Electrical and dielectric properties of epoxy resin/polyaniline-DBSA blends

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The electrical conductivity of a polymer can be increased by addition of a conductive material in the form of particles or fibres. Commonly used fillers for such purpose are carbon fibers (CF) and carbon black (CB) [1, 2]. For a low concentration of the conductive additive, the conductivity of the composite remains at the level of the insulating matrix. As the concentration of the conductive filler is increased and reaches a critical value V_c, a sharp drop in volume resistivity by several orders of magnitude is observed [3].

Interesting properties can be achieved when an intrinsically conductive polymer (ICP) is chosen to play the role of the conductive phase. ICPs exhibit advantages versus fillers such as CB and CF, as they can offer smoother increase of electrical conductivity (especially in the range for electrostatic discharge (ESD) applications: 10^{-9} and 10^{-6} S/cm), all polymeric composites with low density, and mechanical properties similar to the unfilled matrix. Polyaniline (PANI) is one of the most intensively studied among the ICPs. It can be obtained by the protonation the non-conductive emeraldine base (EB), with a strong acid (H^+A), such as dodecylbenzenesulphonic acid (DBSA) and camphorsulphonic acid (CSA) to give the conductive emeraldine salt [4, 5].

The work to be described herein was undertaking with the aim of studying the dc conductivity and the dielectric properties in low frequency range of EP/PANI-DBSA blends. As thermosetting matrix a bisphenol F epoxy resin (Epikote 862, Resolution Performance Products) was used with viscosity equal to 2.5–4.5 Pa s, density of 1.17 g/cm^3 and epoxide equivalent weight (EEW) of 166–177. A BF_3-complex catalytic curing agent (Anchor 1170, Air Products) was chosen as curing agent. PANI doped with DBSA in a moral ratio of about 1.1 to polymer repeat unit PhN (Panipol F) was obtained from Panipol, Finland. Due to the excess of DBSA this salt had improved solubility in common organic solvents. The electrical conductivity of the conductive salt was determined at around 1 S/cm as a pressed pellet.

PANI-DBSA was dispersed in toluene and then mixed with the epoxy resin in a dissolver (Dispermat AE, VMA-Getzmann GmbH) under vacuum, until the whole toluene was evaporated from the blend. The curing agent was finally added in ratio 10 phr EP, and the blends were cured in an oven at temperatures up to 130 °C. The total curing time was 4 hr. The differential scanning calorimetric (DSC) analysis of the final samples proved their complete curing [6]. In this way, blends containing various amounts of PANI-DBSA were prepared. The dc conductivity of the EP/PANI-DBSA blends was determined by volume resistivity measurements at room temperature. A resistivity meter, Hiresta UP, Mitsubishi Chemicals, was used, in connection with a ring probe, UR-SS Type, Mitsubishi Chemicals. The volume resistivity was measured on both surfaces of the slices, and the average value was obtained. The dielectric properties of the cured samples were measured by an Eumetric® System III microdielectrometer (Micromet Instruments, Inc.). A midconductivity inter-digitated electrode sensor (IDEX) was attached onto the samples surface and values of the dielectric constant ε' (or relative permittivity) and loss factor ε'' were determined over the frequency range from 0.075 to 10^6 Hz, at room temperature.

Fig. 1 shows the electrical conductivity versus PANI-DBSA weight content. The expected tendency is observed. The electrical conductivity of the blends increases as the concentration of PANI-DBSA is increasing, from the value of 10^{-16} S/cm (responds to the neat EP matrix) to about 10^{-7} S/cm for 11.1 vol.% PANI-DBSA. For low concentrations of PANI-DBSA the electrical conductivity of the blends remains to low levels. This can occur due to the encapsulation of the dispersed PANI-DBSA from the EP matrix. By increasing the PANI-DBSA content, continuous conductive pathways are allowed to be formed, leading to a steady rise of the conductivity values. Nevertheless, it can be observed that after a volume content of 7.8% PANI-DBSA the conductivity reaches a plateau and no significant enhancement of its values takes place by further addition of the conductive salt.

In an alternating electric field, the electrical behavior of materials is characterized by the complex dielectric constant or complex permittivity, ε^*:

$$\varepsilon^* = \varepsilon' + j \cdot \varepsilon''$$

where ε' is the dielectric constant and ε'' the dielectric loss.

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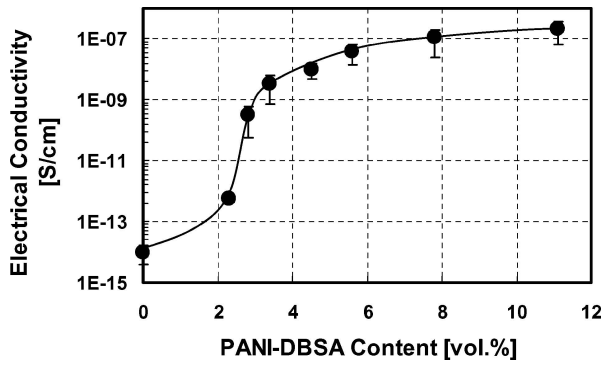

Figure 1 The dependence of conductivity of blends on the volume fraction of PANI-DBSA.

