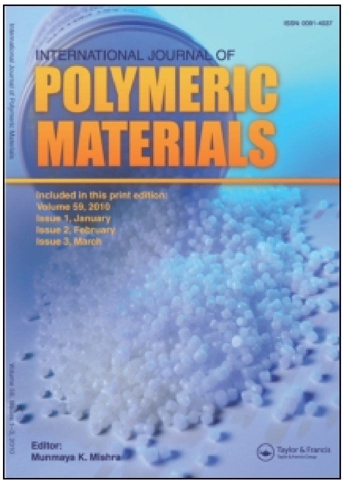

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Micromechanical studies on binary and ternary blends of polyethylene, polypropylene, and polyamide 66: Influence of the compatibilizer

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MICROMECHANICAL STUDIES ON BINARY AND TERNARY BLENDS OF POLYETHYLENE, POLYPROPYLENE, AND POLYAMIDE 66: INFLUENCE OF THE COMPATIBILIZER

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The microhardness H of PE/PP/PA blends prepared by one-Step and two-step mixing processes was determined. The microhardness of the blends was markedly affected by the composition. Results reveal that the presence of compatibilizers induces a remarkable decrease in the H of the blends. It is shown that the large deviation of H from the additivity law of the single components is mainly due to the depression of the crystal hardness values of polymer crystals. However, the decrease in crystallinity of the individual components in each blend also has to be considered. Comparison of experimental and calculated H data and analysis of DSC results in all the blends suggest that the surface free energy of the crystals increases as a consequence of the blending process. Results are discussed in light of the changes occurring in the defective boundary surface of the crystals. Finally, a linear relationship between the hardness H and the yield stress σ_y*, as well as*

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between H and the Young's modulus E, are found. The deviation of the H/σ_y *and the* H/E *ratios from the theoretical predictions are discussed in the light of the strain rate used and the compatibilizer effects on the blend structural properties.*

Keywords: binary and ternary blends, polyethylene, polypropylene, polyamide, compatibilizer, blend composition, processing conditions, crystallinity, microhardness, tensile properties

1. INTRODUCTION

Blending of two or more thermoplastic polymers is a convenient way to upgrade the properties of a given polymer and to achieve totally new and unique property combinations. Most thermoplastic polymers are immiscible and poorly compatible with each other, and, in most cases, another component (compatibilizer) is needed to resolve this problem. The most common compatibilizers are block and graft copolymers, which are presumed to locate at the blend interface (1). They reduce the interfacial tension, increasing the adhesion between the separate phases, promoting the dispersivity, and controlling the particle size of the dispersed phase.

The role of thermoplastic rubber as compatibilizer in polyolefin/polyamide blends has been the subject of many reviews and publications (2-6), but few of them deal with their application in ternary systems (7, 8). The SEBS (Styrene-Ethylene/Butylene-Styrene) type block copolymers, consisting of styrene end blocks and ethylene/butylene midblocks, are thermoplastic elastomers exhibiting physical properties typical for rubbers but melt processability similar to conventional thermoplastics. These properties arise from the fact that styrene is thermodynamically incompatible with the elastomeric midblock, and therefore micro-phase separation of the material occurs. The hard polystyrene micro-domains act as physical crosslinks between the elastomeric sequences providing high strength; on the other hand, soft midblocks elasticity (similar to conventional vulcanized rubber) is achieved. It has been reported that the use of maleic anhydride grafted SEBS (SEBS-g-MAH) as a compatibilizer improves the physical properties, and a much finer dispersion of the minor phase in the matrix can be achieved (9, 10). The chemical compatibilization reaction affecting the graft copolymer formation is expected to take place between the anhydride or carboxyl groups of the functionalized SEBS and the amine end groups of the polyamide.

Microhardness has proven to be a very useful technique for the microstructural investigation of glassy and semicrystalline polymers, copolymers, and polymeric blends of known composition, providing a bridge between their macroscopic mechanical properties (modulus, yield strength) and their microstructural characteristics (such as crystal size, crystallinity, etc.) (11-19).

Binary blends of thermoplastics (polyamide PA, polypropylene PP, polyethylene PE) have been the subject of several studies due to the commercial interest of these materials. Thus, PA/PP (2-6) as well as PP/PE (20, 21) and PE/PA (7, 8) are found to result in interesting engineering materials. The present work deals with the study of the microhardness and the thermal behavior of binary and ternary blends of PE, PP and PA prepared via reactive blending process (twin-screw extrusion) at different compositions. Ternary blends are of special interest, since they are expected to give tough and high-impact resistant materials as their respective binary blends.

The aim of this paper is twofold: 1) to examine the influence of the preparation method and the presence of compatibilizers upon the microstructure (crystallinity) and mechanical and micromechanical (microhardness) properties of the blends, 2) to study the correlation between the microhardness and the mechanical properties, namely yield stress and Young's modulus.

2. EXPERIMENTAL

2.1. Materials

High density polyethylene (HDPE) LUPOLEN 6031M from BASF, polypropylene (PP) VESTOLEN P5000 from Chemische Werke Hüls, and the polyamide 66 (PA66) DURETANE A30 from BAYER were used in this study.

The compatibilizers used were SEBS: KRATON G1652 and SEBS-g-MAH: KRATON FGX1901X from Shell.

Preparation of Blends

Blends of dried PA and preblends of PE/PP were prepared by melt mixing using a HAAKE co-rotating twin screw extruder. The screw speed was 140 rpm and, except for the feed zone, the barrel setting temperature was 270°C for blends containing polyamide and 230°C for polyolefin blends. The residence time was about 2 min. The hot extrudates were immediately quenched in water and pelletized. The polyamide as well as the blends containing polyamide were dried at 65°C for a period of 24 hours to remove the absorbed water.

