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Erstveröffentlichung in / First published in:

Journal of Elastomers & Plastics. 2017, 49(7), S. 595 - 608 [Zugriff am: 15.08.2019]. SAGE journals. ISSN 1530-8006.

DOI: <https://doi.org/10.1177/0095244316677849>

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Journal of Elastomers & Plastics

2017, Vol. 49(7) 595–608

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DOI: 10.1177/0095244316677849

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Abstract

This work, conceived as a second step in the development of high-performance damping materials suitable for seismic application, describes the preparation and characterization of complex natural rubber-based composites containing hybrid nano- and conventional fillers. The cluster–cluster aggregation model was used to assess the apparent filler networking energy. The values obtained suggested that the presence of the hybrid nanofiller strengthens the filler networking. The same model was used to understand the mechanisms of energy dissipation. The damping coefficient was found to be in the sought range between 10% and 20% (at 0.5 Hz and high shear strain).

Keywords

Natural rubber, hybrid composites, carbon nanotubes, nanoclays, filler networking, energy dissipation

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Introduction

Base isolation technique, which implies isolation of the base of a structure from the ground by use of flexible devices (rubber bearings), placed between the superstructure and its foundations, is widely used nowadays to mitigate seismic effects. The function of the bearings is to reduce the translational natural frequency of the structure to a region well below that of most significant earthquake energy. The base isolated structure moves like a rigid body over its isolation system, and deformations and energy dissipation are mostly concentrated in the isolators. Thus, a seismic isolator must possess high vertical stiffness (to support the dead load of the superstructure), to be flexible in the horizontal plane (to allow for large relative displacements between the superstructures and the ground) and, preferably, to be able to dissipate energy.¹ The design procedures for seismic isolated buildings and bridges have matured over the last 40 years. Since then, the theoretical underpinning of the seismic isolation has been firmly established and the technology has been verified by extensive experimental work. The relevant material is covered in many technical reports, publications, and journal articles. Our intention here is not to give a detailed literature review. The interested reader may refer to, for example, the literature review by Taylor et al.,² Kelly and Naeim,³ and some recent publications.⁴

However, in spite of all this extensive work, seismic isolation technology is applied almost exclusively to large, expensive buildings housing sensitive internal equipment, for example, computer centers, chip fabrication factories, emergency operation centers, hospitals, and nuclear plants. The isolators used in these applications are large, expensive, and heavy. To extend this valuable earthquake-resistant strategy to common households and commercial buildings, it is necessary to reduce the costs and weight of the isolators. This can be done by the optimization of the rubber material, especially with emphasize on the use of the novel nanofillers and the results from the rapidly growing field of elastomer nanocomposites. For this purpose, it is necessary to change the approach from rather engineering insight of the macroscopic properties of the material covered in the available literature to a deeper bottom-up approach. If properties of the rubber are finely tuned and controlled, the bearings can provide protection without requiring additional mechanical devices to enhance damping or strengthen the structure.³

The implementation of novel nanofiller systems in elastomeric matrices is a subject of an intense research. The most investigated, thanks to their unique properties and with demonstrated abilities to enhance the mechanical properties of elastomers, are layered silicates^{5–12} and carbon nanotubes (CNT).^{13–16} Montmorillonite (Mt) is widely used due to its large availability, low cost, high surface area, and high cation exchange capacity. CNT, on their behalf, evoke great interest owing to their exceptional combinations of physical attributes such as high aspect ratio, large flexibility, low density, and superior electrical and thermal properties.¹⁷ Furthermore, the combination of these two nanofillers engenders synergism which results in their better dispersion.^{18–20} This in turn enhances the mechanical properties of the rubber, something that was confirmed in recent publications.^{21,22}

Therefore in our study,²² preceding this one, a series of natural rubber (NR)-based nanocomposites containing these two most exploited nanofillers, organo-montmorillonite (OMt) which layers were further expanded for better dispersion

(EOMt) and multiwall carbon nanotubes (MWCNT), were prepared. The thorough mechanical and morphological analyses confirmed that the obtained nanocomposites have superior properties. The optimum ratio of the nanofillers in this system was set to be 2 phr of MWCNT and 16 phr of EOMt. With these results, the goal of the first step in obtaining high-performance damping material suitable for seismic application, a material with excellent strength and elasticity, was achieved.

