

Article

Fabrication of Extrinsicly Conductive Silicone Rubbers with High Elasticity and Analysis of Their Mechanical and Electrical Characteristics

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Abstract: Conductive plastics are attracting more and more interest in electronics due to their light weight and inability to rust, which are common problems associated with metals. The field of conducting plastics is not new. Much work has been done to impart electrical conductivity to mechanically strong polymers such as polypropylene, polycarbonate and epoxies, *etc.* However there is a need to fabricate more flexible and elastic conductive polymers such as conducting silicone rubbers for use in various applications. In this work silicone rubbers reinforced with conductive fillers have been fabricated for use as sensors in textiles to detect the resistance change produced by stretching or relaxing. The variations of electrical resistance have been investigated by stretching and releasing the strands of conductive rubbers as a function of time. Two types of silicone rubbers—addition cured and condensation cured—were compounded with different electrically conductive fillers, among which carbon fibers have shown the best results. The carbon fibers improved the electrical conductance of the rubbers, even in very low weight percentages. The increasing concentration of fillers decreases the elasticity of the rubber. In order to keep the original properties of silicones, the filler concentration was kept as low as possible to produce a significantly detectable signal. The fabricated compounds were analyzed for their mechanical properties by stress strain curves. Such materials find their applications in electronics, antistatic applications, sports and the automotive industry where they can be used as deformation sensors.

Keywords: conductive; silicones; carbon fibers

1. Introduction

Silicones are polymers containing silicon along with carbon, hydrogen, oxygen, and sometimes other elements. They have a repeat unit of alternating silicone–oxygen (Si-O) siloxane in the backbone and have unique chemistry without carbon in the backbone $(R_2-SiO)_n$. Many organic groups such as methyl or the benzene ring may be bonded to the silicones [1]. Depending upon their degree of polymerization and the complexity of the attached organic groups, silicones can occur in the form of oils, greases, rubbers, adhesives and gels [2]. All forms of silicones have their own varied applications. They are not only used in medical technology but also in a broad range of industrial and manufacturing areas. The properties that make them a popular choice are water, UV, ozone and oxygen resistance, thermal stability over a wide range of temperatures, resiliency and flexibility even after curing, usability as solid or liquid and chemical resistance [3]. Such properties are very attractive for the applications where safety and flexibility are primary requirements [4].

A lot of past research is available where polymers are made conductive by dispersing conductive fillers in them [5,6]. The electrical resistivity of such composites depends critically on the volume fraction of the conducting filler particles and is explained well by percolation theory [7]. As silicones are electric insulators, they can be made conductive extrinsically by the addition of conductive materials. The resulting conductive silicones have a number of advantages over other polymeric materials, e.g. epoxies and thermoplastic adhesives [8], which have poor quality and soft oily appearance. The epoxies and thermoplastic adhesives adhere to the conductors and leave a residue after removal. Some polymeric materials are also soldered to the connections which become permanent interconnections between the conductors [9]. Conductive silicones help to overcome these problems. They are flexible, with sufficient cohesive forces and viscosity. They can be housed in cavities without leakage. They are self healing when connected or disconnected to the conductors and also do not adhere to the connections. Such materials find applications also as sealants in electromagnetic shields, office equipment and as antistatic members [10–13].

The research work presented in this contribution aims to develop a flexible and elastic conductive polymer with resistance in kOhm range which upon stretching and releasing gives almost the same values of resistance. Such material has applications in the textile industry, where it can act as an electrical resistance sensor which changes if the textile is stretched or relaxed. Under a certain degree of stress, the material changes its resistance and comes back to the nearly original value when the stress is removed. From the previous available literature and applications it is very clear that the silicone rubbers are quite flexible above their glass transition temperature and have excellent elasticity. Therefore two types of silicone rubbers were selected and made conductive by dispersing conductive materials such as carbon fibers (CF), carbon black (CP), nickel coated graphite (NG), copper fibers (Cu) and a combination of CP and CF. Some of the conductive silicones showed a significant decrease in resistance without losing their flexibility. However certain desirable attributes of the silicones, e.g. flexibility, are diminished as the concentration of conductive fillers increases. Therefore an attempt

