Study of EPDM/PP polymeric blends: mechanical behavior and effects of compatibilization

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Abstract

A blend of Ethylene Propylene Diene Monomer (EPDM) rubber reinforced by polypropylene (PP) particles has been processed and its hyperelastic behavior has been characterized under cyclic uni-axial tensile tests. The experimental results show a significant effect of the fraction of polypropylene particles (10%, 25% and 30% by weight). Moreover, from another series of tests conducted on materials containing compatibilizers at different mass concentration, it is observed that the introduction of a compatibilizer increases the rigidity of the blends and affects notably their macroscopic behavior. These observations are interpreted as a consequence of the modification at microlevel of adherence between particles and matrix phases. The use of a nonlinear micromechanical model allows us to confirm this interpretation. ***To cite this article: V. Bouchart et al., C. R. Mecanique 336 (2008).***
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Résumé

Etude de mélanges EPDM/PP : comportement mécanique et effets de compatibilization. Un matériau constitué d'une matrice d'Ethylene Propylène Diene Monomer (EPDM) renforcée par des particules de Polypropylène (PP) a été élaboré et son comportement hyperélastique a été caractérisé sous sollicitations de traction uni-axiale cyclique. Les résultats expérimentaux montrent un effet significatif de la fraction de particules de polypropylène (10 %, 25 % et 30 % en masse). De plus, à partir d'une autre série de tests réalisés sur des matériaux auxquels sont adjoints des compatibiliseurs à différentes concentrations en masse, il est observé que l'introduction de tels compatibiliseurs accroît la rigidité des mélanges et affecte notablement leur comportement macroscopique. Ces observations expérimentales sont interprétées comme une conséquence de la modification à l'échelle microscopique de l'adhérence entre les particules et la matrice. La mise en oeuvre d'un modèle micromécanique non linéaire permet de confirmer cette interprétation. ***Pour citer cet article : V. Bouchart et al., C. R. Mecanique 336 (2008).***
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1. Introduction

The use of EPDM-PP blends is continuously growing in various industrial domains since several decades. As it is possible to mix Ethylene Propylene Diene Monomer (EPDM) and polypropylene (PP) in any ratio, there is theoretically a wide spectrum of materials from elastified PP to EPDM rubber reinforced with thermoplastics. In order to gain a better understanding of the mechanical behavior of such blends and to provide a physical basis for their modeling an experimental campaign was conducted with the following particular objectives: (i) to quantify the reinforcing effects of polypropylene particles dispersed in the EPDM; (ii) to characterize the macroscopic effect of a compatibilization of the particles-matrix interface by assessing the difference in the macroscopic behavior of rubber-like blend systems prepared with and without compatibilizer. The last part of the study is devoted to a modeling of the behavior of these blends. To this end, we will implement the second order homogenization method proposed by [1] and adapted to hyperelastic composites by [2]. This method assumes a perfect adhesion between the phases and a random dispersion of PP reinforcements in the EPDM matrix. Comparison between the predictions of the homogenization model and the experimental data (obtained for different types and concentrations of compatibilizers in the EPDM/PP blends) is then presented.

2. Test specimens preparation and studied materials

Blends considered in the present study are constituted of polypropylene (PP) procured from Reliance Ind. Ltd., grade REPOL HO33MG and of an EPDM rubber procured from Du Pont, grade NORDEL 4770R.

In the present study, investigations are performed on different types of blend systems prepared with different quantity of PP and EPDM and with or without compatibilizer. This results in properties variations of the blend systems. Moreover, two different compatibilizers are considered: a Maleic anhydride grafted PP one (MAgPP, from Pluss polymers (India) MFI 50) and an Ionomer called Surlyn (from Du Pont Ltd MFI 16) being chemically known as, Ethylene-co-methacrylic acid neutralized by sodium ion. Thus, each compatibilizer and a combination by mixture of both together in the PP/EPDM blends are tested and the results are analyzed. These variations are checked because both the compatibilizers are of different types. More specifically, Ma-g-PP is a chemical compatibilizer that attacks at the unsaturated locations in the chain; this is provided by norbornane ring that is attached to EPDM chain structure. However, for the compatibilizer Surlyn, only physical interactions take place through ion interactions [3–5].

