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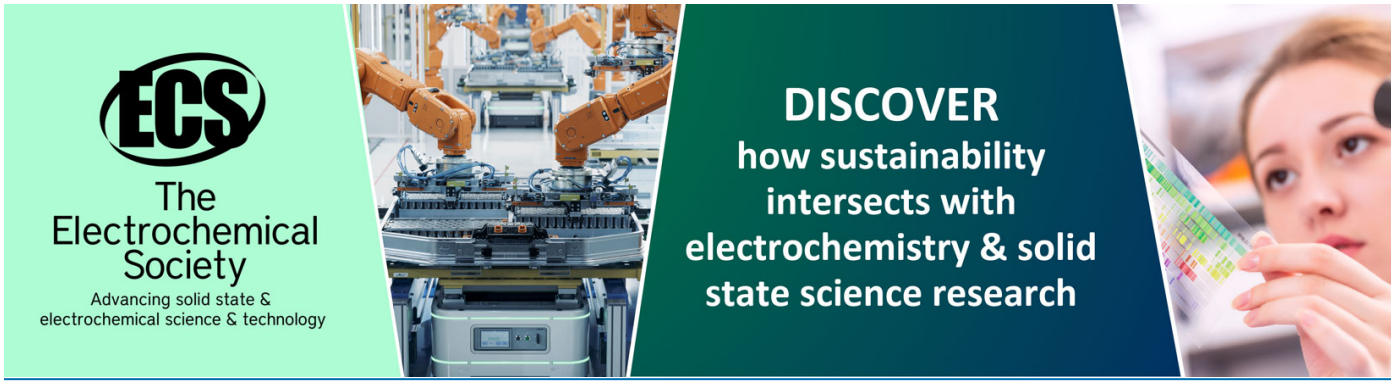

Conductive properties of flexible polymer composites with different carbon-based fillers

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Abstract. This paper is devoted to the comparative study of conductive properties of three types of flexible polymer composites consisting of styrene-butadiene rubber (SBR) as a matrix and graphite, graphene or single-walled carbon nanotubes as fillers. The dependences of the resistivity on the mass fraction of different fillers are measured and analyzed within the framework of the statistical percolation theory. The percolation parameters (the values of the percolation threshold and the critical exponent) are calculated for all studied composites. Their variation depending on the filler type is discussed, taking into account a geometric shape of filler particles and the nature of the conduction process in composites in the percolation range. The sensitivity of the resistivity of synthesized composites to axial deformation at different mass fraction of fillers is also investigated. Using graphite or graphene fillers is observed to result in a higher sensitivity compared to the carbon nanotubes filler. The highest value of the gauge factor is observed when using 23 mass.% graphene filler that indicates graphene/SBR composites to be most promising for creating strain sensors.

1. Introduction

In recent years, polymer composites with different carbon-based structures as fillers have attracted increased interest among researchers. Polymer materials have a number of unique properties, such as low density, flexibility, wear resistance, chemical and radiation resistance, etc., that provides a very wide range of their practical use. Using a polymer material as a matrix and various particles as fillers allows one to significantly modify parameters of the resulting composites, first of all, to improve their mechanical and conductive properties. Conventional electronic composites containing such fillers as short carbon fibers or carbon flakes, require using a high content of filler, that can make the composite brittle and unsuitable for many applications. This is why using nanoparticles as fillers has undoubted advantages. Potential applications of nanocomposites include organic field emitting displays, photovoltaic cells, electromagnetic-wave interference materials, flexible thermoelectric devices, and others [1, 2]. The use of polymer composites to create flexible strain sensors [3, 4] is one of such promising applications, which are currently being intensively studied.