In order to study the effect of processing and that of the compatibilizer on the properties of the PP/PE/PA blends, the PA was mixed with PE and PP in two different ways:

-*One step mixing*: Preparation of PP/PE/PA blends with and without compatibilizers by introducing all components into the extruder.

-*Two step mixing*: 1) Preparation of the extruded polyolefin blends (1st mixing step). 2) Blending the SEBS-g-MAH compatibilizer and the PA in different compositions with the extrudates of the step 1 (2nd mixing step).

Blend Compositions

The blend compositions are presented in Table 1. We have used the following symbols to indicate particular compositions:

TABLE 1 Blend Compositions and Compatibilizers Used

Blend number First mixing step	Composition PP/PE/PA	Compatibilizer type (wt%)
1	50/50/0	—
2	50/50/0	10% N2
3	50/0/50	—
4	50/0/50	15% N1
5	0/50/50	—
6	0/50/50	15% N1
7	100/0/0	—
8	0/100/0	—
9	0/0/100	—
10	33/33/33	—
11	33/33/33	15% N1
12	33/33/33	15% N2
13	33/33/33	15% N1+10% N2
Second mixing step	Composition b/PA	Compatibilizer type (wt%)
14	90/10	15% N1
15	80/20	15% N1
16	60/40	15% N1
17	50/50	15% N1
18	40/60	15% N1
19	20/80	15% N1
20	10/90	15% N1
21	66/33	—
	Composition a/PA	
22	66/33	—
23	66/33	15% N1

N1 = SEBS-g-MAH.
N2 = SEBS.
a = PP/HDPE (50/50) (1st mixing step).
b = PP/HDPE (50/50) + N2(10%) (1st mixing step).

Ternary blends were prepared by mixing PE, PP, and PA. Samples 10, 11, 12 and 13 were prepared using a single mixing step. Samples 22 and 23 were prepared using two mixing steps (see Table 1 for numeration). These blends have identical composition (with PE, PP and PA in equal amounts) but differ in the content and type of compatibilizer.

Processing

Samples for mechanical testing were prepared in the form of 100−mm−long tensile bars (cross section of 6 × 4 mm) using an ARBURG 270S injection molding machine. The melt temperature and mold temperature were 270°C and 70°C, respectively, for the polyamide and the blends containing polyamide, and 250°C and 60°C for the polyolefins and their blends. All samples were dried for 20 h at 65°C, and preserved in a desiccator until the mechanical measurements were made.

2.2. Techniques

Tensile tests were made using ADAMEL-LHOMARGY DY-25 equipment at 23°C, according to i.f.w. A0120.01-3, at a crosshead speed of 50 mm/min. A minimum of seven samples was tested in each case and the deviation of the data from the mean was less than 5%. Tensile properties (modulus, yield point) were evaluated from the stress-strain data.

Microhardness (H) was measured at room temperature using a Leitz tester equipped with a square-based diamond indenter. (See reference (22) for details). The H-value was derived from the residual projected area of indentation according to: $H = kP/d^2$, where d is the length of the impression diagonal in meters, P is the contact load applied in N, and k is a geometrical factor equal to 1.854. A loading cycle of 0.1 min and loads of 0.5 and 1N were used. 8−10 indentations were made on each sample, and results were averaged. Microhardness measurements were done in the outer surface of the non−oriented part of each dumb-bell shaped sample.

Thermal analysis was performed using a Perkin Elmer differential scanning calorimeter DSC-4. The typical sample weight was 5−10 mg, and the heating rate 20°C/min. The range of temperature was 40–320°C. All the scans were performed in a N_2 atmosphere.

The degree of crystallinity α was derived from the melting enthalpy data obtained by DSC using the following formula: $\alpha = \Delta H_m/\Delta H_m{}^{\infty}$, where ΔH_m and $\Delta H_m{}^{\infty}$ are the experimental melting enthalpy and the melting enthalpy for an infinitely long crystal, respectively.

3. RESULTS

3.1. Crystallinity

All the samples included in this study show DSC traces in which the melting peak of every component can be clearly distinguished. Figure 1 shows the DSC scans for all the blends of the b-PA series. The con-

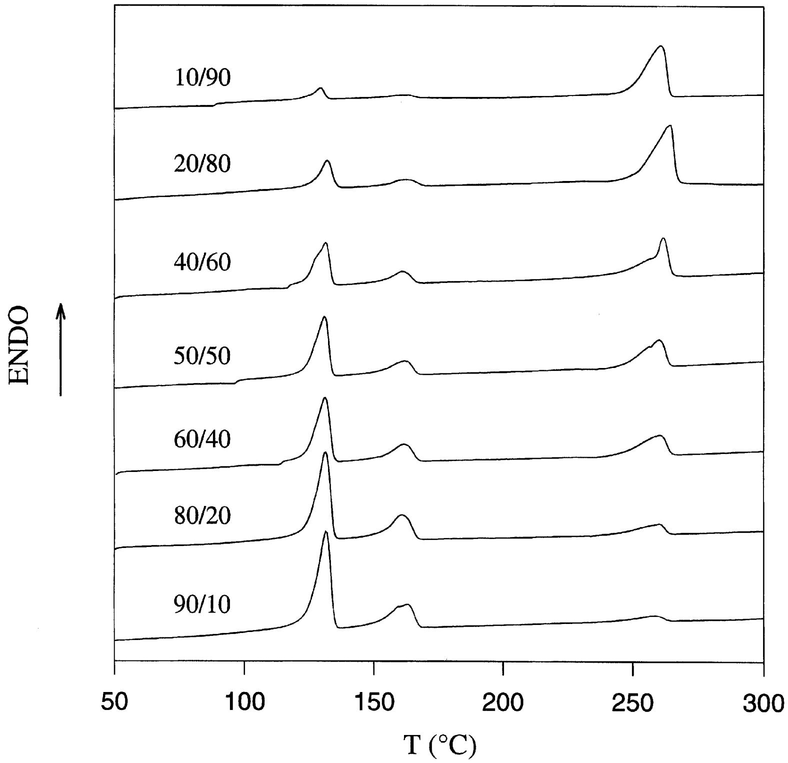

FIGURE 1 DSC traces for the blends of the b-PA series. Blend composition is indicated on each thermogram.

stancy of the position of the melting peaks (near 135°C, 162°C, and 260°C for PE, PP, and PA, respectively) with composition suggests that the crystal thickness of the three components remains nearly unchanged.

