Thermo-mechanical characterization of post-consumer recycled high impact polystyrene from disposable cups: influence of the number of processing cycles.

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Abstract
In this study, the effect of six successive recycling cycles of the recycled material from high impact polystyrene disposable cups on tensile properties, glass transition temperature, flexural, impact strength tests and fluidity were studied. It has been found that after increasing recycling, the molar mass and the viscosity decrease (a slight increase of melt flow index) until the fifth cycle, the maximum yielding stress decreased due to material brittleness. The impact strength has only been relatively influenced by a 17% increase, whereas the elongation at break and the young’s modulus dropped with reprocessing cycles. Glass transition temperature have undergone a remarkable decrease: It dropped in a consistent way, by the sixth cycle we measured a drop of almost 11°C compared to the virgin material, with a notable increase in flexural modulus and hardness. The resulted curves show the reliability of this material to be used after a specific number of processing in several industrial applications.

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Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
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<tr>
<td>Tg</td>
<td>The glass transition temperature</td>
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<td>MFI</td>
<td>Melting flow index</td>
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<td>E</td>
<td>Young’s modulus</td>
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<td>σmax</td>
<td>Maximum load</td>
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<td>εb</td>
<td>Elongation at break</td>
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<td>HB</td>
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<td>A</td>
<td>Shore A hardness</td>
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1. Introduction

Plastics are ubiquitous in our life. Beyond their assets, once consumed, they generate voluminous waste compared to their weight. This waste occupies a large volume in collection points and other waste management facilities including landfills. Their dissemination in nature is durable and unsightly because their biodegradability is, in most cases, low. It is therefore necessary to encourage their recycling. Unfortunately, the
multiplicity of types of plastics and of the composition of the same plastic material, the incompatibility of certain polymers with each other and the difficulty of recognizing and separating the various polymers cause many problems, particularly with regard to selective sorting, especially for post-consumer plastic waste.

In recent decades, Morocco has experienced a sharp increase in the urban population and a proliferation of outlying districts with a consequent increase in the need to access basic services. This situation has made it more difficult to collect and dispose of domestic and industrial waste. It is in this context that the department of the environment and the ministry of the interior with a total amount of 40 billion dirhams jointly launched the national household waste program (NHWP). This program consists of: ensuring the collection and cleaning of household waste, to reach a collection rate of 90% in 2020, to carry out controlled landfills for all urban centers, to rehabilitate all existing wild waste dumps, to develop the "recycling-sorting-valorization” sector, to achieve a recycling rate of 20%, generalize the master plans for all the provinces of the kingdom, as well as to train and sensititize all stakeholders” [1].

Today, Morocco produces 1 million tons of plastic waste, but only 20 to 30% of this amount is valued, but this number is about to change drastically as Morocco embarks on the circular economy and wants to increase its overall recycling rate from 5% to more than 20% (All type of waste combined).[2]

Disposable cups are one of the concerns this policy is facing, as they often end up in the trash after a simple use, sometimes constituting real mounds of waste in some places. In recent years, the phenomenon has grown in importance with the success of the brands offering take-away drinks. It is estimated that hundreds of billions of cups will be used each year.

Mechanical recycling has been proven as the best way to recover a relatively clean and homogenous plastic waste. However, most of the chemical structures, mechanical proprieties, and the behavior’s stability of these materials subjected to multiple degradative cycles are most likely to be altered. The aim of this paper is to demonstrate the effect of multiple post-recycling processing on high impact polystyrene (HIPS) from disposable cups.

It is hence essential to apprehend the degradation mechanisms to which recycled styrene-based plastics are exposed during their life cycle, to better evaluate their potential for further employment in second-market applications [3].

A number of papers have been published on this subject. Mantia and al [4] studied the influence of flow on the polystyrene degradation using samples of different length. The authors also debated the probable breakage of C-C links under elongation flow. Murthy and Raghavendra, [5] established that increased degradation of polystyrene is due to excessive shear in extrusion and palletization processes. Inaba and Inoue [6] examined the alterations of molecular weight of polystyrene degraded at 340-380° C.

Vilaplana and al simulated a period of service life by subjecting virgin HIPS to thermo-oxidative ageing and compared it to nine processing recycling, the results indicate that the mechanical recycling is way less degradative to the material than thermo-oxidative aging and considered HIPS a promising material for mechanical recycling and employment in second-hand applications [7]. Soriano and al repeatedly coextruded 70% of virgin HIPS and 30% of recycled HIPS and confirmed the variation on chemical and physical properties due to microstructural changes in the material attributed to the degradation mechanisms that took place in the PS matrix as well as the rubber phase [8].

Boldizar and al subjected virgin ABS material to a succession of six combined cycles of extrusion and ageing in air at a high temperature, and observed remarkable variations in tensile and flow characteristics due to physical aging of the SAN part and to thermo-oxidative ageing of the polybutadiene phase [9].

