Mechanical behavior of recycled PP composites under tensile, bending and creep loading: experimental and modeling

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Abstract

By the 2000/53/CE directive, the European Union leads to develop the recycling process industry, specially the plastic one, for End of Life Vehicles (ELV). To value these recycled materials by an iso-function use, as for example for car semi structure elements, it is necessary for the mechanical properties to be better known. In this study, the effects of the recycling process on the mechanical behavior of polypropylene (PP)/elastomeric, talc particles filled or not, are presented, through different loading tests: tensile (small and finite strain), bending and creep tests. The failure, plasticity and elasticity parameters modifications are established. Tensile and bending tests lead to some similar characteristics evolution as, for example elastic modulus values. The creep behavior evolution is more complex to understand. Both materials have a near finite strain macroscopic behavior so that, taking account of each component (talc, EPDM or EPR elastomeric part) the intrinsic behavior can be well described in the mechanical model finally presented.

Key words: recycling process, PP compound, HiPP, mechanical behavior, EPDM, EPR.

1 Introduction

Because of their good thermal, mechanical and attractive characteristics, plastics are widely used in the automobile sector. The increasing use of this type of materials results in a large number of publications (Friedrich *et al.* [1], Maiti *et al.* [2], Duffo *et al.* [3], Alonso *et al.* [4], Fond *et al.* [5], Castagnet *et al.*[6], leading to a better understanding of their mechanical behavior. Nevertheless, the recycling process of these materials doesn't lead them, in general, to be used again in the same components.

Today, the recycled PP compound market can increase, through, for example, a more efficient pick up of ELV. Before 2015, companies in automotive industry have to use in their new cars 95% of recoverable materials, with 85% of recyclable ones to agree with the 2000/53/CE European directive [7]. PP compounds represent about 35% of plastics in a vehicle. However, the mechanical properties of the recycled materials have to be better known to allow an iso-function use in the new car generation.

Few studies have been undertaken on the influence of the recycling process on the mechanical behavior. Existing studies relates to rheological aspects (Luda *et al.* [8], Luda *et al.* [9], Guerrica-Echevarria *et al.* [10]) more than on the mechanical characteristics evolution (Bahlouli et al. [11], Pessey et al. [12]). However it is necessary to take into account the recycling effect while designing automotive structures allowing an iso-function use of recycled materials.

Materials studied here are polypropylene reinforced by addition of elastomeric particles and/or talc fillers. They are used for the production of bumpers in car industry. These materials are supposed to support multi axial stresses at different loading rates. The aim of the present study is the characterization of the mechanical behavior of polymer based polypropylene before and after recycling process through different loading tests: tensile, bending and creep tests. Due to the well known high sensibility of polymers to the strain rate, a wide range of the strain rates has also been studied. Two different models of the recycled materials are proposed: one to describe the elastic-visco-plastic behavior under tensile tests and another based on a rheological model to describe creep tests. A good description of the recycling effects for both loadings has been obtained.

2 Experimental study

2.1 Materials

Experimental results have been obtained with polypropylene based composites usually chosen for the manufacturing of semi-structures car elements. They will arrive on the recycling market within 10 years. These materials were provided by SABIC®. The first material is a melt of three phases referenced as compound 7510®. It is a high impact modified filled polypropylene used for rear car bumpers. It contains 20% of EPDM (Ethylene-Propylene-Diene monomer) particles of less than 1 µm diameter, 12% of talc particles of 8 µm mean length, embedded in a PP matrix. The second material is a copolymer PP/EPR (Ethylene-Propylene-Rubber) referenced as 108MF97® obtained by direct synthesis. The elastomeric phase (22%) is made of nodules of less than 1µm diameter.

In order to simulate the recycling process, 6 extrusions/crushing cycles were performed since Guerrica-Echevarria *et al.* [10], Aurrekoetxea *et al.* [13] have shown that the recycling degradation was less important during the first 5 cycles. Samples were machined in 3 mm thick molding sheets obtained by injection process. In the following, 108MF97 (respectively 7510), virgin and 6-time recycled materials, will be referenced as 108MF97 0P and 108MF97 6P (respectively 7510 0P and 7510 6P).

2.2 Experimental procedure

Mechanical behavior of PP based polymers; talc filled or not, as well as the recycling effect on the mechanical behavior is characterized for different loading cases in quasi-static conditions. All the specimens were kept at room temperature at least 72h before mechanical testing.

