respective ternaries were based on ratios 2/1, 1/1 and 1/2 of the binary with the addition of 10 and 20% PEEA. Films were made by compression moulding between teflon sheets at 250°C and 70 kg cm^{-2}, pressure release and quenching to 0°C.

Apparatus and procedures

Tensile tests were performed according to ASTM D882 at 23°C using a J.J. Tensile Tester type T5001 and film strips with dimensions 4.0 cm × 0.65 cm × 0.025 cm. Data reported was obtained at a crosshead speed of 10 cm min^{-1}.

DSC measurements were carried out in an inert atmosphere using a DuPont 910 calorimeter system coupled with a 990 programmer recorder. Calibration was carried out with indium standard. Sample weight was ca. 10 mg and the heating rate was 20°C min^{-1}. The samples were heated up to 250°C, quenched to −80°C followed by heating to 250°C. The second heating scan was recorded.

The DMA data, loss tangent (tanδ) and complex modulus $|E^*|$ was obtained at 110 Hz using a direct-reading viscoelastometer (Rheovibron model DDV II-C). Specimen dimensions were 3.0 cm × 0.20 cm × 0.02 cm.

SEM was carried out with a Jeol model JSM-5200 instrument. Etched surfaces were examined at a tilt angle of 30°.

RESULTS AND DISCUSSION

Binary system of PVOH/Nylon 6

In an attempt to compatibilize PVOH with PEEA copolymer, Nylon 6 was found as the proper polar polymer to facilitate mixing and subsequent reaction of the above mentioned pair. Surprisingly, only a few recent papers relating to the miscibility behavior of copolyamides with vinyl[13] or ethylene-vinyl alcohol[14] have been published. Moreover, few patents referring to the dispersion of mixtures of PVOH/Nylons in polyolefine matrixes[15,16] were found. Since there is no direct evidence for the miscibility behavior of PVOH/Nylon 6 blend it was decided to study this binary.

Mixtures of two crystalline polymers have attracted some attention[17-22] mainly because of the technological interest of these blends. In our case melt-mixed blends of PVOH/Nylon 6 at various compositions were prepared and characterized using dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), tensile testing, scanning electron microscopy (SEM), while the interaction parameter, χ_{12}, was estimated using the observed melting point depression and the simplified equation of Nishi–Wang.

Tensile testing

The mechanical properties under large deformation were examined for this binary system and the results in terms of ultimate stress, σ_b and strain ε_b are given in *Table 1* and *Figure 1*. As the amount of Nylon 6 is increased there is a small reduction of σ_b but except from the composition 1/2, in all other blends high values of σ_b above 50 MPa, were obtained. The ε_b values of PVOH was indeed improved with the addition of Nylon 6 and remained at high levels for all the studied blends. Especially in blend 1/3 the obtained ε_b value exceeded even that of the pure Nylon 6, showing the enhanced mechanical properties of the studied system.

Table 1 Ultimate properties of the binary blends

Blends of PVOH/Nylon 6	σ_y (MPa)	σ_b (MPa)	ε_b (%)
1/0	—	79 ± 13	10 ± 3
3/1	61 ± 4	58 ± 5	330 ± 16
2/1	46 ± 8	56 ± 8	370 ± 67
1/1	20 ± 7	49 ± 8	510 ± 114
1/1[a]	41 ± 6	48 ± 8	24 ± 8
1/2	25 ± 5	36 ± 13	557 ± 74
1/1[a]	—	52 ± 7	17 ± 4
1/3	38 ± 4	60 ± 5	640 ± 31
0/1	35 ± 4	72 ± 7	583 ± 72