2. Materials and methods

In order to simulate the recycling process as accurately as possible, the disposable cups underwent 6 successive grinding / injection cycles as illustrated in figure 1, and during each cycle the tensile, flexural strength, hardness, Charpy, DSC and MFI tests were performed to evaluate the evolution of the properties of the material.
Disposable high impact polystyrene cups were obtained from informal collectors; the disposable cups were initially shredded and extruded by the material provider. The received high impact polystyrene was approximately 5 to 10 mm diameter pellets as shown in figure 2.

The pelletized recycled material was then injection molded into different tests specimens according to ISO 294-1 [10] and ISO 294-2 [11] via a SINTESI molding machine, as shown in figures 3.

### 2.1. Differential scanning calorimetry tests

After each cycle, Differential scanning calorimetry measurements (DSC Machine) were performed on a T-instruments Q20 machine, in order to characterize the melting temperature behavior according to ISO 11357 [12].

Differential scanning calorimetry (DSC) is a technique for detecting changes in the physical state of the material during heating or cooling, by linking the heat output of the device to the enthalpy variations of the material. This apparatus will thus detect any change in the physical state of the sample, as regards semi-crystalline polymers:

- The glass transition of the amorphous part,
- The temperature and the melting enthalpy (endothermic phenomenon) of the crystalline part,
- The temperature and the enthalpy of crystallization (exothermic phenomenon).

The operating principle of the calorimeter is to subject a sample to a controlled thermal cycle (typically a temperature sweep in a neutral atmosphere) and to continuously compare the difference in heat flow needed to maintain the sample and the reference at the same temperature. The reference being an empty capsule placed in the same oven as the sample. The DSC provides access to the thermal characteristics related to the change in physical state (glass transition, melting / crystallization) or chemical change (Figure 4).
A grasp of the thermal properties of polymers thermal properties is in fact very necessary while designing the processing conditions and during the choosing protocol of a suitable material for different purposes. Thermal characterization of polymers, reinforced and hybrid composites [13] [14], include their glass-transition point. Glass transition temperature (Tg) is an essential thermal alteration. Plastics transform from hard vitreous polymers to a rubber-like material or conversely at glass transition temperature. The characteristics of the polymers amorphous portion is causing this shifting in structures [15]. Below this temperature, polymeric chains are in a harden condition. However, their segments gain mobility at glass transition temperature.

2.2. Melt flow index

To analyze the flow properties of the used materials and their interactions with the mechanical properties of the material, an MFI test was carried out. The MFI test in this paper was conducted using the KARG (MeltFlow @on) machine in accordance with ASTM D-1238 [16]. Plastic samples (about 4-5 g) were prepared from the 6 cycles. The materials were packed properly in the cylinder of the melt index machine to avoid air pockets formation. The samples were then preheated for 3 minutes at 190 °C. Afterward, a specific mass was introduced onto the piston. This study applied 2.16 kg as the weight recommended by the standard. Shear weight was applied on the molten material that instantly started to flow through the die. A sample of the melt was taken after the defined period and weighed correctly. MFI was expressed in grams of polymer per 10 minutes flow time.

Melt flow index (MFI) is a widely adopted practical way of measuring the ease of flow of a polymer grade, and so is of use in indicating the relative magnitude of process parameters for shaping the polymer granules or powder to create a finished article [17]. It is inversely related to molecular mass, so that high MFI grades correspond to low molecular masses and vice versa [18]. High molecular mass polymers often possess the best physical properties, which is why the most demanding uses of plastics such as safety helmets and pipe fittings require low MFI grades.

2.3. Mechanical behavior

A mechanical property is a characteristic property of a material that describes its behavior when subjected to one or more mechanical loadings. For materials in general, these properties depend of the temperature, however for polymers; the time is also a factor. The reason for this dependency is that plastics materials are considered viscoelastic, when subjected to mechanical loading, as they are characterized by a transitional state between the two viscous and elastic-solid states. A solid that obeys Hooke’s law is an ideal elastic material [19], i.e., the elongations are proportional to the forces. The mechanical response of plastic materials is usually categorized as short-run mechanical properties, dynamic mechanical properties, and long-term mechanical properties. Short-run mechanical properties indicate the materials mechanical performance of over a short period. The most notable among short-run properties are; tensile strength, impact, and flexural characteristics also called static mechanical tests.