The different compositions were made by means of a co-rotating intermeshing twin-screw extruder. The granules of PP and EPDM were mixed in appropriate ratios prior to being added to the extruder hopper. The screw speed was adjusted to 240 rpm, the die zone temperature was maintained at 210 °C; the filament obtained upon extrusion was immediately quenched in water and later chopped into small granules. The specimens for mechanical testing were prepared by injection molding using LT Demag PFY40-LNC4P Machine. The nozzle temperature was maintained at 210 °C, and the injection pressure at 60 MPa.

SEM micrographs of cryogenically fractured samples of PP/EPDM blends have been performed. The blends showed more or less uniform dispersion of components in which the phase segregation can be seen clearly. PP phase is found to be in dispersed particle phase.

The tests have been carried out by using a uni-axial tension machine (INSTRON 4302) with a low load cell capacity (2 kN). In order to avoid the slippage of the samples, mainly due to the quasi incompressible behavior of the involved materials, the grips used are self tightening based on an eccentric system (Fig. 1(a)). It must be recalled here that the aim of our study is to evaluate the influence of compatibilizer for the considered blends as well as to estimate the accuracy of the considered homogenization method. Thus, even if the influence of the deformation rate might be important in the nature of the mechanical response, it has been decided to perform the mechanical tests at a fixed rate of deformation in order to avoid considering the influence of the rate of deformation and thus the viscosity phenomenon. The measurements of stretch have been performed using a contactless video extensometer at a constant strain rate (10^{-3} s^{-1}) (see adapted samples on Fig. 1(b)). Due to the difficulties to measure the volume variation in large deformation, one has chosen to measure the first Piola–Kirchoff nominal stress ($T_{11} = \frac{F}{S_0}$ where F is the measured force and S_0 the initial section of the sample) rather than the Cauchy true stress. Each test has been performed 5 times and a very good reproducibility was observed; thus, only the average data are presented in the present Note.
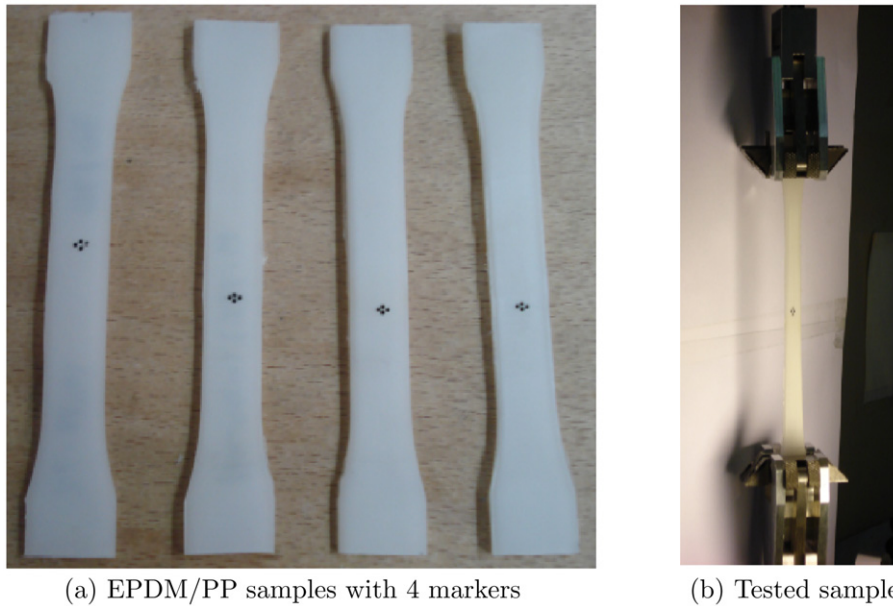
(a) EPDM/PP samples with 4 markers (b) Tested sample
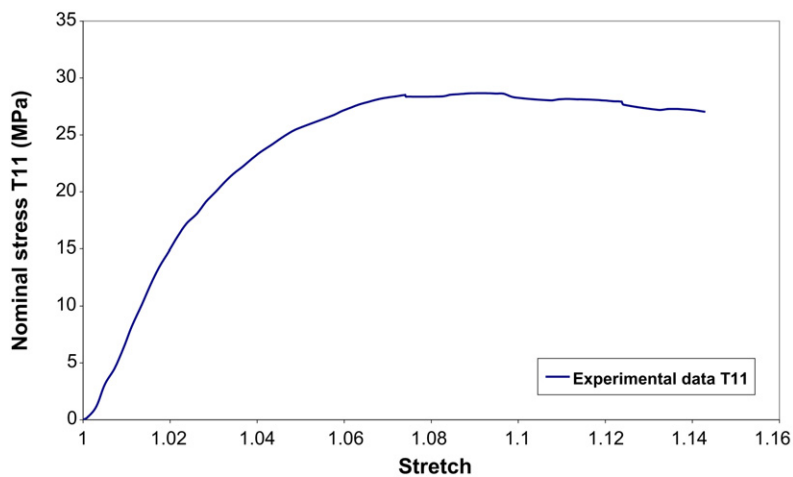
Fig. 1. Tested sample and testing system.

