Developing highly conducting and mechanically durable styrene butadiene rubber composites with tailored microstructural properties by a green approach using ionic liquid modified MWCNTs

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We report the effect of surface modification of multi-walled carbon nanotubes (MWCNTs) by an ionic liquid, 1-ethyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl). An apparent physical (cation−π/π−π) interaction between the ionic liquid and MWCNTs was revealed by Raman and UV-visible spectroscopies. The composite loaded with 10 phr MWCNTs exhibits impressive enhancements in tensile strength (381% increase), hardness (34% increase), and abrasion resistance. High electrical conductivity was also achieved at MWCNT loading levels beyond 3 phr loading, with a low percolation threshold (0.023 vol%) for the composites. The microstructural development of conductive networks and uniform dispersion of MWCNTs in the presence of ionic liquid were analysed by TEM and AFM. The experimentally observed mechanical and electrical properties have been compared with theoretical predictions, and confirm that the dramatic improvement in mechanics and electrical conductivity is the outcome of the extremely fine dispersion, the strong secondary network of MWCNTs and improved interaction at the interface via thermodynamically-induced adsorption and physical interlocking of polymer chains in the nanoscopic MWCNT structure. This study demonstrates a simplified and eco-friendly approach to develop multifunctional advanced materials based on ionic liquid modified MWCNT elastomer composites with a much better balance among mechanical properties, conductivity and filler content.

1. Introduction

Polymer nanocomposites are a relatively new class of composite materials that are nanoparticle-filled polymers, showing improved properties with very small amounts of nano-sized fillers. Major challenges faced during the incorporation of nano-fillers into the polymer matrix include difficulties during their processing and tendency to form agglomerates. The fine dispersion of nano-fillers in the polymer matrices is the most challenging task for their practical and potential applications. Several strategies have been developed for the better dispersion of these fillers in the polymer matrix. Most of the methods demand an additional step of ultrasonication for the dispersion of nano-fillers in organic solvents. However, since the use of such solvents is harmful to the environment, route of green chemistry is preferred. For a more sustainable chemistry and cleaner processes, we can use ionic liquids as the medium for the dispersion of nanofillers in the polymer matrix. The interest in ionic liquids (ILs) has grown dramatically in the past decade since their unique properties have been explored. Over the last few years, ionic liquids have been of immense interest both for academic and industrial fields because they have been widely promoted as green solvents. The term ionic liquids refer to liquids composed entirely of ions, which are fluid around or below 373 K. Their properties can also be adjusted to meet the requirements of a particular process. For this reason, they have been at the same time referred to as “designer solvents”. Another important advantage of ILs is their diverse chemical composition and structure, so better properties can be readily achieved by pairing a variety of organic cations with a wide range of either inorganic or organic anions. Khare et al. discussed the use of ionic liquids as the green dispersant or stabilizers for many nanoparticles. ILs have been used to modify carbon-based nanomaterials especially carbon black, graphene, graphene oxide, clay, MWCNT etc. to improve their dispersion in polymer matrix, which will enhance the overall performance of the nanocomposites. Among various nano-fillers, CNTs modified by...
using ionic liquid can be used as potential reinforcing filler in various polymer matrixes which include elastomers, thermoplastics, thermostets and polyamides.\textsuperscript{14-15}

Fukushima \textit{et al.} succeeded in obtaining a superior dispersion of CNTs in room temperature ionic liquid by mixing single walled carbon nanotubes (SWCNTs) with 1-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF\textsubscript{4}).\textsuperscript{16} It was found that nanotubes were dispersed due to the arrangement of CNTs in IL by possible ‘imidazolium cation–π’ interactions. When MWCNTs and IL are mixed together, the shear force detaches the nanotubes from the bundles and the tubes are then wrapped by IL.\textsuperscript{17} It was found that the π–π stacking interactions of nanotubes are restricted by the high dielectric constants of IL preventing them from re-bundling. Moreover, it is found that IL can disperse a higher concentration of MWCNTs than surfactants or DNA.\textsuperscript{18}

In this regard present paper is focussed on the fabrication of styrene-butadiene rubber–ionic liquid modified MWCNT nanocomposites by using a more sustainable chemistry and a clean process with the use of a green solvent ionic liquid. We report herein the introduction of MWCNTs non-covalently functionalized with 1-ethyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide into SBR matrix and its effect on the cure, morphological, mechanical and electrical properties of the composites. This investigation is concentrated on the development of a stretchable and deformable conducting material which has various electrical applications at low concentration of MWCNT.