Crystallinity values, α, for every component were derived from the DSC data. From the literature (23), we have taken the values $\Delta H_m{}^{\infty}$ (PE) = 70.3 cal/g, $\Delta H_m{}^{\infty}$ (PP) = 49.6 cal/g, and $\Delta H_m{}^{\infty}$ (PA66) = 61.3 cal/g. The crystallinity values of every component in all the blends are presented in Table 2. Figure 2 shows the slight decrease of the total crystallinity of the b-PA blends as a function of the increasing PA content.

TABLE 2 Degree of Crystallinity α for the Individual Components of the Blends Investigated

Blend number First mixing step	Composition PP/PE/PA	Compatibilizer type (wt%)	α^{PP}	α^{PE}	α^{PA}
1	50/50/0	—	0.36	0.59	—
2	50/50/0	10% N2	0.35	0.60	—
3	50/0/50	—	0.46	—	0.32
4	50/0/50	15% N1	0.45	—	0.27
5	0/50/50	—	—	0.79	0.27
6	0/50/50	15% N1	—	0.71	0.29
7	100/0/0	—	0.35	—	—
8	0/100/0	—	—	0.69	—
9	0/0/100	—	—	—	0.29
10	33/33/33	—	0.33	0.65	0.26
11	33/33/33	15% N1	0.31	0.60	0.23
12	33/33/33	15% N2	0.36	0.71	0.27
13	33/33/33	15% N1 + 10% N2	0.40	0.76	0.28
Second mixing step	Composition b/PA	Compatibilizer type (wt%)			
14	90/10	15% N1	0.35	0.66	0.30
15	80/20	15% N1	0.37	0.66	0.28
16	60/40	15% N1	0.36	0.64	0.25
17	50/50	15% N1	0.36	0.70	0.24
18	40/60	15% N1	0.34	0.62	0.29
19	20/80	15% N1	0.47	0.92	0.35
20	10/90	15% N1	0.34	0.69	0.27
21	66/33	—	0.35	0.66	0.33
	Composition a/PA				
22	66/33	—	0.35	0.67	0.33
23	66/33	15% N1	0.34	0.65	0.28

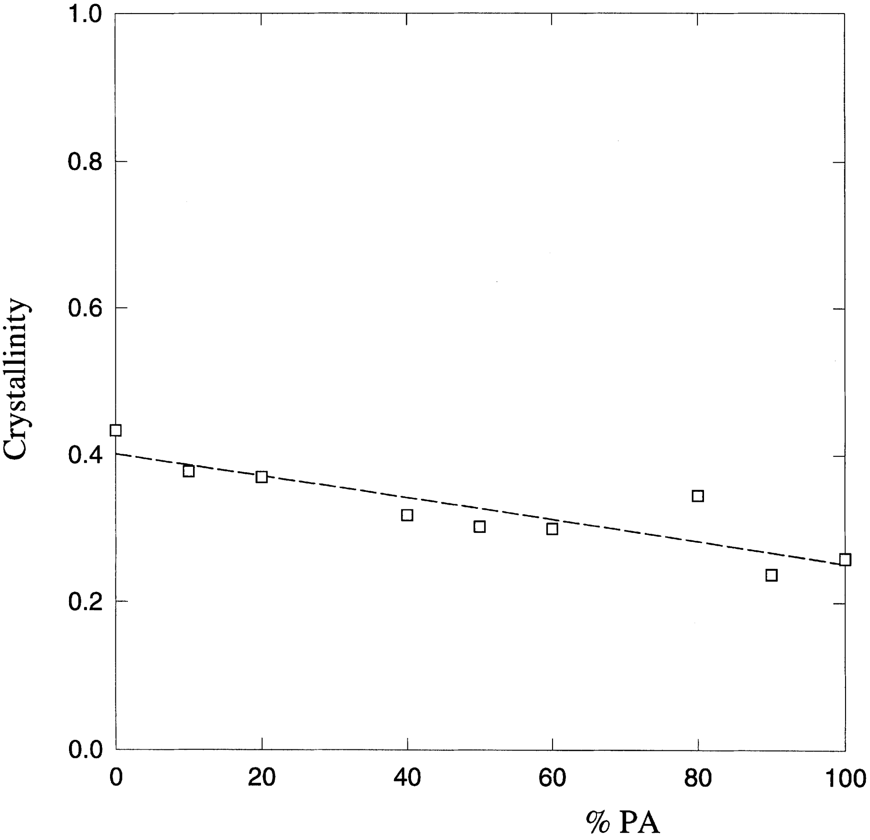

FIGURE 2 Total degree of crystallinity α (from DSC) of the b-PA blends as a function of the PA content.