The charge-carrier transport in considered composites at low filler contents occurs due to the percolation nature of the conduction process. For this reason, it is of interest to study the modification of the electrical properties of polymer composites filled by carbon-based structures, depending on the

types of polymer and filler, as well as on the volume fraction of the filler. It is also needed for their further practical applications. Percolation properties of polymer composites with carbon nanotubes (CNT) or graphene fillers were studied in many papers (see, for examples, reviews [5-7]). However, properties of a specific polymer and the type and morphology of filler particles result in the appearance of many uncontrolled factors affecting the conduction process parameters. This makes is difficult to compare quantitatively the results obtained for different fillers and draw conclusions on advantages of using one or another of them.

Taking the above into account, in this paper we present the results of a comparative study of the conductive properties and their strain sensitivity for polymer composites based on a styrene-butadiene rubber (SBR) matrix with graphite, graphene, and carbon nanotubes as fillers.

2. Samples and experimental details

As the initial components for synthesis, we used styrene-butadiene rubber (SBR) Sigma-Aldrich, graphite powder Super P Conductive Carbon Black, home-made CVD graphene particles, and single-walled carbon nanotubes TUBALL. To synthesize the composites, a filler powder (graphite, graphene or CNT) of the desired mass was stirred in a magnetic stirrer in a CCl_4 solvent in a closed flask to prevent solvent evaporation and air bubbles entering the solution for 10 min for graphite or graphene and for 1 h for CNT. Next, SBR polymer was introduced into the dispersion in an amount of 5.9 wt.% to the solvent and kneading continued for 1 h until the polymer was completely dissolved. The resulting solution was poured into a fluoroplast mold in an amount of 0.1 ml/cm^2 and was dried under a range hood for 1 h. Due to the low wettability of the fluoroplast, the resulting film was easily removed from the mold with tweezers. It should be noted that the use of a mold with low edges for drying the film instead of a conventional substrate led to the fact that all defects in the resulting sample accumulated along edges, which were cut off after sample extraction.

The resistivity was measured by the standard dc four-probe method using the van der Pauw geometry. All measurements were performed twice with changing current and voltage contacts and the resistivity values were calculated using the van der Pauw formula taking into account a correction factor depending on the ratio of two measured values. Contacts to the samples were made by a conductive Ag paste. To study the resistivity sensitivity to the strain, the sample was fixed between two clips coated with polymer for better adhesion to the samples; one of these clips was movable. This clip was moved by a certain step, thereby stretching the sample. After measuring the resistivity, the clip was moved one more step, and the measurements were made again, etc.

3. Experimental results and discussion

Figure 1 shows the dependences of the resistivity value at T = 300 K on the mass fraction of filler, φ, for studied composites. As seen, when the filler fraction increases, the resistivity of all the three composites changes analogously and in a standard way for such systems. At low φ, when all the conductive particles in the polymer matrix are insulated, the resistivity values are extremely high (not shown in figure 1). An increase in φ first leads to the appearance of a small number of complete conductive paths through electrically connected particles that leads to a sharp decrease in the resistivity in accordance with the percolation theory. A further increase in φ results in the formation of a conductive network and the resistivity continues to decrease but rather slightly down to a constant value at a high number of introduced conductive particles. According to the results presented in figure 1, the conductive networks in the studied composites are formed at the mass fractions of fillers approximately equal to 0.37, 0.29, and 0.098 for composites with graphite, graphene, and carbon nanotubes, correspondingly.

As known, in the range of φ corresponding to the percolation process, the conductivity dependence on φ can be adequately described by the percolation power law:

$$\sigma = \sigma_0(\varphi - \varphi_c)^t, \quad (1)$$

where φ_c is the percolation threshold, t is the critical exponent whose value, in the framework of the statistical percolation theory, depends on the system dimensionality, and σ_0 is the adjustable parameter.