2. Experimental

2.1. Materials

Styrene-butadiene rubber (Synaprene 1502) with 25% styrene content was used for this study. MWCNT (NANOCYL NC7000) obtained from Nanocyl; Belgium was used as the filler. The diameter of the tubes ranges from 10 to 20 nm and the average length is 1.5 μm. The carbon content of the material is 90% and the rest is metal oxide (impurity). The ionic liquid 1-ethyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide was used for this study. MWCNT (NANOCYL NC7000) obtained from Nanocyl; Belgium was used as received. Zinc oxide (ZnO), stearic acid, MBTS and sulphur used in this study. MWCNT (NANOCYL NC7000) obtained from Nanocyl; Belgium was used as received. Zinc oxide (ZnO), stearic acid, MBTS and sulphur used in this study. ST1IL1 1 : 1, ST3IL1 1 : 5 and ST5IL1 1 : 10 respectively. 1 g MWCNTs always contains 1 mmol of the corresponding ionic liquid. The amount of MWCNT used in the study is 1, 3, 5, 7 and 10 parts per hundred rubbers (phr).

2.2. Preparation of composites

2.2.1 Modification of MWCNT by ionic liquid. Modification of MWCNT by ionic liquid was done by grinding MWCNT and ionic liquid in an agate mortar (obtained from Fisher Scientific with outer diameter [Metric] 15.24 cm, elastic modulus > 70 GPa and bulk weight around 1.5 kg) for 30 minutes. The above mixture was sonicated for 30 minutes in ethanol, followed by vacuum drying at 50 °C. The modification was done in the following ratios 1 : 1, 1 : 5 and 1 : 10 respectively. 1 g MWCNTs always contains 1 mmol of the corresponding ionic liquid. The amount of MWCNT used in the study is 1, 3, 5, 7 and 10 parts per hundred rubbers (phr).

2.2.2 Preparation of ionic liquid modified MWCNT rubber composites. Mixing of SBR and modified MWCNT was done in laboratory scale two roll mixing mill. The formulations of the different mixes are given in Table 1. Cure properties of the compounded samples were determined by using a moving die rheometer at a temperature 160 °C. Samples were then moulded by electrically heated hydraulic press under a pressure of 120 bars at 160 °C.

2.3. Characterisation

The cure characteristics of the SBR composites were determined with a moving die rheometer (MDR 3000, MonTech, Germany) at 160 °C for 30 min. To assess the quality of filler dispersion and morphological details, the composites were investigated by means of transmission electron microscope (TEM) (JEM-2100 HRTEM). The cryocut specimens prepared using an ultramicrotome (Leica, Ultracut UCT) were placed on 300 mesh Cu grids (35 mm diameter) and were analysed. Atomic force microscopy observations were carried out in air on as-received sample surfaces using Agilent 5500 AFM operated in contact mode. Measurements were carried out using standard triangular silicon nitride cantilevers (MSCT from Bruker). Topography, deflection and friction data were collected simultaneously. The images were taken at 512 × 512 pixels resolution. Dielectric studies were done by using Agilent E4980A precision LCR meter with frequency ranging from 100 Hz to 2 MHz. Volume resistivity studies were done by using Keithley electrometer 6517B. Stress-strain tests were performed with a universal material testing machine (Zwick model 1435) with a crosshead speed of 500 mm min$^{-1}$ according to the standard PN-ISO 37-2005.

3. Results and discussion

3.1. Modification of MWCNT by ionic liquid

3.1.1 Raman spectroscopy. Raman spectra of pristine MWCNT and ionic liquid modified MWCNT are shown in Fig. 1. Raman spectrum of pristine MWCNT shows two characteristic peaks. The peak at the Raman shift of 1318 cm$^{-1}$ named D-band is due to the disordered graphitic structure of MWCNT. The other peak at 1571 cm$^{-1}$ named G-band is due to the tangential vibrations of C=C bond in the graphitic plane. The intensity ratio of D-band to G-band ($I_D/I_G$) can be used for evaluation of graphitic
structure of MWCNTs. Results obtained from Raman spectra of unmodified MWCNT and modified MWCNT are given in Table 2.

