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Production Editor
Advanced properties of multiwalled carbon nanotube elastomer composites

Y. Liu, P. Liu, Z. Fan and H. M. Duong*

Multiwalled carbon nanotube (MWNT)/fluoroelastomer (FKM) composites were synthesised through a simple and cost efficient method. MWNTs were dispersed in the FKM by an open two-roll mill followed by vulcanisation inside a compression moulding machine. The morphologies and rheological and mechanical properties of MWNT/FKM composites with different MWNT mass fractions were systematically investigated. Compared with the carbon black (CB)/FKM composites fabricated via the same method, the MWNT/FKM composites demonstrated higher degree of crosslinking and better mechanical properties. By adding 5 wt-% MWNTs in the FKM matrix, the hardness, tensile strength and abrasion resistance of the FKM were significantly improved by 12, 120 and 13% respectively. Compared to CB, MWNTs show higher reinforcing efficiency due to their higher aspect ratio and surface area that result in higher crosslink density and stronger filler–polymer interaction.

Keywords: Carbon nanotubes, Elastomers, Composites, Mechanical properties

Introduction

Elastomers are one class of polymer, which play a critical role in the industry because of their extensive and potential applications.1,2 In the past decades, different types of filler, such as silica or titania,3,4 clays5 and carbon black (CB),6,7 have been added to strengthen elastomers. However, to obtain an ideal reinforcing effect usually requires a large amount of such conventional fillers, which introduced to some side effects in processing and applications,8 and the current overall reinforcement performance still has a need for improvement.9 Thus, researchers attempt to develop alternatives to reinforce elastomers with lower filler loading and higher reinforcing efficiency. Novel nanomaterials such as carbon nanotubes (CNTs)10–14 and graphene sheets15 show great potential to develop ultralight weight and extremely strong elastomers with a longer service life. Possessing high surface area and short interfiller distance, the nanosized fillers are able to restrain the matrix molecular deformation efficiently under loading.1,16

Since their discovery in 1991,17 CNTs have attracted great interest because of their ultralight weight,18 extremely high stiffness,19 electrical and thermal conductivities20 and their various potential applications.21 The superior mechanical properties and low density make CNT an ideal reinforcement candidate for weight efficient elastomer composites with relatively low filler loadings (<10 wt-%).

Numerous studies have been carried out for various CNT reinforced elastomers, such as natural rubber (NB),22–25 styrene-butadiene rubber (SBR)26–28 and silicone elastomers.12,29 Bhattacharyya et al.23 reported the preparation of reinforced and conducting NB composite materials through incorporation with functionalised multiwalled carbon nanotubes (MWNTs) and showed an increase of 100% in tensile strength and a low percolation threshold (<1 wt-%). Bokobza27 studied the mechanical and electrical properties of the MWNT reinforced SBR, which presented a dramatic increase of 670% in tensile strength. Liu et al.12 dispersed CNTs in a silicone elastomer matrix by a grinding method and reported a 65% enhancement in thermal conductivity with 3.8 wt-% CNT.

Nevertheless, studies on MWNT/fluoroelastomer (FKM) nanocomposites are quite limited. FKM materials are widely used in aerospace,30 petroleum exploration8 and semiconductor industries because they offer robust physical properties and high temperature resistance (up to 250°C). In order to get novel FKM materials with enhanced performance, it is meaningful to study the preparation method and the properties of MWNT/FKM composite materials. This paper aims to develop ultrastong and durable MWNT/FKM composites and compare the reinforcing efficiency of the novel nanofiller (MWNTs) to the conventional filler (CB). In the present work, MWNTs were mixed in FKM by a melt mixing method, which is the most industrially preferred method of composite manufacturing.31 The morphologies and rheological and mechanical properties of MWNT/FKM composites with different MWNT mass fractions were systematically investigated and compared with pure FKM elastomers and CB/FKM composites.

Experimental

Materials

FKM used in this work was DuPont Viton GF-200S, which is widely used as consumables in semiconductor industries.
Diak#7 processing aid was purchased from DuPont Company (Singapore) Pte Ltd. Zinc oxide (ZnO) powder was purchased from Hakusuitech Co. Ltd, and peroxide was purchased from Vanderbilt Chemicals, LLC. Carbon black N990 was manufactured by Cabot Corporation (Japan). MWNT was purchased from Shenzhen Nanotech Port Co. Ltd with tapped density of 0.16 g cm$^{-3}$ and actual density of 1.9–2.0 g cm$^{-3}$. All the chemicals above were used in the condition they were received in, without further purification.

Synthesis of MWNT/FKM composites

The mixing process was completed on an open two-roll mill at 40°C (front roller speed 40 rev min$^{-1}$ and back roller speed 60 rev min$^{-1}$). Viton GF-200S, ZnO, peroxide and Diak#7 processing aid were first mixed by repeated feeding. After the chemicals were entirely mixed with the elastomer, CBs or MWNTs were added by repeated feeding. Subsequently, vulcanisation was done inside a compression moulding machine at 180°C for 10 min.

Characterisations

Morphologies of the pure FKM, MWNT/FKM composites and CB/FKM composites were observed with a field emission scanning electron microscope (FE-SEM; model S-4300, Hitachi).

