

Characterization of aluminized polyethylene blends via mechanical recycling

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Abstract

The use and consumption of polymeric resins is growing around the world because they are easily formed, and can be used in a variety of applications. The increasing consumption results in a great environmental impact because the used plastics are discarded in nature in a non-rational form. Facing all these problems, recycling becomes a powerful strategy regarding the reduction of the environmental impact caused by plastic waste. In this work polymeric blends were prepared by mechanical recycling and characterized. LDPE/Al residues from cartooned packaging were blended with recycled HDPE/LDPE and virgin PE resins. It was observed that processability, mechanical properties, chemical resistance and water absorption are dependent on the blend compositions. Also, an aluminum film was found to remain as isolated particles in the polymeric matrix and the mechanical behavior of the blend depends on the aluminum dispersion. Either, the blend water absorption depends on recycled material contamination, mainly polyamides. Finally, the amount of recycled material added to the blends determines both chemical stability and thermal characteristics.

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1. Introduction

It is not possible to precisely evaluate the total amount of polymer residues that are discarded each year [1]. The processes of recycling and recovering of plastic residues from all sectors always have been associated with their potential to contribute to energy saving and a reduction in CO₂ emissions. This procedure is always better than plastic garbage incineration, procedure largely adopted since 1970s [2]. The benefits of mechanical recycling are even better if virgin polymers also are substituted. Studies in Germany had shown that the combination of mechanical recycling of polymeric residues with the maintenance of recycled raw material supplies points to an economy of 74.10¹⁵ J of

energy, meaning 9% of the energy demand in that country's chemical sector, besides 7.10⁶ t reduction in CO₂ emission, i.e., 13% of the sector emission and 0.8% of Germany total emission for the year of 1995 [1].

From these facts, today Germany is the biggest market for recycled plastics in Europe. However, recycling occurs mainly for plastics of pre-consumer, i.e., industrial shavings. Apparently, in this country, the market of post-consumer plastic residues must be only 20–25% of the overall plastic production. Notice that the post-consumer residues exceed the pre-consumer ones by a factor of 3.5–5. Most of the experience in post-consumer plastic recycling comes from the packing sector, because this sector constitutes 30% in weight and 50% in volume of municipal solid residue. In many countries the areas for landfills are quickly declining and the plastic residues occupy a great amount of their useful area. The pre-consumer residues only include the

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material generated in an industry, either in the companies who manufacture the resin or in companies that use it, transforming the resin into a final product. The pre-consumer residues generally consist of a unique resin. As they are produced inside an industry, its identification, cleanness and homogeneity are very well controlled [2].

In contrast, the residues of post-consumer are a mixture of different plastic resins generally contaminated with dirt or other residues. Recycling of post-consumer residue is then much more difficult. These residues normally follow the normal cycle of solid residues, being then discarded. Most of this residue comes from packings. The post-consumer polymers in the form of containers, bottles and other packings constitute a significant fraction of the total volume of the urban solid residue, ending its cycle in landfills or, a more common process in Brazil, garbage deposits. Moreover, plastic residues quickly have increased their fraction in relation to the total volume of urban solid residues [3].

Plastic residues become problematic due their high volume/mass ratio, besides not being a very attractive material for collection and recycling [4]. Also, some economic factors are associated with plastic recycling, as transport, reprocessing and virgin resin costs. In this way, in countries with minor social development recycling has become a subsistence activity for the sustenance of many families, becoming profitable only for the profiteers. As the biggest volume of plastic residues is of post-consumer kind, normally recycling of this type of residue will only be able to generate end items of low quality. However, some studies have demonstrated that the recycling of post-consumer residues in products of good quality is viable, destroying the myth of recycled material only must be used for secondary purposes [4–7].