It can be seen that there is an upshift of D band after modification. This may be due to the cation–π interaction between cationic part of ionic liquid and π electronic network of the MWCNT. When MWCNTs are mixed with ionic liquid carbon nanotubes are dispersed as shown in Fig. 2. The cationic part of ionic liquid interacts with π electronic network on MWCNT which results in the reduction of van der Waals force of attraction between the individual tubes.\(^\text{19}\) The decrement in the value of intensity ratio for modified MWCNT as opposed to raw MWCNT is due to the rearrangement of the tubes in the modified MWCNT in presence of ionic liquid and this is in good agreement with the literature.\(^\text{20}\) After modification, the intensity of D-band decreases and that of G-band increases. So it can be concluded the graphitic structure of MWCNT is not destroyed after modification.

### 3.1.2 XRD analysis.

The XRD patterns are shown in Fig. 3. Peak at \(2\theta = 26.28^\circ\) corresponding to the distance between walls in MWCNT and diffraction maximum at \(2\theta = 43.48^\circ\) is attributed to the MWCNT inter wall spacing.\(^\text{21}\) Modified MWCNTs are found to have the same cylinder wall structure as raw-MWCNT and inter planar spacing of all samples remained the same.
which also supports the findings from Raman spectroscopy. It can be concluded that the modification process did not alter the structural sidewalls of MWCNTs.

3.1.3 UV-visible spectroscopy. UV-visible spectroscopy was used to understand the interactions between the MWCNTs and the imidazolium group of ionic liquid. As shown in Fig. 4, MWCNT shows a maximum absorption at 224 nm while the modified MWCNT has an obvious blue shift to 217 nm. From this also we can confirm some kind of non-covalent (cation−π) interactions between MWCNTs and the imidazole loop of ionic liquid.23

3.2. Ionic liquid modified MWCNT–SBR composites

3.2.1 Cure characteristics. The rheometric study of elastomers measures the torque response over time during the curing process. The measured torque is related to the modulus of the composite. Fig. 5 shows the vulcanization curves of neat SBR, SBR/MWCNT and of the SBR/MWCNT/IL compounds. From the figure it is observed that there is a remarkable increase in the torque for SBR/MWCNT composites which is due to the immobilization of polymer chains in the rigid MWCNT region. High specific surface area of carbon nanotubes results in high stiffness and torque of the composites. It was also recorded that presence of ionic liquids in the rubber composites influences the cure kinetics by reducing the torque value which is found to be important in processing point of view. It could be due to the fact that ionic liquids act both as plasticizer and as catalyst of the interface cross-linking reactions and thus speed up the cure reaction.24,25 Curatives must dissolve in the rubber and diffuse to the active sites to react effectively for the efficient cross-linking of rubber.26 It can be concluded that ionic liquid improved the dispersion of curing agents particularly zinc oxide in the polymer matrix, so their presence in rubber composites contributed to a considerable decrease of vulcanization time and an increase in the crosslinking efficiency.