Uni-axial tensile tests were performed on an INSTRON servo-hydraulic test system at room temperature (25°C). An Instron strain gage extensometer (referenced as 2360-102) was used to measure the uni-axial tensile strain. Tests were carried out under constant displacement rates of 10^{-4}, 10^{-3} and 10^{-2} $mm.s^{-1}$. The dog bone specimen dimensions were 59 mm in gage length; the calculated corresponding strain rates are therefore assumed to be: $\dot{\varepsilon} =$ 0.17 10^{-4}, 0.17 10^{-3} and 0.17 10^{-2} s^{-1}. All tests have been performed until 15% of strain. For this value, conventional and true strain-stress curves are assumed to be equivalent. Each curve and property represented is an average of five specimens tested.

Three points bending tests at room temperature have been carried out using a set-up specially developed for a tensile INSTRON 6025 device: the beam has been set on two base supports and loaded by a concentrated force providing from the tensile axis. Technical device parameters as supports and awl diameters are in accordance with the EN ISO 178 standard. An LVDT sensor with a maximal range of 10 mm and 1µm precision is located in the middle of the sample, on the strip side down. Bending specimens were 120 mm by 20 mm rectangular samples. The control of the deflection was allowed with two distinct rates: 0.2mm s^{-1} and 2 mm s^{-1}. According with bending classical assumptions and with beam dimensions, it corresponds to strain rates of, respectively, 2.5 10^{-4} s^{-1} and 2.5 10^{-3} s^{-1}. An average of three curves is presented for each type of specimen.

Creep tensile tests were performed, at room controlled temperature, with halter-shaped specimens (effective area: 3 x 10 x 50 mm^3) loaded at 4 MPa. This stress, obtained with standard masses, corresponds to the up-limit of the linear creep behavior. Strains have been measured with a ± 10% extensometer on a 35 mm length basis during 3 days of loading. Then masses have been taken out and, without any loading, the remaining strain had decreased showing a visco-elasto-plastic behavior for virgin and recycled materials. From three tests, a representative curves have been chosen for each material.

2.3 Results

Tensile stress-strain curves obtained for virgin and recycled materials (Fig.1 and Fig. 2) show classical finite strain behavior for thermoplastic polymers. A first elastic linear and reversible phase is observed until a yield stress. The yield point is followed by a light strain softening only for the 7510followed by a plastic strain. Initial elastic modulus, yield stress and yield strain were determined from these curves. Three properties were evaluated from each stress-strain curve: elastic modulus (E), yield stress (σ_y) and yield strain (ε_y). Elastic modulus is assumed as the initial slope of the stress-strain curve. Yield strength (σ_y) is assumed to be the maximum stress observed in each stress-strain curve and the corresponding strain is defined as the yield strain.

Curves obtained for recycled materials differ from one material to the other one (Fig.1 and Fig. 2). Noticeable degradation of the mechanical behavior characterized by a decrease of elastic properties was observed for the 108MF97 recycled material with respect to the virgin one. For the 7510, another remark has to be made. Indeed, as the strain rate increases, the discrepancy between virgin and recycled stress strain curve increases too.

Three points bending tests were performed until a 9.5 mm maximum deflection. Viscoelastic behavior is observed and confirmed during the unloading phase (Fig.3 and Fig.4). This visco-elastic behavior remains for recycled materials since only one loop is shown on the Figure 4. On Fig.3 a slightly weaker slope is observed for the recycled 7510 than for the virgin material. The recycling effect is significantly less important on the 108MF97 behavior since recycled material seems to have a stronger modulus. When the strain rate is increasing from 2.5 10^{-4} s^{-1} to 2.5 10^{-3} s^{-1}, slopes are increasing about 15%. Initial Young modulus for each curve is calculated basing on the elastic model, which is conventionally used to describe stress-strain behavior from flexural measurements. They are presented on Tab.1, showing good agreement with tensile results: recycling impact is greater with 7510 than with 108MF97 and values, even if they are higher, have the same order strain rate dependence.

The Figure 5 shows that creep effect is more important for 108MF97 materials than for 7510 ones. Recycling process is more influent on the 7510 materials creep. The Figure 6 presents the total test, including unloading phase. During the unloading process creep strains are not recoverable, overall for recycled materials: viscoplastic behaviour seems to be observed, with a quicker response for virgin materials.