Fig. 2. Experimental response of the polypropylene (PP) phase under uni-axial loading.

3. Characterization of the mechanical behavior of the blend without compatibilizer

Before presenting the response of the blends, we first present the mechanical behavior of the constituents. Fig. 2 shows the response of the polypropylene (PP) phase; it is observed that the PP phase exhibits a high rigidity while it fails at a relative small strain level (elongation less than 1.15). Let us come now to the EPDM matrix. According to the mechanical response of the pure or reinforced EPDM (see Fig. 3 for the pure EPDM and for the EPDM90-PP10, i.e. 90% EPDM and 10% PP), the materials present a high viscosity (attested by the hysteresis between the loading and unloading) and damage during the first load, known as Mullins effect [6] (characterized on one hand by the important difference between the first cycle and the next ones, and on the other hand by the permanent stretch). For such reasons, and because we aim to study the hyperelastic behavior (without taking into account viscosity), unloading is considered as proposed in [7,8].

Once can notice that the strength of the material increases due to the adjunction of the PP particles in the EPDM. Even if some part of this noticed increase can be attributed to the size effect of the particles on the stress concentration
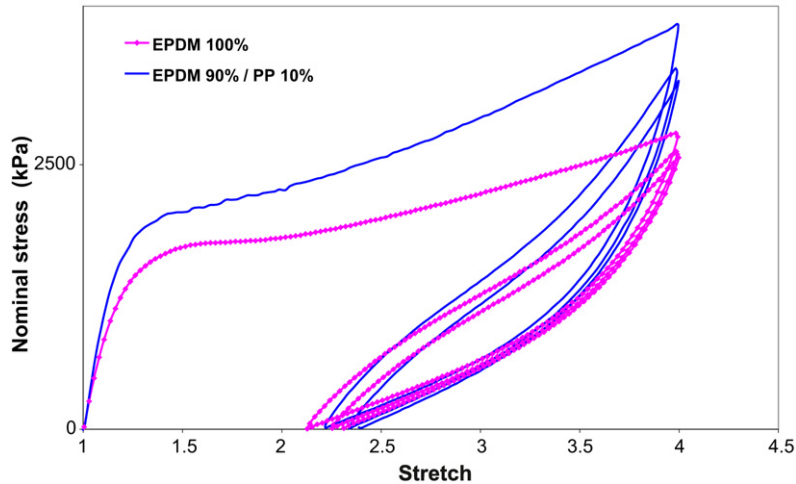
Fig. 3. Mechanical response of the pure EPDM and of the EPDM90-PP10 blend under cyclic uni-axial tensile loading.
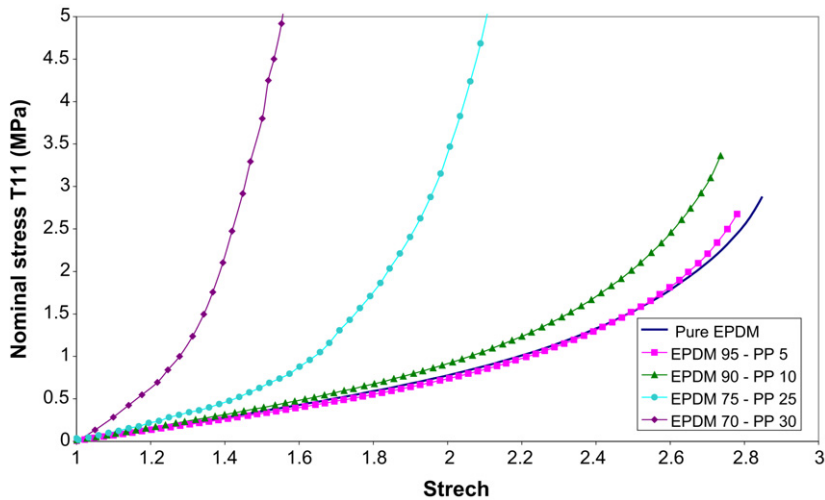