[a] PVOH with 98–100% degree of hydrolysis

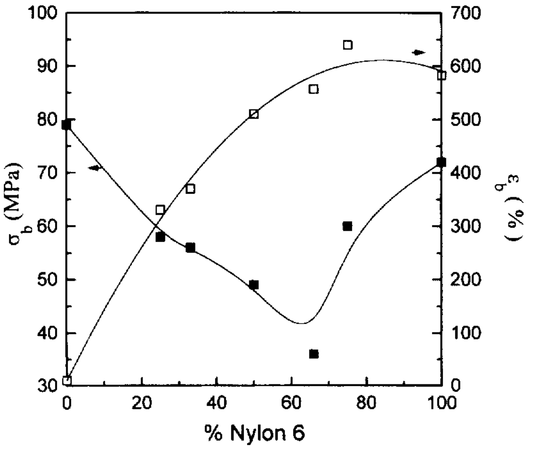

Figure 1 Composition dependence of ultimate properties of PVOH/Nylon 6 blends

Since the PVOH used was partially hydrolyzed the influence of the degree of hydrolysis was also examined. Thus mixtures of PVOH fully hydrolyzed (98–100%) with Nylon 6 at compositions 1/1 and 1/2 were also prepared. The results are presented in *Table 1*, where the significantly reduced values of ε_b show that these mixtures are incompatible. This observation can be attributed either to a more tight structure resulting from the higher degree of intramolecular hydrogen bonding in this type of PVOH, or to a displacement of the phase diagram requiring higher temperatures for the miscibility of the molten components. Moreover it is known from other studies[23] that the higher degree of hydrolysis leads to a lowering of intrinsic viscosity which might have negative influence on melt-mixing of the components.

The results discussed in the next sections refer to blends with lower degree of hydrolysis PVOH.

Dynamic mechanical properties

The dynamic mechanical properties in terms of the temperature dependence of the loss modulus E'' of the quenched blends are presented in *Figure 2*. It is clear that the blends show one broad transition between those of the

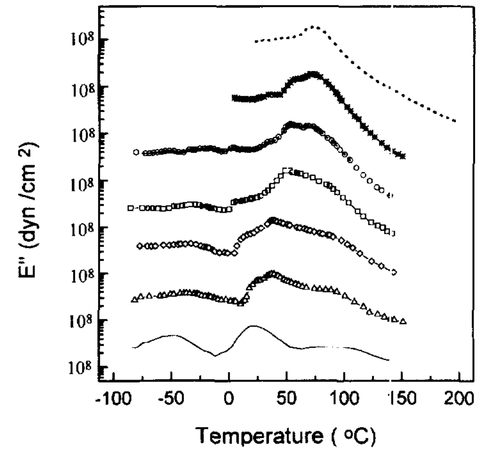

Figure 2 Temperature dependence of the loss modulus (E'') of PVOH/Nylon 6 blends; (·····) PVOH; (—) Nylon 6; (*) 3/1; (○) 2/1; (□) 1/1; (◇) 1/2; (△) 1/3

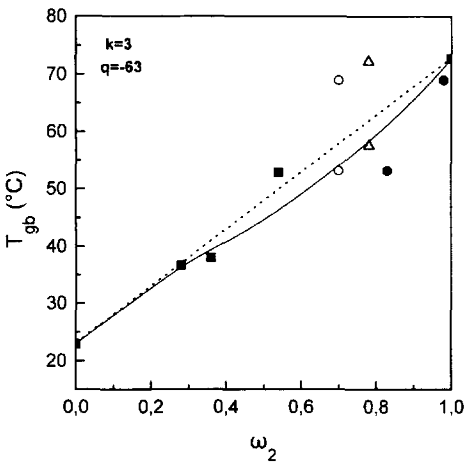

Figure 3 Glass transition temperature (°C) plotted as a function of composition (weight fraction of the amorphous PVOH); (■), (○), (△) experimental data; (●) data derived from Fox equation for 2/1 blend

Table 2 Viscoelastic and thermal properties of blends

Blends of PVOH/ Nylon 6	Glass transition[a] (°C)	Melting point[b] (°C)	Crystallinity[b] of	
			Nylon 6	PVOH
1/0	73	—[c]	—	16
3/1	57–72	209	32	9
2/1	53–69	210	35	13
1/1	53	211	33	15
1/2	38	213	29	14
1/3	37	214	30	14
0/1	23	218	27	—

[a] Results from DMA
[b] Results from DSC
[c] Broad transition

pure components. The broadness of T_g cannot be interpreted as immiscibility[24] since PVOH also shows a broad T_g. The fact that the T_g of the blends is in the region between the transitions of PVOH and Nylon 6 confirms the semi-compatible nature of the quenched blends. This displacement of the T_g as a function of the composition is shown in *Table 2*. For the compositions of 3/1 and 2/1 two distinct transitions appear showing that two phases are present.

