

Influence of Different Grafted Natural Rubbers on Electrical and Mechanical Properties of Natural Rubber/Carbon Nanotubes Composites

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Abstract: This study investigates the augmentation of electrical and mechanical characteristics of natural rubber (NR) film with different forms by integrating carbon nanotubes (CNTs). NR with different forms (i.e., natural rubber grafted with polystyrene (NR-*g*-PS) and polybutyl methacrylate (NR-*g*-PBMA)) were successfully synthesized. The success of these grafting was confirmed through Proton Nuclear Magnetic Resonance (¹H-NMR) and Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) analyses, which showed that the grafting efficiency exceeded 90%. The properties of ungrafted NR and grafted NRs with CNTs were compared and analyzed. It was found that the NR/CNTs composites with grafting displayed significantly improved electrical properties and mechanical strength when compared to the NR/CNTs composites without grafting. It was found that the NR-*g*-PBMA exhibited an 860% increase in electrical conductivity at 100 kHz compared to ungrafted NR. This might be attributed to the synergistic of the high specific surface of CNTs and the high polarization of functional groups, which gave a higher value for the CNTs filled grafted NR than the ungrafted NR. Moreover, the mechanical properties of NR-*g*-PS composites showed a 114% increase in 100% modulus, 127% in tensile strength, and 37% in hardness, while the NR-*g*-PBMA composites exhibited a 159% increase in 100% modulus, 95% in tensile strength, and 34% in hardness compared to ungrafted NR. This enhancement can be attributed to the formation of chemical linkages between the grafted NR matrix and CNTs through functional groups from both. Consequently, it can be concluded that introducing functional groups on grafted NR assists in establishing a crosslinking network, enhancing both the mechanical and electrical properties. Additionally, this research emphasizes the benefits of producing flexible conductive materials with high modulus and enhanced electrical properties.

Keywords: Natural rubber latex, Graft copolymerization, Glutaraldehyde, Natural rubber composites, Electrical properties

1. Introduction

Conductive elastomers are elastic materials designed to transmit electricity, often made from NR or similar alternatives by incorporating conductive materials. NR is a crucial and renewable material known for its outstanding physical properties, including elasticity, high resilience, tackiness, tensile strength, and renewable material [1-3]. To enhance performance, NR composites reinforced with CNTs are explored for their superior mechanical and electrical properties. However, uniform dispersion of CNTs in NR is challenging due to strong Van der Waals forces and high aspect ratio [4,5]. Incorporating CNTs into NR matrices significantly enhances the composite's performance, improving conductivity and mechanical properties even at low CNT concentrations. Improvement of interactions between CNTs and the polymer of the composite is a key to enhance all properties. Several studies have focused on these enhancements, and it is known that modification of NR is a choice to overcome its drawbacks [6-12].

Currently, low-temperature curing of NR using glutaraldehyde as a curing agent has been reported, enabling an easy casting process at around 50 °C without the need for special activators or accelerators. This vulcanization system not only crosslinks rubber molecules but also glutaraldehyde–vinyl groups of monomers via aldol condensation. This method results in low energy consumption and provides a high modulus [13]. Based on these advantages, it is hypothesized that incorporating CNTs into the NR matrix will enhance the material's modulus directly related to the sensitivity of the sensor and electrical properties.

Therefore, this study focuses on enhancing the electrical and mechanical properties of NR composites by adding a functional group on natural rubber molecules in grafted forms (i.e., NR-*g*-PS and NR-*g*-PBMA). The grafting efficiency was confirmed using the Soxhlet extraction method. Grafting copolymerization of grafted NRs were verified by ¹H-NMR and ATR-FTIR analysis. The performance of grafted NR was further enhanced by adding CNTs as conductive fillers, mixing them using sonication, and cured with glutaraldehyde. The electrical and mechanical properties were analyzed to assess the presence and distribution of CNTs within the NR matrix. Swelling experiments confirmed the presence of chemical crosslinking. This study introduces a novel method for producing conductive grafted NR latex films using an easy casting process with glutaraldehyde, enhancing electrical properties.

