A MICROMECHANICS MODEL FOR RUBBER BLENDS FILLED BY A NANO-REINFORCED DEVULCANIZED RECYCLED RUBBER: APPLICATION IN THE AUTOMOTIVE INDUSTRY

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ABSTRACT– The present report proposes a micromechanics model for predicting the dynamic modulus of rubber blends consisting of a base rubber and devulcanized recycled rubbers reinforced by nanofillers. A four-step hierarchical homogenization is established to relate the properties of components from the nano-sized reinforcements to the macro-scaled final blend. The developed model accounts for the effect of agglomeration and geometry of nano-fillers, the quality of the devulcanization process, and the properties of the interphase surrounding the nanofillers on the dynamic modulus of the rubber blend. A comprehensive dimensionless parametric study is performed whose output in terms of graphical maps can be used as a design guideline for practical cases in industries like automotive. A case study for recycled end-of-life tires (ELTs) reinforced by nano clays is presented and it is found that the nano reinforcement of devulcanized rubbers has a remarkable potential to compensate for the weakness compared to its virgin counterpart.

KEY WORDS : Nano reinforcement, End-of-Life Tires (ELTs), Devulcanization, Recycled rubber, Halpin-Tsai (H-T)

1. INTRODUCTION

Tires and automotive component applications, having overall the most rubber demand at the global level, are making very little use of reclaimed rubber from End-of-Life Tires (ELTs) as the main source of reprocessed rubber feedstock, mainly due to technical issues. Consequently, despite the global shortage of this valuable material and the environmental issues related to its consumption, recycling and reuse rates of rubber wastes are still severely low (Markl and Lackner, 2020). The stockpiling and disposal of ELTs as one of the main environmental pollutants create nesting ground for infectious rodents, pollute groundwater with heavy metals that leach underground, and produce flammable landfill sites. Open burning process of ELTs, as a substitute for landfilling, on the other hand, generates Sulphur oxide gases from the oxidation of Sulphur presented in the crosslinked vulcanized rubber (Saputra et al., 2021). Vulcanization as a common process in the rubber industry, especially automotive, although is essential for hardening rubbers, complicates the recycling process to recover the quality of virgin raw material since the vulcanized rubber is persistent to degradation because of the cross-linking of the polymer chains during the vulcanization process. Rubber devulcanization is a process that breaks down the cross-linked sulfur bonded networks in the vulcanized waste rubber by physical, chemical, thermophysical, or biological means to transform it into devulcanized rubber to be used as a high-quality raw material (Asaro et al., 2018; Bockstal et al., 2019). Hence, it has attracted much attention as a powerful method of recycling showing enormous potential to fulfill the technical criteria and reduce the monumental environmental impacts (Zanchet et al., 2012).

On the other hand, the concept of nano-reinforcement has opened a new window to unexpected property improvement even for low volume fractions when compared to traditional micro-reinforcement like high volume fraction fiber reinforced laminated composites (Kayalvizhi Nangai and Saravanan, 2021; Fu et al., 2019). 2D materials like graphene sheets (Valentini et al., 2016) and nano clays (Hong et al., 2005) have received remarkable attention as nano-reinforcements of polymers and particularly rubbers thanks to their high surface-to-volume ratio allowing them to form an efficient widely developed interphase, as a well-understood solution in

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automotive industries for many decades. Hence, the idea of reinforcing devulcanized rubber with nano-platelets emerges to improve its properties before blending with other natural and synthetic rubbers (Fathy et al., 2018). Unlike isotropic materials, evaluation of mechanical properties of nanocomposites based on exclusively experimental approaches is quite costly because of the wide variety of affecting parameters from the properties, the volume fractions, and the possibility of agglomeration of nano reinforcements to the unknown properties of interphases raising from the difficulty of direct measurements. Numerical approaches, such as finite element (Greco, 2020), boundary element (Fedeliński and Górski, 2015), and lattice spring (Shokrieh et al., 2017) methods can reduce experimental costs and difficulties at the cost of long simulations, however, the results are limited to special cases.

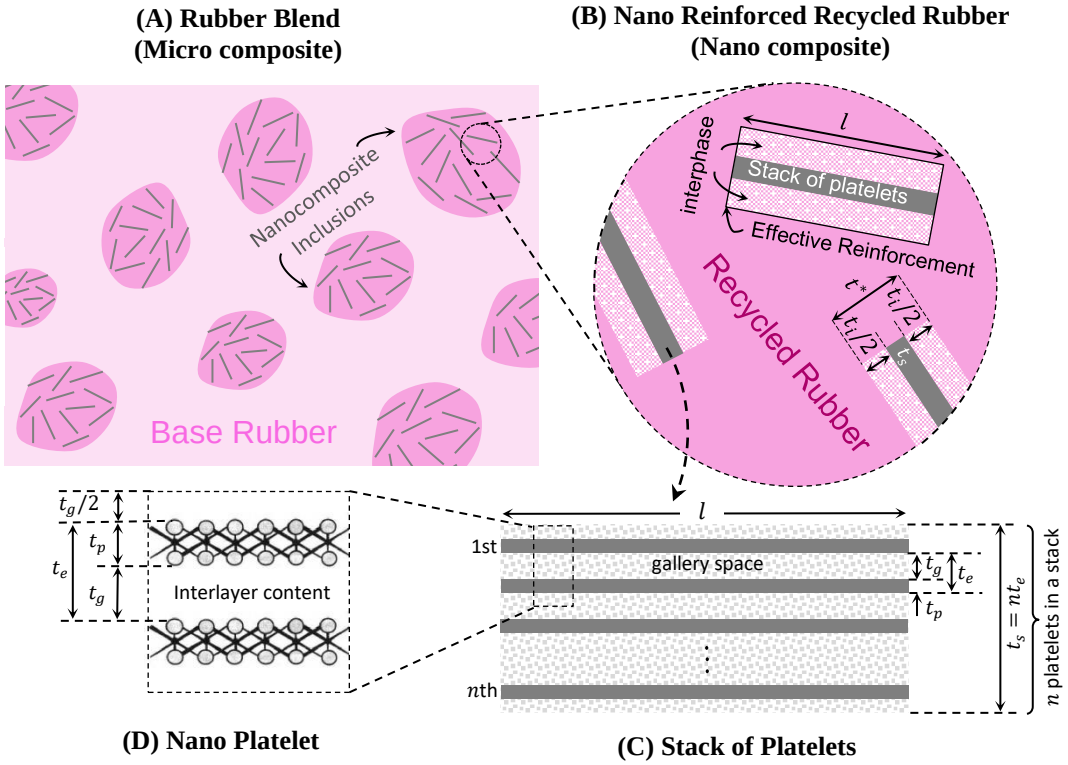

Figure 1. The The schematic of the proposed hierarchical multiscale micromechanics model for rubber blends filled by reinforced recycled rubber. (A) the final rubber blend where the matrix is the base rubber and the fillers are semi-spherical nanocomposite inclusions, (B) the nanocomposite where the matrix is the recycled rubber and the inclusions are the stack of platelets surrounded by interphase defining the effective reinforcement, (C) the stack of nano platelets formed by assembly of n nanoplatelets on the top of each other, (D) schematic atomistic structure of single nanoplates.

