Polymer Mechanical Recycling: Downcycling or Upcycling?

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ABSTRACT

Recycled plastics are considered as materials with physical, mechanical and aesthetic properties worse than the virgin ones. In fact, this is true because degradation during lifetime and during the recycling operations changes the structure and the morphology of the polymers and then the final properties of the secondary material. Several "strategies" are under investigation, and in some cases also applied, in order to avoid further degradation during recycling and, if possible, to repair the macromolecules broken during lifetime and then to restore or to improve the initial properties.

In this paper the more important techniques, already used in industry or under investigation, according to this philosophy are shortly reviewed.

INTRODUCTION

Commonly, recycled materials are thought to be materials with poor properties (physical, aesthetic, and … smelling) with respect to those of the virgin materials: *recycling = downcycling*. Of course, we are referring to mechanical recycling, i.e. the one that allows reusing the material directly in application similar to those of virgin polymers. In fact, for a lot of materials, this common sense coincides with reality, especially when these materials are plastics. It is absolutely true that the most part of recycled polymers follows this rule: the bags for urban waste made in recycled polyethylene are rough if touched and bad smelling (even before use!), PET fibers coming from recycled bottles display worse mechanical properties than the starting material, etc.
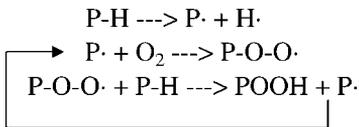
The main reasons of this worsening lay, for plastics, in the degradation both during life cycle and during recycling operations[1]. These two aspects are common to all the recycled polymers, while the incompatibility between different polymeric phases must be added for recycled mixed plastics. This latter problem is so hard that actually the mixed plastic recycling is absolutely reduced and leads to the production of secondary material that can be used only to produce thick items with low economical value.

It is then clear that to avoid further degradation to the recycled material, it is necessary to hinder thermomechanical degradation during the recycling operations and eventually to protect the item from outdoor actions if, for example, it has to remain exposed to UV for a long time. This strategy – that is necessary in several cases – can avoid further structural and morphological modifications and consequently the worsening of the properties. However, certain characteristics lost due to degradation during life cannot be recovered at all.

In this work, after a short discussion on the degradation of polymers, some new recycling methods and new recycling apparatus will be discussed in order to preserve or even to improve the properties of post-consumer plastics: *recycling = upcycling*.

DEGRADATION

During the processing and during the lifetime of the plastic items, heat, mechanical stress and ultraviolet radiations, can deeply change the structure and the morphology of the polymer. The general scheme of the polymer degradation in presence of oxygen can be written as:

$$P\text{-}H \dashrightarrow P\cdot + H\cdot$$
$$P\cdot + O_2 \dashrightarrow P\text{-}O\text{-}O\cdot$$
$$P\text{-}O\text{-}O\cdot + P\text{-}H \dashrightarrow POOH + P\cdot$$

Although photooxidation and thermomechanical degradation can cause different changes in the structure of the plastic materials, it is possible to schematically collect the effects of these degradative processes as:

• variation in molecular weight and molecular weight distribution

• formation of chain branching

• formation of oxygenated compounds, unsaturations, etc.

It is worth to notice that the change of molecular weight can induce also changes in the crystallinity.

The degree and type of degradation depend on the processing conditions and on the nature of the polymer, but, of course, all the changes undergone by the chemical structure will cause variations of the properties of the material. Most

processing operations use fairly gentle processing conditions and polymers of moderate molecular weight: under these conditions degradation phenomena are, generally, modest. Nevertheless, more severe processing conditions, polymers with high molecular weight, or repeated processing operations can cause significant decreases in polymer characteristics.

As for the degradation during lifetime, the influence of the photooxidative degradation is very dramatic on the elongation at break of the polymers. This effect has been attributed to the degradation of the macromolecules but also to the formation of physical and chemical defects on the surface. This latter result does not mean that the properties of the recycled photooxidised polymers are much lower than those of the virgin or slightly photooxidised materials. Indeed, it has been stated above that physical defects, like a different concentration of oxidized species along the thickness of the item, can be considered as responsible for the brittleness of the polymer.

