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Influence of impurities on the performances of HIPS recycled from Waste Electric and Electronic Equipment (WEEE)

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ABSTRACT

In order to produce a high quality recycled material from real deposits of electric and electronic equipment, the rate of impurities in different blended grades of reclaimed materials has to be reduced. Setting up industrial recycling procedures requires to deal with the main types of polymers presents in WEEE (Waste Electric and Electronic Equipment), particularly High Impact Polystyrene (HIPS) as well as other styrenic polymers such as Acrylonitrile-Butadiene-Styrene (ABS), Polystyrene (PS) but also polyolefin which are present into WEEE deposit as Polypropylene (PP). The production of a substantial quantity of recycled materials implies to improve and master the compatibility of different HIPS grades. The influence of polymeric impurities has to be studied since automatic sorting techniques are not able to remove completely these fractions. Investigation of the influence of minor ABS, PS and PP polymer fractions as impurities has been done on microstructure and mechanical properties of HIPS using environmental scanning electron microscopy (ESEM) in order to determine the maximum tolerated rate for each of them into HIPS after sorting and recycling operations.

1. Introduction

Plastics waste represents a great source of pollution in the case of landfilling or incineration for some materials. If the expected properties of recycled plastics would be really taken into account, a tremendous wastage could be avoided by considering such materials as garbage. Although many studies on polymer recycling from DEEE have been carried out over the past few years (Mantaux and et al., 2004; Balart et al., 2004; Larsson and Bertilsson, 1995; Wäger and Hischier, 2015; Wang and Xu, 2014), only a small increase in the use of recycled polymers has been observed. One explanation for that could be related to requirements for a recycled matter, regardless of the pollutants contained within it.

Recycled plastics could meet stringent specifications (Leroy et al., 2006) if separation techniques could be improved. However, sorting, especially by Near InfraRed Spectroscopy (NIR) for different polymer grades or additivated polymers remains difficult or not yet possible. Hence, it would be easier to improve the blending process and the re-additivation of recycled polymers (Murakami, 2001; Wang et al., 2015; Pospisil et al., 2005). As a matter of fact, there is a lack of studies about the mechanical performance of recycled polymers with minor fractions of other polymers. Mastering the influence of impurities could be of prime interest for enhancing the quality and the stability of the recycled polymer structural properties. Thus, the impact of impurities on the microstructure and on the properties of the matrix/impurity interface has to be studied. This study focused on one styrenic polymer: HIPS (High Impact polystyrene). This commodity polymer is used when both aspect and impact strength specifications are required and is largely used for electric housings and fridge fittings. Consequently, HIPS is widely present in WEEE (Waste of Electric and Electronic Equipment) and ELV (End of Life Vehicles). HIPS is a multiphase polymer composed of a rigid polystyrene matrix containing butadiene rubber nodules (from 0.5 to 10 μm in diameter) (Alfarraj and Bruce Nauman, 2004; Vilaplana et al., 2006). Many commercial grades of HIPS can be found with different viscosity and butadiene rate. It should be noted that although HIPS represents 19% of the overall plastic WEEE content, only 1% of HIPS is recycled today in Europe (Dillon and Aqua, 2000; Xu et al., 2002). The recycling rate of HIPS could increase provided that (i) the effect of impurities on this material would be completely mastered (Gent et al., 2015), (ii) no added compatibilizer could

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modify the behavior of the material and (iii) the processing parameters could remain close to virgin HIPS (Boldizar and Möller, 2003; Luzuriaga et al., 2006). Because of the difficulties in sorting HIPS fractions with different additives after grinding, recycling this polymer requires the different grades to be blended. In addition, the quality of styrenic thermoplastic resins can be affected by a small content of impurities (Tall et al., 1998) or by the extrusion process (Tang and Chaffey, 1989; Jamil and Shubber, 1988; Liu and Bertilsson, 1999). This can be explained especially by the degradation of the butadiene phase which induces an embrittlement of the polymer. Tarantili et al. (2010) showed that the degradation of butadiene phase generates a significant decrease in the *trans*-1-4 functional group and the apparition of hydroxyl and carboxyl groups. In addition, other studies have shown that impact strength and elongation at break of ABS and HIPS were affected by chain scission phenomena during recycling or ageing (Tarantili et al., 2010; Vilaplana et al., 2007, 2010; Vilaplana and Ribes-Greus, 2007; Luzuriaga et al., 2006). Although some authors (Tjong and Jiang, 1999) showed that ABS and HIPS could be miscible in specific proportions, generally a small amount of ABS lowers the impact strength of HIPS. So, in order to study the mechanical behavior of recycled HIPS regarding different sources and the influence of impurities, the first part of this work is dedicated to the study of the mixing of different grades of HIPS recycled from real deposits. In the second part, the sensitivity of HIPS to different polymer-impurities such as ABS, Polystyrene (PS) and Polypropylene (PP) is investigated through impact testing and original in-situ tensile measurements using an Environmental Scanning Electron Microscope (ESEM). Formulations of recycled materials have been simulated by incorporating only a single polymer impurity (PP, ABS or PS) in each mixture.