Because the nanofillers were added to the elastomer matrix in low quantities, they did not contribute much to the mechanism of energy dissipation, where the conventional reinforcing fillers, their networking, and their interaction with the matrix play the main role. Wang²³ suggested that breakdown and reformation of the filler network, accompanied by the releasing of the trapped rubber from filler network, causes an energy dissipation process during dynamic strain. This mechanism suggests that the Payne effect or strain dependence of dynamic modulus of filled rubber can serve as a measure of filler networking which originates from filler–filler interaction as well as polymer–filler interaction.²³

The goal of this work, conceived as a second step in the process of obtaining high-performance damping material suitable for seismic application, is to tune the $\tan \delta$ or damping coefficient of the material to a level between 10% and 20% (at 0.5 Hz and high shear strain), which is a precondition for the material to be classified as high damping.³

This is achieved by the addition of conventional fillers (different by nature) to the system containing the hybrid nanofiller with an optimum ratio of MWCNT and EOMt as obtained in the first step. The analysis of the dynamic mechanical properties was used to understand the reinforcing effect of the different combinations of fillers on the elastomeric matrix. The cluster–cluster aggregation (CCA) model was used to assess the apparent filler networking energy. Strain sweep measurements, carried out by applying cyclic deformations in the shear mode, were used to determine $\tan \delta$ and G' (storage) modulus. The CCA model was used to understand more deeply the Payne effect, the strain dependency of the storage modulus, which is considered to be one of the mechanisms of energy dissipation.

Experimental

Materials

The rubber compounds were based on NR using a Standard Malaysian Rubber grade 10. The OMt used was Nanofil 15 supplied from Süd-Chemie AG (Moosburg, Germany). Distearyl dimethylammonium chloride (QUAT) was used as an organic modifier. The density of this OMt was 1.8 g/cm^{-3} with an average particle size of $25 \text{ }\mu\text{m}$. CNTs, NC7000, a MWCNTs produced by catalytic carbon vapor deposition process, were supplied by NANOCYL S. A. (Belgium). They were 90% pure containing 10% metal oxides and had an average diameter of 9.5 nm and an average length of $1.5 \text{ }\mu\text{m}$. The stearic acid was purchased from ACROS Organics (Geel, Belgium) with 97% purity. The vulcanizing accelerators *N*-tert-butyl-2-benzothiazolesulphenamide (TBBS) and *N*-cyclohexyl-2-benzothiazolesulphenamide (CBS) were kindly provided from Rhein

Table 1. Formulation of the NR compounds.

Sample code	NR ^a	MWCNT	EOMt	N330	Ultrasil VN3
NR-gum	100	0	0	0	0
NR-h-CB40-S0	100	2	16	40	0
NR-h-CB20-S20	100	2	16	20	20
NR-h-CB0-S40	100	2	16	0	40
NR-CB58	100	0	0	58	0

MWCNT: multiwall carbon nanotubes; EOMt: expanded organo-montmorillonite; NR: natural rubber; CB: carbon black; ZnO: zinc oxide; 6PPD: *N*-(1,3-dimethylbutyl)-*N'*-phenyl-*p*-phenylenediamine; CBS: *N*-cyclohexyl-2-benzothiazolesulphenamide; TBBS: *N*-tert-butyl-2-benzothiazolesulphenamide.

^aMass of the ingredients was taken in parts per hundred of rubber (phr). The ingredients which amounts were kept constant were ZnO 5 phr, stearic acid 2 phr, 6PPD 1 phr, CBS 1.5 phr, TBBS 0.2 phr, and sulfur 1.5 phr.

