

# Constitutive Modeling of the Tensile Behavior of Recycled Polypropylene Based Composites

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## Abstract

The effect of reprocessing on the quasi-static uniaxial tensile behavior of two commercial polypropylene (PP) based composites is experimentally investigated and modeled. In particular, the studied materials consist of an unfilled high-impact PP and a talc-filled high-impact PP. These PP composites are subjected to repeated processing cycles including a grinding step and an extrusion step to simulate recycling at the laboratory level, the selected reprocessing numbers for this study being 0, 3, 6, 9 and 12. Because the repeated reprocessing leads to thermo-mechanical degradation by chain scission mechanisms, the tensile behavior of the two materials exhibits a continuous decrease of elastic modulus and failure strain with increasing number of reprocessing. A physically consistent three-dimensional constitutive model is used to predict the tensile response of non-recycled materials with strain rate dependence. For the recycled materials, the reprocessing

effect is accounted by incorporating the reprocessing sensitive coefficient into the constitutive model for Young's modulus, failure strain, softening and hardening equations. Our predictions of true stress - true strain curves for non-recycled and recycled 108MF97 and 7510 are in a good agreement with experimental data.

**Keywords:** Polypropylene; Composite; Constitutive model; Reprocessing; Mechanical properties; Strain rate.

## 1. Introduction

Polypropylene (PP) based composites are increasingly utilized in the automotive industry and in particular for both exterior and interior components. These materials have attractive mechanical properties, low density, excellent chemical resistance and effectiveness price [1]. For manufacturing car bumpers tolerant to high loading rate, elastomers such as ethylene-propylene-copolymer (EPC) and ethylene-propylene-diene-monomer (EPDM) are generally mixed with neat PP to improve the impact properties [2]. However, these rubber particles lead to a decrease of stiffness and strength of the materials. In order to alleviate these decreases induced by the addition of rubber particles, mineral rigid reinforcements such as talc are usually added to the binary composite of PP/elastomer [3].

The increasing use of PP-based composites results in huge plastic wastes from end-of-life vehicles (ELV), while the re-use and recovery of these wastes are quite limited [4]. For both environmental protection and waste management considerations, the European directive 2000/53/UE has been legislated to increase the re-use and recovery rate of these plastic wastes. Among the different end-of-life scenarios of plastic, the mechanical recycling is the simplest and

most ecological one, where the post-used ELV plastics were mechanically crushed and re-processed to product new structural parts [5].

It is well known that reprocessing at high temperature, with intensive shearing conditions and with the presence of oxygen and impurities, could lead to thermal, thermo-oxidative and thermo-mechanical degradations of the materials affecting their properties. The mechanical reprocessing effects on the properties of PP-based composites have been studied [6, 7]. Most of the previous arts focus on the characterization of rheological, chemical, physical and mechanical properties of the materials with the number of reprocessing. Briefly, recycling induces a reduction of molecular weight that is attributed to chain scission mechanisms [8, 9]. The lower molecular weight of recycled materials results in an increase in crystallinity of PP matrix [10, 11]. The oxidative state of recycled composites depends on the presence of oxygen during the melted state as well as on the presence of anti-oxidative agents in PP matrix [12]. Even though the reprocessed materials underwent critical reprocessing conditions, the decomposition temperature of the composite is little influenced by the reprocessing [13]. However, the evolution of the composite mechanical behavior during the mechanical recycling is not consistent in the open literature. The reasons for this are, on the one hand, the experimental conditions are drastically varying from one study to another one, on the other hand, the reprocessing not only leads to the degradation of the matrix but also changes the composite morphology and the filler properties. The reinforcement effects on the recycled PP based composites have been recently investigated in our previous works [14-17]. We found that the ethylene octene copolymer (EOC) inclusions stabilize the tensile elongation at break up to 3 recycling number due to a decrease of their size and a homogenization of their shape during the reprocessing. Otherwise, the talc fillers increase the stiffness and the strength of the composite with the number of recycling number due to a decrease of their geometry

and an increase of their aspect ratio. Although the experimental characterization indicates the evolution of different properties of the composite during the mechanical recycling, the modeling of mechanical responses of recycled PP-based composites is less investigated. To this end, a micromechanical modeling may enable to predict the maximum reprocessing number until which the quality of the material would be retained for a targeted application.

In this work, the main objective is to experimentally determine and model the tensile behavior of two commercial PP-based composites as a function of the number of mechanical reprocessing. These two materials are commonly used for the manufacturing of car bumpers in automotive industry, requiring optimizing their end-of-life scenario and utilization. To simulate mechanical recycling, the materials were subjected to multiple reprocessing procedures including a grinding step, an extrusion step and an injection step. The experimental evaluation involves low strain rate uniaxial tensile testing up to failure. The analysis of the recycling dependent tensile behavior has guided the development of a constitutive model including the recycling correlative physical parameters.

## **2. Experimental study**

### **2.1. Materials and processing**

Two commercial grades of PP based composites used for producing bumpers are studied in the present paper. The first one is a two-phase material referenced as Sabic PP compound, grade 108MF97. It contains 22 wt. % of EPC inclusions whose diameter is lower than 1  $\mu\text{m}$ . The second one is a three-phase composite referenced as Sabic PP compound, grade 7510, which contains 12 wt. % of talc powder and 20 wt. % of EPDM particles. In this grade, talc fillers size is around 8  $\mu\text{m}$  and EPDM particles diameter is less than 1  $\mu\text{m}$ .

To simulate the procedure of mechanical recycling, the raw materials initially in the form of pellets are extruded by a Clextral BC 21 twin-screw extruder with a flow rate of 10 kg/h and at a final die temperature of 230 °C. The obtained extruded strands are quenched in a cold-water bath and are subsequently pelletized using a rapid granulator. The obtained pellets are dried in an air circulating oven to eliminate moisture for the next step. A total of 12 cycles of extrusion and pelletization is conducted by using the same machines and under the same processing conditions. The following numbers of reprocessing are chosen: 0, 3, 6, 9 and 12. We note that 12 cycles reprocessing can clearly show the recycling effect [5]. Finally, the pellets of selected materials were molded by an injection machine Billion Visumat 1000 at 230 °C into plates of dimensions 300 mm × 100 mm × 3 mm. Tensile samples (ASTM D638 type V) were carefully machined from the injected plates along the flow direction. In the following, these two PP based composites were denoted with the number of extrusion as 108MF97 0P, 3P, 6P, etc., and 7510 0P, 3P, 6P, etc. It is to be noted that 0P is linked with the non-recycled materials.