The above considerations **-** decrease of the molecular weight and reduction of the mechanical properties with respect to the virgin material **-** suggest that in many cases the "secondary material" can not be used for the same processing operations employed for the virgin material or the same kind of products. Its use, however, is allowed for processing operations requiring lower viscosity and applications requiring lower mechanical properties. The life of the polymeric materials can be thus extended through recycling, but their end applications are continuously worsening.

INFLUENCE OF STRUCTURE AND MORPHOLOGY ON THE BEHAVIOUR OF POLYMERS

In this part a short review of the influence of the structure and morphology on the melt and solid properties of the polymers is reported to supply some qualitative information about the change (reduction) of the properties with recycling steps.

The changes undergone by the structure of the polymers during degradation processes, produce, in their turn, changes in the properties of the materials, but of course, each single modification influences differently the behavior of the polymeric materials. Indeed, changes of molecular weight, MW, of molecular weight distribution, MWD, and formation of long and short chain branching induce remarkable changes in the molten properties of the polymers and smaller variations in the solid properties. On the contrary, the formation of long and short chain branches and the increase of crystallinity dramatically

influence the solid properties. Finally, the formation of new chemical bonds and new chemical groups (in particular double bonds and oxygenated groups) strongly influence the chemical and physical resistance and in particular the photooxidation behavior. All these considerations are schematically reported in Table 1.

Table 1 Influence of the structure and morphology on rheological and mechanical properties and on the photooxidation resistance

Parameter	Properties		
	Rheological	Mechanical	Photooxidation resistance
MW, MWD	– –	–	–
Branching (long)	– –	– –	– –
Branching (short)	–	–	– –
New Chemical Groups	=	=	– –
Crystallinity	=	– –	–
– –strongly influenced, – influenced, = not influenced or unpredictable			

STRATEGIES FOR UPGRADING RECYCLED PLASTICS

Stabilization

The degradation during the recycling operation in the molten state can be stopped or at least reduced by using suitable stabilizers. Indeed, the stabilizers added to the virgin polymers are decreasing during lifetime and successive processing steps. A good stabilizing system has to be studied and prepared for each single polymer. For this reason not all the stabilizers for the virgin polymers can be directly used for recycled materials. New formulations of stabilizers and new compositions of existing stabilizers are now studied and some results have been obtained on some recycled systems.

Figure 1 reports the elongation at break and the molecular weight of an extrusion grade polypropylene, RPP, as a function of the number of extrusion steps[2]. Both elongation at break and molecular weight of the unstabilized sample decrease remarkably with increasing the processing steps while the changes of the restabilized samples (RPP+AO1 and RPP+AO2) are much more modest.
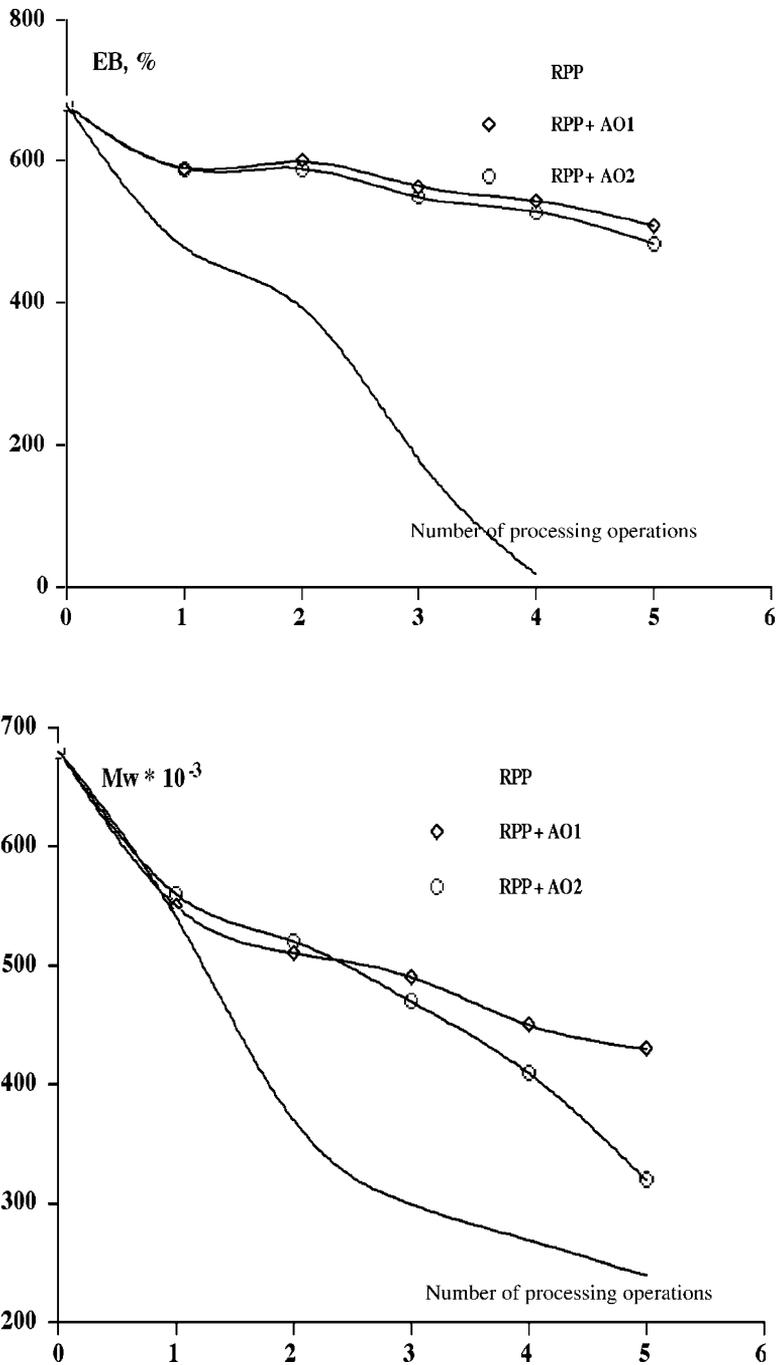
Figure 1 Elongation at break and molecular weight of an extrusion grade polypropylene as a function of the number of extrusion steps

