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Effect of modified nanographene oxide (mGO)/carbon nanotubes (CNTs) hybrid filler on the cure, mechanical and swelling properties of silicone rubber composites

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Abstract

In this study, modified nanographene oxide (mGO) and carbon nanotubes (CNTs) reinforced phenyl silicone rubber (PSR) composites were created and studied. On the mechanical characteristics of the PSR hybrid composites, the synergistic impact of mGO and CNTs was investigated. The PSR hybrid composites were assessed for their tensile strength, elongation at break, 100% modulus, tear strength, hardness, rebound resilience, abrasion resistance, compression set, swelling resistance, and microstructure. The micro-structural, mechanical, and other properties of the nanocomposites are greatly influenced by the concentration of CNTs and mGO. According to the study, the nanocomposites with 6 phr of mGO and 3 phr of CNTs exhibit the highest mechanical property as well as properties that make them resistant to swelling and abrasion.

Keywords: PSR; mGO/CNTs; Nanocomposites; Mechanical properties; Swelling resistance

1. Introduction

Due to its exceptional reinforcing qualities based on the structure and physical bonding with the polymer, carbon black (CB) is the filler that is most frequently employed in rubber compounds [1]. However, it also has limitations, such as in dynamic properties, which control many items' essential characteristics, like tyres. Silica has long been used to enhance the elastic characteristics of rubbers [2]. The friction qualities of the rubber are improved when silica is used in place of CB. Therefore, silica-filled rubber is better suited for tyre applications than CB-filled rubber since it produces less rolling resistance when utilised in tyre treads. The adhesion and interaction between the nonpolar rubber and the polar filler are poor, which is one disadvantage of using silica. To fully benefit from silica, surface modification is therefore
necessary. Additionally, many phases of mixing are necessary for a good dispersion of silica particles into rubber matrix, which lengthens processing times and raises processing costs [3].

With novel filler systems that provide a proper dispersion and a good polymer-filler interaction, the problems of CB and silica may be avoided. Since Toyota introduced the nanoclay-filled polyamides in 1991, nanocomposites have been the focus of polymer research [4-6]. Technology to replace a significant portion of CB with alternative fillers without losing the impact on the characteristics of the composites is constantly being developed by researchers [3].

Polymer composites are the most promising options for flexible devices and components, yet they don’t work well on their own. As a result, nanofillers are utilised to enhance the undesirable properties of the polymer matrix. As nanofillers, carbon allotropes are frequently employed, including sp² hybridised 1D carbon nanotubes (CNTs) [7], 2D graphene [8], and 3D graphite [9]. Transparent conductors, nanoelectronic devices, pharmaceutical delivery, biomolecular detection, and other uses for carbon nanomaterials (CNTs, graphene, and graphite) abound.

Nanographene functions as a lubricant and, at very low concentrations, can increase the fracture strain and stretchability in rubber nanocomposites due to Vander-Waals interactions. A modest content of nanofillers results in a significant improvement in electrical and mechanical properties because of their low density, exceptional mechanical qualities, high thermal conductivity, and high electron mobility [10].

Nanographene oxide (GO) is used as a precursor in elastomeric matrices to enhance their electrical and thermal properties. These nano sheets can be employed as a matrix stiffening agent even though they have strong mechanical characteristics in elastomeric matrices [11]. To promote dispersion in various solvents (aromatic, aliphatic, and chlorinated) and compatibility with elastomer matrices, the surface of graphene nanosheets is functionalized with the proper agents. Epoxies, hydroxyl groups on the surface of nanosheets, and carbonyl, carboxyl groups at the margins of GO sheets enable these materials to disperse in polar liquids [12]. The dispersion of GO nanosheets in nonpolar media has been the subject of numerous studies. Alkylated melamine (ADDT), which is made from cyanuric chloride, was utilised by Tang et al. [13] to covalently functionalize the surface of GO nano sheets. The resulting GO-ADDT was very soluble in organic solvents. They looked at the GO-thermal ADDT’s stability and found that it was more thermally stable than GO. Phase transfer was used by Yu et al [14] to disperse GO in
n-octane solvent. As a suspending agent in the solvent, they utilised oleylamine. Oleylamine and GO therefore formed a solid bond. The presence of oleylamine on the GO sheets was confirmed by FT-IR spectra. Huang et al. [15] introduced decyl groups to a range of imperfection spots on the surface of decreased GO. Polar GO consequently dispersed in non-polar solvents like toluene. They found that the presence of these alkyl chains can prevent the re-aggregation of graphene sheets in non-polar fluids.

The electrical conductivity and gas barrier of the nanocomposites were improved by Kim et al's [16] methods of treating GO with phenyl isocyanate and subsequently integrating this modified GO with polyurethane. Deshmukh et al. [17] employed GO to enhance the thermal and mechanical properties of polyvinyl chloride (PVC). Wang et al. [18] created GO/silicone rubber nano-composites to increase the thermal stability of the nano-composites. Ozbas et al. [19] employ functionalized graphene sheets (FGSs) to improve the mechanical properties, gas permeability, and electrical conductivity of polydimethylsiloxane (PDMS). Electrical percolation was detected in composite materials with a conductivity of 0.8 wt% FGS. Silicone rubber-graphene nanoribbon nanocomposites' mechanical and thermal properties were enhanced by Gan et al. [20]. Natural graphite oxide was converted into GO, a two-dimensional carbon sheet, using a modified Hummers technique. The GO has a large number of oxygen-containing groups on its surface, which allows it to diffuse in water and create a stable colloid solution. This enables the development of a brand-new class of platforms for chemical reactions made of solution-dispersible aromatic hydrocarbons. Covalent connection epoxide and hydroxyl functional groups are present on each side of the basal plane in GO, while carboxyl functional groups are present at the edge sites [21]. Due to the presence of oxygen-containing functional groups, the surface property of GO may change from non-polar to polar, boosting the adsorption of ionic and non-ionic pollutants [22]. Through hydrogen bonding, electron donor-acceptor interactions, and dispersive interactions, GO may be able to absorb organic contaminants [23].