2. Methodology

2.1 Materials

The NR latex in the form of high ammonia (HA latex) with 60% dry rubber content (DRC) was sourced from Chalong Latex Industry in Songkhla, Thailand. MMA and styrene monomer, with a purity of 99.0%, was obtained from Sigma-Aldrich Chemie in Munich, Germany. Tetraethylenepentamine (TEPA) and *tert*-butyl hydroperoxide (*tert*-BuHP) were used as redox initiators, and sodium dodecyl sulfate (SDS) was employed as a stabilizer for NR latex, all of which were also supplied by Sigma-Aldrich Chemie in Munich, Germany. The solvents, petroleum ether, methyl ethyl ketone (MEK), and acetone used for solvent extraction, were purchased from Fisher Scientific in Loughborough, United Kingdom, Ajax Finechem, Australia, and Zen Point, Thailand, respectively. Glutaraldehyde, used as a curing agent for NR latex, was procured from Loba Chemie Pvt in Maharashtra, India. For the fabrication of conductive rubber, CNTs used as a conductive filler were produced by Nanocyl S.A. in Sambreville, Belgium. Toluene solvent for the swelling measurement was procured from Geefin Rubber Tech Co., Ltd., Songkhla, Thailand.

2.2 Preparation of grafted NR and chemical characterization

The grafted NR with various monomers was performed using redox emulsion polymerization. In a main reactor, high ammonia latex with 60% (90 phr), 85% TEPA (1 phr), 20% SDS (1.5 phr), and deionized water were first added and then mechanically stirred at 50 °C for 30 min under a nitrogen atmosphere. The monomer (10 phr) and 80% *tert*-BuHP (1 phr) were continuously dropped into the main reactor. The mixture was maintained for 2 h to ensure the success of the copolymerization reaction. To evaluate the grafting efficiency, the grafted NR latex was dried in a hot air oven 40 °C for 48 h to remove the unreacted monomer and moisture in the film. Soxhlet extraction procedures were carried out with free NR and homopolymer. Free NR was extracted with petroleum ether at 60 °C for 24 h, and

the remaining product was dried in an oven at 40 °C for 24 hours. The residues were further extracted with acetone at 80 °C for 24 h to remove free homopolymers. The copolymer of grafted NR was finally obtained and characterized. The grafting efficiency of the grafted NR was measured by evaluating the remaining weight of the sample after extraction by using Equation (1) [14].

$$\% \text{ grafting efficiency} = \frac{\text{post-extraction weight of copolymer}}{\text{the total initial weight of the polymer}} \times 100 \quad (1)$$

To verify the grafting copolymerization of monomers onto NR molecules, the grafted NR was measured by Proton nuclear magnetic resonance (¹H-NMR). The samples were dissolved in Chloroform-D (CDCl₃) before characterization using the 500 MHz Fourier Transform NMR spectrometer (Varian, Munich, Germany). The functional group on NR molecular chains was confirmed by Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR), Bruker (Model Tensor 207, Ettlingen, Germany) spectrometer. The spectra were detected in the 4000–500 cm⁻¹ range with 64 scans at a resolution of 4 cm⁻¹.

2.3 Preparation of cured grafted NR/CNTs composites

The 1 phr of CNTs and 2 phr of 20 wt% SDS were added into deionized water and then sonicated using an ultrasonic bath for 30 min. This CNT dispersion and 12.5 % of glutaraldehyde were added into the grafted NR latex during mechanical stirring at 200 rpm for 30 min. After that, the mixture was cast into a glass plate and dried in a hot air oven at 50 °C for 24 h. The cured grafted-NR/CNTs composite films were removed and introduced for electrical, mechanical, and swelling characterizations.