- **Tensile tests:**

Plastics stress-strain (tensile) characterization indicates an extensive range of stress-strain behavior. It goes from a soft, weak rubbery material to tough and stiff polystyrene. Significant parameters determined from a stress-strain curve are maximum load endured by the material, which is tensile strength σ_max, their resistance to deformation quantified by the modulus, and elongation at fracture ε_0. These characteristics are easily linked to the microstructure of plastics. Polymeric materials properties can be altered with temperature in addition to testing speed [20]. Their behavior at low temperature is much correlated with an elevated testing speed. Plastics behave as rigid solids at lower temperatures considerably inferior to the Tg temperature, and the loading increases to the rupture point at very little elongation. At much elevated temperatures significantly higher than Tg, the materials are rubber-like [21]. They stretch out consequent to a minor loading application, and the deformation required to fracture the specimen is higher. They also display certain transitional behavior, where a yield point preceding fracture can be noted. Tensile tests were carried out on a Zwick Roell tensile machine according to ISO 527-1 [22], 5 specimens were used on each cycle.
The test consists of subjecting a test piece to a tensile stress along its axis, generally to breaking, in order to determine one or more mechanical characteristics. The standard recommends machines with constant traction speed (controlled on the move). Efforts are measured by strain gauges.

The elongations are measured by an extensometer. The device for attaching the specimens is designed so that, at the least effort, the specimen will align with the axis of the tensile force.

- **Flexural tests:**

Flexural tests differ from the tensile tests regarding the type of loading application to the specimen. Based on the materials category, it as well indicates various sorts of behaviors.

Flexural tests were carried out on a LLOYD LR50K tensile/flexion machine according to ISO178 [23], 5 specimens were used on each cycle. The test consist on the deformation of a rectangular bar, resting on two supports by means of a beam applied at equal distances from the supports and moving at a constant speed to measure the properties of rigid plastics and composites because this type of test reproduces well the real solicitations of the parts. The applied force and the deformation of the test piece are simultaneously measured.

- **Charpy tests:**

Impact strength is one of the main mechanical property that describes the materials ability to resist a mechanical shock or impact loading, traditionally used in fracture mechanics [24] [25] [26]. This property is highly temperature-dependent. At temperatures inferior to Tg, plastics tend to have a brittle behavior and low impact resistance [27].

Charpy tests were carried out on a CEAST Charpy test machine, according to ISO179 [28], five specimens were as well used on each cycle. The Charpy test makes it possible to characterize very quickly the type of brittle or ductile fracture by determining the energy required for the rupture. It is a shock test with high deformation rate. The test is performed on a pendulum. The energy consumed by the impact is evaluated from the initial angle of release of the pendulum and the maximum angle of ascent. The specimens are positioned on two supports and hit by the pendulum in their plane of symmetry.

- **Hardness tests:**

The hardness of a material defines the resistance of a surface of the sample to the penetration of a harder body, for example the ball or tip of a durometer. Unlike minerals whose hardness is characterized by scratching, bounce or penetration tests are often used to characterize the hardness of plastics and elastomers [29]. These tests have the advantage of being simpler to perform and give reproducible results.

There is a wide variety of possible hardness tests: Brinell (HB hardness symbol), Rockwell (HR), Vickers (HV), Shore A and D, etc. They are particularly used in quality control to compare or estimate the strength or stiffness of materials [30].

Hardness tests were performed via a BAIEISS portable device to directly measure the hardness Shore D of plastic materials, according to NF ISO 48-5 [31]. The test for determining the apparent hardness consists in applying, via a calibrated spring, a force tending to drive a penetrant of defined shape into the material to be tested. The penetration depth varies in the opposite direction of the hardness. The displacement of the penetrator is read on a scale of measurement, graduated from zero to 100, in such a way that the mark 100 corresponds to a zero penetration and the mark 0 to the maximum penetration allowed by the apparatus.

The tests after each cycle were performed on different spots on the specimen, at least 4 spots.

3. Results and discussion

3.1. MFI results:

The melting flow index (MFI), was measured after each of the six processes. Figure 5 shows the increase of the MFI with the number of reprocessing cycles: at the first cycle we observed a remarkable rise of the MFI (About +19%) followed by a slight increase during each reprocessing cycle. The results could be attributed to the chain scission mechanism induced by thermos-mechanical degradation due to successive processing cycles (Figure 6), which causes the molecular weight of the recycled HIPS to drop and affect the mechanical properties as well. However, the resulted melt flow range is still suitable for most of industrial applications requiring injection moulding, especially thin-walled articles [32].
3.2. DSC results:

The evolution of glass transition temperature during the six reprocessing cycles is illustrated in figure 7. The $T_g$ dropped in rather a consistent way, by the sixth cycle we measured a drop of almost 11°C compared to the virgin material. These results are in perfect concordance with the results from the MFI tests, as there is a noteworthy dependence between the glass transition temperature and the molecular weight of HIPS and polymers in general [33], in fact, the polymer's chain has two chain ends, and therefore each chain end at any temperature has higher mobility. With decreasing molecular weight induced by chains scission, the concentration of chain ends increases [34], hence the enhancement of chains mobility that is responsible for decreasing the glass transition temperature $T_g$ after each cycle.

