Characterization and Application of Nanomaterials (2019) Volume 2 Issue 2
doi:10.24294/can.v2i2.644

ORIGINAL RESEARCH ARTICLE

Synthesis and characterization of electrically conductive silicone rubber — TiB_2 composites

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ABSTRACT

In this paper, electrically conductive composites comprised of silicone rubber and titanium diboride (TiB_2) were synthesized by conventional mixing methods. Fine particles of TiB_2 (in micron size) and 10 parts per hundred parts of rubber (phr) proportion of carbon black (XC-72) were used to make the composites with HTV silicone rubber. The composites were cured at appropriate temperature and pressure and the effect on the electrical properties was studied. The resistance of the silicone rubber is ~ $10^{15}\Omega$ which decreases to 1–2 kΩ in case of composites with negligible effect of heat ageing. The hardness increases by ~ 35% simultaneous to the decrease of ~ 47% in the tensile strength. Morphological characterization indicates the homogeneous dispersion of the fillers in the composite.

Keywords: Silicone Rubber; Electrical Conductivity; Titanium Diboride; Composite

ARTICLE INFO

Article history:
Received 18 July 2019
Received in revised form 12 August 2019
Accepted 16 August 2019
Available online 3 September 2019

1. Introduction

Electrically conductive silicone rubber composites have great potential towards various applications[1], such as rollers used in printing, fibre weaving, conductive coatings, electronics communication industry, light emitting devices, gas and pressure sensors, EMI shielding etc. Silicone rubber, as an insulating material, has very large application horizon and inducing electrical conductivity into such a versatile material is adding to its value. Electrically conductive composites of silicone rubber with conductive carbon such as XC-72 are well known and can be easily synthesized using conventional mixing methods. XC-72 imparts electrical conductivity to the composites by tunnelling effect of the free electrons on carbon from one aggregate to another through the polymer molecules[2]. These electrons interact with polymer and also with the peroxide used as the curing agent when the composites are subjected to temperature or prolonged storing. Other conductive materials that are reported to impart electrical conductivity to the rubbers are metal powders and graphite etc. The limitations to the use of metal powders are poor process ability of the composites[3,4]. Graphite, when used in rubbers, renders conductivity to the composites, however upon high temperature curing of the composites, the conductivity is lost due to penetration of polymer molecules into graphite layers[5,6]. TiB_2-silicone rubber composite is reported as a piezoresistive material with 70 % of TiB_2[7]. Similar to the metal powders, the ease in the process ability of the composites is reduced. TiB_2 is stable chemically, thermally and physically with a superconductive behaviour at cryogenic temperatures[8].

In the present work, an electrically conductive ceramic material, TiB_2, has been used in conjugation with XC-72 to synthesize conductive composites (SITB). The resultant composites are thermally stable with very good physical and electrical properties under ambient conditions.

2. Experimental

Silicone rubber grade TSE 221-3-U from Momentive Performance Ltd., Japan, TiB_2 with mean particle size of 14 μm from Momentive India, XC-72 from Cabot corporation-India and Luperox 101-45 were used for synthesizing the composites. The composites were prepared on a two roll laboratory mixing mill. The silicone rubber was first masticated for few minutes followed by addition of 10 phr of XC-72, 5 phr of TiB_2 and 1.8 phr of Luperox–101/45 slowly one after the other with continuous rolling on mill. After complete addition, the whole mass was rolled again for 5-10 minutes to attain homogeneity and form a nice band on the mill. The composites were cured by compression moulding in appropriate moulds at 170ºC for 10 mins, and characterized for their electrical, mechanical, morphological and thermal properties after cooling the specimens to room temperature. The specimens were kept as such for 24 hrs before the testing was carried out.

3. Characterization

3.1 Electrical conductivity

Surface resistance was measured by using a 2 probe digital Multimeter from Agilent with 1 cm distance between the probes. Surface resistance of samples was measured both before and after curing. In rubber elastomers, the surface resistance was measured as the surface may conduct electricity more easily than the bulk[9,10].

3.2 Electrical conductivity after heat ageing

The influence of heat ageing on the conductivity of the samples was investigated at 90ºC for 100 hrs in oven. The resistance of the samples was recorded at an interval of 3 hrs.

3.3 Specific gravity

ASTM standard D297–93–Hydrostatic weighing method was utilized for specific gravity measurements with a ratio of mass of a unit volume of composite to mass of a unit volume of water.

3.4 Hardness

The specimens with 6 mm diameter and thickness both were loaded on Type–2 durometer Shore A operating stand to measure the hardness in Shore A by ASTM standard D 2240 method. GSE Testing Instrument with indenter of type “A” was used for measuring the hardness.

3.5 Tensile strength

Computerized Tensile Testing machine by Star Testing Systems was used for measuring the tensile strength by ASTM standard D-412 method. A sheet of size $150\times150\times2$ mm^3 was used to prepare five dumbbell shaped specimens which were punched in a Die–C. Punching machine was used to get a single impact stroke, the strength of all five specimens were measured, the extreme high and extreme low readings were discarded and average of three specimens were taken.