The recycling of polyethylene (from high or low densities) was already studied by some authors [5,7] and, in general, if the reprocessing conditions are adjusted, the properties of the recycled material are next to the ones of products made from virgin polyethylene. In these studies it was observed that the properties of products created with mixing resins, i.e., blends, are better than those of individual resins, virgin or recycled [6]. Recycling of polymeric residues in blends or even composites had found good acceptance in the market, resulting in products with acceptable final characteristics. Natural staple fibers and even polymer fibers have been used successfully in some applications [8,9]. The reprocessing of recycled resins also was studied for the determination of the “useful life” of a resin for continuous recycling [10,11]. Finally, statistical analysis and recycling project have been used in diverse recycled products [12,13].

Considering the great number of garbage areas in Brazil, the urban polymeric residues normally are deposited without any concern about technical, economical or environmental order in drains, rivers, fens and lagoons, among others, located in the peripheries of the cities. Such practice causes an irrational waste of these materials, besides visual pollution and clogging of canals and ditches. When the disposal is made in landfills, the plastics make difficult the compaction

and harm the decomposition of materials biologically degradable, because they create impermeable layers that affect the exchanges of liquids and gases generated in the process of organic substance biodegradation [14]. Although there are, in certain cases, some limitations and restrictions for the use of polymers from urban solid residues (food packings, pharmaceutical and hospital products and some types of toys), if adequately treated, these materials can be used in the manufacture of many products, keeping almost the same properties of those products made from virgin raw material. It must be emphasized that there are technical standards and specifications that must be followed, even if the raw material is virgin or recycled [15].

Recycling has been a promising route to avoid residue deposition in garbage areas and landfills. However, this area of knowledge is still recent, requiring yet much research. With the aim to study reuse and recycling, a research group focusing mechanical recycling processes of polymeric materials and its characterization was created at UNESC, University of the Extreme South of Santa Catarina, located at Criciúma, Brazil. This work deals with recycling of cartooned packings blended with LDPE and HDPE recycled and LDPE virgin resins.

2. Materials and methods

Initially, blends were prepared using polymeric materials from cartooned packings (TetraPak[®] packings). Three layers that can be totally recycled form these packings: paper (75 wt.%), low-density polyethylene (20 wt.%) and aluminum (5 wt.%). The only packing layer used was the aluminized polyethylene, previously prepared. The cellulose layer was separated from the polyethylene/aluminum layers by a mechanical process using equipment called Hidrapulper[®], process that separates the paper fibers from the others by hydration, where the paper forms a pulp of high consistency, using residence times of 30 min to 40 min. The fibers detach the packing and remain suspended, being possible to be removed by pumping. The dissolution of this type of material does not require the use of any chemical additives or heat in the process.

The blends were formed using high-density and low-density polyethylene collected in the University campus. These materials were chosen because they represent the biggest volume of polymers in use. They form almost 50% in weight of the campus polymeric residues, being widely used in packings. They are light, easily processed, of low cost and present excellent chemical resistance. Also, a virgin resin (LDP—Ipiranga trend) was added to the LDPE/Al layer to compare the properties obtained with all the blends and to get the best composition/mechanical properties. The polymeric solid residues collected consist mainly of diverse packing films, recyclable cups and bottles, among others.

In this work, 50 kg of residue collected in the campus were used. The material was washed with pure water for

decontamination. As it was observed that some dirt residues remained in the material, the washing step was repeated. The material was immersed in water containing sodium hypochlorite (10:1 in volume) during 30 min, rinsed in water and dried in air. In sequence, the dried material was agglutinated. The agglutination is more efficient when compared with a simple milling. The agglutinated pellets were extruded in spaghettis in a single spindle extruder (OZ-E-EX-L-22, Orizon). The processing parameters used, such as temperature and spindle speed, were adjusted in accordance with the blend compositions and kept constant for each blend; spindle rotation was varied between 80 and 120 rpm and temperatures between 140 and 155 °C with 5 °C increments among the four heating zones. All blends were prepared in this stage. The aluminized polyethylene of the cartooned packings was the matrix. The collected LDPE/HDPE formed a group of blends and virgin LDPE formed another one. Both groups were added in 10 wt.% fractions until a maximum of 90 wt.% addition for each group of blends.