Chemie Rheinau GmbH (Mannheim, Germany). The carbon black (CB) was Corax N 330 (ORION Engineered Carbons GmbH, Köln, Germany) and silica filler used was Ultrasil VN3 (Evonik Industries AG, Germany). Sulfur (S), *N*-(1,3-dimethylbutyl)-*N'*-phenyl-*p*-phenylenediamine (6PPD), and zinc oxide (ZnO) used in this study were of industrial grade.

Preparation of the hybrid rubber composites

The procedure of preparation of the EOMt by grinding OMt with stearic acid in weight ratio 1:1 is described in detail in the study by Rooj et al.²¹ For the compounds containing nanofillers, the MWCNTs were mixed with ethanol in a ratio 1:20 by weight to form a paste in order for their safe handling. Then, the batch composed of 100 phr NR and 10 phr MWCNT was mixed in an internal mixer (Haake Rheomix, Thermo Electron GmbH, Karlsruhe, Germany) at a fixed rotor speed of 60 r/min, at 90°C for 20 min. The ethanol evaporated during this stage of mixing. Afterwards, this masterbatch was diluted with NR to a target of 2 phr MWCNT and was mixed together with 16 phr of EOMt, N330, and Ultrasil VN3 (for both fillers content was varied from 0 to 40 phr), ZnO, 6PPD, and stearic acid in the internal mixer at 90°C with 60 r/min rotor speed for 10 min. For the compound containing only conventional filler, the NR was mixed together with 58 phr N330, ZnO, 6PPD, and stearic acid in the internal mixer at 90°C with 60 r/min rotor speed for 10 min. In the last step of the preparation, the vulcanization accelerators TBBS and CBS together with the sulfur were added in an open two-roll mill (Polymix 110 L, size: 203 × 102 mm²; Servitec GmbH, Wustermark, Germany) at 90°C. The milling was performed at 0.5 mm and later at 0.3 mm nip gap for 5 min. The formulations of NR compounds expressed as parts per hundred of rubber (phr) are shown in Table 1. The test samples were molded and cured to 2 mm thick plates by compression molding (150 kN) on an electrically heated hydraulic press at 150°C. The rubber samples were vulcanized up to their respective optimum cure time (t_{90}), previously determined with a vulcameter (Scarabaeus, Langgöns, Germany), and then stored for 24 h before the tests were performed.

Table 2. Physical properties of the NR-based compounds.

Compound	100% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
NR-gum	0.77 ± 0.08	2.04 ± 0.17	22.38 ± 4.32	632 ± 24
NR-CB58	3.44 ± 0.13	18.69 ± 0.61	27.39 ± 0.94	430 ± 8
NR-h-CB40-S0	3.42 ± 0.20	14.71 ± 0.85	26.68 ± 2.02	462 ± 32
NR-h-CB20-S20	2.59 ± 0.18	9.49 ± 0.62	28.15 ± 1.42	576 ± 16
NR-h-CB0-S40	2.32 ± 0.11	6.55 ± 0.32	27.16 ± 0.61	636 ± 18

NR: natural rubber; CB: carbon black.

Characterization

The state of the dispersion of the hybrid nanofillers in the rubber matrix was investigated using transmission electron microscopy (TEM) with the microscope JEM 2010 model (JOEL Ltd., Japan). The ultrathin sections of the samples were prepared by ultramicrotomy (Leica Ultracut UCT) at -120°C with a thickness of a section of 100 nm.

Tensile tests of cured samples were carried out using Zwick 1456 (model 1456, Z1010, Ulm, Germany) with a crosshead speed 200 mm/min.

