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RECYCLING OF POLYOLEFINS: PART 1: BLENDS OF TWO POLYMERS

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ABSTRACT

The recovery of plastic waste may be an incentive to industry, since the use of such plastics represents a cheaper source of raw material. The aim of the present paper is to study the feasibility of recycling polyolefins with copolymer additives to improve the mechanical properties and increase the useful life of the blends. The values obtained for the mechanical and thermal properties for polypropylene (PP) with recycled high density polyethylene (HDPE) show that it is possible to use recycled HDPE up to 30% w/w. The properties and applications are similar to those obtained with PP alone, thereby reducing the cost of the raw material. The addition of the compatibilizer at 5% represents the optimal concentration for improving the final properties of the finished product. Analysis of the mechanical and thermal behavior of the low density polyethylene (LDPE) with recycled HDPE blends lead us to conclude that it is possible to use recycled HDPE because the properties of the finished product are thereby enhanced.

INTRODUCTION

Polymers are very important materials in industry, and are increasingly used thanks to their wide range of properties. As the production of new polymers becomes increasingly expensive, blends of these compounds become attractive for research and industrial applications. The main goal of combining two or more polymers is to obtain a material with appropriate features and conditions for processing. Post-used polymers are mixed in order to recycle such materials, and to reduce the environmental impact generated by these solid residues.

Plastics are an important and irreplaceable part of the range of materials required by society, and because of their non-degradable features represent a serious environmental problem when they become waste at the end of their useful lifetime. In the last decades, total consumption of plastics, as well as the range of applications and visibility have shown a meaningful increase. This phenomenon is due to the properties of plastic materials, as well as their adaptability, and the use of economical manufacturing techniques. Nowadays, plastics are used in a great deal of consumer goods and industries such as packaging, construction, transport, vehicle manufacture, electronics, agriculture, and for many household uses. As a result, it is impossible to avoid the generation of a great amount of plastic waste, or the resulting severe environmental, ecological and economic problems brought about by their long permanence in the environment.

The most commonly used plastics, specifically in packing and wrapping, are polyolefins (PP, HDPE, LDPE, etc.). This is shown in Table 1, which reflects the total consumption expressed as a percentage of the different plastics used in the European Union and Venezuela. These polymers represent about 70% of the plastics used. This high consumption is reflected in waste levels which consequently cause environmental problems, and for this reason researchers are studying ways to solve this serious ecological situation [1-6].

Reinink [7] carried out a study on the generation of plastic waste in Western Europe (EEC) and projected that by the year 2000, the volume will grow to 20 million tons compared to 13 million tons produced in 1989.

In Venezuela, as far as household waste and its plastics content are concerned, volumes grow almost linearly in direct relation with population growth. However, plastic waste component has increased quickly as a result of the increase in the consumption of plastic products. During the 1983-1988 period, consumption rose from 188,000 to 346,000 tons [2]. Therefore, consumption of plastics increased by 84%, whereas population growth was 14%. This high level of consumption results in an increase in the volume of plastics in household waste.

Among the options suggested to reduce pollution, the most notable are those involving sanitary garbage dumps, biodegradable plastics, incineration and recycling. Disposal of plastic waste in sanitary garbage dumps reduces the capacity

TABLE 1: Total Consumption of Plastics (%) used for Packaging in Venezuela and the European Economic Community Buekens (1992), Avipla (1993), Rodríguez (1992)

Plastics	EEC	Venezuela
LDPE	37.9	28.9
HDPE	17.5	20.8
PP	11.2	14.5
PS+ABS	11.7	12.4
LLDPE	6.6	-----
PET	3.5	-----
Other	1.2	3.2
PVC	10.4	20.2

of those deposits, due to the huge volume generated by polymers and the difficulties involved in compacting the material. The disposal of plastics hinders the future use of the land used as garbage lots, while the incineration of plastics provokes severe environmental pollution due to the concentration and hazard levels of gases and the level of heat generated throughout the combustion process. Moreover, biodegradable plastics are extremely expensive for Venezuela. Therefore, we came to the conclusion that recycling would represent the most feasible option for avoiding further increases in levels of plastic residues, and could be economically profitable, since it reduces the costs involved in plastic waste and the cost of manufacturing finished products.

