Evaluation of Viscoelastic Performance and Molecular Structures of Natural Rubber/NBR Blends Reinforced by Carbon Black and Nano-Silica

Amel Chelli[1], Hamza Mechakra[2], Ahmed Chellil[2], Djalel Eddine Tria[3], Wissam Bessa[1], Kamel Ikkache[2], Brahim Safi[4*]

[1] High School of Material, Science and Technology Research Direction, Beaulieu, 16004 El Harrach, Algeria
[2] Motor Dynamics and Vibroacoustics Laboratory, Faculty of Technology, M'hamed Bougara University of Boumerdes, Frantz Fanon City, 35000 Boumerdes, Algeria
[3] Materials Engineering Laboratory, Polytechnic Military School, 16046 Bordj El Bahri, Algeria
[4] Process Engineering Department, Faculty of Technology, M'hamed Bougara University of Boumerdes, Frantz Fanon City, 35000 Boumerdes, Algeria
* Corresponding author, e-mail: safi_b73@univ-boumerdes.dz

Abstract

This study focuses on the evaluation of the dynamic mechanical properties, molecular structure, density, hardness, swelling behavior of natural rubber blends (NR) and nitrile rubber (NBR) reinforced with carbon black and/or nano-silica. An experimental work has been conducted to study of the effects of increasing NR content and incorporating nano-silica on the mechanical properties and molecular structure were studied using dynamic mechanical analysis (DMA) and Fourier transform infrared (FTIR) spectroscopy. The results show that increasing the NR content and/or incorporating nano-silica into the elastomer leads to a higher storage modulus with no significant change in the glass transition temperature. FTIR analysis indicates the compatibility of the polyblends and the presence of oxidation of the main polymer chain generated during the grinding of the rubber. Additionally, the results of the swelling study demonstrate that stronger molecular interactions occur on the surface of the nano-silica between the nitrile radicals in the NBR and the silanol (Si-OH) radicals. These findings suggest that blending NR and NBR with carbon black and/or nano-silica can improve the mechanical properties and compatibility of the resulting polyblends, with potential applications in the development of advanced elastomeric materials.

Keywords

naturel rubber, acrylonitrile butadiene rubber, nano filler, nano silica, DMA, FTIR spectroscopy, swelling behaviour

1 Introduction

Nowadays, rubber products are ubiquitous and essential in many applications such as car and truck tires, rubber belts, seals, gaskets, electrical insulation, footwear, and washer sealants [1–3]. Polymer blending has been widely studied for years as an easy and highly efficient way to obtain new materials with improved properties. Additionally, mixing two different polymers typically results in a new material with new and interesting features. Consequently, investigation of polymer blends has garnered the attention of many researchers for specific applications [4–8].

Synthetic rubbers, such as acrylonitrile-butadiene rubber (NBR), offer high resistance to fuels, water, animal and vegetable oils, and alcohols. They are also known for

their outstanding characteristics, which make them useful in various application fields [9–11]. Besides, natural rubber (NR) has the enormous advantage of being a bio-based and renewable product. However, it possesses a very low resistance to material release and stresses, which make it unsuitable for many applications on its own [12, 13]. In this context, it would be highly advantageous to blend natural rubber with synthetic rubber to expand its range of applications and improve its properties. Many efforts have been made to strengthen the material and reduce material losses, and one of the most effective approaches has been the incorporation of fillers [14, 15], typically carbon black and silica, into the rubber. Indeed, the inclusion of nano-fillers

in elastomer blends provides superior mechanical characteristics compared to the use of micro and macro-fillers, despite a smaller amount of nano-filler ratio [16, 17].

The addition of carbon black alone improves the mechanical properties of natural rubber (NR) and some synthetic rubbers, such as acrylonitrile-butadiene rubber (NBR), by enhancing interface adhesion and increasing resistance to abrasion, as well as tensile and tear strength, and modulus [18, 19]. When investigating the effect of reinforcing rubbers with carbon black and silica, it was found that carbon black ensures a high modulus, while silica offers interesting aging, tear, and abrasion resistance properties. Furthermore, silica has been observed to enhance certain rubber characteristics, such as hardness, tensile strength, and tear strength [20, 21].

It is presumed that incorporating both carbon black and silica into the vulcanizates at optimal ratios may provide superior mechanical properties compared to using a single filler [22]. Previous studies have reported the potential of incorporating precipitated silica in elastomeric carbon black fillers for various applications. However, due to the differences in surface properties of the two fillers, their mixture may form agglomerates that affect their dispersibility [23]. Carbon black is primarily held together by Van Der Waal forces, which are relatively weak and easily disrupted during the mixing process [19]. In contrast, silica generates stronger charge-charge interactions due to physical interaction, hydrogen bonding, and Van Der Waal forces [23].

Nanoscale silica particles have a tendency to aggregate, even at low concentrations [20]. These primary aggregates can further develop into larger agglomerates through secondary interactions. This is due to the presence of surface hydroxyl groups on the silica particles, which allow for weak hydrogen bonding and bonding with the surrounding mixture [24–33]. In our study, we utilized both carbon black and nano silica as fillers to reinforce our NR/NBR blend.

