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Impact of the interphase dielectric properties on the electric field distribution in LDPE/BN nanocomposites

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Abstract- Designing a new electrical insulating nanocomposite with chosen nanoparticles and matrix while targeting specific dielectric properties is still the Holy Grail in the domain of electrical engineering. The main challenge remains to understand the physical processes at the interphase between the nanoparticle and the matrix, at the nanoscale, and the impact of this interphase on the nanocomposite behavior at the macroscale. An interphase properties investigation has been developed, combining well-controlled low density polyethylene (LDPE)/ boron nitride (BN) nanoparticles films, and dielectric properties characterizations at the nanoscale. To do so, two derived modes of the Atomic Force Microscopy (AFM) are used. Peak Force Quantitative Nanomechanical Microscopy (PF-QNM) allows obtaining the interphase width, while Electrostatic Force Microscopy (EFM) measurements allow deducing the interphase relative permittivity. Based on these investigations, an electrostatic 3D model is then proposed to account for interphase properties at the microscopic scale, and to overcome the bridge between nanoscale and macroscale measurements.

I. INTRODUCTION

The emergence of nanocomposite (NC) materials in the domain of electrical engineering is closely related to the aim of developing new insulating materials with high electrical, thermal and/or mechanical performances. According to the literature [1-4], improvements observed in the electrical/mechanical/chemical properties of these nanocomposites are mainly due to the interphase existing between the matrix and the nanoparticles. It is thus essential to understand and control the interphase features to design new high performance electrical insulating materials. In the present paper, low density polyethylene /boron-nitride nanocomposites were first prepared with different amount of nanoparticles. They were characterized as regards morphological and dielectric properties at the nanoscale, using the atomic force microscopy (AFM) with two derived modes: the Peak Force Quantitative Nanomechanical (PF-QNM) and the Electrostatic Force Microscopy (EFM). The interphase characteristics were thus deduced. Based on these experimental data, 3D Finite Element Model (FEM) simulations were performed to calculate the electric field characteristics in the different samples.

II. MATERIALS AND METHODS

Commercial boron nitride (BN) nanoparticles (Sigma Aldrich, CAS 10043-11-5, 99%) were incorporated into a low density polyethylene (LDPE) matrix (Borealis). 1.0 gr of LDPE was dissolved in 10 mL of hot toluene and stirred at 80 ° C. 100 mg of BN (150 nm avg. size) for a 10 wt. % LDPE/BN and 10 mg of BN for a 1 wt. % LDPE/BN were added to the hot PE in toluene and continued stirring at 80 °C for 3h. Thin films with thickness from 6 to 20 µm were then prepared by knife casting at 90 °C. For preparation of the reference film (pure LDPE), the same procedure was followed using the casting solution with no BN (1.0 gr LDPE in 10 mL toluene). The LDPE/BN nanocomposite morphology was characterized by Atomic Force Microscopy (AFM Multimode 8 - Bruker) in tapping mode on the surface, and by Scanning Electron Microscopy (SEM) (SEM FEI Hélios nanolab 600i using an acceleration voltage of 2 kV) on cross-section.

PF-QNM AFM mode was used to probe surface topography and to map mechanical properties of NC films. As the LDPE Young modulus value is around 300 MPa, a RTESPA-150 tip (resonance frequency $f_0 = 150$ kHz, spring constant $k = 6$ N.m⁻¹) was used. The Young modulus was calculated directly by NanoScope software using the Derjaguin–Muller–Toropov (DMT) model [5]. The contact force was tuned to obtain on all samples a deformation of around 8 nm over LDPE. To insure reliable and quantitative results a three steps calibration process [6] was applied:

- Force Distance Curves are used to determine static and dynamic deflection sensitivity on hard silicon sample;
- The calibration of the real cantilever spring constant is done using thermal tune included in Nanoscope software for probes with low k ;
- The effective tip radius was determined using the LDPE reference film.