3.2.1. Microhardness of Binary Blends

Table 3 includes the experimental and calculated microhardness values, applying the hardness additivity law: $H = \Sigma_i H_i \Phi_i$ (22) to the binary blends. In this expression, Φ_i is the weight fraction of each component, and H_i its respective hardness value. From inspection of this table, it can be clearly seen that only binary blends 1, 2 and 5 behave according to the hardness additivity law. In case of samples 3, 4 and 6, the experimental values are much lower than the calculated ones. In all cases, the presence of a compatibilizer results in hardness values that are notably lower than those corresponding to the blends without additives (see Figures 3–5).

TABLE 3 Comparison between the Experimental Microhardness Values, Those Calculated from the Additivity Law, and H Values Calculated Taking into Account the Contribution of α

Blend number First mixing step	Composition PP/PE/PA	Compatibilizer type (wt%)	Calculated Microhardness (additivity law) (MPa)	H values from Eq. 2	Experimental microhardness (MPa)
1	50/50/0	—	74	—	74
2	50/50/0	10% N2	67	—	61
3	50/0/50	—	133	147	113
4	50/0/50	15% N1	113	116	78
5	0/50/50	—	122	—	119
6	0/50/50	15% N1	103	103	79
7	100/0/0	—	—	—	85
8	0/100/0	—	—	—	63
9	0/0/100	—	—	—	180
10	33/33/33	—	108	—	102
11	33/33/33	15% N1	93	83	49
12	33/33/33	15% N2	93	91	62
13	33/33/33	15% N1 + 10% N2	82	85	67
Blend number Second mixing step	Composition a/PA				
22	66/33	—	108	—	106
23	66/33	15% N1	93	91	72

3.2.2. Microhardness of ternary blends

Table 3 also includes the experimental and calculated hardness values for the PE, PP and PA blends with the same composition (samples 10, 11, 12, 13, prepared using one−step mixing, and samples 22 and 23, prepared using two−steps mixing). It can be seen that only samples 10 and 22 follow the additivity law. Again the presence of a compatibilizer, particularly that of N1, strongly depresses the H-value. Table 3 additionally shows that there is not a great influence of the preparation method on the H-values of the blends without additives (compare the H-values for the samples 10, one-step method, and 22, two-step method). However, in case of the blends prepared with additives, the two-step process seems to provide materials with improved mechanical properties. For instance, sample 23 (two-step blending) shows a higher H-value than sample 11 (one-step blending), both samples having the same composition.

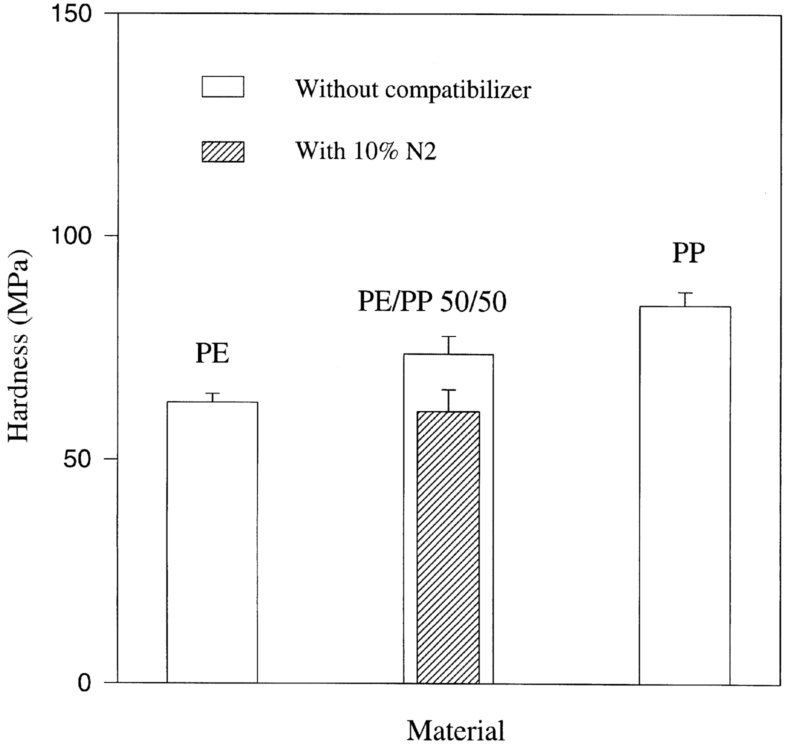

FIGURE 3 Hardness of PE/PP blends. Influence of the compatibilizer (N2).

We have centered our interest especially on the samples prepared by the two-step method, using the constant b (PP/PE 50/50 + 10% N2) composition and the PA component in different proportions, plus 15% of N1. The hardness variation of these blends as a function of polyamide content is illustrated in Figure 6. Here, it is clearly seen that all the experimental H-values are lower than those predicted by the additivity law (straight line 1).

3.3. Tensile Properties

Table 4 shows the experimental Young's modulus E, the yield stress σ_y and the H-values for the investigated blends. It is noteworthy that blend no. 19 (20/18 b-PA composition) presents a peculiar behavior: it shows the highest values for α, E, σ_y and H among the different ternary blends investigated in this work.

