Compatibility of HDPE/Postconsumer HDPE Blends Using Compatibilizing Agents

E. Ramírez-Vargas,[1] Z. Sandoval-Arellano,[2] J. S. Hernández-Valdez,[1] J. G. Martínez-Colunga,[1] S. Sánchez-Valdés[1]

[1]Centro de Investigación en Química Aplicada, Blvd. Enrique Reyna 140, Saltillo Coahuila, 25100, México
[2]Instituto Tecnológico de Saltillo, Blvd. V. Carranza 2400, Saltillo Coahuila, 25270, México

Received 15 July 2005; accepted 17 September 2005
DOI 10.1002/app.23214
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Mechanical properties, molecular weight, X-ray diffraction, and differential scanning calorimetry (DSC) characterization of blends of virgin high-density polyethylene (HDPE) with two types of recycled material were investigated. The recycled came from urban plastic waste; one kind was only washed and grounded and the other was extruded and pelletized to remove most of contaminant particles. Starting with the 30/70 virgin/grounded recycled and 50/50 virgin/pelletized recycled blends the recycled content was increased in both blends and compatibilizing agents were used to increase the blend performance. A mixture of phenolic antioxidants and phosphite costabilizers under the name of Recycloblend™, ethylene vinyl acetate (EVA) copolymer, low-density polyethylene (LDPE), and linear low density polyethylene (LLDPE) were used as compatibilizers. The effect of these additives and the recycled content on the performance of extrusion blow-molded bottles was determined. The results suggest that blends of virgin/grounded recycled and virgin/pelletized recycled HDPE, in general, were not significantly different among each other and both had a quite similar behavior than the virgin HDPE when compatibilizing agents were used. The addition of compatibilizing agents yielded a material with properties similar to those for the virgin HDPE, helping to reduce the effect of polymers degradation on the rheological and mechanical behavior, with Recycloblend and LLDPE being the most effective for the blends with grounded recycled material, and LLDPE y EVA, for the blends with pelletized recycled. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 3696–3706, 2006

Key words: high density polyethylene; blends; recycling; mechanical properties; compatibilizing

INTRODUCTION

The increased consumption of plastic materials worldwide has promoted the increase of these materials in the urban waste due to its short period of use. Thus, it is important to consider the environment pollution they make. Because of environmental concerns the recycling of waste or rejected plastics is nowadays highly encouraged to reduce the increasing amounts of pollutants. In recent years, the recollection and reusing of solid plastic wastes, especially polyolefins, have been considered. A particular case is the high-density polyethylene (HDPE) containers for the packaging of liquids such as milk and other lacteous products and juices, which represents the 35% of all the plastics waste.[1] This is an important issue from two points of view; the protection of the environment and the cost reduction with the recycling of the wasted material. Several approaches to the recovery of thermoplastics have been proposed: (1) incineration, (2) pyrolysis, and (3) recycling. Of these three, incineration and pyrolysis are the less effective methods in terms of recovering the value of the thermoplastics and because of the environmental pollution with toxic fumes. It is well established that recycled polymers have inferior properties compared with the virgin counterpart and that the magnitude of these effects depends mainly upon the polymer type and upon the number of cycles and conditions that exist during reprocessing.[2] Recycling is an option for reducing the volume of solid waste. Among the principal aspects that has to be considered when using a recycled material is that it has to cover the performance characteristics required for the final application. The properties of recycled/virgin blends must be almost the same as that of the virgin material.[3]

The restabilization of virgin and postconsumer HDPE blends with antioxidants and UV stabilizers can produce a significant improvement on the blend characteristics even when using different processing temperatures, with the exception of higher temperatures that can promote the thermal degradation of the

Correspondence to: S. Sánchez-Valdés (saul@ciqa.mx) or E. Ramírez-Vargas (evargas@ciqa.mx).

Contract grant sponsor: Mexican National Council of Science and Technology (CONACYT); contract grant number: 28,554-U.

Journal of Applied Polymer Science, Vol. 100, 3696–3706 (2006)

polymers.[4] Some studies on plastic recycling report the use of a mixture of phenolic and phosphite antioxidants to safe processing of recycled HDPE or low-density polyethylene (LDPE) and to enhance their long-term heat stability, effectively.[5] In other studies about the incorporation of additives and compatibilizing agents to HDPE/postconsumer HDPE blends, the results show that the mechanical properties, such as impact strength and elongation, can be maintained in adequate values compared with the blend without additives in which lower impact strength was observed.[6] In a study of Abad et al.[7] it was found by FTIR that the degradation of HDPE samples after the fifth extrusion cycle produced an increase in the number of carbonyl groups at 1760 cm^{-1}, indicating the material degradation. They also confirmed the effectiveness of a mixture of antioxidants on the reduction of the intensity of the peak at 1760 cm^{-1} in the sample without additives. Similar results were obtained by Cruz and Zanin[8] in the degradation studies of postconsumer recycled HDPE, while analyzing the requirements of restabilization and demonstrating the efficiency of the amount and type of the stabilizer used.

Results on the thermal characterization showed that only one peak was present for melting as well as for crystallization for recycled HDPE modified by LDPE and linear low density polyethylene (LLDPE),[9] which was related with an extensive cocrystallization at contents of 5–23% of LDPE. Other studies about thermal degradation of polyethylene reported a broadening of the endotherm peak and appearance of a new absorption peak between 75 and 100°C for PE samples degraded by accelerated aging, which were attributed to changes in crystallite sizes, molecular weight differences that are brought about by chain breaking, and secondary recrystallization.[10–12]

Studies on the postconsumer HDPE morphology have been focused on changes on the surface (such as color, holes, cracks, etc.) of the recycled materials while it is degraded by accelerated aging, as well as the observed improvements when stabilizers are used.

A morphology analysis by transmission electron microscopy (TEM) showed that there is not a complete integration of the recycled HDPE phase in the LDPE phase, which indicates a partial miscibility that is reflected in the improvement of the mechanical properties. However, in blends of 50% recycled HDPE it was observed that the thickness of the lamellae is not increased and that influenced negatively on tensile properties.[13] Ram et al.[14] reported that when pure PE is blended with PS it presents a fibrillar texture and the addition of small amounts of ethylene vinyl acetate (EVA) or EPDM seems to homogenize the structure. However, on increasing the concentration of these additives, reappearance of the fibrillar structure of heterogeneous blends was observed. Mechanical properties of virgin/recycled materials have been studied by various authors. Kartalis et al.[15] reported that the addition of restabilization systems to postconsumer HDPE is essential to improve the mechanical properties, especially elongation. On the other hand, it has been reported that the mechanical properties of recycled HDPE modified by LLDPE and LDPE depends upon the MFI and molecular weight of the components of the blend.[9] The rheological properties of a PE melt determine the processing techniques to be used, as well as the feasible applications of it.[16] In this way some authors like Kostadinova-Loutlcheva et al.,[17] in a study of the recycling of HDPE containers, found that flow curves of the polymer recycled in the twin screw extruder were very near each other, besides of a continuous but slight decrease in the viscosity with an increasing number of extrusions at high shear rates. In contrast, the samples reprocessed in a single screw showed a reduction in the viscosity over the whole shear rate range with increasing reprocessing steps; remarking the importance of the processing apparatus for these systems.

