Recycling Study of End of Life Products Made of ABS Resin

O.Mantaux[1)†], *T.Lorriot*[1)], *L.Chibalon*[1)], *J.Aurrekoetxea*[2)], *A.Puerto*[2)], *A.Arostegi*[2)] *and I.Urrutibeascoa*[2)]

1) Laboratoire de Génie Mécanique et Matériaux de Bordeaux, Université Bordeaux 1 Domaine Universitaire 33405 Talence, France

2) Mondragon Unibertsitatea, Goi Eskola Politeknikoa, Loramendi 4, 20500 MondragÓn, Spain

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Former studies about ABS recycling show a very slight decrease of performances after several cycles of accelerated ageing and reprocessing, which proves the benefit of ABS as a recyclable material. Nevertheless, few studies consider ABS properties after real service ageing. The study proposed here is focused on properties of ABS after service and reprocessing. This work evaluates mechanical, thermal and chemical properties of ABS products that have been heated and cooled many times after two types of recycling processes: a recycling process involving grinding and extrusion is compared to a chemical recycling process with the use of a solvent. This study shows that it is possible to optimize treatment and reprocessing conditions in order to produce a recycled ABS corresponding to performance specifications of ABS users.

KEY WORDS: ABS resin; Recycling; Mechanical performance; Strong ageing

1. Introduction

ABS is one of the most currently used polymers, particularly in the fields of electrical and electronical equipment and automotive industry. ABS products represent a substantial volume of material to be recycled at the end of life of these products. The increasing utilization of this polymer and the new European standards mean that to make end-of-life treatment of ABS products is becoming a major economical and environmental issue.

Former studies about ABS recycling have been focused on the impact of the recycling process on the mechanical and physical properties of the material[1~7]. However, few studies have been published concerning the combination of recycling and accelerated ageing of the material. In order to develop a real industry of ABS products recycling, it was important to study the performance of recycling ABS from products that have been used for several years[2,8]. It was interesting to compare two recycling ways: a mechanical recycling process and a solvent based process have been experimented on ABS products with the same background.

2. Virgin and Aged ABS

In order to compare the mechanical and solvent based recycling processes proposed here, the present study was focused on ABS products for which the service was identical. The material concerned by this study is extracted from drying trays for fruits out of order after one year of intensive service. In order to enhance the influence of service time, the properties of semiaged samples (6 month) were also evaluated. The current service cycle of these products is a succession of heatings to 70°C and cooling at 4°C in wet atmosphere, heating to 50C with chloride (cleaning). This corresponds to a very strong ageing and the success in recycling these products would open the way for recycling many ABS products, *e.g.* household applications.

3. Mechanical Recycling

The most current methods for plastic recycling are mechanical methods *e.g.* cleaning, grinding, extrusion, granulation and injection. These kinds of methods give satisfying results with polyethylene, polypropylene, polyester and polyamide. Thus, it was all the more interesting to prove the feasibility of this method for used ABS products, these good results were found in the literature for virgin ABS mechanical recycling. ABS, especially when aged, can be thermo-sensible, consequently, the processing parameters of recycled materials are not obviously the same than those required for the virgin material so that samples molded with a 40°C and 50°C mold have been studied.

The products to be recycled were cleaned with pressurized water and the cut parts were ground in a rotating grinder to produce flakes approximately 5 mm×5 mm×2 mm. The flakes were dried at 80°C in air for one hour.

The extrusion has been made on a single screw ϕ 30 mm extruder. The extruder was heated at four zones: 190°C , 195°C, 200°C and 205°C. The rotational velocity of the screw was kept at 30 r/min and the die was ϕ 4 mm, which corresponds to a shearing rate of 12 s^{-1}. The extruded ϕ 3 mm material was milled to produce 2 mm length granulates.

4. Solvent-based Recycling

Nowadays, a new method for recycling polymers has being developed based on the solution of polymers. Solvent-based processes include stage of treating plastic waste with solvent so that the polymeric materials are dissolved and then recovered by reprecipitation. Separating and recycling plastic waste through this route appears technologically feasible and of considerable commercial interest for the following reasons:

(1) Insoluble contaminant and additives can be removed by filtration, leaving pure material. These additives can be reused.

