Microhardness of Ternary Blends of Polyolefins with Recycled Polymer Components

K. Berdjane,[1] Z. Berdjane,[2]* D.R. Rueda,[2] D. Bénachour,[1] F.J. Baltá-Calleja[2]

[1]*Faculté des Sciences de l'ingénieur, Département de Génie des Procédés, Université Ferhat Abbas de Sétif, Sétif 19000, Algérie*
[2]*Instituto de Estructura de la Materia, CSIC, Serrano 119, 28006 Madrid, Spain*

ABSTRACT: Microhardness tests, Fourier transform infrared spectroscopy (FTIR), and differential scanning calorimetry (DSC) measurements were performed on melt-pressed films of multicomponent blends based on low-density polyethylene (LDPE), linear LDPE (LLDPE), high-density polyethylene (HDPE), and polypropylene (PP), and their recycled homologues. Some of the PE blends also contained ethylene-propylene-diene monomer (EPDM) as compatibilizer. In all cases, the variation of microhardness as a function of content of the recycled component follows the additivity law of components. Thus, the range of hardness values of polyolefin blends can be controlled by choice of both components and their relative content in the blend. The hardness of the components increases from LDPE, to LLDPE, to HDPE, to PP and increases from 20 to 84 MPa. For recycled components, the hardness values are reduced by ~15%. According to DSC results, all the blends are immiscible. Results are discussed in terms of the levels of crystallinity reached for the different blends. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 2046–2050, 2003

Key words: polyolefins; blending; compatibility; recycling; hardness

INTRODUCTION

In recent years, interest in the recycling of plastic materials has increased notably because of environmental as well as economic concerns. Polyolefins occupy the largest share of the plastics market [1] and are becoming the most recycled polymeric materials. Binary and ternary blends based on recycled polyethylene (PE) are already very important as "new" materials for industrial packaging. During recycling processes, photo- and thermal oxidation and/or mechanical treatments result in structural and morphological changes (chain scission, crosslinking, branching, oxidation, recrystallization, etc.) in the plastic materials. Combining different plastics, with or without the help of additives (compatibilizer), is a convenient way to upgrade the properties of recycled materials.

Polymer blends are becoming commercially important because they offer a property balance not found in either homopolymer. These properties depend mainly on the polymeric blend microstructure. The mechanical behavior of these multicomponent materials, in relation to their formulation composition and phase,

has been the subject of much work.[2] Drummond et al. recently investigated the behavior of low-density PE (LDPE)–linear LDPE (LLDPE) blends from the point of view of morphology and crystallization.[3]

PE films are important for modern agriculture. These films, which are easy to collect after use, are reused as blown films and molded objects with low mechanical properties. For outdoor applications, LLDPE is preferred to LDPE because of its higher stability that is related to the linearity of the main chains. Commercial LLDPE is, however, more expensive than LDPE. Thus, it would be of interest to investigate blends of LDPE and LLDPE to find materials of moderate costs with some convenient, specific mechanical properties.[4]

Polypropylene (PP) is used extensively as a commercial polymer, but its applications are limited because of weak impact strength, environmental stress cracking, etc.[5] These weaknesses can be overcome by blending PP with PE. Indeed, blends of these two polymers exhibit improved properties. Mechanical mixing is considered to be a better and more economic way than the use of a compatibilizer to prepare PE–PP blends.[6]

From a scientific standpoint, the microhardness is becoming a characterization technique that may contribute to an increased understanding of the ways polymers mix. In addition to methodological contributions, microhardness has been successfully used to provide a detailed understanding of its correlation to the nanostructure of polymers, copolymers, and com-

TABLE I
Density, Melt Flow Index (MFI), Melting Point (T_m), Enthalpy of Fusion (ΔH_m), Crystallinity Index (X_{DSC}), and Microhardness (H) of the Starting Materials

