Silicone Rubber Composites with Improved Electrical Conductivity/Hardness Using Hybrid Fillers: Carbon Black-Expanded Graphite/Polyaniline

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Abstract: Silicone rubber composites have been synthesized using two different systems of hybrid fillers such as expanded graphite (EG)-conductive carbon (XC-72) abbreviated as SICEG for electrical conductivity and camphor sulfonic acid doped polyaniline (PANI)-XC-72 abbreviated as SICP for improved hardness without altering the electrical properties. Addition of EG or PANI in absence of conductive carbon does not yield conductive composites. Composites of silicone rubber with 20 phr of XC-72 show a resistance of 26-30 kΩ. Incorporation of 10 phr of EG leads to a sharp increase in electrical conductivity with the resistance decreasing by two orders i.e. 90-100 Ω. Addition of PANI (5 phr) improves the mechanical properties without altering the conductivity of the composites. Hardness increases by ~6 Shore A. SEM images show even dispersion of fillers in the composites, Rheological studies indicate good cure characteristics. TGA and DSC plots reveal the thermal stability of the composites with the positive shift in the thermogram which is the added advantage of the hybrid fillers.

Key words: Silicone rubber, hybrid fillers, carbon, expanded graphite, camphor sulfonic acid doped polyaniline, electrical conductivity.

1. Introduction

Silicone rubber is a material of commercial importance due to its well known insulating nature, flexibility and excellent weather resistance. Its application potential could be extended, especially for electrical purposes [1] if made electrically conductive. Fillers such as conductive carbon, graphite, expanded graphite, metal powders etc. when added to silicone rubber yield conductive composites. Composites comprised of silicone rubber and conductive carbons are less stable thermally and also exhibit curing retardation [2-3]. Graphite and expanded graphite are excellent conductors of electricity [4] and when added to silicone rubber, render electrical conductivity prior to curing however, on curing the composite a complete loss of conductivity is observed [5]. Metal powders render electrical conductivity to rubbers only when added in large amount and also the process ability is lost [6, 7] with respect to the moulding of the compound. Use of conductive polymers as fillers is also restricted as the composites gain poor environmental and thermal stability together with weak conductive network formation [8, 9].

In the present work, attempts have been made to obtain conductive composites by addition of hybrid fillers without compromising the thermal and mechanical properties. Composite of silicone rubber with carbon (XC-72) and EG (SICEG) shows enhanced conductivity while that with XC-72 and PANI (SICP) exhibits improved mechanical properties. SICEG and SICP can be used in the fields where soft composites and reinforced composites are required, respectively.
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2. Experiments

Grade NE-7140 of methyl vinyl silicone rubber (VMQ), 2,5, dimethyl-2,5di (tert butyl peroxy) hexane (Luperox 101 for cross linking), conductive carbon, Vulcan XC-72 (XC-72) and Expanded graphite were purchased locally. The expanded graphite as purchased has vermiform flakes like structure with the circumference of the worm ~1/4 to 1/2 inch and length up to 2-4 mm. The distance between intercalated layers of EG was ~3 to 6 Å. PANI with resistance of 40-60 kΩ was purchased from Aldrich and used as such. The composites of silicone rubber with various compositions of XC-72, EG and PANI in the proportions of 5 to 30 phr each were prepared on a two roll open mixing mill at room temperature with a continuous and slow addition of the components in the sequence given in Table 1, which represents the formulations of positive results (20 phr, XC-72; 10 phr, EG and 5 phr, PANI) with respect to electrical conductivity and hardness.

A master batch (MB) of silicone rubber, Luperox and XC-72 was prepared. The silicone rubber was rolled on a two roll mill at room temperature for 1-2 min, followed by addition of Luperox and XC-72 in small portions at a time. MB was rolled for several minutes before addition of EG or PANI. A very slow addition of these chemicals with continuous rolling of rubber matrix on mill was necessary to ensure homogeneous mixing of these hybrid fillers. The whole mass was rolled for 20-25 min after addition of all the ingredients.

The composites were characterized for various properties after curing the specimens by compression moulding for 10 min at 170 °C under pressure of 10.34 MPa. The composites were then characterized for various tests after 24 h [10, 11].

The electrical resistance of the composites was measured on “Agilent U 1252 A” two probe multimeter from Germany. Sample buttons of 4 mm thickness and 6 mm diameter were used for this purpose. As the electrical resistance is higher at surface in case of rubbers [12, 13], the surface resistance was measured keeping the probes 1 cm apart.