3.6 Tear strength

ASTM standard D-624 was adopted for tear strength testing. Three dumbbells were punched from the sheet of same size as that for tensile strength with a single impact stroke punching machine to ensure smooth cut surfaces in Die-C with dimensions as per ASTM standard D-624. These specimens were tested and average of them was taken. Tear strength was measured on Star Testing Systems-Mumbai machine.

3.7 Rebound resilience

Rebound resilience was tested using ASTM standard D 2632-01. The specimen of 12 mm thickness and 6 mm diameter was used. Impact resilience was measured by Vertical Rebound Resiliometer by The Shore Instrument and Manufacturing Co., Mumbai, India.

3.8 Morphological characterization

Very thin films of 0.5×0.5 cm were cut from the cured samples and coated with platinum for scanning under JEOL-JSM 6360A electron microscope from Japan for SEM analysis.

3.9 Swelling resistance

The degree of swelling in solvents is the key property in case of polymer composites. The solvent used for testing the swelling resistance was ASTM Fuel B, which is a combination of 70% isopropyl alcohol and 30% toluene. Specimens of 1.5cm×2cm×2mm were weighed and immersed in the solvent for 24 hrs. The difference in the weight of specimens in air and water before and after immersion were recorded. The solvent resistance was measured using the equation (1):

$$Q = \frac{W_i - W_0}{W_0} \times 100 \qquad (1)$$

Where Q represents the degree of swelling; W_i and W_0 represent the mass of specimen before and after immersion in the solvent respectively.

3.10 Thermal characterization (TGA)

Thermograms of the specimens were recorded on the thermogravimetric analyser model TA-60 WS of Shimadzu—Japan in the range between RT-1000°C at a scanning rate of 10°C min^{-1} under nitrogen atmosphere with a flow rate of 50 ml min^{-1}.

4. Results and discussion

The electrical resistance of virgin silicone rubber is known to be ~$10^{15}\Omega$. When TiB_2 along with XC-72 is added to this material, the resistance was observed to decrease by an order of ~$10^{12\text{-}13}\Omega$. Various proportions of XC-72 and TiB_2 were added to silicone rubber, however, in order to achieve conductive composites optimum proportion of XC-72 and TiB_2 was found to be 10 phr and 5 phr respectively. The surface resistance of the composite was recorded to be 15-18 kΩ.

TiB_2, being a ceramic material, has good thermal stability. SITB composites are observed to show a negligible loss in the electrical conductivity when subjected to 90°C for 100 hrs, as is shown in **Figure 1**. There is a loss of ~2-3 kΩ in the resistance of the specimens of SITB at these conditions of temperature and time. **Figure 1** depicts the changes in the surface resistance upon heat ageing.

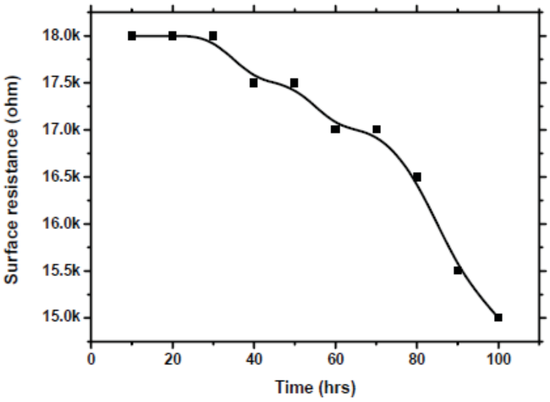

Figure 1. Effect of heat ageing on surface resistance of SITB composite.

The specific gravity of the composites is increased to some extent. Addition of TiB_2 and XC-72 enhances the specific gravity. Blank silicone rubber has a specific gravity of 1.07 while that of the composite is 1.14.

The ceramic material — TiB_2 is extremely hard (as hard as diamonds). This property is seen to be reflected in the hardness of the composites. The hardness of silicone rubber is 40 Shore A. Hardness of silicone rubber with carbon alone is 45 Shore A and that along with TiB_2 is 50 Shore A.

Every component in a composite contributes to the tensile strength of the composite and is the maximum stress experienced by the composites when stretched at the point of rupture. Tensile strength is the property of elastic materials; and addition of non-elastic fillers reduces this property. TiB_2, as a hard-ceramic material, resists stretching and ultimately reduces the tensile strength of the composite. The composites show ~ 47% reduction in tensile strength compared to silicone rubber with a standard deviation in the value of ± 1.1.

Tear is initiated in rubbers at the notch in the specimen and depends on the filler-matrix interaction. Stronger interaction leads to a higher tear strength. In the case of SITB composite, the tear strength is observed to increase compared to the blank silicone rubber. This can be attributed to the better interaction between TiB_2 and the silicone rubber. The tear strength of the composite is 15 kNm^{-1} with the standard deviation of ± 0.50.

The rebound resilience shows an inverse proportion to hardness of rubber material. In case of SITB composites, the rebound resilience is decreased to 39 % from 67% for the blank rubber. Hardness of TiB_2 affects the elasticity of the composite, thereby decreasing the rebound impact.