Material	Trade mark	Density (g/cm^3)	MFI (g/10min)	T_m (°C)	ΔH_m (kJ/mol)	X_{DSC} (%)	H (MPa)
LDPE	PEBD B21 ENIP, Skikda	0.923	0.19	110.3	1.39	33.8	19.9
LLDPE	DSM Stamylan LL011 8BN00	0.918	1.00	119.7	1.49	36.0	28.4
HDPE	TR 140 Alcudia	0.950	0.20	127.3	2.31	56.4	49.0
PP	Inspire Dow Plastics	—	3.91	157.3	3.64	41.8	83.9
PE_R	ENPC, Sétif	—	0.41	108.9	1.29	31.6	17.0
$Bl_{O/R}$	ENPC, Sétif	—	0.51	125.8	1.97	47.9	33.9
PP_R	ENPC, Sétif	—	4.4	157.7	3.39	39.0	71.2

posites.[7] In preceding studies, we examined the microhardness and other properties of blends based on scraps of LDPE (agriculture films and packaging) and of high-density PE (HDPE; industrial scraps).[8] A linear relationship between microhardness and stress at yield point was obtained. We have also used the microhardness technique to examine the influence of gel blending on the properties of PE–PP blends.[9] We found that the creep effect is important for polymeric materials with regard to the mechanism of surface indentation; therefore, plastic deformation during the indentation period should be taken into consideration.[10,11]

Differential scanning calorimetry (DSC) is considered an ideal tool for characterization of thermal properties of blends. Information about the miscibility of blend components is rapidly derived from the endotherm shape and peak temperature. The area of endothermic peaks can be used to derive the level of crystallinity of samples, X_{DSC}.

The aim of the present study is to report novel results on some mechanical (microhardness) and thermal properties (melting behavior) of multicomponent blends of PE, PP, and their recycled homologues. Blend samples covering the whole range of composition with regard to the recycled component were investigated. Particularly, blends based on PE were prepared with and without ethylene-propylene-diene monomer (EPDM) as compatibilizer. The results are correlated to the levels of crystallinity presented by the different samples.

EXPERIMENTAL

Materials

Three grades of PE, LDPE, LLDPE, and HDPE, and a sample of PP were kindly provided by ENIP, DSM, Alcudia, and Dow Plastics, respectively. The density and the melt flow index of the starting materials are collected in Table I. The recycled polymer materials were supplied by ENPC, Sétif, Algeria. A thermoplastic elastomer from EPDM (Du Pont) was used as a compatibilizer. The blends were mixed in a single-screw extruder. To insure good homogeneity, the samples were extruded twice. The films were prepared by compression molding. The nomenclature and description of the compatibilizer, recycled components, and blends are presented in Table II. The polymer components, with a fixed relative proportion throughout the blend composition, are given in parenthesis and/or brackets. For example, in the case of blend-1, the sample with 30% recycled greenhouse film (PE_R) will contain 7% EPDM, and the remaining 63% will be shared by LDPE and LLDPE in a 4:1 ratio.

TABLE II
Nomenclature of Compounds and Blends

| Category	Compound/Blend	Description
Compatibilizer	EPDM ter-polymer^a	Thermoplastic elastomer from EPDM; C_2/C_3 = 55:40; ENB, 5 wt %; Mooney viscosity (ML 125) = 40
Recycled component	PE_R	Greenhouse film made of nonstabilized LDPE; in use for 1 year
	PP_R	Recycled PP from salt containers
	$Bl_{O/R}$	Mixture of original and recycled PE; HDPE–LDPE–waste = 50:25:25; waste is from milk bottles made of HDPE–LDPE (2:1)
Blend	1: [(LDPE–LLDPE)–EPDM]–PE_R	[(4:1):7]–PE_R
	2: [(LDPE–LLDPE)–PE_R)]–EPDM	[(4:1):30]–EPDM
	3: [HDPE–LDPE]–$Bl_{O/R}$	(2:1)/$Bl_{O/R}$
	4: [HDPE–LLDPE]–$Bl_{O/R}$	(1:1)/$Bl_{O/R}$
	5: [PP–LLDPE]–PP_R	(1:4)/PP_R
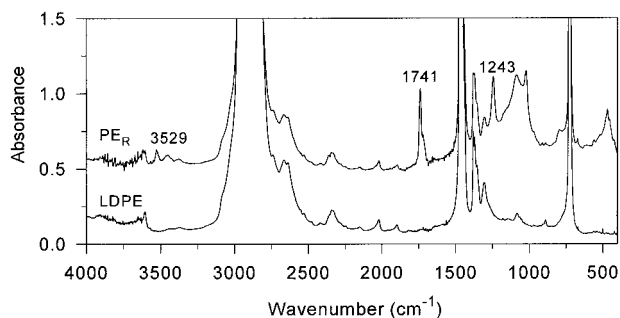
Figure 1 FTIR transmission spectra of LDPE and PE_R.