We can view the recycling of polymers as an essential process. It is, however, important to determine the behavior of these materials in order to optimize the non-used polymer/recycled polymer relation and to obtain suitable properties that do not result in a deterioration of the finished product.

One of the goals pursued in the current study is to develop new materials, especially those most produced and used in Venezuela, i.e. polyolefins. Therefore, the main goal of the present paper is to study the technical feasibility of polyolefin recycling through the evaluation of the mechanical, thermal and morphological properties of recycled polyolefins with non-recycled polymers. In order to reach this goal, two blends were mixed: a) PP with recycled HDPE and b) LDPE with recycled HDPE.

Table 2: Variation of the Mechanical Properties of PP with Recycled HDPE (E: Young's Modulus, σ_B: Ultimate tensile strength, ε_B: Elongation at break, IS: Impact Strength)

HDPE(%)	E (Kg/mm^2)	σ_B (Kg/mm^2)	ε_B(%)	IS(J/m)
0	63.6	3.6	12.6	7.0
5	68.4	3.6	10.1	9.3
10	72.6	3.4	8.6	8.5
20	72.0	3.1	7.1	6.5
30	71.0	3.2	6.9	9.3
40	64.7	3.1	8.3	7.5
50	69.2	2.9	7.1	7.0
100	55.2	1.6	560.0	38.3

EXPERIMENTAL

During the first part of the experiment, non-used polymers (PP, ρ:0.903 gr/cm^3, LDPE, ρ:0.925 gr/cm^3) and recycled polymers were mixed in an extruding machine, at different compositions. Mechanical properties after compression molding were measured using an Instron Tensiles tester with a crosshead of 25 mm/min. Impact strength measurements were made on notched samples using a fractoscope apparatus (Zwick) in the Izod mode. Differential scanning calorimetry (DSC, Perkin Elmer) was used to observe melting behavior. To erase thermal history, the first cooling and the second heating thermograms were detected with the following scanning rate: 5°C/min in the first cooling and 10°C/min in the second heating. The morphology of each sample was observed through a transmission electron microscope (TEM).

RESULTS AND DISCUSSION

PP/recycled HDPE

The results of the Young's Modulus for the PP and recycled HDPE blend are presented in Table 2. There is a slight synergism in the 0–50% range of HDPE, although this property largely does not depend on the nature of the compound. The