2.4 Characterization of cured grafted NR/CNTs composites

Electrical properties were used LCR meter (Agilent 4285A, Yokogawa Hewlett Packard, Inc., California, USA) analyzed in terms of dielectric constant (ϵ') and electrical conductivity (σ). The samples used for electrical measurements had a thickness ranging from 1.25 to 1.50 mm. The thickness of the samples was controlled during the latex film casting process. For electrical properties testing, the samples with thickness ranging from 1.25 to 1.50 mm were placed between two parallel plates of a dielectric test fixture with a 5 mm electrode diameter, and the measurements were conducted over a frequency range of 100 to 1050 kHz. No pressure was applied during the testing. The two parallel plates of the dielectric test fixture were simply in contact with the sample's surface. The capacitance (C_p) and the resistance (R_p) were used to calculate the dielectric constant and electrical conductivity. The dielectric constant (ϵ') and electrical conductivity (σ) of the NR samples were calculated using Equations (2) and (3), respectively.

$$\epsilon' = \frac{C_p \cdot d}{A \cdot \epsilon_0} \quad (2)$$

$$\sigma = \frac{1}{\rho} = \frac{d}{(R_p) \cdot A} \quad (3)$$

where ϵ_0 is the dielectric constant of free space, which is 8.854×10^{-12} F/m. The symbols d and A are the sample thickness and the area of an electrode, respectively. The factor ρ is the volume resistivity, i.e., the reciprocal of conductivity [15].

The tensile testing of the cured sample was performed at room temperature according to the ASTM D 412 method with dumbbell-shaped test specimens at a crosshead speed of 500 mm/min using a universal testing machine (Model H10KS, Hounsfield, England). The case of hardness was tested using a Shore A durometer (Frank GmbH, Hamburg, Germany) in accordance with ASTM D2240.

Swelling behavior was examined according to ASTM D471, determined by the change in mass. The rubber-cured pieces of known weight (W_0) were immersed in toluene for 24 h at room temperature. Samples were kept and quickly wiped using tissue paper and reweighted (W_s). The degree of swelling was calculated using the following equation (Equation (4)), and the average of five test results was reported.

$$\% \text{ Change in weight} = \left(\frac{W_s - W_0}{W_0} \right) \times 100 \quad (4)$$

3. Results and discussion

Chemical characterization of grafted NR

The grafting efficiency of NR molecules in the grafted NR samples was initially characterized using the extraction method. The grafting efficiency of the grafted NR was measured by evaluating the remaining weight of the grafted NR after extraction, as determined by Equation (1). It was found that the NR-*g*-PBMA and NR-*g*-PS samples exhibited a high grafting efficiency of 90.36 and 90.97%, respectively (Figure 1). This result confirmed the effectiveness of the graft copolymerization using this technique for preparing both different forms of grafted NRs.

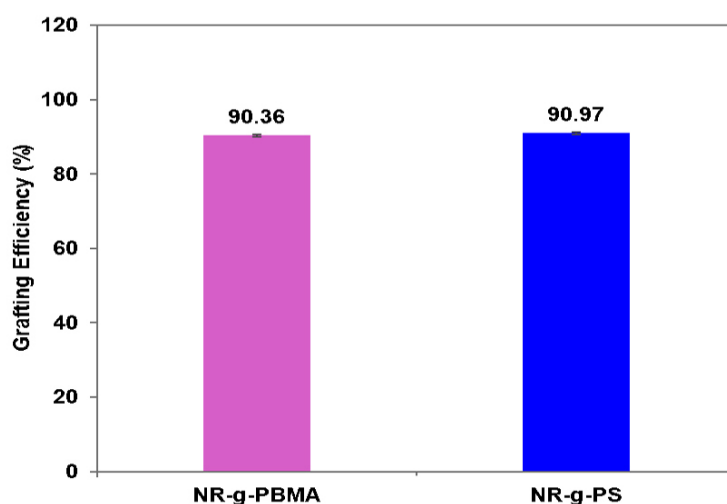


Figure 1 Percentage of grafting efficiency of the grafted NRs, grafted NR-*g*-PS, and grafted NR-*g*-PBMA.

To demonstrate the graft copolymer of the functional group on the NR main chains, the $^1\text{H-NMR}$ spectra of ungrafted NR and grafted NR were represented in Figure 2. The respective signals of isoprene in ungrafted NR are shown at 5.12, 2.04, and 1.68 ppm, which referred to olefinic protons $=\text{CH}$ (a), methylene protons $-\text{CH}_2$ (b) and methyl protons $-\text{CH}_3$ (c) groups in isoprene units, respectively. After grafted NR-*g*-PS, new signals are prominent after the copolymerization process. The signal appeared at 7.1 ppm, corresponding to the aromatic protons $-\text{C}_6\text{H}_5$ (d) of the styrene monomer. For $^1\text{H-NMR}$ spectra of NR-*g*-PBMA, there was a significant signal at 2.30 ppm, attributed to the presence of the methine proton $-\text{CH}$ (e) of BMA monomer [16,17]. This confirm the formation of BMA and styrene monomer on the NR main chains during polymerization successfully.