Elastomers are known as viscoelastic materials that exhibit both elastic and damping behavior. DMA (Dynamic Mechanical Analysis) is the most widely used technique for determining the viscoelastic behavior of elastomeric materials. It is particularly effective in identifying the molecular mechanisms of polymeric materials, reinforcement, and filler dispersion in polymeric composite systems [34–36]. For instance, Jacob et al. [36] reported that the storage modulus of natural rubber (NR) composites is greater with the addition of fillers due to their strengthening capacity, which leads to a strong and stiff interface. Furthermore, the research group revealed that the damping performances of the composites are reduced when fillers are added since they act as a barrier to the free movement of macromolecular chains. Spectrometry is one of the most suitable and appropriate methods for studying the atomic, molecular, and polar group structures, their location, and consequently, the bonds created.

The study of dynamic mechanical analysis (DMA) properties, atomic and molecular structures, polar group levels, and rubber vulcanizate swelling behavior are currently being investigated, especially with the addition of fillers in rubber formulations, as there is limited information available in the literature. This study builds upon our previous work [37] on the effect of silica nano fillers on the physical and thermal properties of rubber composites.

In this paper, we prepared composites of natural rubber (NR) and nitrile rubber (NBR) in varying proportions and reinforced them with 20% carbon black and/or 3% nano silica. The resulting materials were evaluated for density, hardness, dynamic mechanical properties, molecular structures, and swelling behavior.

2 Materials and methods
2.1 Materials preparation
The natural rubber and nitrile rubber used in this study were obtained from Technoflex-Algeria (Fig. 1). Standard rubber compounding substances, including sulphur, TMTM (tetra methyl thiuram mono-sulphide), ZnO (zinc oxide), carbon black (220), stearic acid, and N-cyclohexyl-2-benzothiazyl sulphonamide (CBS), were used as vulcanizing agents in the compounding process. In some blends, the rubber compounds were further reinforced with 3% of nano-silica. The composition of the rubber compound was determined in parts per hundred rubber (phr) and consisted of stearic acid (2.5 phr), zinc oxide (5 phr), MBT (0.5 phr), TMQ (2 phr), sulphur (2 phr), IPPD (2 phr), TMTM (0.5 phr), and CBS (2.2 phr). Table 1 gives the composition of different blends, with the corresponding samples codes.
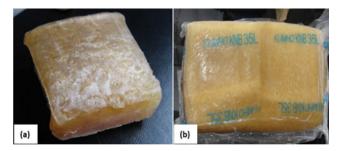

Fig. 1 (a) Natural rubber and (b) nitrile rubber used in this study

Table 1 Mixture composition

Compounds	Specimen code					
	NCS1	NC1	NCS2	NC2	NCS3	NC3
	Weight (wt.%)					
Natural rubber	85	85	75	75	65	65
Nitrile rubber	15	15	25	25	35	35
Carbon Black 220	20	20	20	20	20	20
Nano silica	3	–	3	–	3	–
PEG	0.075	–	0.075	–	0.075	–

2.2 Cure characteristics

The vulcanization process was conducted at TECHNOFLEX using a type R100S rheometer in accordance with ASTM D2084-07, which specifies the vulcanization characteristics of rubber, including the optimal time and temperature. The samples were placed on an oscillating rotor inside a closed pressure chamber preheated to 150 °C, and subjected to low shear stress for 30 minutes. This rheological characterization was performed to determine the ideal conditions before the mixtures were formed.

2.3 Density measurement

The density of the samples was determined using the ASTM D2591-07(2020) standard [38], which involves measuring the ratio of mass to bulk volume. To obtain the mass, a precision balance with an accuracy of 0.1 mg was used to weigh the samples. The apparent volume was determined by measuring the volume of water displaced when the sample was immersed.

2.4 Evolution of hardness

The hardness of the samples was measured using a Shore A hardness tester, which is a standard method for measuring the hardness of elastomers according to the ASTM D2240-15(2021) standard [39]. Three measurements were taken for each specimen, and the average was calculated.

2.5 Dynamic mechanical analysis

The dynamic mechanical analyses were conducted using a NETZSCH DMA 242 instrument. The instrument allows for various monotonic and dynamic test configurations such as tension, three-point bending, shear, compression, among others. The temperature range can vary between −160 °C to 600 °C, while the frequency ranges from 0.001 to 200 Hz. The dynamic mechanical analyses (DMA) spectra were recorded on rectangular samples with dimensions of 40 × 10 × 2 mm in bending mode (Fig. 2). The measurements were carried out as a function of temperature ranging from −100 °C to +100 °C and at a frequency of 1 Hz under a controlled nitrogen atmosphere. The tests were performed at a heating rate of 2 °C/min.

2.6 FTIR characterization

The Fourier Transform Infrared Spectroscopy (FTIR) technique is utilized to obtain the absorption spectrum of a sample, whether it is solid, liquid, or gas. This analytical method is conducted using an FTIR instrument of type FT/IR-4700 typeA at room temperature. The IR spectra are collected in the range of 4000–500 cm^{-1} using transmission mode. The resolution of the spectra is 4 cm^{-1} and the number of scans required to record the IR spectra is 32.