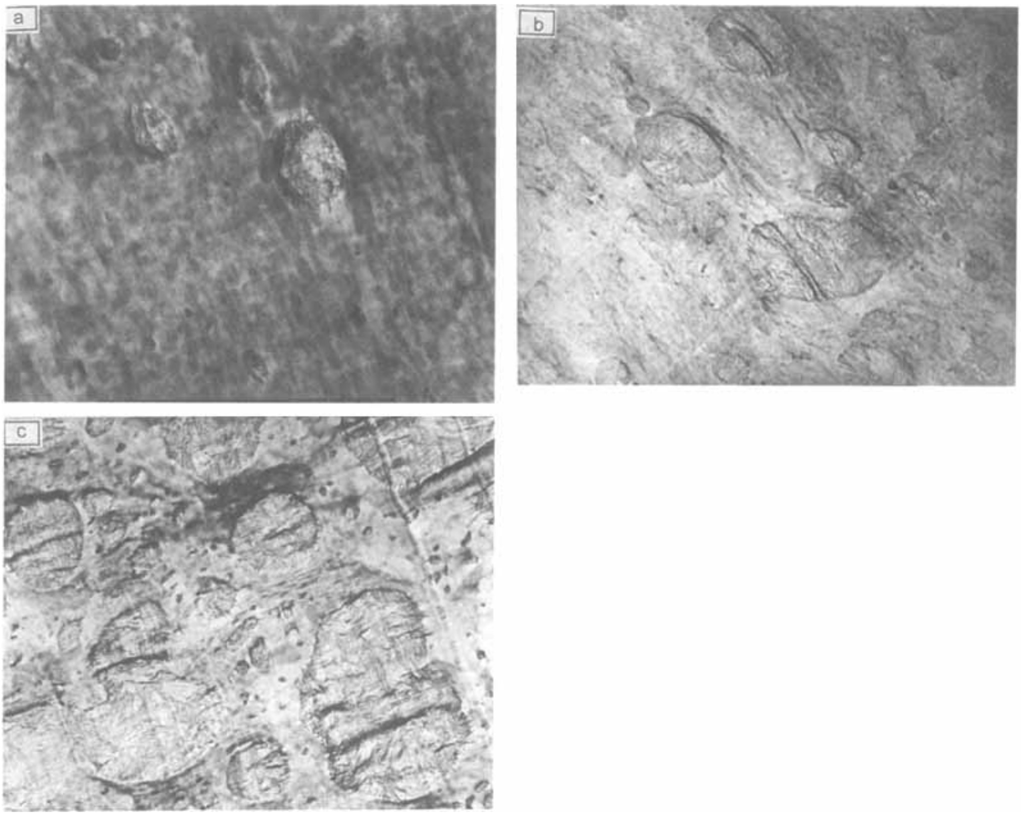

Figure 1. TEM micrographs of PP with recycled HDPE blends. a) 90/10, b) 70/30 and c) 50/50. Scale bar 2.8 um (—).

morphology obtained by optical microscopy agrees with the values of the Young's Modulus, due to the small size of the spherulites. Based upon these results, one can deduce that due to the HDPE, there is a great amount of interlinking of molecules in the interface. This behavior is also due to the fact that in the process of decomposition of HDPE there are some rupture and intercrossing reactions that cause rigidity in the samples.

The values of elongation at break reflect the incompatibility of the blends. The resistance to rupture does not show meaningful changes.

With respect to the results of impact strength, it can be stated that interface adhesion is poor. This can be attributed to the fact that there is no continuity in the

TABLE 3: Values Obtained from Thermal Studies of Virgin PP with Recycled HDPE Blends. (T_f: Fusion Temperature, ΔH_f: Fusion Heat, t: Theoretical, e: Experimental, X: Crystallinity)

HDPE (%)	Tf_1 (°C)	Tf_2 (°C)	X (%)	ΔH_{fe} (J/g)	ΔH_{ft} (J/g)
0	-------	163	72	150	----
5	134	156	38	80	151
10	130	158	38	81	153
20	130	162	38	83	157
30	130	159	49	109	160
40	131	160	41	95	164
50	131	159	38	90	167
100	133	----	73	189	-----

interface, as shown in Figure 1. The micrographs obtained by TEM are shown in Figure 1, as well as the presence of holes in the interface and the poor dispersion of the minority component in the matrix phase. In addition, when the disperse particles are large, they are more effective in bringing about a process of cracking (Figure 1).

Table 3 shows the results of the thermal analysis carried out on the samples studied. The fusion temperatures of PP as well as HDPE decrease slightly due to the presence of the latter polymer in the blends. This small decrease can be due to the effect of the interplasticizing action caused by a molecule of one of the components, that acts as a diluent inside the crystalline of the other component. Reduction of the spherulitic order could also cause this behavior.

The fusion enthalpy values of the blends are shown below those of the components. The table also presents the theoretical fusion enthalpies calculated by means of the additivity rule [8] from the experimental data of the homopolymers. The results obtained show that the values theoretically calculated are higher than the values experimentally obtained.

If the theoretical values match the experimental values to within ±5%, the species would crystallize separately or together, and the process of crystallization would not affect them. Therefore, in this case study characterized by a reduction of the fusion enthalpy values, it can be said that crystallization ability of a component is hindered by the presence of the other component. With respect to the crystallinity, similar behavior is evidenced.

TABLE 4: Variation of the Mechanical Properties of PP with Recycled HDPE (70/30) with Composition of Copolymer. (E: Young's Modulus, σ_B: Ultimate Tensile Strength, ε_B: Elongation at Break, IS: Impact Strength)

Copolymer (%)	E Kg/mm2	σ_B Kg/mm2	ε_B (%)	IS (J/m)
0	68.9	3.2	6.8	9.3
5	11.4	1.7	15.9	16.8
7	79.6	1.7	2.8	10.2
10	78.4	2.7	6.1	10.2
12	80.9	2.8	5.7	10.6
15	83.6	3.7	7.0	13.0
20	76.3	2.9	6.3	12.1

The results obtained from the study of fusion temperatures of the blend components show that the process of previous degradation of the HDPE does not significantly affect the size of the chains. The results of the study of the mechanical and thermal properties of the PP with recycled HDPE blends have shown that it is possible to reuse waste HDPE up to a composition of 30% in weight, so decreasing the cost of raw material in the finished product.

