Electric field induced permittivity increase of carbon particle aggregates/silicone oil suspension

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Abstract. Permittivity percolation threshold of carbon particle aggregates/silicone oil (CPA/SO) suspension was determined (ΦC = 2.6 wt%). A direct current electric field induced permittivity increase versus time for the suspension containing 0.2 wt% of the CPA was measured at different field strengths. It was found that the electric field at 200 V/cm increases the permittivity of the CPA/SO suspension (ε' = 3.2 at 1 kHz) by three orders of magnitude in 30 min. At 800V/cm the same permittivity increase was reached in 1.5 min.

1. Introduction

Obtaining composites with desirable mechanical, thermal and electrical properties is a driving force for the research of polymer composites with aligned particle structure. Electroconductive particles/liquid dielectric matrix composites provide an opportunity for convenient studies of particle alignment dynamics [1,2] and electrical properties of the composites [1-4]. The alignment process can be accomplished using alternating current [1,2,5,6], direct current (DC) [3,4], and pulsed electric fields [7]. The influence of applied electric field strength [2-4], frequency [2,6], filler content [2-6] and matrix viscosity [2-4] has been determined. The main focus of the aligned liquid composite studies, overwhelmingly, is the electrical conductivity. In the present research, the DC electric field induced permittivity increase of the carbon particle aggregates/silicone oil (CPA/SO) suspension was studied.

2. Materials and methods

Medium viscosity (μ = 970 mPa s) SO AK1000 (ε' = 2.75 at 1 kHz, σDC = 2⋅10^{-13} S/m) from Wacker Chemie AG was used as a matrix for the suspensions. Printex EX-2 carbon black (CB) (average particle size 30 nm, surface area 950 m²/g, σDC = 370 S/m [8]) from Degussa AG was used as a filler. The suspensions were prepared as follows. The CB pellets were manually crushed into fine powder using pestle and mortar. The powder was gradually added to the SO while stirring. Subsequently, the filler was additionally dispersed using the pestle and, thus, the CPA/SO suspension was obtained. Suspensions containing from 0.1 wt% to 2 wt% of the CPA were prepared and used to determine a permittivity percolation threshold. The suspension containing 0.2 wt% of the CPA was used for all the alignment experiments. The CPA size in the suspension was estimated using size analyser Zetasizer Nano ZS90 from Malvern and Eclipse LV150 optical microscope from Nikon. It was found that the suspension contains 135 nm (peak) CPA and CPA agglomerates in sizes around 1-4 μm.

Permittivity measurements of the CPA/SO suspension were carried out in a custom-made measurement cell (Figure 1). The size of the copper electrodes is 25 mm x 40 mm. U-shaped 2 mm thick silicone rubber spacer was used to separate the electrodes while holding the suspension. The
suspension was injected into the cell using a syringe. Measurements of a capacitance (measurement voltage 0.2 Vrms) and a DC conductance were accomplished using Agilent E4980A LCR meter. The LCR meter was also used as a source of the DC alignment voltage (for field strengths above 200 V/cm a separate power supply was used). A measurement sequence: electric field was applied for a chosen time interval, electric field was switched off for 30 s, data readings, the field switched on, etc. A flat polytetrafluoroethylene (PTFE) substrate equipped with 5 mm wide copper electrodes separated by 2 mm gap was used to image the aligning CPA network in the suspension layer through the microscope while, simultaneously, receiving readings from the LCR meter.

3. Results and discussion
In order to choose the CPA/SO suspension with a potentially large permittivity change during the alignment, a permittivity percolation threshold was determined. The relative permittivity (at 1 kHz) versus CPA filler concentration for unaligned suspensions is shown in Figure 2. From the work of Dubrov et al [9] it follows that the permittivity can be calculated using equation:

\[ \varepsilon' = \varepsilon'_1 \left( \frac{\Phi - \Phi_C}{\Phi_C} \right)^s \tag{1} \]