Oscillating disc rheometer manufactured by Future Foundation (Delhi-India) was used for rheological analysis. 12 g of raw composite was kept in the sealed cavity under positive pressure and maintained at 170 °C. The rotor (biconical disc) was embedded in the test piece and oscillated at small amplitude. This action exerts a shear strain on test piece and the torque required to oscillate the disc varied with time was measured. The test was run for 12 min.

The composites were thermally characterized using TGA and DSC techniques. Thermogravimetric analyzer model TA-60 WS of Shimadzu, Japan was used for TGA analysis. TGA were recorded in the range between room temperature (R.T.)-1,000 °C at a scanning rate of 10 °C·min⁻¹ under nitrogen atmosphere with a flow rate of 50 ml·min⁻¹.

DSC analysis was performed on a differential scanning calorimeter model DCS 60 from Shimadzu-Japan under nitrogen atmosphere with a flow rate of 50 ml·min⁻¹ and scanning rate of 10 °C·min⁻¹ up to 500 °C.

Morphology of the composites was studied under scanning electron microscope. For this purpose thin test specimens of size 0.5 × 0.5 cm were coated with Pt and observed under JEOL JSM 6360, A SEM analyzer from Japan.

ASTM standard D297-93 by hydrostatic weighing method was adopted for specific gravity measurement. The ratio of mass of a unit volume of composite to mass of a unit volume of water was directly obtained using this method [14] by using a weighing balance from “Contech Instruments, India”.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>phr</th>
<th>phr</th>
<th>phr</th>
<th>phr</th>
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<tbody>
<tr>
<td>VMQ</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Luperox 101</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>XC-72</td>
<td>-</td>
<td>20</td>
<td>20</td>
<td>30</td>
<td>-</td>
</tr>
<tr>
<td>EG</td>
<td>-</td>
<td>-</td>
<td>10</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PANI</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5</td>
<td>-</td>
</tr>
</tbody>
</table>
Hardness was recorded on the specimen with 6 mm thickness and diameter each. Resistance to indentation is the measure of hardness. Indenter is a calibrated spring needle [15]. Shore A (ASTM standard D 2240) method was used for measuring the hardness of specimens with “GSE Testing Instrument (Mumbai, India)”, with indenter of type “A” on Type-2 durometer Shore A operating stand.

The mechanical parameters such as tensile, elongation and tear strength were characterized, particular ASTM standards such as ASTM standard D-412 and ASTM standard D-624 were adopted for measuring the tensile and tear strength respectively. Five dumbbell shaped specimens with ASTM standard dimensions for respective tests were punched from already cured sheets of size 150 × 150 × 2 mm in a Die-C with a single impact stroke punching machine. The strength of all five specimens for both the tests was measured, the extreme high and extreme low readings were omitted and average of rest of the three specimens for each was taken. Star Testing Systems make Computerized Testing machine-Mumbai, India, was used for measuring the tensile and tear strength. Elongation was measured as a % of original distance between extensometers of the tensile machine at the time of rupture during tensile test. 100% modulus i.e., applied stress was also measured.

Impact resilience was measured on Vertical Rebound Resiliometer by The Shore Instrument and Manufacturing Co, India as per ASTM standard D 2632-01 using specimens with 12 mm thickness and 6 mm diameter.

3. Results and Discussion

It was observed that the percolation threshold of the fillers such as XC-72, EG and PANI with respect to electrical conductivity of the silicone rubber composites is 20, 10 and 5 phr respectively, hence all the results and discussions are given only for these combinations.

3.1 Electrical Resistance

The variation in the electrical resistance of the samples (blank silicone rubber and the composites) can be observed as in Fig. 1. Silicone rubber is highly insulating in nature with a resistance of ~ $10^{15}$ Ω, however, composites of silicone rubber with EG and PANI hybridized with XC-72 are observed to be conducting in nature.