PVC is a thermolabile polymer and is rapidly degraded when the temperature is higher than 180 °C and the initial stabilizing system is lost after the first processing operations. The stabilization is then a necessary step for successive recycling operations. Figure 2 shows the effect of adding a lead stabilizer in the recycling of PVC bottles[3]. The maximum working time - the time at which the torque curve starts to increase - of this PVC sample increases by adding small amounts of stabilizer.

The restabilization of recycled polymers has to be designed not only for protecting the material during processing but also during the end application: weathering resistance, heat stability, etc.

Fillers and Impact Modifiers

Some mechanical properties of recycled materials can be improved by using fillers and polymeric modifiers. Among the first compounds, calcium carbonate, sawdust, wollastonite and glass fiber can be used. Polymeric modifiers are, in general, elastomeric compounds like, rubbers, etc.
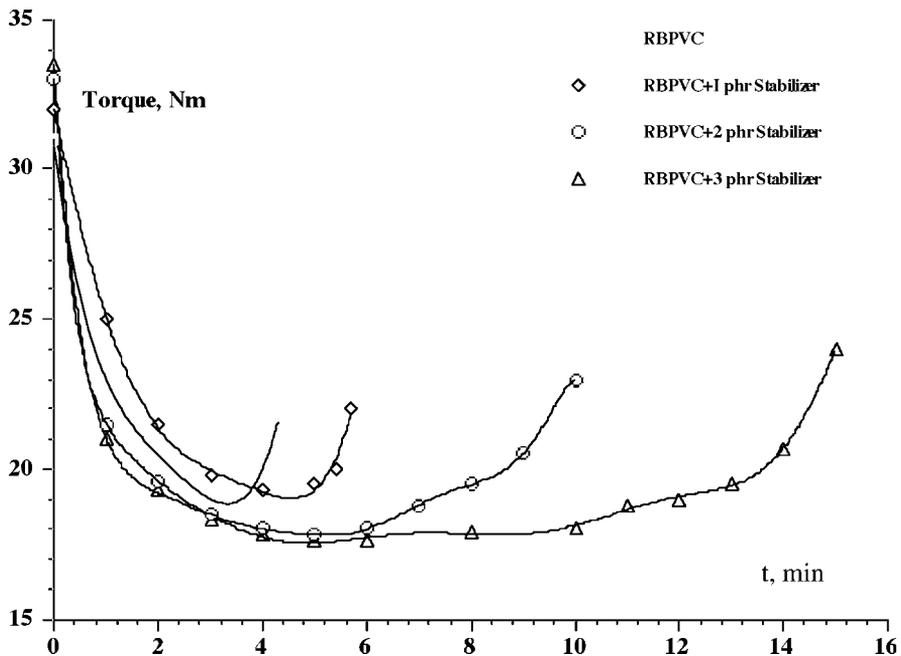

