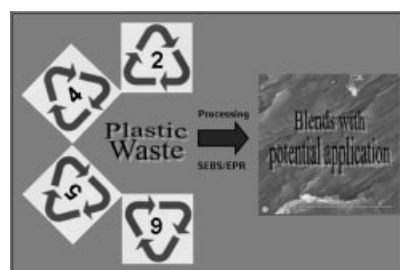


Use of SEBS/EPR and SBR/EPR as Binary Compatibilizers for PE/PP/PS/HIPS Blends: A Work Oriented to the Recycling of Thermoplastic Wastes

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Recycling of thermoplastic wastes consisting of PE/PP/PS/HIPS blends was investigated by using SEBS/EPR and SBR/EPR as compatibilizers. The effect of the binary compatibilizer systems and processing conditions on the mechanical properties and morphology of the blends are discussed. The SEBS/EPR system allowed blends with better mechanical properties to be obtained than the SBR/EPR system; this was attributed to the chemical structure similarity between compatibilizers and recycled materials. The optimal conditions for processing of the recycled thermoplastics (blends) were found to be 190 °C, 14 min of processing time and 3.5 wt.-% of compatibilizer. The morphology and mechanical properties of the blends were discussed using theoretical phase diagrams and models proposed in the literature, and good agreements between these properties were found.



Introduction

Thermoplastic materials have become an integral part of our life. Most of these materials constitute a family of

commodities and their uses are growing due to their low density, good mechanical properties, user-friendliness and low cost. As is known, these materials have many applications in different industrial as well as domestic areas. Their versatility has induced the replacement of conventional materials such as metals and wood.^[1] Although new plastic (polymeric) materials are being developed, traditional materials are still being used to prepare new materials (blends) with different and improved properties.^[2,3]

Many plastic materials, after being used, are still discarded in the landfill together with solid waste, generating a large amount of waste which exceeds the capacity of the deposits created for this purpose. Plastic waste disposed in the landfill has an evident environmental impact, characterized by resistance to degradation, environmental impact due to the use of the stabilizers, plasticizers, fillers, colorants, etc. and the high cost of separation process due to the existence of different plastic materials.^[4]

In general, solid waste deposited in the landfill can be treated by recycling and pyrolysis.^[1,5,6] However, due to

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their properties, plastic wastes can be treated by incineration, controlled depolymerization, pyrolysis and/or hydrogenation and recycling.^[1,7-13] Although the recycling of plastics has been considered economically and environmentally friendly, problems associated with industrial application, especially during the separation of plastic materials from the solid waste, have been detected. The plastic waste could be easily classified, but this has an additional cost in the industrial operation because it is composed of different materials such as polyethylene (PE), poly(propylene) (PP), polystyrene (PS), poly(vinyl chloride) (PVC), poly(ethylene terephthalate) (PET), etc.,^[4,9,13,14] which makes recycling difficult. Therefore, this problem has led to the study and development of polymeric blends from different thermoplastics. De Melo et al.^[15] studied blends of PP and high impact polystyrene (HIPS) by using poly(styrene-*b*-ethylene-*co*-butylene-*b*-styrene) (SEBS) as compatibilizer, wherein an improvement of mechanical properties was observed. Halimatudahliana et al.^[16,17] used different compatibilizers in the preparation of PP/PS blends and concluded that SEBS is appropriate as compatibilizer. La Mantia et al.^[18-21] reprocessed films from low density polyethylene (LDPE) and linear low density polyethylene (LLDPE) and demonstrated that the rheological and mechanical properties were not affected significantly. They also showed an improvement in mechanical properties by fusion and homogenization of the degraded parts of the recycled LDPE films. Bertin and Robin^[22] have compatibilized LDPE/PP blends by using ethylene-propylene-monomer (EPM) and ethylene-propylene-diene-monomer (EPDM) as compatibilizer. They concluded that the behavior of these copolymers is quite different, and the blends exhibited good mechanical properties. Ha et al.^[23] studied PE/PP/PS/PVC blends from virgin and recycled materials. They used cellulose reinforcement and found an improvement in thermal stability and mechanical properties. Sakata et al.^[24] reported thermal degradation of plastic waste and a mixed plastic model (PE/PP/PS/PVC/PET). Avila et al.^[25] analyzed PET/HDPE blends and concluded that polymer matrix blends seems to have potential use not only in engineering application but also in our daily life.

As outlined above, in order to recycle the plastic waste, many works have been focused on the preparation of blends from different thermoplastics. The domestic plastic wastes are mainly constituted of PP, LDPE, LLDPE, HDPE, PS, PET and PVC, and therefore separation is very important during the recycling process. Actually, PET is easily recycled on a large scale but not PVC due to it being present in a small amount, thus a good way to consider the plastic waste is preparing materials constituted by different type of polymers such as PE, PP and PS. Fortelny et al.^[9,26-29] have worked on this subject and demonstrated that the mechanical properties of the materials

obtained from the plastic waste were mainly affected by the degree of compatibility between them. They used poly(styrene-*b*-butadiene-*b*-styrene) (SBS), EPM, EPDM and ethylene-propylene-rubber (EPR) as compatibilizers to improve these properties. They concluded that the use of compatibilizers allows materials to be obtained that have adequate mechanical properties and they proposed an efficient method for recycling municipal plastic waste. Although many studies have been focused on the recycling of plastic wastes, the use of SEBS/EPR and SBR/EPR as binary compatibilizers for PE/PP/PS/HIPS blends from plastic wastes is not reported in the literature.