3.2.2 Transmission electron microscopy. The extent of dispersion of nanofillers in rubber matrix is one of the most critical parameter which controls the overall performance of the composites. The main reason for filler aggregate is its inherent tendency to reduce the surface free energy. Presence of aggregates or agglomeration of filler particles in the rubber matrix leads to stress concentration points resulting in premature and early failure. TEM images of the MWCNT containing rubber composites in the presence and absence of ionic liquid are shown in the Fig. 6. It can be seen from the images of the composites that MWCNTs are highly entangled with one another and form interconnecting structures with agglomerates (Fig. 6A). It may be due to greater differences in surface energy between the SBR rubber and MWCNT as well as strong filler–filler interaction due to van der Waals force of attraction between the individual tubes of MWCNT at nanoscale level. Fig. 6B shows the morphology of ST5IL1 composites in which MWCNTs did not assemble into tangled ropes after functionalization of the surface with the ionic liquid. As expected, the dispersion and distribution of MWCNTs are better for modified ST5IL1 in comparison with unmodified ST5IL0 where the dispersion state of the tubes is not good and a range of small to big agglomerates (represented by black circles) were seen in different magnifications. This shows a substantial dispersion of modified MWCNT with less agglomerates throughout the SBR matrix which could be attributed to the molecular ordering of ionic liquids between individual tubes. In this case surface treatment of MWCNT by ionic liquid reduces the surface energy and also continuous percolating networks are formed with modified MWNT loading and no agglomeration of the MWNTs has been observed. It is well known that the shielding effect of ionic liquids against the π–π stacking interaction among MWCNTs plays a key role in dispersing the MWCNTs. Ionic liquids interact with MWCNT through weak van der Waals interaction. The interactions between modified MWCNT and rubber chains are mainly due to interfacial adhesion between nano-filler and elastomer matrix. Furthermore, prominent black regions are visualized indicate the interlocking structure of modified MWNTs, which confirms that the nanotubes are strongly adhered to the SBR matrix and form a special type of bound rubber aggregations within the rubber matrix. The incorporated MWCNTs should have a certain extent of ability to adsorb rubbery chains onto their surface through physical adsorption.
3.2.3 Atomic force microscopy. Atomic force microscopy (AFM) is used to evaluate the surface roughness of the composites. Fig. 7 illustrates the surface topographical features of unmodified and modified MWCNT composites in 2D and 3D view. The raised features on the topography images indicate the nano MWCNT embedded in the SBR matrix and it is also clear

![AFM images](image-url)

Fig. 6  Transmission electron microscopy images of unmodified and modified composites at different magnifications.

Fig. 7  AFM topography (A) and deflection (B) images and the 3D view (C) of the sample surface and schematic representation of their cross sections.
that SBR surface is modified by the incorporation of MWCNT. However, for ST3IL1 sample the distribution and the dimensions of the heaps/hills are almost homogeneous, indicating a good dispersion of MWCNT in the polymeric matrix. \( R_a \) and \( R_{\text{rms}} \) values are summarized in Table 3. The increase in surface roughness value for unmodified composite can be attributed to the aggregation of the nanotubes, as shown in the schematic image in Fig. 7. The roughness value of ST3IL1 is less than that of ST3IL0 because of the reduction in the size of the aggregates of the modified MWCNT. The attachment of the ionic liquid on the sidewalls of the MWCNT made them denser than unmodified nanotubes. Therefore, modified MWCNT had less volume than pristine MWCNT and consequently the aggregated nanotubes for the modified MWCNT were confined. This is attributed to the better dispersion of carbon nanotubes by ionic liquid due to cation–π interaction.

### 3.2.4 Dielectric properties.

The variations of dielectric permittivity as a function of frequency for different composites are shown in Fig. 8. It can be seen that for pure SBR, the permittivity value remains constant in the whole frequency range. For the SBR modified MWCNT composites, the dielectric constant is almost independent of frequency when \( f_{\text{CNT}} < f_{\text{c}} \), indicating that there is no plentiful accumulation of interfacial charges inside the composites. As soon as the percolation process takes place, a sudden increase in dielectric constant at low frequencies can be observed. This means that there were many modified MWCNT separated by very thin SBR layers. For composites with higher MWCNT loading, there is a clear reduction in the permittivity value with increase in frequency. It is known that permittivity of a composite is determined by the number of orientable dipoles within the system and their ability to orient under an applied electric field. At low frequencies most of the dipoles in composites are able to orientate under applied electric field. When the frequency of the applied voltage increases polymer chains can’t orient themselves. Therefore the effective permittivity of net elastomer will decrease with increasing frequency in the measured frequency range.