1 SEM images of a pure FKM, b 5 wt-% CB/FKM composite and c 5 wt-% MWNT/FKM composite

The crosslink densities of the samples were characterised by swelling analysis (ASTM D2765). The vulcanised samples were soaked in acetone for 24 h and dried in an oven at 160°C for 20 min. The degree of crosslinking was calculated according to equation (1):

$$\alpha = \frac{W_1 - W_2}{W_1} \times 100\%$$

where $\alpha$ is the degree of crosslinking and $W_1$ and $W_2$ are the weights of the testing specimen before and after extraction respectively.

Rheological properties were studied by a Rotorless Rheology meter using ASTM D6204. Vulcanising curves were obtained at 180°C. Hardness tests were carried out on a Roteq DigiTest Shore A hardness tester using ASTM D2240. Tensile strength of the specimens was measured by an Instron 5965 tensile meter with an extension rate of 40 mm min$^{-1}$. Abrasion resistance was measured by a Kemet 15 lapping machine using ASTM D5963. Abrasion rate was calculated by equation (2):

$$\frac{W_1 - W_2}{W_1} \times 100\%$$

where $W_1$ and $W_2$ are the weights of the testing specimen before and after lapping process respectively.

Results and discussion

Morphologies of pure FKM, CB/FKM composites and MWNT/FKM composites

The fractured surfaces of the pure FKM, 5 wt-% CB/FKM composite and 5 wt-% MWNT/FKM composite were investigated through SEM, shown in Fig. 1. Figure 16 shows the fracture surface of 5 wt-% CB/FKM composite in which CB particles with particle size of 250–350 nm are uniformly distributed inside the FKM matrix. Compared with CB/FKM composite, the distribution of MWNTs in 5 wt-% MWNT/FKM composite (Fig. 1c) is less uniform. Unlike conventional spherical particles like CB, MWNTs are cylindrical nanofilms with high aspect ratio and surface area, which result in a strong van der Waals force among the nanotube surfaces, favouring the formation of agglomerates and poor dispersion states. In addition, the non-uniform distribution of MWNTs may be due to the melt mixing method in which a high degree of shear force was applied to disperse the MWNTs. Although this non-solvent method is simple and cost effective compared to solution mixing method, it showed difficulties to obtain

Table 1 Rheological properties of pure FKM, CB/FKM composites and MWNT/FKM composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_1$ $\cdot$ $M_2$ L N m</th>
<th>$t_{50}/s$</th>
<th>$t_{90}/s$</th>
<th>$t_{90}$–$t_{50}$ s/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure</td>
<td>0.20</td>
<td>25.8</td>
<td>55.8</td>
<td>30.0</td>
</tr>
<tr>
<td>1 wt-% CB</td>
<td>0.22</td>
<td>26.4</td>
<td>60.6</td>
<td>34.2</td>
</tr>
<tr>
<td>5 wt-% CB</td>
<td>0.18</td>
<td>25.8</td>
<td>58.4</td>
<td>33.0</td>
</tr>
<tr>
<td>1 wt-% MWNT</td>
<td>0.22</td>
<td>27.0</td>
<td>61.8</td>
<td>34.8</td>
</tr>
<tr>
<td>5 wt-% MWNT</td>
<td>0.27</td>
<td>27.0</td>
<td>66.6</td>
<td>39.6</td>
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Table 2 Mechanical properties of pure FKM, CB/FKM composites and MWNT/FKM composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Degree of crosslinking/%</th>
<th>Shore A hardness</th>
<th>Tensile strength/MPa</th>
<th>Abrasion rate/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure</td>
<td>82.11</td>
<td>53.7 ± 0.13</td>
<td>3.08 ± 0.12</td>
<td>3.1</td>
</tr>
<tr>
<td>1 wt-% CB</td>
<td>84.35</td>
<td>54.5 ± 0.34</td>
<td>3.95 ± 0.44</td>
<td>2.9</td>
</tr>
<tr>
<td>5 wt-% CB</td>
<td>84.05</td>
<td>57.0 ± 0.41</td>
<td>4.89 ± 0.14</td>
<td>2.8</td>
</tr>
<tr>
<td>1 wt-% MWNT</td>
<td>86.10</td>
<td>55.7 ± 0.45</td>
<td>4.64 ± 0.38</td>
<td>2.7</td>
</tr>
<tr>
<td>5 wt-% MWNT</td>
<td>86.41</td>
<td>59.9 ± 0.30</td>
<td>6.59 ± 0.57</td>
<td>2.7</td>
</tr>
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a homogenous distribution via this method because of the extreme high viscosity of the composites with a large MWNT mass fraction.\(^1\)\(^,\)\(^3\)