## 2.2. Experimental procedures

Tensile testing is performed on a MTS 810 testing machine with the Videotraction system at room temperature [18]. This system has been developed to assess the true stress – true strain tensile curve based on optical extensometer with a control of strain rate. Accordingly, all the materials were tested at a constant true strain rate of  $0.001\text{ s}^{-1}$  until failure. In order to investigate the strain rate sensitivity of both materials, 108MF97 0P and 6P, 7510 0P and 6P were tested with additional strain rates of  $0.01\text{ s}^{-1}$  and  $0.0001\text{ s}^{-1}$ .

## 2.3. Experimental results

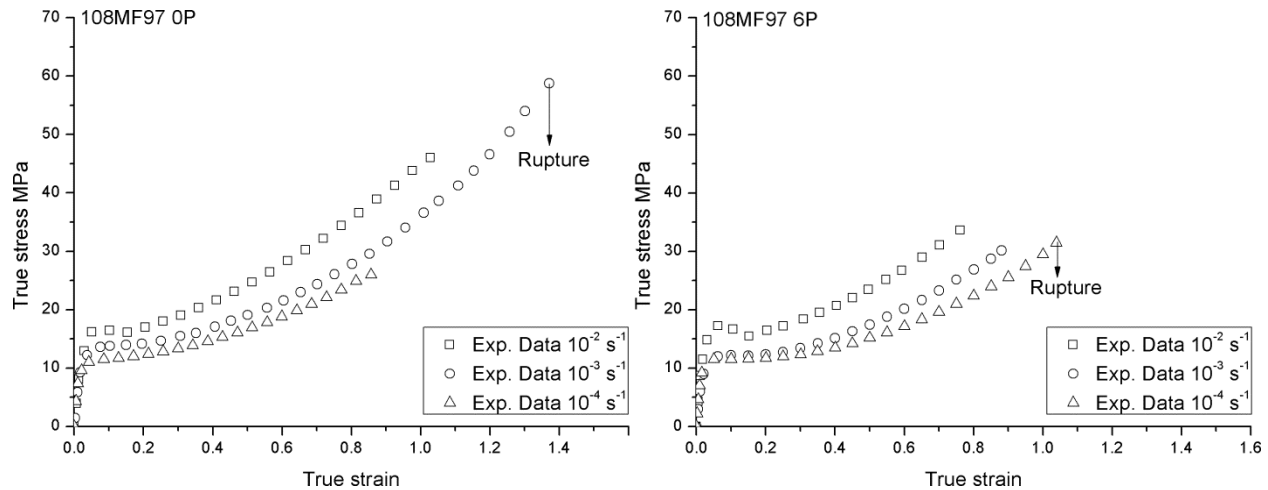


Figure 1: True stress vs. true strain responses of 108MF97 0P and 6P at three different strain rates.

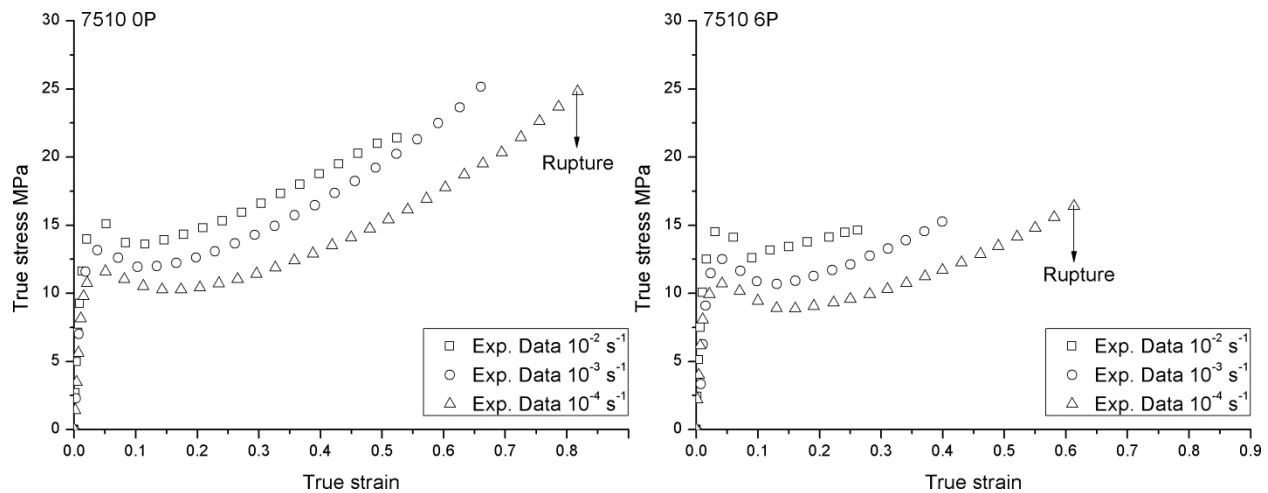


Figure 2: True stress vs. true strain responses of 7510 0P and 6P at three different strain rates.

Fig.1 and 2 show true stress – true strain responses in the case of 108MF97 and 7510 at three different strain rates with the recycling number 0P and 6P, respectively. In these two figures, all the curves exhibit typical features of stress–strain curves in which the curves can be divided into four parts: an initial linear elastic response, a visco-elastic transition to yield, a strain softening after the yielding point and a strain hardening till to the failure [19]. In addition, in Fig.1 and 2, all materials present a strain rate sensitivity in which the yield and flow stresses increase with the

strain rates. The increase of strain rate leads to the hardening of the material due to less time for the molecular network to withstand the imposed strain. However, the mechanical responses at the highest strain rate show a greater post-yield strain softening attributing mainly to self-heating effect [20]. Indeed, during the plastic deformation, due to the low chain mobility coupled with internal friction, a great part of the plastic deformation work is converted into heat in the materials [21]. Comparing the mechanical responses of 108MF97 and 7510 (0P or 6P) at same strain rates, the curves of 7510 show the more important post-yield strain softening. This is probably due to the presence of talc filler. Indeed, the localized shearing deformation in the matrix as well as at the filler/matrix interfaces may generate much more heat during the plastic deformation [19].

Concerning the failure behavior of 108MF97 and 7510 in Fig.1 and Fig.2, the higher strain rate decreases the failure strain in the case of the two materials (0P or 6P, excepted for 108MF97 0P at the strain rate of  $0.0001\text{ s}^{-1}$ , due to the experimental error). The higher strain rate leads to fast crack propagation in tensile sample and consequently, a smaller failure strain of the materials [22]. Comparing 108MF97 and 7510 (Fig.1 and 2), under the same strain rate and with the same recycling number, 108MF97 shows the larger ductility. Although the presence of elastomer particles has a toughening effect on both materials, the talc filler in 7510 may induce cavitation mechanisms by matrix/filler debonding.