Thus, the motivation for developing analytical models suggesting closed-form formulations for prediction of mechanical properties of nanocomposites is growing. A micromechanics model for comparison of tensile and compressive elastic moduli, and prediction of effects of incomplete exfoliation and imperfect alignment on the modulus of nanocomposites was presented by (Brune and Bicerano, 2002) and it was shown that incomplete exfoliation has a very significant detrimental effect on the reinforcement efficiency. The effects of the interphase and strain gradients on the elasticity of layer-by-layer polymer/clay nanocomposites was analytically investigated by developing a size-dependent strain gradient Mori–Tanaka model and an inverse method was presented to determine the effective thickness and stiffness of the interphase layer using finite element simulations and experimental data available in the literature (Li et al., 2011b). A static/dynamic micromechanical model of graphene-reinforced polymer matrix nanocomposites with consideration of the nanoscale interphase and random orientations of graphene sheets was introduced by (Gao et al., 2021) to effectively predict the static and dynamic mechanical behavior. A new form of Halpin–Tsai (H-T) micromechanical model for characterizing the mechanical properties of carbon nanotube-reinforced polymer nanocomposites to show the effects of volume fraction, non-straight shape, aspect ratio, mechanical characteristics, and non-uniform dispersion of nanotubes was proposed by

(Hassanzadeh-Aghdam and Jamali, 2019). A simple micromechanical approach to predict mechanical behavior of polypropylene-organoclay nanocomposites based on representative volume element was developed and calibrated using finite element analysis by (Dong and Bhattacharyya, 2010) and a significant modulus enhancement in the exfoliated nanocomposites was demonstrated. A modified H-T model for polymer nanocomposites considering the effects of interphase properties and spherical nanofiller size was developed by (Zare, 2016). The results showed that the developed model could accurately predict the experimentally measured Young's modulus of polymer particulate nanocomposites assuming the role of the interphase as a calibration parameter. A closed-form, hierarchical, multi-interphase model for nanocomposites was derived to study the influence of the interphase around nanofillers on the enhancement mechanism of nanocomposites in the elastic regime employing the Mori–Tanaka model and the verification was performed through a set of 3D finite element simulations (Li et al., 2011a). An extended micromechanics method for probing the effect of interphase and its overlapping condition on the stiffness of linear elastic and viscoelastic heterogeneous material was presented by (Liu et al., 2016) and applied to viscoelastic polymer nanocomposite with interphase regions to estimate the properties and thickness of the interphase region based on experimental data.

This study aims to establish a hierarchical multiscale framework to propose a closed-form solution for predicting the stiffness of rubber blends containing devulcanized rubber reinforced by nano reinforcements. First, the equivalent properties of a stack of nano platelets are evaluated and an effective reinforcement is introduced to homogenize the properties of the interphase and the stacks. Then, as a nested composite, a two-step H-T equation is implemented to predict the properties of the nano-reinforced recycled rubber and afterward the properties of the final rubber blend. The exact formulation for the critical volume fraction of the nanofiller which reinforces enough the recycled rubber to be equivalent to the base rubber and not to reduce the quality of the final rubber blend, is presented. A simple approximation for the properties and the thickness of the interphase considering the degree of cross-linking in the presence of surface modifiers is suggested. In addition, an exact inverse solution for the properties of the interphase is presented which is useful for back calculating when the experimental measurements on the properties of the rubber blend and/or reinforced devulcanized recycled rubber are available.

2. DEVELOPMENT OF THE PROPOSED MICRO-MECHANICS MODEL

In this section a micromechanices model is developed for predicting the dynamic (complex) modulus of rubber blends reinforced by nano platelets. Frequency-dependent dynamic modulus of a rubber consists of a storage and a loss moduli as the real and imaginary parts of its complex representation, shown here with underlined parameters. Although the developed model uses the complex modulus, however, in fact, it is two separate formulations for the storage and the loss moduli which are presented as a compact complex form. Similarly, the dimensionless moduli which will be defined as the ratio of a modulus to the modulus of a virgin rubber, shown by superscript $\widehat{\ }$, indeed reperesent two storage and loss dimensionless moduli obtained by separately dividing the real and imaginary part of moduli which should not be confused with the standard division of two complex number.

Consider a rubber blend consisting of a base rubber of complex modulus $\underline{E}_{BR}$ filled by a recycled rubber of complex modulus $\underline{E}_{RR}$. This filler is obtained by recycling an end-of-life rubber product through a devulcanization treatment whose virgin counterpart has the complex modulus of $\underline{E}_{VR}$ before vulcanization. Success in the devulcanization process can be quantified through how many fractions of the vulcanized polymer chains have become soluble after the treatment. It may be obtained by measuring the difference between the rubber's crosslink density before and after the treatment. The modulus of the devulcanized recycled rubber after possible revulcanization and implementing treatments like self-healing can be related to the virgin one, by defining a devulcanization parameter, λ, that reflects the quality of the treatment:

$$\underline{E}_{RR} = \lambda \underline{E}_{VR} \tag{1}$$

The quality parameter, $\lambda = 1$, represents an ideal devulcanization that completely recovers the complex modulus of recycled rubber where all the vulcanized polymer chains are soluble, while $\lambda = 0$ is the worst state of no soluble chain. In between, $0 < \lambda < 1$, as the real situations, it is proposed to enhance the complex modulus of the recycled rubber by adding nano platelets to form a rubber-based nanocomposites as the filler of the base rubber. Although the loss contribution from the modulus of nano platelets is insignificant, however, adding them may alter the loss modulus of the rubber as the matrix. Hence, the modulus of nanoplatelets is assumed to be complex whose imaginary contribution is responsible for its effect on the loss modulus of the rubbers. The schematic of the hierarchical assembly of the problem from a single nano platelet as a nano-scaled 2D material to the final macro-scaled rubber blend is depicted in Fig. 1. Four levels of homogenization are introduced to relate the dynamic modulus of the components as a multiscale approach. First, single nano platelets of thickness t_p, length l, and aspect ratio $\alpha_p = l/t_p$ with an interlayer gallery space of t_g resulting in an equivalent thickness of $t_e = t_p + t_g$ (known in the literature of 2D materials as d_{00}), and an

equivalent aspect ratio of $\alpha_e = (l/t_e)$ are assembled on the top of each other to form a stack of nano platelets of the total thickness of $t_s = nt_e$ and aspect ratio $\alpha_s = (l/t_s) = (\alpha_e/n)$ where n is the number of platelets in the stack, see Fig. 1(C) and (D). Considering the fact that the modulus of interlayer contents in the gallery space is ignored when compared to the modulus of stand-alone platelet, $\underline{E_p}$, as the first homogenization step, one can estimate the equivalent modulus of platelets, $\underline{E_e}$, applying a direct rule of mixture. Note that the equivalent modulus of nano platelet is equal to the modulus of a stack, $\underline{E_s}$, since a stack is a parallel assembly of n equivalent platelets, see Fig. 1(C):

$$\underline{E_s} = \underline{E_e} = \underline{E_p}(t_p/t_e) \tag{2}$$

When the stacks are mixed with the recycled rubber, in agreement with the literature of nanocomposites, a thick enough interphase zone is expected to surround the stacks due to bonding the rubber chains to the surface of nano platelets stacks thanks to their high surface-to-volume ratio. In the present model it is assumed that a uniform interphase layer of the thickness of $t_i/2$ is equally formed on both wide surfaces of the stack, while the interphase zone on the lateral surfaces is ignored due to the high aspect ratio, as shown in Fig. 1(B). Since the base material in the interphase zone is the recycled rubber, it is assumed that its dynamic modulus, $\underline{E_i}$, is proportional to the dynamic modulus of the recycled rubber, $\underline{E_{RR}}$:

$$\underline{E_i} = \kappa \underline{E_{RR}} = \kappa\lambda \underline{E_{VR}} \tag{3a}$$

where κ is the dimensionless interphase modulus coefficient. Besides, its thickness, t_i, is normalized to the equivalent thickness of platelet, t_e, by defining the dimensionless β coefficient:

$$\beta = t_i/t_e \tag{3b}$$

It is noted that both κ and β coefficients are related to the degree of cross linking and the presence of surfactants in case of surface functionalization. Consider a recycled rubber with the density of ρ_{RR} and the average length of polymeric chains of $\bar{L}_{RR}$ reinforced by a nano platelet whose surface may be covered by an organic modifier with the density of ρ_{mod}, and the average length of polymeric chains of $\bar{L}_{mod}$ resulting in formation of an interphase zone. It is assumed that the modifier has occupied a fraction of $0 < \phi_{mod} < 1$ of the total surface of the nano platelet. Fig. 2 schematically depicts the interaction of the components in the interphase zone. The density of interphase zone is defined as the weighted summation of the density of recycled rubber and the modifier as the modifier chains penetrate in the intermediate spaces of recycled rubber:

$$\rho_i = (\rho_{RR} + \phi_{mod}\rho_{mod}) \tag{4a}$$

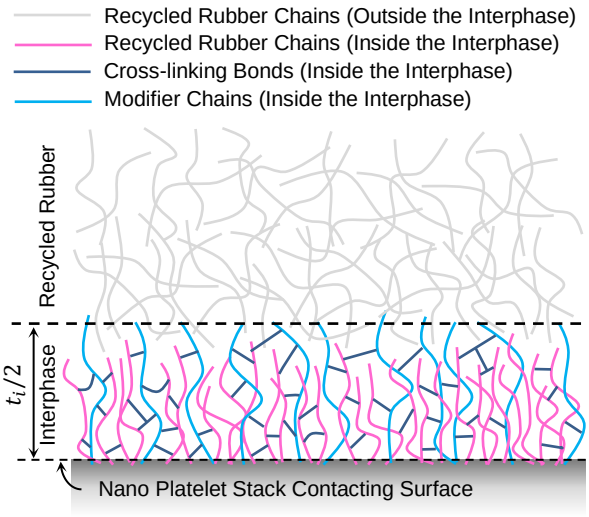

Figure 2. The schematic representation of components within the interphase zone.

Then, making an analogy between the network of molecular chains topology in the interphase and a random 3D cellular solid, the relationship between the density and the modulus of interphase is suggested through a power law equation (Robisson, 2010). In addition, the effect of degree of cross-linking on the complex modulus is taken into account by introducing the cross-liking coefficient, C_κ:

$$\underline{E_i} = \underline{E_{RR}} C_\kappa \left(\frac{\rho_i}{\rho_{RR}}\right)^m \tag{4b}$$

Comparing to Eq. (3a), the interphase modulus coefficient, κ, is:

$$\kappa = C_\kappa(1 + \phi_{mod}\hat{\rho}_{mod})^m \tag{4c}$$

in which, $\hat{\rho}_{mod} = \rho_{mod}/\rho_{RR}$ is the normalized density of modifier with respect to the recycled rubber matrix.

For the thickness of the interphase, t_i, a minimum thickness of t_0 corresponding to a nano platelet without surface modifier is assumed. A term representing the effect of surface modifier is added to this minimum which is suggested to grow by increasing the normalized density, $\hat{\rho}_{mod}$, and the normalized length of modifier chains with respect to the recycled rubber monomer, $\hat{L}_{mod} = \bar{L}_{mod}/\bar{L}_{RR}$, keeping in mind the fact that the thickness of interphase is proportional to the moment of inertia of the polymeric chains. Besides, the expansion coefficient, C_β, is introduced as a fitting parameter that can tune the degree of expansion of interphase due to the modifier. In a dimensionless sense, according to Eq. (3b), the dimensionless thickness coefficient, β, is:

$$\beta = \beta_0 + C_\beta \phi_{mod}\hat{\rho}_{mod}\left(\hat{L}_{mod}\right)^p \tag{4d}$$

where $\beta_0 = t_0/t_e$. In the proposed analytical formulation for the modulus and the thickness of the interphase, the

cross-linking coefficient, C_κ, the modifier expanding coefficient, C_β, and the powers m, and p remain as the calibrating parameters when the experimental and/or molecular simulations are available. Note that the modulus and the thickness of interphase for the nano platelets without surface modification can be obtained from Eqs. (4a) to (4d) by setting ϕ_{mod}=0, as $\kappa = C_\kappa$, and $\beta = \beta_0$.

Before homogenization of the nanocomposite, it is necessary to clarify the definition of the volume fractions within the recycled rubber, which should not be confused with the overall volume fractions of all components in the final blend. If the volume fraction of stand-alone nano platelets in the recycled rubber is v_p, the equivalent volume fraction of the platelet, v_e, and similarly the volume fraction of the stacks, v_s, are higher than v_p due to gallery space:

$$v_s = v_e = v_p(t_e/t_p) \tag{5a}$$

However, the volume fraction of the interphase zone is affected by the number of platelets in the stack, n, and in other words by the degree of exfoliation, as schematically demonstrated in Fig. 3 for $n = 5$. The maximum volume fraction of the interphase happens when the platelets are fully exfoliated, $n = 1$, corresponds to the maximum total contact surface between the platelets and the recycled rubber, and the volume fraction is inversely proportional to the number of platelets in the stack, n:

$$v_i = \frac{(t_i/t_e)v_s}{n} = \frac{\beta}{n}v_s \tag{5b}$$

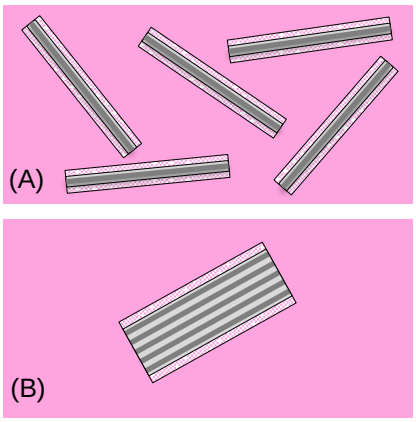

Figure 3. The effect of exfoliation of the platelets on the volume fraction of the interphase. (A) a fully exfoliated mixture with the maximum of interphase volume fraction, (B) Reduction in the volume fraction of interphase in an intercalated mixture with *n*=5 platelet in every stack.

Note that the maximum possible value for the volume fraction of the interphase, v_i^{max}, happens when the recycled rubber as the matrix is completely converted to the interphase. It means that:

$$v_i^{max} = 1 - v_s = 1 - v_p(t_e/t_p) \tag{5c}$$

Having v_i from Eq. (5b), the volume fraction of the effective reinforcement, v^*, consisting of the stack and the interphase can be obtained:

$$v^* = v_s + v_i = v_s(1 + \beta/n) = v_p(t_e/t_p)(1 + \beta/n) \tag{5d}$$

In addition, as the thickness of effective reinforcement is $t^* = t_s + t_i$, its aspect ratio, α^*, is calculated as:

$$\alpha^* = \frac{l}{t^*} = \frac{l}{t_e(n+\beta)} = \frac{\alpha_e}{(n+\beta)} \tag{5e}$$

Now, the second step of homogenization is applied to introduce the dynamic modulus of the effective reinforcement, $\underline{E}^*$, again by implementing the direct rule of mixture:

$$\underline{E}^* = \frac{v_s\underline{E}_s + v_i\underline{E}_i}{v^*} \tag{5f}$$

Substituting from Eqs. (3a), (5b), and (5d) gives:

$$\underline{E}^* = \frac{\underline{E}_s + (\beta/n)\kappa\lambda\underline{E}_{YR}}{1 + (\beta/n)} \tag{5g}$$

If $\hat{E}_s = \underline{E}_s/\underline{E}_{YR} \gg 1$, that is the modulus of the virgin rubber is insignificant in comparison to the stack of nano platelet, it simplifies to:

$$\underline{E}^* \cong \frac{\underline{E}_s}{1 + (\beta/n)} \tag{5h}$$

The dimensionless effective modulus, $\hat{E}^* = \underline{E}^*/\underline{E}_{YR}$, is obtained by normalizing the effective modulus with respect to the modulus of virgin rubber:

$$\hat{E}^* = \frac{\hat{E}_s + (\beta/n)\kappa\lambda}{1 + (\beta/n)} \tag{5i}$$