The relative dielectric permittivity (ϵ_r) of the LDPE/BN nanocomposites were deduced from EFM phase shift ($\Delta\Phi$) measurements. The phase shift parameter $\alpha_{\Delta\Phi}$ is computed from the experimental data using the following equation [7]:

$$\alpha_{\Delta\Phi} = \frac{[\Delta\Phi(V_1) - \Delta\Phi(V_2)]}{V_1^2 - V_2^2} \quad (1)$$

where $\Delta\Phi(V_i)$ is the phase shift measured with a bias voltage V_i applied on the tip which is equal to 0 V and 10 V respectively. In this experiment a PtIr-coated silicon tip (resonance frequency $f_0 = 63.2$ kHz, spring constant $k = 6.7$ N.m⁻¹, quality factor $Q = 355$ and curvature radius $R_c = 26$ nm) and a 50nm-lift were used.

III. INTERPHASE PROPERTIES

A. LDPE/BN nanocomposite morphology

Fig. 1.a presents the surface topography of a 1 wt.% LDPE/BN nanocomposite measured with the AFM, where both single nanoparticles (white arrow) and aggregates (red arrow) can be observed. Single BN nanoparticles are also observed for 10 wt.% LDPE/BN nanocomposite, although the results are not presented here. However, the surface roughness increases from 25 nm for 1 wt.% to 85 nm for 10 wt.%. In the following, only results performed on the 1 wt.% NC are presented. Fig. 1.b presents a SEM picture of a 1 wt.% LDPE/BN nanocomposite observed in cross-section. As for Fig.1.a, single nanoparticles are observed in the case of SEM. This demonstrates that BN nanoparticles are well dispersed in the volume of the matrix. Moreover, a statistical analysis of the BN nanoparticle radius based on 4 SEM pictures leads to a mean value of the order of $17 \text{ nm} \pm 6 \text{ nm}$ (inset Fig. 1.b).

B. Interphase thickness measurement by PF-QNM

The PF-QNM mode is used to measure the interphase thickness (W_i). Indeed, the interphase is a transition zone where the presence of a NP affects the matrix properties (chains rearrangement, chemical bonds, crystallinity degree ...). Consequently, the interphase presents different mechanical (among others) properties from both the matrix and the NP [6]. Fig. 2.a and 2.b present respectively the surface topography and the related Young modulus (E) maps obtained by PF-QNM for the 1 wt.% NC. From the topography map, it is possible to identify an isolated NP (white arrow). From the modulus map,

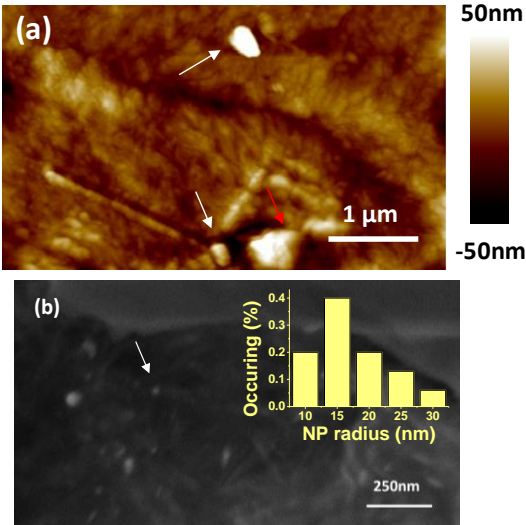


Fig. 1. (a) Surface topography probed by AFM and (b) cross-section SEM picture of 1 wt.% LDPE/BN nanocomposite