Fig. 4. First unloading of the pure EPDM and of different blends EPDM-PP.

in the matrix, such increase might be mainly due to the reinforcement effect of the PP particles. This is confirmed for the blends with different fractions of particles (see Fig. 4). As expected, the reinforcing effect increases with the volume fraction of the particles. However, it is observed that the value of the maximum strain which can be reached in the blend decreases with particles concentration. This is probably due to the brittle character of the PP phase.

4. Effects of compatibilization on the mechanical behavior

It is well known that the adherence between particles (PP) and matrix (EPDM) plays a crucial role in the mechanical behavior of the blends, even if the two phases have been melt blended together. It is therefore essential to quantitatively evaluate the role of compatibilizers by introducing them in the blend in order to increase the adherence between each polymer chains and EPDM macromolecules.

The results, reported on Fig. 5 for the Ma-g-PP and Surlyn, reveal a significant influence of these compatibilizers on the mechanical response of the EPDM-PP blend. It is noted that the efficiency of the two compatibilizers (Surlyn and Ma-g-PP) is quite equivalent. Moreover, it is observed that increasing the concentration of a compatibilizer leads to a higher strength of the blends. From physical point of view, this can be interpreted as a consequence at the macroscopic scale of the improvement of the adherence (due to the presence of a compatibilizer) between the two
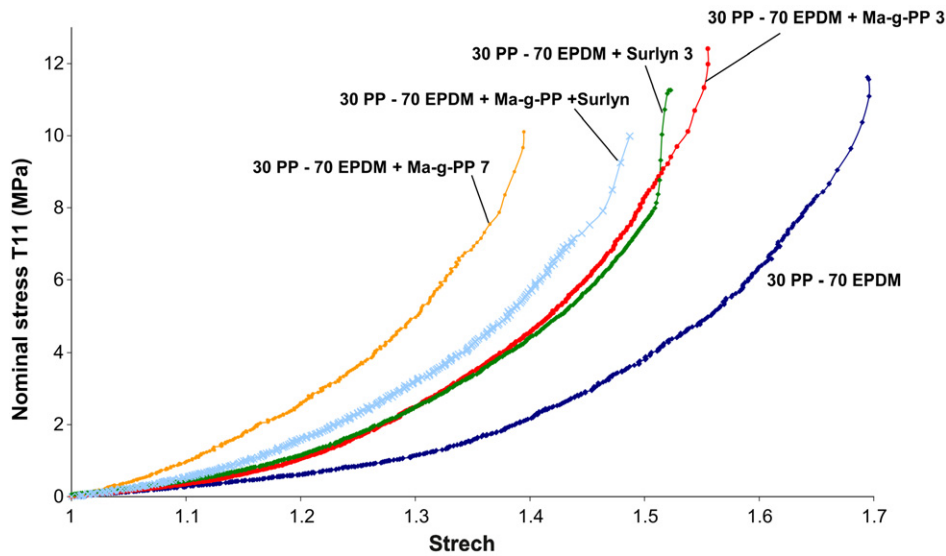
Fig. 5. Comparison of the effect of compatibilizers on the macroscopic response of the hyperelastic blend.