The third step of homogenization employs the H-T equation to evaluate the modulus of nanocomposite, $\underline{E}_{nc}$, where the matrix is the recycled rubber with the modulus of $\underline{E}_{RR}$ and the inclusion is the effective reinforcement with the modulus of $\underline{E}^*$, the volume fraction of v^*, and the aspect ratio of α^*. The H-T model has long been popular for predicting properties of nano platelets polymer nanocomposites because of its validity over a wide range of elastic (Tucker and Liang, 1999) and viscoelastic (Suarez *et al*., 1986) properties and filler volume fractions. As a semi-empirical approach, H-T is developed as a simple equation based on elasticity theories (Chow and Hermans, 1969; Hill, 1965) by introducing a curve fitting parameter carry physical meaning. With the fitting parameter of $2\alpha^*$, the modulus of nanocomposite consisting of randomly oriented effective reinforcements within a recycled rubber matrix can be estimated as (Fornes and Paul, 2003):

$$\underline{E}_{nc} = \omega_1 \left(\underline{E}_{nc}\right)^A + \omega_2 \left(\underline{E}_{nc}\right)^T \quad (6a)$$

where ω_1 and ω_2 are the coefficients obtained from averaging over the orientation. For platelets randomly oriented in a 3D space, ω_1=0.49, and $\omega_2 = 0.51$, however, for simplicity of following analytical formulation, it is assumed that ω_1=ω_2=0.5. In Eq. (6a), the terms $\left(\underline{E}_{nc}\right)^A$ and $\left(\underline{E}_{nc}\right)^T$ are the modulus of a nanocomposite with aligned effective reinforcements along the axial and the transverse directions, respectively, as follows:

$$\left(\underline{E}_{nc}\right)^A = \underline{E}_{RR}\left(\frac{1 + 2\alpha^* v^* \eta_A^*}{1 - v^* \eta_A^*}\right) \quad (6b)$$

$$\left(\underline{E}_{nc}\right)^T = \underline{E}_{RR}\left(\frac{1 + 2v^* \eta_T^*}{1 - v^* \eta_T^*}\right) \quad (6c)$$

$$\eta_A^* = \frac{\left(\hat{E}^*/\lambda\right) - 1}{\left(\hat{E}^*/\lambda\right) + 2\alpha^*}, \qquad \eta_T^* = \frac{\left(\hat{E}^*/\lambda\right) - 1}{\left(\hat{E}^*/\lambda\right) + 2} \quad (6d)$$

or in a dimensionless normalized form of $\hat{E}_{nc} = \underline{E}_{nc}/\underline{E}_{VR}$ one can rewrite Eq. (6a) as:

$$\hat{E}_{nc} = 0.5\lambda\left[\left(\frac{1 + 2\alpha^* v^* \eta_A^*}{1 - v^* \eta_A^*}\right) + \left(\frac{1 + 2v^* \eta_T^*}{1 - v^* \eta_T^*}\right)\right] \quad (6e)$$

For the special case where $\hat{E}^* \gg 1$, $\alpha^* \gg 1$, and $v^* \ll 1$, it simplifies to:

$$\hat{E}_{nc} \cong \lambda\left(1 + \frac{\alpha^* \hat{E}^*}{\hat{E}^* + 2\lambda\alpha^*} v^*\right) \quad (6f)$$

It is worth mentioning that Eq. (6f) suggests a linear variation of the modulus of nanocomposite with respect to the volume fraction of effective reinforcement, v^*.

Finally, as a nested composite, the fourth step of homogenization is applied to find the modulus of the final rubber blend, $\underline{E}$, where the base rubber with the modulus of $\underline{E}_{BR}$ is the matrix with the volume fraction of v_{BR}, and the nanocomposite with the modulus of $\underline{E}_{nc}$ plays the role of inclusion with the volume fraction of v_{nc}. Note that $v_{nc} + v_{BR} = 1$. Again, a standard H-T equation is implemented with the fitting parameter equals to 2, supporting the assumption of an average spherical shape (aspect ratio equals to one) for the nanocomposite inclusions, see Fig. 1(A).

$$\underline{E} = \underline{E}_{BR}\left\{\frac{1 + 2v_{nc}\eta_{nc}}{1 - v_{nc}\eta_{nc}}\right\} \quad (7a)$$

$$\eta_{nc} = \frac{\left(\underline{E}_{nc}/\underline{E}_{BR}\right) - 1}{\left(\underline{E}_{nc}/\underline{E}_{BR}\right) + 2}, \quad (7b)$$

Considering the normalized modulus of the base rubber, $\hat{E}_r = \underline{E}_{BR}/\underline{E}_{VR}$, and the final blend, $\hat{E} = \underline{E}/\underline{E}_{VR}$ with respect to the virgin rubber, one can obtain the dimensionless form of Eq. (7a) and (7b) as:

$$\hat{E} = \hat{E}_r\left(\frac{1 + 2\hat{\eta}_{nc} v_{nc}}{1 - \hat{\eta}_{nc} v_{nc}}\right) \quad (7c)$$

$$\hat{\eta}_{nc} = \frac{\left(\hat{E}_{nc}/\hat{E}_r\right) - 1}{\left(\hat{E}_{nc}/\hat{E}_r\right) + 2} \quad (7d)$$

As the modulus of nano platelets is significantly greater than of rubber, increasing its volume fraction, v_p, will result in stiffening of the recycled rubber. Hence, it is possible to find a critical volume fraction of v_p^{cr} corresponding to a critical volume fraction of effective reinforcement, v_{cr}^*, where the modulus of reinforced recycled rubber is equal to the modulus of the base rubber, $\underline{E}_{nc} = \underline{E}_{BR}$, and consequently the modulus of final blend is identical to the base rubber, $\underline{E} = \underline{E}_{BR}$. Regarding Eq. (7), in terms of dimensionless parameters, it happens where $\hat{\eta}_{nc} = 0$, and $\hat{E}_{nc} = \hat{E}_r$. For the volume fractions higher than the critical value, $v^* > v_{cr}^*$ the reinforced recycled rubber acts as a stiffener while for $v^* < v_{cr}^*$ it reduces the modulus of the final blend with respect to the base rubber regardless of volume fractions, v_{nc}. This critical volume fraction can be obtained by replacing $\hat{E}_{nc}$ by $\hat{E}_r$ in Eq. (6e) and solving for v^* which results in a quadratic equation with the following roots:

$$v_{cr}^* = \frac{-c_2 \pm \sqrt{c_2^2 - 4c_1c_3}}{2c_1} \qquad 0 < v^* < 1 \quad (8a)$$

where

$$c_1 = 2\eta_A^*\eta_T^*\left(\frac{\hat{E}_r}{\lambda} + \alpha^* + 1\right) \quad (8b)$$

$$c_2 = -\left(\frac{2\hat{E}_r}{\lambda}\left(\eta_A^* + \eta_T^*\right) + \eta_A^*(2\alpha^* - 1) + \eta_T^*\right) \quad (8c)$$

$$c_3 = 2\left(\frac{\hat{E}_r}{\lambda} - 1\right) \quad (8d)$$

For $\hat{E}^* \gg 1$, $\alpha^* \gg 1$, and $v^* \ll 1$, from Eq. (6f):

$$v_{cr}^* = c_3 \frac{\hat{E}^* + 2\lambda\alpha^*}{2\alpha^*\hat{E}^*} \quad (8e)$$

As seen in Eqs. (8a) to (8e), the critical volume fraction is directly related to the modulus ratio of the base rubber to the virgin rubber, $\hat{E}_r$. When $\hat{E}_r > 1$, the virgin rubber is naturally softer than the base rubber and the nanofiller is responsible for compensating modulus due to both intrinsic softening and the one from recycling. In contrast, when

$\hat{E}_r < 1$, the virgin rubber is naturally stiffer than the base rubber and the quality of recycling, λ, play the main role. In this way, there is a critical value for the recycling quality parameter, λ_{cr}, where the recycled rubber is as stiff as the base rubber:

$$\underline{E}_{RR} = \underline{E}_{BR} \rightarrow \lambda_{cr} = \hat{E}_r \qquad (8f)$$

One should notice that for $\lambda = \lambda_{cr}$, the coefficient c_3 equals zero which results in $v_{cr}^* = 0$ for both Eqs. (8a) and (8e), which means no need for reinforcing nanofillers as expected.