It is known that the similarity of the chemical structure between polymers and compatibilizer is very important to have good enhancement in the final properties of the blends. In our research group, after having studied blends of PP with EPR,^[30] PE with EPR^[31] and PP with PET,^[32] we thought that the use of binary compatibilizer systems with similar structures as those of polymeric wastes would help to improve the compatibility and hence the mechanical properties of the blends. In this work, we report the use of SEBS/EPR and SBR/EPR as compatibilizers to obtain PE/PP/PS, PE/PP/HIPS and PE/PP/PS/HIPS blends. The processing conditions as well as the mechanical and morphological properties of the blends are discussed. In addition, this work is aimed to the recycling of domestic thermoplastic wastes (PE/PP/PS/HIPS) in Bolivia. This study was firstly carried out on blends prepared from virgin raw materials which can be considered a model of thermoplastic waste, and then blends from domestic plastic wastes collected from solid waste were prepared.

Experimental Part

Materials and Polymer Characterization

Low density polyethylene (PE) from Ipiranga, Brazil (melt flow index $MFI = 1 \text{ g} \cdot (10 \text{ min})^{-1}$, molecular weight $\bar{M}_w = 122 \text{ kg} \cdot \text{mol}^{-1}$ and melt temperature $T_m = 122 \text{ }^\circ\text{C}$), Polypropylene (PP) from Petroquim S.A., Chile ($MFI = 14 \text{ g} \cdot (10 \text{ min})^{-1}$, $\bar{M}_w = 346 \text{ kg} \cdot \text{mol}^{-1}$ and $T_m = 168 \text{ }^\circ\text{C}$), Polystyrene (crystal) (PS) from Lustrex ($MFI = 28 \text{ (g} \cdot 10 \text{ min)}^{-1}$ and $\bar{M}_w = 262 \text{ kg} \cdot \text{mol}^{-1}$) and high impact polystyrene (HIPS) from Innova ($MFI = 9 \text{ g} \cdot (10 \text{ min})^{-1}$ and $\bar{M}_w = 190 \text{ kg} \cdot \text{mol}^{-1}$) were used to simulate thermoplastic waste.

Real domestic plastic waste was selected from solid waste which can be easily found in cities. The classification was done following the American Society of Plastics Industry (SPI) code.

Ethylene-propylene-rubber (EPR) from Dutral ($\bar{M}_w = 275 \text{ kg} \cdot \text{mol}^{-1}$ with 41 mol-% of propylene), poly(styrene-*b*-ethylene-*co*-butylene-*b*-styrene) (SEBS) from Calprene ($\bar{M}_w = 100 \text{ kg} \cdot \text{mol}^{-1}$ with 30 mol-% of styrene) and styrene-butadiene-rubber (SBR) from Europrene ($\bar{M}_w = 364 \text{ kg} \cdot \text{mol}^{-1}$ with 24 mol-% of styrene) were used to prepare binary compatibilizers.

In order to prevent the degradation of polymer materials, a binary system of Irganox 1010 and Irgafos 168 in a 2/1 weight ratio was used as antioxidant.

The MFI data were determined according to the ASTM 1238–95 (standard) in a melt flow indexer Ray-Ran Polytest Model 2. The molecular weights of the polymers were determined by high temperature gel permeation chromatography (GPC) using a Waters Alliance 2000 system equipped with a differential refractometer detector. Three GPC columns, HT6E, HT5 and HT3, previously calibrated with polystyrene standards of narrow molecular weight distributions were used. 1,2,4-trichlorobenzene was used as a solvent and the flow rate for analysis was 1 mL·min⁻¹ at 135 °C. The melt temperature was determined with a differential scanning calorimeter (DSC) from TA Instruments Model DSC 290 connected to a cooling system with different standards.

Blends Preparation

PE/PP/PS, PE/PP/HIPS and PE/PP/PS/HIPS blends with composition of 70/20/10% by weight were prepared by melt mixing in a Brabender Plasticorder equipped with high-shear roller-type rotors, this composition was determined from real case of recycling (Bolivia). The compatibilizer amount, temperature of the mixing chamber and blending time were changed according to experimental design, and the rotor speed was set to 80 rpm. Immediately after the completion of mixing, the blend was compressed and molded in a press at 190 °C for 14 min into plaques according to the samples required.^[33] The recycled plastic material was also prepared under the same conditions described here.

Mechanical Tests

Mechanical characterization was carried out by tensile testing and impact measurement. Tensile testing was performed at room temperature on a HP D500 dynamometer according to ASTM D 638M–93 methods. However, the tests were carried out at a crosshead of 10 mm·min⁻¹, the samples had 0.34 mm thickness, 5 mm width and the distance between the gages was 30 mm.

The impact experiments were carried out according to ASTM 256–93a, but due to the impossibility of breaking the samples, it was necessary to decrease the temperature of samples to –165 °C by immersion in liquid nitrogen. Samples of 120 × 12.6 × 3.4 mm were used to measure the impact properties in a HP Charpy pendulum.

All mechanical data presented here are the average of at least 10 samples, which can be considered sufficient for engineering cases.

Morphological Analysis

The resulting morphology of the blends was analyzed using a TESLA scanning electron microscopy (SEM) model BS343A at an accelerating voltage of 15 kV. The samples were fractured in liquid nitrogen, and then polymer soluble in toluene was extracted at 50 °C overnight. Before the SEM analysis and in order to examine their cross-section, the samples were mounted on an aluminum support and sputter-coated with gold (20 nm thick layer) by using an EMS-550 automated sputter coater.

Theoretical Analysis of Phase Diagram

A PE/PP/PS theoretical ternary phase diagram based on spinodal curve was built using the Flory-Huggins equation. The mathematical expressions used and considerations to build this phase diagram were those reported by Horst and Wolf.^[34–36] This diagram was used to discuss the results. However, before using this method it was necessary to check the assumptions and results presented in those references. The calculations were carried out using Excel and Matlab software.

Results and Discussion

Processing Conditions

In order to analyze the effect of the processing conditions during blends preparation, a factorial design of experiments with two levels and three factors was used. The data were analyzed by ANOVA (analysis of variance) following the Fischer “*F*” coefficient, where the significance was assumed if $P < 0.05\%$.