The dependence of T_g on blend composition can be evaluated using the Kwei equation[25]

$$T_{\mathrm{gblend}} = \frac{T_{\mathrm{g1}} + \omega_2\left(kT_{\mathrm{g2}} - T_{\mathrm{g1}}\right)}{1 + \omega_2(k-1)} + q(\omega_2 - \omega_2^2) \qquad (1)$$

where T_{g1} and T_{g2} are the T_g's of the Nylon 6 and PVOH, respectively, and ω_2 is the weight fraction of PVOH in the amorphous phase. Parameter k is formally equal to $\Delta\alpha_2/\Delta\alpha_1$ where $\Delta\alpha$ is the change in the expansion coefficient at T_g, and it is generally used as an empirical fitting parameter. Parameter q is also determined as an empirical fitting parameter and is relevant to the stabilization energy of the backbones in the blend and takes positive or negative values.

Figure 3 shows the glass transitions of the blends as a function of PVOH composition. For the composition 3/1 two T_g's are observed, one very close to the T_g of PVOH and another one in the region between those of the pure materials. This blend was excepted from the following analysis as one of the phases formed seemed to be pure PVOH and thus made it difficult to determine the composition of the other phase. For the composition 2/1 the percentage of the components in each phase was estimated according to the Fox equation[26] for the observed T_g's. The resulting compositions were included in the experimental data and the full line represents the Kwei equation, which produces the best fit of the data for $k \neq 1$ and $q < 0$ ($k = 3$ and $q = -63$). This line is S shaped which means that the system changes from a state of increased to a state of decreased backbone stabilization. In the amorphous matrix the two states must correspond to different molecular morphologies. Such values of k and q are reported[25] for systems which have strong tendency to phase separate. In such cases microphase separation occurs and consequently the hydrogen bonding interactions are active only across the phase boundaries. These interactions tend to maximize the interphase surface and to minimize the volumes of the individual phases. As a result, the system is a state reminiscent of that encountered in some segmented block copolymers.

Thermal properties

T_g values obtained by DSC resemble those obtained by DMA. The melting temperatures of Nylon 6 in the blends are reported in *Table 2*, where a significant melting point depression is evident. PVOH has a broad T_m which is difficult to determine with accuracy.

The crystallinity of both semicrystalline polymers was calculated and the results are also shown in *Table 2*. Crystallinity of Nylon 6 seems to be increased in the blends as Nylon 6 crystallizes in the presence of molten PVOH which probably facilitates the crystallization process. On the other hand, PVOH shows a slightly reduced degree of crystallinity showing that crystallization of PVOH is more difficult in the presence of the crystallites of Nylon 6.

As mentioned above, Nylon 6 shows a T_m depression in its blends with PVOH. The analysis of the melting behavior of a crystalline component in semicrystalline polymer blends is an important tool in assessing polymer miscibility. In miscible blends, the melting point of a crystalline component is usually lowered with respect to the pure polymer as a result of thermodynamically favorable interactions. The extent of the melting point depression in such systems provides means for measuring the interaction parameter χ_{12}[27] as described by Nishi and Wang[28]. However, the melting point of a polymer is affected not only by thermodynamic factors but also by morphological

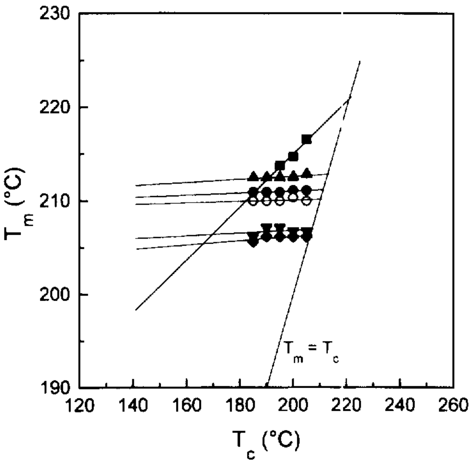

Figure 4 Hoffman–Weeks plots for Nylon 6 in its blends with PVOH at various compositions; (■) Nylon 6; (◆) 3/1; (▼) 2/1; (○) 1/1; (●) 1/2; (▲) 1/3