Dynamic mechanical analysis (DMA) was performed on samples with dimensions $10 \times 35 \text{ mm}^2$ using a dynamic mechanical thermal spectrometer (model Eplexor-2000 N; Gabo Qualimeter, Ahlden, Germany) in the tension mode. Temperature sweep analysis was carried out using a constant frequency of 10 Hz in a temperature range of -80°C to $+80^{\circ}\text{C}$. For the measurement of the complex modulus (E^*), a static tensile load of 1% pre-strain was applied and then the samples were oscillated to a dynamic load of 0.5% strain. Measurements were performed with a heating rate of 2 K/min under liquid nitrogen flow.

Amplitude sweep measurements were also performed on Eplexor 2000 N in the shear mode at room temperature on circular samples with 10 mm diameter. The samples were oscillated at a constant frequency of 0.5 Hz to a double shear strain from 0% to 50%.

Results and discussion

The influence of the different combinations of fillers on the physical properties of the NR vulcanizates is given in Table 2. As obvious, the modulus values (stresses at 100% for M100 and 300% elongation for M300) significantly increase (347% for M100 and 816% for M300) in case when CB is loaded into compound. Then, the partial replacement of CB with the hybrid nanofiller causes a slight decrease in these moduli which continue to decrease with addition of silica.

On the contrary, the ultimate tensile properties show a different trend. A typical stress-strain plot of the vulcanizates is shown in Figure 1. The strength at break stays almost unchanged when CB is partially replaced with hybrid nanofiller and also stays unchanged while changing the ratio between the conventional fillers (CB and silica).

Figure 1. Stress–strain curves of NR-gum and different NR-based composites. NR: natural rubber.

This is due to the strong interaction of MWCNT with the NR matrix. In the study that preceded this one,²¹ the apparent polymer–filler interaction parameter B was calculated. This phenomenological parameter represents the relative increase in volume of the filler particle due to the adherent interface of the immobilized polymer matrix; the larger the relative increase in volume or value of B , the stronger the interfacial interaction between the polymer matrix and filler. For the nanocomposite containing MWCNT, a very high value of 27.6 was found which implies a very strong physical interfacial interaction between NR and MWCNT.²¹ This means that the MWCNT have the predominant role in the reinforcement due to the polymer–filler interaction. Even after addition of high quantity (40 phr) of silica without silane modifier, the tensile strength is as high as for NR-CB58 composite containing 58 phr CB and no hybrid filler. At the same time, the elongation at break increases for 7% when CB is partly replaced with the hybrid nanofiller, 34% for NR-h-CB20-S20 composite and 48% for NR-h-CB0-S40 composite. Due to the inorganic nature of the silica particles, they exhibit mainly physical adsorptions with the elastomeric matrix, and hence a higher mobility of the rubber chains.²⁴

To further analyze the reinforcing effect of the hybrid nano and conventional fillers on the elastomeric matrix, the DMA temperature sweep measurements were performed. Figure 2(a) shows the storage modulus (E') and Figure 2(b) the $\tan \delta$ values of the compounds as a function of the temperature.

It is observed that in the rubbery plateau, all the combinations of fillers significantly increase the E' values in comparison with the unfilled NR-gum. The curves for all filled compounds are almost overlapping with only slight changes; this suggests that the

Figure 2. Temperature dependence of the (a) storage modulus, E' , and (b) loss tangent, $\tan \delta$, of the NR-gum and NR-based composites. NR: natural rubber.

combination of hybrid nanofillers with the conventional fillers, regardless whether it is reinforcing CB or unmodified silica, gives the same reinforcing effect as if only 58 phr CB are used. This is valid even for the compound NR-h-CB0-S40 containing only silica and hybrid nanofiller. At the same time, almost the same reduction of $\tan \delta$ peak is observed (Figure 2(b)) for all compounds when the fillers are added, confirming a predominant role of the hybrid nanofiller in the polymer–filler interactions.

