Electron microscopy of multi-layered polymer-nanocomposite based dielectrics

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Abstract. Vacuum deposited polymer-nanocomposites (PNCs) comprising alternate layers of metal (Al/Ag) (filler) and polymer (nylon-6) (matrix) have been investigated using chemical, impedance spectroscopy and microstructural characterisation techniques. Electron microscopy investigations revealed the morphology, nanostructure and phases of nano-scale core (metal)-shell (oxide) particles and metallic nano-islands in Al and Ag based PNCs respectively. Evaporation of Al yielded islands of angular core-shell nanoparticles in an Al-oxide/nylon-6 matrix whereas Ag yielded rounded, discrete nanoparticles in nylon-6 matrix. The high particle surface area and an affinity for oxygen formed oxide shells in Al nanoparticles and was critical to charge accumulation and enhanced dielectric behaviour; in contrast, Ag showed little oxidation and less charge accumulation. With an increase in the thickness of the deposited metal layer, Al formed a continuous film of particles whereas Ag condensed to form interconnected nano-islands. This microstructural study is useful in conceptualising better dielectrics based on PNCs.

1. Introduction
Polymer-nanocomposites (PNCs) consisting of a highly polarisable minority phase (filler) in an easily processable polymer (matrix) are promising dielectrics for capacitive applications. Recently, core-shell particles have been used as fillers to yield PNCs with a high dielectric constant $k$ of up to $\sim 60$ [1]. Experimental insights [2] and computational studies [3] have suggested that the shell thickness of the core-shell particles influences their polarisability, along with filler shape, size, and size distribution [4–6]. Therefore, knowledge of the chemical and structural arrangement of phases at fine-scale is crucial to understand capacitative mechanisms in PNCs and to guide the design and fabrication of polymer-based capacitors with enhanced properties.

In this paper, we use a simple vacuum based deposition technique to fabricate Al/Ag and nylon-6 based PNCs. The formation and growth of Al/Ag nanoparticles on the nylon-6 surface and their encapsulation is studied by employing various electron microscopy techniques and microstructure is correlated with the PNC dielectric response. Based on the importance of the formation of in-situ interfacial layers on reactive metals for charge accumulation, different nanoarrangements of Al and Ag are proposed, and the resulting dielectric behaviour is described and compared.

2. Experimental
Alternately-deposited nanocomposite (ANC) films were fabricated by tandem deposition of five individual layers of metal and nylon-6 in an Edwards Auto 306 Cryo evaporator, where the
The evaporator-chamber was evacuated to a pressure of $5 \times 10^{-4}$ Pa before evaporation. Aluminium wire (99.999% pure, Alfa Aesar, 0.5 mm diameter) and nylon-6 (Aldrich) were thermally evaporated alternatively using two different tungsten boats onto a glass slide at a deposition rate of 0.5 nm/s and 0.1 nm/s respectively. The top and bottom (1st and 5th) layers of Al (40 nm each) formed the electrodes of a simple parallel-plate capacitor. The growth of Al (3rd layer), sandwiched in between the nylon-6 layers (2nd and 4th - 20 nm each), was studied at various thicknesses (5, 10, and 15 nm). Silver based ANCs were fabricated by replacing Al with Ag (99.99% pure, Advent, 0.125 mm diameter) in the W-boat with a similar procedure. The resulting capacitors were dried at 400°C for 20 hours to negate any water vapour effects, and then the dielectric properties were studied using a Solartron SI 1260 impedance analyzer operating at 1 kHz. The thickness of the ANC films was measured using a DekTak 6M profilometer (Veeco Instruments, Inc) and allowed estimation of $k$ from the impedance data.

JEOL transmission electron microscopes, JEM-2000FX and JEM-3000F, operating at 200 kV and 300 kV respectively were used for ANC characterisation on identical samples produced in parallel but with no top/bottom Al-electrodes. Energy dispersive X-ray spectroscopy (EDS) and scanning transmission electron microscopy (STEM) were carried out via the 3000F.

### 3. Results and discussion

Figure 1 shows the variation of dielectric constant of Al (■) and Ag (●) of the ANCs with the thickness $t$ of deposited metal layer at 1 kHz and 400°C. For reference, $k$ of “pure” deposited nylon-6 was $\sim 4.3$. At $t=15$ nm, $k$ of Al-ANCs was approximately twice that of Ag-ANCs; the $k$ of both ANCs also tended to increase with increasing $t$.

![Figure 1](image1.png)

**Figure 1:** Variations of dielectric constant $k$ of Al (■) and Ag (●) of the ANCs with the thickness $t$ of metal layer at 1 kHz and 400°C.