Figure 3 presents the ATR-FTIR spectra of both ungrafted and grafted NR, displaying absorption peaks at various wavenumbers. The spectra distinctly reveal the characteristic peaks of the isoprene molecule, identified at specific absorption peaks: 836 cm^{-1} for $-\text{C}-\text{H}$ out-of-plane bending vibrations, 1446 cm^{-1} for $-\text{C}-\text{H}$ bending vibrations, 1670 cm^{-1} for $-\text{C}=\text{C}$ stretching vibrations, and 2960 cm^{-1} for $-\text{C}-\text{H}$ stretching vibrations in the aliphatic bonds of the isoprene units. After grafted NR-*g*-PS, a new peak at 696 cm^{-1} was assigned to out-of-plane bending

vibrations of aromatic $-CH$ in styrene structure. In the ATR-FTIR spectrum of grafted NR-*g*-PBMA, characteristic peaks are observed around 1250 cm^{-1} for $-C-O-C$ asymmetric stretching vibration and around 1730 cm^{-1} $-C=O$ stretching vibration of the ester group in BMA structure. This clarifies the presence of both NR and monomer in the grafted copolymer, indicating successful grafting of the monomer onto NR molecules [18,19]. Furthermore, after the glutaraldehyde vulcanization process, new peaks appeared at $1090\text{--}1020$ and 1558 cm^{-1} , corresponding to $-C-N$ stretching and $-N-H$ bending vibrations of secondary amine, respectively [20]. It confirms the crosslinking of NR molecules with pentane-1,5-diylidenediamine by *ene* reaction.

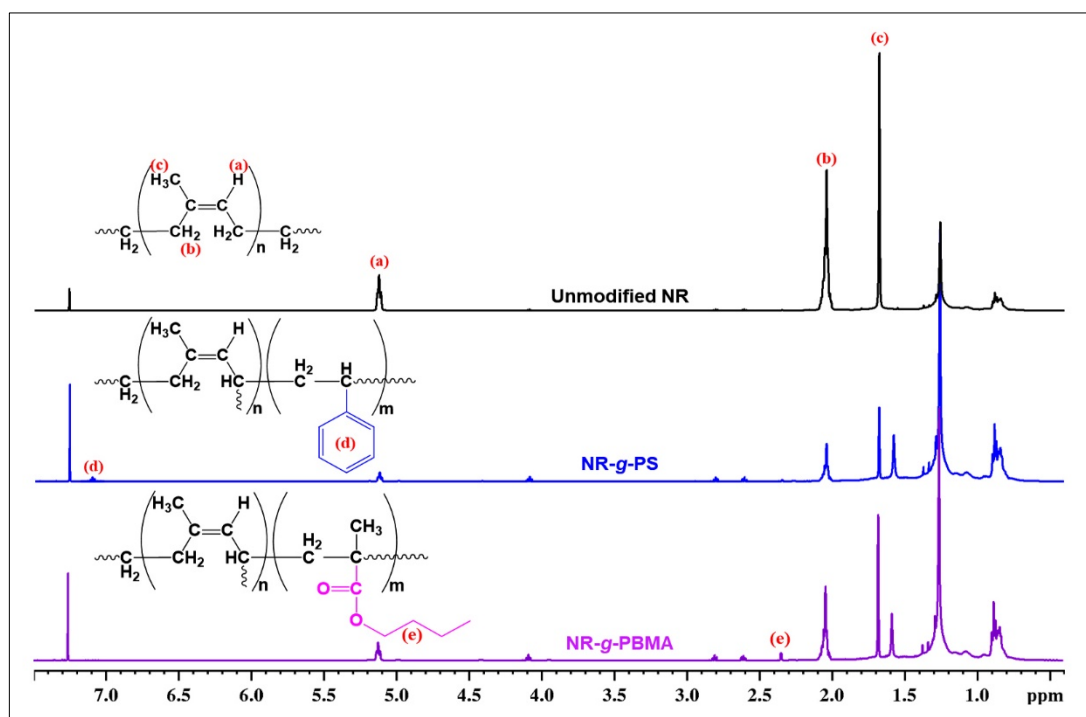


Figure 2 $^1\text{H-NMR}$ spectra of ungrafted NRs, grafted NR-*g*-PS, and grafted NR-*g*-PBMA.