As the MWCNT loading increases, permittivity of composites increases which is well understood from the Fig. 8. The significant increment in dielectric constant of SBR/modified MWCNT nano composites can be mainly attributed to the homogenous dispersion of MWCNT in the SBR polymer matrix in the presence of ionic liquid and gradual formation of the micro capacitor networks in the SBR/MWCNT composites as the MWCNT content increases. Initially, when small amount of MWCNT is incorporated into the SBR matrix, some micro capacitance structures are formed, resulting in a slight increase of dielectric constant relative to that of pure SBR. As the MWCNT content increases, dielectric constant gradually increases because there are so many conductive MWCNT nanoparticles which are isolated by dielectric insulating rubber layers with in the nanocomposite. At low frequencies, the high \( \varepsilon' \) values might be correlated to Maxwell–Wagner–Sillars relaxation that occurs due to accumulation of ions at the interfaces in inhomogeneous media. The interfacial polarization leads to an increase in \( \varepsilon' \) due to the motion of virtual charges, which get trapped at the interface of components of a multiphase material of different conductivity.

AC conductivity also increases with increase in MWCNT loading. This is due to the formation of filler network at higher loading of MWCNT. As the MWCNT loading increases, distance between adjacent tubes decreases so tunnelling of electrons through nanoscopic gap between MWCNT is possible, which results in high conductivity. As per literature, an increase in dielectric constant and ac conductivity of the SBR composites was observed with increase in MWCNT content and ac frequency. The conductivity of the polymer/conductive-filler composites originates from two mechanisms: (1) ohmic conduction which is by direct contact of conductive fillers, and (2) non-ohmic conduction, by the barrier-tunnelling effect between the conductive fillers separated by thin polymer layer. At percolation threshold there is the transition from non-ohmic conduction to ohmic conduction.

To determine the electrical percolation following power law equation can be used

\[
\sigma \propto (p - p_c)^\alpha
\]

where \( \sigma \) is the electrical conductivity, \( p \) is the volume fraction of MWCNT, \( p_c \) is the electrical percolation threshold value and \( \alpha \) is critical exponent in conducting region. The best linear fits of the conductivity data to the log–log plots of the power laws for eqn (1) gave \( p_c = 0.023, \alpha = 3.62 \) (Fig. 9). Critical exponent gives an idea about system dimensionality. In literature it is shown that for 2D and 3D systems values of critical exponents are 1.4 and 1.94 respectively. From this study we got an average value about 3.62 which shows that ionic liquid modified MWCNT forms a quasi-network structure near percolation threshold. This low value of \( p_c \) is due to the uniform dispersion of MWCNT with the

<table>
<thead>
<tr>
<th>Sample</th>
<th>( R_{\text{rms}} ) (root mean squared) (μm)</th>
<th>( R_a ) (average surface roughness) (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ST3IL0</td>
<td>0.27</td>
<td>0.21</td>
</tr>
<tr>
<td>ST3IL1</td>
<td>0.2</td>
<td>0.15</td>
</tr>
</tbody>
</table>

Fig. 8 Effect of MWCNT loading on the dielectric permittivity of nanocomposites.
aid of ionic liquid in SBR. In SBR composites with higher MWCNT contents, MWCNT are more densely dispersed in the polymer matrix and the interfacial thickness of polymer wrapped MWCNT are also even thinner, which facilitates the electron tunnelling among MWCNT for the efficient electrical conduction.

### 3.2.5 Comparison between the experimental and theoretical $p_c$

Percolation threshold is correlated to the aspect ratio of the fillers as per excluded volume theory, higher the aspect ratio, lower the $p_c$.\(^{31,32}\) In isotropic case of randomly oriented long sticks the following linear relationship is true.\(^{33}\)

\[
\left(\frac{l}{d}\right)_{p_c} \approx 0.6
\]

where $l/d$ is the aspect ratio of the MWCNT. For Nanocyl NC7000 average length of the tube is 1.5 μm and average diameter is 9.5 nm, $p_c \approx 0.0387$ is obtained which is in the range of experimental value. This confirms that there is not that much breakage of MWCNTs during the processing of nano composites by two roll mill mixing technique.