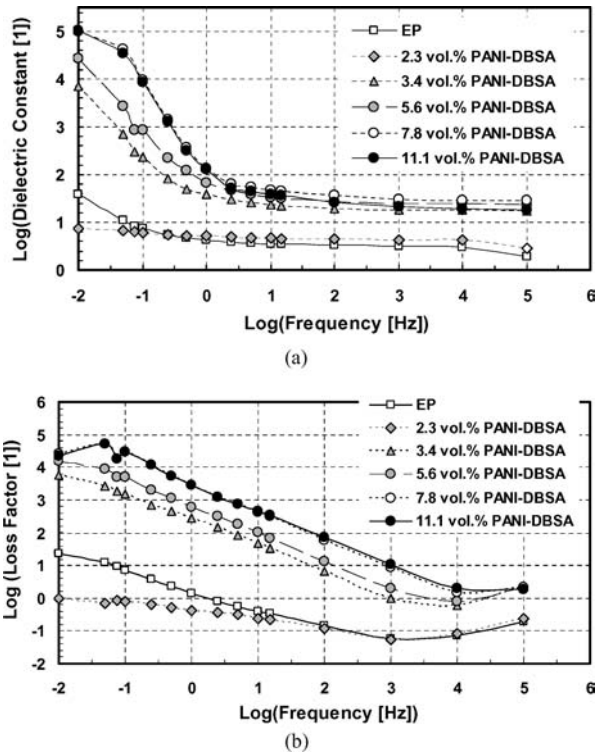

Figure 2 Frequency dependence of (a) dielectric constant and (b) dielectric loss factor for blends with different PANI-DBSA concentrations.

Fig. 2 shows the values of ε' and ε'' as function of frequency, f, for the various EP/PANI-DBSA blends. For PANI-DBSA concentrations below the percolation threshold (<2.4 vol.%) both values are almost independent of frequency. As the blends become more conductive, the permittivity increases due to the space charge build up at the interfaces between PANI-DBSA and EP as result of the difference in conductivity of the two phases. At higher concentrations, ε' and ε'' reach high values at low frequencies, which drop to lower values as frequency increases, indicating the existence of a dielectric relaxation. This behavior may be attributed to an interfacial polarization, known as the Maxwell–Wanger–Sillars effect (MWS) [7, 8], a phenomenon appearing in heterogeneous media due to the accumulation of virtual charge at the interfaces of the media [9–11]. However, the loss peaks related to this relaxation are not evident in Fig. 2.

In order to obtain further information about the dielectric relaxation of the blends, the ε'^* is transformed to the electric modulus, or inverse complex dielectric

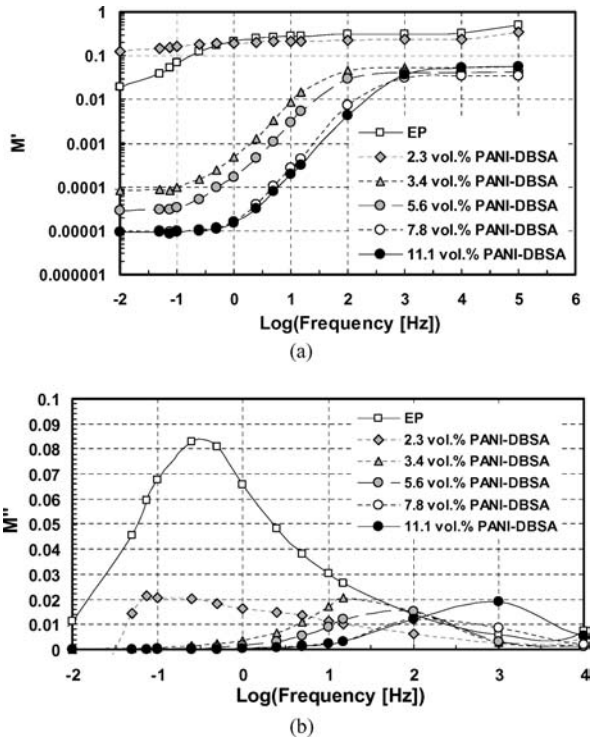

Figure 3 Frequency dependence of (a) the real part M' and (b) the imaginary part $M''$of the electric modulus for blends with different PANI-DBSA concentrations.

constant, M^*, by the equation:

$$M^* = \frac{1}{\varepsilon^*} = \frac{1}{\varepsilon' - j \cdot \varepsilon''} = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2} + j \cdot \frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2}$$
$$= M' + j \cdot M''$$

where M' and M'' are the real and the imaginary part of electric modulus, respectively.

The calculated values of M' and M'' are presented in Fig. 3 for the various PANI-DBSA concentrations as a function of frequency. M' approaches the value of zero at low frequencies, showing that the electrode polarization gives a negligible contribution to the real part of electric modulus and can be ignored when the permittivity data are expressed in this form. The values of M' are almost frequency independent for PANI-DBSA concentrations below V_c, while for higher concentrations they increase with frequency, and then reach a rather constant value. Furthermore, increase in the PANI-DBSA volume content results in decreasing M' values, as result of the increase in the real part of permittivity. The step-wise transition of M' from low to high values is apparent at PANI-DBSA concentrations above the percolation threshold. On the frequency range of this transition, the values of M'' exhibit a peak, at a characteristic relaxation frequency f_{max}, which indicates a relaxation process. It can be clearly seen that the maximum of the relaxation peaks in M'' is reduced as the PANI-DBSA content increases, and it is shifted towards higher frequencies. The appearance of these peaks in higher frequencies means enhanced dc conductivity values. Similar curves have been presented for epoxy resin-metal particles [9, 10] and polyaniline-polyvinyl alcohol composites [11].

EP-based composites containing PANI-DBSA as conductive phase were prepared. The electrical conductivity of the blends increased with the increase of the PANI-DBSA concentration. Both dielectric constant and loss factor increased with the addition of PANI-DBSA in the EP matrix. The electric modulus showed relaxation process in the dielectric spectra measured. Depending on the frequency at which the blends will be used, the dielectric properties can be drastically different. This is mostly important when the volume fraction of the conducting phase is near the percolation threshold.

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