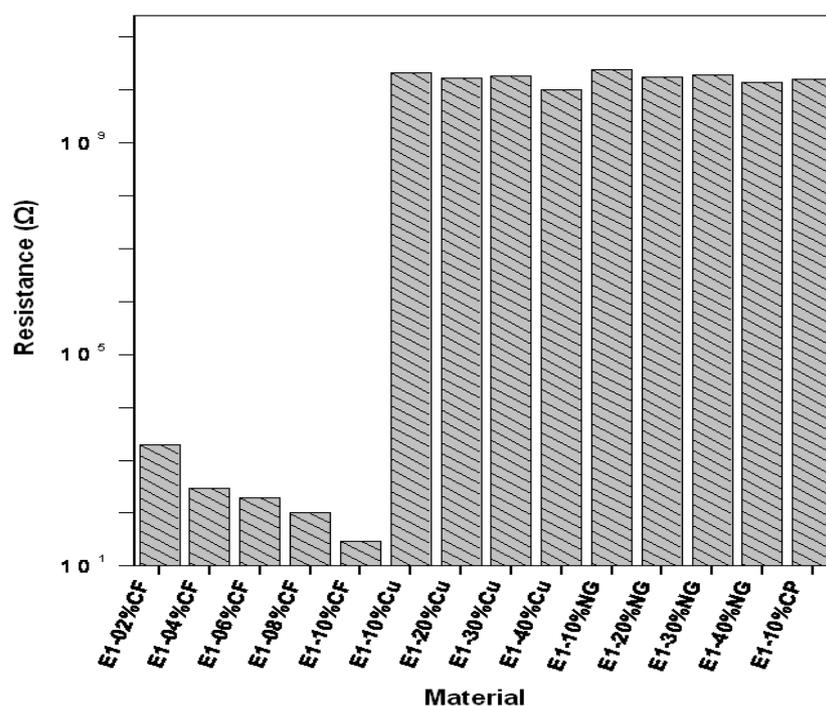
was made to keep the concentration of fillers at the level where they decrease the silicone resistance while keeping the silicones as close to the original as possible. These textiles based on such conductive silicone rubbers have potential applications in the field of sports and automobile industry where they can detect various deformations present in structures e.g. shoes, gloves, *etc.*

2. Results and Discussion

2.1. Electrical Resistance

Electrical resistance of the cured rubbers in bone shaped probes was measured by two instruments: Agilent 4339B and DigitekDT4000ZC. The Agilent is a high resistance meter and it can measure resistance from 103 to 1,016 Ω . It was used to check the resistance for pure rubbers and for electrically conductive filler-reinforced rubber with high resistance, which was out of the range of Digitek (measuring range: ohm to 4 M Ω). Figure 1 is showing the results for E1 reinforced with different conductive fillers. The resistance of pure E1 measured by the Agilent unit was $2 \times 10^{12} \Omega$.

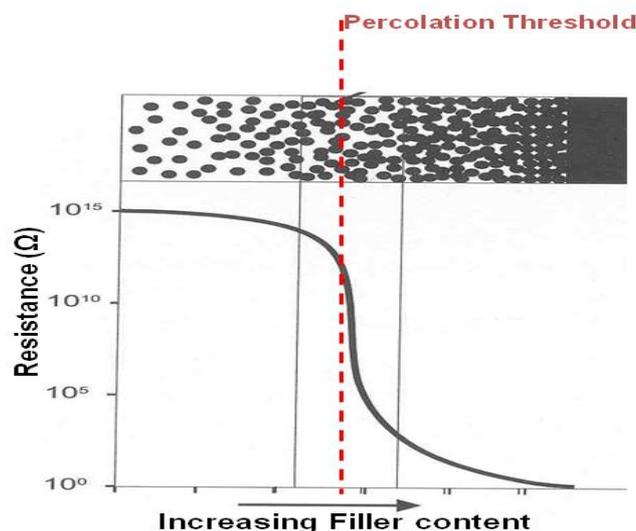
Figure 1. Resistance of E1 reinforced with conductive fillers.



The results for E1 show that carbon fibers have significantly reduced the resistance. At 2 weight% CF the compound has a resistance of 2 k Ω , whereas other fillers have not shown any conductivity, even at high concentrations of 30 and 40 weight%. There can be many reasons for such results. Metals undergo oxidation in open air, and therefore, it is possible that due to oxidation CuF was no longer conductive [15]. Moreover the aspect ratio of fillers is also a reason why some fillers are so efficient in imparting electrical conductivity to the materials. The higher aspect ratio (length/diameter) of carbon fibers may have allowed the better connections between fillers [16]. Electricity can pass through a material only if there is a sufficiently conducting network. This concentration, where a conductive

network is established among the fillers is called the percolation threshold (Figure 2). It might be possible that for the other fillers no connections developed or the connections between fillers were not effective even at high concentrations due to their geometry and low aspect ratio that did not allow the formation of conducting paths [17].