AC conductivity of the nanocomposites is function of frequency as well as nanofiller loading. This increase in $\sigma_{ac}$ with frequency can be explained in terms of hopping and tunnelling mechanism. As the frequency of the applied field increases, hopping of charge carriers also increases thereby increasing the conductivity. Fig. 10 shows some linear relationship between logarithm of conductivity value and volume fraction of fillers at higher amount of modified MWCNT. The linear relation $\log(\sigma)$ vs. $\phi^{-1/3}$ is a consequence of a hopping mechanism between nearest MWCNTs.\(^{34}\) At higher loading of MWCNT it forms percolative network by contact between adjacent tubes. The effect of ionic liquid at fixed loading of the nanotubes was also studied. As the ionic liquid increases, both dielectric constant and conductivity increases. Effect of high dielectric constant value for ionic liquids on the dispersion of MWCNTs is well known in literature. Ionic liquid acts as a dispersing agent for MWCNT. In fact, the imidazolium ion non-covalently wraps the MWCNTs to cause better dispersion of MWCNT in polymer matrices. The improved conductivity of composites is due to two factors (1) inherent dielectric nature of ionic liquid (2) formation of conductive network of MWCNT in the presence of ionic liquid. Modification of MWCNT leads to decreased van der Waals interaction between individual tubes, so tubes are disentangled and a continuous network is formed in the elastomer matrix. So modification of MWCNTs by ionic liquid leads to an increased conductivity that is related to smaller gap distance between neighbouring MWCNTs and a better dispersion due to a physical coupling between MWCNTs and rubber matrix.

Ionic liquid has an inherent property of ionic conductivity. Even though ionic liquid is ion conducting their ability to make the insulating rubber matrix to conductive is negligible which is evident from ac conductivity values of SBR composites containing ionic liquid without CNT (Fig. 11C). As we increase in the ionic liquid loading variation conductivity is too low and the values are very close to rubber sample without anyfiller. In the literature it is well stated that the conductivity of the composite is the synergistic effect of electrons and ions. It is seen that the dispersion of the tubes in the matrix is enhanced with the modification with ionic liquid by the cation–π interaction between cationic part of the ionic liquid and π electronic
surface of MWCNT. So the presence of tube–tube contact and improved dispersion in the case of modified MWCNT/SBR composites is the reason behind good electrical conductivity. The improved dispersion and the formation of percolating CNTs network with the ionic liquid modified tubes also leads to increased conductivity.

3.2.6 Volume resistivity measurements. Volume resistivity of nanocomposites with 3 phr MWCNT modified with different loadings of ionic loading are presented in Fig. 12. The electrical volume resistivity of the composite at constant loading of the tubes with variations in ionic liquid (ratio) also shows a drastic decrease initially and a marginal difference is noted later on. Presence of ionic liquid favours the formation of a continuous network of MWCNT in the elastomer matrix enabling the passage of current through the system thus making the system conductive. For composites with unmodified MWCNT, filler particles act like conductive islands in a sea of electrically insulating polymer as shown in schematic diagram in Fig. 12. When ionic liquid is added, the conductive particles come in contact with each other by cation–π interaction between ionic liquid and MWCNT and so a conductive network is formed.

3.2.7 Mechanical behaviour. The mechanical properties of SBR vulcanizates with different MWCNT contents are summarized in Table 4. From the figure it is evident that the stress/strain ratio increases continuously with the MWCNT content. It is important to note that values of tensile strength and M100 (modulus at 100 percent strain) have a marginal improvement from 1.409 and 2.58 to 6.798 and 9.26. Girun N. et al. has reported that tensile strength MWCNT/SBR composite has a maximum 150% increment when adding 10 phr of MWCNT. Ali Atieh et al. reported that tensile strength carboxyl functionalised MWCNT/SBR composite has a maximum 273% increment when adding 10 phr of functionalised MWCNT. However in the present study tensile strength of SBR vulcanizate reaches 382% of the unfilled SBR with the addition of ionic liquid modified MWCNT. Here the ionic liquid acts as a dispersant for MWCNT. It prevents the π–π stacking of MWCNT and leads to good and homogeneous dispersion of
MWCNT in the rubber matrix as shown in Fig. 13 which shows the exfoliation of the bundles of entangled MWCNT in the presence of ionic liquid leads to a better dispersion of the tubes. Because of high intrinsic modulus of MWCNT, they act as rigid reinforcement to the polymer matrix. High surface area of MWCNT renders large surface area for the adsorption of polymer molecules. Here reinforcing efficiency of MWCNT increases with increase in the amount of filler. This is due to the proper transfer of the applied stress to MWCNTs. At high concentration of MWCNT it forms local network in the polymer matrix so that external stress can be uniformly distributed to avoid stress concentration. The uncommon increase observed in the elongation at break of ST1IL1 compared to unfilled one is due to the fact that some rubber chains are not cross linked with sulphur in presence of MWCNT. These uncross linked rubber chains are responsible for increment in elongation of composites at break. Further addition of MWCNT leads to decrease of elongation at break to a relatively small degree. This is due to the restricted movement of rubber chains in the presence of MWCNT (Fig. 14).