Figure 2 Torque curves of stabilized and unstabilized recycled PVC from bottles

The first compounds improve modulus, tensile strength and, in some cases, impact strength; the elastomers improve elongation at break and impact strength. On the contrary, fillers worsen elongation at break, while the impact modifiers decrease the rigidity of the polymer.

Wood fillers are a new filler type that continuously rises the interest of scientists and industry. Wood fibers, very cheap and "environment friendly", can be used with the same scope of other fibers and with similar results. In Figure 3 the values of elastic modulus, E, tensile strength, TS, impact strength, IS, and elongation at break, EB, of a sample of recycled post-consumer mixture (LF) of PE (about 80%) and PP in presence of different types of fillers are compared[4].

The effect of the three fillers is quite similar for tensile strength, elongation at break and impact strength. In particular tensile strength and impact strength show values similar to those of the unfilled material, whereas the elongation at break is lower. On the contrary, the elastic modulus increases with the filler and wood fibers and glass fibers show the best results. The addition of inert fillers strongly improves the rigidity of this plastic waste mixture, whereas the reduction of the elongation at break does not infirm the possible applications of this system in injection molding.
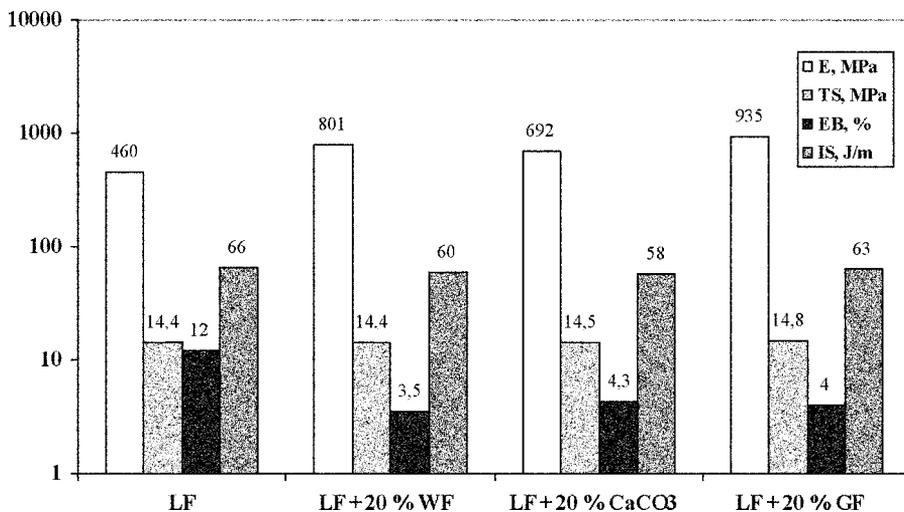

Figure 3 Mechanical properties of the unfilled and filled PE/PP recycled blends

The effect of mineral fillers can be more important for recycled commingled plastics[5]. Indeed, these systems are incompatible and their properties are very poor. Elastic modulus, E, tensile strength, TS, impact strength, IS, elongation at break, EB, and heat distortion temperature, HDT, of incompatible PET/HDPE bends are reported in Table 2 as a function of the content of added glass fibers[5].

Mechanical and thermomechanical properties of the blend rise with increasing the GF content, but for the elongation at break that is almost constant.

Table 2 Mechanical properties and HDT values of glass fibres filled PET/HDPE blends

Sample	E, GPa	TS, MPa	EB, %	IS, J/m	HDT, °C
PET/HDPE	1.6	12	1.3	19	120
PET/HDPE + 10% GF	1.95	21	1.4	28	158
PET/HDPE + 20% GF	2.35	26	1.5	33	233
PET/HDPE + 40% GF	3.1	30	1.4	39	239

Repair

This is a new concept in the plastic recycling field and means that not only the molecular architecture is preserved, but also improved by enlarging the molecular weight. This is achieved by adding molecules able to build-up molecular weight, for example: bis-oxazolines (PET)[6] and bifunctional oxiranes (PA)[7] or by optimising the processing conditions, for example avoiding oxygen and moisture during processing[8].