In recent times, nanofillers like multiwalled carbon nanotubes (MWCNTs) have emerged as a possible substitute for the substantial amount of CB necessary to provide the best reinforcing qualities [24]. When compared to CB with high filler content, MWCNTs have higher mechanical and electrical properties [25]. In order to enhance the characteristics of polymer composites, MWCNTs are frequently utilised as a reinforcing nanofiller [26].
The use of MWCNTs to reinforce a polymer matrix is not without its difficulties, though, including nanotubes compatibility with the polymer matrix [27], nanotubes dispersion [28], nanotubes aggregation [29], and nanotubes-polymer interaction [30]. Among these, the MWCNTs reinforcement in a polymer matrix is severely constrained by MWCNTs polymer interfacial interaction and MWCNTs dispersion. MWCNTs characteristics including the surface area, aspect ratio, roughness, surface energy, and morphological characteristics like shape have an impact on the dispersion state of MWCNTs and their interaction with the polymer matrix [31]. Improvements to nanotubes surface modification [32], processing conditions [33], and polymer matrix modification [34] are techniques utilised to enhance MWCNTs dispersion and their interaction with the rubber matrix. However, there hasn't been much progress in areas like flexible and elastic electronics [35] or electromagnetic interference shielding [36].

Numerous polymer matrixes, including thermoplastics [37], thermosets [38], and elastomers [39] are investigated for reinforcing with MWCNTs-based nanofiller [40–41]. Elastomers come in a variety of forms, including silicone rubber [42], natural rubbers [43], and diene rubbers [44]. Due to its simple processing, low viscosity, high tensile strength, ideal curing, and reinforcing qualities, silicone rubber is frequently employed [45]. The widespread usage of silicone rubber in many industrial applications, including actuators and sensors, is just one of its many benefits [46-47]. Numerous studies have demonstrated that silicone rubber reinforced with MWCNTs nanofillers has improved mechanical strength, electrical characteristics, filler dispersion, and compatibility with silicone rubber in industrial applications like actuators [48].

Many researchers employed MWCNTs or modified MWCNTs for numerous industrial applications [49–51]. High actuation for MWCNTs-based composites was demonstrated [52–53], as well as actuation for MWCNTs and few layer graphene-based composites. Halloysite nanotube composites made from silicone rubber have also been investigated for use in a variety of industrial applications [54]. Silicone rubber-based piezo-resistive strain sensors based on mGO-MWCNTs hybrids, however, have not yet been studied. As a result, new, highly flexible and stretchable devices based on silicone rubber packed with carbon family members (mGO/MWCNTs hybrid) were created in this work for use as strain sensors and actuators. Structure-property relationships of the composites were established by earlier researchers [52]. The mGO particles were alone used as the reinforcement in silicone rubber nanocomposites
which results in improved mechanical properties, ageing, abrasion and swelling resistances as stated by Aravinth et al. [55]. In this study, a new hybrid composite was created using a silicone rubber matrix and reinforced with various mGO and MWCNTs particle concentrations. The utilisation of mGO/MWCNTs hybrid filler in this work along with chemical treatment will provide fresh experimental findings for commercial use. As a result, this study is safe for the environment and eco-friendly.

2. Experimental

2.1 Materials

Graphite-flakes (99% carbon basis; formula: C; 12.01 (g/mol) formula weight; 325 mesh particle size (≥ 99%); natural), multiwalled carbon nanotubes (MWCNTs; 20-30% MWCNT basis; outer diameter x length – 7-12 nm x 0.5-10 μm; 5-30 graphene layers), 4,4’-Diphenylmethane diisocyanate (MDI; empirical formula – C_{15}H_{10}N_{2}O_{2}; molecular weight – 250.25; density – 1.237 kg/m³ at 20 °C; isomer diisocyanates - ≤ 10% (area%); triisocyanate – 20% (area%)) and N,N-dimethylacetamide (linear formula – CH₂CON(CH₃)₂; molecular weight - 87.12) was purchased from Sigma-Aldrich, Puducherry. Phenyl silicone rubber and dicumyl peroxide (DCP) was supplied by Vignesh Chemical, Chennai, India. All of the other chemicals (acetone, NaNO₃, H₂SO₄, KMnO₄, H₂O₂, HCl, dibutyltin dilaurate (C₃₂H₆₄O₄Sn)), and solvents (C₆H₆, C₈H₁₀, C₇H₈, CH₂Cl₂, C₉H₁₂, C₆C₁₄, C₅H₁₂, C₈H₁₈, C₇H₁₆, CCl₄, and CHCl₃) [56] were of exploratory grade and were used without further decontamination.

2.2 Preparation of graphene oxide

First, graphene oxide (GO) was made using a modified Hummers process [57]. Graphene oxide preparation is shown in Figure 1. 5 g of graphite flake 30–50 μm, 3.75 g of NaNO₃, and 230 mL of H₂SO₄ were combined at 0 °C. After stirring for two hours in an ice-water bath, the mixture received 15 g of KMnO₄ gradually over the course of one hour. After five days of continuous stirring at 23 °C, a half litre of 5 wt.% H₂SO₄ was added in one hour. The resulting mixture was stirred for an additional 2 hours at 98 °C. 15 mL of diluted hydrogen peroxide (H₂O₂) was added once the temperature was lowered to 60 °C. The mixture was stirred for two hours at 23 °C, precipitated, and repeatedly washed with an aqueous solution of 3 wt.% H₂SO₄ and 0.5 wt.% H₂O₂ before filtering. After that, the solid was three times washed with a 3 wt.%
and 0.6 wt.% HCl solution. After being rinsed with deionized water until the pH level reached almost 7 [58–59], the GO material was filtered and dried for a week in a vacuum oven.

Figure 1. Preparation of graphene oxide

2.3 Preparation of modified GO

The creation of modified graphene oxide is depicted in Figure 2. In a vacuum oven, GO was dehydrated/dried for 3 hours at 80 °C. To create a homogenous dispersion, GO was ultrasonically sonicated in anhydrous N,N-dimethylacetamide (DMAc). The mixture was stirred under nitrogen while being heated to 80 °C. A few drops of dibutyltin dilaurate (DBTDL) were added to the dispersion after MDI was dissolved in anhydrous DMAc. The reaction was maintained at 80 °C for 4 hours. After cooling to room temperature, the mixture was centrifuged and repeatedly rinsed with acetone to remove any leftover MDI. 24 hours were spent drying the
solid product in a vacuum oven set at 50 °C. Figure 3 shows the GO functionalization using MDI procedure.