Here after surface modification cation–π interaction between cationic part of the ionic liquid and π electronic surface of CNT favours de-bundling of MWCNT to individual tubes and the resulting individual MWCNTs tubes are finely separated and well dispersed in SBR. The interfacial bonding between CNT and SBR has enhanced and thus there will be a better load transfer from the matrix to the filler. This provide an attractive interface which allows the composite to bear a higher applied load and it improved the interaction of these two phases and compatibility and thereby resulting a composite with superior mechanical properties. After modification with ionic liquid there is a slight increase in the elongation at break is observed which is due to the plasticizing effect of ionic liquid. From the mechanical characteristics it can be concluded that surface modification with ionic liquid is an effective method to prepare flexible composites without compromising the mechanical strength.

DIN abrasion test results and Shore A hardness of the rubber composites are represented in Fig. 15. Abrasion of elastomer is a complex phenomenon which involves the combination of three processes such as mechanical, mechano chemical and thermo chemical. Factors which influence abrasion resistance of elastomers include strength of the matrix, resistance to thermo-oxidative ageing, resistance to crack growth etc. By the incorporation of reinforcing MWCNT into the rubber matrix, wear resistance of unfilled rubber can be increased. Wear mechanism rely upon the effective hardness of the polymer. The presence of rigid reinforcing nanofiller in the matrix increases the effective hardness of the composite; it resulted in the decrease of mass removal. Incorporation of f-MWCNT in a SBR matrix led to an increase in the hardness and the maximum hardness of 62.82 for 10 phr f-MWCNT loaded sample was observed as compared to 47 for

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**Table 4** Mechanical properties of SBR/modified MWCNT nanocomposite membranes with different concentration of MWCNT (values of unmodified composites are given in bracket)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (EB%)</th>
<th>Young’s modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ST0IL0</td>
<td>1.41 ± 0.12</td>
<td>120.83 ± 14</td>
<td>2.58 ± 0.3</td>
</tr>
<tr>
<td>ST1IL1</td>
<td>2.25 ± 0.01(2.07 ± 0.1)</td>
<td>143.05 ± 6(124.99 ± 7)</td>
<td>2.84 ± 0.03(2.45 ± 0.2)</td>
</tr>
<tr>
<td>ST3IL1</td>
<td>3.32 ± 0.1(3.01 ± 0.2)</td>
<td>131.94 ± 6.5(123.62 ± 6)</td>
<td>4.25 ± 0.3(3.95 ± 0.3)</td>
</tr>
<tr>
<td>ST5IL1</td>
<td>4.22 ± 0.3(3.78 ± 0.2)</td>
<td>123.61 ± 16(118.34 ± 7)</td>
<td>5.74 ± 0.2(5.24 ± 0.3)</td>
</tr>
<tr>
<td>ST7IL1</td>
<td>5.14 ± 0.4(4.69 ± 0.3)</td>
<td>122.07 ± 7(112.49 ± 5)</td>
<td>6.38 ± 0.3(5.97 ± 0.2)</td>
</tr>
<tr>
<td>ST10IL1</td>
<td>6.79 ± 0.4(6.10 ± 0.2)</td>
<td>106.05 ± 16(93.05 ± 6)</td>
<td>9.26 ± 0.6(8.39 ± 0.3)</td>
</tr>
</tbody>
</table>

*a* Values of unmodified CNT composites.

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**Fig. 13** Stress–strain curve of SBR/modified MWCNT composites.