In order to assess the effect of the addition of a compatibilizer to the PP/recycled HDPE blend (70/30), a block copolymer (formed by monomers of ethylene and propylene at a 6% composition of ethylene) was added to different compositions, varying between 5 and 20% in weight.

In Table 4, the mechanical properties of the blend under study are shown using different concentrations of block copolymer. Elongation at break presents an atypical behavior. Impact strength presents similar characteristics. That is, a maximum value is achieved at a 5% composition of the copolymer, and similar values to those obtained in a blend without copolymer are subsequently maintained.

In the case of the Young's Modulus, a drastic decrease to 5% of the copolymer is observed, and subsequently module values similar to those seen in the blend without copolymer are maintained.

Resistance to rupture slightly decreases at up a 5% composition of the copolymer; at higher copolymer compositions this increases until reaching the values of the blend without compatibilizer.

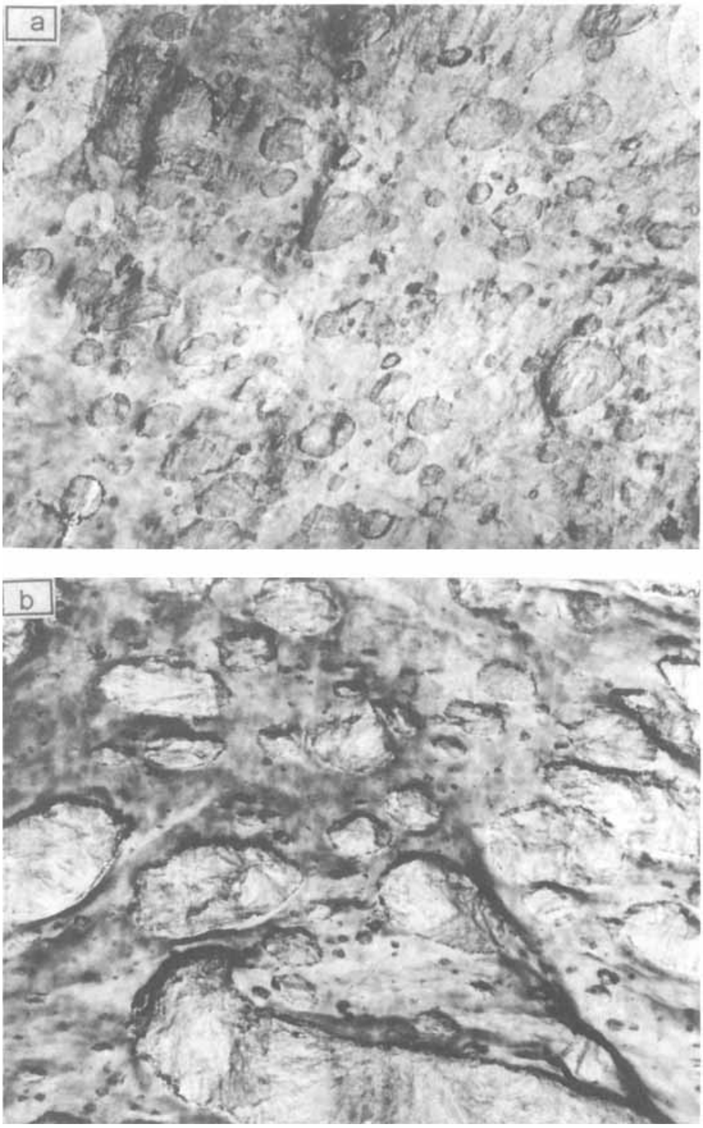

Figure 2. TEM micrographs of PP with recycled HDPE (70/30) with copolymer blend system. a) 5% copolymer and b) 15% copolymer. Scale bar: 1.7 um (—).

In the analysis of the micrographs of the 70% PP with 30% recycled HDPE blend (Figures 1 and 2) without and with copolymer, it can be seen that the addition of a compatibilizer at 5% composition decreases particle size as well as the thickness of the interface.