Even though the recycling of materials from postconsumer milk bottles has been studied by some authors, in this work we studied the effect of compatibilizing agents with different characteristics to that reported in literature such as: EVA (25% of VA) and Recycloblend™ (synergistic mixture of primary and secondary antioxidants from last generation), and some of those used in previous works, such as LLDPE and LDPE (at different contents), on the final properties of bottles made with blends of virgin HDPE/post consumer HDPE from milk bottles. In this work two types of blends were studied, one using grounded recycled material and the other using pelletized recycled material, both blended with virgin material. In this study a more complete characterization of thermal properties, crystallinity, phase morphology, molecular size, and flow and mechanical properties was performed. The purpose of this investigation is to obtain virgin/grounded recycled blends and virgin/pelletized recycled blends with high contents of recycled material, by using compatibilizing agents, trying to not affect the final properties and selecting the most adequate blends for the extrusion blow molding of a bottle for nonfood-packaging application, with the final properties needed for an adequate performance and with a lower cost of the materials used.

EXPERIMENTAL

Materials and preparation of blends

The polymers and compatibilizing agents employed in this work are shown in Table I. It can be observed that two types of recycled materials were used; pelletized (material with low impurities and contaminant con-

TABLE I
Main Characteristics of the Raw Materials

Trade name	Description	MFR (g/10 min)
HDPE Fortiflex B53–35H-011	High-density polyethylene	0.35[a]
Pelletized recycled material	Pelletized recycled HDPE	0.49[a]
Grounded recycled material	Grounded recycled HDPE	0.61[a]
LLDPE 2045 Dow Chemical	Linear low-density polyethylene	1.0
LDPE 20020 Pemex	Low-density polyethylene	1.95
Elvax DuPont	Ethylene/vinyl acetate (25% VA)	1.9
Recycloblend Ciba Gegy	Mixture of phenolic antioxidant and phosphite co-stabilizers	—

[a] Data obtained in laboratory.

tent) and grounded (material with high impurities and contaminant content from labels, adhesives, dust, etc.) from urban plastic waste. With these polymers different virgin/pelletized or grounded recycled blends with and without compatibilizers were prepared.

Figure 1 shows the washing procedure and selection of the recycled material grounded and pelletized that was used in this study. It is important to notice that this washing procedure removes only part of the contaminant materials.

The bottle samples were prepared using virgin and recycled materials and blends with and without compatibilizing agents, in a blow molding extruder model 1203 with a screw speed of 65% of its maximum capacity with a barrel temperature between 180 and 185°C and between 182 and 192°C for the die. ASTM test specimens were obtained from the bottles.

With these conditions, bottles were prepared with virgin HDPE, virgin/grounded recycled blends (70/30), virgin/pelletized recycled blends (50/50), and blends of recycled materials with compatibilizers. The above blend compositions were taken as a reference and were the ones that, without any additive, had an adequate behavior of the final product. The compositions and designations for each of the blends are listed in Table II.

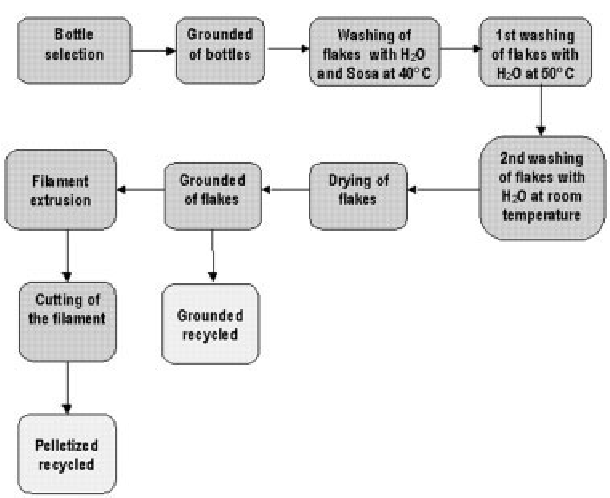


Figure 1 Schematic of the procedure used to obtain the recycled material.

Techniques and methods

To determine the characteristic IR bands of the polymers, recycled materials and compatibilizing agents used, a FTIR Nicolet Nexus 470 spectrometer was used. These tests were performed on hot-pressed film samples, scanned 30 times with 4 cm^{-1} resolution. The formation of carbonyl due to degradation process was also detected by FTIR.

Differential scanning calorimetry (DSC) analyses were performed with a TA instruments model 920. The thermograms were obtained at a temperature range between 5 and 180°C with a heating rate of 10°C/min in nitrogen atmosphere. The melting and crystallization temperatures (T_m and T_c) and the heat of fusion and crystallization (ΔH_m and ΔH_c) were measured.

To determine the gel content, the virgin, grounded, and pelletized recycled samples were Soxhlet extracted for 20 h in hot xylene, which is a solvent for HDPE. Once extracted, the samples were weighed to determine the final gel content (wt %) and other contaminates in each of the samples.

To visual analyze the gels and contaminants in the samples, a Leica MZ-6 spectroscope attached to an image analyzer using the Pro Plus 3.0 program was used. The 10× and 40× magnifications and micro images were obtained from the nonsoluble materials in the samples. The molecular weights of the virgin, recycled materials, and the different bottles elaborated from the blends of virgin/recycled material with compatibilizing agents were determined by GPC in an Alliance GPCV-2000 from Waters at 145°C using polystyrene standards.

X-ray diffraction of the materials and bottles elaborated from blends of virgin/recycled (grounded or pelletized) with and without additives was performed in a Siemens D5000 with Ni filter and using CuKα X-ray radiation. The X-ray samples were obtained at a 2θ range between 5 and 45° and with an angular rate of 0.4°/min at 35 kV and 25 amp.

TABLE II
Compositions and Designation of the Blends

Designation	Bottle composition
BRVHDPE	100% Virgin HDPE
B70V/30G	70% Virgin/30% grounded recycled
B50V/50P	50% Virgin/50% pelletized recycled
B27V/70G/3EVA	27% Virgin/70% grounded recycled/3% EVA
B27V/70P/3EVA	27% Virgin/70% pelletized recycled/3% EVA
B29.6V/70G/0.4RB	29.6 Virgin/70% grounded recycled/0.4% recycloblend
B25V/70P/5LLDPE	25% Virgin/70% pelletized recycled/5% LLDPE
B49.6V/50G/0.4RB	49.6% Virgin/50% grounded recycled/0.4% recycloblend
B47V/50G/3EVA	47% Virgin/50% grounded recycled/3% EVA
B45V/50G/5LLDPE	45% Virgin/50% grounded recycled/5% LLDPE
B40V/50G/10LDPE	40% Virgin/50% grounded recycled/10% LDPE

The morphology of the samples was analyzed using a scanning electron microscope Topcon SN510. The samples were fractured after at least 4 h in liquid nitrogen, near −150°C. The fracture was done under nitrogen, and the sample thickness was 0.5 mm. This method was used for all the scanning electron microscopy (SEM) samples. The surfaces were Au-Pd coated by vacuum deposition. All the micrographs were obtained at 600× with 15 kV and with a working distance of 18 mm. The reported SEM micrographs were selected from at least five measurements.