† Ph.D., to whom correspondence should be addressed,
E-mail: olivier. mantaux@iut.u-bordeaux1.fr.

(2) Any defective material, such as gelling lumps, due to the previous degradation history, can be removed during the dissolution stage.

(3) Except heating for dissolving (also related to the solvent and the conditions chosen) no further degradation, due to the recycling process itself, is anticipated.

(4) The value added during the polymerization stage is maintained intact and the recycled polymers, free of any contaminants, can be used for any kind of application, since the final product is of competitive quality compared with the virgin material.

(5) Solvent-based processes have the potential to deal with mixtures of polymers or polymer alloys, based on the principle of 'selective dissolution'.

The solvent/precipitation system developed for recycling ABS consists in solving the polymer in acetone at 25°C with a 25 g/100 ml concentration, and recovering it by means of the evaporation of solvent at 80°C during 150 min. The ABS is recovered in solid state, so it is ground in order to be reprocessed.

5. Mechanical Properties

The mechanical tests have been performed at a room temperature of 21°C (±2°C) with 50% (±10) relative humidity.

5.1 Tensile measurements

Tensile measurements were performed according to ISO 527-5A with a MTS RF/100 testing machine at a crosshead speed 0.2 mm/min. The elongation has been measured with a video extensometer to get free of any notch effect due to the blades of a mechanical extensometer.

The samples of virgin and aged material were machined in the trays for fruits. The mechanically and solvent-based recycled material samples were injected with a DK 50 press. The sample geometry was the same in both cases (machined or injected).

Figure 1 shows that the tensile properties are very little affected by the recycling process, either mechanical or by dissolution. Indeed, the modulus and the maximum stress show a slight decrease of 2.5% after ageing and it is noteworthy that after recycling the tensile properties are regenerated at their former level. This recovery of mechanical properties could be interpreted by the occurrence of a noticeable service induced damage disappearing after reprocessing of the material. Furthermore, the higher the mold temperature during injection, the stronger the material strength and the lower the Young′s modulus. That proves the necessity of studying further the influence of processing parameters on material properties.

The elongation at break has not been studied because of the sensitivity of the machined samples to very small defects induced by the injection process of the tray.

5.2 Impact strength

The impact strength test was determined with a 50 J Charpy impact tester using 4 mm×10 mm×80 mm unnotched samples. The average value of 8 test results is shown in Fig.2. The typical deviation is less than 17%.

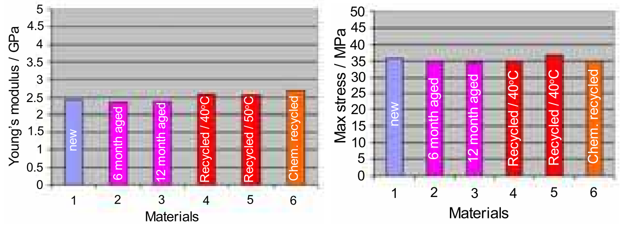

Fig.1 Tensile properties of recycled ABS compared to new ABS and aged ABS

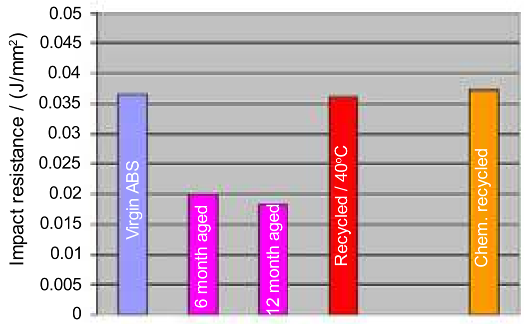

Fig.2 Impact strength of recycled ABS

The impact strength of the recycled materials is comparable to the one of virgin material with even a slight increase for the solvent based process. The difference between the two recycling process be attributed to the difference of butadiene content (see chap. 8) which is the governing additive for impact strength. The impact resistance provided by the solvent based recycling process seems to be better than the one of virgin material, this may be due to the machining of the virgin and aged material samples which possibly damages the material. It is possible to conclude that both of the recycling processes are able to recover the impact properties of the material even after a strong ageing of the material. It can be noted that the service imposed to this material damages severely the impact strength (50% lost). The recovery of the impact strength after recycling proves that it is due to microcracks at the material surface (see chap.9).