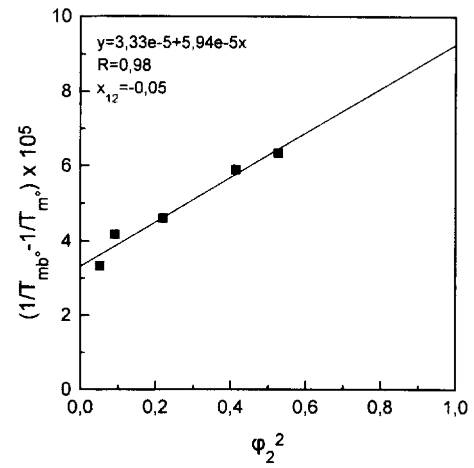

Figure 5 Melting point depression of Nylon 6 as a function of blend composition, plotted according to the simplified Kwei equation

Table 3 Results of the Hoffman–Weeks analysis of the melting behavior of the Nylon 6 component in PVOH/Nylon 6 blends

Blends of PVOH/Nylon 6	Equilibrium Melting point (°C)	Slope, η
3/1	206	0.023
2/1	207	0.015
1/1	210	0.008
1/2	211	0.011
1/3	213	0.017
0/1	221	0.283

parameters such as the crystal thickness. So, in order to eliminate the morphological effects in melting point depression analysis, the equilibrium melting points were estimated.

The equilibrium melting point of a polymer, T_m^0, is conveniently determined using the Hoffman–Weeks analysis[29]. This method involves isothermal crystallization of the sample at various temperatures T_c and plotting the observed melting point T_m as a function of T_c. The Hoffman–Weeks equation

$$T_m = \eta T_c + (1 - \eta) T_m^0 \tag{2}$$

predicts a linear relation of T_m vs T_c. The equilibrium melting point T_m^0 is obtained from the intersection of this line with the $T_m = T_c$ equation. The slope of the Hoffman–Weeks plot, η, assumes values between 0 and 1 and may be regarded as a measure of the stability of the crystals undergoing the melting process[29]. The obtained value for η of ca. 0 (see *Table 3*) implies that the crystals are perfectly stable ($T_m = T_m^0$ for all T_c), whereas a value of $\eta = 1$ reflects inherently unstable crystals.

In order to assure that PVOH is in amorphous state (melt), in this study the annealing temperatures range between 185–205°C. Because of the low thermal stability of PVOH short annealing times were employed. The samples after a heating scan up to 250°C remained at the crystallization temperature for 15 min, followed by quenching to 5°C and then heated again up to 250°C with a heating rate of 10°C/min.

Figure 4 shows the Hoffman–Weeks plots for Nylon 6 in the bulk as well as in its blends with PVOH and the results are summarized in *Table 3*. It is seen that, in the blends, the equilibrium melting point of Nylon 6 phase decreases steadily with PVOH content. The maximum extent of this melting point depression is 15 deg at the 3/1 (PVOH/Nylon 6) blend, where the T_m^0 of Nylon 6 is determined to be 206°C.

Thermodynamics predict that the chemical potential of the crystallizable polymer is decreased due to the presence of the miscible amorphous polymer, resulting in a decrease in the melting point. Using relevant theory from Nishi and Wang[28] showed that the following relationship may be used to obtain the χ_{12} interaction parameter:

$$\frac{1}{T_m^0(\text{blend})} - \frac{1}{T_m^0(\text{pure})} = -\frac{RV_1}{\Delta H_f^0 V_2}\chi_{12}\varphi_2^2 \tag{3}$$

In equation (3) T_m^0(pure) and T_m^0(blend) are the equilibrium melting points of the crystallizable polymer in the bulk and in the blends, ΔH_f^0 is the heat of fusion of the crystalline component, V and ϕ are the molar volume and the volume fraction of the components, respectively. Subscripts 1 and 2 refer to the crystalline (Nylon 6) and noncrystalline (PVOH) polymers, respectively. It should be noted that, since the melting point of Nylon 6 is well above that of PVOH ($\simeq$180°C), the latter is a noncrystalline polymer at the temperatures of interest so that this equation may be applied to the melting point data of the Nylon 6 phase. If the interaction parameter is independent of blend composition, a plot of the left-hand side of the above equation vs ϕ_2^2 should give a straight line[30], passing through the origin, with a slope from which χ_{12} can be obtained. From the interaction parameter, the interaction energy density B, may be also derived.