Graphene oxide (dried for 3 h at 80 °C)
\[ \rightarrow \]
N,N-dimethylacetamide (DMAc)
\[ \rightarrow \]
Processed GO
\[ \rightarrow \]
80 °C
\[ \rightarrow \]
Adding
4,4'-diphenylmethane diisocyanate (MDI) + Dibutyltin dilaurate (DBTDL)
\[ \rightarrow \]
Washed with acetone
\[ \rightarrow \]
80 °C for 4 h
\[ \rightarrow \]
Excess MDI removed
\[ \rightarrow \]
50 °C for 24 h
\[ \rightarrow \]
Modified GO

Figure 2. Preparation of MDI-GO
2.4 Preparation of silicone-mGO/CNTs nanocomposite

In accordance with ASTM D-3182 specifications, a silicone elastomer was used to prepare the necessary sample. It was combined with other materials in a laboratory-sized open mill mixing apparatus at a speed ratio of 1:1.4. (i) Silicone rubber – 100 phr; (ii) CNTs – varied (0, 1, 2, 3, 4, 5, and 6 phr); (iii) mGO – 6 phr (iv) dicumyl peroxide (DCP) – 4 phr are used to determine the ratios of the ingredients during mixing. The temperature was maintained between 60 and 70 °C throughout the mixing process, as were the cutting, nip gap, and mixing times (15 to 25 min) (for proper mixing of rubber (silicone rubber), reinforcement (mGO/MWCNTs) and vulcanizing agent (DCP)). Under the same circumstances, the prepared samples were electrically
heated and subsequently moulded in a semi-automated hydraulic press (pressure: 30 MPa, temperature: 160 °C, and time: optimal cure time).

2.5 Characterizations

The cure rate index (CRI) of the nanocomposites, which is calculated as CRI (min⁻¹) = 100/(t_{s2} - t_{90}), the scorch time (t_{s2}, min), the optimum cure time (t_{90}, min), the minimum torque (M_l, dNm), the maximum torque (M_h, dNm), and the torque difference (ΔM, dNm), were all measured using an oscillating die rheometer with ASTM D-2048 at a temperature of 160 °C [61].

According to ASTM D-412, the tensile properties were evaluated using Instron 4302 testing equipment at room temperature (23 °C). The same machine was used to test the rubber nanocomposites' tear strength in accordance with ASTM D-624 testing guidelines. Tensile and tear strength tests on all specimens were performed at 500 mm/min [62]. The tear and tensile process was performed five times in order to limit the random error. In line with ASTM D-2240, hardness was assessed using a Shore A durometer. Using ASTM D-2632 techniques, the vertical rebound resilience of each sample was used to examine the rebound resilience of all rubber nanocomposites [63].

The abrasion resistance of the nanocomposites was assessed using a DIN abrader and grade 60 emery paper at room temperature (23 °C), 10 N force (constant), and 0.32 m/s speed (constant). Abrasion resistance was investigated in terms of volume loss using the ASTM D-5963 standard [64].

The button-shaped compression set sample had a thickness of 12 ± 0.5 mm and a diameter of 29 ± 0.5 mm. The permanent compression set was measured using a compression instrument. The specimens were pressed at 23 °C with a 25% deformation rate for 1, 2, and 3 days. The specimen was then removed from the compression apparatus and allowed to rest at room temperature for 30 minutes. The permanent compression set (C) [65] was found to be

\[
\text{Permanent compression set (C)} = \frac{H_0 - H_1}{H_0 - H_n} \times 100\%
\]

where, \(H_0\) - original height, \(H_1\) - final height of the sample and \(H_n\) - spacer height.

According to ASTM D-471 standard, the solvent immersion method was utilised to conduct the swelling test. To examine the behaviour of silicone/mGO/MWCNTs...
nanocomposites after swelling, samples from a sheet of rubber nano-composites were cut into squares with rounded corners (25 mm in size and 2 mm thick). The samples were then immersed in various solvents for varying lengths of time after the weight of each sample was calculated using extremely sensitive weighing equipment. The solvents used in this experiment included dichloromethane, benzene, xylene, toluene, mesitylene, n-hexane, n-pentane, n-octane, and n-heptane as well as carbon tetrachloride and chloroform. After the time limit had passed, the samples were removed from the solvent, cleaned, and weighed once more. The mole percent uptake [66] was calculated using the calculation shown below:

$$Q_t = \frac{(M_t-M_0)/MW}{M_0} \times 100$$

(2)

where, MW - molecular weight of the penetrant, M₀ – samples weight before swelling, and Mₜ - swelled samples weight after time 72 h of immersion.

A SEM was utilised to explore the morphological features of silicone nanocomposites using micro-photomicrographs (ZEISS EVO 18 MA s SEM). The samples first received a gold sputter coating.

The thermal ageing properties of silicone nanocomposites were examined by ageing for 96 hours at 70 °C (the remainder for a similar amount of time at 100 °C and 125 °C, in accordance with ASTM D-865) and 100 °C and 125 °C in accordance with ASTM D-573. The parameters of accelerated ageing were measured following a 96-hour ageing test. To determine how well the silicone nanocomposites withstood ageing, their tensile strength, 100% modulus, tear strength, elongation at break, abrasion resistance, hardness, and rebound resilience were measured. The following formula is used to calculate the percentage of retention in specimen properties:

$$\text{Percentage retention} = \frac{\text{Value after aging}}{\text{Value before aging}} \times 100$$

(3)

3. Results and discussion

3.1 Cure characteristics

Figures 4, 5, 6, 7, 8, and 9 show the minimum torque (M₁), maximum torque (M₉), torque difference (ΔM: delta torque), scorch time (t₂), optimum cure time (t₉₀), and cure rate index
(CRI) of silicone rubber composites reinforced with mGO and MWCNTs and crosslinked with peroxide.

The viscosity of the substances at the test temperature directly relates to the \( M_l \). The masticated rubber's viscosity can be determined using the \( M_l \) unit of measurement. According to Figure 4, the \( M_l \) rises as the MWCNTs content does. This suggests that the addition of MWCNTs to the nanocomposites had a negative impact on their processability. Nanocomposites filled with hybrid nanofiller (6 phr mGO + 6 phr MWCNTs) exhibit a slightly higher viscosity than those filled with mGO filler. The improved interaction between MWCNTs and the silicone rubber-mGO compounds may be the cause of the higher viscosity of the nanocomposites. MWCNTs' tubular structure has a greater surface area, which can lead to better interactions. The stock modulus measurement can be related to the \( M_h \) value. The silicone rubber-mGO composites with MWCNT loading demonstrate that \( M_h \) rises as MWCNT concentration is increased, as illustrated in Figure 5. The \( \Delta M \) serves as a proximate indicator of the rubber vulcanizates' degree of crosslinking. This demonstrates that \( \Delta M \) rises steadily as MWCNT content rises, as illustrated in Figure 6.