2.4 Discussion

The two materials, despite a great similarity in the mechanical behavior, demonstrate a significant difference with the presence of a "knee" for the 7510, due to the addition of a third phase of talc (Pessey *et al.* [14]). Indeed, one of the effects of the elastomeric phase is a softening of the mechanical behavior while increasing the ductility of the material and reducing the peak at the threshold are observed (Denac *et al.* [15], Liang *et al.* [16]). The elastic modulus and the yield stress thus decrease with the addition of the elastomeric phase, while the deformation at break is slightly modified by the presence of two phases (Denac *et al.* [15]. Both recycled and virgin high impact PP seems to have the same deformation mechanisms.

On the contrary, it is reported that the talc particles rigidify the mechanical behavior and decrease the yield stress and the deformation at break (Oksuz *et al.* [17], Hadal *et al.* [18]). But in these multi-component materials, several deformation mechanisms at different scales of observation exist: the elastic deformation of the composite, the cavitation of rubber particles, the debonding between matrix and particles and the shear deformation of the matrix (Collyer [19]). As explained in a previous paper (Bahlouli *et al.* [11]), cavitation was observed by SEM on all the virgin specimens and occurs at very low level of stress and strain before yield stress (whitening of the reference length during tensile testing). The deformation mechanisms of such materials include multi micro cracking of the matrix, shear flow, micro-voids and cavitation (G'Sell *et al.* [20]). For the 7510, as the strain rate increases, the discrepancy between virgin and recycled material increases.

A comparison between tensile and bending tests is possible. Using the hypothesis of Strength of Materials (SOM), it is possible to link deflection, load and Young modulus whose values once calculated are in agreement with those of tensile tests. It has been noted (Trantina [21]) that SOM tends to over predict the bending modulus in relation to those obtained by tensile test. It is due to the fundamental hypothesis used on SOM: the formula needed to calculate Young modulus from load displacement and geometry of the specimen is true if mechanical behavior is assumed to be linear. But figures 3 and 4 show the behavior is non linear. Thus the young modulus is always over estimated when it is measured from flexural tests.

Recycling has altered various mechanisms involved during the tensile test cited above. Thus, the Young modulus and the threshold stress decrease after recycling (Fig.1 and Fig. 2) An explanation of these effects is found in the recycling process. Several degradation mechanisms are involved: thermal, mechanical and chemical degradation (Aurrekoetxea *et al.* [13]). The different extrusion runs have modified the structure of polymers by cutting chains during successive grindings. The degraded chains are mainly part of the amorphous matrix of polypropylene. But this phase plays a role in the deformation mechanisms solicited after the yield point (Addiego *et al.* [22]. In this study, we show that the elastic properties are degraded by the recycling process. These degradations are not followed by a modification of the initial morphology as explained in Pessey et al, Icrach. In the open literature, it is reported that the recycling increases the elastic properties of the PP (Aurrekoetxea *et al.* [13])

Indeed, only the effects of strain rates are clearly identified by observation under scanning electron microscope (Bahlouli *et al.* [11]. In the same way, the effects of time, highlighted during the creep tests, are different depending on whether the material is virgin or recycled. Thus, the relaxation time of the recycled material, determined by a conventional "four parameters" modeling, is approximately equal to 1.3 times that of virgin material in the case of 7510 and 4 times in the case of 108MF97. The chains cut during the successive extrusion runs would be much more movable than in the virgin materials and even more so in the absence of talc fillers. After unloading, some structural modifications still permit the samples to be strained and they are more important for recycled materials. The total recoverable can be hopped for virgin materials but it had not been, already, measured.

3 Simulation of the mechanical behavior

In this part, a first modeling of the macroscopic mechanical behavior for tensile tests and for creep tests of our materials is proposed. Tensile tests are modeled using a non-linear law originally developed for particulate reinforced PP talc and proposed by Zhou *et al* [23]. Creep tests are modeled using a conventional "four parameters" modeling, since a visco-elasto-plastic behavior has been observed.

An elastic-visco-plastic model has been proposed by Zhou *et al.* in order to describe the stress strain curves obtained experimentally. This model describes the strain rate effects. A modification of this model is proposed to include recycling effect by the way of elastic modulus and yield stress, properties more affected by the reprocessed effects.