Addition of 10 phr XC-72 to silicone rubber shows a negligible decrease in the electrical resistance, while addition of 20 phr resulted in a sharp decrease in resistance of the order of ~$10^{12}$ of the composite. XC-72 imparts conductivity to the composites through tunneling [16] but addition of carbon more than 20 phr leads to curing retardation indicating that the percolation threshold of carbon (XC-72) is 20 phr with a resistance of 26-30 kΩ. This observation is in good agreement with rheometer studies of the composites as shown in Table 2. The process of curing is probably inhibited in the composite due to the loss of peroxide free radicals (cross linking agents) which react with the $\pi$ electrons on carbon [17]. Composite obtained by adding EG to silicone rubber does not exhibit conductivity. The reason for this can be attributed to the lack of establishment of connecting links between silicone rubber and EG (Fig. 2) especially during curing at a pressure of 10.34 MPa.
Table 2  Rheometric properties.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Blank</th>
<th>SIC (20 phr)</th>
<th>SIC (30 phr)</th>
<th>SICEG</th>
<th>SICP</th>
</tr>
</thead>
<tbody>
<tr>
<td>MI (dNm)</td>
<td>8.40</td>
<td>26.36</td>
<td>25.81</td>
<td>23.07</td>
<td>24.22</td>
</tr>
<tr>
<td>ML (dNm)</td>
<td>6.50</td>
<td>13.06</td>
<td>11.59</td>
<td>7.86</td>
<td>9.01</td>
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<tr>
<td>MH (dNm)</td>
<td>54.67</td>
<td>35.52</td>
<td>11.73</td>
<td>24.48</td>
<td>35.05</td>
</tr>
<tr>
<td>ts2 (min)</td>
<td>1.32</td>
<td>2.45</td>
<td>0</td>
<td>2.47</td>
<td>2.00</td>
</tr>
<tr>
<td>tc90 (min)</td>
<td>6.06</td>
<td>9.68</td>
<td>11.99</td>
<td>10.83</td>
<td>7.50</td>
</tr>
<tr>
<td>CR (min⁻¹)</td>
<td>21.00</td>
<td>13.80</td>
<td>8.33</td>
<td>10.23</td>
<td>15.00</td>
</tr>
</tbody>
</table>

when compaction occurs, the rubber polymer penetrates into the EG layers.

A combination of 10 phr of EG along with 20 phr of XC-72 results in a conductive composite with the reduction in the surface resistance by the order of $10^5 \Omega$. From Fig. 3 it can be noted that SICEG with 10 phr of EG shows a resistance of 90-100 $\Omega$. The composite with 5 phr of EG is unaltered with respect to resistance and addition of 15 phr EG yields a dry composite. EG and carbon when present together, they react with each other rendering conductive nature to the composite. EG has 100% $sp^2$ hybridization with aromatic electrons and carbon has $sp^2/sp^3$ hybridization in a ratio of ~ 77:23 [18] with localized electrons. The combined effect of aromatic electrons on EG and localized electrons on carbon make the
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Fig. 3  Resistance of a) SICEG and b) SICP versus the phr of EG and PANI added to SIC respectively.

composites strikingly conductive. Dispersion of fillers in the composites is another major aspect responsible for electrical conductivity which can be observed from morphological characterization.

Further, composites were prepared by adding conducting polyaniline together with carbon (20 phr). Results indicated that the resistance of the composite does not seem to change, the resistance being same as that for silicone rubber, XC-72 composites (SIC) which is ~26-30 kΩ. However, the hardness is observed to increase by 6 Shore A for a combination of 5 phr PANI and 20 phr XC-72. Hence, this composite has been considered for further analysis. PANI though electrically conductive in its emeraldine salt phase probably does not reduce the resistance when added to silicone rubber or SIC as it undergoes oxidation in presence of peroxide which is used as a curative in the composite.

3.2 Rheology

The stiffness of rubber specimen increases when cross links are formed during cure. The direct proportionality of shear modulus and crosslink density depends upon statistical theory of rubber elasticity[19]. Table 2 gives a comparative account of the cure characteristics from the rheological analysis of blank silicone rubber and the SIC (with 20 phr and 30 phr of XC-72), SICEG (20 phr XC-72 and 10 phr EG) and SICP (20 phr XC-72 and 5 phr PANI). From Fig. 4 it can be observed that silicone rubber shows lowest cure time (tc90, time required for 90% cure) and highest cure rate (CR).

The Luperox, which is the curative in the system, is completely available for the cross linking reaction of polymeric chains with no other additives in the system. In case of composites, the cross linking reaction is affected due to the presence of fillers, so also the curing rate. The magnitude of effect varies with the type and proportion of fillers. SIC composite with 20 phr XC-72 shows better cure characteristics compared to that with 30 phr XC-72 as cure retardation takes place. Similarly, in case of SICEG composites the difference in ML and MH is 16.62 dNm and tc90 is higher compared to SIC with 30 phr XC-72.