2. Waste materials and sorting techniques

In this study, manually sorted (from PS, HIPS and SB (styrene butadiene) marking) batches of plastics waste came from Waste of Electric and Electronic Equipment (WEEE), particularly computer housings dismantled in the Bordeaux region – France (7 batches noted “HIPSWE3EMV1” to HIPSWE3EMV3 and “HIPSW3ETP1 to HIPSW3ETP4”). On the average, the mean age of these products is around ten years old. The manual sorting by marking was carried out using a Phazir® NIR hand-detector test. The 7 batches represented 25 kg of matter, considered as pure recycled HIPS. Nevertheless, the HIPS may contain different rates of polybutadiene (PB).

Another batch of impure HIPS was obtained by grinding refrigerator fittings called “HIPSFridgeAC”. This batch was sorted automatically using a NIR facility (Pellenc ST®) based on IR spectra recognition and air ejection of the separated pellets regarding their IR spectrum. This batch also contained a lot of polymer impurities and foreign bodies (foam, glue, labels, and pieces of rubber) and was considered as a low quality for recycled HIPS.

After automatic sorting by IR spectroscopy, it is supposed that polymer impurities result from:

(a) Trajectory errors during the ejection of undesirable chips; some of the most common polymer found in WEEE deposits are then likely to be found as impurities, so Polypropylene (PP) was which is used in small household equipment, was selected.
(b) Errors due to close NIR spectra. Consequently, this led to the selection of two polymers as impurities:
    (i) PS because it may lower the impact strength of HIPS.
    (ii) ABS which may not be compatible with HIPS.

These impurities were manually added to pure HIPS (obtained by decontamination of previous batches) at rates corresponding to realistic sorting errors defined below.

3. Recycling and mixing process

Each batch of recycled matter was decontaminated manually (stickers, glue, metallic inserts) and was cleaned by immersion during 4 h in a mixture of water and 4 vol% of 100% biodegradable detergent. 1 kg batches of matter were then constituted after the grinding process. The flakes of matter were extruded, pure or mixed with a determined rate of impurity (PP, PS or HIPS). The impurity rate was chosen within the range of capacity of an industrial sorting facility. One run of sorting induces an impurity rate of around 5 wt% whether 2 runs of sorting allow less than 3 wt% impurity. As a consequence, impurities in the range 1–8 wt% were added. Before drying, the flakes were mixed slowly by hand with the flakes of matrix in order to lower electrostatic phenomena.

Before extrusion, the flakes were dried for 40 min: 20 min under air, then under vacuum at 85 °C. Extrusion was performed in a single-screw extruder SCAMEX VM 30/26 L/D. The screw speed was 60 rpm; the extrusion temperature in the die was 225 °C. Before injection molding, the pellets were dried (once more) for 40 min similarly. The samples for mechanical testing were injected using a DK 50/200 NGH injection molding machine at a 210 °C injection temperature and 50 °C mold temperature.

Several SEM images (Fig. 1) at a magnification of 5000× were taken on cryo-fractured cross-sections of samples, prior to the tensile tests, in order to evaluate the influence of the different impurities as function as both the nature and the rate of impurity. Impurities appear in white and the matrix in black.

The nature of the impurity strongly influences the final topographic morphology of the material. Observations highlight that the nodules of PS within the HIPS matrix present a similar morphology from 1 to 8 wt% of PS. It is also possible to consider that a few numbers of micrometric PS nodules reveal a possible partial miscibility of PS into HIPS. Moreover, no PS nodules pullout is noticeable which indicates a good interfacial adhesion with the HIPS matrix.

4. Mechanical characterization

4.1. Charpy impact test (unnotched samples)

Upon ageing and recycling of a polymer, the impact strength is one of the most damaged mechanical property (Xu et al., 2002; Gent et al., 2015). To investigate loss of HIPS impact resistance due to impurities and recycling, Charpy impact tests according to ISO 179 standard were performed on unnotched samples. Samples were temperature stabilized for 16 h at 23 °C before testing.

4.2. Uniaxial tensile tests with environmental scanning electron microscopy (ESEM)

New tailor made method based on ESEM in-situ tensile tests were conducted to view the damage sequence of the studied samples.

The nature of the impurity influences the final topographic morphology of the material significantly and thus corroborates both the values of the impact strength of unnotched impact tests as well as the analysis of the fracture aspect.

Tensile tests were carried out by ESEM Quanta FEG 200 on rectangular shaped samples (30 × 10 × 4 mm) with a 10 mm gauge length and repeated three times. Two notches (depth 0.5 mm ± 0.02 mm) were performed symmetrically on each side