In order to calculate the left-hand side of the simplified Nishi–Wang equation from the experimental melting point data, the following constants have been used: ΔH_f^0 = 5200 cal/mol[31], V_1 = 104.3 cm^3/mol[31], and V_2 = 35.0 cm^3/mol[31]. Weight fractions were converted to volume fractions using ρ(Nylon 6) = 1.123 g/cm^3 and ρ(PVOH) = 1.274 g/cm^3 (calculated based on the crystallinity observed and on the densities of the pure amorphous and pure crystalline polymers—ρ_{aNylon6} = 1.084 g/cm^3, ρ_{cNylon6} = 1.23 g/cm^3, ρ_{aPVOH} = 1.26 g/cm^3 and ρ_{cPVOH} = 1.35 g/cm^3)[31]. The plot of the Nishi–Wang equation using the experimental melting point data for Nylon 6 in its mixtures with PVOH is shown in *Figure 5*. It is seen that the straight line passing through the experimental points, intercepts the axis at 3.33 × 10^{-5} with a slope of 5.94 × 10^{-5}. The fact that this line does not

Table 4 Ultimate properties of the ternary blends and of he respective binaries

Blends of PVOH/ Nylon 6	PEEA (%)	σ_y (MPa)	σ_b (MPa)	ϵ_b (%)
1/0	0	—	79 ± 13	10 ± 3
1/0	10	64 ± 4	51 ± 1	17 ± 8
1/0	20	—	15 ± 6	3 ± 1
2/1	0	46 ± 8	56 ± 8	370 ± 67
2/1	10	53 ± 6	46 ± 12	267 ± 67
2/1[a]	10	52 ± 3	49 ± 4	8 ± 1
2/1	20	25 ± 3	33 ± 9	334 ± 67
1/1	0	20 ± 7	49 ± 8	510 ± 114
1/1	10	28 ± 4	44 ± 3	399 ± 27
1/1	20	33 ± 3	24 ± 2	95 ± 45
1/2	0	25 ± 5	36 ± 13	557 ± 74
1/2	10	14 ± 4	37 ± 5	444 ± 42
1/2	20	16 ± 4	34 ± 3	393 ± 18
0/1	0	35 ± 4	72 ± 7	583 ± 72
0/1	10	37 ± 3	47 ± 4	358 ± 57
0/1	20	12 ± 1	30 ± 1	393 ± 17

[a]without added catalyst

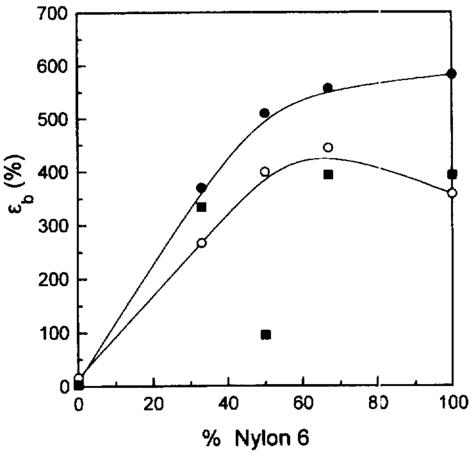

Figure 6 Elogation at break, ε_b (%) of the blends of PVOH/Nylon 6 with 0 (●); 10 (○) or 20% (■) PEEA

pass through the origin is usually attributed to a residual entropic effect which is neglected in the derivation of the equation. Such results have already been reported elsewhere[32–35]. Considering the value of the intercept as very small, we can derive from the slope of the obtained line, the parameters χ_{12} and B, as follows:

$$\chi_{12} = -0.05 \text{ (at 221°C)}$$

$$B = -6.12 \text{ J/cm}^3 \text{ (of PVOH)}$$

The negative value for χ_{12} at 221°C implies that the PVOH/Nylon 6 polymer pair is thermodynamically miscible in the melt[36,37] but the fact that this value is so close to zero indicates that no strong interaction forces are involved. This is further corroborated by the results of DMA where the quenched blends with high PVOH concentrations show in the solid state two distinct T_g's resulting from the amorphous phases of the two components.

Ternary system of PVOH/Nylon 6/PEEA

The composition series studied in this ternary were those of PVOH/Nylon 6 with ratio 2/1, 1/1 and 1/2 with 10 and 20% PEEA. These blends were prepared in the presence of an appropriate catalyst for the aminolysis reaction[38]. For comparison blends of PVOH/PEEA were also studied. The results in terms of ultimate tensile properties σ_b, ε_b and σ_y are summarized in *Table 4* and *Figure 6*. Since ε_b is accepted[39,40] as a practical criterion of adhesion between different polymer phases, the tensile properties are of great importance for the application of the ternaries studied.