2.7 Swelling study

To measure the swelling behaviour of the vulcanized specimens, a steady-state swelling method using toluene was employed. Square samples with dimensions of 20 mm × 20 mm × 2 mm were cut and immersed in pure toluene at ambient temperature for one week. Every 24 hours, the toluene was replaced with fresh solvent. If necessary, the samples were removed from the solution and quickly wiped with absorbent paper to remove any adhering liquid. The cross-link density was determined by measuring the molar percentage of solvent uptake (Q_t) at a given time using Eq. (1) [40]:

$$Q_t = \frac{\dfrac{(W_t - W_0)}{W_0}}{M_w} \times 100, \tag{1}$$

where W_0 is the weight of dry samples, W_t is the weight of swollen samples and M_w is the molar mass of toluene (92.14 g mole^{-1}).
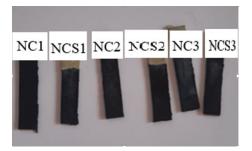

Fig. 2 Samples with dimensions of 40 × 10 × 2 mm

3 Results and discussions

3.1 Cure characteristics results

The R100S rheometer analysis shown in Fig. 3 indicated that the optimal curing time and temperature for our materials were 420 s and 140 °C, respectively. The beginning of vulcanization, indicated by the heating time ts2, was found to be irreversible and was evaluated at 185.4 s. After the optimal curing time, the systematic destruction of the formed bridges occurs, leading to a phenomenon known as reversion. The reversion is more significant when cross-linking occurs rapidly. The tc90, the time required to reach 90% of the optimum crosslink density, was estimated to be 261 s.

3.2 Density of the rubber samples

Table 2 presents the density values of the various samples, which vary depending on the nitrile rubber content and the addition of nano-silica. So adding nitril rubber increases density whereas incorporating nano silica decreases density, except for NC1.

3.3 Hardness of the rubber samples

The results in Table 2 reveals that the increase in nitrile rubber (NBR) content is accompanied by a decrease in the elasticity of the elastomer blend's vulcanizate, which is consistent with the findings of Pittayavin et al [41]. This can be an attributed to a combination of reduced cross-linking density and dispersion effects resulting from the increase in NBR [42].

On the other hand, adding hard particles such as silica to a ductile solution like elastomer increases the vulcanisate's
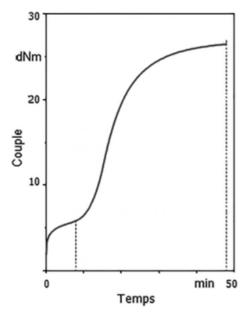
Fig. 3 Torque-time curves of the mixture [1]

Table 2 Density and hardness of vulcanised rubber

Samples	NCS1	NC1	NCS2	NC2	NCS3	NC3
Density d (g/cm³)	1.24	1.17	0.78	1.22	1.13	1.23
Hardness (Shore A)	59±1.4	54±1.4	59±1.4	56±1.4	63±1.4	64±1.5

hardness [43, 44]. In these studies, researchers found that including silica in the mixture with a sufficiently high filler close the space between the silica aggregates, inducing a strong interaction between the aggregates that results in further cross-linking. This interaction between the filler and the rubber should lead to a significant increase in hardness. However, carbon black also contributes to one-third of the rubber hardness, whereas silica represents half of the rubber hardness [44]. It is worth noting that the addition of silica particles has little influence on the NCS3 elastomer. We assume that the nitrile rubber content in the compound has more influence on the hardness of the NCS3 material due to the amorphous structure of the nitrile rubber (NBR), making the compound less rigid and therefore less hard [45].

3.4 Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) involves measuring a material's response to dynamic loading as a function of frequency and temperature. It provides information on the storage modulus (E'), the loss modulus (E''), and the tangent of the loss angle δ.

The storage modulus (E') refers to the stiffness and elastic part of the material, indicating its capacity to retain the mechanical energy of the load and release it completely in the form of elastic deformation. The loss modulus (E'') indicates the viscous part of the material and its ability to dissipate mechanical energy irreversibly as heat. This behavior is related to the friction of the chains of molecules and their flow. The loss factor, also known as the internal friction coefficient, corresponds to the fraction of energy dissipated in viscous form.

The dynamic mechanical analysis of rubber composites provides valuable information on the effect of reinforcement, the compatibility of the rubber compound, and the interaction between rubber and filler. Fig. 4 shows the temperature dependence of the storage modulus of all samples.

The storage modulus of a rubber compound can be influenced by various factors, including the modulus of each component, the composition of the compound, the interactions among the components, and, most importantly, the nature of the filler and how it interacts with the polymers.
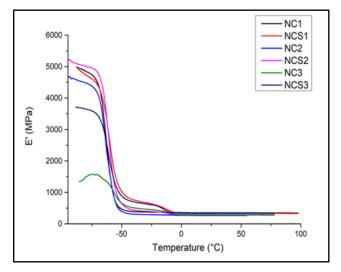
Fig. 4 DMA graph of the E′ storage module as a function of temperature

The data presented in Fig. 4 indicates a significant increase in storage modulus upon the addition of nano-silica to the elastomer blend. This is attributed to the strong interaction between the mixture of the two rubbers and the nano-silica filler, which has been reported previously in the study by Bansod et al. [43]. Moreover, as reported by Sengloyluan et al. [19] and Wu et al. [3], the elasticity of the elastomer blend, as represented by the storage modulus, increases with an increase in Naturel rubber (NR) content. This is because NR rubbers are known to exhibit high elasticity, good damping, and other excellent properties.

