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RECYCLING OF POLYOLEFINS: PART 2: BLENDS OF SEVERAL POLYMERS

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ABSTRACT

The aim of the present paper is to study the feasibility of recycling polyolefins with some additives, such as copolymers in order to improve the mechanical properties and increase the useful life of the blends. From analysis of the results of blends of polypropylene(PP) with POD(Blend of recycled Polyolefins), it can be concluded that it is possible to recycle POD up to 20%, the addition of a copolymer to the 12% composition improving the interfacial adhesion. In the case of low density polyethylene(LDPE) mixtures with POD, the optimum improvement in properties is obtained with approximately 10% of POD. The addition of copolymers did not yield any improvement in the properties.

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 principal objective of combining two or more polymers is to obtain a material with appropriate features and conditions for processing. On the other hand, 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. Over the last decades, total consumption of plastics, as well as the wide range of applications and visibility, has shown a meaningful increase. This phenomenon is the result of the properties of plastic materials, as well as their adaptability, and the use of economical manufacturing techniques. Nowadays, plastics are used a great deal in consumer goods and industries such as packaging, construction, transportation, vehicle manufacture, electronics, agriculture, and for many household uses. Therefore, it is impossible to avoid the generation of great amounts of plastic waste, or the resulting severe environmental, ecological and economic problems brought about by their long permanence in the environment.

The production and consumption levels of plastics are extremely high. In Venezuela, consumption averages 340,000 to 390,000 tons per year, whereas in the industrial countries figures vary between 11 and 30 million tons/year [1]. This could lead us to think that there are no pollution problems in Venezuela caused by the use of plastics. However, if Venezuelan consumption is analyzed on a per capita basis [2], it is evident that Venezuela presents similar figures to the rest of the world as far as consumption is concerned (See Table 1).

The most commonly used plastics, specifically in packing and wrapping, are polyolefins (PP, HDPE, LDPE, etc.). These polymers represent about 70% of the plastics used. Because of this high rate of usage, which is reflected in waste levels and consequently provokes environmental problems, researchers are studying ways of solving this serious ecological problem [3-6].

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 plastics products. During the 1983-1988 period, consumption rose from 188,000 to 346,000 tons [2]. Therefore, plastics consumption increased by 84%, whereas population grew by 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

TABLE 1: Consumption Per Capita of Plastic Products in Venezuela with Respect to World Consumption (Plásticos Hoy, May-July 1993)

Year	1988	1989	1990	1991
World(Kg/inhabitant)	18.5	11.3	10.0	16.1
Venezuela(Kg/inhabitant)	17.3	17.9	18.5	19.8

recycling. The disposal of plastic waste in sanitary garbage dumps reduces the capacity of those deposits, due to the huge volume generated by polymers and the difficulties 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 increase 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 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 attain this goal, several blends were mixed: a) PP with a blend of recycled polyolefins (POD), formed by 23% of PP, 45% of high density polyethylene(HDPE) and 32% of LDPE and b) LDPE with the POD blend.

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

TABLE 2: Variation of the Mechanical and Thermal Properties of PP with POD (Temp.: Temperature, ΔHf: Fusion Heat, E: Young's Modulus, UTS: Ultimate Tensile Strength, ε_B: Elongation at Break, IS: Impact Strength)

Material	Thermal Properties			Mechanical Properties			
PP (%)	Temp.1 (°C)	Temp.2 (°C)	ΔHf (J/g)	E (Kg/mm^2)	UTS (Kg/mm^2)	ε_B (%)	IS (J/m)
100	----	162	89	96.5	4.0	16.6	15.5
90	126	161	75	110.4	3.6	10.1	12.8
80	126	161	78	93.6	3.7	7.6	12.0
70	125	159	78	98.2	3.6	8.2	9.9
60	126	160	77	85.7	3.2	6.7	7.9
50	128	159	65	77.4	2.7	5.4	7.2
0	128	160	106	46.3	2.9	11.5	10.5

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 scanning electron microscope (SEM). After being fractured cryogenically, all samples were treated with gold coating to avoid charging by electron beams.