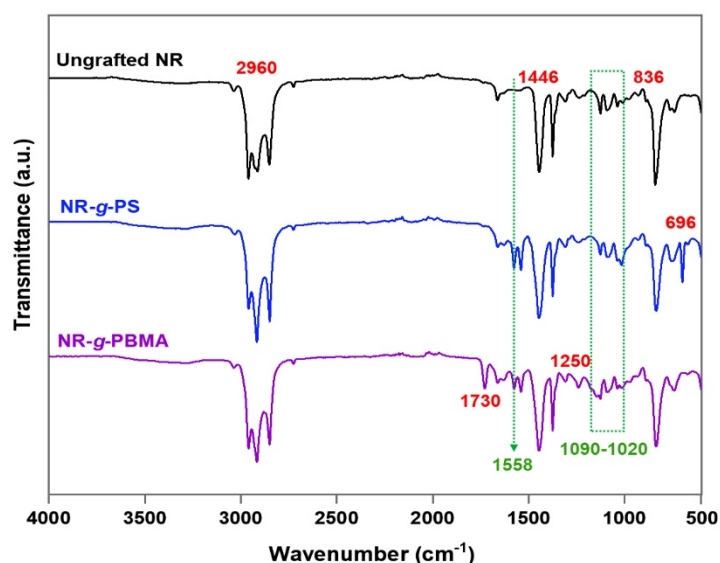


Figure 3 ATR-FTIR spectra of ungrafted NR, grafted NR-*g*-PS, and grafted NR-*g*-PBMA.

Mechanical properties of cured composites

The mechanical properties of the cured NRs using glutaraldehyde as a curing agent were evaluated through tensile testing according to the ASTM D 412 method. The 100%, 300%, and 500% modulus refer to the stress values at specific levels of strain, along with tensile strength, elongation at break, and hardness, as shown in Table 1. The stress-strain curves of the cured composites (Figure 4) clearly show that at strains below 100%, the stress increases sharply, which is consistent with the principles of the Neo-Hookean theory. This phenomenon might be attributed to the chain entanglement of NR molecules, which contributes to the strength of the composites against extension [10]. Beyond 300% strain, the stress of the cured grafted composites increases again until reaching maximum stress. This behavior indicates strain-induced crystallization of the cured grafted composites [7, 21]. Moreover, it was found that the grafted vulcanizates exhibited higher 100, 300, and 500% modulus, tensile strength, and hardness than the ungrafted NR vulcanizate. The mechanical properties of NR-g-PS composites significantly improved and showed a 114% increase in modulus at 100% strain, 127% in tensile strength, and 37% in hardness.

Table 1 Mechanical properties of CNTs filled ungrafted, NR-g-PS and NR-g-PBMA composited vulcanizates using glutaraldehyde as curing agent

Samples	Ungrafted NR/CNTs	NR-g-PS/CNTs	NR-g-PBMA/CNTs
100% modulus (MPa)	1.40 ± 0.05	3.00 ± 0.04	3.63 ± 0.05
300% modulus (MPa)	1.57 ± 0.03	3.54 ± 0.05	3.87 ± 0.01
500% modulus (MPa)	2.57 ± 0.20	4.91 ± 0.24	5.52 ± 0.20
Tensile strength (MPa)	8.81 ± 0.13	20.08 ± 0.18	17.24 ± 0.15
Elongation at break (%)	960.60 ± 33.81	940.08 ± 23.30	894.18 ± 8.48
Hardness (Shore A)	46.8 ± 0.4	64.4 ± 0.5	62.8 ± 0.4