Bright field (BF) TEM images of Al-ANCs at $t=5$ nm and $t=15$ nm are shown in Figs. 2(a) and (b) respectively. The images show dark nanoparticles of 5-60 nm diameter dispersed in a relatively bright matrix. The presence of any Al-oxide shell was not resolvable from the nylon-6 matrix in the BF-TEM images and both were expected to be substantially or wholly amorphous. Nonetheless, previous work involving the evaporation of Al [7] and the pervious nature of nylon-6 strongly suggested the oxidation of Al. Figure 2 suggested that the increase in $k$ from $17 \pm 1$ (at $t=5$ nm) to $23 \pm 1.5$ (at $t=15$ nm) was due to an increase in the size of the Al nanoparticles. Figure 2(c) shows a high resolution transmission electron microscopy (HRTEM) image of the Al-ANC. The $d$-spacings measured from the HRTEM image and the spots from the fast Fourier transform (FFT) of the image [Fig. 2(d)] corresponded to Al [$d \sim 0.23$ nm (111) and $d \sim 0.2$ nm (002)].
Figure 2: Bright field (BF) TEM images of Al-ANCs at (a) $t=5$ nm and (b) $t=15$ nm with a bright matrix containing relatively dark nanoparticles; (c) a HRTEM image of the Al-ANC and (d) corresponding FFT from highlighted region.

A further BF-TEM image of Al-ANC at $t=5$ nm is shown in Fig. 3(a) with the marked region containing nanoparticles. This region was darker than the nylon-6 "matrix", which appeared as a light contrast, branched dendritic continuous phase separating dark regions. The contrast was due to differences in atomic number $Z$ of Al and lighter elements in nylon-6 which is shown more clearly in the annular dark field (ADF)-STEM image in Fig. 3(b). The crystalline nanoparticles appeared very bright due to high diffraction contrast. The corresponding EDS map in Fig. 3(c) revealed that Al was also distributed throughout the film, not only in the nanoparticles, and suggested that the evaporated Al not only formed discrete, crystalline nanoparticles but was also relatively uniformly deposited as aluminium oxide-based islands delineated by the branched nylon-6 "matrix". A cross-sectional schematic representation of this arrangement is shown in Fig. 3(d).

Figures 4(a) and (c) show BF-TEM images of Ag-ANCs at $t=5$ and 15 nm respectively. Spherical nano-islands of Ag formed at $t=5$ nm, and these spheres grew and formed interconnected islands at $t=15$ nm due to Volmer-Weber growth [8]. The corresponding ADF-STEM image in Fig. 4(b) confirmed discrete Ag-islands (bright) in a nylon-6 matrix (dark). A cross-sectional schematic representation of Ag-ANC based capacitor at $t=5$ nm is shown in Fig. 4(d).

The enhancement in $k$ for Al was primarily due to the differences in the oxygen reactivity of Al ($\Delta G_{\text{Al}_2\text{O}_3}=-1582.3$ kJ/mol at 25°C) and Ag ($\Delta G_{\text{Ag}_2\text{O}}=-11.21$ kJ/mol at 25°C). Although the ANCs were processed in vacuum, it is well-known that Al will nonetheless undergo some

Figure 3: (a) A BF-TEM image of Al-ANC at $t=5$ nm, (b) corresponding ADF-STEM image, (c) corresponding EDS map and (d) a cross-sectional schematic of the Al-ANC microstructure.
oxidation either *in-situ* [7] or on removal from vacuum. In this case, deposited Al particles formed Al (core)-aluminium oxide (shell) particles. The presence of Al (core)-aluminium oxide (shell) particles leads to an enhancement in interfacial polarisability resulting in high-$k$. Interfacial polarisation takes place due to the piling up of charges at the heterogeneous interfaces of the core-shell particles and polymer. Although there were interfacial polarisation effects in the Ag-ANCs, the increase in $k$ was less pronounced, since oxide formation was much reduced or absent.

4. Conclusions
Dielectric materials consisting of Al or Ag in nylon-6 films were fabricated by an alternate vacuum deposition technique. Electron microscopy studies revealed that the deposition of Al led to the formation of aluminium (core)-aluminium oxide (shell) nanoparticles, a branched nylon-6 matrix with fine-scale aluminium oxide “islands”. On the other hand, because Ag was much less-reactive with ambient gases (especially oxygen), it formed well-separated, spherical Ag-nanoparticles. Enhanced interfacial polarisation in Al-ANCs resulted in $k$ that was two-times higher than Ag-ANCs, attributed to the formation of a comparatively polarisable oxide containing shell around an aluminium nanoparticle core.

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