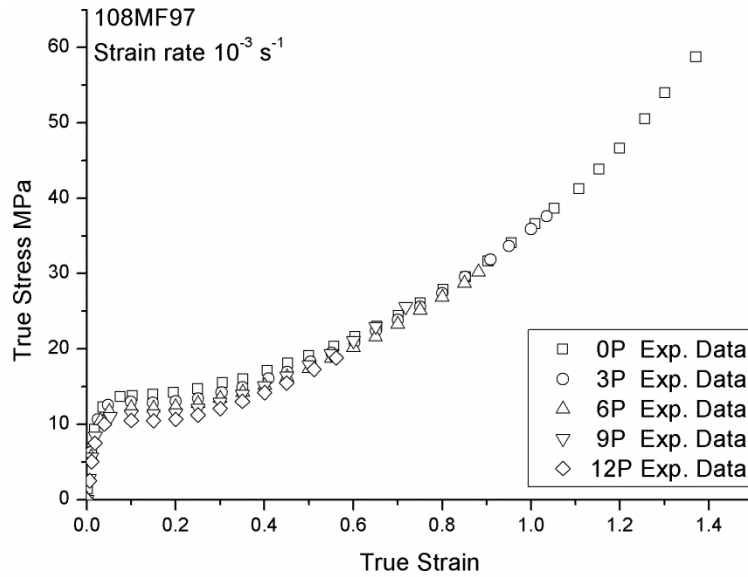


Figure 3: True stress vs. true strain responses of 108MF97 at different recycling numbers under a strain rate of  $0.001 \text{ s}^{-1}$

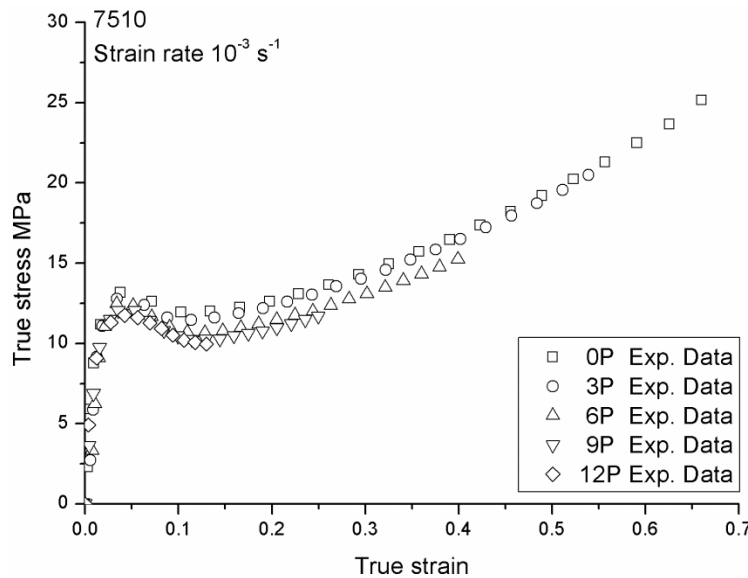


Figure 4: True stress vs. true strain responses of 7510 with different recycling numbers under strain rate of  $0.001 \text{ s}^{-1}$

The mechanical responses of 108MF97 and 7510 with different recycling numbers under strain rate  $0.001 \text{ s}^{-1}$  are shown in Fig.3 and Fig.4, respectively. These two figures show that the yield stress and Young's modulus of both materials continuously decrease with the recycling



numbers. Indeed, mechanical recycling conducted under intensive shearing at high temperature, and with the presence of oxygen and impurities, generally leads to thermal, thermo-oxidative and thermo-mechanical degradations of the materials. At the molecular level, the mechanical properties decrease is mainly due to the chain scission mechanisms caused by the reprocessing [5]. Our previous studies have found a decrease of average molecular weight with the recycling numbers for 108MF97 and a significant increase of melt flow index (MFI) with reprocessing number in the case of for 7510. This increase of MFI also relates to a decrease of molecular weight of PP matrix for 7510 [5]. In fact, the mechanical recycling shortens polymer chains, and hence, increases chains mobility. This higher mobility can result in an increase of crystallinity content of PP matrix and consequently, to stiffen materials [15]. As shown in Fig.3 and Fig.4, the stiffer recycled materials show greater strain hardening effect than the non-recycled ones. This effect is more significant for 108MF97. In addition, the failure strain has a continuous decrease with reprocessing number for both materials. This is due to the shortening of the molecular chains of PP matrix, inducing disentanglement in the amorphous phase and decreasing the inter-connection between the crystalline phase and the amorphous phase of materials. As a result, the failure strain of both materials decreases with the reprocessing number.

### 3. Constitutive relation

The constitutive model considered in this work is based on the previous work of Wu and Ahzi [23]. In their work, the authors have developed a physically consistent model to describe the strain rate and temperature dependency of the large inelastic deformation response of non-filled and silica filled cured resin. They used a molecular theory for the plastic flow and an orientational model for the deformation of polymer chains at large strain rate. In our study, we have chosen to

describe the elastic behavior of materials by the strain rate dependent equation of Zhou et al. [24]. The yield and post-yield behavior was described by the strain rate and temperature dependent flow rule of Boyce et al. [25]. The orientational hardening was modeled through the eight-chains rubber-elasticity law [26].

### 3.1. Strain rate dependent of Young's modulus and failure strain

Non-recycled 108MF97 and 7510 are strain rate sensitive materials (Fig.1 and 2). The linear relationships between the Young's modulus ( $E$ ) and natural logarithm strain rate  $\ln(\dot{\epsilon})$ , and between the failure strain  $\epsilon_R$  and  $\ln(\dot{\epsilon})$  can be described as follows [24]:

$$E(\dot{\epsilon}) = E_0(1 + \lambda_E \cdot \ln \frac{\dot{\epsilon}}{\dot{\epsilon}_0}) \quad (1)$$

$$\epsilon_R(\dot{\epsilon}) = \epsilon_{R_0}(1 + \lambda_{\epsilon_R} \cdot \ln \frac{\dot{\epsilon}}{\dot{\epsilon}_0}) \quad (2)$$

where  $E_0$ ,  $\epsilon_{R_0}$ ,  $\dot{\epsilon}_0$  are the reference elastic modulus, reference failure strain and reference strain rate of non-recycled materials, respectively. The parameters  $\lambda_E$  and  $\lambda_{\epsilon_R}$  are defined as strain rate strengthening coefficient of Young's modulus and failure strain of non-recycled materials, respectively.