6. Viscosity

The viscosity curves have been traced on a Dynisco LCR 7000 capillary rheometer. The shear rate range between 6 and 3640 s^{-1} represents the shearing conditions of extrusion and injection.

Figure 3 shows that the viscosity is not modified by ageing of the material, although the viscosity of the recycled polymer is slightly affected for the very low shearing rates. This can be explained by molecular scission due to cutting and grinding of the products. Since the viscosity of the recycled material is not modified for the highest shearing rates, the oxidation of the aged material is expected to be moderate. We can then expect the recycled material to present a high molecular weight. This conclusion has to be studied further with measurements of the molecular mass evolution according to recycling processes.

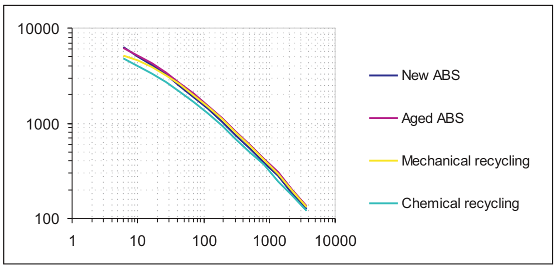

Fig.3 Viscosity of recycled ABS compared to new ABS and aged ABS

7. Thermal Properties

This result confirms that the polymer microstructure is very few affected by the recycling processes. (Fig.4).

8. Molecular Properties

The ABS impact strength is achieved due to the addition of butadiene in the brittle SAN matrix. Thus, a loss of butadiene content during recycling would induce a resilience drop. RMN analysis were performed for evaluating the initial butadiene content in the virgin ABS and the FTIR analysis allowed to compare the butadiene content of recycled, aged and virgin materials.

8.1 RMN analysis

Polymer flakes were dissolved in THF with deuterium and heated. The RMN carbon 13 analysis spectra at 300 K has been performed to evaluate the 3 monomers contents: styrene, acrylonitrile and butadiene. This analysis sets the initial reference value of butadiene at 24% ±5%, for the FTIR analysis.

8.2 FTIR analysis

Five IR spectra of each material have been carried out (Fig.5(a)). The ratio between the 2919 cm^{-1} wavelength peak (carbonyl) and the 1637 cm^{-1} wavelength peak (butadiene) is proportional to the butadiene percent of the material[9]. The dispersion on the results is ±1% butadiene.

The Fig.5(b) shows that the strong ageing of the material involves a butadiene content decrease from 24% to 23% after 6 month of service. This can be explained by the chemical attack by chlorine on butadiene at the material surface. The chemical recycled material presents the same butadiene percent (23%) than the aged material. It proves the efficiency of the solvent based process and its weak impact on the mechanical properties. The mechanical recycling process is more butadiene consuming (21.5%) because of heating during extrusion. As butadiene is the governing additive for the ABS impact strength, this explains the slight degradation of impact properties of the mechanical recycled material.

9. Microscopic Observations

The observations made by SEM point out the presence of microcracks in the aged ABS samples. These microcracks are revealed by the tensile tests and can give an explanation for the mechanical properties drop of the aged material. (Fig.6). These microcracks are due to the strong ageing and the effect of chlorinated solvents and they are no more present in the recycled material by both mechanical and solvent based recycling processes.