Table 5 Tensile properties of PVOH/Nylon 6 2/1 blends with 10% of different polyethylene copolymers

Blends of PVOH/ Nylon 6 2/1	σ_y (MPa)	σ_b (MPa)	ϵ_b (%)
0%copolymer	46 ± 8	56 ± 8	370 ± 67
10%PEEA	53 ± 6	46 ± 12	267 ± 67
10%PEMA-g-MA	44 ± 3	37 ± 7	249 ± 125
10%SEBS-g-MA	46 ± 3	50 ± 3	396 ± 49

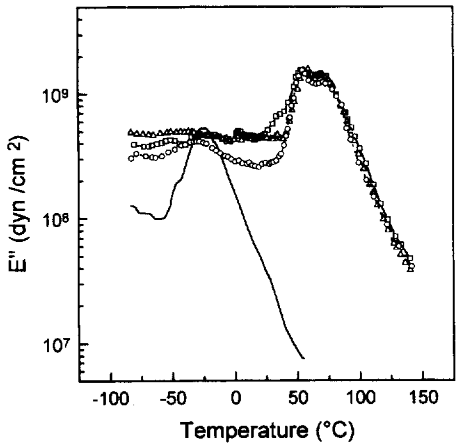

Figure 7 Temperature dependence of the loss modulus (E'') of PVOH/Nylon 6 2/1 with PEEA blends; (—) PEEA; (□) 2/1 + 0%; (△) 2/1 + 10%; (○) 2/1 + 20%

As shown in *Table 4* addition of PEEA to PVOH resulted in a drastic decrease of ε_b. On the contrary, addition of PEEA to Nylon 6 does not affect the mechanical properties[11]. The addition of 10 or 20% PEEA with PVOH/Nylon 6 2/1 blend led to blends with similar ε_b values and slightly reduced σ_b values, as expected because of the incorporation of a 'soft' material. Blends of PEEA with PVOH/Nylon 6 in the ratio 1/2, show ε_b values lower than the binary with the same ratio. Blends of PVOH/Nylon 6 1/1 with 10% PEEA have good mechanical properties although the analogous blend with 20% PEEA has poor properties, showing the poor adhesion between the components of this blend.

As mentioned previously, PEEA can be reactively blended with Nylon 6 and this is expected to be the reason for the good mechanical properties of the ternaries studied. To prove that, blends without added catalyst were also prepared. The results for the latter in terms of mechanical properties, for the composition 2/1 with 10% PEEA are included in *Table 4*; and one can see that they are very poor. This fact further supports the view that the good properties of the ternary are due to the reactive process which takes place during blending when the catalyst is present.

Other polyethylene copolymers, like PEMA-g-MA and SEBS-g-MA, were also used instead of the PEEA and their effectiveness were compared for the composition of PVOH/Nylon 6 2/1 + 10% PEEA. The results are reported in *Table 5*. Conditioning of these blends at constant humidity showed that the water absorption increased ε_b values but decreased σ_b, probably due to the plasticization effect of the water on this system.

In comparison to the respective binary and the pure PEEA, dynamic mechanical data, in terms of the temperature dependence of the loss modulus E' of the quenched blends of PVOH/Nylon 6 2/1 with 0, 10 and 20% PEEA, are presented in *Figure 7*. The broad transition observed in the binary remains in the blends with 10 and 20% PEEA. Moreover, the transition of PEEA also appears in the blend with 20% PEEA. These results lead to the conclusion that two phases are present. Taking into account the good mechanical properties of these blends, it is evident that a two-phase system with very good component adhesion is obtained.

Finally, morphological examination was performed on the above mentioned samples PVOH/Nylon 6 2/1 with 0, 10 and 20% PEEA after etching for 24 h with hot water (80°C). The micrographs are presented in *Figure 8* showing that a more uniform structure is obtained with the addition of the hydrophobic PEEA. Similar results were observed for ternary blends of PVOH/Nylon 6 in ratios 1/1 and 1/2.