The variations in surface free energy, surface topology, and surface area of the reinforcements are thought to be effective parameters in our instance where several forms of carbon nanoparticles, particularly hybrid filler, i.e. mGO and MWCNTs, are used. The substantially greater bound rubber (glassy layer plus occluded rubber) for mGO-6 phr MWCNTs can be attributed to the higher \( M_l \) and \( \Delta M \) values for silicone rubber/mGO-6 phr MWCNTs because of its extremely high specific surface area and highly structured nature (Saatchi and Shojaei provide more information about the bound rubber calculations [67]). According to their dispersive component of surface free energy, particles with higher specific surface areas can actually produce a stronger rubber-filler interaction, resulting in more bound rubber and higher compound viscosities.

The results (Figures 7 and 8) demonstrate that the rubber composite's \( t_{52} \) and \( t_{90} \) decrease as its MWCNTs content rises. The CRI of the silicone rubber nanocomposites is displayed in Figure 9. With more MWCNTs present, CRI for the silicone rubber nanocomposites was found to rise. A high CRI result indicates a higher rate of vulcanization. The systems with a higher filler loading were found to have the highest cure rates. The literature, however, offers no
definitive justification for this observation. One potential mechanism is the adsorption of peroxide on the surface of mGO and MWCNTs.

**Figure 4. Minimum torque of silicone rubber-mGO/MWCNTs composites**

**Figure 5. Maximum torque of silicone rubber-mGO/MWCNTs composites**
Figure 6. Torque difference of silicone rubber-mGO/MWCNTs composites

Figure 7. Scorch time of silicone rubber-mGO/MWCNTs composites
3.2 Mechanical properties

The composite's tensile strength (TS), tensile modulus (TM), hardness (HD), and tear strength (TAS) are all improved by the addition of fillers to the matrix. The impact of reinforcement on polymer materials depends on the nature of the specific interactions between the polymer matrix and reinforcing fillers and is strongly related to the interphase characteristics [68-69]. The filler-filled composite materials are given various beneficial features by the addition of filler to the polymer materials. The characteristics, such as particle size, surface area, surface
activity, aggregate structure, and rubber-filler interactions, are largely dependent on the dispersion conditions of filler particles [70-71]. The benefit of filler being better disseminated in the rubber matrix allows for optimal reinforcing control. Another crucial component of the reinforcing effect is the chemical or physical interaction between the filler and the rubber [72]. The properties of rubber composite are significantly influenced by the interaction between the reinforcing fillers and rubber matrix. In contrast to filler-filler and filler-rubber interactions, rubber-rubber interactions primarily occur when rubber blends are utilised in composites. While filler-rubber interactions are described by the compatibility of the filler with the rubber, filler-filler interactions are explained by the attraction of filler to filler and capacity to create a network. One of the most crucial mechanisms in reinforcement is filler-filler interactions, especially at high filler loading. These interactions depend on filler volume percentage, filler network architecture, chemical interactions between the filler particle surfaces, such as filler-filler and filler-rubber, physical interactions, such as Vander Waals forces, and hydrogen bonding.

Figure 10 displays the graph for the TS of mGO and MWCNTs-reinforced silicone rubber nanocomposites. The TS of the silicone rubber nanocomposites increases initially as the concentration of MWCNTs rises, and then slowly declines as the concentration of MWCNTs rises further. It is also clear from Figure 10 that the MWCNTs concentration needed to be at its peak for 3 phr before the TS began to decline. This was caused by the higher crosslink density (CLD) seen in MWCNTs at 3 phr, as illustrated in Figure 17. The efficiency of MWCNTs was enhanced by the presence of mGO, as demonstrated in Figure 10. This was brought about by improved MWCNT–silicone rubber matrix interaction via the mGO surface. MWCNTs have a well-known strong filler-filler interaction. The interaction between MWCNTs and other MWCNTs should therefore grow as MWCNTs content increases, which in turn should result in a decrease in the interaction between MWCNTs and silicone rubber/mGO.
In Figure 11, the silicone rubber nanocomposites' reduced elongation at break (EB) is depicted. As the concentration of MWCNTs in the silicone rubber nanocomposites increases, the EB of those materials gradually declines up to a point of 3 phr before falling off quickly. The features of dissimilar constituent phases like silicone rubber, mGO, MWCNTs, and their interfacial region combine to produce the EB of the MWCNTs filled hybrid rubber composites. The characteristics of the hybrid composites are improved as a result of the MWCNTs' increased strength of interaction with silicone rubber-mGO and MWCNTs.
The TM of the silicone rubber nanocomposites augmented with mGO and MWCNTs particles is shown in Figure 12. The TM of the silicone rubber nanocomposites including MWCNTs steps-up with an increase in filler content up to 3 phr and then gradually declines with nanoparticle integration. This was brought on by a rise in CLD and a restriction on the mobility of molecular chains.

![Figure 12. Tensile modulus of silicone rubber-mGO/MWCNTs composites](image)

In Figure 13, the hybrid composites' TAS was displayed. When MWCNT concentration was raised, it resulted in higher TAS for silicone rubber hybrid composites containing both mGO and MWCNTs. The increased polymer chain stiffness, CLD, and interactions between them were the causes of the improvement in TAS.
As illustrated in Figure 14, the HD of a silicone rubber hybrid composite reinforced with mGO and MWCNTs increases as the concentration of MWCNTs increases. The increase in contact, CLD, and polymer chain rigidity in the polymer were the causes of the HD increase [73]. The two nanoparticles (mGO and MWCNTs) in the composite penetrate the matrix void and interact with the matrix, acting as a physical crosslink to increase CLD [74-75]. The composite sample's highest HD is correlated with higher CLD. The softer matrix becomes harder because to the CLD.
Figure 15 displays the hybrid composites' rebound resilience (RR). Low RR hybrid composites are harder than those with greater RR. The RR of the silicone rubber hybrid composites decreases with an increase in MWCNT content due to their integration. This resulted from a decrease in the polymer chain's mobility and an increase in the composite's CLD. Due to MWCNTs' critical involvement in the silicone rubber composite, the RR was limited for the MWCNT-enriched composite.