From all the blend compositions the extruded spaghettis were pressed into test specimens via hot pressing (180 °C, 50 kgf/cm², 3 s). The test specimens were then subject to tensile testing strength determination in a universal testing machine model EMIC DL10 (10 mm min⁻¹ traction rate; 50 kgf load cell; great deformation strain gauges). Also, microscopic analysis was carried out to visualize the fractions of the dispersed aluminum using a scanning electron microscope (Philips X30) with an EDS (EDAX) probe. Finally, it was carried out the determination of blend water absorption (ASTM D570), chemical compatibility (ASTM D543) and thermal analysis. For thermal analysis a differential scanning calorimeter (DSC) Netzsch model STA409 (5 °C min⁻¹ heating rate) was employed in this work.

3. Results and discussion

Fig. 1 shows the variation in plastic deformation for the blend composed by aluminized LDPE (TetraPak[®]) combined with recycled LDPE/HDPE. The blend composed of aluminized LDPE combined with virgin LDPE (data not showed) presented a similar behavior to the previous one, showing that these resins have good recycling characteristics (Fig. 1). However, during blend preparation and initial testing it was perceived an enormous variation in mechanical behavior due to heterogeneities of the post-processed material. Diverse factors can contribute for this: presence of humidity, presence of other polymers and the kind of extruder used in the work (simple spindle). Only when the processing conditions had been adjusted the results were satisfactory.

The microscopic analysis (SEM) clearly reveals the presence of aluminum fragments (Fig. 2a) dispersed in the polymeric matrix. The material heterogeneities show some fractions of addition of recycled and virgin resins. As the microscopic analyses show, the mechanical behavior seems to be associated to the degree of dispersion of the aluminized

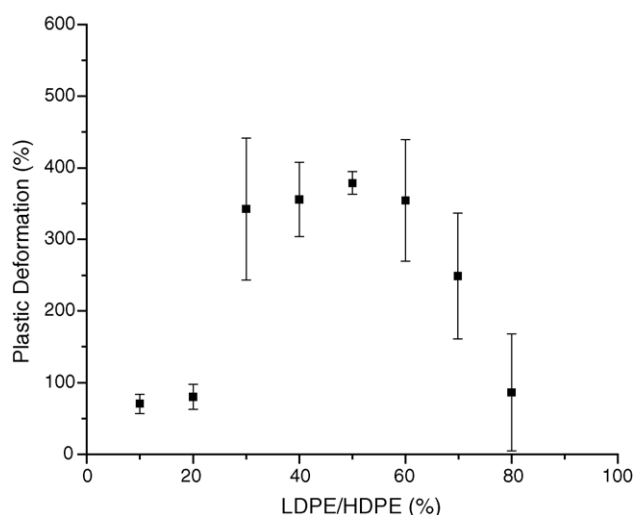


Fig. 1. Maximum deformation as a function of the amount of recycled polymer; blend formed by aluminized LDPE added with recycled LDPE/HDPE.

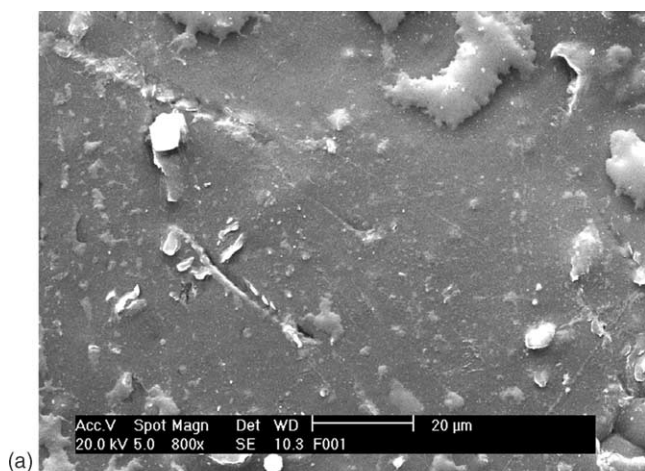
LDPE. In addition, the microanalysis, carried out with a microprobe, shows an intense peak in 1.50 keV, indicating the presence of Al in the material, as expected (Fig. 2b).