In Fig. 5, two glass transition temperatures corresponding to the naturel rubber (NR) and nitrile rubber (NBR) phases are clearly observed in each plot, which is in agreement with the findings of Bansod et al. [43]. The height of the tan δ peak is indicative 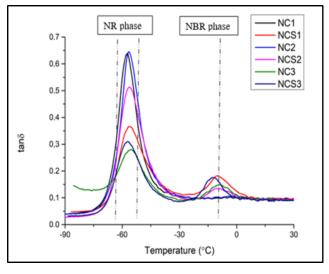of molecular mobility, with the addition of nanosilica limiting and reducing the mobility of the molecules. As a result, the intensity of the tan δ peak decreases, which is evident in samples NCS1, NCS2, and NCS3, indicating increased cross-linking and a strong rubber-filler interaction in the mixture. This can be attributed to the compatibility of silica with polar elastomers such as nitrile rubber (NBR) [46–51]. The glass transition temperature (T_g) was determined using the delta tangent peak, and the results are presented in the Table 3.

3.5 Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared (FTIR) spectroscopy is an analytical technique that measures the amount of light absorbed by a sample as a function of the wavelength emitted by an infrared beam. When a sample is subjected to infrared radiation, the organic molecules within the sample absorb the radiation and undergo changes in their vibrational energies. Depending on the types of chemical bonds and functional groups present in the sample, an infrared spectrum characteristic of the sample or its surface under analysis is obtained. Fig. 6 shows the IR spectra of

Table 3 Glass transition temperature of vulcanisates

Samples	Glass transition phase of NR T_g (°C)	Glass transition phase of NBR T_g (°C)
NCS1	−56.34	−10.16
NC1	−57.11	no pick
NCS2	−56.49	−10.36
NC2	no pick	no pick
NCS3	−56.92	−12.44
NC3	−55.50	−9.05

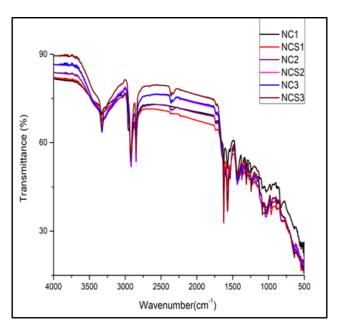**Fig. 5** Loss tangents (tan δ) versus temperature

Fig. 6 Spectra IR cm-1 of blends

the different samples analyzed in this study. Based on the study by Gunasekaran et al. [52], it is suggested that the peak observed at 3325 cm^{-1} in Fig. 6 may be attributed to the O-H bond resulting from the use of stearic acid.

By analyzing the double bond and all C-H valence vibrations, the strong asymmetric (v as CH2) and symmetric (vs CH2) vibrations of the methylene group present in naturel rubber(NR) are visible at around 2917 and 2850 cm^{-1}, respectively (Fig. 7), as confirmed in the study by Arroyo et al. [53].

The band observed at 2230 cm^{-1} in Fig. 8 is attributed to the stretching vibrations of the C≡N alkyl of acrylonitrile,
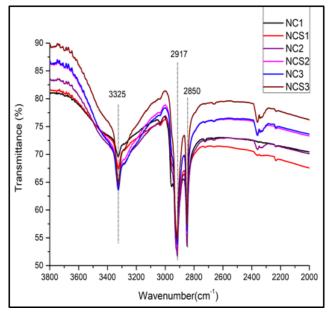
which is present in NBR, and the band at 960 cm^{-1} in Fig. 8 is attributed to the vibrations of the swinging motion of C-H of butadiene [52]. Both bands are still present in the blend, indicating the compatibility of the polyblends.

In line with the work of Padella et al. [54], the peak in the vicinity of 1730 cm^{-1} in Fig. 8 (C=O stretching peak) suggests that oxidation of the main polymer chain occurred during the grinding of the rubber.

The peak at 1085 cm^{-1} in Fig. 9 is attributed to the symmetric stretching vibrations of the C-S-C group in the two C-S bonds [55, 56]. The addition of sulfur during the vulcanization process breaks the double bonds between the carbon atoms and the sulfur atoms and fills the gaps between the two chains by creating cross-links within the chains.

In the work of Das and Kapgate [57] the characteristic peak at 1412 cm^{-1}, shown in Fig. 10 for organosilanes, corresponds to the bending mode of Si-CH$_2$, and the peak at 814 cm^{-1} is due to Si-OH.

3.6 Swelling study

The diffusion of solvents into an elastomer mixture is affected by various factors, including the shape, size, concentration, orientation, and distribution of the fillers, as well as the properties of the matrix and the interaction between the matrix and fillers [58]. The toluene uptake rate was observed to be relatively rapid during the initial phase for all samples studied, stabilizing at around $t_{1/2} = 20$ min, as depicted in Fig. 11. At steady state, the swelling rate of vulcanizates decreases with decreasing amount of naturel rubber (NR) and increasing amount of nitrile rubber (NBR), as shown in Fig. 11. This is due
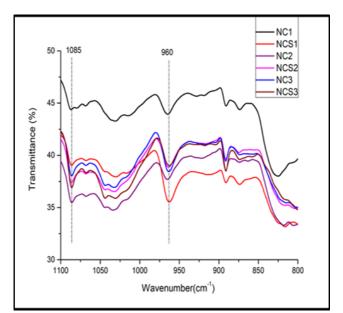

Fig. 7 IR spectra from 3800–2000 cm^{-1} of blends

Fig. 8 IR spectra from 2300–1700 cm^{-1} of blends

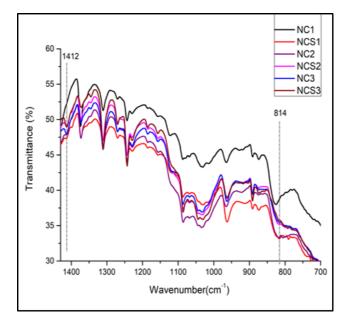Fig. 9 IR spectra from 1100–800 cm^{-1} of blends