![Graph showing rebound resilience vs. MWCNT loading](image)

Figure 15. Rebound resilience of silicone rubber-mGO/MWCNTs composites

The graph for the DIN abrasion test in terms of volume loss for the rubber hybrid composites is shown in Figure 16. Up until a concentration of 3 phr MWCNTs, the wear resistance rises with an increase in MWCNT concentration before beginning to decline. The MWCNTs, which can prevent the composite from deforming during the abrasion process, were responsible for this. The abrasion property of silicone rubber-mGO/MWCNTs composites will be significantly impacted by the combination of mGO and MWCNTs. Because the dual reinforcement was distributed uniformly throughout the silicone rubber matrix and had a positive contact with the matrix, the wear property was improved. A silicone rubber-mGO/MWCNTs hybrid composite, which displays a minimal wear loss compared to other composites at a 3 phr MWCNTs content, was in line with the material's HD and tensile property. The modulus, strength, resilience, frictional behaviour (friction coefficient), and fatigability [76-78] of the
composite sample all influence the silicone rubber hybrid composites' wear resistance. The hybrid composite's maximum wear resistance may be a result of the system's several nanoparticles working together synergistically. The composite's higher CLD was what gave it greater abrasion resistance (AR). The softer rubber matrix becomes a harder one as the CLD rises. It was evident that the composite with a uniform distribution of nanoparticles had higher wear resistance than the one with agglomerated ones (Figure 17).

![Figure 16. Abrasion loss of silicone rubber-mGO/MWCNTs composites](image)

However, the impact of ambient oxygen or other gases on silicone rubber compounds is quite minimal at room temperature (between approximately -2 and 38 °C in India). This can be done using heat. Thermal ageing of compounds, which affects a variety of natural rubber and synthetic rubber (SBR, EPDM, NBR, etc.), including silicone rubber, is the deteriorating of favourable properties when in use or storage conditions [79]. The conditions in which rubber components are used or stored can cause a variety of modifications [80–81]. Age the materials at 70 °C, 100 °C, and 125 °C for 72 h (3 days) to 144 h (6 days) to determine the old values of the cured rubber's mechanical properties. After being aged at high temperatures (70 °C, 100 °C, and 125 °C) for 96 hours, the mechanical properties of samples of cured rubber were tested. The effects of ageing on physical characteristics including modulus of elasticity, TS, and HD are important from an industrial perspective. If the conditions are too severe, the rubber can quickly lose its usability.
As with all polymeric materials, silicone rubbers are prone to deterioration over time when exposed to various chemical and environmental irritants (as detailed in swelling experiments) and high temperatures [82-83]. Age-related degradation of a material's intended properties eventually results in failure [84], which can be calamitous or cause significant financial loss. Therefore, it is essential to comprehend how ageing affects material qualities in order to anticipate product lifetimes and constantly improve products and processes [85]. The amount of material property changes is frequently assessed using accelerated thermal ageing studies. Such studies have attracted the attention of academic and industrial researchers in an effort to collect quantitative and qualitative information on the long-term organisation of materials in various service environments. The three primary goals of accelerated ageing are to (i) select the best material for the given environment and exposure period, (ii) pinpoint existing degradation mechanisms before application, and (iii) forecast a material's service life and activity over time [86]. It is vital to understand the changes in properties brought on by in-service circumstances over time, though, as silicone rubbers are increasingly used in a variety of industrial machinery and process applications. Engineers can use these studies to prevent unplanned equipment failures and process halts. For instance, recent studies have examined the deterioration of silicone rubber with regard to its use as a sealing agent in machinery [87]. Silicone rubber parts in many technical machineries come into contact with lubricants and oils, as well as heat transfer fluids, at high temperatures. These elements may alter the properties of the rubber and shorten its lifespan.

Despite the complexity of silicone rubber's ageing process, it is widely known that oxidation is a significant mechanism for degradation. The rate of degradation accelerates significantly at higher temperatures. We tested and compared the mechanical properties of silicone nanocomposites with those of their thermally aged equivalents. The final cured silicone rubber goods' physical characteristics, notably their mechanical characteristics, can change at high temperatures. Rubbers' mechanical properties are crucial to their performance in a variety of applications, especially whether they are utilised as structural materials or in industrial operations [88]. In the industrial setting, rubber samples are frequently only cured to 90% of their Mₘ [89]. The 10% restriction is normally maintained to allow for the insertion of crosslinks into the rubber matrix throughout service. The impact of temperature on ageing property must therefore be evaluated. EB, TS, TAS, HD, TM, RR and AR are shown in Tables 1-7. The results
of thermal ageing at three different temperatures—70 °C, 100 °C, and 125 °C—for 96 hours (4 days) reveal that silicone rubber-mGO nanocomposites reinforced with varying amounts of MWCNTs start to exhibit sharp values of the aforementioned properties at 125 °C, whereas for nanocomposites at 100 °C and 70 °C, a significant decrease in the aforementioned properties was observed. The values of TS, TM, TAS, HD, and AR increased at 70 °C of ageing temperature, while the values of EB and RR dropped.

As the ageing temperature increases from 100 °C to 125 °C, the rate of the aforementioned qualities decreases; nevertheless, the rate of TS, TM, and HD increases as the ageing temperature increases from 70 °C to 100 °C. Ageing temperature affects TS, TM, and HD because of the complex processes occurring in the vulcanised elastomer material. This shift in behaviour can also be caused by polymer chain scission in MWCNTs nanotube-filled mGO-silicone rubber nanocomposites with high CLD due to lower molecular weight and molecular entanglement. This last one minimises energy loss through molecular mobility restriction. The TS and TAS properties of the material are impacted by the CLD. Table 7 demonstrates that when the MWCNTs content rises, the CLD of mGO-silicone rubber nanocomposites filled with varying amounts of MWCNTs nanofillers continuously increases. This post-vulcanizing effect tends to worsen as the temperature of ageing increases. In their study on the ageing kinetics of TS of natural rubber compound, Clarke et al. [90] found that both scission and cross-linking processes increase with increasing ageing temperature. When MWCNTs-filled and mGO-silicone rubber nanocomposites are present in samples at varied loadings, TS, TAS, EB, TM, HD, RR, and AR all decline with ageing. These qualities quickly degrade after 96 hours of ageing at 125 °C. Property values are declining, which is a sign of damage brought on by rapid ageing. As MWCNTs loading rises, the properties of nanocomposite materials seem to get better. When exposed to high temperatures, a rubber material only degrades in the rubber section [91]. The degradable rubber component is diluted as the quantity of MWCNTs in silicone rubber nanocomposites is raised, leading to a higher value over time. Silicone rubbers containing Si-O connections typically lose some of their strength properties as they age more quickly.