Table 1 presents all the results obtained in this stage. The samples named as B1, B2, B3, etc. mean blend sample 1, 2, 3, etc. The inferior and superior levels of temperature (*T*) were assumed as 190 and 210 °C, the processing times (*t*) were 6 and 14 min and the concentration of compatibilizer (*C*) was varied between 2 and 5 wt.-% (SBR/EPR, 60/40 wt/wt). It is seen in this table that the mechanical properties change when these factors (*T*, *t* and *C*) are simultaneously varied. However, the Yield stress (σ_y), Young’s modulus (*E*) and strain at break (ϵ_r) of the specimens did not show statistically significant differences, and the effect of the processing conditions could not be discussed through these properties. Thus, one can conclude that yield stress and Young’s modulus can not help in the determination of the main factors during blend processing. A similar result was reported by Fortenly

Table 1. Yield stress (σ_y), Young’s modulus (*E*), strain at break (ϵ_r) and impact resistance (*IR*) of different samples as a function of temperature (*T*), time (*t*) and compatibilizer concentration (*C*).

Sample	<i>T</i>	<i>t</i>	<i>C</i>	σ_y	<i>E</i>	ϵ_r	<i>IR</i>
	°C	min	wt.-%	MPa	MPa	%	J·mol ⁻¹
B1	190	6	2	16	2.2	260	64.7
B2	210	6	2	17	2.4	245	95.1
B3	190	14	2	16	2.5	231	91.8
B4	210	14	2	17	2.6	131	82.2
B5	190	6	5	15	1.7	259	78.0
B6	210	6	5	14	1.9	296	99.2
B7	190	14	5	15	1.6	294	99.6
B8	210	14	5	15	1.8	294	97.6

et al.^[9,27], and they showed that the response of the tensile analysis usually is not used to discuss the behavior of polymer blends. However, the impact resistance (IR) showed significant differences between each experiment. Thus, through the IR (response variable) it is possible to analyze the effects of the factors (control variables) on the blend preparation process.

According to Table 1, when the temperature is varied from 190 to 210 °C at short processing time (6 min), the IR values of the blends are enhanced, and at longer time (14 min) this property shows lower values. This result can be due to the degradation of the polymers, since the polymeric chains at high temperature and long time can be degraded.^[29] This assumption can be checked by analyzing the IR values corresponding to blends processed at 190 °C and different processing time, where the tensile impact is improved, whereas at 210 °C the IR is deteriorated. In addition, the MFI of the polymer after processing increased, indicating that degradation of the polymer has occurred (decreasing of the molecular weight).^[14] On the other hand, it is clearly observed that an increase of the compatibilizer in the blends from 2 to 5 wt.-% improve the impact resistance.

After this stage, statistical analysis showed that the main factor which significantly affects the IR values was the compatibilizer concentration.^[14] The statistical analysis carried out is not presented here. However, it is necessary to mention that ANOVA was used as a powerful tool to decide about the next step to be taken in this work.

Optimal Conditions of Processing

Although the compatibilizer concentration is the main factor which affects the IR of blends, the temperature and the time of processing are also very important from engineering point of view. A temperature of 190 °C can be considered adequate since all polymers under study can be processed at this temperature. Many researchers have studied and reported that this temperature is adequate for processing this kind of materials^[9,15,23–29] and therefore one could assume that this temperature is also optimal for our work due to the fact that higher temperatures can degrade these materials.

As discussed above, the impact resistance deteriorated with increase of processing time and temperature. Nevertheless, at lower processing temperature this property was improved (see Table 1), thus we can consider that the processing time and compatibilizer concentration should be optimized. Additional experiments were carried out in order to complete the experiments for the factorial design, which is by carrying out experiments in the central point (10 min and 3.5 wt.-% of compatibilizer) at 190 °C. Figure 1a shows the IR behavior of the blends as function of compatibilizer concentration at different times of proces-

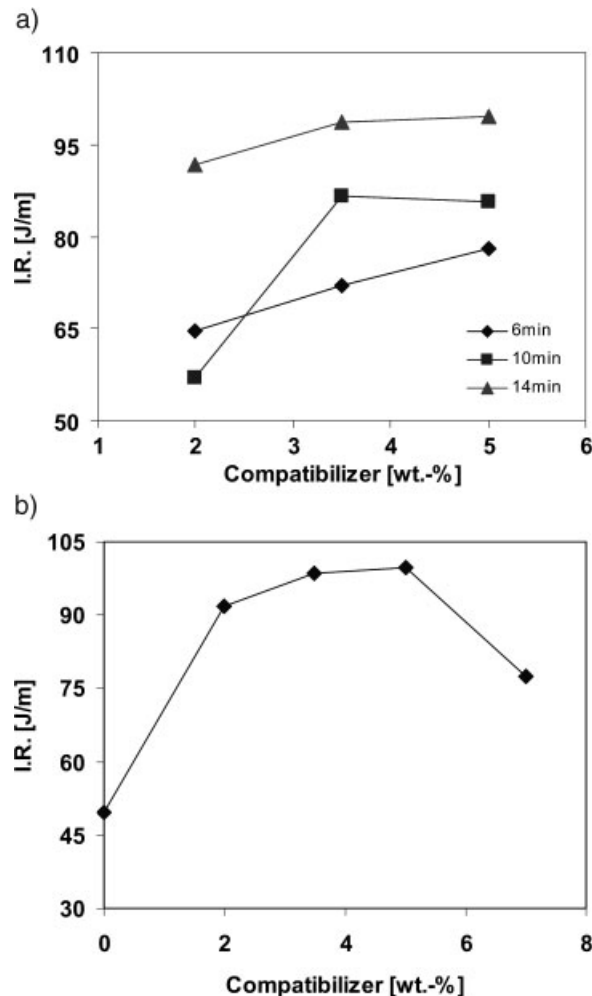


Figure 1. a) Impact resistance (IR) as a function of the compatibilizer concentration at different processing times. b) Effect of the compatibilizer concentration on IR at 190 °C and 14 min of processing.

ing (6, 10 and 14 min). The IR values at 14 min of processing are higher than at 10 and 6 min and, the compatibilizer does not have a significant effect beyond 4 wt.-%. Therefore, 14 min of processing time can be considered optimal since a longer time could degrade the polymers. However, although 14 min of processing time is considered optimal in this work, for industrial applications the degradation of polymers as a function of processing time should be minimized from the economic point of view.