Figure 2. A sketch showing resistance decrease with sufficient filler connections.



For E2, even lower concentrations of CF were prepared and it was found that the material was conductive at 0.5 weight% CF (Figure 3). Resistance decreased almost 100% when pure E2 (1,012 Ω) was reinforced with 0.5 weight% of CF. At 1 weight% CF the resistance decreased again drastically. However with further addition of CF the resistance remained almost the same. A possible explanation can be that effective conductive networks have been formed at 1 weight% CF and further addition of fibers did not help further decrease the resistance.

Figure 3. Resistance of CF reinforced E2.

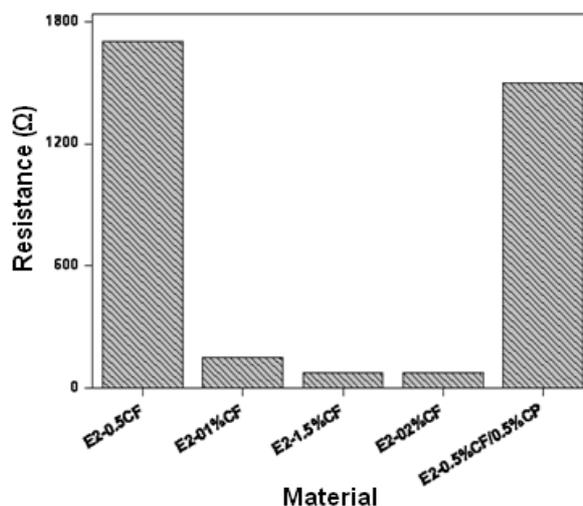
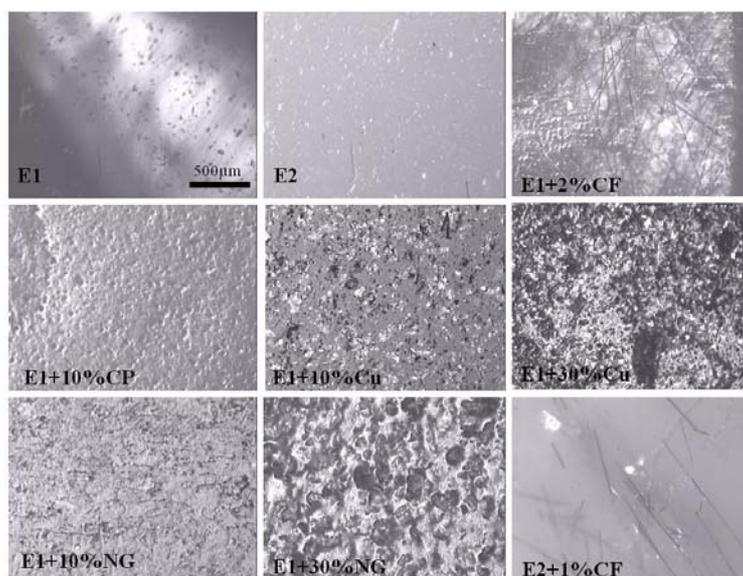


Figure 4 shows optical microscope images of the compounds. These pictures also support the idea that fibers have better conductive networks as compare to the particles. The fiber geometry allows the

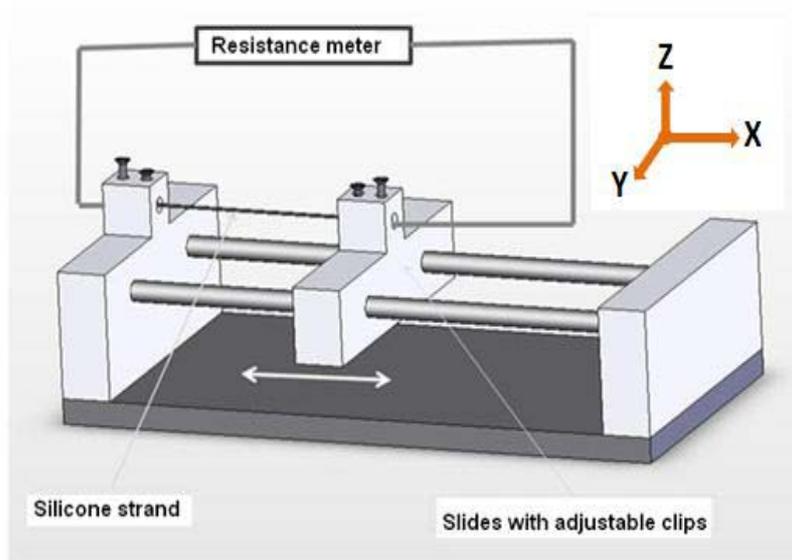
effective interconnections as compare to the particles which also tend to agglomerate and thereby breaking the contacts at certain places. However Cu fibers have not produced conductive composites even at 30 weight%. The reason could be the oxidation of metals due to which Cu fibers are no longer conductive.