phases. It is expected that with an adequate concentration of compatibilizer a perfect contact might be reached. In our experiments the rate of Surlyn or Ma-g-PP beyond 7% by wt. was found to provide no supplementary benefit. Thus, one can conclude that adhesion between PP and EPDM is almost perfectly achieved.

5. Micromechanical interpretation

5.1. Basic principles and implementation

As explained in Section 2, the injection process of the blends considered induces PP phase as distributed particles in the EPDM matrix. Moreover, since no information allows us to consider that the particles are periodically embedded in the matrix, it has been assumed that the particles are randomly distributed in the matrix. Then, the blends considered can be thought of as composite materials whose heterogeneous and nonlinear behaviors are modeled with a nonlinear homogenization method devoted to composites with random microstructure. The adopted approach is based on the second order method developed by P. Ponte Castañeda [1] and thereafter extended to the hyperelastic behavior by [2].

Let us consider a representative elementary volume (R.E.V.), denoted Ω_0, and composed of an hyperelastic matrix reinforced by a random distribution of particles. This R.E.V. is assumed to occupy a volume V_0 in the reference configuration and to satisfy the standard scale separation conditions. The reinforced material is subjected to homogeneous boundary strain conditions: $\underline{u} = (\bar{\mathbf{F}} - \mathbf{I}) \cdot \underline{x}$ on $\partial\Omega_0$. The heterogeneous deformation gradient tensor $\mathbf{F}$ satisfies then $\bar{\mathbf{F}} = \langle \mathbf{F} \rangle$ with $\langle \cdot \rangle$ the volume average over Ω_0.

The particles, randomly distributed in the R.E.V., are assumed, as well as the matrix, to have hyperelastic constitutive behaviors which are determined by their strain energy densities $\mathrm{W}^{(r)}(\mathbf{F})$[1] ($r = 1, \ldots, N$). It has been shown by Hill [9] that the homogenized constitutive law, giving the macroscopic first Piola–Kirchoff stress tensor $\bar{\mathbf{T}} = \langle \mathbf{T} \rangle$, is determined by a macroscopic strain energy density $\widetilde{\mathrm{W}}$ such that:

$$\bar{\mathbf{T}}(\bar{\mathbf{F}}) = \frac{\partial \widetilde{\mathrm{W}}(\bar{\mathbf{F}})}{\partial \bar{\mathbf{F}}} \tag{1}$$

In order to assess the homogenized energy in the case of nonlinear materials various approaches are developed in Ponte Castañeda and Suquet [10]. In particular, the second order homogenization procedure which provides estimates of $\widetilde{\mathrm{W}}$ and is based on a linearization of the strain energy densities of each phase, $\mathrm{W}^{(r)}(\mathbf{F})$, by using a Taylor expansion.

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[1] The superscript (r) stands for a constituent r.

Let us denote by "1" the hyperelastic matrix containing a unique population of spherical particles, denoted by "2". For this two-phase hyperelastic composite, the second order method can be specialized and provides the following estimate of the macroscopic strain energy density (see [2]):

$$\widetilde{W}(\bar{\mathbf{F}}) \simeq \sum_{r=1}^{2} c^{(r)} \big\{ W^{(r)}(\bar{\mathbf{F}}^{(r)}) + \frac{1}{2}(\bar{\mathbf{F}} - \bar{\mathbf{F}}^{(r)}) : \mathbf{T}^{(r)}(\bar{\mathbf{F}}^{(r)}) \big\} \tag{2}$$

where $\mathbf{T}^{(r)}(\bar{\mathbf{F}}^{(r)}) = \frac{\partial W^{(r)}}{\partial \mathbf{F}}(\bar{\mathbf{F}}^{(r)})$ and $c^{(r)}$ the volume fraction of phase r.