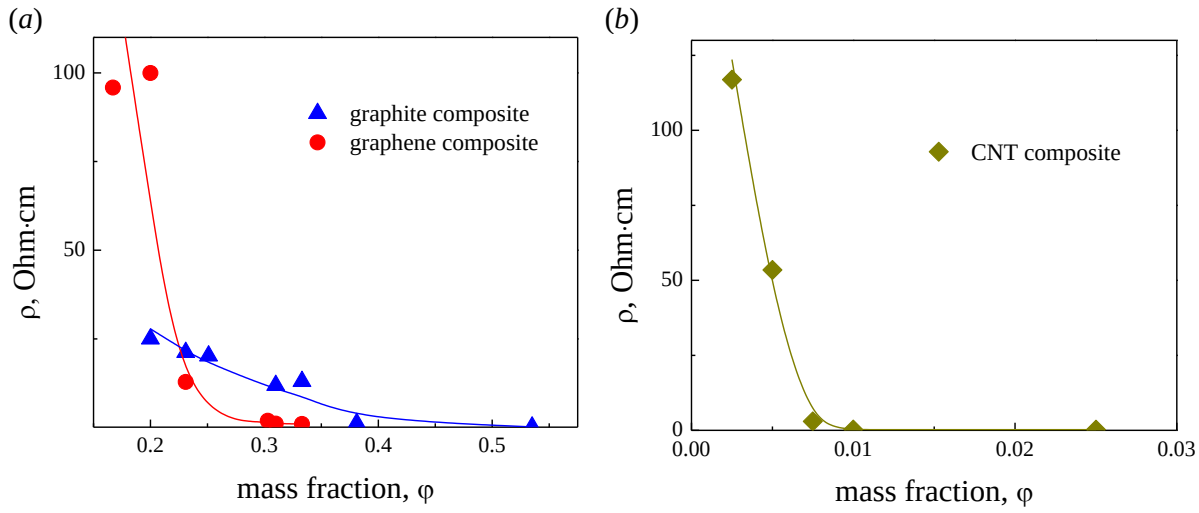

Figure 1. Resistivity at T = 300 K vs mass fraction of fillers for composites containing graphite and graphene (*a*); carbon nanotubes (*b*)