The constitutive relation is described by the following equation:

$$\sigma = \frac{E(\dot{\varepsilon}) \cdot \varepsilon}{1 + E(\dot{\varepsilon}) \cdot \beta(\dot{\varepsilon}) \cdot \varepsilon^m} \tag{1}$$

Where E is the elastic modulus of the material, and σ is the stress. Both depend on strain rate as mentioned before and as represented in Figures 7 to 10. β represents a compliance parameter and m is a strain exponent. β and m are calculated from the equation (2) and from its partial derivative. We obtain the expressions given by:

$$\begin{cases} m = \dfrac{E\varepsilon_y}{E\varepsilon_y - \sigma_y} & (2) \\ \\ \beta = \dfrac{1}{(m-1)E\varepsilon_y^m} & (3) \end{cases}$$

The degradation of the mechanical properties (E, σ_y) of the unfilled and talc-filled high impact modified polypropylene for the recycling passes under different strain rates has been described in Figures 7 to 10. It is obvious that a simple linear law can give a good description of the recycling effects. We showed that for virgin materials, the Young modulus and the yield stress are calculated respectively by equation (4) and equation (5) :

$$E(\dot{\varepsilon}) = E_0\left(1+\lambda_1 \cdot \ln\frac{\dot{\varepsilon}}{\dot{\varepsilon}_0}\right) \tag{4}$$

$$\sigma_Y(\dot{\varepsilon}) = \sigma_{Y_0}\left(1+\lambda_2 \cdot \ln\frac{\dot{\varepsilon}}{\dot{\varepsilon}_0}\right) \tag{5}$$

These equations have two materials parameters based on experimental results: a mechanical reference parameter and a strain rate strengthening coefficient. Figures 7 and 8 showed the evolution of the reference Young Modulus and the reference yield stress with the number of recycling passes at this strain rate. From these figures, a linear evolution of these parameters with the number of recycling passes is assumed. Therefore the mechanical reference parameters can be written as follows:

$$E_0(n) = \kappa_1 n + E_0^{REF} \tag{6}$$

$$\sigma_{Y_0}(n) = \kappa_2 n + \sigma_{Y_0}^{REF} \tag{7}$$

where *n* is the number of recycling passes, E_0^{REF} and $\sigma_{Y_0}^{REF}$ are the mechanical reference parameters for virgins materials and κ_1, and κ_2 are the recycling strengthening coefficients calculated by fitting the experimental results plotted in using the least square method.

Figures 11 and 12 report the comparison between the modeling and the experimental stress strain curves for the 108MF97 and the 7510 materials, respectively. The predicted responses for each material at the three strain rates are in fair agreement with the experimental results. Overall the recycling effects observed in the experimental part are well reproduced.

These are rather encouraging preliminary results for the modeling. However, the simulation under finite strain is in progress as well as a description of the degradation due to cavitation during tensile testing. It is also well known that at large strains, molecular orientation plays an important role in the material response and needs to be accounted for the capture the hardening effects.

The chosen model to describe creep tests is a set composed with a Maxwell set and three Kelvin-Voigt sets (Fig. 13)

The equation of the compliance for this model is a sum of 3 parts, the elastic compliance, the visco-plastic compliance and the visco-elastic compliance:

$$J(t)=\frac{\varepsilon(t)}{\sigma_0}=\frac{1}{E_1}+\frac{t}{\eta_1}+\frac{1}{E_2}\left(1-e^{-\frac{E_2 t}{\eta_2}}\right)+\frac{1}{E_3}\left(1-e^{-\frac{E_3 t}{\eta_3}}\right)+\frac{1}{E_4}\left(1-e^{-\frac{E_4 t}{\eta_4}}\right) \qquad (8)$$

E_1 is the elastic spring stiffness; η_1 is the plastic viscosity; E_2, E_3 and E_4 are the spring stiffness of each Kelvin-Voigt set and η_2, η_3 and η_4 are the viscosities of them. E_1 and η_1 are calculated by a direct method, and E_2, E_3, E_4, η_2, η_3, η_4 are calculated by an indirect method, the Gauss-Newton algorithm

In addition of these parameters, the creep retardation time τ can be used. τ is the conventional retardation time such as:

$$J(\tau)=0.63\ J(\infty) \qquad (9)$$

The comparison of this model with the experimental data is proposed Figure14. The fit is quite good between the experimental data and the model.