Once the optimum processing time was established, the next step was to optimize the amount of compatibilizer. The effect of the compatibilizer on the IR values of the blends prepared at 190 °C and 14 min of processing are shown in Figure 1b. The IR values are improved when the amount of compatibilizer reaches 5 wt.-%. However, the IR decreases when the amount of compatibilizer is higher

than 5 wt.-%. This behavior can be due to the phase separation of the compatibilizer from the blend matrix, it is as result of its incompatibility and therefore its effect as compatibilizer is reduced.

Important results are the IR values between 3.5 and 5 wt.-% of compatibilizer. The IR between these values does not change significantly, and it allows us to conclude that 3.5 wt.-% could be considered optimal because a smaller amount of the compatibilizer represents lower cost during blends production.

The optimization technique by using graphical and experimental data is still used in different optimization processes. For example, Kokta et al.^[37] maximized impact strength, tensile and modulus of polypropylene/aspens/liquid polybutadiene composite by statistical experimental design. Yave et al.^[38] found good agreement between experimental and theoretical data during polypropylene production, and they concluded that it is a good method of optimization. Therefore, using this method the optimal conditions for PE/PP/PS blends processing was determined as $T = 190\text{ }^{\circ}\text{C}$, $t = 14\text{ min}$ and 3.5 wt.-% of compatibilizer.

Effect of the Compatibilizer System on the Blend Properties

In order to obtain results close to the real case, three types of blends from PE/PP/PS, PE/PP/HIPS and PE/PP/PS/HIPS were prepared at $190\text{ }^{\circ}\text{C}$, 14 min of processing and 3.5 wt.-% of compatibilizer. This has been done usually with different grades of PE, PP, PS and HIPS present in the waste.

The impact resistance (IR) of the blends prepared by using SEBS/EPR and SBR/EPR mixture as compatibilizer is compared in Figure 2a. As seen in this figure, the impact resistance of these blends is clearly different when compatibilizers with different structures are used. The SEBS/EPR system showed a better improvement of the IR respect to SBR/EPR, which would indicate a better compatibilization between the three polymeric phases. The high values of IR in PE/PP/HIPS were expected because this system contains HIPS, a high impact material. Therefore, by adding SEBS/EPR system as compatibilizer to this blend, an improvement is expected in the interaction between the polymers of the blends, and thus, better dispersion of the polymers within the PE matrix is obtained. De Melo et al.^[15] reported that SEBS is an adequate compatibilizer for PP/HIPS blends and leads to materials with improved mechanical properties. On the other hand, Fortelny^[9] showed that SB/EPDM is a more efficient compatibilizer than the neat SB. The use of binary SEBS/EPR system as compatibilizer in our blends allows obtaining recycled materials with acceptable mechanical properties due to the presence of similar chemical structures between the

blend components and those of the compatibilizers. Consequently, interaction between the polymers comprising the blend and compatibilizers is favored.

Figure 2b shows the effectiveness of the SEBS as compatibilizer for PE/PP/PS, PE/PP/HIPS and PE/PP/PS/HIPS blends prepared from virgin and recycled materials, as well as the IR values for PE, PP, and HIPS. The impact resistance of PS sample was not determined due to the fragile nature of this polymer.

Using SEBS/EPR as compatibilizer, the PE/PP/PS blends showed behavior close to that of PE/PP/HIPS. The recycled material exhibited IR values lower than those of ternary blends from virgin materials but similar to the PE/PP/PS/HIPS simulated blend, which has been represented as thermoplastic waste. The entire blends exhibited intermediate IR values compared to those of pure polymers, which is expected if the blends are correctly processed. The recycled material was collected from solid wastes following the SPI code, and it was mainly composed of PE, PP, PS and HIPS. However, in these materials the presence of additives such as stabilizers, plasticizers, fillers, colorants, etc. could have contributed to the dispersion and compatibility between the blend components, and thus, the impact strength was improved.

On the other hand, in order to characterize the resulting plastic materials, the MFI of all blends was measured, because MFI data are important for industrial applications, especially during processing. As seen in Table 2, all blends prepared from virgin material presented MFI values lower than those from recycled plastics. These differences can be due to the fact that recycled materials have already been processed, and thus, their MFI values are higher than that of pure polymers. However, all samples presented intermediate MFI compared to the pure PE, PP, PS and HIPS, producing a plastic material with potential application.