**Fig. 14** Schematic diagrams showing the prevention of π–π stacking of MWCNT in presence of ionic liquid.

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pure SBR (an overall improvement of 34%) composites incorporating ionic liquid modified MWCNT displayed considerably improved abrasion resistance, ascribed to the high stiffness and strength. Their chemical inertness and hollow tube structure that provides certain elasticity and lubrication capability, combined with a synergistic effect. As evidenced from AFM images the addition of multi-walled carbon nanotubes modified by ionic liquid affords the maximum reduction in surface roughness thereby increasing the abrasion resistance as compared to composites with unmodified MWCNT.

3.2.8 Reinforcement mechanism and mechanical modelling of composites. In order to understand the reinforcing mechanism in filled composites several reinforcement models have been proposed by various researchers. Guth introduced a shape factor \( f \) in order to understand the stiffness caused by chain like particles. According to this modulus enhancement \( E/E_0 \) is given by the equation

\[
E/E_0 = 1 + 0.67f + 1.62f^2
\]

(3)

Halpin–Tsai equation,\(^\text{41}\) another way to estimate the reinforcement mechanism in filled composites is given below

\[
E_0 = E_i/E_m = 1 + 2f\eta\phi/1 - \eta\phi
\]

(4)

Here we plotted the reinforcement factor as a function of volume fraction of MWCNT and found that reinforcement factor increases with increase in filler loading (Fig. 16). At low filler loading both model shows good agreement with experimental values. But at higher filler loading Guth–Gold model deviates from experimental results. But Halpin–Tsai model fits moderately well at all concentrations of MWCNT.

An attempt has been made to apply Cunneen & Russell\(^\text{42}\) equations to find the extent of reinforcement of fillers in the matrix.

According to Cunneen and Russell equation,

\[
V_{ro}/V_{rf} = ae^{-z} + b
\]

(5)

where \( V_{ro} \) and \( V_{rf} \) are the volume fraction of the solvent swollen rubber in the fully swollen unfilled sample and in the fully swollen filled sample respectively. A plot of \( V_{ro}/V_{rf} \) versus \( e^{-z} \) should give a straight line with a slope that is a measure of the reinforcing ability of the filler. The experimental findings reported here showed a unique reinforcement of MWCNT in polymer matrix. This reinforcing mechanism corresponds to an immobilization of polymer chains at the surface of the nanotubes. A significant portion of the bulk polymer is immobilized at the nanotube surface due to its large surface area. Thus, this

![Fig. 15](image1.png)

Fig. 15  DIN abrasion test results and Shore A hardness of the rubber composites.

![Fig. 16](image2.png)

Fig. 16  Theoretical modelling of Young’s modulus – comparison with experimental data.

![Fig. 17](image3.png)

Fig. 17  Plot of \( V_{ro}/V_{rf} \) versus \( e^{-z} \) of SBR vulcanizates.
immobilized polymer can be regarded as a third phase in the composite which has a major role in determining the mechanical behaviour of composites. Micro mechanical modelling can be used to estimate the properties of this interphase region based on the measured effective properties of the nanotube–polymer composite (Fig. 17).

4. Conclusion

The present study could prove the attraction between MWCNT and ionic liquid by physical interaction between cationic part of the ionic liquid and graphitic surface of MWCNT with evidence from various characterization techniques. This study also examined the cure, morphological, conducting and mechanical behaviour of SBR composites containing ionic liquid modified MWCNT. It has found that ionic liquid acted as cure accelerator thereby improving the efficiency of vulcanization. With this novel dispersion method using ionic liquid we were able to prepare homogeneously dispersed MWCNT composites with less agglomerates since ionic liquid prevents the π–π stacking of MWCNTs. Enhanced dispersion of MWCNT and the formation of secondary network of MWCNT in presence of ionic liquid was the basic reason behind the increased conductivity and mechanical properties such as tensile strength, modulus, abrasion resistance and hardness of the prepared composites. Composite fabrication by using ionic liquid is an eco-friendly method to get high performance composites. Merging processing techniques of composites with ionic liquid for effective dispersion of nanotubes facilitates the development of new, high performance materials which are highly flexible and conducting. Since molecular dynamics simulations would really complement the experimental characterization done on these systems, simulations studies will be very informative as an extension of present work.

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