Techniques

A Perkin Elmer Fourier transform infrared (FTIR) instrument (1725X) was used for chemical characterization, particularly of recycled in relation to pristine polymer materials. The FTIR transmission spectra of thin films of LDPE and PE_R are shown in Figure 1. In addition to the bands characteristic of PE, new bands related to oxidized groups appear in the case of PE_R because of photooxidation during weathering. The weak band at 3529 cm^{-1} is assigned to the hydroperoxide group formed during the degradation of PE.[13,14] The strong band at 1741 cm^{-1} is related to the carbonyl group of either the ester or carboxylic group. The latter is also confirmed by the band at 1243 cm^{-1}.[15] The reduced peak absorbance of some of these bands compared with the nominal composition of the recycled component (Fig. 2) is an indication of blend formation.

DSC thermograms of 5–10 mg of sample were recorded with a Perkin-Elmer 4B calorimeter at a heating rate of 20 K/min. Indium and zinc standards were used for calibration. Crystallinity of samples was calculated from the observed endothermic peaks. Fusion enthalpy values of 4.1 and 8.7 kJ/mol were used for fully crystalline PE and fully crystalline PP, respectively.

The specimens used for microhardness measurements were films of 300–400 μm thickness that were prepared by hot pressing of the materials near the melting points of the blend components. The Vickers hardness of the blends was measured on a standard Leitz microhardness tester. The indenter was a square-shaped diamond pyramid with an angle of 136°. Loads of 0.4, 0.6, 0.8, and 1.0 N, to correct for instant elastic recovery, were employed. A loading cycle of 0.1 min was used. The standard Vickers microhardness, H, was determined from

$$H = k \cdot P / d^2 \tag{1}$$

where P is the applied load, k is a geometric factor equal to 1.854, and d is the mean diagonal length of the imprint after removing the indenter. At least 10 inden-

tations were made under each load. The H values were determined in the range $\Delta H / H = 0.05$–0.1.

RESULTS AND DISCUSSION

The thermal properties (corrected melting point, T_m, and fusion enthalpy, ΔH_m), the crystallinity derived from DSC, as well as the experimental hardness values of the neat components (LDPE, LLDPE, HDPE, and PP) and of the recycled components (PE_R, $Bl_{O/R}$, and PP_R) are collected in Table I. The blends based on LDPE and LLDPE components present broad DSC endothermic maxima, whereas the blend samples based on HDPE and PP components exhibit two maxima corresponding to the melting point of each component.

The dependence of the experimental hardness values on blend composition for the uncompatibilized (blend 3) and compatibilized blends (blends 1 and 2) of PE is presented in Figures 3 and 4. The hardness values of blend 3 are larger than those of blend 1 mainly because the HDPE component is harder than the other PE grades (LDPE and LLDPE) (see Table I) and also because 7% of blend 1 is a rubbery component. The hardness decrease shown in Figure 4 for the samples with 30% PE_R (blend 2) should be related to the amorphous nature of the compatibilizer EPDM. The hardness variation of the PP blends (blend 5) with the PP_R content is presented in Figure 5.

In contrast to preceding studies[8,9] where we found a deviation from additivity of the H data for binary blends, the linear dependence observed for all the multicomponent blend systems investigated in the present work is remarkable. The straight lines represent the hardness additivity law of a single component according to the following equation:
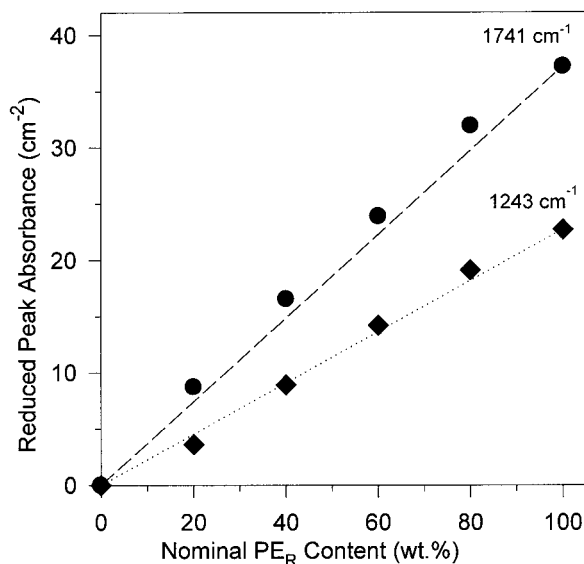