Morphology of the Blends

The resulting morphology of the PE/PP/PS blends studied by scanning electron microscopy (SEM) is presented in Figure 3. Three separated phases are clearly observed: 1) porous structure; 2) nonporous semi-spherical structure; and, 3) superposed lacy structure (see Figure 3a). One could consider that the pore, semi-spherical and lacy structures would represent PS and PP dispersed in PE matrix, respectively; that is because PE constitutes 70 wt.-% of the blend. The porous structure could represent the PS phase because the samples were cleaned by extraction with toluene at $50\text{ }^{\circ}\text{C}$ overnight before performing the SEM analysis; therefore, PS phase was removed during this procedure leading to the pore formation. The semi-spherical and lacy structure could correspond to the isotactic PP phase because it is not soluble in toluene at

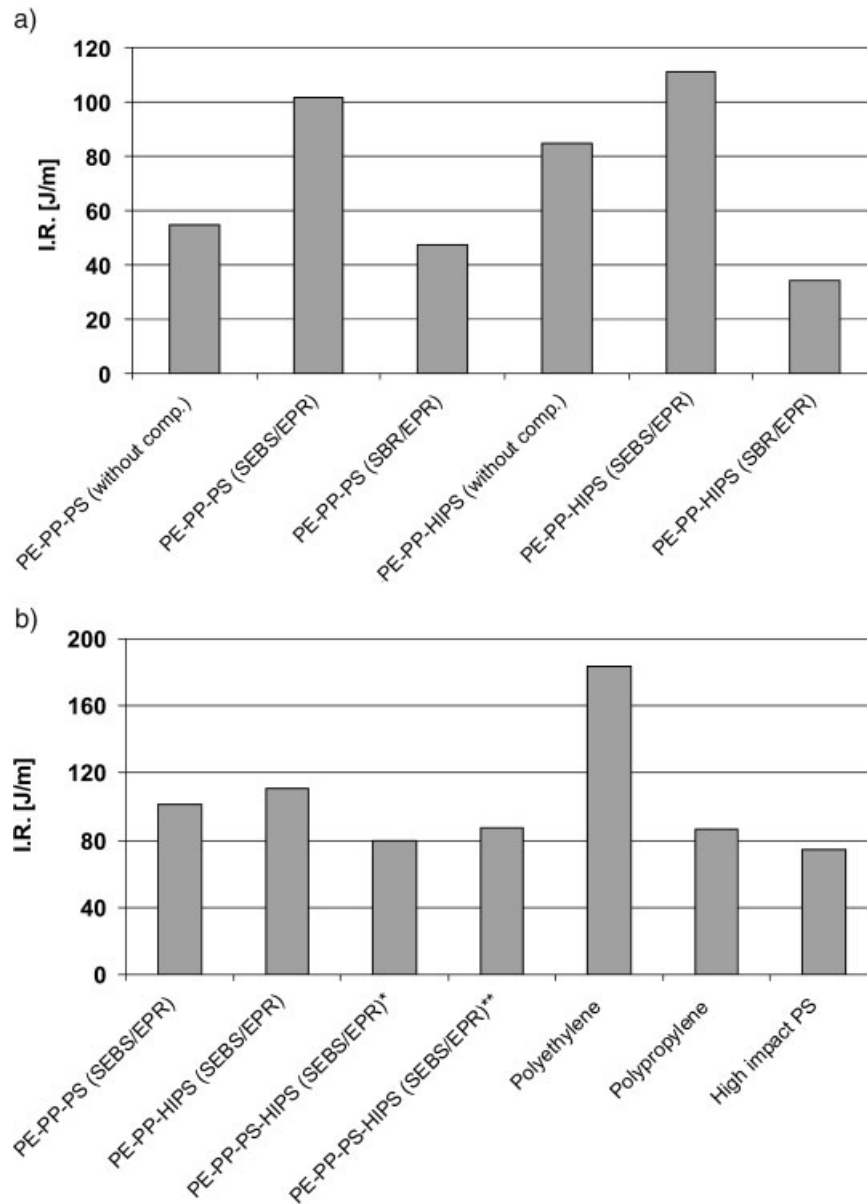


Figure 2. a) Impact resistance (IR) of the blends prepared without and with different compatibilizers. b) IR values showing the effectiveness of the SEBS (* recycled material and ** virgin material).

50 °C, and thus, it remains within the PE matrix. On the other hand, the decrease in size of these structures (Figure 3b and c) indicates the role of the SEBS/EPR and SBR/EPR as compatibilizers. Although the lacy structure disappeared, the pore size did not change too much, therefore a large decrease of the dispersed phase in this blend is not really observed.

Figure 3d–f shows SEM micrographs of the PE/PP/HIPS blends. In this case the compatibilizer action was forceful, since the pores, semi-spherical nonporous and lacy structures decreased considerably. This is seen by compar-

ing the Figure 3e and f with Figure 3d. A homogeneous distribution of the phases is observed when SEBS/EPR was used as compatibilizer (Figure 3e) indicating a good agreement with IR values found for this blend (Figure 2). This result could be explained by considering that SEBS facilitates the dispersion of the HIPS in the PE matrix and good compatibility between PP and HIPS.^[15] This is mainly because they contain common chemical groups in their main chain, which are ethylene, styrene and butadiene, and the EPR could have only contributed to the PP dispersion in the PE matrix. Therefore, the morphology of

Table 2. Melt flow index of PE/PP/PS, PE/PP/HIPS and PE/PP/PS/HIPS blends, and recycled plastic.

Blends	MFI
	$\text{g} \cdot (\text{10 min})^{-1}$
PE/PP/PS - without compatibilizer	3.14
PE/PP/PS - SEBS/EPR	3.51
PE/PP/PS - SBR/EPR	3.64
PE/PP/HIPS - without compatibilizer	3.54
PE/PP/HIPS - SEBS/EPR	3.63
PE/PP/HIPS - SBR/EPR	3.27
PE/PP/PS/HIPS - SEBS/EPR	3.50
Recycled plastic - without compatibilizer	16.22
Recycled plastic - SEBS/EPR	11.27
Polyethylene	1.00
Polypropylene	13.98
Polystyrene	28.17
High impact polystyrene	9.18

the blends results from homogeneously well-dispersed PS and PP in the PE matrix. The IR values and morphological properties can be well correlated and understood by analyzing the results shown in Figure 2 and 3. However, to have results close to the real cases, samples from recycled materials (plastic waste) were prepared. The resulting morphology of the blend obtained by using plastic waste is shown in Figure 3g and h. The effectiveness of SEBS/EPR as compatibilizer is clearly observed, since almost homogeneous blends were obtained.