RESULTS AND DISCUSSION

PP with POD

The temperatures of the thermograms made in the DSC for PP with POD blends are shown in Table 2. It can be seen that the fusion temperatures of the phases do not change considerably, and that the fusion endotherms registered belong to the PP and polyethylene phases. These results show a co-crystallization of poly-ethylene, and also indicate the presence of poor interaction between the phases. There is also a decrease of the fusion heat. This effect is deeper at a 50% concentration of POD.

The polyblend of PP/POD presents a synergism in Young's Modulus (Table 2) for a 90% composition of PP, behaving in an additive form for the rest of the compositions. This is probably due to the change of morphology presented, because in the micrographs of optical microscopy, there is, at this composition, a decrease in the size of the PP spherulites, due to an increase in the nuclei density caused by the polyethylenes that form part of POD. This results in the nuclei of the spherulites approaching each other and in an increase of internuclear attraction forces, reflected in the increase of the aforementioned modulus.

The fact that the fusion temperatures found for the blend do not change with the composition shows that the increase of the Young's Modulus is due to morphological causes alone, as has already been explained.

The properties more affected by the PP/POD blend are elongation to break and impact strength (Table 2). It behaves similarly to the binary blend polyolefins. This is shown by the results of the thermograms presented in Table 2. With the purpose of improving the mechanical properties of the PP/POD blend, a random copolymer of propylene-ethylene was added. The copolymer had 97% of propylene and 3% of ethylene. The composition chosen to be compatibilized is 80% of PP and 20% of POD, because at this composition the properties of the blend present a similar value to the one obtained by pure PP. In addition, at this proportion the composition contains the greatest possible amount of recycling material.

In order to assess the effect of the addition of the compatibilizer to the PP/POD blend (80/20), a copolymer was added to different compositions varying between 5 to 20% in weight.

From the mechanical test (Table 3), it can be concluded that the optimal concentration of the compatibilizer is 12%, because at this composition the elongation to break and the impact strength are improved, without greatly affecting rigidity. This is probably due to the fact that the copolymer serves as an agent that improves interfacial adhesion through a mechanism that increases the transference of stresses among the phases. The results also suggest that the increase in the adhesion force among the phases could be a consequence of the partial miscibility of the copolymer in both phases. This is reflected in the temperature values of the thermograms (Table 3), where two fusion peaks, practically at the same temperatures, are observed: one for the compatibilized blend and the other one for

TABLE 3: Variation of Thermal and Mechanical Properties of PP with POD (80/20) with Copolymer Composition (Temp.: Temperature, ΔHf: Fusion Heat, E: Young's Modulus, UTS: Ultimate Tensile Strength, ε_B: Elongation at Break, IS: Impact Strength)

Material	Thermal Properties			Mechanical Properties			
Copolym (%)	Temp.1 (°C)	Temp.2 (°C)	ΔHf (J/g)	E (Kg/mm^2)	UTS (Kg/mm^2)	ε_B (%)	IS (J/m)
0	128	161	78	93.6	3.6	7.6	12.1
5	126	160	82	71.3	3.1	8.8	11.6
7	127	160	81	67.1	3.2	9.1	12.7
10	126	160	80	67.5	3.1	9.4	13.6
12	126	160	80	67.3	2.9	9.6	15.5
15	127	161	81	70.4	2.5	9.7	15,4
20	126	161	81	68.8	2.6	9.9	16.0
100	147	------	63	109.4	3.3	11.0	65.0

the incompatibilized, in spite of the fact that the fusion peak of the copolymer is placed among the fusion temperatures of the phases conforming the blends without the copolymer.

