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Effect of thermal treatment conditions on the properties of onion-like carbon based polymer composite

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ABSTRACT

Dielectric properties of onion-like carbon (OLC) and polyurethane composite prepared using different procedures were investigated in the frequency range up to 1 MHz. We show that broadband dielectric spectroscopy is powerful tool to determine technological fingerprints in the studied materials. It is demonstrated that cured samples annealed at temperature close to the melting point (450 K) exhibit substantially higher dielectric permittivity and electrical conductivity in comparison with untreated samples. With the increase of temperature of an untreated sample, its dielectric permittivity, electric conductivity and critical frequency increase, while Maxwell–Wagner mean relaxation time and aggregate sizes of OLC decreases. Annealing of the composite at temperature close to the melting temperature produce sample with more homogeneous distribution of OLC. The temperature dependence of conductivity of the homogeneous sample is mainly caused by a weak positive temperature coefficient effect.

1. Introduction

Electrically percolative polymer-based composites have been attracting much attention because of their potential applications such as electroactive materials, sensitive materials, and electromagnetic coatings. Owing to the advanced electrical, thermal, and mechanical properties, various carbon nanoparticles like carbon nanotubes or carbon black have been widely studied and often used as nanofillers in the past few years. The main advantage of carbon nanotubes versus other carbon nanofillers is their extremely low percolation threshold [1]. Nevertheless, the percolation threshold in carbon nanotubes based composites dependents on many factors such as polymer type and dispersion method [2]. The onion-like carbons (OLCs), consisting of stable defected multishell fullerenes, exhibit high conductivity similar to carbon nanotubes [3]. The OLC have a rare structure allowing for hierarchical assembly of conductive structural units and high concentration of electrically active defects, being able to absorb a wideband of electromagnetic radiation [4]. Nevertheless, the first investigations of OLC based composites have shown low dielectric permittivity and electrical conductivity similar to the pure polymer matrix parameters [5–7]. It was observed, however, that the dielectric permittivity and electrical conductivity drastically increase in onion-like-based composite approaching the percolation point [8]. It is interesting to note that in the OLC polyurethane (PU) composite, the percolation point of a 10% volume fraction is estimated [8], and this is lower than a prediction from an effective medium approximation for the inclusions with a spherical shape (the percolation threshold for spherical inclusions is close to 1/3 volume fraction [9]). Carbon black topology is similar to OLC. For carbon black, the percolation threshold depends on the preparation technology and can be similar to carbon nanotubes, i.e., it can be also very low [10]. Therefore, for OLC applications it is very important to find optimal technological ways to further reduce the percolation threshold [8] and to study the effect of technological procedures on the electrical/dielectrical properties of the structures.

In this paper, we therefore, investigate an influence of preparation conditions on OLC/PU dielectric properties in order to find a most favorable technology for producing coatings with a low percolation threshold. In more detail, we explore the role of heating of the samples during mixing of OLC and PU solution as well as annealing effect of the cured films.

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2. Sample preparation technology and experimental part

The OLC material was produced by annealing of detonation nanodiamond powder in vacuum at 1800 K, as it described by Kuznetsov et al. [3]. Nanodiamonds were purchased from New Technologies, Chelyabinsk. Average primary particle size of DND was 4 nm and the average volumetric aggregate size was 120 nm. To achieve fully transformed DND into OLC, DNDs were heated in vacuum 10^{-4} torr at 1800 K for 2 h. Size of primary OLC particles is around 6–7 nm, while average aggregate size is 130 nm for OLC dispersed in *N*-methylpyrrolidone solvent as measured by dynamic light scattering technique.

Samples of OLC were mixed with commercial formulation of oil-based polyurethane "Minwax clear satin" containing 60% of volatile compounds. All samples contained 15 wt.% of OLC. Six samples were prepared under different thermal treatment conditions (more detailed information can be found in Table 1). First, after manual mixing with the OLC powder, the polymer suspension was magnetically stirred at 400 rpm during 24 h at 50 °C. Then, before casting a suspension, samples 2 and 3 were additionally heated at 70 °C and 90 °C, correspondingly, on a hot plate with a purpose to improve uniformity in distribution of OLC in a polymer solution with a lower viscosity. Then suspensions were casted on a Teflon substrate and dried at ambient conditions at 45 °C overnight. Half of the dried samples ("b" series) were additionally annealed at 150 °C during 1 h under pressure in an oven. A motivation for this treatment originated from our observation that after testing of dielectric properties of the samples at high temperatures (for example, 450 K), dielectric constants and conductivities of the samples, when cooled to the room temperature, were increased. Thus, we introduced an annealing stage during sample preparation. Thickness of OLC/PU films varied between 250 and 700 μm. Distribution of OLC in PU matrix was characterized by scanning electron microscope SEM Zeiss Supra 25.