TABLE 5: Mechanical Properties of Virgin LDPE with Recycled HDPE Blends (E: Young's Modulus, σ_B: Ultimate Tensile Strength, ε_B: Elongation at Break, σ_f and ε_f: Yield Properties, IS: Impact Strength)

HDPE (%)	E Kg/mm^2	σ_B Kg/mm^2	ε_B (%)	σ_f Kg/mm^2	ε_f (%)	IS (J/m)
0	15.0	0.9	83.0	1.0	18.4	>200
10	20.9	0.9	251.6	1.2	14.8	117
20	26.0	1.0	325.1	1.2	14.9	62
30	35.2	1.1	487.4	1.4	14.3	32
40	41.1	1.1	514.6	1.6	13.5	23
50	354	0.5	9.0	1.2	8.2	22
100	54.8	1.6	560.0	2.3	10.9	38

This leads to the conclusion that the addition of this agent to the above mentioned composition (5%) represents the optimal concentration for improving the final properties of the finished product.

LDPE/recycled HDPE

In Table 5, Young's Modulus is shown. There is also an increase of this property related to the increase in the HDPE levels used in the composition. From these results, it can be concluded that the blends become more rigid due to the presence of HDPE.

The modulus of crystalline polymers greatly depends on its spherulitic morphology, the size of spherulites, and the lamellar thickness [9]. These polymers present a high nucleation velocity. Therefore, the size of the spherulites is small, and they have a granular aspect. For this reason, the increase in the modulus can be explained by the change in the size of the lamellas, depending on the HDPE content. Finally, it can be deduced that the HDPE and LDPE lamellas present different thicknesses.

In Table 5, elongation to break is shown. There is an increase of this property, up to 40% compositions of recycled polymer. Subsequently, there is a steep decline of this property in the case of 50% compositions. The behavior of these blends, with the exception of that having 50% of recycled HDPE, shows a certain degree of interaction in the amorphous phase, or compatibility. The reduction detected at a 50% composition may be due to the previous degradation of high density polyethylene that weakens the tying molecules. Therefore, the material becomes weaker and rupture occurs before expected.

Breaking strength increases slightly and, in the case of a 50% composition of HDPE, there is a sudden decrease.

The increase in breaking strength can be attributed to the fact that the HDPE presents more tying molecules and intercrystal bonds. These types of links play an important role in the transmission of efforts between the lamellas, because the increase of HDPE results in a growth of resistance. However, in blends of 50% recycled HDPE, the tying molecules weaken or break up, and the material has less resistance; that is, it becomes weaker and breaks up earlier due to previous degradation reactions.

Analysis of the morphology obtained through transmission electron microscopy (Figure 3) shows that there is no apparent dispersed phase of the HDPE observable in the matrix of LDPE. This shows that there is some compatibility or a partial miscibility that improves the mechanical properties with an increase in the concentration of HDPE. At a 50% composition of recycled HDPE, this polymer does not increase the thickness of the lamellas. This factor influences negatively on tensile properties. This fact could explain the behavior observed at this particular composition of this recycled material.

Table 5 shows resistance to the impact of the studied blends. The first notable fact is that the values for this property are extremely high in the case of LDPE, and could not be measured with available test equipment. This is evidence of the higher tenacity of LDPE in relation to HDPE.

As the concentration of recycled HDPE increases in the LDPE blends, impact strength decreases. As a result, the compound material loses tenacity, since its behavior becomes less ductile. This leads to the conclusion that recycled HDPE does not provide the mechanism of energy dissipation. However, the compounds behave in a similar way to a polymer that receives a rigid load. Thus, impact strength is subject to a counteracting force.

The results of thermal behavior are shown on Table 6. Fusion temperatures of both components of the blends diminish. This behavior is related to an interplasticizing effect, caused by some molecules of one of the components acting as diluents in the crystalline zone of the other component.

In compositions formed by 90 to 70% LDPE, a third endothermic peak is observed. This is probably due to a new crystalline phase being formed in the