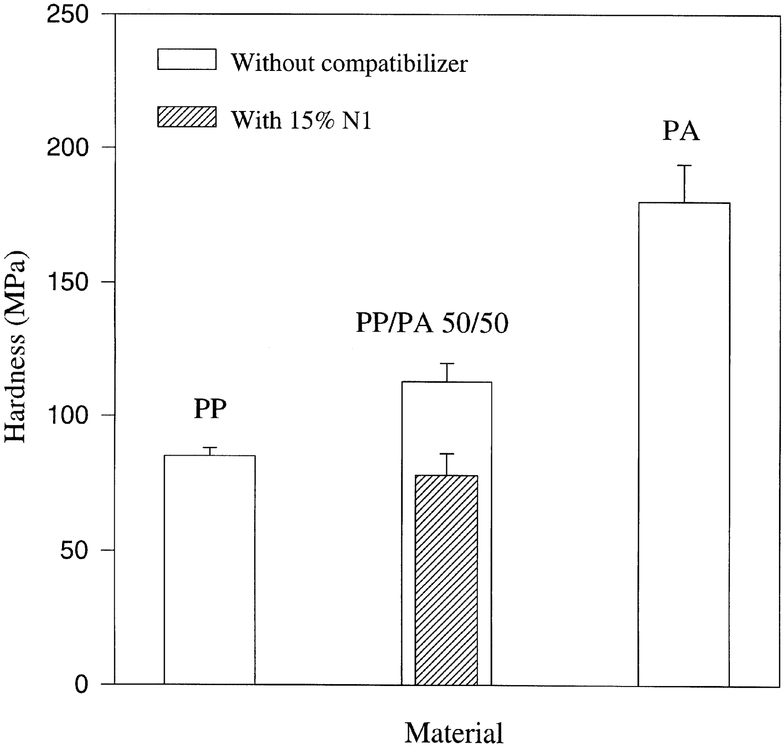

FIGURE 4 Hardness of PP/PA blends. Influence of the compatibilizer (N1).

It is of interest to study the correlation between H, σ_y, and E. Figure 7 shows the relationship between hardness and yield stress for all the blends, without and with compatibilizer. The regression line follows: $H = 1.8288\sigma_y$. As is well known, according to Tabor (24), the relationship between microhardness and yield stress is $\mathrm{H}/\sigma_y \approx 3$. Figure 8 shows the plot of H as a function of the Young's modulus, E. In this case, the equation relating E and H is: $\mathrm{H} = \mathrm{E}/16.5$. In a recent study (25), PE samples with different molecular weight and thermal history (compression molded, annealed at atmospheric pressure, chain extended and melt-crystallized samples) were found to follow the $\mathrm{H} \approx \mathrm{E}/10$ relationship. On the other hand, the blends investigated in the present study obey Struik's predictions (26). Struik's model relates the yield stress to the Young's modulus, in tension, according to the expression $\sigma_y \approx E/30$. This relationship has been shown to apply for amorphous and semicrystalline homopolymers (26).

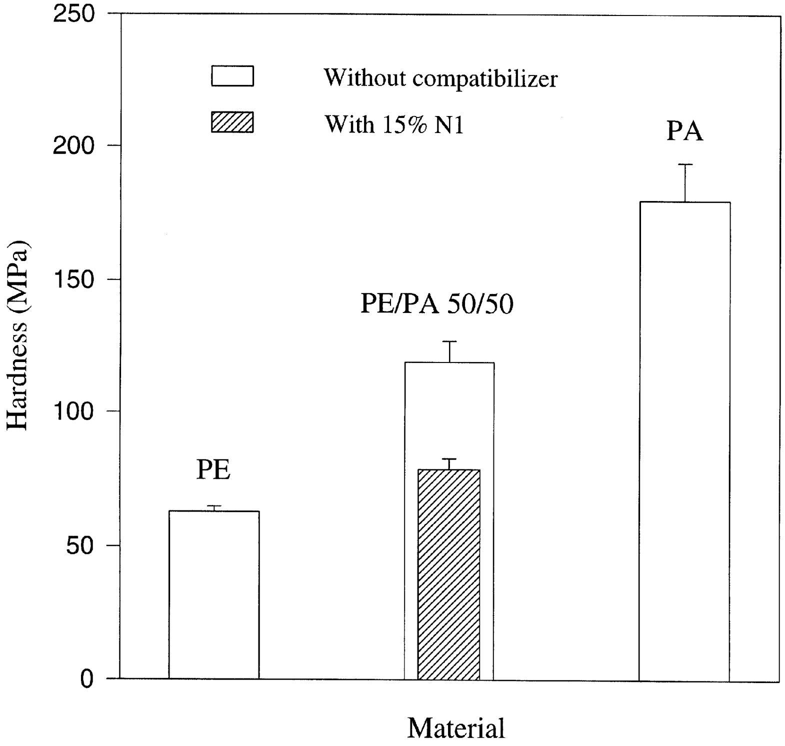

FIGURE 5 Hardness of PE/PA blends. Influence of the compatibilizer (N1).

4. DISCUSSION

The obtained results show that only samples 1, 2, 5, 10 and 22 follow the additivity law. To explain the behavior of the rest of samples, we assume the two phase model for the hardness of a semicrystalline polymer:

$$H = H_c\alpha + H_a(1 - \alpha) \qquad [1]$$

where H_c and H_a are the intrinsic hardness values for the crystalline and amorphous phases, respectively, and α is the volume fraction of the crystalline material. By combination of the additivity law and equation [1], we are led to the expression:

$$\begin{aligned} H = {} & \left[H_c^{PE}\alpha^{PE} + H_a^{PE}(1 - \alpha^{PE})\right]\Phi^{PE} + \left[H_c^{PP}\alpha^{PP} + H_a^{PP}(1 - \alpha^{PP})\right]\Phi^{PP} \\ & + \left[H_c^{PA}\alpha + H_a^{PA}(1 - \alpha^{PA})\right]\Phi^{PA} \end{aligned} \qquad [2]$$