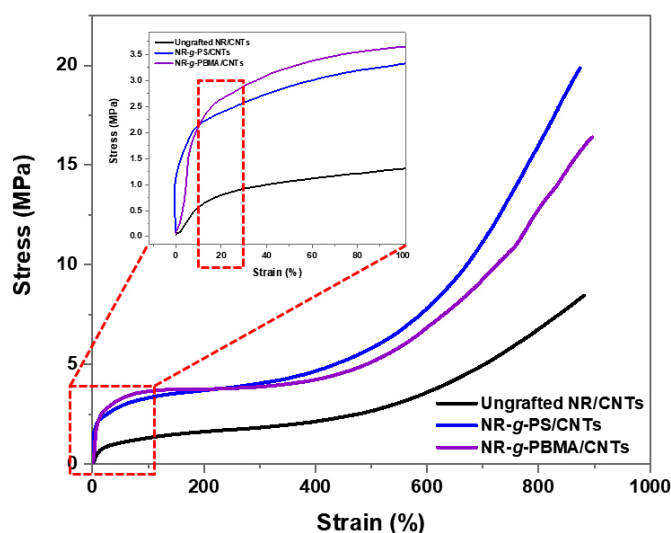


Figure 4 Stress-strain curves of cured ungrafted, NR-g-PS and NR-g-PBMA composited using glutaraldehyde as curing agent.

Similarly, NR-g-PBMA composites also exhibited enhancements, with a 159% increase in modulus at 100% strain, 95% in tensile strength, and 34% in hardness. The mechanical properties of the NR had strongly increased upon grafting functional groups on NR molecules. Functional group is often grafted onto NR to improve the chemical interaction between its molecules [20]. On the other hand, the lowest values of elongation at break were observed for the cured grafted NR compared to cured ungrafted NR. This is due to the presence of brittle and thermoplastic

components that reduce the strain at the break of NR. The hardness values of cured ungrafted and grafted NR/CNTs composite were also summarized in Table 1. It is clearly seen that the hardness value of the composites is increased upon grafting the functional group. This is due to the incorporation of CNT nanofillers and rigid components of functional group (styrene and BMA) into the NR matrix by reducing the elasticity of NR chains and making the composite more rigid [8]. This increases hardness when adding the CNTs nanofiller and grafting monomer to the rubber matrix.

Furthermore, considering modulus at low strain (10–30% strain) directly related to the range of use for motion sensor applications, that showed the modulus at low strain of cured NR-*g*-PBMA significantly increased (Figure 4). This can be attributed to the rubber chain entanglement of NR and the high polarity of functional groups in the molecular chains of NR-*g*-PBMA, which can be explained by the glutaraldehyde-rubber crosslink through the covalent bond between two carbon atoms and glutaraldehyde-ester crosslink through the active functional groups of grafted NR molecules [22]. Therefore, cured NR-*g*-PBMA composite provides a high modulus at low strain, resulting in advantages for improving the sensitivity of the rubber composites.

Swelling properties of cured composites

The chemical crosslinking of the NR samples was elucidated through swelling experiments using a toluene solvent. Figure 5 indicates the swelling degree of the samples. It is seen that the degree of swelling for all grafted NRs showed lower values compared to ungrafted NRs. A lower value indicates the material with better chemical resistance. This can be attributed to the chemical interaction between polar functional groups in its molecules [23]. Among different grafted NR samples, NR-*g*-PBMA exhibited higher chemical resistance, followed by NR-*g*-PS. This can be attributed to the higher dipole moment of PBMA ($\mu = 1.6\text{--}1.97$ Debye) compared to the dipole moment of styrene ($\mu = 0.13$ Debye) molecule in the grafted forms [19]. A higher dipole moment corresponds to higher polar-polar interactions in its molecule. The higher interaction between polar functional groups of the grafted NR (NR-*g*-PBMA) contains butylmetacrylate that polar functional groups (from PBMA) behave as a barrier which does not allow the chains to rearrange easily under chemical stress. Also, after vulcanization using glutaraldehyde, the crosslinked structure resists the movement of solvent through the vulcanized rubber. This can be explained by the interaction between polar functional groups present in the molecules with a robust interface that developed and restricts the penetration of the solvent, causing the lower swelling degree of the grafted NR. According to previously published articles, the glutaraldehyde vulcanized rubber phase does not allow the chains to rearrange easily under the solvent stress [13,14,24]. This occurrence can be understood through the chemical linkage between polar functional groups within the NR molecules. Therefore, high modulus at low strain and higher interaction between polar functional groups, from these reason the NR-*g*-PBMA was chosen to further investigated in electrical conductivity for future development in sensor applications.