The rheological measurements of melt flow index and capillary rheometry were evaluated in a Tinius Olsen UEA-78 plastometer according to ASTM D1238 and in capillary rheometer Instron 4467 according to ASTM D3835, respectively. With the data from capillary rheometry, flow curves of apparent shear stress and shear rate versus viscosity were obtained. The test temperature was 190°C for all the measurements.

The mechanical properties of elongation at break and tensile strength were evaluated with an Instron tester model 4301 according to ASTM D638. The sample specimens were cut out from the bottles elaborated by extrusion blow-molding. The crosshead speed was 200 mm/min and the gauge length was 63.5 mm. Elmendorf tear strength was determined according to ASTM D1004 with a crosshead speed of 51 mm/min.

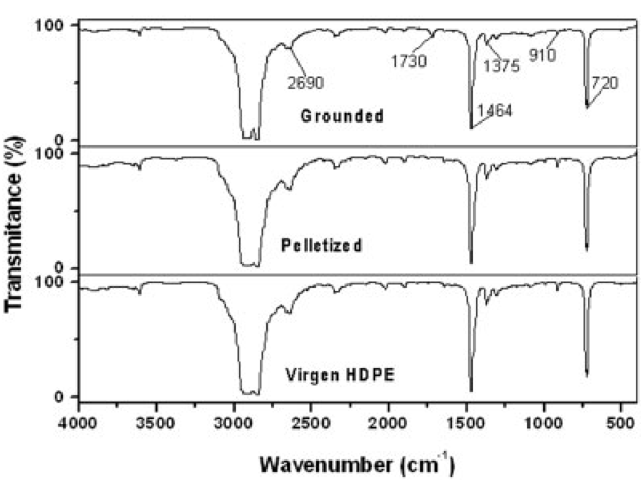


Figure 2 FTIR curve of virgin, grounded, and pelletized recycled materials.

RESULTS AND DISCUSSION

Sample characterization

Figure 2 shows the FTIR results obtained for the different samples. The characteristic signals for the HDPE for the three samples are shown in this figure. For the grounded recycled sample an additional peak could be seen at 1730 cm^{-1}, attributed to carbonyl groups (C=O) formation. This indicates that this sample is highly degraded.[7] This peak was not visible for the pelletized recycled material, because the degraded material was eliminated during the extrusion process when passing through the barrel meshes.

The thermal characteristics, molecular weights, melt flow index, and content of insoluble material (gels) for the three samples are shown in Table III. DSC results show that the melting and crystallization temperatures, as well as the heat of fusion and crystallization, are higher for the pelletized recycled material, indicating a higher crystallinity. This could be related with

TABLE III
Materials Characteristics

Property	Virgin material	Pelletized recycled	Grounded recycled
T_m (°C)	133.5	138.3	132.8
ΔH_f (J/g)	156.8	189.6	163.4
T_c (°C)	114.4	115.9	116.2
ΔH_c (J/g)	189.2	214.2	198.8
M_n (g/mol)	24726	15147	20376
M_w (g/mol)	129537	107695	113099
M_w/M_n	5.2	7.1	5.5
MFR (dg/min)	0.374	0.50	0.613
Gel content (%)	0.08	0.13	0.49

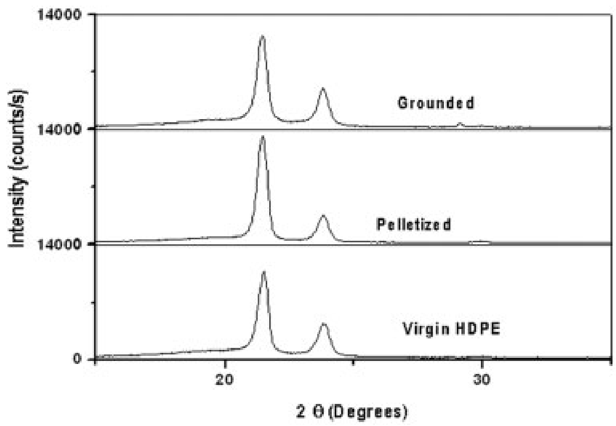


Figure 3 XRD patterns of virgin, grounded, and pelletized recycled materials.

the lower molecular weight of this sample. The difference in molecular weights between virgin and recycled materials is because they come from different sample materials. The X-ray diffraction patterns for the three samples are shown in Figure 3. A higher intensity signal (higher crystallinity) in the pelletized recycled material can be observed, which is in agreement with the DSC results. This pattern shows the HDPE characteristic peaks at 2θ of 110 and 220°.[18] Rheological properties were evaluated by MFR and viscosity measurements. MFR results are shown in this table and viscosity versus shear rate in Figure 4. These results show low MFR and high viscosity for the virgin material. The highest MFR was for the grounded recycled, which can be related with the contaminants in this sample that could be acting like flow modifiers through the barrel. The flow curves show a continuous decrease in viscosity with an increase in shear rate, and at higher shear rates, the curves seem to be very near each other with almost the

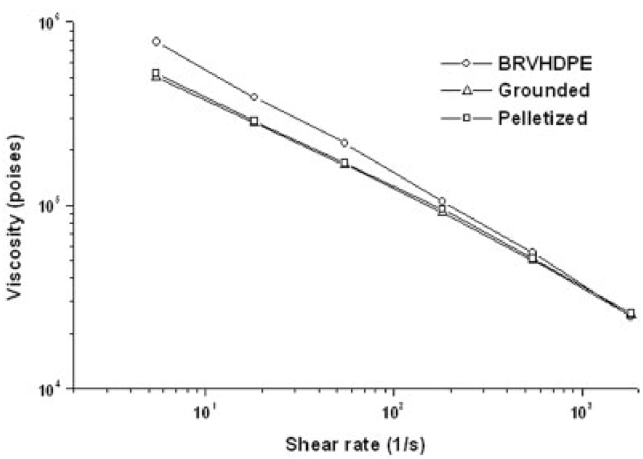


Figure 4 Apparent viscosity as a function of shear rate for virgin HDPE, grounded, and pelletized recycled.