3.3 Thermo gravimetric Analysis

The thermograms of blank silicone rubber and the composites SICEG and SICP are shown in Fig. 5; the specimens were analyzed between R.T. and 1,000 °C. A comparison of thermograms reveals that the samples are stable up to a temperature of ~400-470°C, the stability being slightly higher in composites compared to blank silicone rubber with a negligible weight loss of ~ 5 weight %. Addition of XC-72, EG and PANI seem to improve the thermal stability of the composites. Above ~ 450°C silicone rubber shows a sharp weight loss of ~ 70 % in a single step and after
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600 °C the weight appears to be constant indicating that the cross links and backbone decompose simultaneously. The residual weight corresponds to silicon.

On the other hand, the composites SICEG and SICP exhibit a two stage decomposition process with weight losses of ~37% and 45% up to 600 °C with further gradual loss of 20% each, from 600 °C to 900 °C. The first step includes the loss of carbon and other volatiles while the latter step corresponds to the decomposition of backbone.

This can be attributed to reinforcement due to carbon, expanded graphite and PANI. Conductive carbon alone is less stable thermally and it also reacts with the polymer reducing the conductivity however the hybrid fillers and their interaction with silicone rubber increase the physical and chemical crosslinks [20] improving the thermal stability of the composites.

3.4 Differential Scanning Calorimetry

Fig. 6 depicts the differential scanning calorimetric plots of blank silicone rubber, SICEG and SICP. Blank rubber shows endothermic transitions with a heat flow towards the rubber. In case of composites, the transitions are shifted towards right implying improved thermal stability due to reinforcement. In SICEG, the heat flow toward the composite is reduced due to exothermic transitions as a result of stronger interactive forces between silicone rubber, carbon and expanded graphite which are enhanced with the increasing temperature releasing the heat up to 100°C. Above this temperature, an endothermic peak is observed which may be due to increased heat requirement during degradation of the composite. SICP shows lowest heat flow with an exothermic transition up to 60 °C. Intermolecular interactions in SICP are large as both are polymeric materials reinforcing the composite. The endothermic path above 300 °C can be attributed to Tg of PANI and decomposition of the composite. Data of DSC analysis is given in Table 3.

3.5 Morphological Characterization

The dispersion of carbon, EG and PANI in SICEG and SICP respectively can be seen from the scanning electron microscopic images. Expanded graphite, which exhibits an exfoliated structure, is seen to be evenly dispersed in composite as shown in Fig. 7a. The composite shows compaction with reasonable inter particle connection sufficient enough to impart the conductivity. Polyaniline being a polymer forms a smooth blend with silicone rubber resulting into a homogeneous composite which can be observed from Fig. 7b. This interaction is also in good agreement with the reinforcement in the hardness.
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Table 3  Data of DSC analysis.

<table>
<thead>
<tr>
<th></th>
<th>M.P (°C)</th>
<th>Onset (°C)</th>
<th>End set (°C)</th>
<th>Heat (mJ)</th>
<th>Height (mW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>108</td>
<td>101</td>
<td>111</td>
<td>-0.13</td>
<td>-0.01</td>
</tr>
<tr>
<td>Step1</td>
<td>113</td>
<td>111</td>
<td>120</td>
<td>-0.09</td>
<td>-0.01</td>
</tr>
<tr>
<td>Step2</td>
<td>128</td>
<td>123</td>
<td>139</td>
<td>-0.15</td>
<td>-0.00</td>
</tr>
<tr>
<td>SICEG</td>
<td>193</td>
<td>185</td>
<td>205</td>
<td>-1.16</td>
<td>-0.03</td>
</tr>
<tr>
<td>SICP</td>
<td>186</td>
<td>182</td>
<td>183</td>
<td>-1.17</td>
<td>-0.05</td>
</tr>
</tbody>
</table>

Fig. 7  SEM images of (a) SICEG and (b) SICP.

Table 4  Mechanical properties of composites.