The chemical process of vulcanisation transforms the rubber from weak plastic-like material into the strong and durable elastomer by building up crosslinks between the long chain molecules together. Degree of crosslinking is a critical property that determines the stiffness of the elastomer products.\(^1\)\(^,\)\(^3\) As shown in Fig. 2, the degree of crosslinking of pure FKM is ~82%. With increasing of MWNT mass fraction, the crosslinking increases up to 86.4% in 5 wt-% MWNT/FKM composites. MWNT/FKM composites provide higher degree of crosslinking at both 1 and 5 wt-% MWNT loadings compared with CB/FKM composites at the same mass fractions. This increase in degree of crosslinking can be attributed to higher aspect ratio and surface area of MWNTs, compared with CB, thus creating more matrix-filler interactions.\(^3\)\(^,\)\(^6\)

Rheological properties of pure FKM, CB/FKM composites and MWNT/FKM composites

Vulcanisation characteristics are important for material development in the rubber industry. The rheological properties, including the difference between maximum and minimum torque value (\(M_H - M_L\)), scorch time (\(t_{95}\)) and optimum cure time (\(t_{c90}\)), of pure FKM, CB/FKM composites and MWNT/FKM composites were obtained from vulcanising curves and listed in Table 1. The difference between maximum and minimum torque value increases while the mass fraction of MWNTs increases, which is due to the increased stiffness of molecular chains in the rubbers with the presence of CNTs.\(^3\)\(^,\)\(^3\)\(^3\) There is a slight increase in scorch time for the MWNT/FKM composites and the CB/FKM composites compared to the pure FKM.

The optimum cure time obviously increases with the increase of MWNT mass fraction. Meanwhile, the MWNT/FKM composites present longer optimum cure time compared with the CB/FKM composites. The possible reason for the increase of optimum cure time might be attributed to the slower curing reaction rate of CNT/rubber composites.\(^3\)\(^,\)\(^3\)\(^3\) Due to their higher aspect ratio compared with CB, the better interaction between the MWNTs and the FKM may restrict the movement of molecular chains in the rubbers.\(^3\)\(^,\)\(^3\)\(^3\) As a result, more energy is required for curing the MWNT/FKM composites, which leads to a longer optimum cure time.

Mechanical properties of pure FKM, CB/FKM composites and MWNT/FKM composites

Mechanical properties of the pure elastomers and the composites are summarised in Table 2. It is found that, at any given filler mass fraction, the FKM reinforced by MWNTs exhibits higher hardness, tensile strength and abrasion resistance compared to the ones reinforced by CB, which indicates that MWNTs possess a higher reinforcing efficiency.

As shown in Fig. 3, the Shore A hardness of the composites increases with the increase of mass fraction of CB or MWNT. Obviously, the hardness of elastomers has been dramatically improved by 6–12% with < 5 wt-% MWNT loading. Compared with the CB/FKM composites at the same mass fraction, the MWNT/FKM composites present higher hardness, because MWNT/FKM composites have higher crosslink density and higher stiffness of molecular chains, which provide more resistance to the indentation of hardness indenter.

Figure 4 shows the comparison of tensile strength between the pure FKM and the composites. It is predictable that the tensile strength increases when the mass fraction of CB or MWNT increases. MWNTs (5 wt-%) in FKM provides 120% improvement in tensile strength, indicating the better reinforcement performance of MWNTs compared with CB. The dramatic reinforcement performance of MWNTs is attributed to their high aspect ratio,\(^3\)\(^,\)\(^3\) which provides a good interface to stand the stress. In addition, MWNTs can carry most of the applied force from the matrix due to their better mechanical properties compared with other types of fillers.

The relationship between abrasion rate and the filler type with different mass fractions is shown in Fig. 5. Composites with higher mass fraction of fillers (CB or MWNT) demonstrate lower abrasion rates because the polymer chains in the composites are reinforced by nanoparticles. Compared to CB/FKM composites, MWNT/FKM composites have better wear resistance due to their higher tensile strength and better elastic expansion, thus significantly preventing the formation of surface crack.

As a summary, the mechanical properties of the FKM have been significantly enhanced by incorporation with
5 wt-% MWNTs. The possible reason for the great enhancement can be the strong interaction between MWNTs and FKM, which includes the physical bonding (van der Waals force) of CNT percolation network and the adhesion of the FKM on the MWNT surface due to the defects and potential functional groups of the MWNTs. This filler–polymer interaction restrains the movement of the polymer chains and promotes the stress transfer from the matrices to the fillers under loading. However, the formation mechanism of the interaction between MWNTs and FKM requires further investigation.

Conclusions

MWNT/FKM composites were synthesised by an industrial applicable and cost efficient method. FKM, chemical additives and two types of fillers (MWNT and CB) were mixed by melt mixing method followed by vulcanisation. The morphologies and rheological and mechanical properties of the composites were systemically investigated. Compared to CB/FKM composites, MWNT/FKM composites demonstrate higher degrees of crosslinking and better mechanical properties. The hardness, tensile strength and abrasion resistance of the FKM were significantly enhanced by a small amount of MWNTs. MWNTs showed higher reinforcing efficiency due to their higher aspect ratio and better filler–polymer interaction between MWNTs and FKM. To further enhance the mechanical properties of MWNT/FKM composites, new synthesis approaches are currently under development for homogenous dispersion of CNTs in FKM matrices using functionalised CNTs and solution mixing method. The interaction between CNTs and FKM should also be investigated in the future work.

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References

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