Fig. 7. Evolution of glass transition temperature $T_g$ as function of recycling number.

3.3. Tensile tests results:

Tensile tests until fracture were carried out for the virgin material as well as the recycled material after each reprocessing cycle; the results are illustrated in figure 8.

Young’s modulus underwent a drastic decrease until reprocessing cycle 2, followed by a small variation up to the sixth cycle. Young's modulus is an indicator of the strength of the polymer. As shown in figure 9, Young's modulus (E) decreases with the number of recycling cycles of disposable cups, a decrease that is not very significant. Indeed, the tensile results are very well correlated with those of MFI. Used plastic cups after each recycling stage undergo thermo-mechanical degradation as a result of repeated extrusion and may induce changes in the chemical microstructure of HIPS, resulting in a slightly more brittle material with lower ductility.
Fig. 8. Stress-strain curves of high impact polystyrene after each reprocessing cycle (the most representative samples). The maximum stress and elongation at break were clearly affected by the reprocessing cycles, but not at the same degree, the reason behind the drastic drop of elongation at break as illustrated in figures 10 and 11, is that the chain scission induced by reprocessing mechanisms, did leave the material with an enormous amount of short length chains, which means more chain ends and therefore, more inhomogeneities where the fracture finds its way and we start to observe a brittle behavior of the material [35].

Fig. 9. Evolution of Young’s modulus as function of recycling number.

Fig. 10. Evolution of maximum stress as function of recycling number.

Fig. 11. Evolution of strain as function of recycling number.

3.4. Flexural modulus and hardness Shore “D” tests results:

The results of flexural modulus and hardness indicate a notable level of brittleness. As the figure shows a miner increase in flexural modulus (Figure 12), the hardness of the recycled HIPS underwent a strong shift (Figure 13).

Compared to tensile tests results, the flexural and hardness tests suggest that the reprocessed material undergoes chain deterioration as well as crosslinking with every cycle. All of these factors
result in the material’s brittleness and resistance to bending and penetration, but not in favor of tensile properties, as in polymers: crosslinking may slightly increase young’s modulus; on the other hand, it decreases the ability of the material to resist fracturing. Thus, the material loses its elasticity with each cycle due to chain scission, which confirms the tensile tests results clearly indicated on figure 8.

![Graph showing flexural modulus vs. number of cycles](image1)

**Fig. 12.** Evolution of flexural modulus as function of recycling number.

![Graph showing hardness (Shore D) vs. number of cycles](image2)

**Fig. 13.** Evolution of hardness “Shore D” as function of recycling number.

### 3.5. Impact strength tests results:

The results from the impact strength tests, on the hand were quite different from the literature [7] [8] [9]. In fact there was a miner increase of the toughness of recycled HIPS (Figure 14). This is basically related to the shortest molecular chains with extremely low molecular weight acting like plasticizers and hence slightly improving the impact strength. Additionally the repeated reprocessing of the recycled material is most likely to assure better distribution of the rubber phase within the high impact polystyrene as a result of mechanical attrition, the polybutadiene phase (the rubber phase) is responsible for the fracture resistance of the material, increasing thus the impact strength. This result suggests an amount of entanglement density leading to rubber particles size modification [36].

![Graph showing impact strength vs. number of cycles](image3)

**Fig. 14.** Evolution of impact strength “Charpy” as function of recycling number.

### 4. Conclusion

Repetitive mechanical recycling of high impact polystyrene (HIPS) induce changes in the chemical structure of the material; these chemical changes are related to modifications at a macroscopic scale in the mechanical and viscoelastic behavior. Thermo-mechanical degradation triggered by numerous reprocessing cycles may cause changes of the physical microstructure, in addition to chain scission and chains redisposition in the HIPS. High impact polystyrene is a promising material for mechanical recycling, since its properties are not all drastically affected by the six reprocessing cycles.
Given the life cycle, and the mechanical recycling prospective of HIPS, previous service life seems, therefore, to determine the degradation degree of HIPS recyclates and its further potentials for reuse in second-market uses, as Morocco is moving towards a policy of environmental protection by recently banning the production of non-biodegradable plastic bags and embarks on the circular economy by encouraging the recycling of commercial, industrial and agricultural plastic waste and limiting the export plastic waste. This study is part of the initiative to strengthen the competitiveness of the recycling industry through the development of reused HIPS from disposable cups, the development of the different control methods associated with the different characteristics of HIPS recyclates. The final material is intended to be used for the production of different parts, the future aim is to develop a standard designed for suppliers and customers to guide them to better target the potential applications of recycled HIPS according to specifications and legislation.

References


