TECHNICAL BULLETIN: IMPROVEMENT OF PROPERTIES OF RECYCLED MATERIAL WITH ADDITIVES

1 Introduction

The current growing world market is increasingly closely linked to the use of plastic, since world consumption has gone from 1.5 to 280 million tons per year from 1950 to 20121, therefore the generation of waste has increased despite the increase in employment of post-consumer materials (recycled or reused). Around 63% of the waste generated comes from the packaging sector, which makes it imperative to search for alternatives to improve this situation.

On the other hand, it is important to note that even a 25% of the energy used in the useful life of a PE container (which includes the production of plastic, processing, transportation, among others) for household consumption product can be recovered (Figure 1) through any of the recovery techniques named2, which shows the importance of the recycling process.

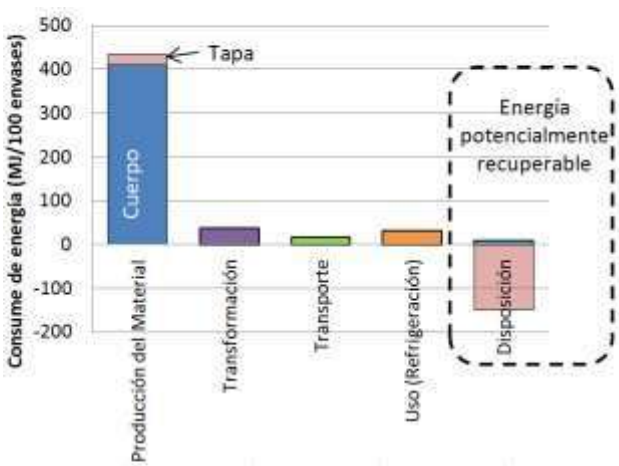

Figure 1. Energy consumption and recovery potential in the life cycle of PE containers

2 Types of recycling

There are five ways of recovery for plastics [3,4] (Figure 2), one of them refers to re-use of the product and the other four ways are related to recycling; the type depends on where it starts from (for example, from the final product) and what the destination would be (for example, the raw material or pellets).

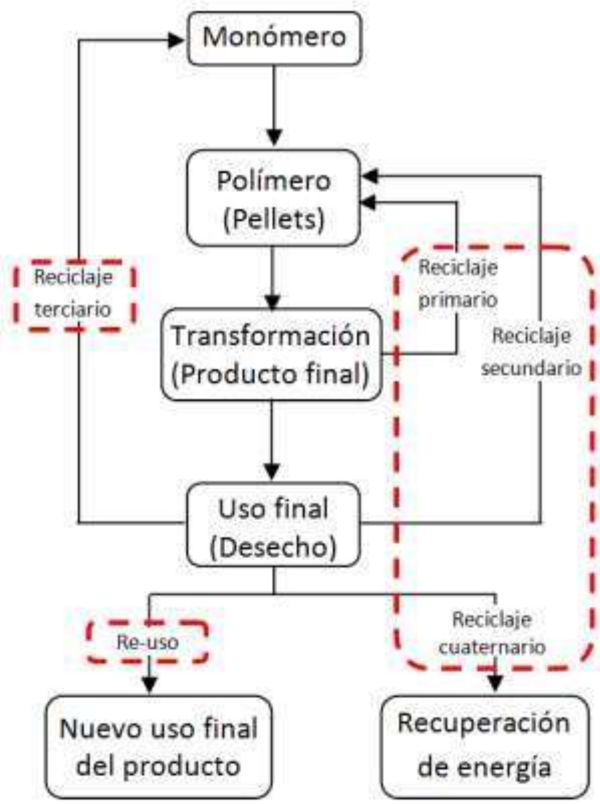

Figure 2. Recycling levels in plastics

2.1 Re-use of the product

This is the simplest method, since it refers to allocating a product that has already fulfilled its initial function for a new purpose; This can range from things as simple as, for example, using a plastic bag as a waste bag or using a paint container as a planter or flower pot, to adapting a rotomolded desk (which, for example, has been damaged) to be reused as a chair or even as the same desk, reprocessing it again.