Tables 1 and 2 display the silicone rubber nanocomposites' reduction in TS and EB as well as their decreasing (reduction) rate. After being exposed to silicone rubber nanocomposites for 4 days (92 hours) at a high temperature (125 °C), the TS and EB of the silicone rubber nanocomposites decreased by 51.7 and 48.3%, from 32.87 to 16.98 MPa and from 721 to 348%,
respectively. It's important to note that the decline rate of TS exhibits a significant stepwise increase of 105.1% at 70 °C of ageing before keeping fairly constant up to 100 °C. But from 100 °C to 125 °C, the rate of TS drastically dropped, reaching only 51.7%. However, the reduction rate of EB progressively dropped to 76% at 70 °C and then continued to drop until it reached 67.8% when the experiment reached 100 °C. From 100 °C to 125 °C, the drop rate changed significantly. Similar to TS, the ultimate EB's rate of fall decreased noticeably from 100 °C to 125 °C. These results indicate that silicone rubber nanocomposite's tensile properties and EB are impacted by ageing after reaching a certain temperature for ageing (100 °C).

Table 1 Effect of MWCNTs loading on TS of mGO/MWCNTs-silicone rubber nanocomposites before/after aging

<table>
<thead>
<tr>
<th>MWCNTs loading</th>
<th>Unaged value</th>
<th>Aging temperature (condition: 70 °C, 96 h)</th>
<th>Percentage retention</th>
<th>Aging temperature (condition: 100 °C, 96 h)</th>
<th>Percentage retention</th>
<th>Aging temperature (condition: 125 °C, 96 h)</th>
<th>Percentage retention</th>
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<tbody>
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Table 2 Effect of MWCNTs loading on EB of mGO/MWCNTs-silicone rubber nanocomposites before/after aging

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<td>81.5</td>
<td>440</td>
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</table>
Silicone rubber nanocomposites' HD (Table 3) and TM (Table 4) showed a slight increase at the beginning of the ageing process, followed by a general dropping tendency, comparable to the TS behaviour versus ageing temperature. The HD of the unaged sample went from 65 Shore A in the aged sample at 70 °C to 66 Shore A, to 70 Shore A in the aged sample at 100 °C, and finally dropped to 62 Shore A. Similar to this, the TM increased from 2.98 MPa in the unaged sample to 3.18 MPa in the sample that was aged at 70 °C, 3.35 MPa in the sample that was aged at 100 °C, and finally decreased to 2.54 MPa in the sample that was aged at 125 °C. Tables 3 and 4 demonstrate that silicone rubber initially becomes harder due to exposure to high temperatures, increasing EM and HD, before becoming a flexible compound and losing its ability to withstand indentation or penetration as ageing proceeds. Wu et al. [92] conducted research on the thermal oxidation ageing of silicone rubber and discovered a growing trend in the rubber's TM, HD, and compression set (CS) as a function of temperature (the rubber aged between 120 and 180 °C) and time (ageing time range of 45-81 h). The struggle between continuous crosslinking in the rubber and macromolecule chain disintegration is indicated by the observed increasing-decreasing TAS and HD pattern [92]. Early in the exposure, crosslinking may be favoured, but after 100 °C, polymer chain breakage may prevail.

Table 3 Effect of MWCNTs content on HD of mGO/MWCNTs-silicone rubber nanocomposites before/after aging

<table>
<thead>
<tr>
<th>MWCNTs loading</th>
<th>Unaged value</th>
<th>Aging temperature (condition: 70 °C, 96 h)</th>
<th>Percentage retention</th>
<th>Aging temperature (condition: 100 °C, 96 h)</th>
<th>Percentage retention</th>
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<th>Percentage retention</th>
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Table 4 Effect of MWCNTs loading on TM of mGO/MWCNTs-silicone rubber nanocomposites before/after aging

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<th>Percentage retention</th>
<th>Aging temperature (condition: 100 °C, 96 h)</th>
<th>Percentage retention</th>
<th>Aging temperature (condition: 125 °C, 96 h)</th>
<th>Percentage retention</th>
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</table>

Table 5 Effect of MWCNTs loading on TAS of mGO/MWCNTs-silicone rubber nanocomposites before/after aging

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<tr>
<td>5</td>
<td>3.3</td>
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</tbody>
</table>
Table 6 Effect of MWCNTs loading on RR of mGO/MWCNTs-silicone rubber nanocomposites before/after aging

<table>
<thead>
<tr>
<th>MWCNTs loading</th>
<th>Unaged value</th>
<th>Aging temperature (condition: 70 °C, 96 h)</th>
<th>Percentage retention</th>
<th>Aging temperature (condition: 100 °C, 96 h)</th>
<th>Percentage retention</th>
<th>Aging temperature (condition: 125 °C, 96 h)</th>
<th>Percentage retention</th>
</tr>
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<td>80</td>
<td>14</td>
<td>70</td>
<td>12</td>
<td>60</td>
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</table>

Table 6 displays the variations in RR versus ageing temperatures for silicone rubber nanocomposites with various MWCNT loadings. Since the findings are normally reliable, it can be concluded that the RR test is sensitive and repeatable enough to detect heat damage. It is evident that the RR value of each type of filled compound decreases as ageing temperatures increase. Strong crosslinks are created, and the specimen's surface develops an oxidising skin as a result of oxygen absorption [95]. As a result, the RR of nanocomposites diminishes as the ageing temperature increases.
Table 7 Effect of MWCNTs loading on AR of mGO/MWCNTs-silicone rubber nanocomposites before/after aging