TABLE IV
Thermal Characteristics of the Bottles of Virgin/Recycled Blends with and without Compatibilizing Agents

Sample	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)
BRVHDPE	131.5	160.2	117.1	193.0
70V/30G	131.2	161.9	117.8	185.9
50V/50P	132.6	165.2	121.0	194.3
29.6V/70G/0.4RB	131.6	161.9	119.2	191.4
27V/70G/3EVA	131.3	164.5	122.1	193.4
49.6V/50G/0.4RB	131.1	163.2	118.5	190.0
47V/50G/3EVA	131.8	164.0	118.8	193.1
45V/50G/5LLDPE	132.5	163.3	118.4	194.2
40V/50G/10LDPE	131.9	160.1	118.8	191.3
25V/70P/5LLDPE	131.1	164.8	119.4	194.7
27V/70P/3EVA	132.4	166.2	119.4	194.6

same viscosity among them. This behavior is in agreement with that reported by Kukaleva et al.[9] Finally, the gel or insoluble material content was higher for the grounded recycled; almost six times the value obtained for virgin material. The gel content in the pelletized material was almost two times the value from virgin material, and as expected, the lowest value was for the virgin material.

Effect of addition of compatibilizing agents on the virgin/recycled bottles

Thermal properties

To determine the effect of compatibilizing additives on melting and crystallization temperatures, as well as on the heat of fusion and crystallization, DSC analysis was done for each of the bottles with and without additives and with low and high content of recycled material. The DSC results are shown in Table IV.

It could be seen in this table that there is a slight difference in heat of fusion and crystallization between the virgin material and virgin/recycled material blends, showing slightly higher values for the blend with pelletized material compared with that of the samples with virgin and grounded materials. This could be related with the fact that pelletized material has lower molecular weight and higher crystallinity, as was shown in Table III; nevertheless, these differences in crystallinity are relatively low.

On the other hand, if we compare the thermal values of the blends without additives with the ones with additives, there is not significant differences between them. Considering that the blends with additives have higher recycled material content it is observed that only the blend with higher compatibilizing agent (10% of LDPE) has lower heat of fusion and crystallization, showing a very similar thermal behavior among the rest, indicating similar crystallinities among them.

Molecular weights

The weight–average molecular weight (M_w) and number–average molecular weight (M_n), as well as poly-

TABLE V
Molecular Weights and Polydispersity

Sample	M_n (g/mol)	M_w (g/mol)	M_w/M_n
BRVHDPE	25,154	128,335	5.1
70V/30M	22,067	119,920	5.3
50V/50P	18,479	123,921	6.7
27V/70G/3EVA	20,718	121,578	5.8
29.6V/70G/0.4RB	19,182	118,757	6.2
48V/50G/0.4RB	24,179	122,526	5.1
47V/50G/3EVA	23,424	117,970	5.0
45V/50G/5LLDPE	25,004	115,007	4.6
40V/50G/10LDPE	23,496	109,313	4.7
27V/70P/3EVA	20,901	111,272	5.3
25V/70P/5LLDPE	20,766	118,403	5.7

dispersity for each of the virgin/recycled blends with and without additives bottle samples, obtained by GPC, are shown in Table V. If we compare the bottle samples made with virgin material with those made with virgin/recycled blends with and without compatibilizing additives, the blends show only a slight tendency to lower number–average molecular weights (M_n) and weight–average molecular weights (M_w) and a slight broadening in the curve of MW distribution, as can be seen from polydispersity values. This could be related with the lower molecular weight of the recycled materials compared with that of the virgin material and also could be related with the possible competition between chain scission and chain crosslinking during processing, as was reported by other authors.[17,19]

Morphology

Some authors such as Gupta et al.[20] have studied the morphology of PE blends and have reported that in the surface of tensile-fractured surfaces of HDPE/LLDPE samples a fibrillar structure (observed mainly in HDPE) with transverse connections between the fibrils (observed in LLDPE) was observed. The authors concluded that LLDPE has an important effect in reducing the fibrillation tendency of HDPE. Some other works had reported a fibrillar morphology for tensile-fractured surfaces of PE/PS samples, which tends to become a homogeneous structure when compatibilizing agents were added in low contents. When using higher contents of these additives, fibrillar structures tends to reappear, which was in agreement with mechanical properties.[14] Albano et al. reported changes in mechanical properties related with the morphology, obtained by TEM, for LDPE/HDPE blends.[13]

Figures 5–8 show micrographs of the fractured surface morphology from each of the samples. Figure 5 shows the SEM micrographs for the virgin material and virgin/recycled (grounded and pelletized) blends without additives. When comparing the virgin HDPE with the recycled materials, the differences in the fractured surface morphology can be observed. The micrograph of the virgin material shows a homogenous surface; meanwhile, in the image of the blends a less homogeneous surface with discontinuous flows can be seen, which may be related with the different flow patterns of the blend components.

In the blends with EVA copolymer (47V/50G/3EVA, 27V/70G/3EVA, and 27V/70P/3EVA; Fig. 6) and in the blends with LLDPE and Recycloblend (45V/50G/5LLDPE, 25V/70P/5LLDPE, and 48V/50M/2RB; Fig. 7) a more homogeneous morphology and a continuous flow pattern could be observed, suggesting a better integration of the blend components. This behavior should be proven with the mechanical results further obtained for these blends. On the other hand, the micrographs of the samples with