Theoretical Analysis of the Blends

A theoretical analysis of the experimental results was performed with the aim of elucidating the phase behavior and properties of the blends. In this part of the paper some theoretical aspects concerning the phase diagram and final morphology related to the mechanical properties are presented.

Phase Diagram

It is well known that phase diagrams can have two or more phases. In polymer systems these diagrams are characterized by two curves, which are binodal and spinodal, respectively. The binodal curve is that which separates the homogenous phase (stable region) from separated phase (instable region). The spinodal curve is that which separates the unstable region from a meta-stable phase.^[34–36] The knowledge of phase diagrams

allows understanding of the phase separation and the resulting morphology in heterogeneous materials. For example, meta-stable systems present a slow phase separation and produce dispersed phase within the matrix.^[39]

Building of the phase diagrams from experimental data can be troublesome in some cases; however, mathematical expressions can help to obtain easily such diagrams. As was mentioned in the experimental part, the mathematic procedure and considerations developed by Horst and Wolf was used to build the phase diagram in this work. The phase diagram obtained following the Flory-Huggins theory based on spinodal curve at 190 °C is presented in Figure 4. The areas of the binary systems represent non-stable regions (φ_1 PS-PE, φ_2 PP-PE and φ_3 PS-PP), which have two separated phases in equilibrium. On the other hand, the intersection areas constitute unstable and meta-stable regions (where the spinodal areas coalesce). In our case, the sample PE/PP/PS (70/20/10) is in the non-stable region, and therefore, the use of SEBS/EPR as compatibilizer to increase the phase miscibility (compatibility) is justified, and thus, it would lead to the system towards a meta-stable region.

When the system is in a meta-stable region, one would expect that the resulting morphology could consist of phases dispersed within a matrix; this is because the polymeric phases are not completely homogenous. As is observed in Figure 3, the blends presented characteristic morphology of dispersed phases in a matrix; therefore, this result shows a good agreement between the phase diagram and morphology of the blends, which is PP and PS dispersed in PE matrix.

Morphology and Mechanical Properties

Kolarik et al.^[40,41] have proposed a scheme to predict the blends morphology using mechanical properties, which is by synchronized calculation of the Young's modulus and yield stress for a ternary system. In this procedure, the authors used two mathematical models for binary systems according to continuous and non-continuous phases with the following considerations: i) use of equivalent box model in the co-continuous phases, wherein relations from percolation theory are used; and, ii) effects of the dispersed phases on continuous phase and mechanical properties are treated like dispersed systems. This procedure relates the Young's modulus and yield stress estimated for a ternary system based on the same parameters of a specific blend structure.

The SEBS/EPR used in the PE/PP/PS blends would give rise to a system of six components, but as SEBS and EPR are the minor phases (small amounts), the resulting blend could be considered to be only PE, PP and PS. The SEBS and EPR would be between the polymeric phases contributing to the compatibility and dispersion of PP and PS within the

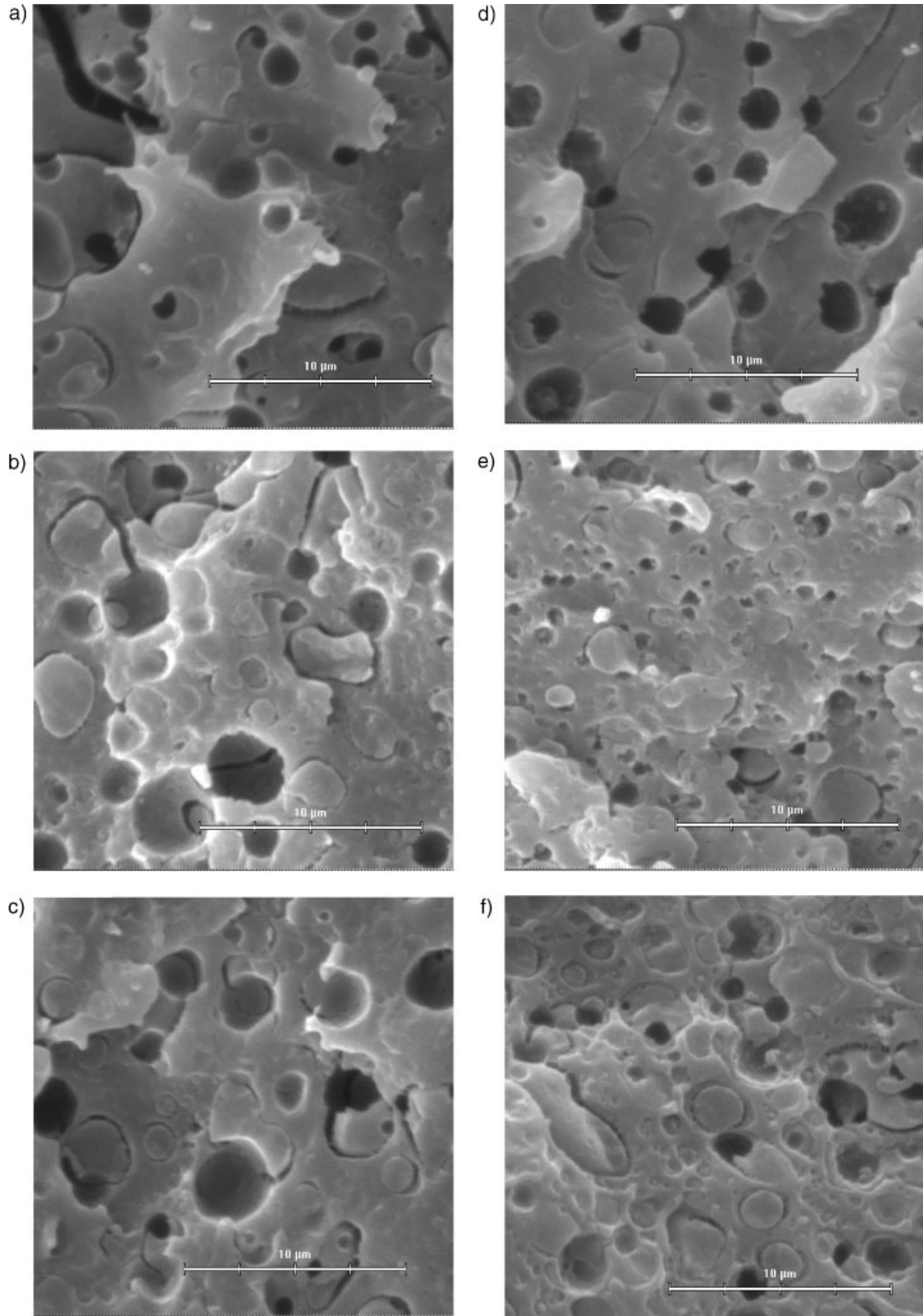
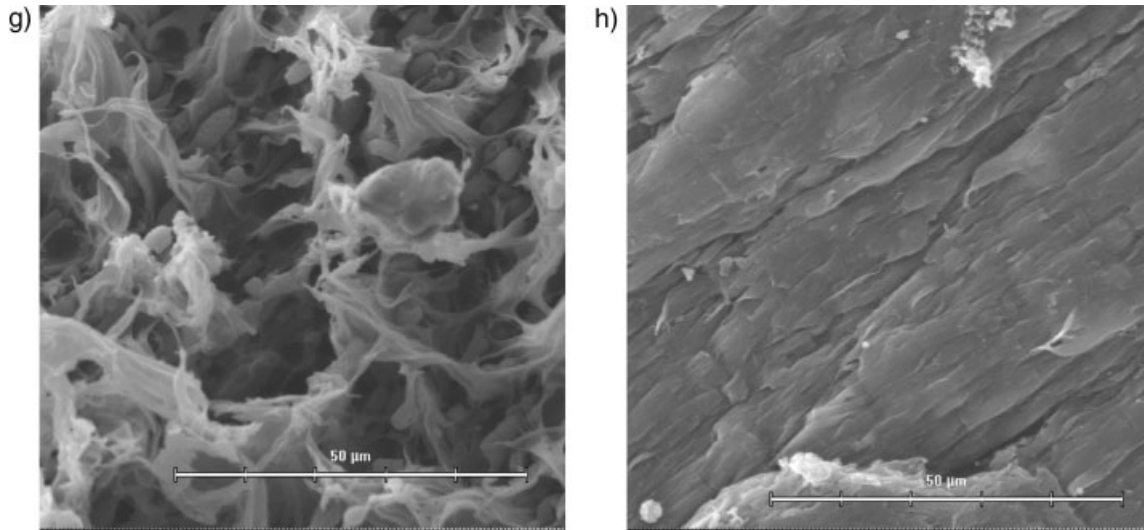