<table>
<thead>
<tr>
<th>Property</th>
<th>Blank</th>
<th>SIC (20 phr)</th>
<th>SICEG</th>
<th>SICP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness, Shore A</td>
<td>40</td>
<td>60</td>
<td>61</td>
<td>66</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>1.11</td>
<td>1.22</td>
<td>1.24</td>
<td>1.21</td>
</tr>
<tr>
<td>Tensile strength (Kg·cm⁻²)</td>
<td>64.7</td>
<td>47.2</td>
<td>23.1</td>
<td>31.15</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>632</td>
<td>256</td>
<td>160</td>
<td>280</td>
</tr>
<tr>
<td>Modulus (100%)</td>
<td>9.968</td>
<td>25.672</td>
<td>22.822</td>
<td>17.602</td>
</tr>
<tr>
<td>Tear strength (Kg·cm⁻¹)</td>
<td>15.04</td>
<td>13.7</td>
<td>12.1</td>
<td>11.70</td>
</tr>
<tr>
<td>Rebound resilience (%)</td>
<td>67</td>
<td>28</td>
<td>26</td>
<td>22</td>
</tr>
</tbody>
</table>

3.6 Physical, Short Term and Dynamic Stress, Strain Properties

The values of all the above parameters for silicone rubber, silicone rubber with 20 phr XC-72 (SIC, 20 phr), SICEG and SICP are given in Table 4.

Specific gravity, which is a contribution of all the components in a composite, shows variation in the values as expected. Addition of carbon increases the specific gravity by 0.1, however, no significant change is observed upon incorporation of EG or PANI into the composite.

Hardness, which is a short term stress-strain property is increased by 20 Shore A with 20 phr XC-72 due to reinforcement. Carbon forms chain like structures due to van der Waals forces between inter particles and polymer matrix [21]. EG being a soft and lubricating material does not add to the hardness of SICEG composite, however in SICP, cross linking between rubber and PANI molecules due to van der Waals forces leads to a rigid structure enhancing the hardness by 6 Shore A.

Tensile strength is proportional to the elastic nature of a polymer and is a sum of all the components in a composite. It is highest in case of blank rubber which gradually reduces depending upon the type of fillers used. Table 4 shows the results that are in good agreement with this behaviour. The polymeric content
of the composites is reduced upon incorporation of 
carbon, EG and PANI. EG reduces the tensile strength 
of SIC by ~24 Kg·cm⁻², whereas PANI reduces by ~17 
Kg·cm⁻². PANI being a polymer, exhibits a better 
cross linking with rubber imparting rigidity to the 
composite, however being a non elastic polymer, 
contribution towards tensile strength is reduced to 
some extent. 

Silicone rubber has a maximum elongation which is 
a property of elasticity of a polymer. Incorporation of 
fillers reduces the elongation. There is a major 
reduction in elongation of SIC as the polymeric 
content in the composite is reduced. The elongation is 
seen to increase upon addition of PANI to SIC. 
Though PANI is an organic polymer while silicone 
rubber has an inorganic back bone, both being 
polymeric molecules blend with each other in a better 
way. This phenomenon explains the increase in the 
elongation of SICP compared to SIC. In case of 
SICEG, EG being a soft, lubricating, heterogeneous 
material reduces the polymeric content when added to 
SIC. This is the major cause of decrease in the 
elongation of SICEG. Modulus which is a stress 
required to elongate is smallest for blank rubber. The 
modulus of SIC has a marginal rise in the value as 
carbon reinforces the composite reducing the overall 
elasticity, when PANI is added to SIC the modulus 
shows an improvement, this is because the polymeric 
filler (PANI), even though forms a rigid cross linked 
structure with silicone polymer, blends well thereby 
reducing the stress required to elongate the composite 
material. EG has a negligible effect on modulus of 
SIC as it is a lubricating, heterogeneous material 
compared to polymers. Table 4 gives the exact values 
of elongation and 100% modulus.

Tear strength of rubber depends on the extent of 
compactness of the base polymer, it is maximum in 
the blank rubber and is negligibly altered upon 
incorporation of carbon, EG and PANI as shown in 
Table 4. The drop in tear strength of composites can 
be attributed to the lack of continuity in the silicone polymer molecules due to the fillers. The filler 
molecules arrange themselves in the polymer matrix 
as shown in Fig. 2 disturbing the basic polymer 
structure.

The dynamic impact resistance of the composites 
has decreasing trend in the sequence of SI > SIC > 
SICEG > SICP, this observation is in good agreement 
with the fact that greater the reinforcement and 
hardness, lower is the resistance to dynamic impact 
which is rebound resilience in this case as given in 
Table 4.

4. Conclusions

Conductive fillers XC-72 (20 phr), EG (10 phr) and 
PANI (5 phr) are responsible for the improved 
properties of the composites with respect to electrical 
conductivity and hardness when hybridized. SICEG 
composite shows a resistance of 90-100 Ω while the 
SICP composite shows the increase in hardness by 6 
Shore A without altering the electrical conductivity. 
The composites are thermally stable with negligible 
changes in physical, short term and dynamic 
properties.

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