Figure 4. Optical microscopy of E1 and E2 filled with conductive fillers.



The requirement of the research work was to have a highly elastic material with resistance in the $k\Omega$ range. E2 with 1 weight% CF has both the required features. E2 + 1 weight% CF and E1 + 2 weight% CF were tested for resistance changes upon stretching and releasing. For these tests 100 mm long strands with 3×1 mm (width \times thickness) dimensions were cut from the cured rubbers. These strands were mounted on a setup (Figure 5) connected to resistance meter (Digitek). All the resistance measurements were done in x-axis direction. The mounted strands were in a relaxed state.

Figure 5. Setup to measure the resistance of conductive strands in stretched and relaxed state.



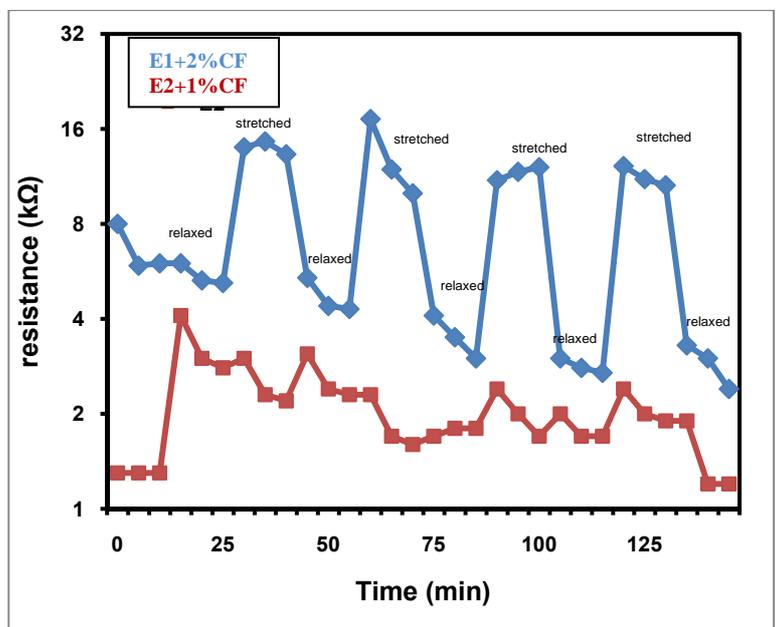
The first resistance value was recorded with the Digitek multimeter as soon as the strands were mounted. Two more resistance values of the strands were recorded in the relaxed state, each after a five minute interval. Thereafter, strands were stretched by 8% (10 to 10.8 cm) of their original length and three resistance values were recorded every 5 minutes. It can be seen (Figure 6) that the materials have shown quite reproducible results after five cycles (stretched-relaxed = one cycle). Both materials were quite elastic and upon releasing came back to the original value in less than a minute. It can be observed that the resistance in relaxed state is less than in the stretched state. This behavior can be due to the reason that in the stretched state some connections between fibers break leading to an increase in resistance. Variations in resistance values for E2 compounds are less than for E1. E2 is more elastic as compared to E1 and its elasticity might be responsible for its fast recovery and less breakage of the conductive paths.

It can also be observed that the resistance is higher for strands as compared to the bone shaped samples. Resistance of the materials is given as:

$$R = \frac{l \times \rho}{A} \quad (1)$$

where R = resistance, ρ = electrical resistivity (Ω m) and A = cross sectional area in m^2 and l = length of the conductor in m [18]. According to the relation (1), when the area of the material decreases, its resistance increases. When material strands were cut from cured rubber samples, the resistance increased compared to the bone shaped samples. This is due to the decreased area.