Figure 2 Reduced peak absorbance at 1741 and 1234 cm^{-1} versus the nominal content PE_R in LDPE–PE_R blends.
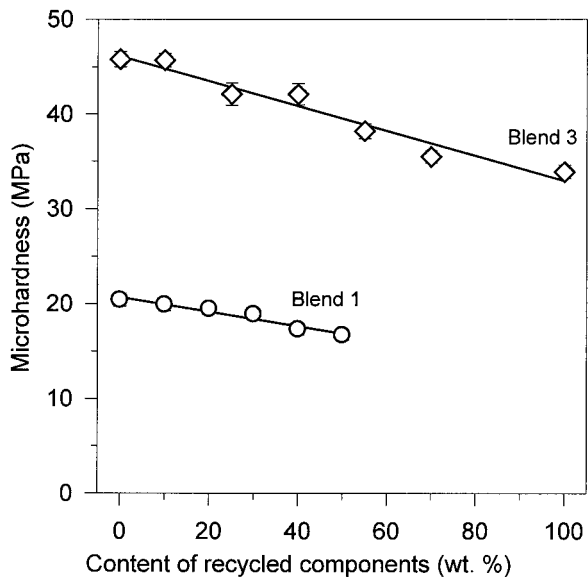
Figure 3

Figure 3 Variation of microhardness of blends 1 and 3 as a function of PE_R and $Bl_{O/R}$ content, respectively.

$$H = H^b w^b + H^R w^R \qquad (2)$$

where H^b and H^R are the experimental hardness values of the PE or PP blends and the recycled PE components (or compatibilizer), respectively, and w^b and w^R are their corresponding weight contents in the blends. In our case of multicomponent blends, the first term of eq. (2) refers to the hardness contribution from the component within the brackets (Table II). The apparent different behavior shown by PE blends in relation to PP blends is due to the different hardnesses corresponding to extreme samples with 0 and 100%
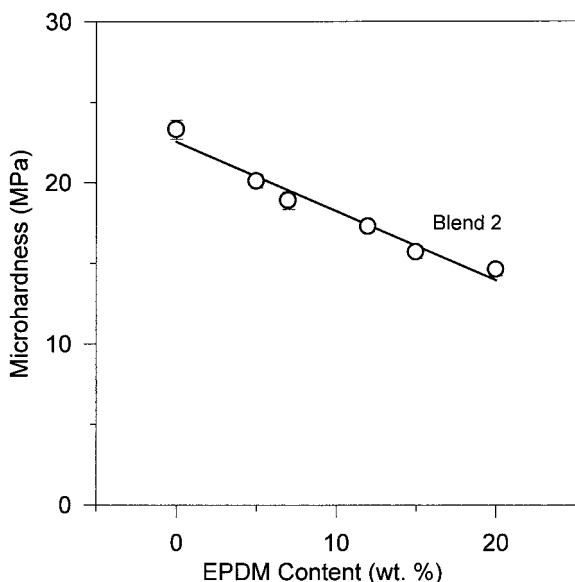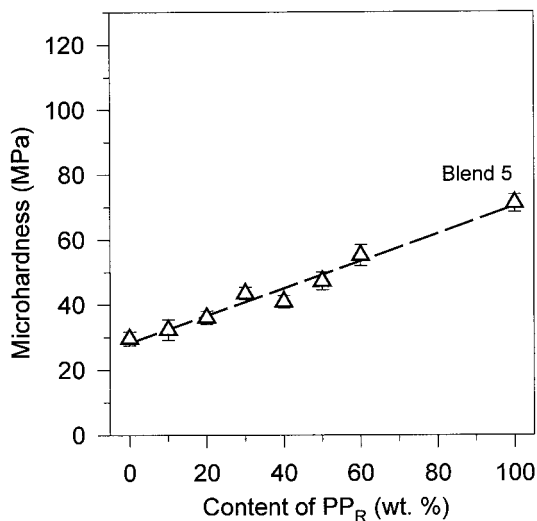