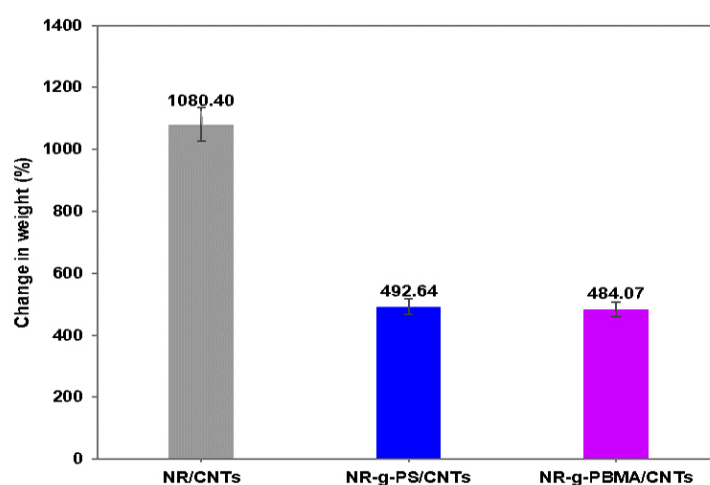


Figure 5 Degree of swelling of cured ungrafted, NR-*g*-PS and NR-*g*-PBMA composited in toluene solvent.

Electrical properties of cured composites

The electrical conductivity of the composites was examined to assess the capability of CNTs to create continuous networks within the NR vulcanizates. In general, the electrical conductivity of a composite increases with conductive filler loading. It provides conductive pathways through the NR matrix and transforms this insulator into an electrical conductor [25]. In this work, the electrical properties of CNTs filled ungrafted and grafted NR vulcanizates were studied by investigation of the dielectric constant (ϵ') and the electrical conductivity (σ), respectively. Figure 6 shows the dielectric constant of CNTs filled ungrafted NR and NR-*g*-PBMA vulcanizates in the frequency range from 100 to 1050 kHz. It is seen that the dielectric constant of the CNTs filled NR-*g*-PBMA vulcanizates significantly increased. This might be attributed to the sp^2 -hybridization in CNTs with plenty of free electrons forming electric dipoles. Interfacial polarization in the CNTs-filled NR vulcanizates was then induced by the dipole-dipole interactions. Also, by adding CNTs as fillers in the NR matrix, space charge polarization originated at the conductor-insulator interfaces. In this case, the fillers conduct while the NR insulates, generating a dielectrically heterogeneous system [26]. Hence, space charges accumulate at the interface between the polymer and the filler, contributing to what is known as interfacial polarization, following the Maxwell-Wagner-Sillars effect [25].