Figure 6. Resistance variations upon stretching and relaxing the conductive rubber strands.



2.2. Mechanical Analysis

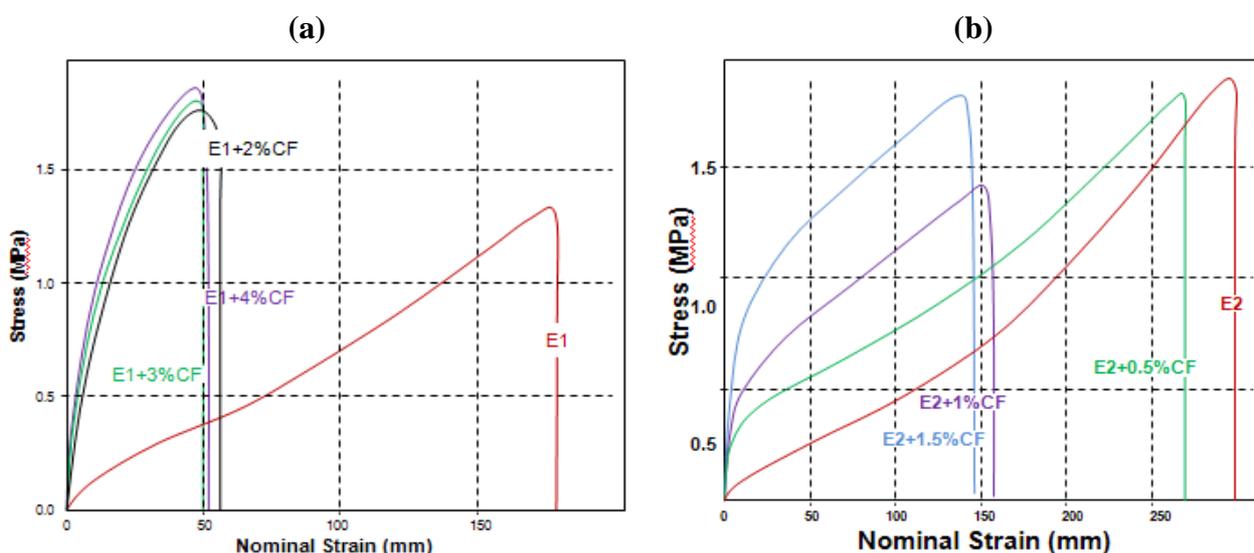
Stress-strain curves are very important to measure a material's mechanical ability. These tests measure the force required to break a specimen and the extent to which the specimen stretches or elongates to that breaking point [18]. This data was important to specify the material, to design the parts where this material is able to withstand the applied forces, and for the quality control of the

material. The stress strain curves for the silicone rubbers are shown in Figure 7. These tests were done using a Zwick Roell Z250 testing machine on bone shaped samples with $14.5 \times 1(\text{centre}) \times 0.4$ cm dimensions according to the standard DIN EN ISO 527-4. Samples were placed in the grips of the instrument with a relaxation of 90 mm and pulled to failure. Testing speed was 20 mm/min and preload was 0.8 N.

Figure 7a shows stress strain curves for E1 and its compounds with 2 weight% CF and 4 weight% CF. The maximum nominal strain for E1 was 180 mm and after which the material fails. However presence of carbon fibers diminishes the elasticity of the material and changes its behavior more towards brittleness. Therefore it was thought best to keep the CF concentration as low as possible to maintain the material properties more like the original E1.

Similar behavior has been observed for E2 and its compounds with CF (Figure 7b). With an increasing concentration of filler, the material loses its flexibility and the brittle behavior becomes pronounced. Therefore the material with 1weight% CF was selected for further tests as its nominal strain is 45% less than pure E2. E2 + 1weight% CF has reasonable elasticity while at the same time giving very good value for resistance.

Figure 7. (a) Stress-strain curve for E1 and E1-CF compounds. (b) Stress-strain Curves for E2-CF compounds.



Modulus of elasticity or E-modulus is an indication of a material's stiffness and is determined by the slope of the stress-strain curves of the material [19]. The E-moduli for the compounds of E1 and E2 with carbon fibers are shown in Figure 8. The stiffness of the materials increases with the increasing filler concentration.