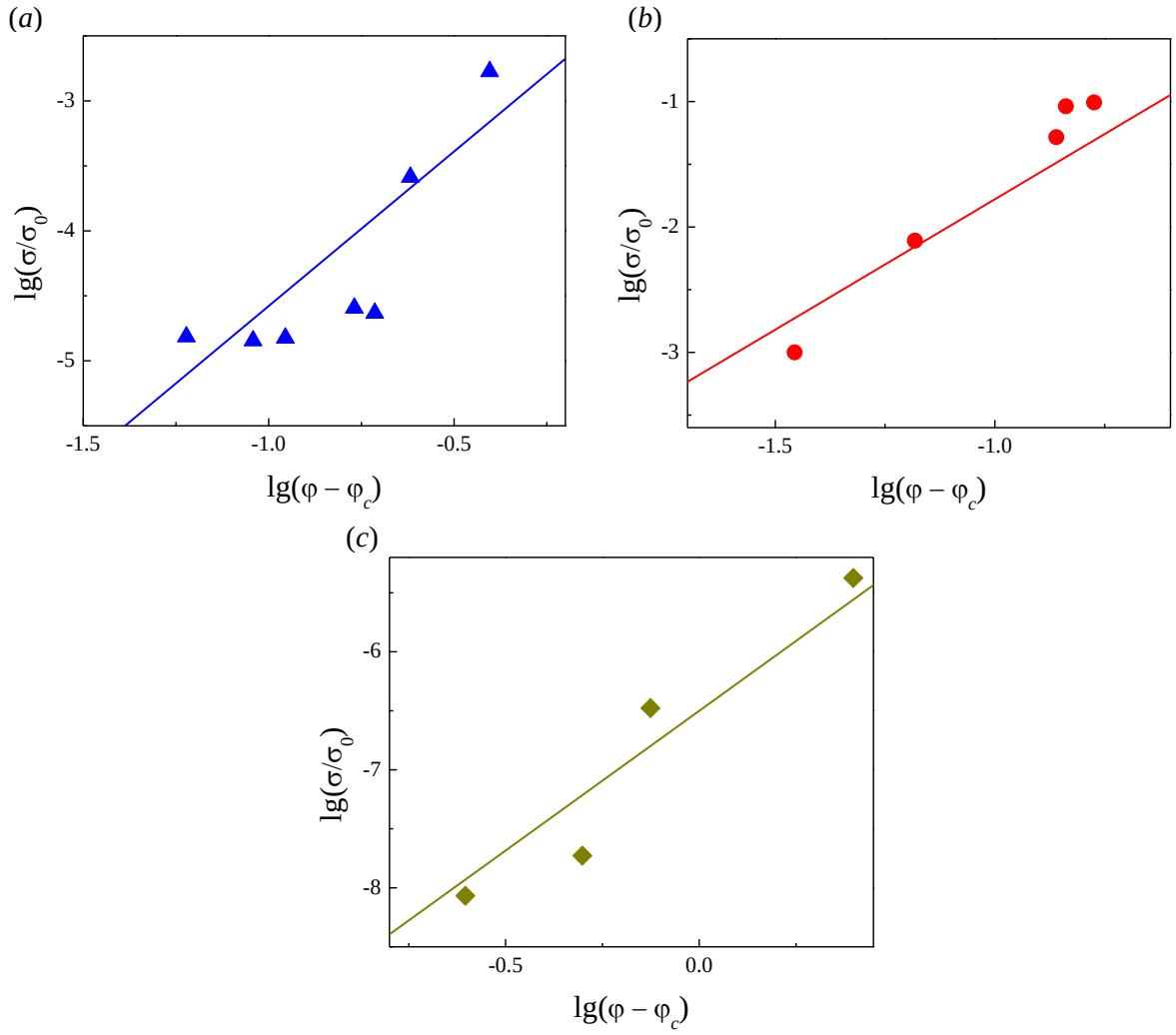

Figure 2. Fitted dependences of $\lg(\sigma/\sigma_0)$ vs $\lg(\varphi - \varphi_c)$ for composites with different fillers: graphite (*a*), graphene (*b*), and carbon nanotubes (*c*)

To calculate the percolation parameters, we have fitted the experimental results to Eq. (1). The obtained dependences of $\lg(\sigma/\sigma_0)$ on $\lg(\varphi - \varphi_c)$ for the studied composites are shown in figure 2. The slopes of the presented lines correspond to the critical exponent values of 2.38, 2.08, and 2.37 for composites with graphite, graphene, and carbon nanotubes, correspondingly. According to the statistical percolation theory, the calculated t values should be about $t \approx 1.33$ for two-dimension systems and $t \approx 2.0$ for three-dimensional ones, while the t values obtained for all studied composites are higher. Note, that investigations of various polymer composites filled by carbon nanotubes of different morphologies revealed the critical exponent value to be in a range of $t = 1.2–4.0$ peaking around $t \approx 2.0$, which corresponds well to our results for this filler ($t = 2.37$). Different approaches were proposed to explain this finding, but the main conclusion was that in such composites the t value ceases to unambiguously depend on the geometrical characteristics of carbon nanotubes and thus cannot be used to extract information of the system dimensionality [5, 6]. The probable reason for this phenomenon can be that in the range of low filler concentrations, there is no direct electrical contact between conductive particles in composite so that the conduction is carried out due to tunneling transitions of charge carriers between filler particles. Since the distances between different filler particles are different, the Eq. (1) loses its universal nature. Our resilts show that if graphite and graphene are used as fillers the t value also exceeds 2, i. e., in these cases the conduction in a mixture at low filler concentrations also arises due to the tunneling effect.