Homogeneity of the composites can be observed from the scanning electron microscopic image shown in **Figure 2**. A homogeneous dispersion of TiB_2 in the rubber matrix leads to the better interaction between the materials leading to the rise in electrical conductivity which is the result of inter particle connection and also increases the physical properties such as hardness and tear strength.

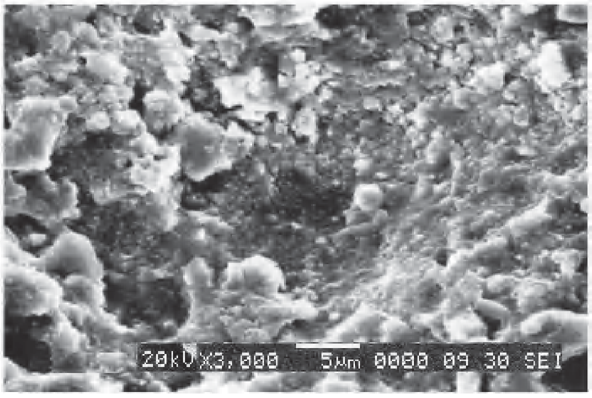

Figure 2. SEM image of the composite SITB.

Degree of swelling is the indication of the crosslinking density of the polymer composites. The lower the swelling is, the higher the crosslinking density will be. In case of SITB composites, lower degree of swelling shows the compactness and good filler-matrix interaction. Lower degree of swelling of the composites in ASTM Fuel B extends the application potential for high efficiency electronic devices[11]. The degree of swelling is decreased in case of composites than the silicone rubber itself. This can be attributed to the homogeneous dispersion which leads to the better filler-matrix interaction. The solvent resistance of the composite is 11% and that of blank silicone rubber is 17%. **Figure 3** depicts the scanned electron microscopic image of the composite after immersion in ASTM Fuel B for 24 hrs. The voids are due to the solvent penetration into the matrix. Thermal properties of the composites are negligibly altered as the proportion of TiB_2 added is very small.

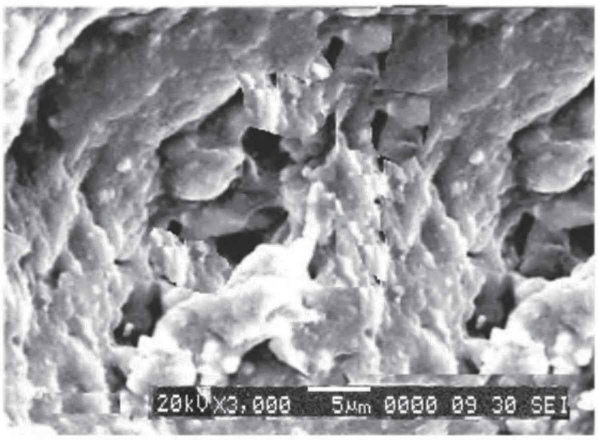

Figure 3. SEM image of the composites after swelling.

As can be seen from **Figure 4**, when the temperature is up to 450ºC, there is a weight loss due to volatile matter and decomposition of organic matter. When the temperature is between 450ºC and 600ºC, the sharp change in weight is due to the decomposition of silicone rubber into silicon and oxygen. The weight gain of ~ 4 % above 600ºC as is seen in **Figure 3** can be attributed to the oxidation of TiB_2 to form TiO_2[12]. TiB_2 combines with the oxygen generated during the decomposition of silicone rubber polymer.

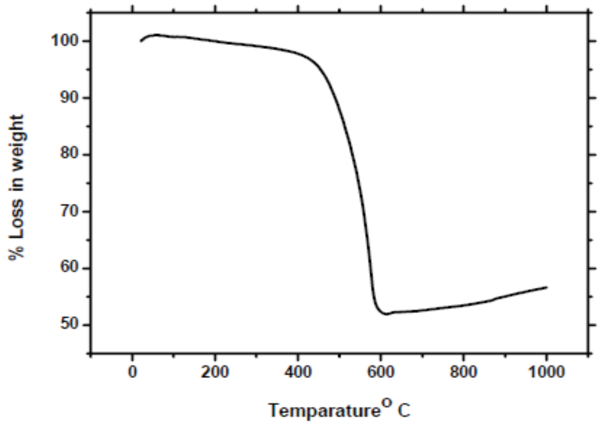

Figure 4. Thermogram of SITB composite.

5. Conclusions

Incorporation of TiB_2 and XC-72 into the silicone rubber gives an electrically conductive composite with the surface resistance of 15–18 kΩ under ambient conditions with a negligible effect of heat ageing on the surface resistance. The hardness and tear strength of the composites are increased with a decrease in the tensile strength and rebound resilience. The composites show an excellent resistance to the solvent — ASTM Fuel B.

Acknowledgements

The authors are thankful to K.D. Joshi Rubber Industries Pvt Ltd. for supporting the project. And the authors would like to extend sincere gratitude to University of Pune — Department of Chemistry for providing the facilities and Department of Physics for SEM facility.

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