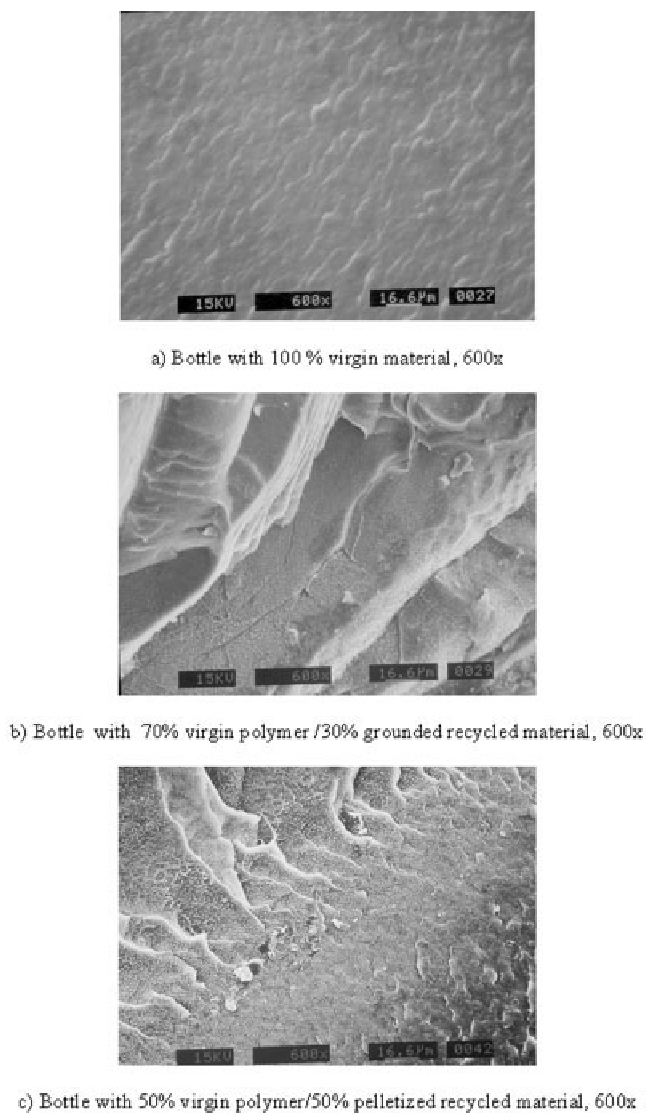
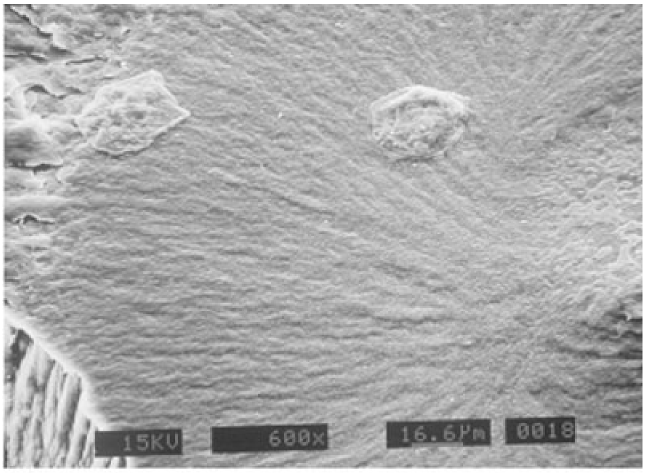
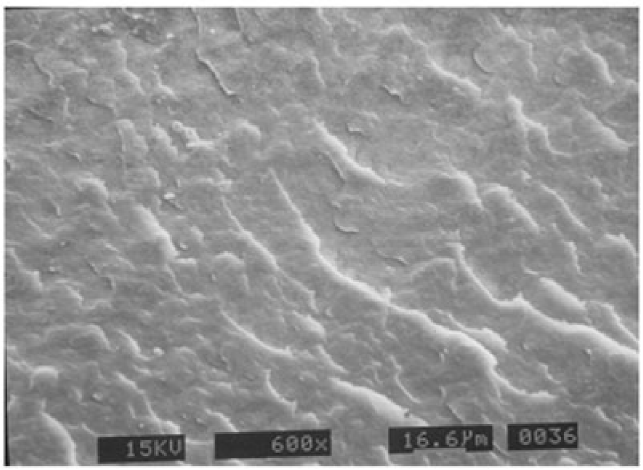


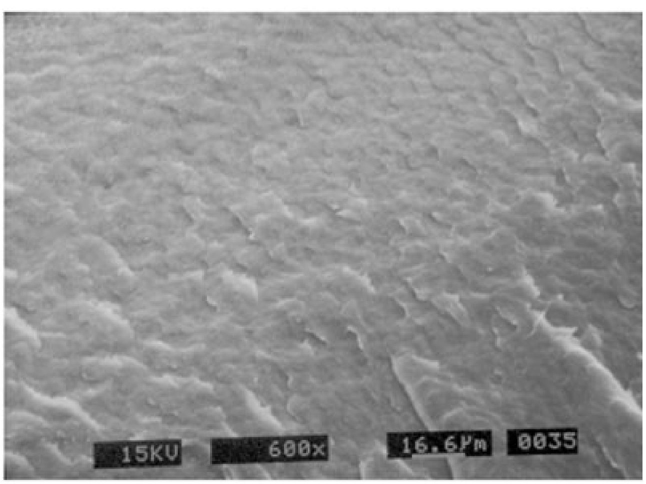
Figure 5 SEM micrograph for 100% virgin, 70/30 virgin/grounded, and 50/50 virgin/pelletized samples surface.



a) Bottle 47V/50G/3EVA, 600x

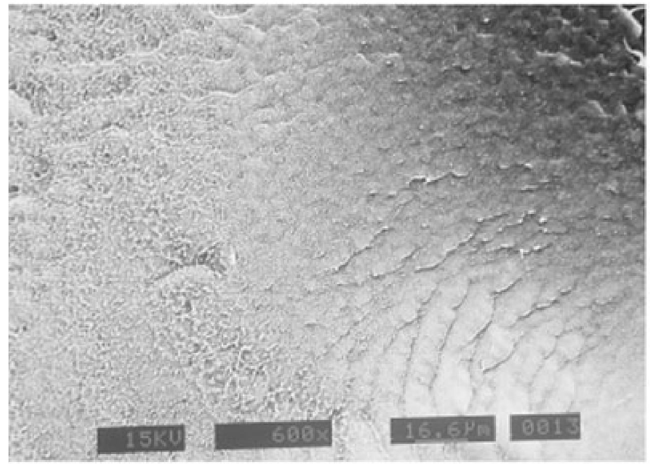


b) Bottle 27V/70G/3EVA, 600x

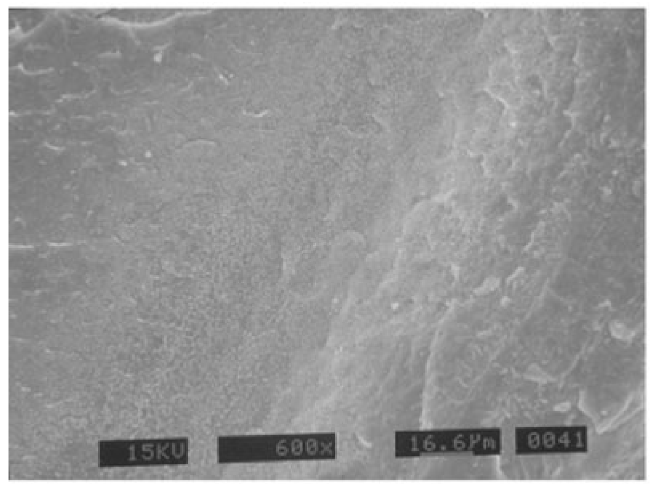


c) Bottle 27V/70P/3EVA, 600x.

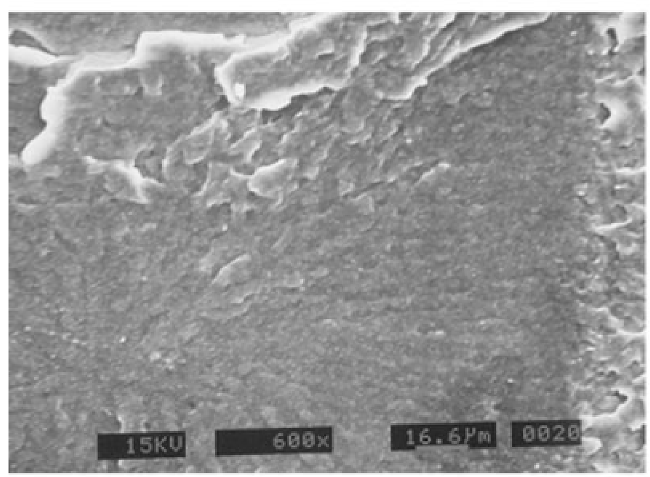
Figure 6 SEM micrograph of samples surface for blends with compatibilizing additive EVA.



a) Bottle 45V/50G/5LLDPE, 600x



b) Bottle 25V/70P/5LLDPE, 600x.



c) Bottlle 48V/50 G/0.4 RB, 600x

Figure 7 SEM micrograph of samples surface for blends with compatibilizing additive LLDPE and Recycloblend.