The inverse solution of the proposed micromechanics model can be obtained which may be of interest when looking for the modulus of the interphase (see Appendix).

3. RESULTS AND DISCUSSION

In this section, the proposed micromechanics model is applied for predicting the properties of rubber blends of a base rubber filled with a nanocomposite consisting of devulcanized recycled rubber reinforced by nano inclusions. First, a parametric investigation is presented where the dimensionless results in form of graphs can be considered as a design guideline in rubber industries like automotive. Then, a practical case study on recycled rubbers obtained from end-of-life tires (ELTs) filled with nano clays is performed to demonstrate the potential of nano platelets for enhancing the properties of recycled rubbers before blending with a raw base rubber. It is shown that this approach can be considered as a solution to technical issues against further use of this material in manufacturing high-quality rubber products in automotive industries.

Fig. 4 shows the effect of adding nano fillers on the normalized modulus of reinforced recycled rubber with respect to its virgin counterpart, $\hat{E}_{nc}$, for different quality of devulcanization treatment, from low, $\lambda = 0.1$, to high, $\lambda = 1$, corresponding to the first H-T homogenization for nanocomposite presented in Eqs. (6a) to (6f). The normalized modulus of effective reinforcement and its aspect ratio is assumed, $\hat{E}^* = 1000$, and $\alpha^* = 100$. It is seen that every plot starts at $\hat{E}_{nc} = \lambda$, where there is no reinforcement, $v^* = 0$, and rises by increasing the volume fraction of effective reinforcement. For the ideal case of devulcanization, $\lambda = 1$, the modulus is always higher than the virgin, $\hat{E}_{nc} \geq 1$, while for the realistic devulcanization, $\lambda < 1$, a minimum of reinforcement is needed to recover the lost modulus of virgin rubber where $\hat{E}_{nc} = 1$. The shaded area determines the whole wide space of design for the modulus of reinforced recycled rubber. Fig. 5 compares the exact, Eq. (6e), and the approximate, Eq. (6f), equations for the modulus of reinforced recycled rubber nanocomposite for different aspect ratios of effective reinforcement, α^*.

Fig. 6 depicts the second H-T homogenization for the final blend of the nanocomposite with the base rubber formulated in Eqs. (7a) to (7d). The normalized modulus of the final blend, $\hat{E}$, with respect to the volume fraction of nanocomposite, v_{nc}, is plotted for different modulus of nanocomposite with respect to the base rubber, $\hat{E}_{nc}/\hat{E}r$ (Note that the ratio $\hat{E}_{nc}/\hat{E}r$ equals to E_{nc}/E_{BR} by cancelling $\underline{E}_{YR}$).

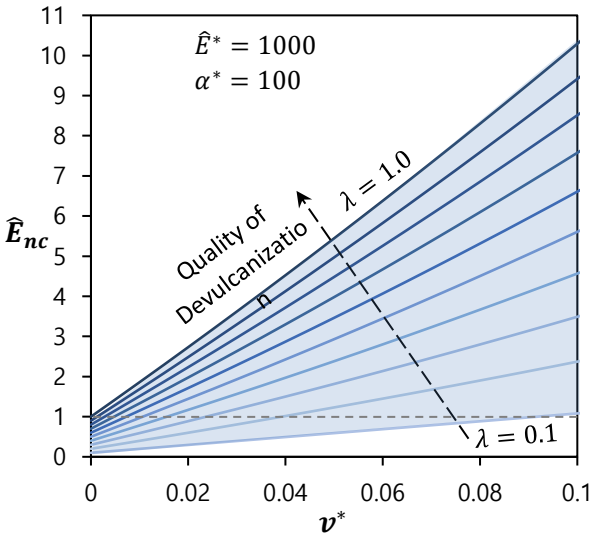

Figure 4. The effect of efficiency of devulcanization on the variation of normalized modulus of reinforced recycled rubber (nanocomposite) with respect to virgin rubber, $\hat{E}_{nc}$, versus the volume fraction of effective reinforcement, v^*.

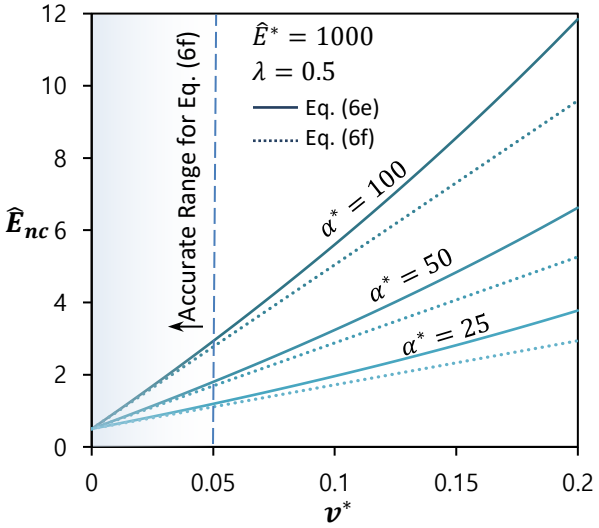

Figure 5. The comparison between the exact, Eq. (6e), and the approximate, Eq. (6f), equations for the modulus of reinforced recycled rubber (nanocomposite).

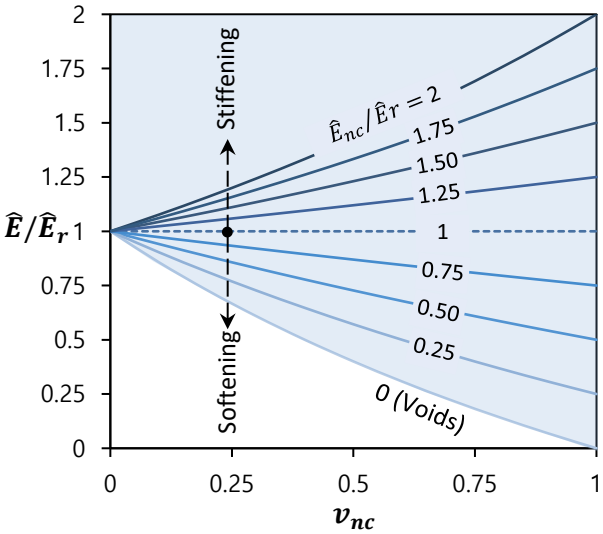

Figure 6. The variation of normalized modulus of final blend with respect to the volume fraction of the nanocomposite as the final step of homogenization.

It is seen that the assumption of linear increase in the modulus with respect to the volume fraction of nanofiller suggested in Eq. (6f), shows an acceptable accuracy when $v^* < 0.05$ and the error increases by increasing v^*.

It is observed that for $(\hat{E}_{nc}/\hat{E}r) < 1$ the nanocomposite acts as a softener while for $(\hat{E}_{nc}/\hat{E}r) > 1$ it will enhance the modulus of blend as a reinforcement. The design space (shaded area in the graph) is limited by the lower bound $(\hat{E}_{nc}/\hat{E}r) = 0$ where the modulus of the recycled rubber is insignificant, in other words, when the recycled rubber inclusions behave as voids in the blend.