On the other hand, the morphology of the blends obtained by SEM (Figure 1) confirm the fact that the disperse phase POD is more embedded in the matrix phase of PP when it is compatibilized, presenting also a slightly smaller particle size, giving rise to a decrease in interfacial tension.

As a result, one can conclude that is possible to recycle the POD up to 20% with PP. This implies a reduction of cost in raw materials. The addition of a copolymer to the 12% composition improves the interfacial adhesion.

LDPE with POD

Table 4 shows the results obtained by the mechanical and thermal behavior of the LDPE/POD blends.

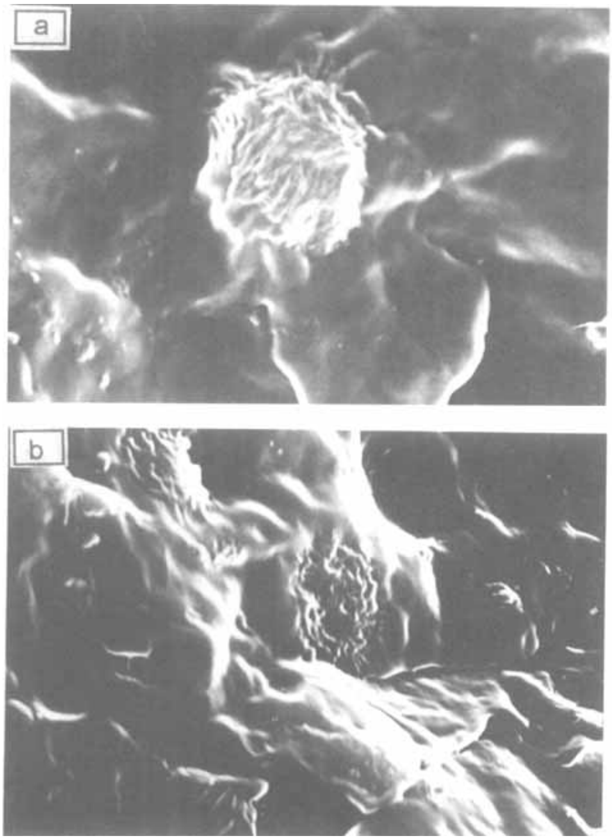

Figure 1. SEM micrographs of the PP/POD (80/20). a) without copolymer and b) 12% copolymer. Scale bar: 1um (—).

With respect to the results in the yield point, the study showed that the elongation to yield and the yield strength (12-15%, 1-2 K/mm^2, respectively) did not change meaningfully with the addition of POD to the LDPE, and the with the composition of the POD mechanical properties remain practically unchanged. It is worthwhile to point out that the POD did not present a yield point.

Young's Modulus shows an additive behavior, since at a greater concentration of POD the values of this property increase linearly. This is due to the rigidity of the POD induced by the greater crystallinity presented by this blend of recycled polyolefins.

The additive behavior observed in the values of the strength at break can be explained as being due to the tying molecules that link the lamellas pertaining to the phase of the LDPE, and the cocrystalline phase of the LDPE-HDPE.

TABLE 4: Variation of Mechanical and Thermal Properties of LDPE with POD (Temp.: Temperature, ΔHf: Fusion Heat, E: Young's Modulus, UTS: Ultimate Tensile Strength, ε_B: Elongation at Break, IS: Impact Strength)

Material	Thermal Properties					Mechanical Properties			
LDPE (%)	Temp.1 (^oC)	Temp.2 (^oC)	Temp.3 (^oC)	Temp.4 (^oC)	ΔH_f (J/g)	E (Kg/mm^2)	σ_B (Kg/mm^2	ε_B (%)	IS (J/m)
100	110.7	-----	-----	-------	77.3	13.0	0.7	98.0	166.0
90	109	117	123	162	96.0	11.0	0.5	84.7	74.4
80	109	119	124	162	97.0	20.0	0.9	50.2	22.9
70	110	-----	124	163	91.0	25.9	1.0	57.4	20.4
60	109	-----	125	162	92.0	27.2	1.8	20.3	20.2
50	109	-----	127	162	100.0	30.4	1.9	20.2	13.7
0	-----	-----	128	160	106.0	45.9	2.8	12.1	14.0