### 3.2. Flow rule

For large elastic-viscoplastic deformation of glassy polymers, Boyce et al. [25] extended Argon's model and proposed a three-dimensional constitutive model. This model contains the yield and post-yield behavior of the material with the pressure, strain rate and temperature dependency. The extended model is expressed as [25]:

$$\dot{\gamma}^P = \dot{\gamma}_0 \exp \left[ -\frac{AS_0}{T} \left( 1 - \left( \frac{\tau}{S_0} \right)^{\frac{5}{6}} \right) \right] \quad \text{with} \quad A = \frac{39\pi\omega^2\alpha^3}{16k}h \quad (3)$$

where  $\dot{\gamma}^P$  is plastic strain rate,  $\dot{\gamma}_0$  is the pre-exponential shear strain rate factor,  $\omega$  is the net angle of rotation of the molecular segment,  $\alpha$  is the mean molecular radius,  $k$  is the Boltzmann constant.  $T$  is the absolute temperature,  $\tau$  is the shear yield strength, The athermal shear yield strength of the material ( $S_0$ ) at absolute zero is approximated given by:

$$S_0 = \frac{0.077\mu}{1-\nu} \quad (4)$$

Here  $\mu$  is the shear modulus and  $\nu$  is the Poisson's ratio of the material.

### 3.3. Strain softening

In the constitutive model of Boyce et al. [25], strain softening is incorporated into the constitutive law by modifying the athermal yield strength,  $S_0$ , of the material as plastic straining occurs. It is based on the assumption that as the material begins to undergo plastic deformation, there is some average restructuring of the molecular chains in the flow state that causes an actual fall in the athermal shear resistance of the material. Thus, the phenomenological evaluation of the shear resistance during strain softening is defined as:

$$\dot{S} = h \left( 1 - \frac{S}{S_{ss}} \right) \dot{\gamma}^P \quad (5)$$

where  $\dot{S}$  is the softening evolution of the shear resistance,  $h$  is the softening slope,  $S$  is the current athermal deformation resistance of the material,  $S_{ss}$  is the resistance referring to the preferred structure determined by temperature and strain rate [27].

### 3.4. Orientational hardening

The hardening effect is determined by computing the external stress state that results when the material is stretched at temperatures above its glass transition ( $T_g$ ), and assuming that this state represents an internal resistance which is locked in the material. The locked internal resistance

related to an applied external stress state is therefore named back stress of materials when undergoing deformation. Arruda and Boyce developed an eight-chain model to describe this network stress tensor as [26]:

$$B_i = \frac{C_R}{3} \sqrt{N} L^{-1} \left( \frac{\lambda_{chain}}{\sqrt{N}} \right) \frac{\lambda_i^{p^2 - \frac{1}{3} I_1}}{\lambda_{chain}} \quad (6)$$

where  $B_i$  is a principal value of the deviatoric back stress tensor, the subscript  $i = 1, 2, 3$  designates one of the three principal direction.  $C_R$  is a temperature dependent rubber modulus [28],  $N$  is the number of rigid links of the entanglement of chains,  $\lambda_{chain} = ((\lambda_1^2 + \lambda_2^2 + \lambda_3^2)/3)^{1/2}$  and  $\lambda_i$  is the imposed principal stretch,  $\lambda_i^p$  are the principal values of the left Cauchy stretch tensor  $V_p$ , the subscript  $p$  designates the plastic part.  $I_1$  is the stretch tensor with  $I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2$ . The Langevin function is defined by  $L(y) = \coth(y) - \frac{1}{y} = x$ , with its inverse form  $L^{-1}(x) = y$ .

### 3.5. Recycling effect

As shown in Fig. 3 and 4, the Young's modulus,  $E$ , and failure strain,  $\varepsilon_R$ , of 108MF97 and 7510 have a continuous decrease with the reprocessing number. Thus, we have assumed a linear evolution of these two parameters with strain rate and reprocessing dependencies, based on equations (1) and (2):

$$E(N_p, \dot{\varepsilon}) = (k_1 N_p + E_0) \cdot (1 + (\xi_1 \cdot N_p + \lambda_E) \cdot \ln \frac{\dot{\varepsilon}}{\dot{\varepsilon}_0}) \quad (7)$$

$$\varepsilon_R(N_p, \dot{\varepsilon}) = (k_2 N_p + \varepsilon_{R_0}) \cdot (1 + (\xi_2 \cdot N_p + \lambda_{\varepsilon_R}) \cdot \ln \frac{\dot{\varepsilon}}{\dot{\varepsilon}_0}) \quad (8)$$

where  $N_p$  is the number of reprocessing.  $k_1$  and  $k_2$  are the reprocessing strengthening coefficient of Young's modulus and failure strain, respectively.  $\xi_1$  and  $\xi_2$  are the recycling strengthening

coefficient of strain rate. For the non-recycled materials,  $N_p$  is equal to zero, Equations (7) and (8) reduce to the same form of Equations (1) and (2).

The mechanical recycling induces microstructure changes of the materials, i.e., the chain length, the crystallinity content, with the need to exhibit mathematical simplicity, we have assumed a linear evolution of  $C_R$ ,  $N$  and  $R_s$  with reprocessing number as follows:

$$C_R(N_p) = k_3 N_p + C_{R_0}^{ref} \quad (9)$$

$$N(N_p) = k_4 N_p + N_0^{ref} \quad (10)$$

$$R_s(N_p) = k_5 N_p + R_{S_0}^{ref} \quad (11)$$

where  $R_s$  is the ratio of  $S_{ss}/S_0$ .  $k_3$ ,  $k_4$  and  $k_5$  are the reprocessing strengthening coefficients of these three parameters.  $C_{R_0}^{ref}$ ,  $N_0^{ref}$  and  $R_{S_0}^{ref}$  are the reference parameters for the non-recycled materials.

## 4. Constitutive modeling

### 4.1. Kinematics of finite strain

The kinematics and kinetics of the finite deformation elastic-viscoplastic model for our materials are briefly presented below. The elastic-plastic deformation gradient tensor  $\mathbf{F}$  is multiplicatively decomposed into two parts as [23]:

$$\mathbf{F} = \mathbf{F}^e \mathbf{F}^p \quad (12)$$

where the subscript  $e$  and  $p$  designate the elastic and plastic part, respectively.