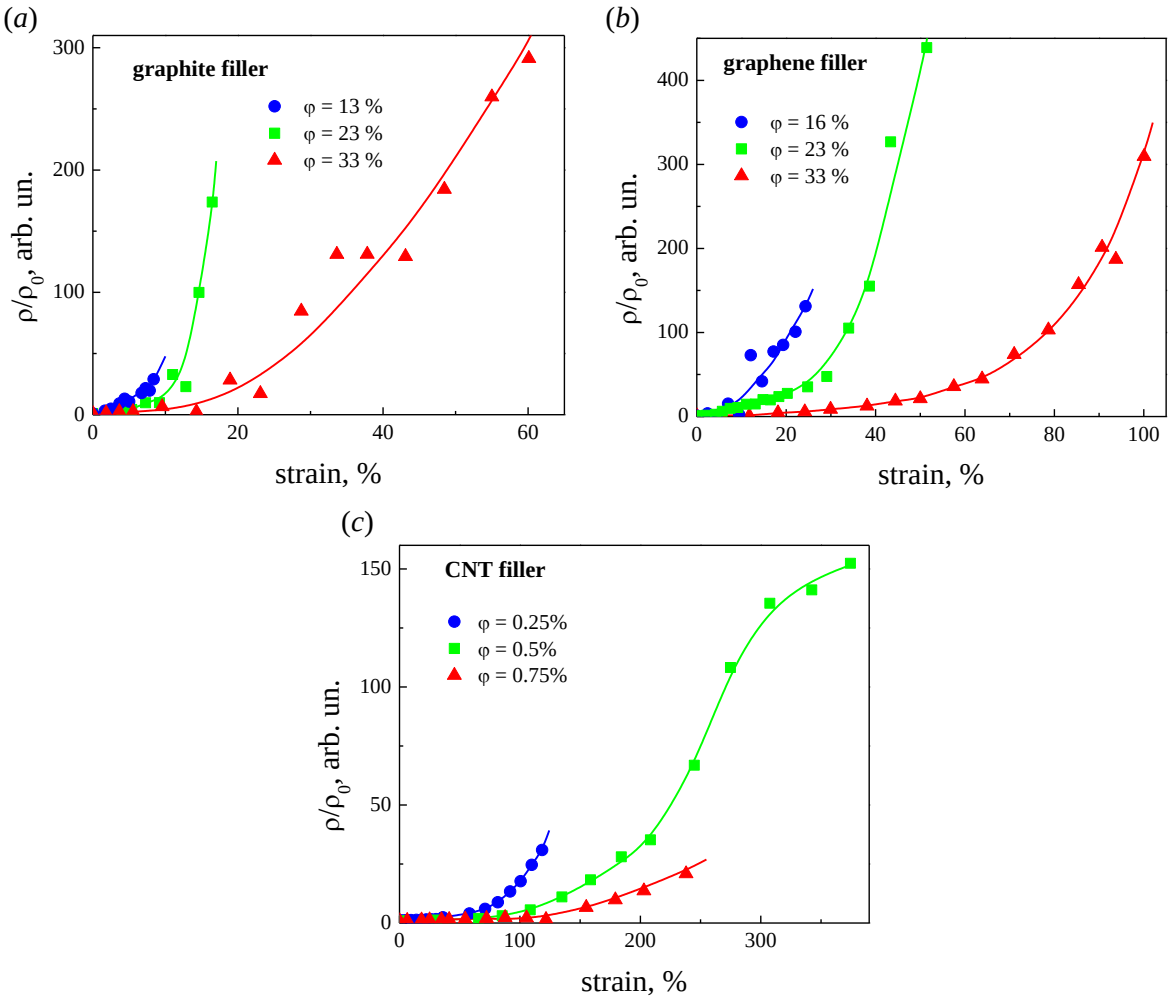

Figure 3. Variation of the resistivity with increasing strain for composites with different fillers: graphite (*a*), graphene (*b*), and carbon nanotubes (*c*)