Figure 5 Variation of microhardness of blend 5 as a function of PP_R content.

recycled material. Furthermore, the hardness window observed for the different blends investigated is obviously dependent on the hardness values for the extreme composition samples. Thus, the hardness window for PP–PE blends is considerably larger than that observed for blends based exclusively on PE.

The correlation between hardness and crystallinity in polymer materials is well known.[7] The variation of microhardness as a function of crystallinity for the different blends of Table II is shown in Figure 6. The data clearly segregate into two sets corresponding to blends containing PE and PP, respectively. In the case of the PE blends, the data fit a linear relationship and are separated in two main groups with crystallinity values of ~30 and 45%, respectively. Among the latter
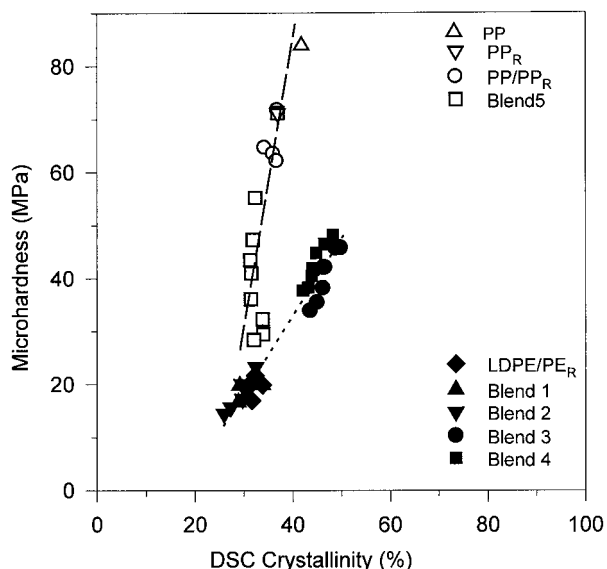

Figure 4 Variation of microhardness of blend 2 as a function of EPDM content.

Figure 6 Microhardness–crystallinity relationship for both blends series of PE and PP.
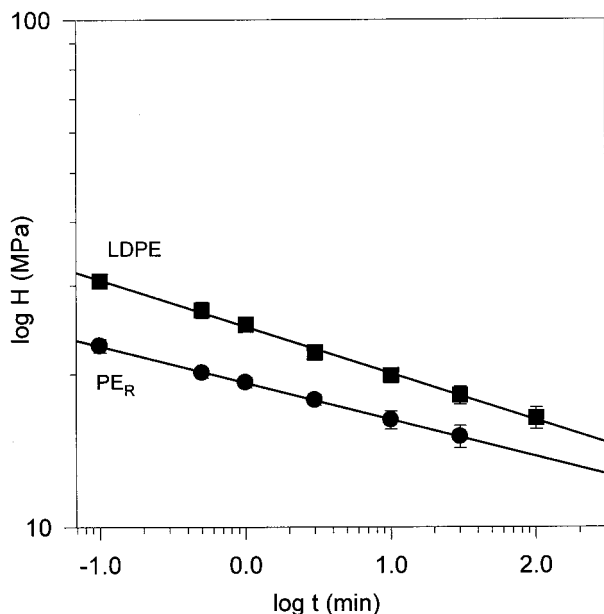
Figure 7 Double logarithmic plot of hardness versus indentation time for LDPE and PE$_R$.

group, corresponding to blends containing HDPE (blends 3 and 4), there is an additional segregation of data corresponding to blends also containing LDPE (blend 3) and LLDPE (blend 4). On the other hand, in the case of the PP blends, as we have already mentioned, there is a larger variation of hardness in relation to PE blends even if the range of crystallinity variation is smaller. Particularly, data for blend 5 (PP–LLPDE–PP$_R$) tend to approach those of PE blends for samples with a low content of PP$_R$. This result is due to the low hardness of the starting LLDPE–PP (4:1) material ($\sim$30 MPa). This value dramatically increases with the increasing content of the recycled PP$_R$ component, which exhibits a relatively high hardness value of 71 MPa.