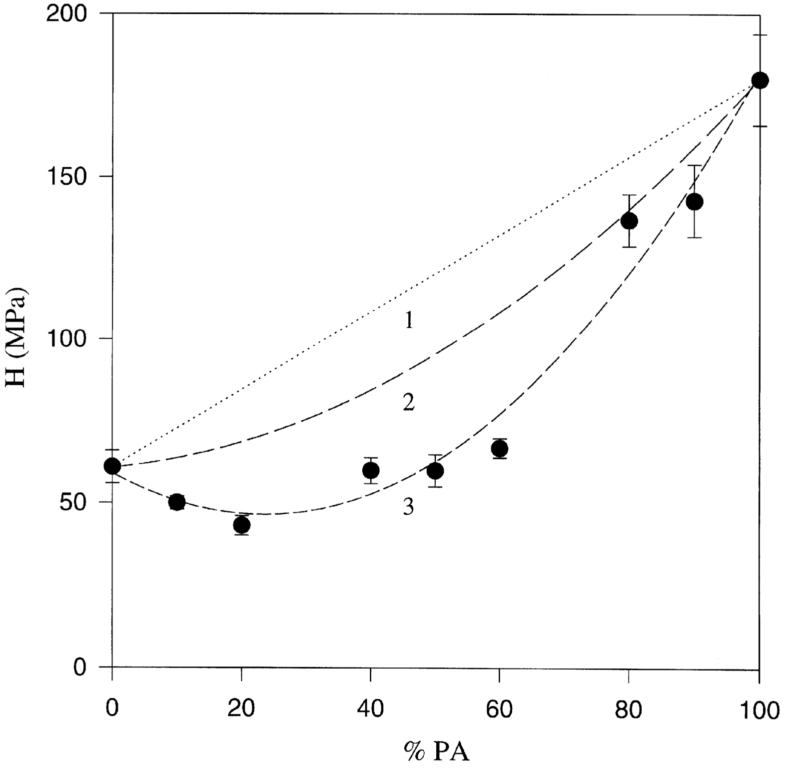

FIGURE 6 Hardness variation in b-PA blends as a function of PA content. ●: experimental values, straight dotted line 1: additivity law, dotted line 2: H-values calculated from Eq. (2) using, α^{PE}, α^{PP} and α^{PA} data (Table 2) for each blend.

which describes the microhardness of the binary or ternary blends in terms of the hardness values of the independent crystalline and amorphous components. In the case of PE, as $H_a^{PE} \lll H_c^{PE}$, we can approximate $H^{PE} \cong H_c^{PE}\alpha$. For PP we assume a value of $H_a^{PP} = 30$ MPa (27). Taking into account the recently found relationship between H and the glass transition temperature (T_g) in amorphous polymers (28), we can attempt to derive the hardness for the amorphous phase of the PA66 from its T_g value. Thus, if we let $T_g^{PA} = 50°\text{C}$ (23), we obtain for $H_a^{PA} \cong 65$ MPa. We have calculated $H_c^{PE} = 91$ MPa, $H_c^{PP} = 187$ MPa and $H_c^{PA} = 463$ MPa for the three homopolymers from their experimental H values using eq. [1]. By substituting α^{PE}, α^{PP}, α^{PA} in eq. [2] for their experimental crystallinity values (see Table 2), the calculated H values for every composition can be obtained.

TABLE 4 Young's Modulus, E, Yield Stress σ_y and Microhardness H for All the Blends Investigated

Blend number First mixing step	Composition PP/PE/PA	Compatibilizer type (wt%)	E (MPa) 10^{-3}	σ_y(Mpa)	H(MPa)
1	50/50/0	—	1.65	40.12	74
2	50/50/0	10% N2	1.48	33.56	61
3	50/0/50	—	1.83	56.4	113
4	50/0/50	15% N1	0.414	61	78
5	0/50/50	—	2.25	58.6	119
6	0/50/50	15% N1	0.899	35	79
7	100/0/0	—	1.802	40.22	85
8	0/100/0	—	1.518	31.3	63
9	0/0/100	—	2.71	99.62	180
10	33/33/33	—	1.81	62.5	102
11	33/33/33	15% N1	0.18	30.87	48
12	33/33/33	15% N2	1.63	51.8	62
13	33/33/33	15% N1 + 10% N2	0.374	32.75	67
Second mixing step	Composition b/PA	Compatibilizer type (wt%)			
14	90/10	15% N1	0.837	27	50
15	80/20	15% N1	0.324	24.3	43
16	60/40	15% N1	0.691	26	60
17	50/50	15% N1	0.363	32.25	60
18	40/60	15% N1	1.04	40.9	67
19	20/80	15% N1	2.08	83.6	137
20	10/90	15% N1	1.59	61	143
21	66/33	—	1.12	48.5	93
Second mixing step	Composition a/PA				
22	66/33	—	1.81	44	106
23	66/33	15% N1	0.449	33.58	72

In Figure 6, the H values calculated using eq. [2] for the different b-PA compositions are indicated by the dotted line 2. From inspection of this figure, it can be seen that the experimental values are even lower than those calculated taken into account the α values of every component for each blend. The same is true for the blends 3, 4, 6, 11, 12, 13 and 23, not shown in Figure 6 (see Table 3).