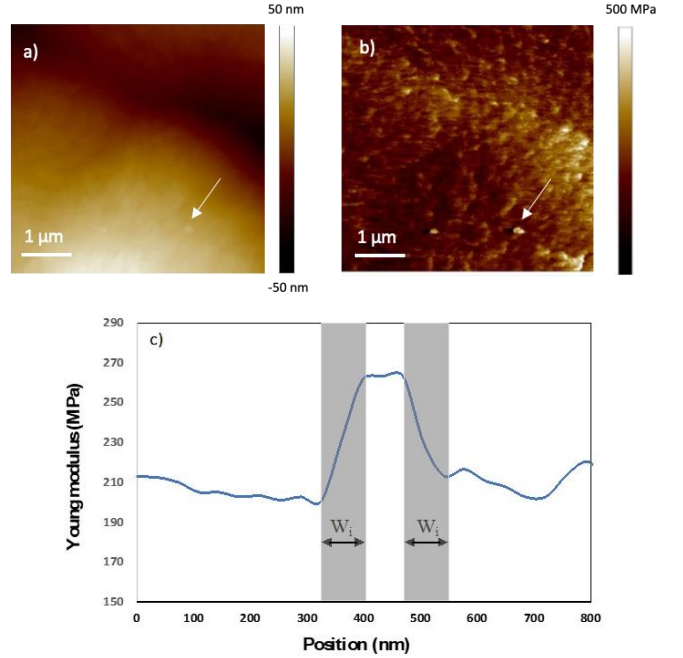


Fig. 2. (a) Surface topography and (b) Young modulus maps probed by PF-QNM on 1 wt.% LDPE/BN nanocomposite. (c) Modulus profile probed over a single NP identified with the arrow.

it is possible to draw the modulus (E) profile over the NP as shown on Fig. 2.c. Results show that the Young modulus gradually changes between the neat LDPE ($201 \text{ MPa} < E_{LDPE} < 213 \text{ MPa}$) and the LDPE over BN ($E_{LDPE+BN} \sim 263 \text{ MPa}$) modulus values. Indeed, the BN nanoparticles Young modulus is much greater than the LDPE one and the measured modulus over the nanoparticle is higher than for neat LDPE [8]. The interphase area corresponds to the average of both slope distances from each particle side as shown on Fig 3.c (grey zone) [6]. The obtained interphase thickness value is of $82 \text{ nm} \pm 8 \text{ nm}$.

C. Interphase relative dielectric permittivity measurement by EFM

Surface topography, performed on a 1 wt.% LDPE/BN (Fig. 3.a), exhibits a single BN nanoparticle close to the surface. The related phase shift parameter map (Fig. 3b), performed exactly in the same zone as the surface topography, shows that $a_{\Delta\Phi}$ is lower, in absolute value, over the nanoparticle (black arrow on Fig. 3.b), compared to its value on LDPE. Fig. 3.c resumes the previous results obtained on the topography and phase shift, and shows a good correlation between the position of the identified nanoparticle and the increase, in absolute value, of the phase shift parameter. $a_{\Delta\Phi}$ is equal to $-0.11 \pm 0.01 \text{ } ^\circ/\text{V}^2$ over the matrix and $-0.07 \pm 0.01 \text{ } ^\circ/\text{V}^2$ over the NP.

The interphase relative dielectric permittivity is calculated from the measured phase shift parameter $a_{\Delta\Phi}$ using a 2D-axisymmetric Finite Element Model (FEM), developed with COMSOL Multiphysics®. The nanocomposite film is modelled by 20μm-thick LDPE ($\epsilon_{r-LDPE} = 2.2$), a single BN nanoparticle close to surface (NP radius fixed at 20nm according to Fig. 1.b, $\epsilon_{r-BN} = 4$) and the interphase (thickness $W_i = 82 \text{ nm}$ probed by

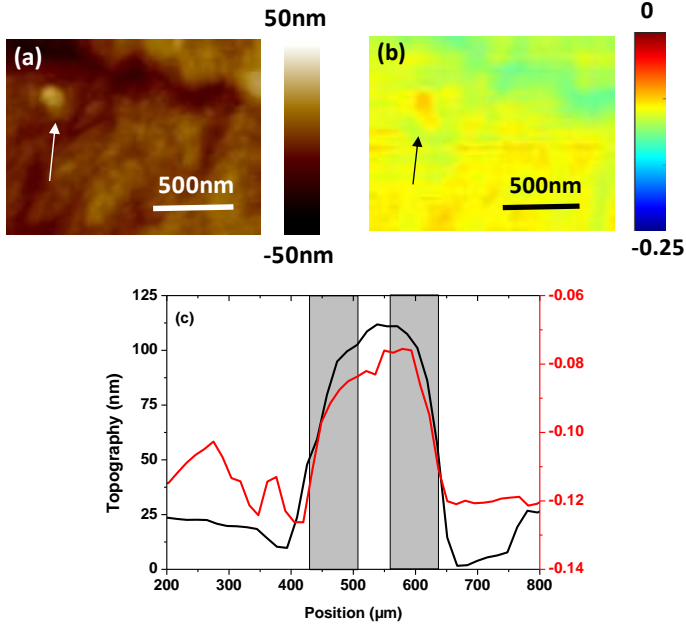


Fig. 3. (a) Surface topography and (b) $a_{\Delta\Phi}$ probed by EFM on a 1 wt.% LDPE/BN nanocomposite. (c) Topography and $a_{\Delta\Phi}$ profiles probed over single NP identified by arrows on a and b).