Fig. 7 illustrates the critical volume fraction of the effective reinforcement, v^*, as a function of quality of devulcanization, λ. In Figs. (7A) and (7B) it is assumed that the virgin and the base rubber are identical, $\hat{E}_r = 1$, and the effective aspect ratio, α^*, and the normalized modulus of effective reinforcement, E^*, are investigated, respectively, while Fig. (7C) demonstrates the case of different properties of virgin and base rubbers, $\hat{E}_r \neq 1$. It is seen that increasing both effective aspect ratio and modulus reduces the critical amount of nanofiller to keep the modulus of final blend equal to the base rubber. Besides, increasing the quality of devulcanization, λ, dramaticaly drops the critical volume fraction (tending to zero when $\hat{E}_r = 1$ for the ideal case of $\lambda = 1$).

From Fig. (7C) it is observed that for $\hat{E}_r = 1.5$ where the virgin rubber is softer than the base rubber a critical volume fraction of nanofiller is needed even for the ideal devulcanization. However, for $\hat{E}_r = 0.5$, the virgin rubber is naturally stiffer and according to Eq. (8f) for $\lambda < \lambda_{cr}$ adding nanofillers are requested while for $\lambda > \lambda_{cr}$ the blend is stiffer than the base rubber even without the nano

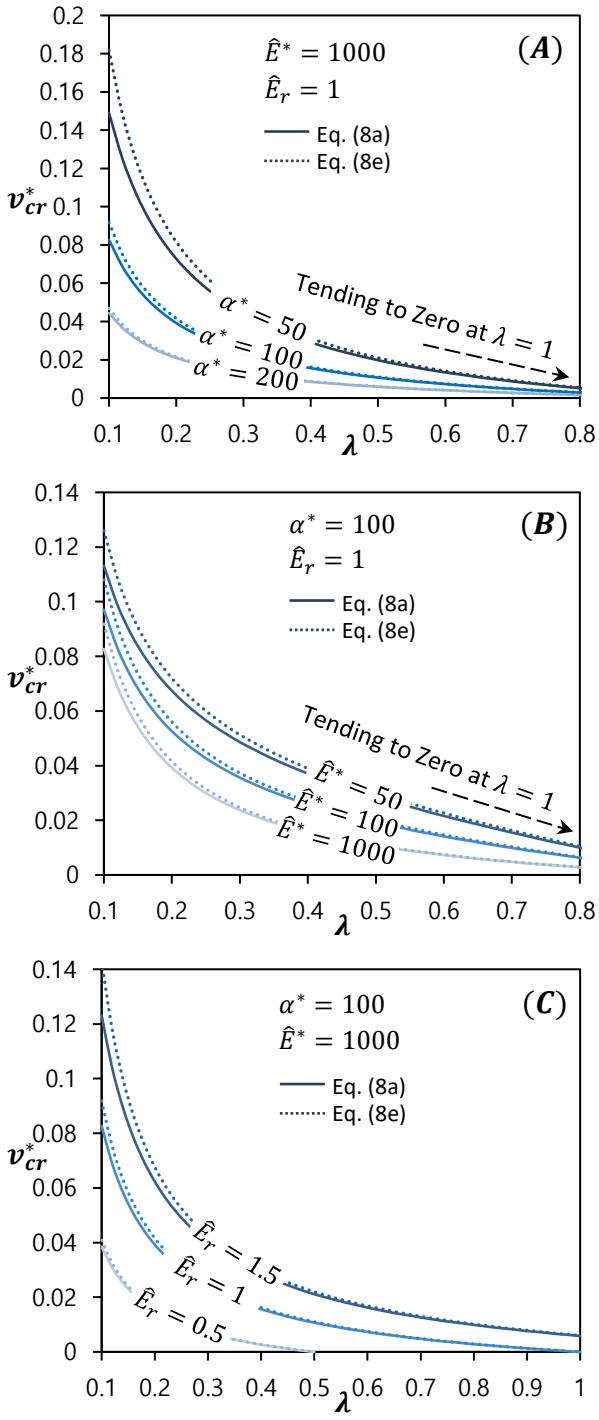

Figure 7. The critical volume fraction of effective reinforcement versus the quality of devulcanization for variation of (A) the effective aspect ratio, (B) the modulus of effective reinforcement, (C) the normalized modulus of the base rubber.

reinforcement. In this case, to keep the modulus of blend equal to the base rubber, softenning additives should be

used in the blend. It is noted that the proposed approximate equation for v^* in Eq. (8e) provides accurate enough estimation especially when the quality of devulcanization is high ($\lambda > 0.5$).

After the dimensionless parametric investigations, a practical case study on the recycled rubbers obtained from ELTs is presented. Nano clays, which are well-known in automotive industry, are selected as the nano reinforcement. In spite of general complex form of the developed model, the case study is limited to the the real part of the modulus, i.e., storage modulus, which is shown by the same parameters, however, without underline. It is assumed that the virgin and the base rubber are identical with the equal storage modulus of $E_{VR} = E_{BR}$ =10 MPa, and an average devulcanization quality, $\lambda = 0.5$, is selected resulting in the storage modulus of the recycled rubber, E_{RR}=5 MPa. The nanofiller is assumed to be a typical clay with the thickness of t_p=1 nm, the gallery space of t_g=0.5 nm, length of l=100 nm, and density of ρ_p =3000 Kg/m^3 (Jlassi *et al.*, 2017), resulting in the modulus of E_p=190 GPa according to the semi-empirical equation E_p(GPa) = 0.189ρ_p (Kg/m^3) – 377, suggested by (Chen and Evans, 2006). Regarding the surface functionalization, two cases named the Bare-Clay (unmodified), and the Organo-Clay (surface modified) are considered. For the latter, a typical organic modifier covering 50% of the clay surface, ϕ_{mod} =0.5, with the density of ρ_{mod}=700 Kg/m^3 comparing to the density of recycled rubber, ρ_{RR}=1440 Kg/m^3 resulting in $\hat{\rho}_{mod}$=0.614, and the normalized length of molecular chain, $\hat{L}_{mod}$=3, is selected. The fitting parameters are set as follows: The crosslinking coefficient C_κ is set to 2, which means cross-linking increases the modulus by 100% in the interphase zone. The power m in Eq. (4b) is set to 2, considering an analogy between the structure of cross-linked polymeric chains in the interphase and a 3D open-cell porous structure. In Eq. (4d), the minimum dimensionless thickness of the interphase is β_0=2, taking a minimum thickness in every side of clay equals to the equivalent thickness of clay, ($t_0/2) = t_e$, even without any modifications, and the power p is set to 2, considering an analogy between the moment of inertia of the modifier molecular chains and the moment of inertia of a bar, which is proportional to the square of its length. The interphase expansion coefficient, C_β, is set to 1.

According to Eqs. (4c) and (4d), these selection results in the dimensionless parameters of interphase, κ=2, and 3.42, and β =2, and 4.76, for the Bare-Clay, and the Organo-Clay, respectively. Furthermore, to take into account the quality of dispersion, three different scenarios, i.e., exfoliated (n=1), intercalated (n=5), and agglomerated (n=10) are defined.

Therefore, six cases of study (three different dispersions for two different modifications) are introduced which are compared in Fig. 8 by plotting the storage modulus ratio of blend to base rubber, E/E_{BR} (equivalent to the dimensionless form of $\hat{E}/\hat{E}_r$), with respect to the volume fraction of nano clay, v_p. One can conclude that the quality of dispersion of nano clays in the recycled rubber has a remarkable influence on the storage modulus of final blend since by increasing the number of nano platelets in stacks, the reinforcing effect dramatically drops. It is also observed that the surface modified Organo-Clays present higher enhancing effect which is more noticeable when the nano clays are exfoliated, n=1. It is of interest to mention that surface modification improves the quality of dispersion, therefore, the case of exfoliated Bare-Clay is difficult to achieve in practice.