where \( \varepsilon' \) is the relative permittivity of the composite, \( \varepsilon'_1 \) is the relative permittivity of the matrix, \( \Phi \) is the filler concentration, \( \Phi_C \) is the critical filler concentration (the percolation threshold), \( s \) is the critical exponent. The results for the permittivity measurements were found using a linear fit for \( \log(\varepsilon') \) versus \( \log(|\Phi - \Phi_C|/\Phi) \) (Figure 2, the insert). The best fit was obtained at \( \Phi_C = 2.6 \text{ wt}\% \ (s = 4.73) \). In the case of a DC conductivity, previously determined \( \Phi_C \) value [4] for the suspension was 0.6 wt\% (exponent 11.48). Thus, the \( \Phi_C \) for the conductivity is significantly lower than for the permittivity. As pointed by Grady [10], percolation thresholds for carbon nanotube/polymer composites, which are calculated from the dielectric constant and conductivity, are identical or nearly identical. As mentioned by Knaapila et al [6], percolation depends on particle topology and is also determined by the interactions among particles and between particles and matrix. The dissimilar percolation threshold values for the suspension suggest that, although the filler at small concentrations quickly forms conductive channels with tunneling conductivity, these channels are long and sparse and, unlike it is in case of solid composites, they form a smaller series connection capacitance and provide a small contribution to the permittivity.

![Figure 1. Components of the suspension permittivity measurement cell and the cell in the PTFE holder.](image)

![Figure 2. Permittivity vs. filler concentration for unaligned CPA/SO suspensions. The continuous line is a theoretical fit obtained using Eq. (1).](image)
The electric field induced relative permittivity (1 kHz) and a DC conductivity change for the CPA/SO suspension is shown in Figures 3 and 4, respectively. Application of the field increases the permittivity by up to almost 3 orders of magnitude in 1.5 min (for 800 V/cm). At the same time, the DC conductivity of the suspension increases by over 4 orders of magnitude.

During repeated experiments, it was observed that a large (up to 1 order of magnitude or more) dispersion for the $\varepsilon'$ and the $\sigma_{DC}$ saturation values was obtained (not seen in the Figures due to averaging) for each field strength. In addition, it was often observed that the permittivity decreased after reaching the saturation value (as seen in 400 V/cm graph). This effect, most likely, is caused by two factors: 1) expansion of the SO matrix due to significant Joule heating (up to 50°C) at the end of the alignment; 2) over-densification of the particle agglomerate network, which excludes a space for micro-capacitors formed by nearby particles. Here, it is important to note that if the field was off for about 10 min, the permittivity increased by up to 15% (further lack of the aligning field led to suspension permittivity decrease).

![Figure 3. The relative permittivity (at 1 kHz) versus time for the CPA/SO suspension containing 0.2 wt% of the CPA depending on the DC field strength.](image1)

![Figure 4. The DC conductivity versus time for the CPA/SO suspension containing 0.2 wt% of the CPA depending on the DC field strength.](image2)

![Figure 5. Alignment (200 V/cm) of a thin (~0.2 mm) layer of the CPA/SO suspension containing 0.2 wt% of the CPA on the PTFE substrate with simultaneous capacitance and conductance measurements while taking snapshots of the aligning particle network through the microscope. The field direction on the micrograph is vertical.](image3)
To follow a correlation between the emerging aligned CPA network and the change in the electrical properties, micrographs of the suspension were taken during the alignment while performing measurements of the capacitance and the DC conductance (Figure 5), simultaneously. It can be seen that the capacitance curve is closely related to the conductance curve although the C increase is around one order of magnitude, but the G_{DC} increase is around 2 orders of magnitude. The micrographs show that the CPA agglomerates reallocate forming chains, which are predominantly aligned along the electric field lines (the CPA particle chaining process is thought to be similar as described by Oliva-Avilés et al [1]). In terms of an equivalent circuit, series (and to less extent parallel) connection capacitor-resistor chains are formed causing the observed permittivity and conductivity increase of the suspension.

4. Conclusions
Application of the DC electric field (200 V/cm and higher) leads to the permittivity increase of the CPA/SO suspension (containing 0.2wt% of the CPA) by up to three orders of magnitude. At lower field strength (100 V/cm) the permittivity increase reduces to two orders of magnitude. The increase of the permittivity is caused by the alignment of initially randomly positioned CPA and their agglomerates, which form a network of a branched structure of microcapacitor chains, which densify upon increasing electric field strength and time.

5. Acknowledgements
This research was supported by the Latvian National Research Programme in Materials Science (IMIS2). The authors also would like to thank “IMCD Baltics UAB” for supplying the silicone oil.

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