The velocity gradient  $\mathbf{L}$  and the plastic velocity gradient  $\mathbf{L}^p$  are given by:

$$\mathbf{L} = \dot{\mathbf{F}}\mathbf{F}^{-1} = \dot{\mathbf{F}}^e\mathbf{F}^{e-1} + \mathbf{F}^e\mathbf{L}^p\mathbf{F}^{e-1} \quad (13)$$

and

$$\mathbf{L}^P = \dot{\mathbf{F}}^P \mathbf{F}^{P^{-1}} \cong \mathbf{D}^P \quad (14)$$

where  $\mathbf{D}^P$  is the plastic strain rate gradient, while the plastic spin is considered equal to zero.

Polar decomposition of the plastic deformation gradient is:

$$\mathbf{F}^P = \mathbf{V}^P \mathbf{R}^P \quad (15)$$

and the Cauchy stress tensor is given by:

$$\mathbf{T} = \frac{1}{J} \mathbf{C}^e (\ln \mathbf{F}^e) \quad (16)$$

Where  $J$  is volume change and  $\mathbf{C}^e$  is the elastic constant of the fourth order tensor.

The driving stress tensor is expressed as:

$$\mathbf{T}^* = \mathbf{T} - \frac{1}{J} \mathbf{F}^e \mathbf{B} \mathbf{F}^{eT} \quad (17)$$

where  $\mathbf{B}$  is the back stress tensor given previously.

The rate of plastic straining is constitutively described by:

$$\mathbf{D}^P = \dot{\gamma}^P \mathbf{N} \quad (18)$$

where the plastic strain rate,  $\dot{\gamma}^P$ , is defined in equation (2).

The resulting normalized deviatoric portion of the driving stress tensor is given by:

$$\mathbf{N} = \frac{1}{\sqrt{2}\pi} \mathbf{T}^{*'} \quad (19)$$

where the effective equivalent stress  $\tau = (\mathbf{T}^{*'} \cdot \mathbf{T}^{*'} / 2)^{1/2}$ , here  $\mathbf{T}^{*'}$  is the deviatoric part of the driving stress tensor.

## 4.2. Modeling results

In this constitutive model, several material constants need to be identified experimentally. First, the strain rate dependent Young's modulus and failure strain of non-recycled 108MF97 and

7510 are measured from the experimental true stress - true strain curves for non-recycled state under the strain rate  $0.01 \text{ s}^{-1}$  and  $0.001 \text{ s}^{-1}$  in Fig. 1 and 2. Then, the reference elastic modulus ( $E_0$ ), reference failure strain ( $\varepsilon_{R_0}$ ), the strain rate strengthening coefficient  $\lambda_E$  and  $\lambda_{\varepsilon_R}$  in equations (1) and (2) can be determined by a reference strain rate of  $1 \text{ s}^{-1}$ .

Once the Young's modulus is determined, the athermal shear yield strength of materials,  $S_0$ , in equation (4) can be computed with Poisson ratio for the 108MF97 and 7510 as 0.31 and 0.3, respectively [5]. The values of the  $A$  ( $K/MPa$ ) and  $\dot{\gamma}_0$  ( $\text{s}^{-1}$ ) for non-recycled materials are obtained from the experimental yield stresses in Fig. 1 and 2, by using Equation (3).

Concerning the parameters of the softening effect, by comparing the maximum with the minimum yield stress under strain rate of  $0.001 \text{ s}^{-1}$  during softening in Fig. 1 and 2 for two non-recycled materials, the ratios  $S_{ss}/S_0$  were equal to 0.975 and 0.911 for 108MF97 and 7510, respectively. Thus, the steady state shear resistance can calculate by using  $S_{ss} = S_0 * 0.975$  for non-recycled 108MF97 and  $S_{ss} = S_0 * 0.911$  for non-recycled 7510. Consequently, the rate of the yield drop is measured by  $h \cong S_{ss}/\Delta\gamma^P$  where  $\Delta\gamma^P$  is the strain between the maximum and the minimum yield stresses under strain rate of  $0.001 \text{ s}^{-1}$ .

Concerning the recycling effect parameters, first, the Young's moduli and failure strains are measured from the experimental curves in Figures 3 and 4 for 108MF97 and 7510 with different number of reprocessing. Other parameters, such as  $C_R$ ,  $N$  and  $R_s$  are selected according to the experimental true stress – true strain curves. The reprocessing sensitive parameters are reported in Table 1. Once these parameters are experimentally determined, the reprocessing strengthening coefficients for the Young's modulus and failure strain in Equations (7) and (8) can be calculated. The reprocessing strengthening coefficient and the reference parameters of  $C_R$ ,  $N$  and  $R_s$ , in

Equations (9) - (11) can be chosen by their trendlines which yield the relations with the number of reprocessing as shown in Fig.5.

As reported by Arruda et al. [28], the rubber modulus,  $C_R$ , is taken to be proportional to the chain density ( $n$ ):  $C_R = nkT$ , where  $k$  is Boltzmann constant and  $T$  is absolute temperature. In Fig.5,  $C_R$  increases with reprocessing number. This is due to the reprocessing increases the crystallinity content of materials and consequently, an increase of polymer chain density [29]. This increase of crystallinity content of matrix stiffens materials that generates more heat during the plastic deformation. This is probably the main reason for the decrease of the ratio,  $R_s$ , with the reprocessing number for both composites. Contrarily, the number of rigid links in the entanglement of chains,  $N$ , decreases with the increasing of reprocessing cycle. Because the repeated reprocessing gradually shorten the molecular chains, which decreases chain entanglements [14]. All the coefficients and the reference parameters, used for the modeling are summarized in Table 2.