It is also of interest to analyze the time-dependent part of the plastic deformation during loading (creep) of polymer materials.[10–12] Hardness values reported in the literature usually refer to short indentation times of a few seconds so as to minimize creep. The double logarithmic plot of H as a function of indentation time for the LDPE neat and recycled polymer is shown in Figure 7. The hardness follows a variation of the type

$$H = H_0 t^{-k} \qquad (3)$$

where H_0 is the hardness at a given reference time, t, $t = 0.1$ min, and k is the so-called creep constant.[7] The results show that the creep behavior of the samples varies little after LDPE is used as a greenhouse film for 1 year. Nevertheless, a slight decrease of the creep constant is observed, from $k = 9 \times 10^{-2}$ to 7×10^{-2},

indicating that slip processes within the polymer under the indenter are reduced as a consequence of the presence of oxidative groups in the recycled material. For PP and PP$_R$, however, a similar k value (14×10^{-2}) was observed.

CONCLUSIONS

The study of the microhardness of multicomponent blends of polyolefins as a function of the recycled polymer content demonstrates that the additivity relation of the microhardness of components holds. Therefore, the window of hardness for a polyolefin blend is determined by the hardness value of the two extreme composition samples. Blending of PE and PP considerably enlarges the range of hardness values observed in comparison with the hardness variation observed for the blends based on different PE grades. The results have been interpreted by changes in the crystallinity of the blend samples or blend components. Thus, blends based on PP or PE show a linear dependence of hardness versus DSC crystallinity. The oxidation observed, particularly for the recycled component PE$_R$ (greenhouse film), is responsible for the better creep behavior in relation to that of pristine PE.

References

1. Deanin, R.D.; Manion, M.A. In Polymer Blends and Alloys; Shonaike, G.O.; Simon, G.P., Eds.; Marcel Dekker: New York., 1999; Chapter 1, p. 1.
2. Hull, D. An Introduction to Composites Materials; Cambridge University Press: Cambridge, MA, 1981; Chapter 5, p. 81.
3. Drummond, K.M.; Hopewell, J.L.; Shanks, R.A. J Appl Polym Sci 2000, 78, 1009.
4. Prasad, A. Polym Eng Sci 1998, 38 (10), 1716.
5. Galli, P.; Haslock, J.C.; Simonazzi, T. In Polypropylene: Structure, Blends and Composites, Vol. 2: Copolymers and Blends; Karger-Kocsis, J., Ed.; Chapman & Hall: London, 1995, Chapter 1, p. 1.
6. Shanks, R.A.; Li, J.; Yu, L. Polymer 2000, 41, 2133.
7. Baltá-Calleja, F.J. ; Fakirov, S. Microhardness of Polymers; Cambridge University Press : Cambridge, 2000 ; Chapter 4, p. 80.
8. Rueda, D.R.; Baltá-Calleja, F.J.; Viksne, A.; Malers, L. J Mater Sci 1994, 29, 1109.
9. Baltá-Calleja, F.J.; Santa Cruz, C.; Sawatari, C.; Asano, T. Macromolecules 1990, 23, 5352.
10. Baltá-Calleja, F.J.; Basset, D.C. J Polym Sci: Polym Symp 1977, 58, 157.
11. Baltá-Calleja, F.J.; Flores, A.; Ania, F. J Mater Sci 2000, 35, 1315.
12. Chua, S.M.; Henderson, P.J. J Mater Sci Lett 1991, 10, 1379.
13. Guadagno, L.; Naddeo, C.; Vittoria, V.; Camino, G. ; Cagnani, C. Polym Degrad Stab 2001, 72, 175.
14. Carrasco, F.; Pages, P.; Pascual, S.; Colom, X. Eur Polym J 2001, 37, 1457.
15. Bellamy, L.J. In The Infrared Spectra of Complex Molecules, 2nd Ed.; John Wiley: London, 1958; Chapter 10, p. 161.