As for the first case, the small molecules added to the reclaimed plastics during processing react with the end groups of the macromolecules enlarging the molecular weight. The final result is a remarkable improvement of the mechanical properties of the recycled polymer that can be higher than those of the virgin one. In the second case, the elimination of oxygen and humidity from the processing machines, allows the regradation of the polymer, see Table 3[8].

Also in this case an improvement of the mechanical properties is observed. Of course, these techniques can be used only for polycondensation and for functionalized polymers.

Table 3 Processing Parameters and molecular characteristics for PET

	Under:	T, °C	Time, min	η, dL/g	M_w
Virgin				0.67	35500
Dry	N_2	260	60	0.88	54000
Dry	air	260	5	0.665	35100
Dry	air	260	60	0.37	14200
Humid	N_2	260	60	0.81	49000
Humid	air	260	60	0.33	12400

Compatibilization

It is well-known that only a few polymer pairs are compatible. Moreover, the concept of compatibility is in itself difficult to define and quantify. Although it is not completely correct, for our purposes we can define the compatibility on the basis of the property-composition curve, where properties are taken as macroscopic characteristics such as mechanical or rheological properties, etc.. The property-composition curves for blends can be additive (compatible), intermediate between the properties of the two polymer parents (semicompatible) or can present minimum or maximum (incompatible)[9]. The synergistic effect (maximum in this curve) is found only in blends with strong interactions between the two phases. Instead, the antagonistic effect is typical of those polymer pairs with strong repulsion (for example, apolar polymers and strongly polar polymers). In most cases, the properties of the blends are intermediate between those of the two components, (partially compatible or semicompatible) although most of them show values lower than what might be expected on the basis of an additive law. Moreover, for the same blend not all properties behave in the same way.

Incompatibility and antagonistic effects can arise not only from blending polymers with different structures, but also from blending polymers with very similar structure. This can occur, for example, when the blends are prepared from the same polymer, virgin and recycled, called "homopolymer blends" or "monopolymer blends"[3, 10-12].

Generally speaking therefore, it is not possible to predict the physical properties of a mixture containing recycled material. Consequently when degraded

polymers are used, it is a good idea to add only limited amounts to the virgin material if the mechanical properties of the pure polymer have to be maintained.

To improve adhesion between the polymers - to compatibilize the blends - two main methods can be used:

• physical linking among the phases

• chemical linking among the phases

Both points can be achieved by adding small amounts of a third component to the blend to act as a bonding agent between the two incompatible phases. When the macromolecular compound is a copolymer having monomeric units that are identical to, or at least compatible with each phase, there is a physical bonding. The copolymer is miscible in the two phases, creating a bond between the two completely immiscible phases.

In other cases the third component is a polymer miscible in one of the phases and includes some functional groups grafted on it. This component is then miscible in one of the polymeric phases while the functional group can react with some functional group of the other polymer giving rise to a chemical linking between the two phases.

This latter type of bonding between the phases can be also achieved by inducing chemical reactions between the macromolecules of the different phases during the processing, in this case during recycling. This process is called "reactive processing" or "reactive blending" and the compatibilizing polymer is formed "in situ". This may occur because during processing the applied mechanical stress and temperature may cause the polymer chains to break and the subsequent reactions between different radicals. Of course, this latter system is very appealing but it cannot be applied to all the pairs of polymers and it is very difficult to control the reactions during processing. In fact, the copolymers formed "in situ" may be degraded in turn, reducing their molecular weight and changing from block to graft to random copolymers, thus loosing their capacity to act as compatibilizing agents.

As an example, recycled PET and PP have been compatibilized by adding a functionalized thermoplastic rubber (SEBS-g-MA)[13]. Impact strength, IS, and elongation at break, EB, increases remarkably with increasing the compatibilizer content, Table 4. The reactions between the maleic anhydride and the terminal groups of PET give rise to copolymers linking the two phases.