Since the breakdown and reformation of the filler network is considered to be one of the mechanisms of energy dissipation in filled rubber systems, we will try to assess this filler networking energy for the different combinations of fillers, by using the CCA model. This model contains the assumption of geometrical arrangements of subunits (resulting from the kinetical CCA) in particular filler network structures.²⁵ According to this model, the temperature or frequency dependence of the elastic modulus of the CCA clusters is governed by the immobilized, glassy polymer between adjacent filler particles and is given by that of a glassy polymer. This model of glassy polymer bridges between adjacent filler particles of the filler network yields a physical understanding of the temperature dependence of the Payne effect. It is generally known that the Payne effect decreases with the increasing temperature. In the high temperature range, well above the bulk transition temperature of the polymer system, an Arrhenius temperature behavior for the elastic modulus is expected one that is typically found for polymers in the glassy state. This Arrhenius like behavior, in a somewhat different interpretation, could be understood by referring it to the transition of the glassy polymer bridges between adjacent filler particles of the filler network, that is, the apparent filler networking energy. In Figure 4, the relationships between the natural logarithm of storage modulus, $\ln(E')$ of the different NR-based composites, and the inverse temperature far above the glass–rubber transition region (10^3T approximately $3.4\text{--}2.8 \text{ K}^{-1}$; corresponding T approximately $20\text{--}80^{\circ}\text{C}$) are presented. If the Krause assumption²⁶ that the dynamic modulus is proportional to number of sub unites (e.g. filler aggregates) is used, then the

Figure 3. Natural logarithm of the storage modulus as a function of reciprocal absolute temperature for the different NR compounds. NR: natural rubber.

straight lines obtained have a slope E_c/R , where E_c is the activation energy or, in our case, filler networking energy, and R is the gas constant.

For the NR-CB58 composite containing only CB, there is a one-slope linear relationship between $\ln(E')$ and the inverse temperature. For the composites containing the hybrid nanofiller, there are two distinct mechanisms with different activation energies. One that occurs below approximately 60°C (but still well above the bulk glass transition temperature of the polymer system) gives activation energies between 5.7 and 6.7 kJ/mol, which are within the range of the physical (van der Waals) interactions and correspond to the apparent filler networking energies; another, occurring above approximately 60°C, the temperature near the melting temperature of stearic acid, which was used as an expander of the galleries of OMt layers and is present with 8 phr in these composites²² and is probably connected to the phase transition of the stearic acid. The filler networking energies for the conventional fillers and for the different combinations of fillers are calculated from the slopes and presented in Figure 3. The filler networking energy for the composite containing only CB is 5.94 kJ/mol. The replacement of 18 phr of CB with the hybrid nanofiller increases the filler networking energy for 13%, so the NR-h-CB40-S0 composite have the highest filler networking energy of 6.72 kJ/mol and then it starts to decrease with increase of the silica content. What is interesting is that the NR-h-CB0-S40 composite, which contains hybrid nanofiller and only silica, has a filler networking energy close to the referent CB containing compound. This suggests that the presence of the nanofillers strengthens the filler networking.

Figure 4. TEM images of NR-h-CB40-S0 (a) and NR-h-CB0-S40 (b) with $\times 20,000$ magnification and NR-h-CB40-S0 (c) with $\times 40,000$ magnification. TEM: transmission electron microscopy; NR: natural rubber; CB: carbon black.

To get a visual impression of the distribution of the fillers throughout the NR matrix, we analyze the TEM micrographs presented in Figure 4. In Figure 4(a), the TEM image of the NR-CB40-S0 composite (containing only CB and hybrid nanofiller) are shown, and Figure 4(b) presents the TEM images of NR-CB0-S40 composite (containing only silica and hybrid nanofiller). From these images, we can conclude a good dispersion of the nanofillers up to individual nanoparticles (in case of MWCNT) or layer (in case of EOMt). This was also found for the nanocomposites in our previous study,²¹ and it was mainly attributed to the predispersion of MWCNT in ethanol, but also to the high viscosity of the rubber and occurrence of strong shearing forces during the process of mixing. This fine dispersion of the nanoparticles was not interrupted by the presence of the conventional fillers. Regarding the conventional fillers, a better dispersion of CB can be observed in Figure 4(a), which arises from the better interaction with the polymer matrix compared to the silica filler presented in Figure 4(b). Furthermore, we can conclude that individual nanotubes and individual mineral clay layers (indicated with white rectangles in Figure 4(c)) are bridging the conventional filler aggregates, strengthening the filler network. This supports the aforementioned idea of forming glassy polymer bridges of immobilized rubber in the vicinity of the filler particles, enhanced by the presence of the hybrid nanofiller, and hence the calculated higher filler networking energies.