Finally, Fig. 9 depicts the effect of volume fraction of nanocomposite, v_{nc}, reinforced by Organo-Clay on the storage modulus of the final blend for exfoliated, intercalated, and agglomerated dispersion qualities. It is seen that for the volume fraction of nano clays lower than the critical value, v_p^{cr}, the nanocomposite behaves as a softener and hence, increasing its volume fraction diminish the storage modulus of final blend, while the effect is opposite when $v_p > v_p^{cr}$. Besides, Comparing Figs. (9A), (9B), and (9C), reveals that by reducing the quality of dispersion due to agglomeration of nano clays in the stacks, the critical volume fraction of nano clays, v_p^{cr} increases, which are 0.008, 0.035, 0.06 for exfoliated, intercalated, agglomerated, respectively. The shaded area in the graphs specifies the design space for the storage modulus of final blend while it is filled 50% with the recycled rubber in maximum ($0 < v_{nc} < 0.5$), confirming the potential of concept of nano reinforcement for tuning the properties of the rubber blends including recycled rubbers.

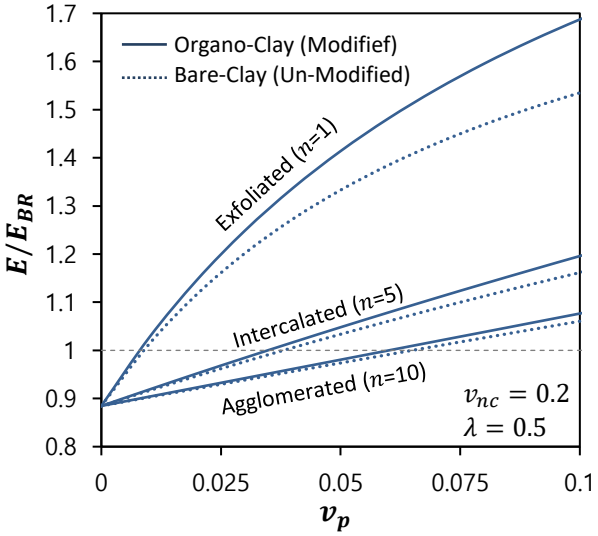

Figure 8. The effect of surface modification and the quality of dispersion of nano clays on the reinforcement of final rubber blend.

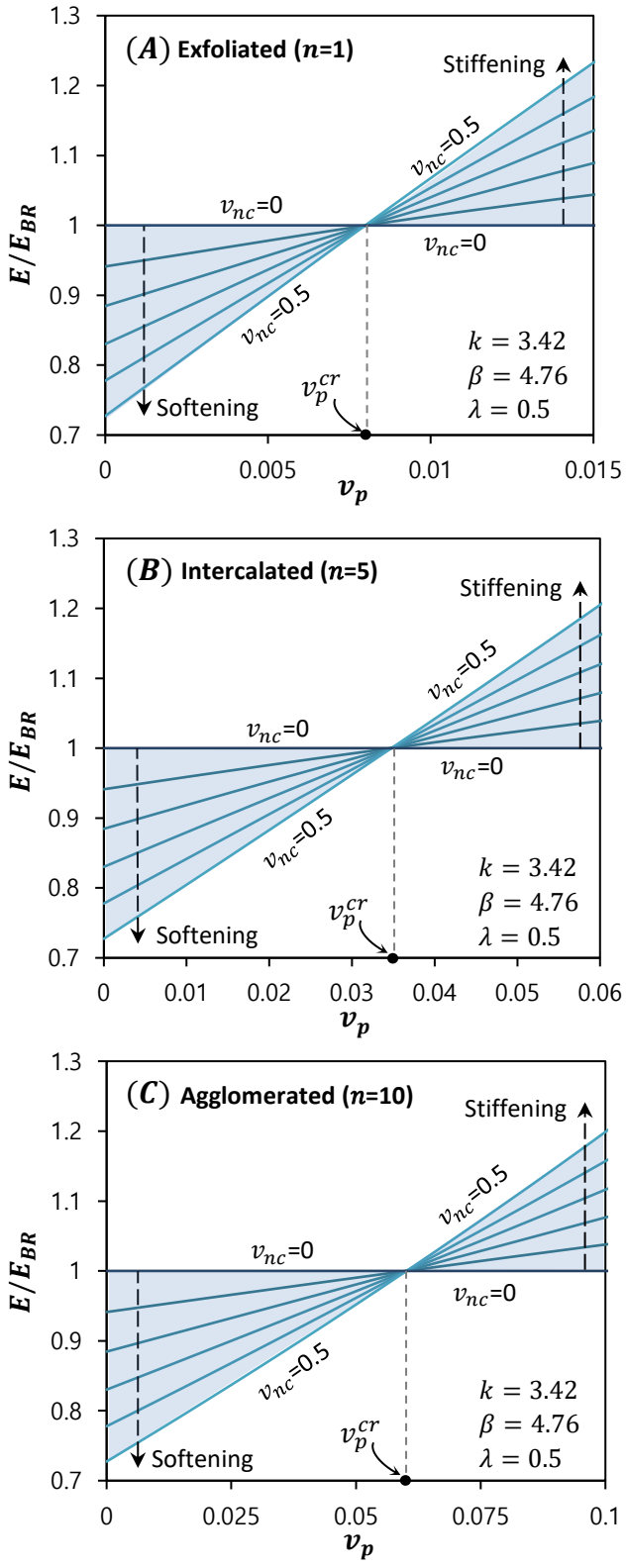

Figure 9. The effect of volume fraction of nanocomposite, v_{nc}, reinforced by Organo-Clay on the storage modulus of the final blend. (A) exfoliated, n=1, (B) intercalated, n=5, (C) agglomerated, n=10.

4. CONCLUSIONS

- An analytical framework is presented for evaluating the modulus of the rubber blends containing a devulcanized recycled rubber reinforced by nanofillers to enhance its lost performance due to the vulcanization-devulcanization treatments compares to its virgin properties.
- Generally, it is concluded that adding proper contents of nanofillers within the devulcanized recycled rubber can countervail its weakness and even enhance its modulus to play a reinforcing role when is blended with a base rubber.
- A practical case study on the recycled rubbers obtained from ELTs filled with nano clays, which are well-known in automotive industry, is presented and the effect of surface modification of nano clays as well as the quality of dispersion is investigated.
- A simple approximation and an inverse solution for evaluting the properties of interphase is proposed.
- The outcomes of this study can be used as a design guideline for practical cases in the industries which are widely using rubber blends like automotives to increase the use of devulcanized recycled rubber for manufacturing high-quality products.

ACKNOWLEDGEMENT–This work was supported by The LIFE programme, Project Title: High performance devulcanized masterbatches for End-of-Life Tire reuse in high-volume technical compounding applications (LIFE GREEN VULCAN, LIFE19 ENV/IT/000213). https://www.lifegreenvulcan.eu/.

REFERENCES

Asaro, L. *et al.* (2018). Recycling of rubber wastes by devulcanization. *Resour. Conserv. Recycl.*, **133**, **February**, 250–262.

Bockstal, L. *et al.* (2019). Devulcanisation and reclaiming of tires and rubber by physical and chemical processes: A review. *J. Clean. Prod.*, **236**, 117574.

Brune, D. A. and Bicerano, J. (2002). Micromechanics of nanocomposites: comparison of tensile and compressive elastic moduli, and prediction of effects of incomplete exfoliation and imperfect alignment on modulus. *Polymer (Guildf).*, **43**, **2**, 369–387.