CONCLUSIONS

Blends of PVOH and Nylon 6 were found to have good mechanical properties in the complete composition range. DSC and DMA measurements showed, in most compositions, one T_g in the region between the T_g's of the pure components and a composition dependent T_m depression of Nylon 6. Analysis of the equilibrium melting point of Nylon 6 as a function of blend composition using the simplified Nishi–Wang equation yields a negative value of $\chi_{12} = -0.05$ for the polymer–polymer interaction parameter. This negative value leads to the conclusion that these blends are miscible in the melt. The glass transition temperatures of these blends were determined as a function of composition, and the T_g versus composition curves were approximated by an empirical equation proposed by Kwei[25]. The curve was found to be S-shaped and the values of the constants k and q where determined to be $k \neq 1$ and $q < 0$. This implies that the system is resembling block copolymer in the solid state. So this partially miscible blend combines good mechanical properties with the barrier properties of PVOH unaffected by the presence of Nylon 6, something that is very important when the polymers are to be used in packaging applications. Finally, melt-mixing of PVOH/Nylon 6 with PEEA in the presence of a catalyst, results in reactive bonding of the polyethylene copolymer onto the miscible in melt blend of PVOH/Nylon 6.

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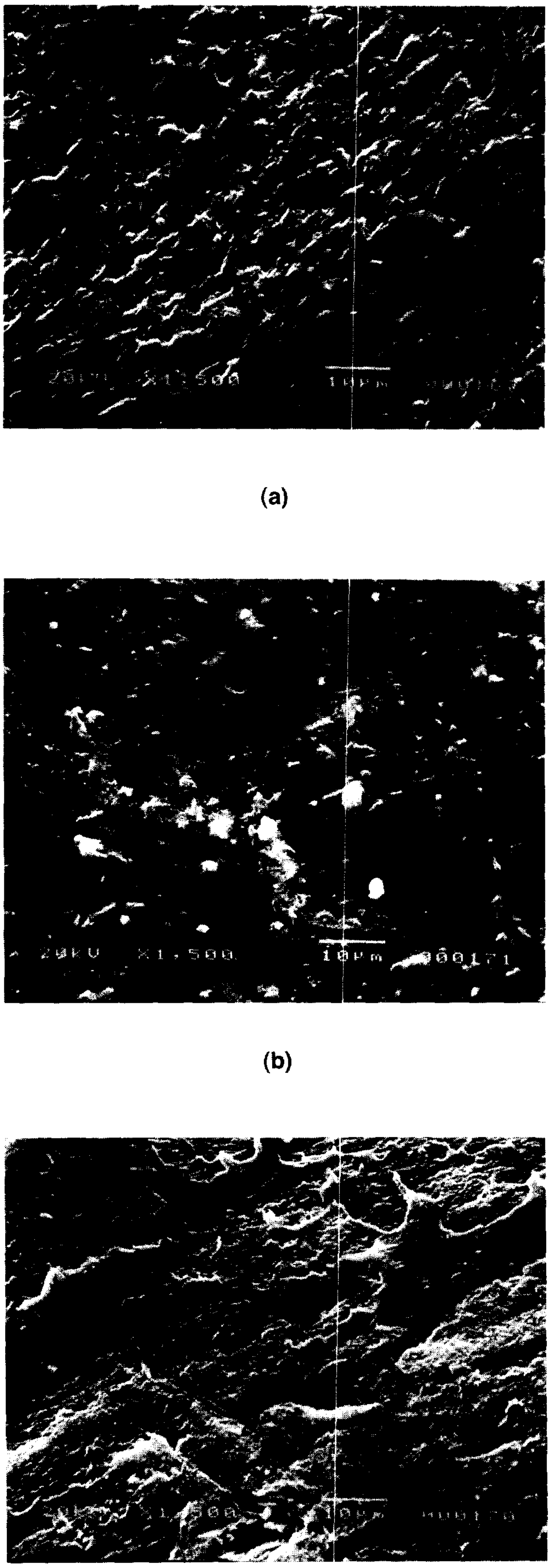

(a)

(b)

(c)

Figure 8 Scanning electron micrographs of PVOH/Nylon 6 2/1 blends with 0 (a); 10 (b); or 20% (c) PEEA after etching with hot water

Stassinopoulos, 'ARGO SA', Athens, for initiating our interest in packaging materials.

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