The amount of humidity absorbed by the blends was measured according to the ASTM D570 standard. The corresponding results are shown in Table 1. Both blends had absorbed water to some extent. The one that presented greater absorption was the blend formed by aluminized LDPE with recycled LDPE/HDPE in the ratio 10 wt.% of aluminized and 90 wt.% of recycled resin. In this case the mixture of LDPE and HDPE was collected in the campus. Moreover, the absorbed amount of water has a strong dependence with the added amount of recycled resin. Thus, another factor that can contribute to the high degree of humidity in blends containing recycled polyethylene is the presence, even in small amounts, of nylon, glue, inks and others, in form of fragments or films, whose nature is polar. These contaminations cause an increase in water absorption. Since polyethylene is a polyolefin, whose polymeric chain does not contain polar radicals.

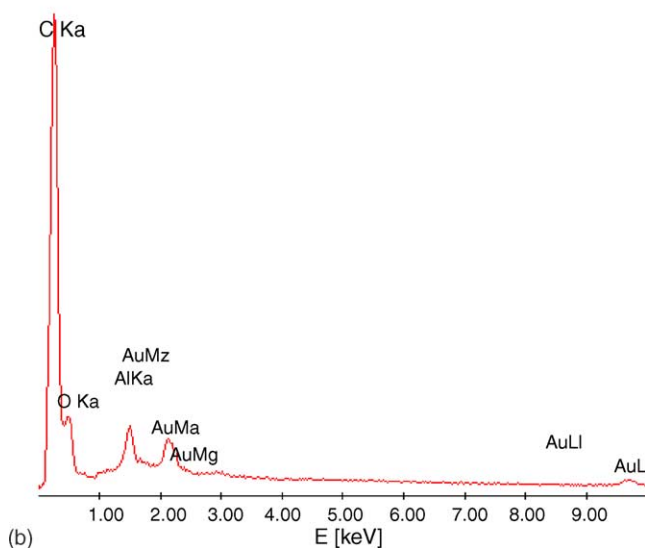
The resistance to chemical attack was determined using the ASTM D543 standard. Although the standard recommends a higher number of chemical reagents, in this study

Table 1
Water absorption results for the studied blends (ASTM D570)

Compositions (wt.%)	Absorbed water (wt.%)
90% aluminized LDPE + 10% recycled LDPE/HDPE	0.20
50% aluminized LDPE + 50% recycled LDPE/HDPE	0.33
10% aluminized LDPE + 90% recycled LDPE/HDPE	0.60
90% aluminized LDPE + 10% virgin LDPE	0.23
50% aluminized LDPE + 50% virgin LDPE	0.26



(a)



(b)

Fig. 2. (a) Micrograph of the blend formed by 70 wt.% aluminized LDPE (TetraPak[®]) added with 30 wt.% LDPE/HDPE (SEM, 800 × magnification); (b) EDS corresponding to aluminum particles immersed in the resin matrix (Au, O and C refers to gold coating and the main elements of the polymer matrix, respectively).

it was chosen a fewer number of them, specifically sodium hydroxide (10 and 1 vol%), concentrated sulphuric and hydrochloric acids, acetone, acetic acid and ethyl alcohol. Table 2 shows the results obtained from chemical attack for the inorganic and organic reagents for both blends studied. Notice that none of the samples presented visual or optical alteration after the chemical attack.