4 Conclusion and perspectives

Recycling process leads to modify some mechanical parameters as Young modulus, failure strain, yield stress, creep parameters. Comparing tensile and bending tests, some evolution are similar as for example, the Young modulus decreasing, a less influence on the 108MF97 behavior and strain rate sensibility. Creep tests show the impact is less important with the talc filled polymer. All these microscopic and macroscopic observations leads to a good modeling of the recycled 108 and 7510 PP compounds, including strain rate effects.

In this study only the recycling effect has been studied. But in a real industrial recycling process, ELV bumpers are covered in dust, soaked in liquids, specially oils and are modified by every physical and chemical elements met in its use. The influence on rheological and mechanical properties of pollutants, as basic engine oil and ethylene glycol, has been performed (Pessey *et al.* [14]). The combination of both: recycling and pollution is under progress and will be presented in a future work.

In addition numerical models have to be integrated with finite element methods in order to study the bumper mechanical behavior.

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6 References

[1] Friedrich, K., and Karsch, U.A., 1983, *Fiber Science and Technology* **18** (1), pp. 37-52.

[2] Maiti, S., and Sharma, N.K.K., 1992, *J. of Materials Science* **27,** pp. 4605-4613.

[3] Duffo, P., Monnase, B., Haudin, J.M., G'Sell, C, and Dahoun, A, 1995, *J. of Materials Science* **30**, pp. 701-711.

[4] Alonso, M., Velasco, J.I. and De Saja, J.A., 1997, *European Polymer Journal* **33,** pp. 255-262.

[5] Fond, C. and G'Sell, C., 2002, *Mécanique et Industries.* **3,** pp. 431-438.

[6] Castagnet, S. and Grandidier, J.C., 2006, *Structural effect in the creep behavior of thermoplastic pressure pipes at high temperature. Role of geometrical defects*, Archive of Applied Mechanics.

[7] Standard, directive 2000/53/EC of the European parliament and of the council, 2000.

[8] Luda, M. P., Ragosta, G., Musto, P., Pollicino, A., Camino, G., Recca A., and Nepote V., 2002, *Macromolecular Materials Engineering* **287,** pp. 404-411.

[9] Luda, M. P., Ragosta, G., Musto, P., Acierno, D. ,Di Maio, L., Camino, G. and Nepote, V., 2003, *Macromolecular Materials Engineering* **288,** pp. 613-411.

[10] Guerrica-Echevarria, G., Eguiazabal, J.I. and Nazabal, J., 1996, *Polymer degradation and stability* **53,** pp. 1-8.

[11] Bahlouli, N., Pessey, D., Ahzi, S. and Rémond**,** Y., 2006, *J. Phys. IV* **134,** pp. 1319-1323.

[12] Pessey, D., Bahlouli, N., Pattofato, S. and Ahzi, S., 2008, I. J. of Crash. 13 (4), pp. 411-424.

[13] Aurrekoetxea J., Sarrionandia M.A., Urrutibeascoa I., and Maspoch, M.L., *J. Mat Sci*. **36,** 2607-2613 (2001).

[14] Pessey, D., Bahlouli, N., Ahzi, S. and Khaleel M.A., 2007, Polym Sci - Series A 50 (6), pp. 690-697.

[15] Denac, M., Musil, V., and Šmit, I., 2005, *Composites Part A: Applied Science and Manufacturing* **36,** 9, pp. 1282-1290.

[16] Liang, J.Z. and Li, R.K.Y., 2000, J. *Appl. Polym. Sci*. **77(2),** pp. 409-417.

[17] Oksuz, M., Eroglu, M. and Yildirim, H., 2006, *J. of App. Pol. Sci.* **101,** pp. 3033-3039.

[18] Hadal R.S., and Misra, R.D.K., 2004, *Materials Science and Eng*. A **374**, pp. 374-389.

[19] Collyer, A.A., 1994, Rubber Toughened Engineering Plastics (Chapman and Hall, London).

[20] G'Sell, C, Hiver, J. M. and Dahoun, A, 2002, A. *Int. J. of Solids and Structures* **39,** 13-14, pp. 3857-3872.

[21] Trantina, G. and Oehler P, 1994, SPE ANTEC proceedings, 3106

[22] Addiego F., G'Sell C., Dahoun A. and Hiver J.M., 2002, Université d'été, APOLLOR 02, Nancy, France.

[23] Zhou Y. and Mallick P. K., 2002, *Polymer engineering and science,* **42**, n°12, pp. 2449-2460.