If the concentration of filler is low as in the compounds of E1 with carbon fiber, the increase in E-modulus is low as well. Although material is not as elastic as the original material, it is elastic enough to give reproducible electrical resistance upon stretching and relaxing. The compounds of E2 with CF were prepared only up to 2 weight% of the filler because the required resistance and elasticity were achieved at 0.5 weight% of filler loading.

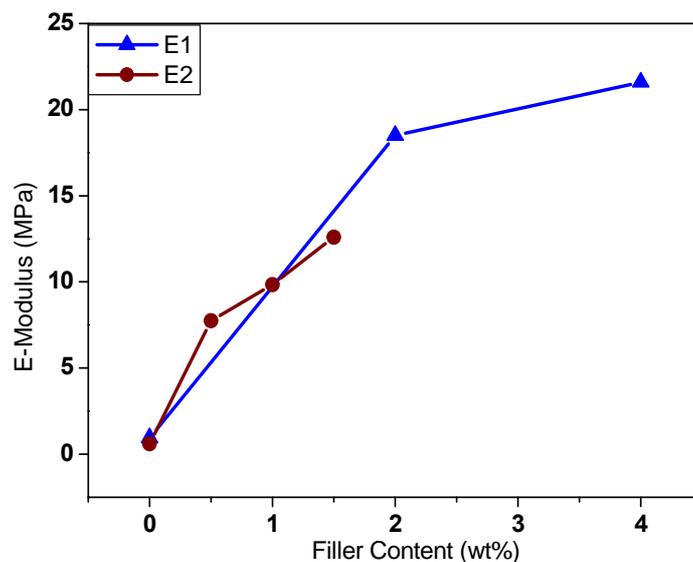
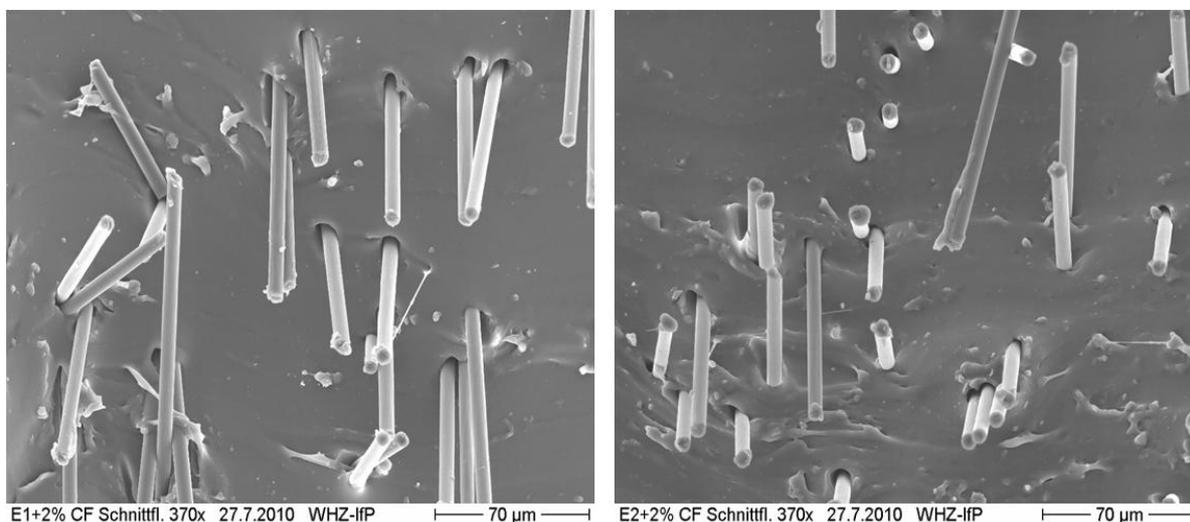
Figure 8. E-moduli for E1 and E2 with CF.

Figure 9 gives an understanding of how fibers adhere to the matrix. The fibers are quite loosely bonded to the E1. The base of the fibers has holes showing that the matrix is not holding them firmly in the place. This might be a reason for the brittle behavior of E2 reinforced with CF. However the fibers seem to be better embedded in the E2 matrix as compared to the E1.

Figure 9. SEM pictures of E1 and E2 reinforced with 2%CF.

3. Experimental

3.1. Material

3.1.1. Silicone Rubbers

The two silicone rubbers from R&G Faserverbunwerkstoffe GmbH (Germany) were selected as matrix material for this research work. The important properties of both materials are given in Table 1.

Table 1. Properties of used silicone rubbers.