The macroscopic stress tensor, given by the derivative of (2) with respect to $\bar{\mathbf{F}}$, is then estimated by:

$$\bar{\mathbf{T}}(\bar{\mathbf{F}}) \simeq \sum_{r=1}^{2} \frac{c^{(r)}}{2} \bigg[\mathbf{T}^{(r)}(\bar{\mathbf{F}}^{(r)}) + \big[\mathbf{T}^{(r)}(\bar{\mathbf{F}}^{(r)}) + \mathbb{L}^r(\bar{\mathbf{F}}^{(r)}) : (\bar{\mathbf{F}} - \bar{\mathbf{F}}^{(r)}) \big] : \frac{\partial \bar{\mathbf{F}}^{(r)}}{\partial \bar{\mathbf{F}}} \bigg] \tag{3}$$

where $\mathbb{L}^r(\bar{\mathbf{F}}^{(r)}) = \mathbb{L}_t^r(\bar{\mathbf{F}}^{(r)}) = \frac{\partial^2 W^{(r)}}{\partial \mathbf{F} \partial \mathbf{F}}(\bar{\mathbf{F}}^{(r)})$.

Note that the only unknowns in (3) are the average deformation gradients in each phase r, $\bar{\mathbf{F}}^{(r)}$, which may be computed from the resolution of a thermoelastic problem linked to a linear comparison composite involved in the method.

In the case of two-phase materials, the resolution of this thermoelastic problem is performed thanks to the Levin's theorem [11] which reads:

$$\bar{\mathbf{F}}^{(r)} = \mathbb{A}^{(r)}(\bar{\mathbf{F}}^{(r)}) : \bar{\mathbf{F}} + \big(\mathbb{A}^{(r)}(\bar{\mathbf{F}}^{(r)}) - \mathbb{I} \big) : (\Delta\mathbb{L})^{-1} : (\Delta\boldsymbol{\tau}); \quad r = 1, 2 \tag{4}$$

where $\Delta\mathbb{L} = \mathbb{L}^{(1)}(\bar{\mathbf{F}}^{(1)}) - \mathbb{L}^{(2)}(\bar{\mathbf{F}}^{(2)})$, $\Delta\boldsymbol{\tau} = \boldsymbol{\tau}^{(1)}(\bar{\mathbf{F}}^{(1)}) - \boldsymbol{\tau}^{(2)}(\bar{\mathbf{F}}^{(2)})$ with $\boldsymbol{\tau}^{(r)} = \mathbf{T}^{(r)}(\bar{\mathbf{F}}^{(r)}) - \mathbb{L}^r : \bar{\mathbf{F}}^r$ polarization tensors which can be seen as fictitious thermal stress tensors and $\mathbb{A}^{(r)}$ is the localization tensor associated to phase (r) in the linear comparison composite. $\mathbb{A}^{(r)}$ depends on the linear homogenization scheme used to solve (4). In the present study, taking into account the matrix-inclusion type morphology of the (reinforced) material, we choose to consider, for the linear comparison composite, the well known Hashin–Shtrikman lower bound [12] since the matrix is more compliant than the particles. The micromechanical model will be then referred as HS-based model.

The implementation of this homogenization model requires the use of several numerical methods, among others, to compute the Hill tensor in the HS-based model, the tangent modulus tensor of each phase $\mathbb{L}^{(r)}$ being anisotropic. Numerical techniques are also needed to solve the system of nonlinear equations (4) associated to the thermoelasticity problem. For this resolution, required to determine $\mathbf{F}^{(1)}$ and $\mathbf{F}^{(2)}$, we then use a Newton–Raphson method. For more details concerning the implementation of the method, the readers may refer to [13] and [14]. Moreover, it has been also shown in these works, that the homogenization technique, when compared to reference solutions obtained by finite element (FE) calculations, leads to very accurate results.