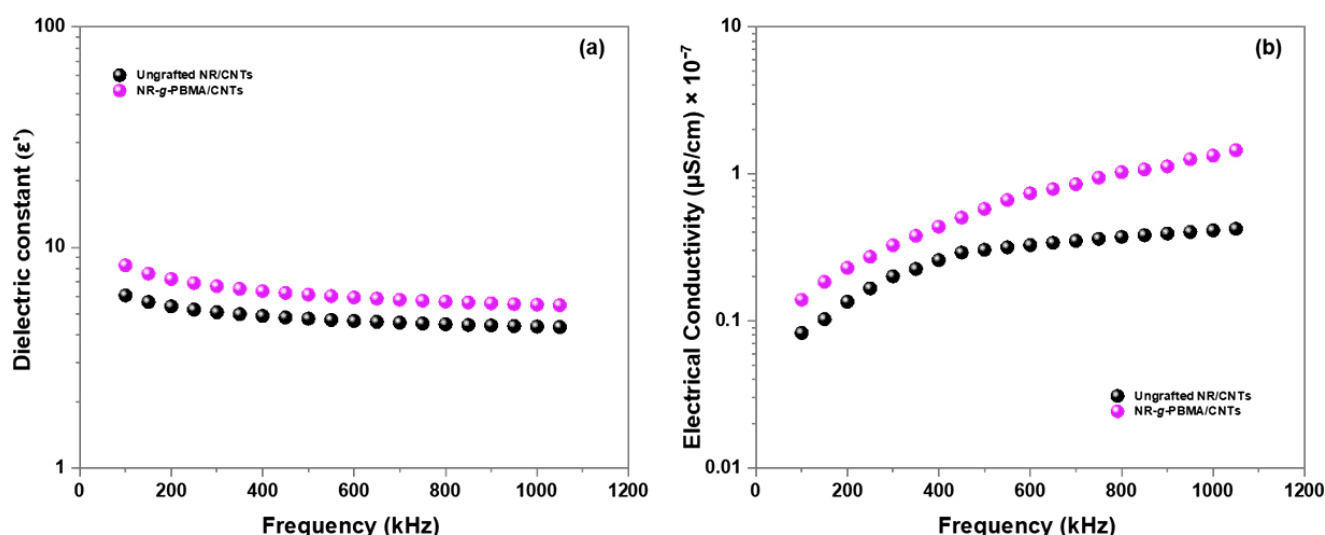


Figure 6 Dielectric constant (a) and electrical conductivity (b) as a function of across frequency for CNTs filled ungrafted and NR-*g*-PBMA vulcanizates.

Furthermore, it was found that the CNTs filled grafted NR vulcanizate demonstrated the highest dielectric constant. This is due to the synergistic of the high specific surface of CNTs and high polarization of BMA functional groups, which gave a higher dielectric constant for the CNTs filled grafted NR vulcanizate than the others. Moreover, the frequency-dependent behavior was observed for the filled ungrafted NR vulcanizates. It was found that the dielectric constant decreased upon frequency increase. This might be due to the lack of a CNT network that occurs at high frequency. This clarifies the formation of dipole-dipole interactions between the NR-*g*-PBMA matrix and the CNT network, causing continuous CNT networks [21]. This indicates a continuous CNT network formed in the grafted NR matrix, giving the frequency-independent dielectric constants in Figure 6(a).

To assess the formation of CNT networks in the NR vulcanizates, the plots of electrical conductivity versus frequency range from 100 to 1050 kHz are discussed in Figure 6(b). It is clearly seen that the electrical conductivity increased with CNTs adding in both ungrafted and grafted NR [9]. This is due to the high electric conductivity of CNTs from its sp^2 hybridized structures. The transition from an insulating to a conducting state occurs when CNTs fill in the matrix, causing an increase in the electrical conductivity of the rubber composites [21]. The CNTs filled NR-*g*-PBMA

demonstrated higher electrical conductivity than the ungrafted NR. This suggests enhanced CNTs dispersion of the grafted NR/CNTs composites because of the interactions of the functional groups in NR-*g*-PBMA molecules and the polar groups on CNTs surfaces. This confirms that the polarity effects of grafted rubber molecules markedly improved CNTs dispersion and electrical properties of the rubber composites.

4. Conclusion

This study successfully utilized graft copolymerization to integrate BMA and styrene onto NR molecules, achieving high grafting efficiency. The grafted NR combined with CNTs and cured using glutaraldehyde exhibited enhanced electrical, mechanical, and swelling properties. The grafted NR composites exhibited significantly better electrical and mechanical properties due to the high specific surface area of CNTs and the high polarization of functional groups. Specifically, NR-*g*-PS composites showed a 114% increase in modulus at 100% strain, 127% in tensile strength, and 37% in hardness. Similarly, NR-*g*-PBMA composites also exhibited enhancements, with a 159% increase in modulus at 100% strain, 95% in tensile strength, and 134% in hardness. These improvements are attributed to enhanced chemical linkages between the grafted NR matrix and CNTs. According to the swelling properties of cured composites, it was found that the cured grafted NR composites had lower swellability compared to the ungrafted NR samples. This is attributed to the absence of butyl methacrylate functional groups on the molecular chains and strong polar-polar interaction among the molecules. The study highlights the potential of grafted NR composites for creating flexible conductive materials with high modulus and enhanced electrical properties.

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