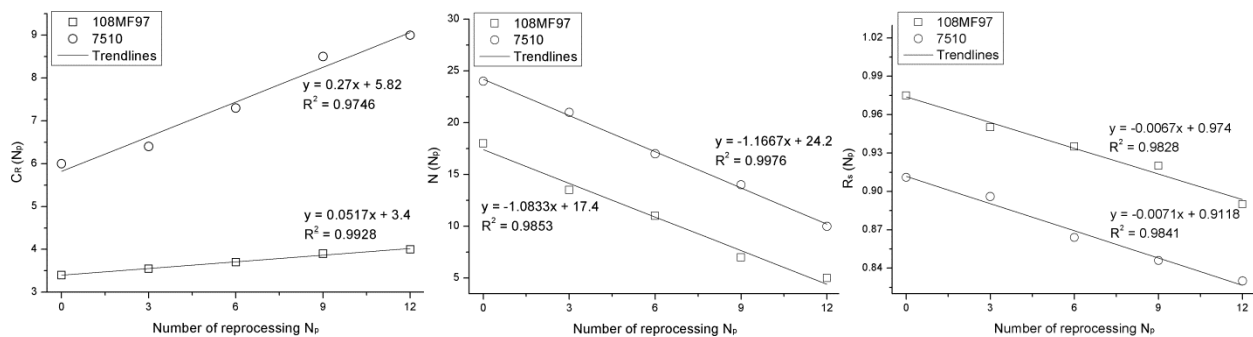


Figure 5: Reprocessing parameters for 108MF97 and 7510

Table 1: Reprocessing sensitive parameters

$N_p$	E (MPa)	$\varepsilon_R$	$C_R$	$N$	$R_s$
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	108MF97	7510	108MF97	7510	108MF97	7510	108MF97	7510	108MF97	7510
0	850	1100	1.37	0.66	3.4	6	18	24	0.975	0.911
3	790	1050	1.04	0.54	3.55	6.4	13.5	21	0.95	0.896
6	730	1000	0.88	0.40	3.7	7.3	11	17	0.935	0.864
9	650	950	0.72	0.25	3.9	8.5	7	14	0.92	0.846
12	590	920	0.56	0.13	4	9	5	10	0.89	0.83

Table 2: The coefficients and the reference parameters for modeling

	$k_1$	$k_2$	$k_3$	$k_4$	$k_5$	$E_0^{ref}$	$\varepsilon_{R0}^{ref}$	$C_{R0}^{ref}$	$N_0^{ref}$	$R_{s0}^{ref}$	$\xi_1$	$\xi_2$	$\lambda_E^{ref}$	$\lambda_{\varepsilon_R}^{ref}$
108MF97	- 31.11	- 0.01	0.05	- 1.08	- 0.01	977.51	0.34	3.4	17.4	0.97	- 0.001	0.02	0.019	-0.43
7510	-9.87	- 0.02	0.27	- 1.17	- 0.01	1250	0.23	5.82	24.2	0.91	0.001	- 0.001	0.017	-0.28

The modeling results are compared to the experimental data for 108MF97 and 7510 at three different strain rates in Fig. 6 and 7. In our simulation, for the purpose of mathematical simplicity as mentioned previously, we considered that the physic meaning parameters,  $C_R$ ,  $N$  and  $R_s$ , are not depend on the strain rate and they are selected in accordance with the experimental curves at strain rate of  $0.001\text{ s}^{-1}$ . Thus, the predictions of hardening part of the true stress – true strain curves under other strain rates have dispersions with the experimental data for both materials. In fact, different strain rates could generate different heat during the plastic deformation. The elevation of temperature affects the  $R_s$  and the rubber modulus,  $C_R$ , which is a temperature dependence parameter [28, 30]. Besides that, our predictions have good correlation with experimental data.

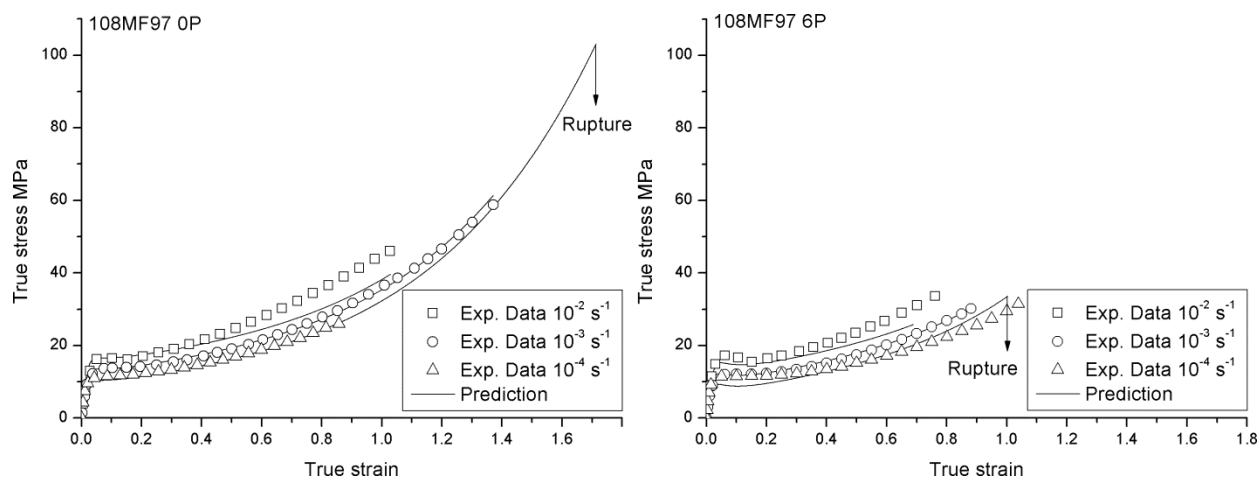


Figure 6: Comparison between the experimental and the predicted tensile behavior of 108MF97 0P and 6P at three different strain rates

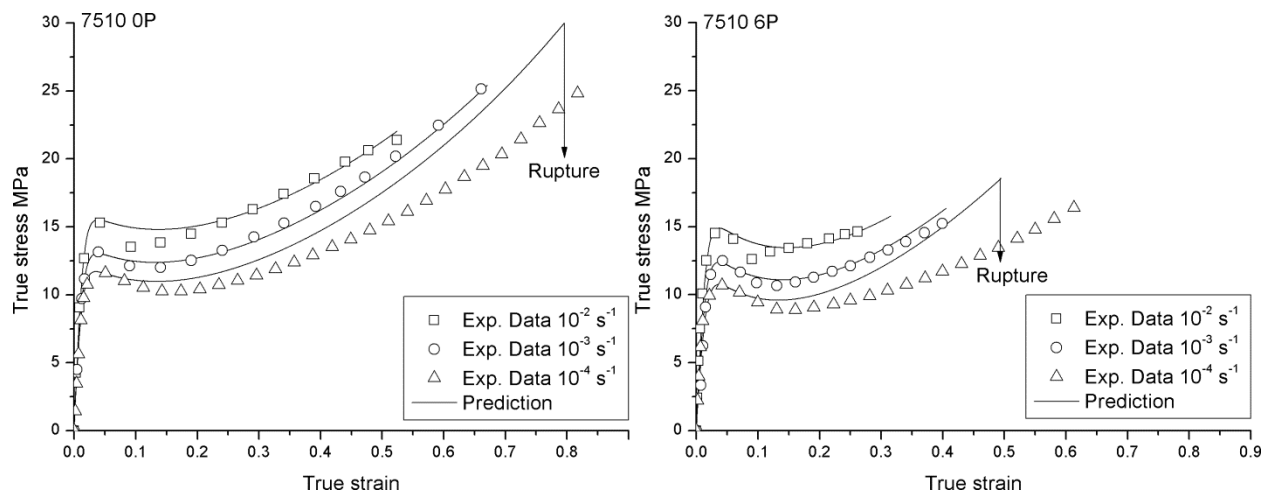


Figure 7: Comparison between the experimental and the predicted tensile behavior of 7510 0P and 6P at three different strain rates