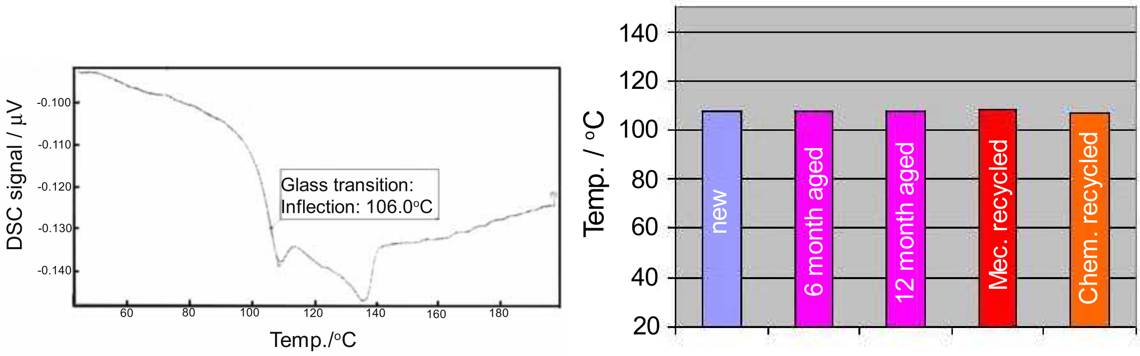

Fig.4 Thermal transitions of recycled ABS compared to virgin ABS and aged ABS

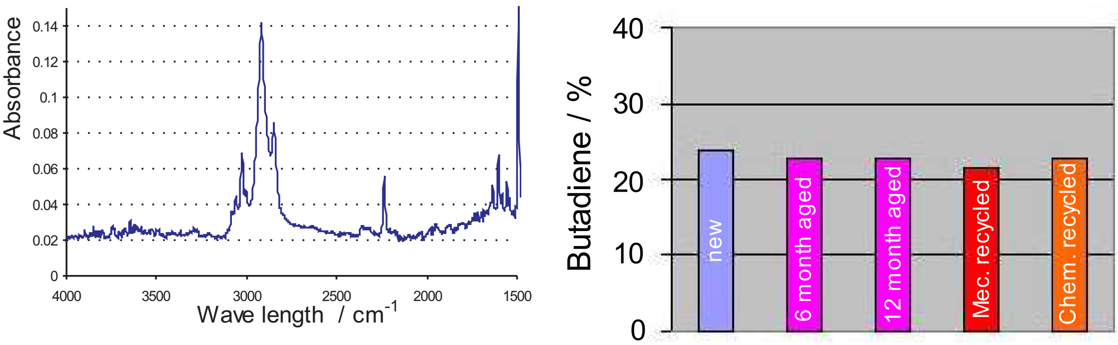

Fig.5 Evolution of butadiene percent during ageing and recycling

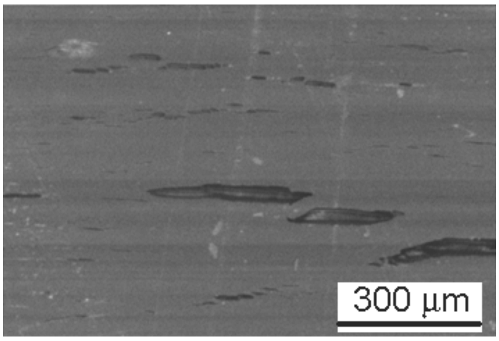

Fig.6 Micrograph of 12 month aged ABS after tensile strength test

10. Conclusions

(1) The analysis of the recycled material by mechanical or chemical process did not reveal any significant change in the thermal and viscous properties. These results lead to think that the ABS microstructure is not affected by the recycling processes. The glass transition temperature remains constant after recycling which is in agreement with former studies about ABS recycling. The viscosity and tensile strength are very slightly reduced during recycling, which indicates that molecular chain scission is only due to grinding.

(2) The impact strength is affected especially by ageing which is interpreted by the appearance of microcraks due to chloride. It was observed a recovery of the impact strength after recycling which proves the efficiency of the recycling processes and that the microstructure of the material is not affected by ageing or recycling. The FTIR analysis shows a butadiene content decrease with ageing and mechanical recycling and gives a good explanation for the slight decrease of the recycled material resilience.

(3) The solvent based recycling process involves no butadiene loss and will be an interesting method for ABS recycling, especially for painted or metallized parts. This method can be improved by minimizing the solvent consummation.

(4) The mechanical recycling process is satisfying and very economical but has to be optimized in order to limit its butadiene consumption.

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