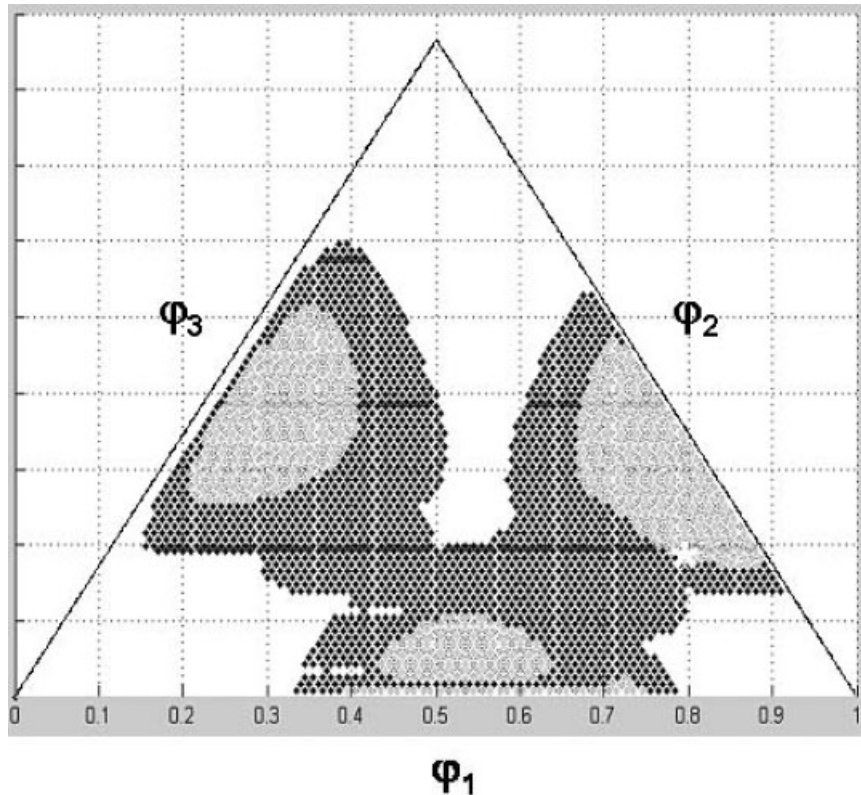
Figure 3. Morphology of different blends: a) PE/PP/PS, b) PE/PP/PS-(SEBS/EPR), c) PE/PP/PS-(SBR/EPR), d) PE/PP/HIPS, e) PE/PP/HIPS-(SEBS/EPR), f) PE/PP/HIPS-(SBR/EPR), g) recycled material (PE/PP/PS/HIPS) and h) recycled material with SEBS/EPR.



■ Figure 3. (Continued)

PE matrix. It is also possible to consider that the two co-continuous phases of PE/PP and PE/PS are present in the blend, although PP/PS phase could also be present. A two-dimensional model representing this supposition is presented in Figure 5, wherein the PP and PS are dispersed within two co-continuous PE phases.