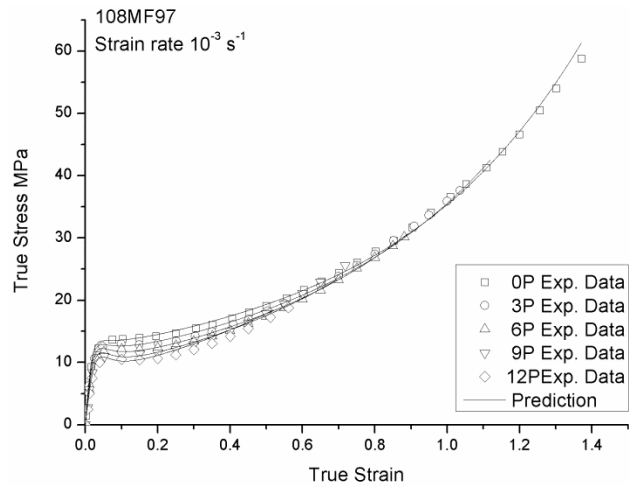


Figure 8: Comparison between the experimental and the predicted tensile behavior of the non-recycled and recycled 108MF97 under the strain rate of  $0.001 \text{ s}^{-1}$

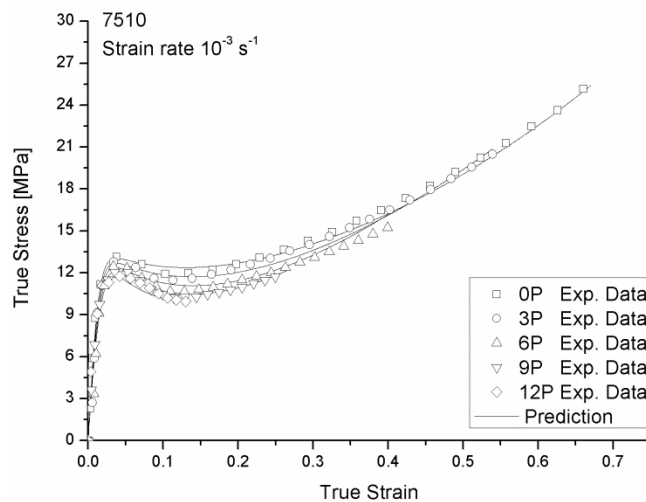


Figure 9: Comparison between the experimental and the predicted tensile behavior of the non-recycled and recycled 7510 under the strain rate of  $0.001 \text{ s}^{-1}$

Figures 8 and 9 show good agreement between the experimental data and the modeling of true stress – true strain curves for the 108MF97 and 7510 with different reprocessing numbers under the strain rate of  $0.001 \text{ s}^{-1}$ , respectively. As shown in figures 8 and 9, the use of strain rate and reprocessing dependent equations for the Young's modulus and failure strain provides correct

description of the tensile behavior of our materials at small strain and at the largest strain, respectively. The incorporated strain softening and hardening effects can reasonably predict the experimental curves for non-recycled materials. The use of reprocessing dependent equations for the rubber modulus,  $C_R$ , the number of rigid link of polymer chain,  $N$ , and the ratio of  $S_{ss}/S_0$ ,  $R_s$ , can well predict the change of strain softening and hardening effects with the number of reprocessing for the recycled materials.

## 5. Conclusions

In order to investigate the effect of mechanical reprocessing on the mechanical properties of PP based composites that are usually used for the manufacturing of car bumpers, two commercially available PP based composites (PP/elastomer, PP/elastomer/talc) are re-grinded and re-extruded up to 12 times. Their mechanical characterizations are performed by quasi-static uniaxial tensile testing in the case of the selected recycling numbers 0, 3, 6, 9 and 12. By using the Videotraction technique, the true stress – true strain curves were recorded till to the failure of materials. Due to the presence of talc filler in 7510, this composite has higher Young's moduli but lower failure strains compared to 108MF97 with the same recycling number and under the same strain rate. The mechanical properties such as yield stress, Young's modulus and failure strain of both materials decrease with increasing reprocessing number. This is because the mechanical reprocessing at high temperature and intensive shearing conditions has led to thermo-mechanical degradations of the materials by chains scission mechanism. For the interest of predicting the mechanical properties of the non-recycled and recycled materials, a three-dimensional constitutive model has been used. In this modeling, the reprocessing strengthening coefficients are incorporated into the constitutive equation for Young's modulus, failure strain as well as the

softening and hardening effects. Our model predictions are compared to the experimental results from the non-recycled and recycled composites and a good agreement has been found.

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## References:

1. Chirayil, C. J.; Joy, J.; Maria, H. J.; Krupa, I.; Thomas, S., Polyolefins in automotive industry. In *Polyolefin Compounds and Materials*, Springer: 2016; pp 265-283.
2. Chow, W. S., Polypropylene Blends: Properties Control by Design. In *Polypropylene Handbook*, Springer: 2019; pp 419-480.
3. Wu, J. H.; Chen, C. W.; Wu, Y. T.; Wu, G. T.; Kuo, M.; Tsai, Y., Mechanical properties, morphology, and crystallization behavior of polypropylene/elastomer/talc composites. *Polym. Compos.* **2015**, 36, (1), 69-77.
4. Sardon, H.; Dove, A. P., Plastics recycling with a difference. *Science* **2018**, 360, (6387), 380-381.
5. Bahlouli, N.; Pessey, D.; Raveyre, C.; Guillet, J.; Ahzi, S.; Dahoun, A.; Hiver, J. M., Recycling effects on the rheological and thermomechanical properties of polypropylene-based composites. *Mater. Des.* **2012**, 33, (0), 451-458.
6. Stan, F.; Sandu, L. I.; Fetecau, C.; Rosculet, R., Effect of reprocessing on the rheological, electrical, and mechanical properties of polypropylene/carbon nanotube composites. *J. Micro Nano Manuf.* **2017**, 5, (2), 021005.
7. Martín-Alfonso, J.; Franco, J., Influence of polymer reprocessing cycles on the microstructure and rheological behavior of polypropylene/mineral oil oleogels. *Polym. Test.* **2015**, 45, 12-19.
8. Soccalingame, L.; Perrin, D.; Bénézet, J.-C.; Mani, S.; Coiffier, F.; Richaud, E.; Bergeret, A., Reprocessing of artificial UV-weathered wood flour reinforced polypropylene composites. *Polym. Degrad. Stab.* **2015**, 120, 313-327.
9. Spicker, C.; Rudolph, N.; Kühnert, I.; Aumnate, C., The use of rheological behavior to monitor the processing and service life properties of recycled polypropylene. *J. Food Pack. Shelf* **2019**, 19, 174-183.