5.2. Results of the blend modeling

For the application of the described homogenization method, the considered EPDM matrix is the same for each blend and since data on mechanical characteristics of compatibilizers are not available, the reinforcement effect of compatibilizers has been neglected in the micro-macro approach. Thus, we need to choose suitable strain energy densities to model the behavior of the matrix phase and of the inclusion one. The chosen density for the EPDM matrix is the one introduced by Lambert-Diani et al. [15]. Even if it seems obvious for the EPDM, such choice is not entirely relevant for pure PP. However, because of the very low rigidity of the EPDM, the PP phase will be subjected to very low strain. Its behavior is described by the strain energy density proposed by Ciarlet and Geymonat [16]. Since, each constituent of the composite being considered isotropic, the strain energy density functions $W^{(1)}$ and $W^{(2)}$ are expressed as functions of the three invariants, I_1, I_2 and I_3 of the dilatation tensor $\mathbf{C} = {}^t\mathbf{F}.\mathbf{F}$ (see for instance [17]).

The Diani-Lambert and Rey's density is then expressed as follow:

$$W^{(1)}(\mathbf{F}) = \int_3^{I_1} e^{(\alpha_0 + \alpha_1(I_1-3) + \alpha_2(I_1-3)^2)} \, dI_1 + \int_3^{I_2} \beta_1 I_2{}^{\beta_2} \, dI_2 \tag{5}$$

(a) Lambert-Diani and Rey density for the EPDM particles
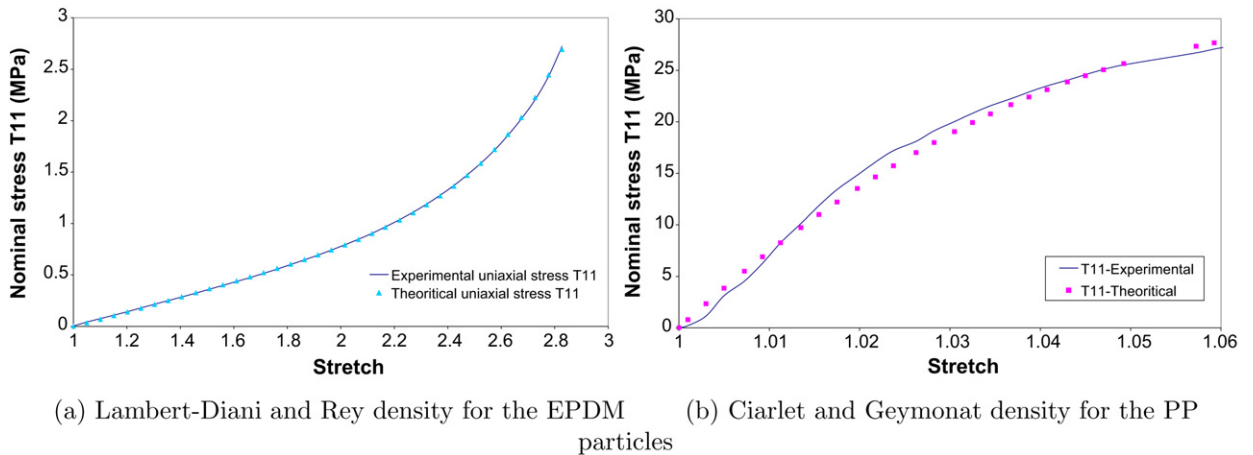
(b) Ciarlet and Geymonat density for the PP