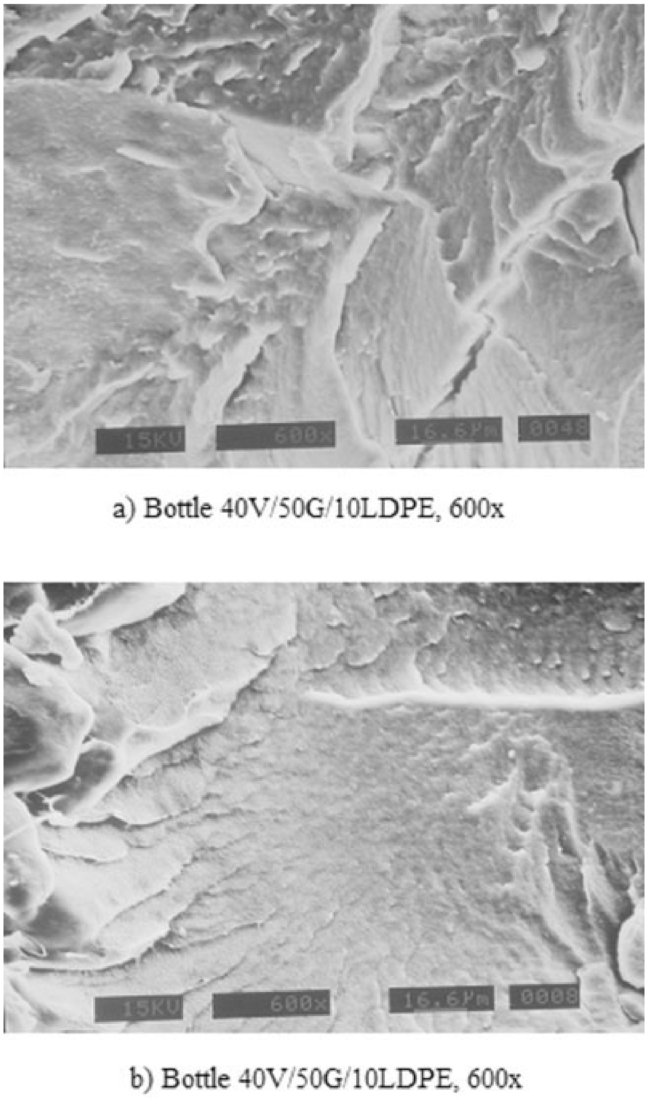


Figure 8 SEM micrograph of samples surface for blends with compatibilizing additive LDPE.

compatibilizing agents LDPE are shown in Figure 8. It can be seen that there was not a complete integration of the blend components (40V/50G/10LDPE). This again should be proven with the mechanical results.

Rheological properties

Melt flow index of bottle samples of virgin HDPE, grounded and pelletized recycled, and blends of virgin/recycled materials with different compatibilizing agents were determined. Table VI shows the variation in MFR. It can be observed that the lowest MFR is for the virgin sample, and the virgin/recycled blends with compatibilizing agents have slightly higher MFR values than those of the virgin material and the reference blends (blends without compatibilizing agents). This is attributed, in first place, to the higher MFR of the recycled materials and to the fact that blends with

TABLE VI
Melt Flow Index of Bottle Samples

Sample	MFI (g/10 min)
BRVHDPE	0.381
70V/30G	0.475
50V/50P	0.434
27V/70G/3EVA	0.579
29.6V/70G/0.4RB	0.544
48V/50G/0.4RB	0.478
47V/50G/3EVA	0.526
45V/50G/5LLDPE	0.506
40V/50G/10LDPE	0.452
27V/70P/3EVA	0.462
25V/70P/5LLDPE	0.545

compatibilizing agents have higher contents of recycled material. On the other hand, the small differences between these samples could be related with the different type and content of compatibilizing agents.

The rheological results of the virgin/recycled material with and without compatibilizing additives bottles, obtained by capillary rheometry, are shown in Figures 9 and 10, as plots of the variation in viscosity with shear rate.

Figure 9 shows the behavior for the bottles of virgin material and the blends of virgin with up to 70% of recycled material (grounded and pelletized) and with different compatibilizing agents. It can be seen in this figure that the recycled material blends have lower viscosity than the virgin polymer, especially at low shear rates, which is in agreement with the MFR results. It can be observed how the blends of virgin with 70% of recycled material with and without compatibilizing agents all have a very similar behavior over the whole shear rate range, being quite similar to the bottle with virgin material. Small differences at low

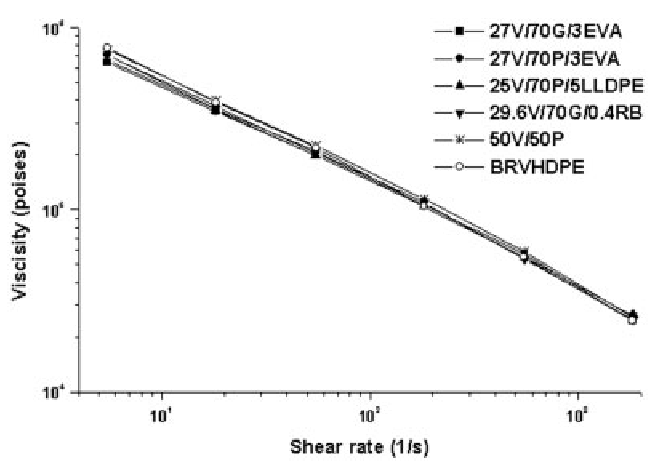


Figure 9 Apparent viscosity as a function of shear rate for virgin HDPE, grounded and pelletized recycled, and blends with 70% of recycled (grounded and pelletized) and different compatibilizing agents.

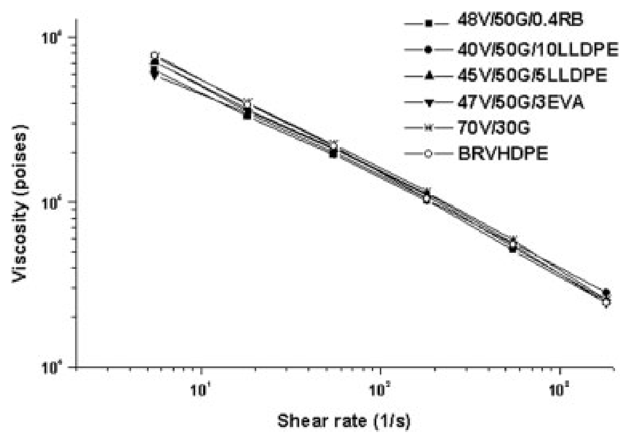


Figure 10 Apparent viscosity as a function of shear rate for virgin HDPE, grounded and pelletized recycled, and blends with 50% of recycled (grounded and pelletized) and different compatibilizing agents.

shear rates can be seen, in particular, for the sample of 27V/70G/EVA, which has lower viscosities; however, when considering the high recycled material content, this variation is quite small.