For many reasons, mainly environmental and economic, this is the most desired form of plastic recovery, since it is the most direct way, and it requires a minimum of energy to be able to convert any article that can be considered waste into something useful.

2.2 Primary recycling

Also known as "plant recycling", and is the one that consists of a reprocessing of the marketable material that is discarded (for example, the extruder cakes), known as "scrap". It is very simple and very low cost.

2.3 Mechanical or secondary recycling

If reuse of the product is not possible, the next option at hand is mechanical or secondary recycling. It consists of the recovery of polymeric plastic waste (not thermosetting) through mechanical processes: separation, grinding, washing, pelletizing and reprocessing of new products.

However, one aspect of care is the properties of the materials, since they could be affected by the homogeneity of the material to be recycled2. Coming from different sources, they can vary, thus affecting the processing conditions and the quality of the finished product.

The main disadvantage of this type of recycling is the deterioration of properties for each process cycle due to material degradation, which can occur due to crosslinking or chain cleavage.

For example, it is known that significant changes in its mechanical properties begin to occur in HDPE from the tenth processing cycle (elastic modulus or G', Figure 3), while the melt flow index (MFI) shows changes after 5 processing cycles5 as seen in Figure 4.

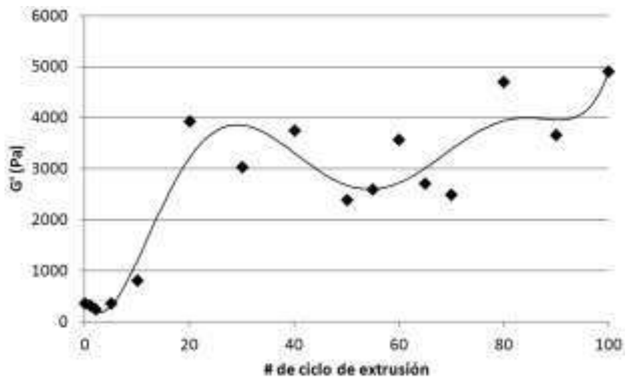

Figure 3. G' with respect to # of cycles of extrusion[5]

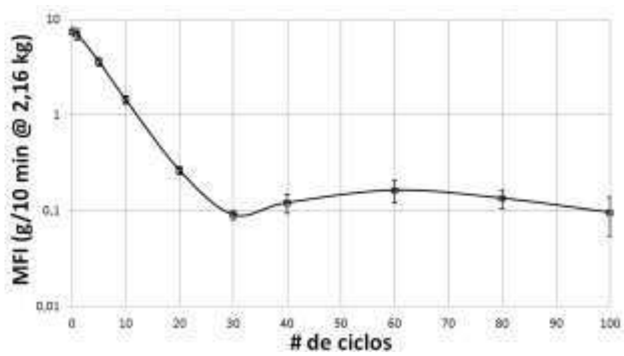

Figura 4. MFI with respect to # extrusion[5]

Although 5 to 10 extrusion cycles may seem like a high amount of recycling, it should be taken into account that in many parts of the world, including Venezuela, it is not possible to determine the number of life cycles of each material obtained for secondary recycling, for what processors consider important to be able to minimize degradation in the medium or long term.

Continuing with the example used previously, this type of recycling would apply when the industrial bag has been damaged in such a way that it cannot be used as a waste bag; that the paint container has become fragile and cannot be used as a pot; or that it is not possible that a person can sit the old plastic desk; and it is at this time that the waste must be disposed of in such a way that it can be recycled.

This form of recycling (since the life cycle of the plastic begins again) is the most economical since it is not necessary to produce the plastic, it only requires the use of (relatively) little energy to adapt the plastic for processing (for example injection, blown or rotational molding) and allocate it to a new application. This means that the energy consumption for the production of matter (first column of Figure 1), which is the one with the greatest environmental impact, is saved.