Fig. 6. Result of the identification of the densities for each phase.
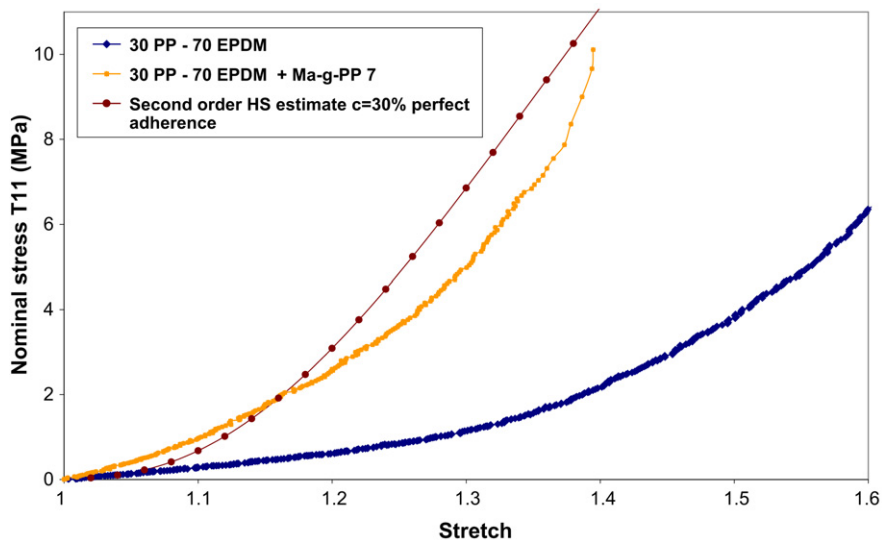

Fig. 7. Comparison of the effect of compatibilizer on the elastic response of the blend.

where α_0, α_1, α_2, β_1, β_2 are the model parameters for the matrix phase which have to be identified on experimental data for the considered EPDM. And for the energy density proposed by Ciarlet and Geymonat, one has:

$$W^{(2)}(\mathbf{F}) = C_1(I_1 - 3) + C_2(I_2 - 3) + C_3(I_3 - 1) - B\ln(I_3) \tag{6}$$

where C_1, C_2, C_3 and B have also to be identified.

The results of the identification procedure are presented on Fig. 6(a) for the pure EPDM and on Fig. 6(b), up to 6% deformation, for the PP. The following values of the parameters are then obtained for the EPDM:

$$e^{\alpha_0} = 0.2246 \text{ MPa}; \quad \alpha_1 = 0.013051; \quad \alpha_2 = 0.024$$
$$e^{\beta_1} = 0.38104 \text{ MPa}; \quad \beta_2 = -2.03234$$

and the following for the PP phase:

$$C_1 = -827 \text{ MPa}; \quad C_2 = 963 \text{ MPa}; \quad C_3 = 100 \text{ MPa} \quad \text{and} \quad B = 1199 \text{ MPa}$$

The results obtained by the nonlinear homogenization technique are presented on Fig. 7 for the EPDM matrix containing 30% of PP particles. It may be noticed that the homogenization model gives results that are not completely in

quantitative agreement with experimental results. Indeed, a discrepancy between model predictions and experimental data is noted, but it is believed that the predictions can be improved by taking into account the rigidity of the compatibilizers. However, it has been proved that this model provides good results when compared to FE computations [13].

From experimental point of view, the blend material studied is far from being ideal. The introduction of the compatibilizer was shown to increase the strength of the material by introducing a better contact between each phase but there is still no guarantee that we have reached the perfect contact between each phase. Damage phenomena which probably occur in the blends during the loading must be taken into account. Indeed, in the absence of the compatibilizer, the interfaces between particles and matrix suffer damage which affects the macroscopic response.

6. Conclusions

The present Note is devoted to an experimental characterization of elastomers-based blends of the type EPDM/PP, the PP phase being in the form of particles. For the particles concentration considered in the study, the results show a significant effect of the reinforcements. Moreover, experiments performed in the second part of the study allow us to quantify the role of compatibilizers in EPDM-PP blend. Indeed, an increase of the rigidity and an improvement of the macroscopic behavior is obtained by introducing a compatibilizer; an optimum concentration of 7% Ma-g-PP has been noticed. In order to evaluate the perfect contact conditions induced by such introduction of compatibilizer, an homogenization method for hyperelastic composites has been implemented. It is shown that the available compatibilizer system is not able to ensure perfect contact between the constituents when the material is loaded. It is desirable to extend the homogenization method in order to take into account damage mechanisms and to model more accurately the compatibilized blends.

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