<i>Material</i>	<i>Abb.</i>	<i>Density</i> (g/cm ³)	<i>Hardness</i>	<i>Heat Resistance</i> (°C)	<i>Elongation</i> <i>at Break</i>	<i>Mixing Ratio</i>	<i>Curing</i> <i>Time (h)</i>
<i>Elastosil</i> <i>M4641</i>	E1	1.07	Shore A 43	Up to 180	300%	10:1 Silicone:hardener	15
<i>Elastosil</i> <i>M4503</i>	E2	1.17	Shore A 25	180	350	100:5	15

E1 is a pourable, addition-cured, highly elastic double constituent silicone rubber vulcanizes at room temperature. E1 has 500 to 1,000 mPa·s viscosity at 23 °C. E1 is a two part curable system, which consists of component A (polydimethyl siloxane with functional groups) and component B (polydimethyl siloxane with functional groups and some additives for additional crosslinking). It has a fast, non-shrink cure at room temperature which can be accelerated by the application of heat [14]. The processing time for E1 is 100 minutes. The cured rubber is transparent.

E2 is a pourable, condensation-cured two component silicone rubber that vulcanizes at room temperature. It has good flowability, great extensibility and elasticity. The characterization shows it is a polysiloxane with functional groups. The viscosity is between 40,000 and 60,000 mPa·s at 23 °C. The vulcanizate has long term mechanical properties [14]. E2 is cured by adding catalyst T35 which was also purchased from R&G. The processing time for E2 is 90 minutes.

3.1.2. Electrically Conductive Fillers

The conductive fillers given in Table 2 were used as reinforcement materials because of their excellent conductivity and successful integration into polymers for enhancing conductivity and mechanical properties of plastics. The properties of the fillers reported in the Table 2 have been provided by the manufacturers.

Table 2. Properties of Conductive fillers.

<i>Filler</i>	<i>Abb.</i>	<i>Trade</i> <i>Name</i>	<i>Manufacturer</i>	<i>Density</i> (g/cm ³)	<i>Length</i> (mm)	<i>Diameter</i> (µm)	<i>Particle</i> <i>Size</i> (µm)
<i>Carbon</i> <i>Fibers</i>	CF	HTA 5131	Toho-Tenax Europe GmbH	1.8	6	7	–
<i>Carbon</i> <i>black</i>	CP	Norit SA Super	Norit, Netherlands	0.25 (tamped)	–	–	>150
<i>Nickel</i> <i>coated</i> <i>graphite</i>	NG	E-fill 2701	Sulzer Metco Ltd.	1.25 to 1.35	–	–	60
<i>Copper</i> <i>Fibers</i>	Cu	E-Cu58	Stax, Deutsches metallfaserwerk GmbH&Co.	–	0.8	60	–

3.2. Fabrication of Conductive Silicone Rubbers

To prepare electrically conducting silicone compounds, first E1 and E2 were compounded with the electrically conductive fillers using an electrical mixer for 5 minutes followed by the addition of hardeners in the mixing ratios recommended by the manufacturers (Table 1) and a further mixing for 5 minutes. The compounds were left to cure at room temperature for 15 hours. E1 was compounded with CF (2, 4, 6, 8 and 10 weight%), Cu (10, 20, 30 and 40 weight%), CP (10 weight%) and NG (10, 20, 30 and 40 weight%). The elasticity of the rubber decreases by the increasing amount of fillers. Therefore fillers were added only up to the concentrations where silicone rubber was still flexible. E2 was compounded with CF (0.1, 1, 1.5, 2, 3 and 4 weight%). In order to check the effect of hybrid fillers, E2 was compounded with a mixture of 0.5 weight% CF and 0.5 weight% CP as well. Bone shaped samples were cut from the cured samples for tensile testing and 100 mm long strands were cut for resistance measurement.

4. Conclusions

Extrinsically conductive silicone rubbers have been produced by adding conductive fillers to the rubbers during processing. Silicone rubbers were cured at room temperature. The aim was to produce compounds with greater elasticity, low resistance and consistent behavior upon stretching and relaxation of the material. The most promising results were obtained by the addition of carbon fibers. The credit goes to the high aspect ratio of carbon fibers that enabled them to develop effective conducting networks. The electrical and mechanical properties of the compounds were measured and compared. Electrical resistance was measured to determine the electrical properties whereas stress – strain curves provided the information about tensile properties.

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