In order to investigate how this influences the strain dependency of the storage modulus or Payne effect, as one of the mechanisms of dissipating energy, we performed strain sweep measurements in shear mode.

The loss factor ($\tan \delta$) or damping coefficient is reported in Figure 5 for the composites containing different combinations of fillers. $\tan \delta$ values for all samples are found to increase by increasing strain amplitude, reaching a maximum, and then start to decline due to the filler network break down and no longer existence of this mechanism of dissipating energy. The NR-CB58 and NR-h-CB40-S0 composites have the highest

Figure 5. Plot of loss factor $\tan \delta$ versus strain amplitude for different NR-based composites. NR: natural rubber.

values of loss factor, with the difference that NR-CB58 composite reaches the maximum value of loss factor at lower strain and then it starts to decline rapidly indicating lower stability of the filler network. For the composites containing hybrid nanofiller, the loss factor decreases with increase of silica content. The obtained damping coefficient for all composites lay between 10% and 20% (at 0.5 Hz and high shear strain). So, for all composites, the precondition for the material to be classified as high damping is fulfilled.² The referent NR-CB58 composite has the lowest damping coefficient of 12% and for all other composites is between 14% and 15%.

To understand deeply the Payne effect as mechanism of energy dissipation and describe this strain dependency of the storage modulus G' , we will use the same CCA model. It is convenient to consider $G'(\gamma_0)$ as a sum of two contributions $G'(\gamma_0) = \Delta G'(\gamma_0) + G'_\infty$, where $\Delta G'(\gamma_0)$ describes the strain dependency of G' that results from a breakdown of the filler network and G'_∞ is the rubber specific contribution including hydrodynamic amplifications due to the presence of the filler. The storage modulus, well above the percolation threshold, can be approximated by a function of the Havriliak-Negami type²⁵:

$$\Delta G'(\gamma_0) \cong \Delta G'_0 \left[1 + \left(\frac{\gamma_0}{\gamma_c} \right)^{2m} \right]^{-\tau} \quad (1)$$

Here, γ_c is the strain amplitude, where half of the clusters are broken, m being an empirical exponent, and $\tau \approx 3.6$ is the elasticity exponent of percolation.²⁷

Figure 6. Plot of storage modulus versus strain amplitude for the different NR-based composites. NR: natural rubber.

Table 3. Material parameters from least square fits of equation (2) to the experimental data shown in Figure 6 ($\tau = 3.6$).

Composite	$\Delta G'_0$ (MPa)	γ_c (%)	m	G'_∞ (MPa)
NR-h-CB40-S0	12.8	15	0.30	1.7
NR-h-CB20-S20	8.8	15	0.38	1.3
NR-h-CB0-S40	6.2	21	0.39	1.2
NR-CB58	8.7	12	0.32	1.6

NR: natural rubber; CB: carbon black.

Already with this approximation, a fairly good description of the Payne effect is possible. Figure 6 shows experimental results of the strain dependency of the modulus G' for the different NR-based composites containing different combinations of fillers. The solids lines correspond to fitted curves according to equation (1).

The fitting parameters $\Delta G'_0$, γ_c , G'_∞ , and m are summarized in Table 3. It becomes obvious that the small strain modulus $G'_0 = \Delta G'_0 + G'_\infty$ is affected by the type of the conventional filler but also by the presence of the hybrid nanofiller. Partial replacement of CB with hybrid nanofiller results in more pronounced Payne effect, which is reflected in high increase of $\Delta G'_0$ of 47%. Addition of silica reduces the $\Delta G'_0$ value which is lowest for NR-h-CB0-S40 composite. This is in correlation with the other obtained results, the highest calculated value of the apparent filler networking energy.