Chen, B. and Evans, J. R. G. (2006). Elastic moduli of clay platelets. *Scr. Mater.*, **54**, **9**, 1581–1585.

Chow, T. S. and Hermans, J. J. (1969). The Elastic Constants of Fiber Reinforced Materials. *J. Compos. Mater.*, **3**, **3**, 382–396.

Dong, Y. and Bhattacharyya, D. (2010). A simple micromechanical approach to predict mechanical behaviour of polypropylene/organoclay

nanocomposites based on representative volume element (RVE). *Comput. Mater. Sci.*, **49**, **1**, 1–8.

Fathy, E. S. *et al.* (2018). Gamma irradiation of (styrene butadiene rubber)/(devulcanized waste rubber) blends modified by organoclay. *J. Vinyl Addit. Technol.*, **24**, **1**, 50–57.

Fedeliński, P. and Górski, R. (2015). Optimal arrangement of reinforcement in composites. *Arch. Civ. Mech. Eng.*, **15**, **2**, 525–531.

Fornes, T. D. and Paul, D. R. (2003). Modeling properties of nylon 6/clay nanocomposites using composite theories. *Polymer (Guildf).*, **44**, **17**, 4993–5013.

Fu, S. *et al.* (2019). Some basic aspects of polymer nanocomposites: A critical review. *Nano Mater. Sci.*, **1**, **1**, 2–30.

Gao, C. *et al.* (2021). A static/dynamic micromechanical model of graphene-reinforced polymer matrix nanocomposites with consideration of the nanoscale interphase. *Mech. Mater.*, **157**, **March**, 103838.

Greco, A. (2020). FEM analysis of the elastic behavior of composites and nanocomposites with arbitrarily oriented reinforcements. *Compos. Struct.*, **241**, **October 2019**, 112095.

Hassanzadeh-Aghdam, M. K. and Jamali, J. (2019). A new form of a Halpin-Tsai micromechanical model for characterizing the mechanical properties of carbon nanotube-reinforced polymer nanocomposites. *Bull. Mater. Sci.*, **42**, **3**, 1–8.

Hill, R. (1965). Theory of mechanical properties of fibre-strengthened materials-III. self-consistent model. *J. Mech. Phys. Solids*, **13**, **4**, 189–198.

Hong, C. H. *et al.* (2005). POLYPROPYLENE/CLAY NANOCOMPOSITES FOR AUTOMOTIVE APPLICATIONS. *Int. J. Automot. Technol.*, **6**, **6**, 665–670.

Jlassi, K. *et al.* (2017). *Overview: Clay Preparation, Properties, Modification*. Elsevier Inc.

Kayalvizhi Nangai, E. and Saravanan, S. (2021). Synthesis, fabrication and testing of polymer nanocomposites: A review. *Mater. Today Proc.*, **xxxx**.

Li, Y. *et al.* (2011a). A closed-form, hierarchical, multi-interphase model for compositesDerivation, verification and application to nanocomposites. *J. Mech. Phys. Solids*, **59**, **1**, 43–63.

Li, Y. *et al.* (2011b). The effects of the interphase and strain gradients on the elasticity of layer by layer (LBL) polymer/clay nanocomposites. *Int. J. Solids Struct.*, **48**, **6**, 1044–1053.

Liu, Z. *et al.* (2016). An extended micromechanics method for probing interphase properties in polymer nanocomposites. *J. Mech. Phys. Solids*, **95**, 663–680.

Markl, E. and Lackner, M. (2020). Devulcanization technologies for recycling of tire-derived rubber: A review. *Materials (Basel).*, **13**, **5**.

Robisson, A. (2010). A simple analogy between carbon black reinforced rubbers and random three-dimensional open-cell solids. *Mech. Mater.*, **42**, **11**, 974–980.

Saputra, R. *et al.* (2021). Current progress in waste tire rubber devulcanization. *Chemosphere*, **265**.

Shokrieh, Z. *et al.* (2017). Simulation of stiffness of randomly-distributed-graphene/epoxy nanocomposites using a combined finite element-micromechanics method. *Mech. Mater.*, **115**, **May**, 16–21.

Tucker, C. L. and Liang, E. (1999). Stiffness predictions for unidirectional short-fiber composites. *Compos. Sci. Technol.*, **59**, 655–671.

Valentini, L. *et al.* (2016). Synergistic effect of graphene nanoplatelets and carbon black in multifunctional EPDM nanocomposites. *Compos. Sci. Technol.*, **128**, 123–130.

Zanchet, A. *et al.* (2012). Use of styrene butadiene rubber industrial waste devulcanized by microwave in rubber composites for automotive application. *Mater. Des.*, **39**, 437–443.

Zare, Y. (2016). Development of Halpin-Tsai model for polymer nanocomposites assuming interphase properties and nanofiller size. *Polym. Test.*, **51**, 69–73.

APPENDIX: INVERSE SOLUTION FOR THE MODULUS OF THE INTERPHASE

As the first backward step, the normalized modulus of the reinforced recycled rubber nanocomposite, $\hat{E}_{nc}$, is back calculated from Eq. (7) for a given modulus of blend $\hat{E}$:

$$\hat{E}_{nc} = \hat{E}_r \left(\frac{-\left(\hat{E}/\hat{E}_r\right)(2+v_{nc}) + 2(1-v_{nc})}{\left(\hat{E}/\hat{E}_r\right)(1-v_{nc}) - (1+2v_{nc})} \right) \quad \text{(A1)}$$

Second, the normalized modulus of effective reinforcement is obtained by solving Eq. (6 a-f) for $\hat{E}^*$ resulting in following solution as the root of the quadratic equation:

$$\hat{E}^* = \frac{-c_5 \pm \sqrt{c_5^2 - 4c_4c_6}}{2c_4} \quad \text{(A2)}$$

$$c_4 = -2\frac{\hat{E}_{nc}}{\lambda^3}\left(1-v^{*2}\right) + \frac{1}{\lambda^2}\left(-2(1+\alpha^*)v^{*2} + 2\alpha^* v^* + 2\right) \quad \text{(A3)}$$

$$c_5 = -4\frac{\hat{E}_{nc}}{\lambda^2}\left(-v^{*2} + \alpha^*(1 - v^*) + 1\right) + \frac{2}{\lambda}\left(2(1 + \alpha^*)v^{*2} + (2\alpha^* - 1)v^* + 2(1 + \alpha^*)\right) \quad \text{(A4)}$$

$$c_6 = -2\frac{\hat{E}_{nc}}{\lambda}\left(v^{*2} + 2(1 + \alpha^*)v^* + 4\alpha^*\right) - 2(1 + \alpha^*)v^{*2} + 2(1 - 3\alpha^*)v^* + 8\alpha^* \quad \text{(A5)}$$

For the special case presented by Eq. (6f), the modulus of effective reinforcement is obtained as:

$$\hat{E}^* = \frac{2\lambda\alpha^*\left(\frac{\hat{E}_{nc}}{\lambda} - 1\right)}{\alpha^* v^* - \left(\frac{\hat{E}_{nc}}{\lambda} - 1\right)} \quad \text{(A6)}$$

Having $\hat{E}^*$ from Eq. (A2) or (A6), the third and last step of back-calculation is to obtain the modulus of the interphase by solving Eq. (5i) for the dimensionless modulus parameter of interphase, κ:

$$\kappa = \frac{\hat{E}^*\left(1 + \frac{\beta}{n}\right) - \hat{E}_s}{\lambda\frac{\beta}{n}} \quad \text{(A7)}$$

Note that in the proposed back calculation it is assumed that the thickness of interphase, β, is known to reduce the degree of freedom to find a unique solution for the inverse problem.