<table>
<thead>
<tr>
<th>MWCNTs loading</th>
<th>Unaged value</th>
<th>Aging temperature (condition: 70 °C, 96 h)</th>
<th>Percentage retention</th>
<th>Aging temperature (condition: 100 °C, 96 h)</th>
<th>Percentage retention</th>
<th>Aging temperature (condition: 125 °C, 96 h)</th>
<th>Percentage retention</th>
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<td>96.5</td>
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</table>

Using the kinetic theory of elasticity, the CLD of silicone rubber nanocomposites was taken into account from the TM [96]. CLD (υ) was calculated using the formula $\sigma/(\lambda - (1/\lambda^2)RT$ [97-98]. Where, TM, extension ratio, gas constant, and absolute temperature are represented by $\sigma$, $\lambda$, R, and T, respectively. Table 7 shows the relationship between abrasion loss and MWCNT content for silicone rubber nanocomposites that have undergone thermal ageing. After being thermally aged at 70 °C, all of the nanocomposites exhibit an increase in AR. This is due to the development of extra crosslinks during the thermal ageing process, as shown by the values in Table 8. When silicone rubber nanocomposites are thermally aged at 100 °C, more crosslinks are encouraged to form. However, the AR decreases in all samples after ageing at 125 °C. The CLD values in Table 8 show that this is because crosslinks deteriorate at high temperatures.

Table 8 Effect of MWCNTs loading on CLD of mGO-silicone rubber nanocomposites before/after aging

<table>
<thead>
<tr>
<th>MWCNTs loading</th>
<th>Unaged value</th>
<th>Aging temperature (condition: 70 °C, 96 h)</th>
<th>Percentage retention</th>
<th>Aging temperature (condition: 100 °C, 96 h)</th>
<th>Percentage retention</th>
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</tbody>
</table>
The swelling characteristics of silicone rubber-mGO/MWCNTs hybrid composites that are penetrant through (benzene, n-pentane, chloroform, etc.) were examined. The kind of rubber matrix, the type of reinforcing material, the temperature, the penetrant, the curing agent, etc. utilised all had an impact on the swelling behaviour of the hybrid composites. The swelling characteristics of the hybrid composites reinforced with mGO and MWCNTs are shown in Figures 17 and 18 as well as Table 9. On the mole percent uptake in the hybrid composites, the impacts of MWCNTs loading, vulcanizing agents, penetrant nature, and temperature were examined. The mole percent uptake \( Q_t \) and the square root of time \( t^{1/2} \) swelling curves are plotted. The mole percent uptake of mesitylene penetrant with various MWCNTs contents is shown in Figure 17 at a temperature of 30 °C. The mole percent absorption initially declines, reaches an optimal level, and then increases as the MWCNTs content rises. According to Figure 17, the optimum MWCNTs concentration was 3 phr, and adding more nanoparticles to the mixture will significantly enhance the mole percent uptake. A strong concentration gradient causes the early steep region of the curve for mole percent absorption to have a high swelling rate, while the last section of the curve has a lowered swelling rate that eventually approaches swelling equilibrium. With an increase in MWCNTs concentration, silicone rubber hybrid composites' equilibrium benzene absorption decreased. Due to the production of MWCNTs agglomerates after 3 phr, the absorption of benzene slightly increases. The fillers (MWCNTs/mGO) and rubber matrix had a good interaction, which improved swelling resistance. The tendency is clearly shown in Table 9 for chlorinated hydrocarbons (dichloromethane, chloroform, and carbon tetrachloride), aliphatic hydrocarbons (n-pentane, n-hexane, n-heptane, and n-octane), and aromatic hydrocarbons (toluene, xylene, and mesitylene). Higher MWCNT concentrations resulted in a decrease in swelling resistance because of an increase in MWCNTs-MWCNTs interaction, which weakens the bond between the reinforcement and the rubber matrix.
Figure 17. Mole percent uptake of mesitylene by different MWCNTs content at 23 °C

Figure 18 depicts the impact of penetrant size on the mole percent uptake of aromatic hydrocarbons (benzene, toluene, xylene, and mesitylene) by composites made of 3 phr MWCNTs. Mesitylene was discovered to have the largest penetrant size, followed by xylene, toluene, and benzene. The lowest uptake is shown in penetrants with a higher molecular weight and vice versa. In general, the relationship between the molecular weight and the penetrant is inverse. Figure 18 made it obvious that the tendency was in the following order: benzene > toluene > xylene > mesitylene. The aliphatic and chlorinated hydrocarbons showed a tendency that was comparable to this, which was listed in Table 9. In comparison to the other chlorinated hydrocarbons (84.93 g/mol for dichloromethane and 119.38 g/mol for chloroform), carbon tetrachloride (153.82 g/mol) has the lowest absorption due to its larger molecular weight.
Figure 18. Mole percent uptake of various solvents via silicone rubber-mGO nanocomposites loaded with 3 phr MWCNTs

Table 9 Mole percent uptake of penetrant (aromatic, aliphatic and chlorinated) via silicone rubber reinforced with MWCNTs composites at 23 °C

<table>
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<th>Chlorinated</th>
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<tr>
<td>mGO/MWCNTs6</td>
<td>1.21</td>
<td>0.9</td>
<td>0.78</td>
</tr>
</tbody>
</table>

Table 10 contains a summary of the silicone rubber hybrid composites' compression set values. Without MWCNTs, the hybrid composite exhibits a lower value in the compression set. With an increase in MWCNTs concentration, the hybrid composites' compression set values rise. This may be because the stiffness of the nanocomposites has increased due to an increase in the
CLD of the composite and a decrease in the mobility of long polymeric chains. The rubber samples were subjected to a set amount of compression (load) that resulted in a 25% strain; the extensive crosslinks attempted to resist this load, which was reported to increase the stiffness of the rubber samples. Some of the crosslinks were broken during the compression resistance; as a result, when the compression was released, fewer crosslinks were needed to restore the strain than were needed to resist it. The samples were no longer recovered to their previous thickness after that. The change to break more crosslinks increases, which results in a high proportion of compression set, as was expected for an increase in crosslinking density. In compression set tests conducted at 23 °C, 70 °C, and 100 °C, a similar pattern was seen. The compression set values likewise grow as the time and temperature rise when MWCNTs are present. In order to make the material more usable, the compression set values were supposed to be lower.