In general it can be observed that all the blends lost mass when in contact with the inorganic reagents and gained mass in contact with organic reagents, and the results are consistent with the literature [13–15]. In order to evaluate the thermal properties of the studied materials, DSC analyses were carried out, and the results are shown in Fig. 3. Fig. 3 corresponds to a thermogram for the blend composed of the mixture of 40% of aluminized LDPE and 60% of recycled LDPE/HDPE (DSC analysis; 5 °C min⁻¹ heating rate; N₂

Table 2

Chemical compatibility for different blends in diverse reagents (ASTM D543)

Composition	Reagent	Mass variation (wt.%)
Aluminized + recycled	NaOH 10%	-2.32
Aluminized + virgin	NaOH 10%	-1.02
Aluminized + recycled	NaOH 1%	-1.60
Aluminized + virgin	NaOH 1%	-0.59
Aluminized + recycled	HCl	-0.67
Aluminized + virgin	HCl	-0.39
Aluminized + recycled	H ₂ SO ₄	-0.37
Aluminized + virgin	H ₂ SO ₄	-0.39
Aluminized + recycled	Acetone	+2.75
Aluminized + virgin	Acetone	+0.99
Aluminized + recycled	Acetic acid	+3.23
Aluminized + virgin	Acetic acid	+1.23
Aluminized + recycled	Ethanol	+0.29
Aluminized + virgin	Ethanol	+0.19

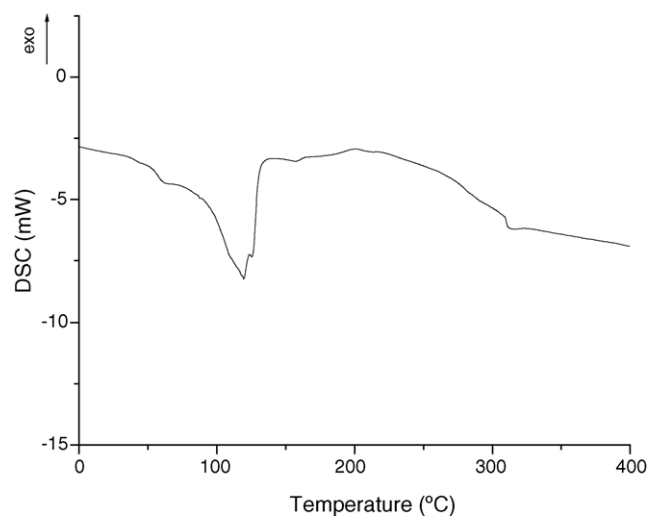


Fig. 3. DSC curve for the blend formed by aluminized LDPE added with recycled LDPE/HDPE (5 °C min⁻¹ heating rate; N₂ inert atmosphere).

atmosphere). During its melting, the polymeric blend shows two peaks next to each other; the peak found at 119 °C is attributed to LDPE melting and the next at 130 °C, attributed to HDPE melting. These temperatures are compatible with those used to extrude the blends. Also, there are two peaks less intense, approximately at 80 and 300 °C. Probably these peaks are related to T_g (glass transition temperature) and T_m (softening temperature) of some polyamide present in the recycled residues. It is common in the packing industry the use of multilayer films of LDPE or HDPE, where one of the layers is composed by polyamides.

4. Conclusions

The main conclusions of this preliminary study are:

It is possible to prepare diverse blends for extrusion, in this case aluminized LDPE (from TetraPak[®] packings) added

with recycled LDPE/HDPE and aluminized LDPE added with virgin LDPE.

Mechanical properties are strong dependent on the blend composition as well as processing conditions.

Regarding chemical compatibility all blends have a bigger chemical resistance to organic agents when compared with inorganic reagents.

The recycled LDPE/HDPE fraction exhibits increasing water absorption, possibly due to the presence of polyamides. The absorbed water is related to the dimensional stability of the plastic components. Thus, this feature becomes, in some situations, a restraining factor in technological applications.

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