Table 4 shows the results obtained in the fusion thermograms. One can observe that at concentrations of 80% and 90% of the LDPE, there are four crystalline phases. As a result, there are four fusion temperatures. For the rest of the compositions there were three peaks corresponding to the phases of PP, LDPE and the cocrystalline phase of the LDPE-HDPE. This is evidence that there is a shift in the fusion temperature (T_2), since the concentration of HDPE in the blends increases.

The values obtained by the elongation at break and the impact strength for this blend reflect the incompatibility between the phases of PP and polyethylene, since at low concentrations of POD, there is a sharp decrease. This is an indication of poor adhesion between the phases of PP and polyethylene.

The incompatibility is also due to the concentration of stresses mainly located in the interface that joins the PP phase with the matrix of polyethylenes. Although the concentration of PP is low, this generates a reduction of ductility due to the formation of weakening zones. In addition, the reduction of tensile strength is due to the fact that the phases of polyethylenes, as a result of their recycling, present

TABLE 5: Variation of the Thermal and Mechanical Properties of LDPE with POD (90/10) with Composition of Copolymer. (Temp.: Temperature, ΔHf: Fusion Heat, E: Young's Modulus, UTS: Ultimate Tensile Strength, ε_B: Elongation at Break, IS: Impact Strength)

Copol. (%)	Temp.1 (°C)	Temp.2 (°C)	Temp.3 (°C)	Temp.4 (°C)	ΔH_f (J/g)	E (Kg/mm^2)	σ_B (Kg/mm^2)	ε_B (%)	IS (J/m)
0	109	116.5	122	161	95.9	11.0	0.5	85.0	74.0
5	108	-------	122	162	103.9	28.4	1.2	35.0	15.0
7	109	-------	122	162	98.3	29.4	1.3	30.2	14.9
10	108	-------	123	162	98.8	30.2	1.3	21.4	14.6
12	109	-------	122	163	96.5	30.9	1.4	25.9	14.6
15	107	-------	123	162	96.4	30.7	1.4	20.1	14.0
20	108	-------	122	163	95.5	31.0	1.4	15.6	13.9
100	147	-------	------	-------	63.4	109.4	3.3	11.0	65.0

some intercrossing that results in the behavior presented in the impact strength since, as has been previously explained, they act as a rigid charge.

Due to the high sensibility of these mechanical properties (elongation at break and impact strength) to the interfacing interactions, it can be deduced that the changes in properties are a consequence of the weak interactions of the PP phase with the rest of the phases. This fact is confirmed through the thermal values. They show that the fusion temperature of the PP does not change as the concentration of POD increases. This implies that there is separate crystallization and no interaction with the rest of the phases.

A composition of 10% of POD with LDPE was selected, and a copolymer randomly based on ethylene-propylene was added. The copolymer consisted of 3% of ethylene and 97% of propylene. Table 5 shows the mechanical and thermal behavior of the LDPE/POD/copolymer blends.

The yield point for compatibilized blends disappears from a concentration of 5% in compatibilizers, since the material breaks the elastic zone, before the yield occurs. The cause of this behavior is the increase in the PP phase in the POB blend. As far as the thermal behavior is concerned, when the concentration of this