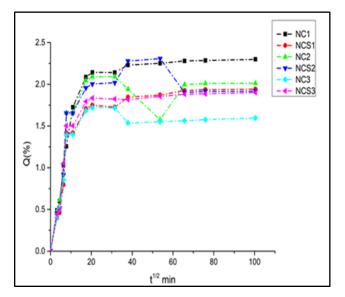**Fig. 10** IR spectra from 1400–700 cm^{-1} of blends

Fig. 11 Toluene sorption curves for the samples

to the increased cross-linking density between the polar NBR and carbon black in a non-polar NR matrix, which restricts molecular movement in the polymer blend [43]. Additionally, the high resistance of NBR to gases, organics, and oil, as well as its higher sticking energy, contributes to this phenomenon. Furthermore, the dissimilar solubility parameters between the solvent and the matrix also result in reduced permeability of NBR [58].

It can also be seen that the degree of swelling decreases with the addition of the nano silica filler in both samples NC1 and NC2, indicating the presence of a solvent diffusion barrier in the polymer matrix. This is due to the strong

molecular interactions between the nitrile groups in NBR, which is a high polarity rubber, and the silanol (Si-OH) groups on the silica surface, which limit the molecular movement of the rubber and make it more difficult for the solvent to migrate through the rubber, resulting a decrease in swelling [46, 58, 59].

An exception in the third case NCS3, where the abnormal diffusion observed may be due to the counteraction between the ability of the rubber compound segments to rearrange in the presence of solvents and the restriction imposed by the reinforced nano silica filler particles [58].

4 Conclusions

This study investigated the effects of incorporating 20% carbon black and 3% nano silica fillers into various mixtures of naturel rubber (NR) and nitrile rubber (NBR) at different proportions, focusing on their impact on dynamic mechanics over a wide temperature range, FTIR spectroscopy, and swelling behavior. Our results indicate that there is a strong interaction between the filler and the rubber, leading to a significant increase in hardness. Moreover, a higher NBR content was found to decrease the cross-linking density and dispersion effects.

Regarding elasticity, the storage modulus was found to increase with increasing NR content. The incorporation of nano silica in the elastomer resulted in a higher storage modulus due to the strong interaction between the two rubber compounds and the nano silica filler. Furthermore, the molecular mobility was limited, and the intensity of the tan δ peak was reduced, indicating increased cross-linking and strong interaction between the rubber and the filler in the mixture. The presence of the C=O stretching peak suggests that oxidation of the polymer main chain occurred during the grinding of the rubber.

In terms of swelling behavior, our findings showed that the degree of swelling of the vulcanisates decreased with decreasing NR content and increasing amount of NBR. Additionally, the addition of the nano silica filler in both samples NC1 and NC2 resulted in a decrease in swelling. These results suggest that solvent diffusion into an elastomer mixture is affected by the form of the fillers, matrix properties, and matrix-filler interaction.

This study provides valuable insights into the effects of incorporating carbon black and nano silica fillers into NR and NBR elastomers. These findings can be useful for the development of new elastomeric materials with improved mechanical and swelling properties.

References

[1] Tippur, H. "Introduction to Plastics Engineering", Journal of Engineering Materials and Technology, 143(3), 036501, 2021.
https://doi.org/10.1115/1.4051082

[2] Chartrand, T. L., Maddux, W. W., Lakin, J. L. "Beyond the perception-behavior link: The ubiquitous utility and motivational moderators of nonconscious mimicry", [e-book] Editor Hassin, R. R., Editor Uleman, J. S., Editor Bargh, J. A. In: The new unconscious, Oxford University Press, 2005, pp. 334–361. ISBN 9780199847488
https://doi.org/10.1093/acprof:oso/9780195307696.001.0001

[3] Wu, M., McIntosh, J., Liu, J. "Current prevalence rate of latex allergy: Why it remains a problem", Journal of Occupational Health, 58(2), pp. 134–144, 2016.
https://doi.org/10.1539/joh.15-0275-RA

[4] Elmendorp, J. J., Maalcke, R. "A study on polymer blending microrheology: Part 1", Polymer Engineering & Science, 25(16), pp. 1041–1047, 1985.
https://doi.org/10.1002/pen.760251608

[5] Scott, C. E., Macosko, C. W. "Morphology development during the initial stages of polymer-polymer blending", Polymer, 36(3), pp. 461–470, 1995.
https://doi.org/10.1016/0032-3861(95)91554-K

[6] Sundararaj, U., Macosko, C. W., Shih, C.-K. "Evidence for inversion of phase continuity during morphology development in polymer blending", Polymer Engineering and Science, 36(13), pp. 1769–1781, 1996.
https://doi.org/10.1002/pen.10572

[7] Ibrahim, B. A.. Kadum, K. M. "Influence of Polymer Blending on Mechanical and Thermal Properties", Modern Applied Science, 4(9), pp. 157–161, 2010.
https://doi.org/10.5539/mas.v4n9p157

[8] Morris, B. A. "Chapter 12 - Polymer blending for packaging applications", In: Multilayer Flexible Packaging: A volume in Plastics Design Library, William Andrew, 2016, pp. 137–162. ISBN 978-0-8155-2021-4
https://doi.org/10.1016/B978-0-8155-2021-4.10012-7