10. Da Costa, H. M.; Ramos, V. D.; De Oliveira, M. G., Degradation of polypropylene (PP) during multiple extrusions: Thermal analysis, mechanical properties and analysis of variance. *Polym. Test.* **2007**, 26, (5), 676-684.
11. Martins, M. H.; De Paoli, M. A., Polypropylene compounding with post-consumer material: II. Reprocessing. *Polym. Degrad. Stab.* **2002**, 78, (3), 491-495.
12. Sarrionandia, M.; Lopez-Arraiza, A.; Aurrekoetxea, J.; Arostegui, A., Structure and mechanical properties of a talc-filled polypropylene/ethylene-propylene-diene composite after reprocessing in the melt state. *J. Appl. Polym. Sci.* **2009**, 114, (2), 1195-1201.
13. Jiménez, A.; Torre, L.; Kenny, J. M., Processing and properties of recycled polypropylene modified with elastomers. *Plast. Rubber Compos.* **2003**, 32, (8-9), 357-367.
14. Wang, K.; Addiego, F.; Bahlouli, N.; Ahzi, S.; Rémond, Y.; Toniazzi, V.; Muller, R., Analysis of thermomechanical reprocessing effects on polypropylene/ethylene octene copolymer blends. *Polym. Degrad. Stab.* **2012**, 97, (8), 1475-1484.
15. Wang, K.; Bahlouli, N.; Addiego, F.; Ahzi, S.; Rémond, Y.; Ruch, D.; Muller, R., Effect of talc content on the degradation of re-extruded polypropylene/talc composites. *Polym. Degrad. Stab.* **2013**, 98, (7), 1275-1286.
16. Wang, K.; Addiego, F.; Bahlouli, N.; Ahzi, S.; Rémond, Y.; Toniazzi, V., Impact response of recycled polypropylene-based composites under a wide range of temperature: Effect of filler content and recycling. *Compos. Sci. Technol.* **2014**, 95, 89-99.
17. Wang, K.; Bahlouli, N.; Addiego, F.; Ahzi, S., Elastic and yield behaviors of recycled polypropylene-based composites: Experimental and modeling study. *Compos. Part B- Eng.* **2016**, 99, 132-153.
18. Addiego, F.; Dahoun, A.; G'Sell, C.; Hiver, J.-M., Characterization of volume strain at large deformation under uniaxial tension in high-density polyethylene. *Polymer* **2006**, 47, (12), 4387-4399.
19. Wang, K.; Boumbimba, R. M.; Bahlouli, N.; Ahzi, S.; Muller, R.; Bouquey, M., Dynamic behaviour of a melt mixing polypropylene organoclay nanocomposites. *J. Eng. Mater. Technol.* **2012**, 134, (1), 010905.
20. Wang, Y.; Arruda, E. M., Constitutive Modeling of a Thermoplastic Olefin Over a Broad Range of Strain Rates. *J. Eng. Mater. Technol.* **2006**, 128, (4), 551-558.
21. Ahzi, S.; Ganesan, A.; Arruda, E. In *Modeling and simulation of deformation texture in semi-crystalline polymers: application to polypropylene and nylon-6*, Mater. Sci. Forum, 2002; Trans Tech Publ: pp 1723-1728.
22. Gensler, R.; Plummer, C. J. G.; Grein, C.; Kausch, H. H., Influence of the loading rate on the fracture resistance of isotactic polypropylene and impact modified isotactic polypropylene. *Polymer* **2000**, 41, (10), 3809-3819.
23. Wu, Z.; Ahzi, S.; Arruda, E.; Makradi, A., Modeling the large inelastic deformation response of non-filled and silica filled SL5170 cured resin. *J. Mater. Sci.* **2005**, 40, (17), 4605-4612.
24. Zhou, Y.; Rangari, V.; Mahfuz, H.; Jeelani, S.; Mallick, P. K., Experimental study on thermal and mechanical behavior of polypropylene, talc/polypropylene and polypropylene/clay nanocomposites. *Mat. Sci. Eng. A-Struct.* **2005**, 402, (1-2), 109-117.
25. Boyce, M. C.; Parks, D. M.; Argon, A. S., Large inelastic deformation of glassy polymers. part I: rate dependent constitutive model. *Mech. Mater.* **1988**, 7, (1), 15-33.
26. Arruda, E. M.; Boyce, M. C., A three-dimensional constitutive model for the large stretch behavior of rubber elastic materials. *J Mech Phys Solids* **1993**, 41, (2), 389-412.
27. Boumbimba, R. M.; Wang, K.; Hablot, E.; Bahlouli, N.; Ahzi, S.; Avérous, L., Renewable biocomposites based on cellulose fibers and dimer fatty acid polyamide: experiments and modeling of the stress-strain behavior. *Polym. Eng. Sci.* **2017**, 57, (1), 95-104.

28. Arruda, E. M.; Boyce, M. C.; Jayachandran, R., Effects of strain rate, temperature and thermomechanical coupling on the finite strain deformation of glassy polymers. *Mech. Mater.* **1995**, 19, (2–3), 193-212.
29. Teegarden, D. M., *Polymer Chemistry: Introduction to an Indispensable Science*. illustrated edition ed.; Natl Science Teachers Assn: virginia, 2004; p 280.
30. Richeton, J.; Ahzi, S.; Vecchio, K. S.; Jiang, F. C.; Makrati, A., Modeling and validation of the large deformation inelastic response of amorphous polymers over a wide range of temperatures and strain rates. *Int. J. Solids. Struct.* **2007**, 44, (24), 7938-7954.