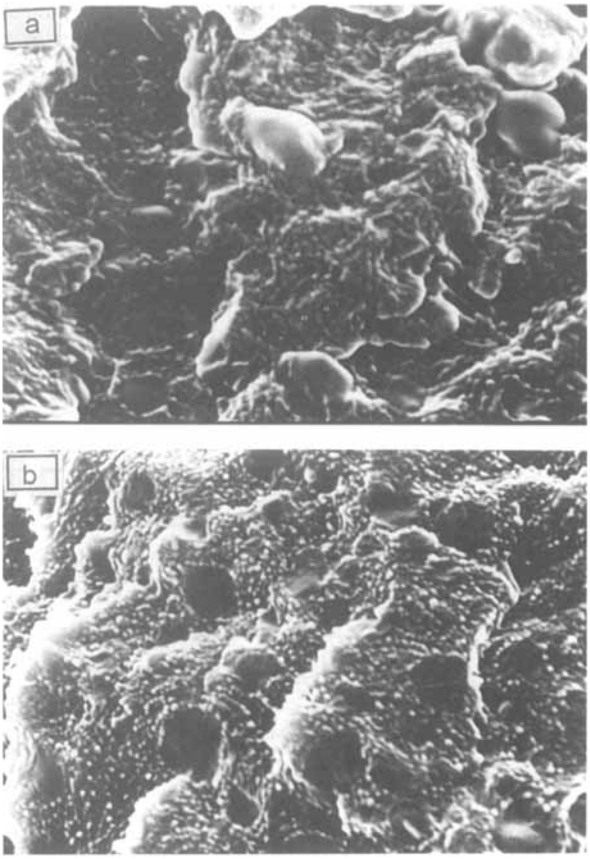

Figure 2. SEM micrographs of LDPE/POD (90/10). a) without copolymer and b) 10% copolymer. Scale bar: a) 1um , b) 0.8um (—).

compatibilizer is increased, the area below the fusion peak of the PP increases, and the absence of the fusion peak corresponding to the compatibilizer, that should appear at a temperature of 146°C, reflects the partial miscibility of the copolymer with the phases that constitute the blend.

On the other hand, the morphology of the material (Figure 2), observed through scanning electron microscopy shows that the dispersed phase is more embedded in the matrix phase for the compatibilized samples.

Young's Modulus and the breaking strength increases with the addition of small quantities of compatibilizer. After that it remains practically constant, from a composition of 10% of the copolymer onward. Elongation at break and impact strength suffer a greater deterioration at lower concentrations of the compatibilizer (lower than 7%). From 10% on, these features remain approximately constant. These properties show that the material becomes rigid, losing ductility. This is mainly due to the increase in the content of PP.

It could be inferred from this that to increase the rigidity of the blends, the optimal concentration would be 10%. However, if this is not the main goal, it is more appropriate to not to add this copolymer, but rather to select another copolymer that improves the target properties for the finished product.

CONCLUSION

From analysis of the blend of PP with POD, it is possible to recycle POD up to 20% with PP. This implies a decrease of the cost in raw materials. From the mechanical test, it can be concluded that the optimal concentration of the compatibility agent is 12%, because at this composition the elongation to break and the impact strength are improved, without greatly affecting rigidity. This is probably due to the fact that the copolymer serves as an agent that improves interfacial adhesion through a mechanism that increases stress transference among the phases.

In the case of LDPE mixtures with POD, optimal improvement in properties is obtained with approximately 10% of POD.

REFERENCES

[1] Avipla , Boletín "Reciclaje y Revalorización de Desechos Plásticos", May 1988.

[2] Avipla, Boletín "Algunas Consideraciones de Avipla Sobre la Creciente Problemática de Desechos Sólidos", April, 1993.

[3] A. Buekens, "*Draft of the Study on Management of Plastic Wastes in the ECE Region*", Economic and Social Council, United Nations, May, 1992.

[4] C. Rodriguez , "Caracterización de los Desechos Sólidos en el Area Metropolitana de Caracas", Instituto de Aseo Urbano para el Area Metropolitana de Caracas, 1992.

[5] P. P. Klemchuk, *Polymer Preprint, 32*, 2, 123 (1991).

[6] *Plásticos Hoy*, May-July, 20 (1993).

[7] A. Reinink, *Plastics, Rubber and Composites Processing and Applications*, *20(5)*, 259 (1993).