[9] Alves, S. M., Mello, V. S., Medeiros, J. S. "Palm and soybean biodiesel compatibility with fuel system elastomers", Tribology International, 65, pp. 74–80, 2013.
https://doi.org/10.1016/j.triboint.2013.03.026

[10] Bertram, H. H. "Developments in Acrylonitrile—Butadiene Rubber (NBR) and Future Prospects", in Developments in Rubber Technology—2, Springer Dordrecht, 1981, pp. 51–85. ISBN 978-0-85334-949-5
https://doi.org/10.1007/978-94-009-8108-9_3

[11] Maciel, A.V., Machado, J. C., Pasa, V. M. D. "The effect of temperature on the properties of the NBR/PVC blend exposed to ethanol fuel and different gasolines", Fuel, 113, pp. 679–689, 2013.
https://doi.org/10.1016/j.fuel.2013.05.101

[12] Chapman, A. "Natural rubber and NR-based polymers: renewable materials with unique properties", presented at 24th International H.F. Mark-Symposium, 'Advances in the Field of Elastomers & Thermoplastic Elastomers', Vienna, Austria, Nov. 15–16, 2007.

[13] Zhao, X., Niu, K., Xu, Y., Peng, Z., Jia, L., Hui, Zhang, L. "Morphology and performance of NR/NBR/ENR ternary rubber composites", Composites Part B: Engineering, 107, pp. 106–112, 2016.
https://doi.org/10.1016/j.compositesb.2016.09.073

[14] Pal, K., Rajasekar, R., Kang, D. K., Zhang, Z. X., Kim, J. K., Das, C. K. "Effect of epoxidized natural rubber–organoclay nanocomposites on NR/high styrene rubber blends with fillers", Materials & Design, 30(10), pp. 4035–4042, 2009.
https://doi.org/10.1016/j.matdes.2009.05.021

[15] Zhao, P., Li, L., Luo, Y., Lv, Z., Xu, K., Li, S., Zhong, J., Wang, Z., Peng, Z. "Effect of blend ratio on the morphology and electromagnetic properties of nanoparticles incorporated natural rubber blends", Composites Part B: Engineering, 99, pp. 216–223, 2016.
https://doi.org/10.1016/j.compositesb.2016.06.017

[16] Hassan Nejad, M. "Improving the Mechanical Properties of Polysaccharide Derivatives through Melt Compounding with Nano-Clays", PhD Dissertation, Universität Berlin, 2011.

[17] Hassan Nejad, M., Ganster, J., Volkert, B. "Starch esters with improved mechanical properties through melt compounding with nanoclays", Journal of Applied Polymer Science, 118(1), pp. 503–510, 2010.
https://doi.org/10.1002/app.32312

[18] Mondal, D., Ghorai, S., Rana, D., De, D., Chattopadhyay, D. "The rubber–filler interaction and reinforcement in styrene butadiene rubber/devulcanize natural rubber composites with silica–graphene oxide", Polymer Composites, 40(S2), pp. E1559–E1572, 2019.
https://doi.org/10.1002/pc.25076

[19] Sengloyluan, K., Sahakaro, K., Dierkes, W. K., Noordermeer, J. W. M. "Silica-reinforced tire tread compounds compatibilized by using epoxidized natural rubber", European Polymer Journal, 51, pp. 69–79, 2014.
https://doi.org/10.1016/j.eurpolymj.2013.12.010

[20] Prasad, T., Halder, S., Dhar, S. "Imidazole-supported silica one-pot processed nanoparticles to enhance toughness of epoxy based nanocomposites", Materials Chemistry and Physics, 231, pp. 75–86, 2019.
https://doi.org/10.1016/j.matchemphys.2019.04.002

[21] Crié, A. "Caractérisation et lois rhéologiques d'élastomères chargés à basse température pour la simulation du procédé d'extrusion" (Characterisation and rheological laws of elastomers filled at low temperature for the simulation of the extrusion process), PhD Thesis, l'École nationale supérieure des mines de Paris, 2014. (in French)

[22] Song, Y.-h., Zeng, L.-b., Zheng, Q. "Understanding the reinforcement and dissipation of natural rubber compounds filled with hybrid filler composed of carbon black and silica", Chinese Journal of Polymer Science, 35(11), pp. 1436–1446, 2017.
https://doi.org/10.1007/s10118-017-1987-5

[23] Seyvet, O., Navard, P. "Collision-induced dispersion of agglomerate suspensions in a shear flow", Journal of Applied Polymer Science, 78(5), pp. 1130–1133, 2000.
https://doi.org/10.1002/1097-4628(20001031)78:5<1130::AID-APP220>3.0.CO;2-I

[24] Meera, A. P., Said, S., Grohens, Y., Luyt, A. S., Thomas, S. "Tensile Stress Relaxation Studies of TiO$_2$ and Nanosilica Filled Natural Rubber Composites", Industrial & Engineering Chemistry Research, 48(7), pp. 3410–3416, 2009.
https://doi.org/10.1021/ie801494s

[25] Boutaleb, S., Zaïri, F., Mesbah, A., Naït-Abdelaziz, M., Gloaguen, J. M., Boukharouba, T., Lefebvre, J. M. "Micromechanics-based modelling of stiffness and yield stress for silica/polymer nanocomposites", International Journal of Solids and Structures, 46(7–8), pp. 1716–1726, 2009.
https://doi.org/10.1016/j.ijsolstr.2008.12.011