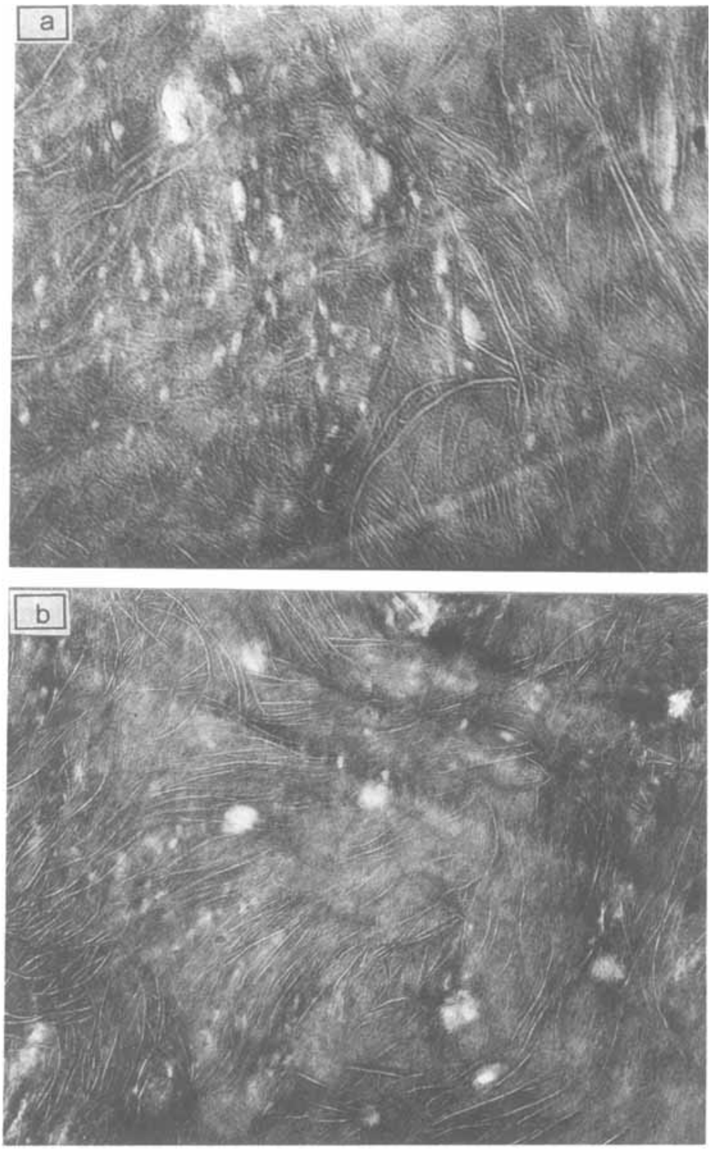

Figure 3. TEM micrographs of LDPE with recycled HDPE. a) 70/30 and b) 50/50. Scale bar: 0.42 um (—).

TABLE 6: Values Obtained from Thermal Studies for Virgin LDPE with Recycled HDPE Blends. (T_f: Fusion Temperature, ΔH_f: Fusion Heat, t: Theoretical, e: Experimental, X: Crystallinity)

LDPE (%)	Tf_1(^{o}C)	Tf_2(^{o}C)	TF_3(^{o}C)	ΔH_{fe}(J/g)	ΔH_{ft} (J/g)	Xe(%)	Xt(%)
100	111	---	---	105	---	35	---
90	108	117	124	126	113	44	40
80	107	120	124	126	121	45	42
70	107	122	125	138	130	48	46
60	108	----	126	146	138	51	49
50	110	----	125	130	146	46	52
0	----	----	133	189	----	73	---

polyblend, as a result of an interaction of both components. In lower concentrations of LDPE, it is assumed that an important run is produced. Consequently, the fusion temperature of the new phase is superposed on that of HDPE.

From the crystallinity values obtained in the experiments, it can be seen that the values of the blend were higher than those for LDPE. However, the experimental crystallinity is lower than that obtained from the additivity rule. Similar results are observed with fusion heat. From these results, an increase of the modulus and of the breaking strength can be deduced, as well as an increase in the elongation at break, because this phase acts as a link in the interface and generally improves all the mechanical properties. In addition, this phase generates an increase in crystallinity that also improves the Young's Modulus.

CONCLUSION

The results of analysis of the PP mechanical and thermal properties with recycled HDPE blends have shown that it is possible to re–use waste HDPE up to a composition of 30% in weight, decreasing the cost of raw material. The addition of block copolymer at 5% composition represents the optimal concentration for improving the final properties of the finish product

The mechanical behavior of the blend of LDPE with recycled material implies that the additional phase behaves as an interface agent, by improving interface adhesion. Therefore, it is possible to use recycled HDPE in blends with LDPE, since it is a productive material and reduces the cost of raw materials, in addition to enhancing the properties of the finished product.

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