PF-QNM and unknown $\epsilon_{r,i}$) surrounding the BN nanoparticle and protruding on surface.

The methodology to compute the theoretical phase shift parameter $a_{\Delta\Phi}$ is composed by three steps [9-10]:

- the electric field distribution in the nanocomposite and in air is computed and the electrostatic force F_e on the AFM-tip is deduced;
- the second derivative of the capacitance between the AFM probe and the sample (d^2C / dz^2) is deduced from F_e .
- the related phase shift parameter $a_{\Delta\Phi}$ is computed using:

$$a_{\Delta\Phi} = \left[\frac{Q}{k} \right] \frac{d^2C}{dz^2} \quad (2)$$

According to the model, a phase shift parameter of -0.11 ± 0.01 $^\circ/\text{V}^2$ corresponds to a relative dielectric permittivity of $2 - 2.2$ which is in agreement with the one of the LDPE matrix values. Considering the interphase width of 82 nm, the phase shift parameter of -0.08 ± 0.01 $^\circ/\text{V}^2$ measured over the BN nanoparticle and its interphase leads to a relative dielectric permittivity of the interphase of 1.4 ± 0.2 . An interphase area with a lower dielectric permittivity than matrix one has already been observed for various nanocomposites, particularly for polyethylene based one, such as PE/TiO₂ [11], PE/Al₂O₃ [12], or polyimide/Si₃N₄ [10]. Results published in [11] on PE/TiO₂ NC have shown practically the same value of the interphase permittivity ($\epsilon_{r,i} = 1.6$). However, the interphase thickness ($W_i = 20$ nm) is lower than the one measured in this study. This difference is probably related to the NP width (100 nm-width TiO₂ NP).

IV. SIMULATION RESULTS

3D Simulations have been performed using a finite element method commercial software coupled with Matlab® to

calculate the electric field distribution in different LDPE/BN nanocomposites. To do so, a cube of side 1 μm is simulated, to account for the LDPE matrix, of relative permittivity 2.3. BN nanoparticles are considered as spherical, and their radius is taken from SEM measurements, i.e. 20 nm. The relative permittivity of the BN nanoparticles is set to 4, which is the BN relative permittivity at macroscopic scale. An interphase zone is also simulated, and has a spherical shape. The radius is the one that has been measured using PF-QNM, and is set to 80 nm in the present simulations. The relative permittivity value, deduced from the EFM measurements, is set to 1.4. Calculations have been performed for a pure LDPE, and for different wt.% LDPE/BN. The number of nanoparticles to simulate in a 1 μm^3 matrix is calculated using the density of each material (i.e. 923 kg/m³ for LDPE and 3450 kg/m³ for BN). As an example for a 1 wt.% LDPE/BN, 80 nanoparticles need to be inserted in the matrix. The position of the nanoparticles in the matrix are then simulated randomly using Matlab®, with no constraints on their position. It means that the nanoparticles can be ‘homogeneously’ dispersed in the cube, or make clusters. An example of geometry of simulation is proposed in Fig. 4, for a 1 wt.% LDPE/BN when the interphase is also accounted for. A large number of simulations have been performed in order to simulate different study cases. The present model is developed with Matlab® and COMSOL Multiphysics®. The electrostatic module of the FEM software is used to calculate the electric field distribution within the nanocomposite. An applied voltage of 40 V is set at the top face, which represents an applied electric field of 40 kV/mm. The bottom face is grounded. A zero charge boundary condition is set on the other faces of the cube.