Figure 10 shows the flow curves of virgin compared with the blends of virgin with 50% of recycled material and with different compatibilizing agents. It can be observed that they showed a similar behavior to that observed in Figure 9 where the flow curves are very near each other showing no significant differences at any shear rate for any of the blends with and without compatibilizing agents. These flow curves suggest that the virgin/recycled blend materials were not significantly degraded, especially by chain scission. According to the study by Kostadinova-Loutlcheva et al.,[17] the degradation process by chain scission tends to make higher differences between the flow curves, especially at low shear rates. These results are also in agreement with those obtained for the molecular weight, which were discussed earlier. From these results we can conclude that there was not a significant reduction in viscosity in the blends with higher recycled content with compatibilizer additive, and this could be attributed to the stabilization effect of the compatibilizer.

Mechanical properties

The results of tensile strength, elongation, tear strength, and tensile modulus are shown in Table VII. According to the mechanical properties shown in this table, we can say that, in general, the blends of virgin/recycled with compatibilizing agents had lower stiffness and a little more deformation than the blends without compatibilizing additives. This becomes more relevant if we consider that the content of recycled material is higher in all the blends with compatibilizing agents.

It can be observed in this table that the blends with the best behavior were those in which pelletized recycled material was used. In the blends with grounded recycled, the blends that showed higher mechanical behavior were those with Recycloblend and EVA as compatibilizing agent. The tensile modulus results for the bottles of virgin/grounded recycled blends and the bottles of virgin/pelletized recycled blends are shown in this table. A reduction in modulus can be seen in this table when comparing the bottles with additives with the reference bottles (grounded and pelletized) without additives. However, similar to the elongation results we have to consider that the bottles with additives have higher recycled material content than the reference bottles without compatibilizing agent (70V/30G and 50V/50P). This slight reduction in modulus could be attributed to the lower toughness of the compatibilizing additives, especially in the blend with 10% of LDPE as a compatibilizing agent. The tear strength results for the bottles of virgin/recycled (grounded and pelletized) with and without compatibilizing additives are shown in this table. It can be observed that there is not a significant variation

TABLE VII
Mechanical Properties

Sample designation	Elongation at break (%)	Tensile modulus (MPa)	Tensile strength (MPa)	Tear resistance (kN/m)
BRVHDPE	880	601.4	25.8	171.2
70V30G	937	558.8	33.4	160.9
50V50P	950	516.1	34.3	160.8
27V/70G/3EVA	875	553.5	19.8	161.0
29.6V/70G/0.4RB	975	552.7	25.7	156.1
48V/50G/0.4RS	962	498.4	34.1	154.1
45V/50G/5LLDPE	965	550.4	27.9	163.2
47V/50G/3EVA	961	534.2	30.0	162.3
40V/50G/10LDPE	875	405.6	19.0	160.4
27V/70P/3EVA	1018	501.9	30.0	149.6
25V/70P/5LLDPE	930	445.9	32.3	168.9

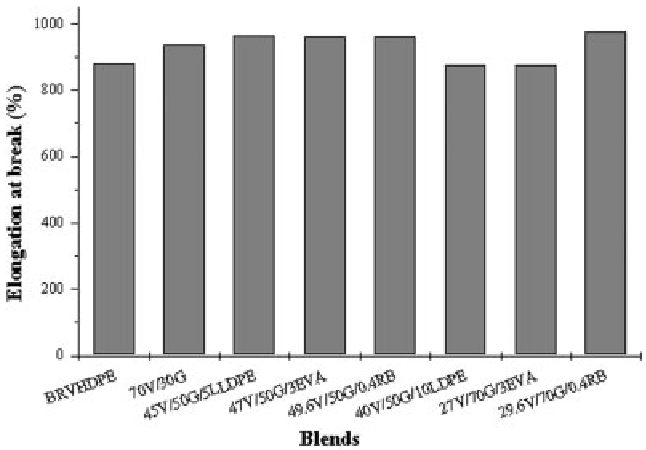


Figure 11 Elongation at break of bottles with blends of virgin HDPE with 70% of recycled material and different compatibilizing agents.

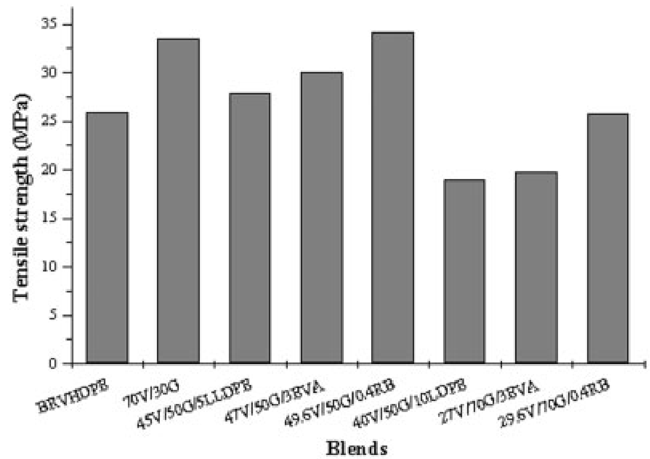


Figure 13 Tensile strength of bottles with virgin/grounded recycled blends with and without compatibilizing additives.

between the blends with and without compatibilizing agent. It is important to see how the higher recycled content, either grounded or pelletized, did not affect the tear strength of the blends.

In Figure 11 the elongation results of the bottles with blends of virgin HDPE with different grounded recycled content (50 and 70%) and with different compatibilizing agents are shown, for comparison of the mechanical results. The bottle sample of the virgin/grounded recycled blend without compatibilizing agent is shown as a reference. In the same way Figure 12 shows the elongation behavior of the bottles from virgin/pelletized recycled blends with different contents of recycled (50 and 70%), and the blend of these materials without the compatibilizing agent is shown as a reference. It can be seen in these figures (Figs. 11 and 12) that the elongation at break is slightly increased with the different compatibilizing agents, even with high contents of recycled material (grounded and pelletized). This result suggests that the deformation behavior of these materials is not significantly affected with the increase in recycled content when the compatibilizing agents are used.