A similar behavior is observed for the large strain G'_{∞} values that are dominated by the pronounced hydrodynamic amplification of structured particles like CB. G'_{∞} slightly increases with partial replacement of CB with hybrid nanofiller and then its value decreases with increase of silica content. On the other hand, structured filler particles lead to a lower stability of the filler network, as seen by the relatively low γ_c values for the NR-CB58 composite. This value of γ_c (the strain amplitude, where half of the clusters are broken) increases when hybrid nanofiller is introduced into the composites indicating that it strengthens the filler network stability. The largest γ_c value of 21% is found for the NR-h-CB0-S40 composite, suggesting the highest stability, which is due to poor compatibility of silica filler to hydrocarbon rubber, its polar character, and the ability to form hydrogen bonds.²⁸ The empirical Kraus parameter m that considers the power law dependency of the number of surviving clusters on the applied strain shows very small variation with the type of applied fillers. Again, its universal value is confirmed indicating that it is mainly a geometrical quantity of the filler network and agglomerates, independent of the specific filler type, although the reasons for its universality still remain unclear.²⁵

Conclusion

Based on the above work, devoted to obtaining a high-performance damping material with excellent strength and elasticity and enhanced energy dissipating capacity, the following conclusions can be drawn.

The tensile tests showed that the presence of the nanofiller (MWCNT/EOMt) enables retention of the high tensile strength of the composites while increasing their elasticity by replacement of CB with unmodified silica filler. The retention of the high tensile strength is due to the very strong interfacial interaction between the elastomer matrix and the well-dispersed hybrid nanofiller, where the MWCNT have the predominant role. The increase of elasticity arises from the inorganic nature of the silica particles, which exhibit mainly physical adsorptions with the elastomeric matrix, and hence a higher mobility of the rubber chains. This means that the hybrid nanofiller played its roll in obtaining material with excellent strength and elasticity.

DMA temperature sweep measurements confirmed nearly the same reinforcing effect for all filler combinations. The values of the apparent filler networking energy, calculated using the CCA model, indicated that the presence of the hybrid nanofiller strengthens the filler networking. This idea of forming glassy polymer bridges of immobilized rubber in the vicinity of the filler particles enhanced by the presence of the hybrid nanofiller was supported by the TEM images. The fine dispersion of the nanoparticles (MWCNT/EOMt) was not interrupted by the presence of the conventional fillers (CB and silica). The individual MWCNT and individual mineral clay layers are bridging the conventional filler aggregates, strengthening the filler network.

The strain sweep measurements in shear mode showed that the damping coefficient of the material is in the sought range between 10% and 20% (at 0.5 Hz and high shear strain) which is a precondition for the material to be classified as high damping.

The CCA model gave a fairly good description of the Payne effect. The calculated parameters $\Delta G'_0$, γ_c , G'_∞ , showed that the partial replacement of CB with hybrid nanofiller (MWCNT/EOMt) resulted in more pronounced Payne effect. On the other hand, structured filler particles lead to a lower stability of the filler network, as seen by the relatively low γ_c values for the composite containing only CB (NR-CB58). This value of γ_c (the strain amplitude, where half of the clusters are broken) increased when hybrid nanofiller is introduced into the composites, indicating again that the presence of hybrid nanofiller strengthens the filler network stability. Since the breakdown and reformation of the filler network is considered to be one of the mechanisms of energy dissipation in filled rubber systems, our approach of obtaining material with excellent strength and elasticity and enhanced energy dissipating capacity by partial replacement of conventional fillers with hybrid nanofiller is justified.

Declaration of Conflicting Interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

Funding

The author(s) received no financial support for the research, authorship, and/or publication of this article.

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