An example of electric field distribution (norm of the electric field) is presented on Fig. 5 for a 2D cut plane. It is first noticeable that a large part of the volume is taken by the interphase, while only 2 BN nanoparticles are clearly visible on Fig.5. The electric field distribution is quite expected, and is consistent with previous simulations proposed in [13]. The electric field value is low in the BN nanoparticle, having a relative permittivity of 4, while the electric field value is high in the interphase zone, having the lowest relative permittivity, compared to LDPE and BN. What is most surprising is the

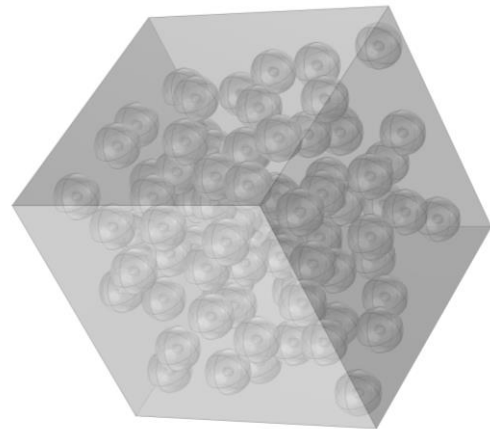


Fig. 4. 3D geometry of a 1%wt LDPE/BN, for a cube of side 1 μm .

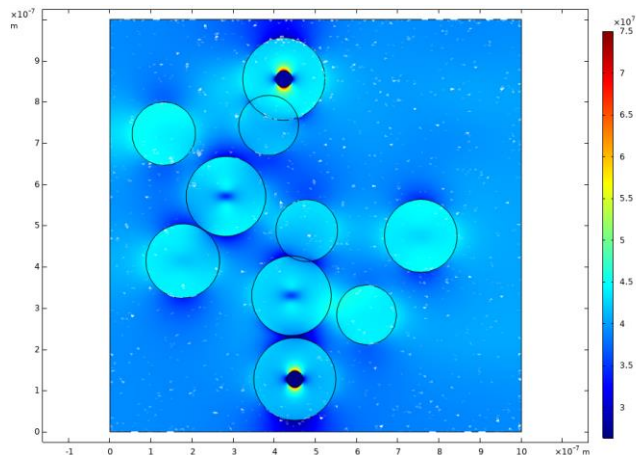


Fig. 5. Norm of the electric field (V/m) for a yz cut plane, calculated for a 1 wt.% LDPE/BN nanocomposite.

maximal electric field calculated within the nanocomposite. The applied electric field is 40 kV/mm. In the present simulation, the maximal electric field is encountered in the interphase zone, and is around 75 kV/mm, almost twice the applied electric field. This leads to a field enhancement factor (FEF) of around 1.9. This FEF is only of the order of 1.3 when only BN nanoparticles are accounted for, and the interphase is not present. The second point is the observable increase of the electric field in the LDPE matrix, for certain configurations (depending of the surrounding nanoparticle/interphase). For the present case, i.e. a 1 wt.% LDPE/BN, the mean value of the maximal electric field obtained in LDPE for different simulations (5) performed is around 50 kV/mm, i.e. a FEF in the matrix of 1.25.

Further calculations, accounting not only for the relative permittivity but also for the electric conductivities of the different materials should emphasize the impact of the interphase on the electric field distribution within the nanocomposite.

V. CONCLUSION

AFM based measurements have been performed on different wt.% LDPE/BN nanocomposites, particularly to characterize the interphase thickness and dielectric properties. It has been found that the interphase thickness is of the order of 80 nm, while the BN nanoparticle radius is around 20 nm. EFM measurements lead to a relative permittivity of the interphase around 1.4, far lower than the BN and the LDPE relative permittivity values. In the case of LDPE/BN particularly, the interphase properties should be of prime importance as the volume of interphase is high compared to the one of the nanoparticles and/or the matrix. A 3D electrostatic model has also been developed to calculate the electric field distribution within the nanocomposite, using the previously measured interphase thickness and relative permittivity. For a 1 wt.% LDPE/BN, the electric field is maximal in the interphase zone, with a high calculated FEF. Further experimental data are necessary to link the nanoscale properties to the macroscopic ones, and verify if the electric field distribution calculated in the

present paper is real, or if other hypotheses, such as an electrical conductivity in the interphase zone, and/or space charge accumulation, lead to other behaviors.

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