Table 4 Effect of SEBS-g-MA copolymer on the properties of the incompatible PET/PP blend

Sample	EB, %	IS, J/m
PET/PP	5	27
PET/PP + 2.5% SEBS-g-MA	140	54
PET/PP + 5%	250	88
PET/PP + 7.5%	285	108
PET/PP + 10%	320	123

New Technologies

New recycling plants have been designed both for homogeneous and heterogeneous recycling. In the first cases, the aim of these new technologies is mainly devoted to improve the homogenization avoiding large thermomechanical stress on the melt. In the second case, the aim is to try to improve the adhesion between the different molten phases forming links among them. This can be achieved by causing some cleavage of the C-C links with the subsequent in-situ formation of new copolymers acting as adhesion promoters. Among these attempts, it is worth to mention the Newplast Process and the S^{3}P Process (Shear Solid State)

Newplast Process

The heart of the process is the homomicroniser. a cylindrical chamber within which a rotor turns at high speed. The mixed plastics particles are molten by the friction developed between the particles as well as that added by the rotor blades and chamber wall.

A sharp increase of the torque indicates that the molten mixture is completely homogenised and is discharged from the chamber. In Figure 4 some properties of a HDPE = 63.75%, PP-PVC-PS-PET= 11.25%, PVC= 4.5%, ABS = 4.5%, PS = 4.5%, PET = 4.5% PP = 5.0%, EVA = 2.0% mixture are reported[14]. NPPA1 is the material reprocessed in the Newplast Process while TSCA1 is the same mixture reprocessed in a laboratory twin screw compounder. The Newplast material shows good properties and, in particular, is ductile while the conventional recycled sample is fragile.
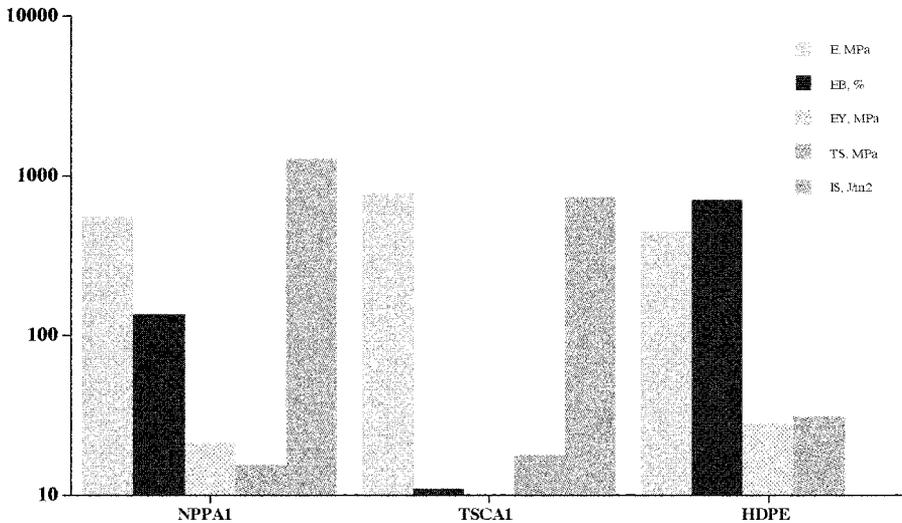
Figure 4 Properties of a commingled mixture reprocessed in the Newplast process and in a laboratory twin screw compounder

S³P Process (Shear Solid State)

A polymeric feedstock is subjected to high shear and compression in a modified twin-screw extruder[15-16]. During the pulverization, elastic energy is stored in the solid polymers until the energy reaches a critical level leading to the formation of a new surface via fragmentation, creating a powder. The S³P process does not involve melting the feedstock; plastics are maintained in their solid state. Frictional heat is rapidly removed by a specially-designed cooling system. By controlling the screw configuration and processing parameters such as screw design, screw speed and feed rate, it is possible to control the particle size and particle size distribution of the powder.

CONCLUSIONS

Homogeneous recycled polymers can show good properties if:

• Degradation during processing is avoided (stabilizers, optimisation processing conditions, etc)

- Molecular weight is enlarged (processing conditions while adding functional molecules)

- Fillers and/or impact modifiers are added

Commingled recycled polymers can show good properties if:

- Fillers and/or impact modifiers are added

- Effective compatibilizers are added

- New ad hoc tailored technologies are used

ACKNOWLEDGEMENT

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