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

Amel Chelli1, Hamza Mechakra2, Ahmed Chellil2, Djalel Eddine Tria3, Wissam Bessa1, Kamel Ikkache2, Brahim Safi4*

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

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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
natural 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 seals [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 vulcanize 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), sulphur (2 phr), TMTM (0.5 phr), IPPD (2 phr), TMQ (2 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](image-url)
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]:

$$Q_t = \frac{W_t - W_0}{W_0 M_w} \times 100,$$

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](image-url)
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 $t_{s2}$, 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 $t_{c90}$, 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 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 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 $\delta$.

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.

| Table 2 Density and hardness of vulcanised rubber |
|-----------------|-------------|-------------|-------------|-------------|-------------|-------------|
| Samples         | NCS1 | NC1 | NCS2 | NC2 | NCS3 | NC3 |
| Density $d$ (g/cm$^3$) | 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 |

Fig. 3 Torque-time curves of the mixture [1]
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>
<thead>
<tr>
<th>Samples</th>
<th>Glass transition phase of NR $T_g$ (°C)</th>
<th>Glass transition phase of NBR $T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCS1</td>
<td>−56.34</td>
<td>−10.16</td>
</tr>
<tr>
<td>NC1</td>
<td>−57.11</td>
<td>no pick</td>
</tr>
<tr>
<td>NCS2</td>
<td>−56.49</td>
<td>−10.36</td>
</tr>
<tr>
<td>NC2</td>
<td>no pick</td>
<td>no pick</td>
</tr>
<tr>
<td>NCS3</td>
<td>−56.92</td>
<td>−12.44</td>
</tr>
<tr>
<td>NC3</td>
<td>−55.50</td>
<td>−9.05</td>
</tr>
</tbody>
</table>

![Fig. 4 DMA graph of the E’ storage module as a function of temperature](image1)

![Fig. 5 Loss tangents (tan δ) versus temperature](image2)

![Fig. 6 Spectra IR cm-1 of blends](image3)
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 ($\nu_{as}$ CH$_2$) and symmetric ($\nu_{s}$ CH$_2$) vibrations of the methylene group present in naturer 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 naturer 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](image7)

![Fig. 8 IR spectra from 2300–1700 cm$^{-1}$ of blends](image8)

![Fig. 9 IR spectra from 1100–800 cm$^{-1}$ of blends](image9)
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 in 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 natural 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.
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References