The values of the percolation threshold φ_c estimated by Eq. (1) are 0.001, 0.12, and 0.165 for composites filled by carbon nanotubes, graphene, and graphite, respectively. A large difference in these values can be explained by an influence of the size ratio of conductive particles in cases of using different filler types. Indeed, carbon nanotubes are characterized by a large aspect ratio (typically about 1000) that decreases significantly the percolation threshold value. According to the excluded volume concept [8], the above value of the aspect ratio, when calculated within the statistical percolation theory, gives a value of $\varphi_c \approx 0.001$ [5] that fully corresponds to our results for the case of CNT filler. In case of using graphene filler, conductive particles have a sheet shape that should increase the φ_c value compared to CNT filler. At last, graphite particles have a rather spherical shape that results in the highest φ_c value among the studied composites.

The synthesized composites were examined for the possibility of their use to build working elements for strain sensors. For this aim, their sensitivity to axial deformation was investigated. Figure 3 shows the relative change in the resistivity of all three studied composites under strain (ρ_0 is the resistance of corresponding composite without applied load). Although polymer composites with CNT filler are considered as most appropriate materials for strain sensor applications, one can clearly see that using both graphite and graphene as fillers makes it possible to achieve a higher sensitivity to deformations. Note that in case of CNT filler, the resistivity value starts increasing strongly only under high strain, while in cases of graphite and graphene fillers, lower strains are required to rise the resistivity. Moreover, the changes in ρ values are already observable even under very low strains. This suggests using graphite or graphene as filler to be more perspective for the creation of strain sensors. Additionally, as can be seen from figure 3(*a, b*), a variation of the filler mass fraction shifts a range of composite sensitivity to strain that makes it possible to adjust a sample composition depending on the specific requirements for the sensor.

Table 1. Influence of the filler type and mass fraction on the gauge factor value

Filler	graphene			graphite			CNT		
Mass fraction (%)	16	23	33	13	23	33	0.25	0.5	0.75
GF	534.7	2661	340.4	6.86	1005	481.9	25.3	40.3	8.4

Based on the results obtained for the composite sensitivity, we have calculated the values of the gauge factor $\mathrm{GF} = (\Delta\rho/\rho)/(\Delta L/L)$, where ρ and L are the resistivity and the length of the sample before applying strain; $\Delta\rho$ and ΔL are the absolute values of changes in these parameters under strain. Table 1 presents the values of the gauge factor for composites with different types and mass fractions of fillers calculated for the maximal strain values used for them in our measurements. One can see that composites with graphite and graphene fillers demonstrate significantly higher GF values compared to the composites with CNT filler. The maximal value of GF = 2660 is found for the composite with graphene filler at its mass fraction of 23 %. Such a GF value is extremely high when comparing to other materials that indicates great prospects for the use of the SBR polymer with graphene filler to create strain sensors.

4. Conclusions

In this paper, we have performed a comparative study of the conductive properties of the polymer composites on the basis of styrene-butadiene rubber and three types of carbon-based filler: graphite, graphene, and single-walled carbon nanotubes of mass fraction varied in a wide range. By analyzing the results within the percolation theory, the values of the percolation thresholds and the critical exponent in the percolation power law were determined. In cases of graphene and graphite fillers, the percolation threshold values were found to be significantly higher than in case of CNT filler. The observed variation of this value with the filler type can be explained by taking into account the geometric shape of particles of different fillers introduced into the polymer matrix. The values of the critical exponent $t \geq 2$ found

for all fillers indicate that the conduction in all studied composites in a percolation range appears because of charge-carrier tunneling between the filler particles. Investigation of the sensitivity of the resistivity to axial deformation revealed higher values of the gauge factor for graphite and graphene fillers with a maximum value of 2660 in cases of introduction of 23 mass.% graphene into the SBR matrix. This indicates the composites with graphene filler to be the best candidates to use for the creation of strain sensors.

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