[26] Bhattacharya, M., Bhowmick, A. K. "Analysis of wear characteristics of natural rubber nanocomposites", Wear, 269(1–2), pp. 152–166, 2010.
https://doi.org/10.1016/j.wear.2010.03.022

[27] Hui, S., Chaki, T. K., Chattopadhyay, S. "Dynamic and capillary rheology of LDPE-EVA–based thermoplastic elastomer: Effect of silica nanofiller", Polymer Composites, 31(3), pp. 377–391, 2010.
https://doi.org/10.1002/pc.20814

[28] Pal, K., Rajasekar, R., Kang, D. J., Zhang, Z. X., Pal, S. K., Das, C. K., Kim, J. K. "Effect of fillers on natural rubber/high styrene rubber blends with nano silica: morphology and wear", Materials & Design, 31(2), pp. 677–686, 2010.
https://doi.org/10.1016/j.matdes.2009.08.014

[29] Cao, X., Xu, C., Wang, Y., Liu, Y., Liu, Y., Chen, Y. "New nanocomposite materials reinforced with cellulose nanocrystals in nitrile rubber", Polymer Testing, 32(5), pp. 819–826, 2013.
https://doi.org/10.1016/j.polymertesting.2013.04.005

[30] Li, Y., Guo, Y., Ge, J., Ma, P. X., Lei, B. "In situ silica nanoparticles-reinforced biodegradable poly(citrate-siloxane) hybrid elastomers with multifunctional properties for simultaneous bioimaging and bone tissue regeneration", Applied Materials Today, 10, pp. 153–163, 2018.
https://doi.org/10.1016/j.apmt.2017.11.007

[31] Zhang, K., Wu, W., Meng, H., Guo, K., Chen, J.-F. "Pickering emulsion polymerization: Preparation of polystyrene/nano-SiO$_2$ composite microspheres with core-shell structure", Powder Technology, 190(3), pp. 393–400, 2009.
https://doi.org/10.1016/j.powtec.2008.08.022

[32] Qi, D., Liu, C., Chen, Z., Dong, G., Cao, Z. "In situ emulsion copolymerization of methyl methacrylate and butyl acrylate in the presence of SiO$_2$ with various surface coupling densities", Colloid and Polymer Science, 293(2), pp. 463–471, 2015.
https://doi.org/10.1007/s00396-014-3433-3

[33] Tang, X., Kang, W., Zhou, B., Gao, Y., Cao, C., Guo, S., Iqbal, M. W., Yang, H. "Characteristics of composite microspheres for in-depth profile control in oilfields and the effects of polymerizable silica nanoparticles", Powder Technology, 359, pp. 205–215, 2020.
https://doi.org/10.1016/j.powtec.2019.09.070

[34] Thongsang, S., Sombatsompop, N., Ansarifar, A. "Effect of fly ash silica and precipitated silica fillers on the viscosity, cure, and viscoelastic properties of natural rubber", Polymers for Advanced Technologies, 19(9), pp. 1296–1304, 2008.
https://doi.org/10.1002/pat.1129

[35] Sae-Oui, P., Rakdee, C., Thanmathorn, P. "Use of rice husk ash as filler in natural rubber vulcanizates: In comparison with other commercial fillers", Journal of Applied Polymer Science, 83(11), pp. 2485–2493, 2002.
https://doi.org/10.1002/app.10249

[36] Jacob, M., Francis, B., Thomas, S., Varughese, K. T. "Dynamical mechanical analysis of sisal/oil palm hybrid fiber-reinforced natural rubber composites", Polymer Composites, 27(6), pp. 671–680, 2006.
https://doi.org/10.1002/pc.20250

[37] Chelli, A., Hemmouche, L., Ait-Sadi, H., Trache, D., Benziane, M., Ait-Sadi, R. "The Effect of Silica Nanofiller on the Physical and Thermal Characteristics of Rubber-Based Composites", International Polymer Processing, 36(1), pp. 60–68, 2021.
https://doi.org/10.1515/ipp-2020-3956

[38] ASTM International "ASTM D2591-07(2020) Standard Test Method for Linear Density of Elastomeric Yarns (Short Length Specimens)", ASTM International, West Conshohocken, PA, USA, 2020.

[39] ASTM International "ASTM D2240-15(2021) Standard Test Method for Rubber Property—Durometer Hardness", ASTM International, West Conshohocken, PA, USA, 2021.

[40] Mathai, A. E., Thomas, S. "Transport of aromatic hydrocarbons through crosslinked nitrile rubber membranes", Journal of Macromolecular Science, Part B: Physics, 35(2), pp. 229–253, 1996.
https://doi.org/10.1080/00222349608212383

[41] Pittayavinai, P., Thanawan, S., Amornsakchai, T. "Comparative study of natural rubber and acrylonitrile rubber reinforced with aligned short aramid fiber", Polymer Testing, 64, pp. 109–116, 2017.
https://doi.org/10.1016/j.polymertesting.2017.09.033

[42] Sae-Oui, P., Sirisinha, C., Hatthapanit, K. "Properties of Natural Rubber Filled with Ultra Fine Acrylate Rubber Powder", Journal of Elastomers & Plastics, 42(2), pp. 139–150, 2010.
https://doi.org/10.1177/0095244310362733