With these considerations and by using the expressions reported by Kolarik, one can estimate the Young's modulus and yield stress of a system considered as two co-continuous phases (PE/PP and PE/PS). The simplified expressions reported by Kolarik are shown below, Equations (1)–(4)



■ Figure 4. Phase diagram for PE/PP/PS system obtained following the Flory-Huggins theory based on spinodal curve (φ_1 PS-PE, φ_2 PP-PE and φ_3 PS-PP) at 190 °C.

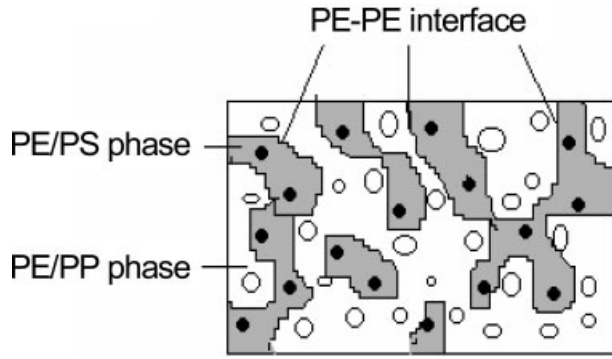


Figure 5. Two-dimensional model of two co-continuous phases of PE/PS and PE/PP present in the blend material; PP and PS are dispersed within the PE matrix.

Co-continuous phase models

$$E_b = E_1v_{1p} + E_2v_{2p} + \frac{v_s^2}{v_{1s}/E_1 + v_{2s}/E_2} \tag{1}$$

$$S_{yb} = (S_{y1}v_{1p} + S_{y2}v_{2p}) + AS_{y1}v_s \tag{2}$$

Where E_b is the modulus of the blend; E_1 and E_2 are the modulus of the components 1 and 2, respectively; v_{ij} are the volume fractions, where i is the component and j corresponds to the coupling type [parallel (p) or series (s)], and the fraction of component 1 and 2 coupled in series is interrelated as $v_s = v_{1s} + v_{2s}$; S_{yb} is the yield stress of the blend; S_{y1} and S_{y2} are yield stresses of components 1 and 2, respectively; and, A is inversely proportional to the extent of interfacial de-bonding.

Continuous and discontinuous phase models:

$$E_b = E_m \left(\frac{1 - P_i B_i v_i}{1 - A_i B_i v_i} \right) \tag{3}$$

$$S_{yb} = S_{ym} \left[1 - \left(\frac{v_f}{v_{fmax}} \right)^{2/3} \right] \tag{4}$$

Where v_i is the volume fraction of the inclusions; A_i , B_i and P_i are constants;^[12,40] S_{ym} is the yield stress of the matrix, v_f is the volume fraction of the dispersed material and v_{fmax} is the maximum fraction of the dispersed material.

According to the calculation of Young’s modulus (E), the theoretical values presented in Table 3 are similar to experimental data; however, the yield stress (σ) values obtained with these models are totally different to experimental values. It leads us to some comments: i) the PE content in the blend is 70 wt.-% and the yield stress could be mainly affected by this component; and, ii) the

Table 3. Yield stress (σ) and Young’s modulus (E) values obtained with Kolarik’s models (* values estimated considering strong PE contribution).

Systems (Blends)	Kolarik’s model		Experimental values	
	σ_y	E	σ_y	E
	MPa	MPa	MPa	MPa
PE/PP + PE/PS	4	1.5	11	1.4
*PE/PP + PE/PS	11	1.5	11	1.4
PE	—	—	11	1.7

connection between PE/PP and PE/PS in series and/or parallel are constituted by PE-PE interface, thus PE really would be contributing to the yield stress of the blends. In this way and with those considerations, the yield stress of the blend was calculated.

Good agreement between theoretical values and experimental data for Young’s modulus and yield stress were found (Table 3, *PE/PP+PE/PS values). Therefore, the co-continuous phase model applied to PE/PP/PS blend can be used to predict the morphology. In addition, it is shown that the morphology and mechanical properties are well correlated. It is worth mentioning that these results and the morphology prediction were performed before SEM analysis.

Conclusion

Blends of PE, PP, PS and HIPS were obtained from virgin raw materials and recycled plastic waste. The optimal conditions for processing of these materials were found as 190 °C, 14 min of processing and 3.5 wt.-% of compatibilizer (SEBS/EPR).

The SEBS/EPR compatibilizer system was better than SBR/EPR, since well dispersed phases and small sizes of separated phases was observed by SEM analysis. The mechanical properties were correlated with morphology, and good agreement was found. The impact resistance of different blends as well as recycled material was improved by using SEBS/EPR mixture as compatibilizer. The characteristics of the recycled material were found as: 1) a soft material; 2) a material with high impact resistance; and, 3) easy processing. Thus the resulting blend material can be considered for some industrial applications such as small containers, plastic plates, polytubes, etc.

The phase diagram showed that the use of compatibilizer is very important for obtaining compatible blends, since the composition of the studied plastic waste (PE/PP/

PS; 70/20/10) is in a non-stable region. Therefore, the use of SEBS/EPR as compatibilizer to increase the phase miscibility (compatibility) was justified.

Under some considerations, the mathematical model of Kolarik for mechanical properties was useful, and the resulting morphology of the blends was predicted as it was expected.

Acknowledgements: The authors acknowledge financial support of Conicyt through projects FONDAP 11980002, FONDECYT 1040927, to J. L. Arias, L. Guajardo and J. Benavides from the University of Chile for SEM and GPC analysis. WY also thanks Deutscher Akademischer Austausch Dienst (DAAD) for the grant "Small equipment for research project 2005" for the Chemical Engineering Department at the Technical University of Oruro.

Keywords: blends; compatibilizers; recycling of plastics; thermo-plastics

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