The very low H values obtained for all the above–mentioned samples could be explained as follows: it is known that the expression that relates the crystalline hardness H_c of a material of crystal thickness lc to the corresponding H_c^{∞} value for an infinitely thick crystal is given by (29):

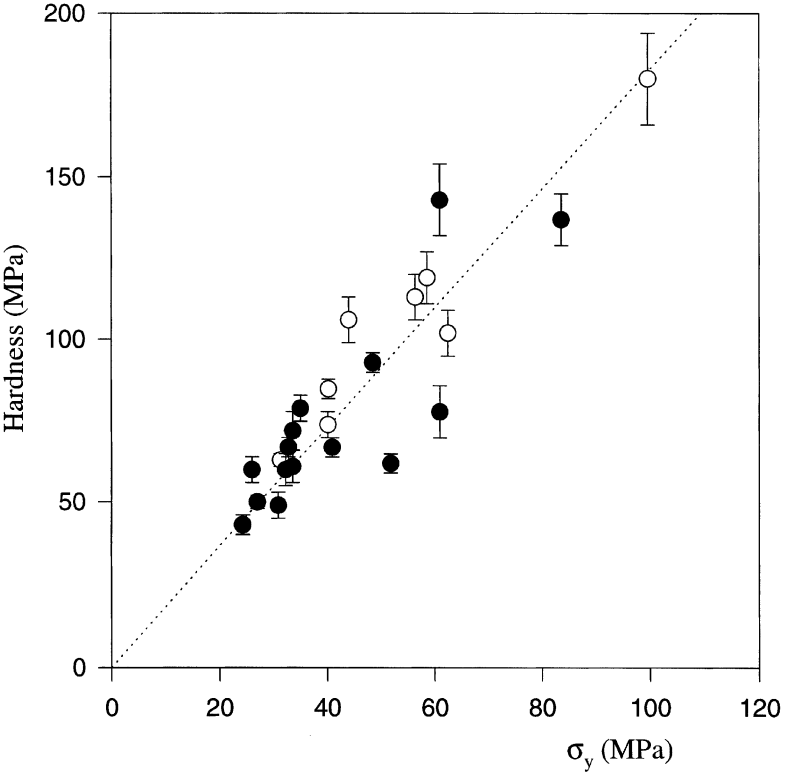

FIGURE 7 Plot of hardness vs. yield stress for the blends investigated. ○: samples without compatibilizer, ●: samples with compatibilizer.

$$H_c = H_c^{\infty}/(1 + b/lc) \quad [3]$$

The b-parameter is here defined as $b = 2\sigma_e/\Delta h$, σ_e being the free surface energy, and Δh the energy required for the plastic deformation of the crystals. The b-value can be influenced by the degree of order at the crystal surface (22). Hence, the blending of the samples, and also the presence of one or two compatibilizers, could well affect the b-value. Compatibilizers are amorphous materials, with flexible chains. These are also branched to some extent. As a consequence of these factors (the influence of blending and the use of compatibilizers), the surface of the crystals within the blends probably becomes more disordered. This could lead to a σ_e increase for each polymer system with reference to the surface free energy of the homopolymers. As a consequence, the b-parameter would also increase in the polymer crystal

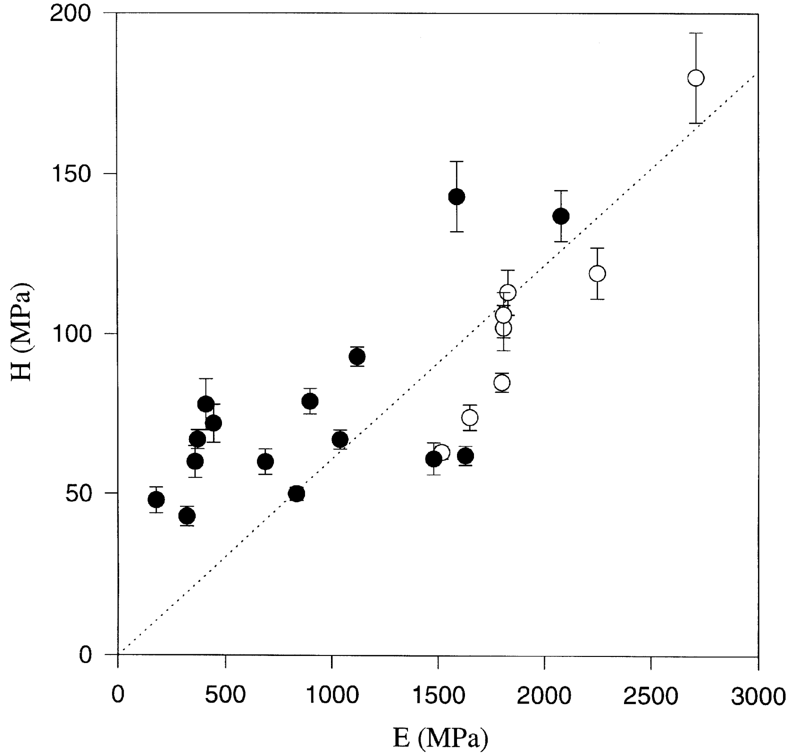

FIGURE 8 Plot of hardness vs. Young's modulus for the blends investigated. Symbols are as in Figure 7.

of the three components, giving rise to a H_c decrease which, therefore, contributes to an overall lower H-value.

The obtained results show that the linear relationship found between H and the yield stress σ_y (see Figure 7) applies reasonably well to the blends studied with a widely varying composition range. The mean value of the H/σ_y ratio obtained is about 1.8, i.e., lower than the value predicted by Tabor's relation (24). This is due to the fact that the yield stress is strain-rate dependent (31). It is known that Tabor's relation is only obeyed when the strain rate used is similar to that employed in the hardness test (31). In the blends studied in the present work, the crosshead speed used in the determination of the tensile properties was 5 cm min^{-1}, that is much higher than the penetration rate of the indenter employed during the hardness indentation tests (0.01-0.02 cm min^{-1}). Similar behavior is observed with the relationship between H and Young's modulus E (see Figure 8).

The mean value of the H/E ratio obtained is about 0.066. The deviation from the reported value of $H/E \approx 0.10$ obtained for PE samples with different morphologies (25) could be due to the same reason, i.e. the effect of strain rate in addition to the compatibilizer effects on the blend structural properties: changes in the overall crystallinity, blend components interactions, etc.