[43] Bansod, N. D., Kapgate, B. P., Das, C., Das, A., Basu, D., Debnath, S. C. "Compatibilization of natural rubber/nitrile rubber blends by sol–gel nano-silica generated by in situ method", Journal of Sol-Gel Science and Technology, 80(2), pp. 548–559, 2016.
https://doi.org/10.1007/s10971-016-4114-0

[44] Ulfah, I. M., Fidyaningsih, R., Rahayu, S., Fitriani, D. A., Saputra, D. A., Winarto, D. A., Wisojodharmo, L. A. "Influence of Carbon Black and Silica Filler on the Rheological and Mechanical Properties of Natural Rubber Compound", Procedia Chemistry, 16, pp. 258–264, 2015.
https://doi.org/10.1016/j.proche.2015.12.053

[45] Arayapranee, W., Rempel, G. L. "Effects of polarity on the filler-rubber interaction and properties of silica filled grafted natural rubber composites", Journal of Polymers, 2013, 279529, 2013.
https://doi.org/10.1155/2013/279529

[46] Choi, S.-S. "Improvement of properties of silica-filled styrene–butadiene rubber compounds using acrylonitrile–butadiene rubber", Journal of Applied Polymer Science, 79(6), pp. 1127–1133, 2001.
https://doi.org/10.1002/1097-4628(20010207)79:6<1127::AID-APP170>3.0.CO;2-8

[47] Le, H. H., Sriharish, M. N., Henning, S., Klehm, J., Menzel, M., Frank, W., Wießner, S., Das, A., Stöckelhuber, K.-W., Heinrich, G., Radusch, H.-J. "Dispersion and distribution of carbon nanotubes in ternary rubber blends", Composites Science and Technology, 90, pp. 180–186, 2014.
https://doi.org/10.1016/j.compscitech.2013.11.008

[48] Le, H. H., Osswald, K., Ilisch, S., Hoang, X. T., Heinrich, G., Radusch, H.-J. "Master curve of filler localization in rubber blends at an equilibrium state", Journal of Materials Science, 47(10), pp. 4270–4281, 2012.
https://doi.org/10.1007/s10853-012-6277-6

[49] Karikal Chozhan, C., Chandramohan, A., Alagar, M. "Benzoxazine modified diglycidyl ether of bisphenol-a/silicon/siliconized epoxy hybrid polymer matrices: Mechanical, thermal, electrical and morphological properties", Journal of Macromolecular Science, Part A: Pure and Applied Chemistry, 56(1), pp. 1–16, 2019.
https://doi.org/10.1080/10601325.2018.1470469

[50] Pothan, L. A., Oommen, Z., Thomas, S. "Dynamic mechanical analysis of banana fiber reinforced polyester composites", Composites Science and Technology, 63(2), pp. 283–293, 2003.
https://doi.org/10.1016/S0266-3538(02)00254-3

[51] Jawaid, M., Abdul Khalil, H. P. S., Hassan, A., Dungani, R., Hadiyane, A. "Effect of jute fibre loading on tensile and dynamic mechanical properties of oil palm epoxy composites", Composites Part B: Engineering, 45(1), pp. 619–624, 2013.
https://doi.org/10.1016/j.compositesb.2012.04.068

[52] Gunasekaran, S., Natarajan, R. K., Kala, A. "FTIR spectra and mechanical strength analysis of some selected rubber derivatives", Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 68(2), pp. 323–330, 2007.
https://doi.org/10.1016/j.saa.2006.11.039

[53] Arroyo, M., López-Manchado, M. A., Herrero, B. "Organomontmorillonite as substitute of carbon black in natural rubber compounds", Polymer, 44(8), pp. 2447–2453, 2003.
https://doi.org/10.1016/S0032-3861(03)00090-9

[54] Padella, F., Cavalieri, F., D'Uva, G., La Barbera, A., Cataldo, F. "Recycling of scrap tires rubber by mechanochemical devulcanization", Polymer Recycling, 6(1), pp. 11–16, 2001.

[55] Yoshizawa, M., Marwanta, E., Ohno, H. "Preparation and characteristics of natural rubber/poly(ethylene oxide) salt hybrid mixtures as novel polymer electrolytes", Polymer, 41(26), pp. 9049–9053, 2000.
https://doi.org/10.1016/S0032-3861(00)00277-9

[56] Rai, A. K., Singh, R., Singh, K. N., Singh, V. B. "FTIR, Raman spectra and ab initio calculations of 2-mercaptobenzothiazole", Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 63(2), pp. 483–490, 2006.
https://doi.org/10.1016/j.saa.2005.05.034

[57] Das, C., Kapgate, B. P. "Preparation and studies of nitrile rubber nanocomposites with silane modified silica nanoparticles", Research Journal of Recent Sciences, 1, pp. 2277–2502.

[58] Maria, H. J., Lyczko, N., Nzihou, A., Mathew, C., George, S. C., Joseph, K., Thomas, S. "Transport of organic solvents through natural rubber/nitrile rubber/organically modified montmorillonite nanocomposites", Journal of Materials Science, 48(15), pp. 5373–5386, 2013.
https://doi.org/10.1007/s10853-013-7332-7

[59] Kumnuantip, C., Sombatsompop, N. "Dynamic mechanical properties and swelling behaviour of NR/reclaimed rubber blends", Materials Letters, 57(21), pp. 3167–3174, 2003.
https://doi.org/10.1016/S0167-577X(03)00019-3