Table 10 Compression set of silicone rubber-mGO/MWCNTs composites

<table>
<thead>
<tr>
<th>MWCNTs loading</th>
<th>For 1 day at 23 °C</th>
<th>For 2 days at 23 °C</th>
<th>For 3 days at 23 °C</th>
<th>For 4 days at 23 °C</th>
<th>For 1 day at 70 °C</th>
<th>For 1 day at 100 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>mGO/MWCNTs_0</td>
<td>2.52</td>
<td>4.04</td>
<td>4.74</td>
<td>5.98</td>
<td>9.87</td>
<td>11.28</td>
</tr>
<tr>
<td>mGO/MWCNTs_1</td>
<td>2.94</td>
<td>4.68</td>
<td>5.12</td>
<td>6.35</td>
<td>10.68</td>
<td>12.56</td>
</tr>
<tr>
<td>mGO/MWCNTs_2</td>
<td>3.15</td>
<td>5.35</td>
<td>5.68</td>
<td>7.47</td>
<td>12.58</td>
<td>14.78</td>
</tr>
<tr>
<td>mGO/MWCNTs_3</td>
<td>3.56</td>
<td>5.89</td>
<td>6.48</td>
<td>7.87</td>
<td>14.68</td>
<td>16.68</td>
</tr>
<tr>
<td>mGO/MWCNTs_4</td>
<td>4.18</td>
<td>7.68</td>
<td>9.47</td>
<td>10.45</td>
<td>18.67</td>
<td>20.14</td>
</tr>
<tr>
<td>mGO/MWCNTs_5</td>
<td>4.84</td>
<td>8.36</td>
<td>10.35</td>
<td>11.36</td>
<td>19.42</td>
<td>21.26</td>
</tr>
<tr>
<td>mGO/MWCNTs_6</td>
<td>5.25</td>
<td>8.74</td>
<td>11.48</td>
<td>13.57</td>
<td>20.24</td>
<td>23.41</td>
</tr>
</tbody>
</table>

Figure 21 (a-c) displays the FESEM pictures of the tensile fractured specimen for each of the various composites. The FESEM micrograph, which is clearly displayed in Figure 21 (a), shows a good dispersion of mGO and MWCNts in the silicone rubber matrix and is composed of 6 phr of mGO and 1 phr of MWCNts. In comparison to nanocomposite with 6 phr MWCNts, the tensile-fractured surface of the former exhibits a much smoother plane. The homogenous phase depicted in these Figures contains fewer tear lines. According to Figure 21 (a), the majority of MWCNts were completely encased in the rubber matrix. It was evident from the observations above that MWCNts dispersed well in the matrix at lower loading settings. Figure 21 (b) depicts the FESEM micrograph, which contains 6 phr of mGO and 3 phr of MWCNts,
and which shows that both fillers are well dispersed in the rubber matrix. When compared to a nanocomposite with a high MWCNT concentration, the one with a low MWCNT content (3 phr) exhibits a smooth surface and superior MWCNTs dispersion (Figure 21b). The tensile strength of 3 phr MWCNTs filled mGO-rubber composites was improved due to greater MWCNTs particle dispersion and distribution inside the silicone rubber matrix. Figure 21(c) illustrates the poor dispersion of MWCNTs nanotubes in the silicone rubber matrix as seen in the micrograph of 6 phr MWCNTs filled composites. Figure 21(c) shows the aggregation of MWCNT particles, which was caused by the intense contact between MWCNTs and their compounds.

Figure 22 illustrates the results of a FESEM investigation into the morphology of samples of thermally aged silicone rubber. It shows that there are no discernible variations in the surface morphology between the thermally aged samples (Figure 22) and the unaged samples (Figure 21). The cracked surfaces of the samples, which were obtained by tensile tests, are depicted in FESEM images in different ways for the thermally unaged and aged samples. The material's considerable elasticity at the time of fracture is shown by the sizeable elastic areas that protruded from the fracture surface of the unaged sample. The surface of the older sample, however, was noticeably flatter and more delicate. A few minor cracks that appear to originate from the silicone rubber's surface texture are depicted in Figure 22(a, b, and C). The concern that the surface may have stress-concentrated regions where cracks begin more quickly as it ages grows as a result.
Figure 21 The tensile fractured surfaces of unaged silicone rubber composites reinforced by mGO/MWCNTs: (a) mGO/MWCNT$_{S_1}$, (b) mGO/MWCNT$_{S_3}$, (c) mGO/MWCNT$_{S_6}$
Figure 22 The tensile fractured surfaces of aged silicone rubber composites by mGO/MWCNTs: (a) mGO/MWCNTs$_1$, (b) mGO/MWCNTs$_3$, (c) mGO/MWCNTs$_6$

4 Conclusions

It was successful in creating a more recent silicone rubber hybrid composite reinforced with mGO and MWCNTs. In silicone rubber nanocomposites, the synergistic effect of mGO and MWCNTs was examined. Compared to silicone rubber-mGO composite, silicone rubber composite's vulcanizing reaction is hastened by the addition of MWCNTs. The hybrid composite that has been created with mGO and MWCNTs exhibits improved TS, EB, TM, TAS, HD, AR, and swelling resistance. The optimum filler content to get the best tensile properties was 3 phr. While the RR of the composites has a detrimental effect on it, the HD, TAS, and compression set of the composite rise with an increase in filler concentration. Silicone rubber nanocomposites were aged more quickly at 70, 100, and 125 °C for 96 hours depending on the amount of MWCNTs nanotubes loaded. In comparison to silicone rubber-mGO nanocomposites, the TS, AR, TAS, and HD for silicone rubber nanocomposites filled with mGO/MWCNTs rise to 24%, 22%, 24%, and 12%, respectively. This research's silicone rubber nanocomposites have potential use as actuators and sensors.

Ethics approval

Not applicable.
Consent to participate

The writers state that participation is not opposed.

Consent for publication

The authors say they have no objections about their consent being published.

Availability of data and materials

This published article contains all of the data that were created or evaluated during this project.

Competing interests

There are no significant financial or non-financial competing interests or conflicts of interest that would prevent any of the authors from publishing the article.

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Authors' contributions

V. Aravinth- Done an experimental work and characterization

S. Vishvanathperumal and V. Navaneethakrishnan - Wrote the main manuscript text and Prepared figures and tables as well as removal of plagiarism

G. Gurumoorthi - Done an experimental work and characterization

*All authors reviewed the manuscript*

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Conflict of interest

The authors declare that there is no conflict of interest.

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