5. CONCLUSIONS

In most of the binary and ternary blends of PP, PE and PA, the crystallinity of the components is affected by the blending process. However, the main effect of the blending process seems to lead to an increase of disorder at the crystals surface, giving rise to hardness values much lower than those calculated taking into account the individual contributions of α. The presence of one or two compatibilizers contributes to magnify this hardness depression effect. Thus, blends without additives show higher H-values than their counterparts with compatibilizers. A linear relationship between H and σ_y following Tabor's relation has been found to apply for the blends studied in a wide varying range of compositions. Additionally, a relationship has been found, as well, between E and H in accordance to Struik's predictions (26).

REFERENCES

[1] Deanin, R. D. and Manion, M. A. (1999). "*Compatibilization of Polymer Blends*," in *Polymer Blends and Alloys*, Shonaike, G. O. and Simon, P. O. (eds.), Marcel Dekker Inc., New York, Chapter 1, pp 1–21.

[2] Holsti-Miettinen, R. and Seppala, J. (1992). *Polym. Eng. Sci.*, **32**, 868–877.

[3] Holsti-Miettinen, R., Seppala, J., Ikkala, O. T. and Reima, I. T. (1994). *Polym. Eng. Sci.*, **34**, 395–404.

[4] Ohlsson, B., Hassander, H. and Tornell, B. (1998). *Polymer*, **39**, 4715–4721.

[5] Heino, M., Hietaoja, P., Seppala, J., Harmia, T. and Friedrich, K. (1997). *J. Appl. Pol. Sci.*, **66**, 2209–2220.

[6] Ohlsson, B., Hassander, H. and Tornell, B. (1998). *Polymer*, **39**, 6705–6714.

[7] Kelar, K. and Jurkowski, B. (2000). *Polymer*, **41**, 1055–1062.

[8] Sheng, J., Ma, H., Yuan, X.-B., Yuan, X.-Y., Shen, N.-X. and Bian, D.-C. (2000). *J. Appl. Pol. Sci.*, **76**, 488–494.

[9] Wong, S.-C. and Mai, Y.-W. (1999). *Polymer*, **40**, 1553–1566.

[10] Amomsakchai, T., Sinpatanapan, B., Bualek-Lincharoen, S. and Meesiri, W. (1999). *Polymer*, **40**, 2993–2999.

[11] Baltá Calleja, F. J., Giri, L., Ezquerra, T. A., Fakirov, S. and Roslaniec, Z. (1997). *J. Macromol. Sci.-Phys.*, **B36**, 655–665.

[12] Baltá Calleja, F. J., Fakirov, S., Roslaniec, Z., Krumova, M., Ezquerra, T. A. and Rueda, D.R. (1998). *J. Macromol. Sci.-Phys.*, **B37**, 219–237.

[13] Baltá Calleja, F. J., Santa Cruz, C., Sawatari, C. and Asano, T. (1990). *Macromolecules*, **23**, 5352–5355.

[14] Santa Cruz, C., Baltá Calleja, F. J., Zachmann, H.G. and Chen, D. (1992). *J. Mater. Sci.*, **27**, 2161–2164.

[15] Flores, A., Ania, F. and Baltá Calleja, F. J. (1997). *Polymer*, **38**, 5447–5453.

[16] Giri, L., Roslaniec, Z., Ezquerra, T. A. and Baltá Calleja, F. J. (1997). *J. Macromol. Sci.-Phys.*, **B36**, 335–343.

[17] Baltá Calleja, F. J. (2000). "Structure-microhardness correlation of polymers and blends" in *Structure Development During Polymer Processing*, Cunha, A. M. and Fakirov, S. (eds.), Kluwer Acad. Pub., NATO Science Series Dordrecht, Vol. 370E, pp 145–162.

[18] Fritz, H. G., Cai, Q., Cagiao, M. E., Giri, L. and Baltá Calleja, F. J. (1995). *J. Mat. Sci.*, **30**, 3300–3306.

[19] Cagiao, M. E., Ania, F., Baltá Calleja, F. J., Hirami, M. and Shimomura, T. (2000). *J. Appl. Pol. Sci.*, **77**, 636–643.

[20] Krache, R. (1995). Master Thesis, Sétif, Algeria.

[21] Bouhelal, S. (1992). Master Thesis, Sétif, Algeria.

[22] Baltá Calleja, F. J. and Fakirov, S. (2000). *Microhardness of Polymers*, Cambridge University Press (Solid State Sciences Series), Cambridge, pp. 1–237.

[23] ATHAS databank.

[24] Tabor, D. (1979). *Gases, Liquids and Solids*, 2nd Ed, Cambridge University Press, Cambridge, p 188.

[25] Flores, A., Baltá Calleja, F. J., Attenburrow, G. E. and Bassett, D. C. (2000). *Polymer*, **41**, 5431–5435.

[26] Struik, L. C. E. (1991). *J. Non-Cryst. Solids*, **131-133**, 395–407.

[27] Martínez Salazar, J., Garcia Tijero, J. M. and Baltá Calleja, F. J. (1988). *J. Mater. Sci.*, **23**, 862–866.

[28] Fakirov, S., Baltá Calleja, F. J. and Krumova, M. (1999). *J. Polym. Sci., Phys.*, **37**, 1413–1419.

[29] Baltá Calleja, F. J. and Kilian, H. G. (1985). *Colloid Polym. Sci.*, **263**, 697–707.

[30] Flores, A., Aurrekoetxea, J., Gensler, R., Kausch, H. H. and Baltá Calleja, F. J. (1998). *Colloid Polym. Sci.*, **276**, 786–793.

[31] Baltá Calleja, F. J., Giri, L., Ward, I. M. and Cansfield, D. L. M. (1995). *J. Mater. Sci.*, **30**, 1139–1143.