2.4 Chemical or tertiary recycling

It consists of taking the polymer to its initial form, to its monomer, through de-polymerization to later re-polymerize and have raw material again. This can only be done profitably for some materials. There are no known commercial PE de-polymerization mechanisms.

2.5 Energy recovery or quaternary recycling

It refers to the recovery of energy by incineration of plastic. This method is currently the most effective for reducing the organic volume of this type of material.

This method has been questioned due to the potential for the release of substances (sometimes toxic) into the environment and for consuming the plastic material that could be recycled in another way (primary or secondary recycling).

3 Increased shelf life by additives

There are basically two strategies for the recovery or recycling of plastic at the level of the transforming sector (secondary recycling); The first and most commonly practiced is to mix virgin resin with post-industrial resin post-consumer. This does not guarantee maintaining the properties of the resin, which allows is to increase the time (or extrusion cycles) in which they begin to observe loss of properties.

The other strategy is the addition of additives that minimize the effects of shear and temperature on the properties, and maintain them over time. The amount of additive to be used will be related to how degraded the PE is and the type of degradation that occurs.

Some of the additives used for this purpose are:

3.1 Processing helpers

They are high molecular weight additives, and for this reason they improve the processability of the material, resulting in better processing. These materials are used for those cases in which degradation crosslinking occurs.

They are classified into three large groups: lubricants, sliders and viscosity controllers. They are usually used in concentrations that vary between 200 and 1000 ppm.

3.2 Loads

They are additives used to improve the mechanical resistance of the resin (tension, bending and impact), and increase the viscosity during processing, therefore the incorporation of this type of additives is desirable in resins with high extrusion cycles to counteract the effect on the flow rate.

In some cases, the addition of fillers to the resin at certain levels can lead to processability problems and can increase brittleness (decreasing the strain at break).

There are two types of loads used for the reuse or recycling of polyethylene:

3.2.1 Organic loads

It is an alternative that has been developed for almost two decades and consists of adding organic fillers to the resin, such as wood fiber or lignocellulose, which, accompanied by suitable compatibilizers, allow the generation of a compound that can be used for outdoor applications with an appearance similar to that of wood as shown in Figure 5.

Figure 5. PE loaded with wood for exteriors

By 2011, this type of material (not only based on PE but also in other cases such as PVC) had 6% of the market for outdoor furniture applications worldwide[6].

An adequate performance in the mechanical properties at tension and impact is normally expected with this type of loads if they are added correctly.

3.2.2 Inorganic loads

They are the most used since their use is similar to other types of additives and a different handling of the resin or the use of compatibilizers is not required in most cases.

The use of organic fillers is focused on improving the rheological properties (viscosity increase) and mechanical properties (modulus of elasticity, effort and creep strain); so its use is suitable for PE with high life cycles.

The most common inorganic fillers in the transformation of PE are calcium carbonate, talc and titanium dioxide, which in turn can function as pigments and UV protectors.

It is important to consider that at high doses of loads, the materials can experience counterproductive effects, since the PE becomes brittle.

4 Commercial additives

Being PE a stable material with high resistance to thermal and shear degradation, it is not very common to find specialized additives focused on maintaining properties; However, commercial houses such as BASF have developed some additives such as Recycloblend, which is a mixture of antioxidants, stabilizers and co-stabilizers in a granular presentation that allows desensitizing the polyolefin to the negative influence of impurities.

On the other hand, commercially there are additives that can be considered as "improver packages" since they are focused on improving the stability and mechanical resistance of polyolefins, since they have the double function of processing and loading assistant; BASF presents the Recyclostab® focused on LDPE and the Recyclosorb® focused on HDPE.

It is noteworthy that if you do not have access to this type of commercial additives, you can also add the resin that is being recovered with the individual additives depending on the specific need; in that case it is highly recommended to carry out laboratory studies to adapt the type and dose of additive.

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To obtain more detailed information on the safety aspects related to the handling and disposal of our products, we invite you to consult the safety data sheets (MSDS) of Venelene® Polyethylenes.