The tensile strength results of the bottles from virgin/grounded recycled and virgin/pelletized recycled blends are shown in Figures 13 and 14. It can be seen in these figures that there is an increase in tensile strength in most of the blends with compatibilizing agents, especially in those with Recycloblend. It is evident that the blends with 50% of recycled material have the highest increase in tensile strength compared with those with 70% of recycled material. This indicates that the efficiency of compatibilizing agents is affected by the increment in recycled material. In the bottles made with blends of virgin/grounded recycled with a content up to 70% of recycled and compatibilizing agent, this increase in tensile strength was not observed. On the other hand, this mechanical property

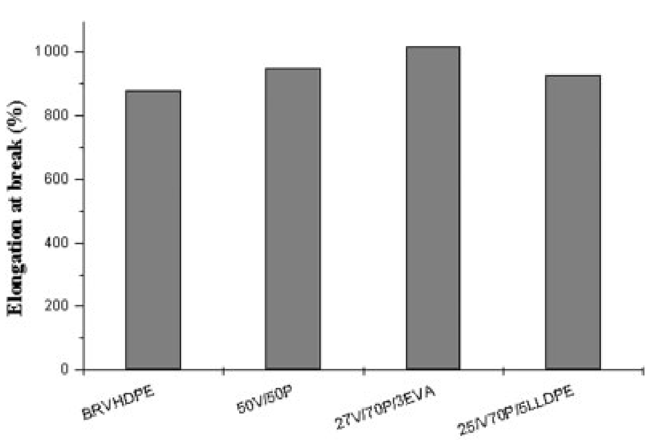


Figure 12 Elongation at break of bottles with virgin/pelletized recycled blends.

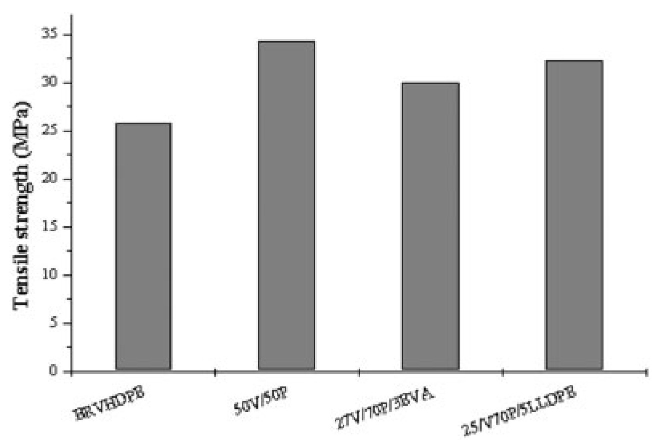


Figure 14 Tensile strength of bottles with virgin/pelletized recycled blends with and without compatibilizing additives.

was kept into acceptable values, similar to those of virgin material, even with the increase in the pelletized recycled content up to 70% (Fig. 14). All this mechanical behaviors are similar to that reported by Kartalis et al.[15] and Blom et al.[21] using other kind of compatibilizing agent between virgin and recycled materials.

It is clear from the above data that the mechanical properties of virgin/recycled blends were enhanced with the addition of the different compatibilizing agents even at higher recycled contents. Therefore, these blends could have a good mechanical performance in applications in which tensile properties are required.

With respect to the appearance of the bottles obtained by extrusion blow-molding with virgin and recycled materials, a change in color (pale dark) was observed in the samples with grounded recycled material. The change of color was less significant in the samples of bottles with pelletized recycled. This change in color could be related with the foreign particles from urban plastic waste. However, as was proven with the mechanical results, these impurities did not affect the mechanical performance. This change in color was not detected when using pigments in the bottles, which makes these materials a good option for the production of pigmented bottles for the packaging of cleaning products and other nonfood applications.

CONCLUSIONS

Blends of virgin/grounded recycled and virgin/pelletized recycled HDPE, in general, were not significantly different from each other and both had a quite similar behavior than the virgin polymer when compatibilizing agents were used, even with recycled contents up to 70%, being higher than the recycled contents of the reference blends (70/30 virgin/grounded and 50/50 virgin/pelletized). Addition of compatibilizing agents yielded a material with properties similar to those for the virgin HDPE, helping to reduce the effect of polymers degradation on the rheological and mechanical behavior, especially Recycloblend and LLDPE, for the blends with grounded recycled material, and LLDPE y EVA, for the blends with pelletized recycled. It can be concluded that it is possible to use blends of virgin HDPE with high contents of recycled (grounded or pelletized) material with the aid of a compatibilizing agent, for the manufacturing of extrusion blow-molded bottles.

References

1. Resins of Modern Plastic 1987, 64, 41.
2. Mitterhofer, F. Polym Eng Sci 1980, 20, 692.
3. Ehring, R. J., Ed. Plastics Recycling: Products and Processes; Hanser: New York, 1992.
4. Pfaendner, R.; Herbst, H.; Hoffmann, K. Macromol Symp 1998, 135, 97.
5. Pospíšil, J.; Nešpùrek, S.; Pfaendner, R.; Zweifel, H. Trends Polym Sci 1997, 5, 294.
6. Pospišil, J.; Sitek, F.; Pfaendner, R. Polym Degrad Stab 1995, 48, 351.
7. Abad, M. J.; Ares, A.; Barral, L.; Cano, J.; Díez, F. J.; García-Garabal, S.; López, J.; Ramírez, C. J Appl Polym Sci 2004, 92, 3910.
8. Cruz, S. A.; Zanin, M. Polym Degrad Stab 2003, 80, 31.
9. Kukaleva, N.; Simon, G. P.; Kosior, E. Polym Eng Sci 2003, 43, 26.
10. Gulmine, J. V. Polym Degrad Stab 2003, 79, 385.
11. Dorner, G.; Lang, R. W. Polym Degrad Stab 1998, 62, 431.
12. Valadez-González, A.; Cervantes-Uc, J. M.; Veleva, L. Polym Degrad Stab 1999, 63, 253.
13. Albano, C.; Sánchez, G.; Ismayel, A. J Macromol Sci Pure Appl Chem 1998, 35(7/8), 1349.
14. Ram, A.; Narkis, M.; Kost, J. Polym Eng Sci 1977, 17, 274.
15. Kartalis, C. N.; Papaspyrides, C. D.; Pfaendner, R.; Hoffmann, K.; Herbst, H. J Appl Polym Sci 1999, 73, 1775.
16. Peacock, A. J., Ed. Handbook of Polyethylene: Structures, Properties and Applications; Marcel Dekker: New York, 2000.
17. Kostadinova-Loutlcheva, M.; Proietto, M.; Jilov, N.; La Mantia, F. P. Polym Degrad Stab 1997, 57, 77.
18. Murthy, N. S.; Minor, H. Polymer 1990, 31, 996.
19. Pattanakul, C.; Selke, S.; Lai, C.; Miltz, J. J Appl Polym Sci 1991, 43, 2147.
20. Gupta, A. K.; Rana, S. K.; Deopura, B. L. J Appl Polym Sci 1992, 46, 99.
21. Blom, H. P.; Teh, J. W.; Rudin, A. J Appl Polym Sci 1998, 70, 2081.