Table 1
List of investigated OLC/PU composites.

Sample	OLC–PU mixing conditions	Treatment of a cured sample
1a	1 day at 50 °C	Untreated
1b	1 day at 50 °C	Annealing at 150 °C
2a	1 day at 50 °C + 70 °C 2 h	Untreated
2b	1 day at 50 °C + 70 °C 2 h	Annealing at 150 °C
3a	1 day at 50 °C + 90 °C 2 h	Untreated
3b	1 day at 50 °C + 90 °C 2 h	Annealing at 150 °C

To characterize the samples we have employed broadband dielectric spectroscopy. This technique was already proved to be powerful tool to characterize these materials [5,6,8]. The complex dielectric permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$ was measured by a capacitance bridge HP4284A in the frequency range 20 Hz–1 MHz. Measurements have been performed on cooling and heating at a rate of about 0.5 K/min. Each measurement started from heating, and after reaching 450 K, the sample was kept at this temperature for ~0.5 h, and then the samples were cooled down to room temperature.

3. Results and discussion

Fig. 1 illustrates SEM images of the top view of the samples 3a and 3b at the same magnification. As can be seen from the images, OLC are uniformly distributed within the matrix and OLC aggregate sizes are smaller in the annealed sample 3b.

The frequency dependence of dielectric permittivity ε' and electrical conductivity σ at room temperature for composites prepared under different conditions with OLC concentration of 15% is shown in Fig. 2. It can be seen that both dielectric permittivity ε' and electrical conductivity σ is strongly influenced by preparation conditions. In particular, it is more pronounced at low frequencies. All annealed samples (1b–3b) exhibit higher electrical conductivity σ and dielectric permittivity ε' in comparison with not treated samples in the frequency range up to 1 MHz. The highest electrical conductivity σ and dielectric permittivity ε' are observed in 3b sample. The increasing of dielectric permittivity ε' at low frequencies (below 300 Hz) in the annealed sample is obviously caused by Maxwell–Wagner relaxation [11]. In order to explain an effect of annealing on the dielectric properties, measurements of dielectric

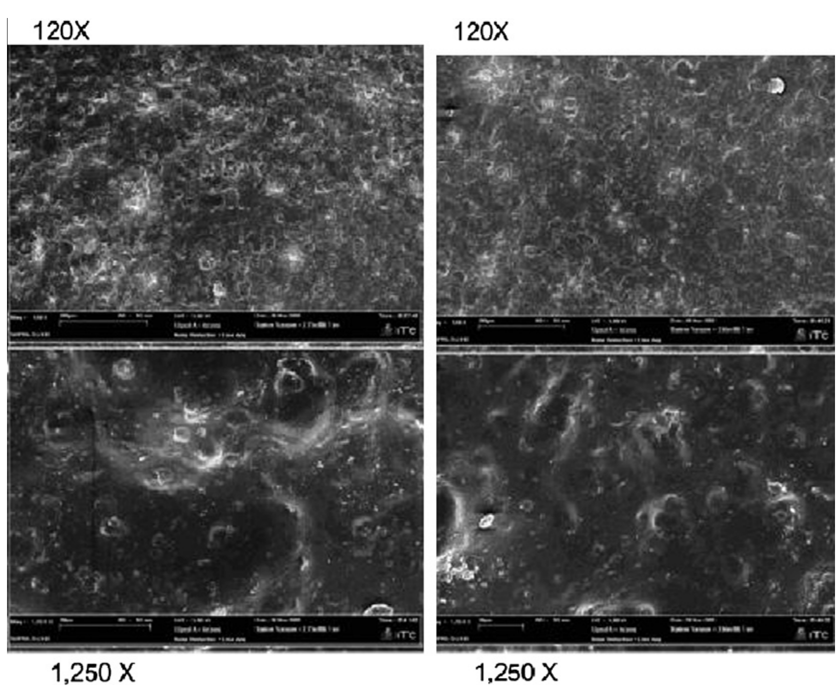

Fig. 1. SEM images of OLC/PU composites prepared under different conditions: untreated sample 3a (a) and sample 3b annealed at 150 °C (b).