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# Polyethylene and Polypropylene compounds Surface NanomorphologyAnalyzed by Differential Evanescent Light Intensity (DELI )

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In this work, the nanometer profile of Polyethylene (PE) and Polypropylene (PP) dielectric materials used typically as insulators in the electrical industry have been investigated by the new optical microscopy method termed Differential Evanescent Light Intensity (DELI). The dielectric materials investigated were of 4 kinds: pure Polyethylene (PE) and Polypropylene (PP) and their compounds doped with 20% Amidon and Cellofiber respectively. The dielectric materials were deposided by melting them on optical glass waveguides for analyzing by DELI which is a version of Evanescent Light Tunneling Microscopy assisted by computer image processing method. The results showed differences in the surface nanostructure profiles and morphology of the films deposited on glass for the various dielectric materials.

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## 1. Introduction

We have investigated the surface morphologies of dielectric materials by a new optical microscopy technique termed Differential Evanescent Light Intensity (DELI). The method is easier to use than AFM or SEM for evaluating large areas of nanometer profiles and nanostructures of several dielectric materials of interest for the insulating materials technology and is based on the phenomenon of Total Internal Reflection(TIR) and evanescent waves in an optical waveguide [1],[2].

As source materials for the investigation of dielectric organic materials we have chosen Polypropylene (PP) and Polyethylene (PE) and two compounds of PP doped with 20% Celofiber and PE with Amidon. Polyethylene is a commercially available insulating material used in the manufacture of high-voltage (HV) extruded cross-linked underground cables [3],[4]. Polypropylene is a material slightly with a higher tensile strength and modulus, tougher, retains its shape to higher temperatures and has a higher melting point (165°C). For Polypropylene (PP) compounds, recent works [5] indicate that being filled with nanosilicates they may present a lower content of space charge and thus higher electric strength.

Investigations are carried out to explain their nanocomposite behaviour and characterize their electrical, thermal and mechanical properties. Investigations are carried out by broad-band dielectric spectroscopy on PP and PE filled with layered nanosized silicates, showing isochronal and isothermal curves of the complex permittivity, and activation energies of the relaxation processes involved. It was found that nanoparticles give rise to substantial changes in the polarization and dielectric loss behavior[2].

Due to these interesting findings we employed a simple and more convenient method to observe the nanometer thickness layers profiles of these dielectrics prepared by melting the source materials onto glass substrates and their surface morphology characterized by DELI microscopy.

## 2. Experimental procedure for depositing the films

The preparation of the dielectric samples for morphological observation was performed as follows: The substrates were slides of Borosilicate glass with dimensions of 76x25x1 mm onto which the dielectric polymeric layers were deposited by melting and spreading with a metal blade.

The source polymeric materials were samples of 4 dielectrics materials: PP and PE, and their doping with 20% Celofiber and Amidon respectively. The specific compositions with Celofiber and Amidon were developed to test new formulations of PP and PE insulators targeted for reduced cost. For each sample preparation we used about 1 gr of the material for investigation.

## 3. Theory of DELI

The advent of Near Field Microscopy (NFM) successfully showed [6], the possibility of surpassing the classical diffraction limit of conventional imaging systems. This new kind of microscopy was aimed at

acquiring information about nanostructures. However, in Scanning Near Field Optical Microscopy (SNOM) all 3 dimensions are measured by a scanning probe and the image of a relatively small field is obtained by reconstruction from an electronic signal [1]. This method [7] has enabled the investigation of the Near Field (NF) of samples, proving a higher optical resolution above the diffraction limit. It is not clear, however, how this high frequency spatial information is encoded in the optical signal [8]. In comparison, Far Field Techniques (FF) although limited to about $\lambda/2$ optical resolution are much easier to perform and interpret.

Our technique of Differential Evanescent Light Imaging (DELI) used in this investigation was based on the far field technique to cover large areas, and has been developed to achieve a high resolution for nanometer features, though only in the z-direction, $i \cdot e$, into the depth of the surface samples. The technique uses basically the technique of Total Internal Reflection (TIR) [9] where evanescent waves give information on the nanostructure on the waveguide.

This technique has the advantage that the close as well as far field images do not include direct transmitted or reflected light [1]. In fact we rely on the evanescent light "extraction power" of the nanoparticles and nanolayers to obtain an image of the waveguide external field. It is especially more simpler and cost effective for investigating large areas samples in excess of hundreds of micrometers on the perimeter. DELI uses the interaction of light beams propagating in transparent waveguides with dielectric nanostructures deposited on the surface to obtain the materials nanostructural profiles on top [10].

The TIR phenomenon occurs when light passes from an optical waveguide of denser medium $n_1$, into a less denser medium $n_2$ such as air. Assuming the material/air interface is perpendicular to the z-direction and the light propagates in the material waveguide in the x direction, the light intensity in the vicinity of the interface is given [2] by:

$$I_{ew}(z) \sim I_0 \cdot e^{-\frac{2 \cdot z}{d}} \tag{1}$$

where the customary defined penetration depth of the evanescent wave is :

$$d = \frac{1}{k_{tz}} = \frac{\lambda_{vac}}{2 \cdot \pi \cdot \sqrt{n_1^2 \cdot \sin^2 \theta_i - n_2^2}} \tag{2}$$

$\lambda_{vac}$ is the light wavelength in vacuum, $n_1$ is the refraction index of the glass, and $n_2$ in the air.

As an example, for TIR of a light beam with *λ=555 nm*, in a glass/air waveguide for the highest reflected mode, i.e., with $\theta_i = \theta_{icrit} = 41.83^o$ and glass with $n_1 = 1.5$, the evanescent wave penetration depth from eqn. (2) is *79 nm*, i.e., much less than one wavelength.

$$d = \frac{\lambda_{vac}}{2 \cdot \pi \cdot \sqrt{\left(n_1^2 \cdot \sin^2 \theta_{\max} - n_2^2\right)}} = \frac{555}{2 \cdot \pi \cdot \sqrt{\left(1.5^2 - 1\right)}} \cong 79 \quad (nm) \tag{3}$$

The electric field in the lower index medium with exponentially decaying amplitude is termed an evanescent field. Such a field stores energy but does not transfer photons in the direction of $z$, unless it interacts with particles or layers deposited on the optical waveguide [2].

In our experimental cases we used the evanescent wave propagation combined with the light extraction power of the nanomaterial deposited on the glass substrate by scattering, refraction or other surface optical mechanism. It can be done formally by assuming the following simple phenomenological model where the evanescent light intensity in the near field zone can be estimated by the following eqn:

$$I_z(h) = \int_0^h K(z) \cdot e^{-\frac{2 \cdot z}{d}} dz \tag{4}$$

The nanoparticles are modeled by an aggregate of spherical particles on the waveguide surface and $K(z)$ is the light extraction efficiency of the aggregate due to the optical interactions prevailing at the interface between the nanoparticles and light in the waveguide below.

The optical response of a CCD camera acquiring the scattered evanescent light is proportional to the normalized light intensity which for the simplest case of constant light extraction efficiency model has the form:

$$\eta = I_z(h) = \frac{1}{2} Kd \cdot (1 - e^{-\delta h}), \quad with \quad \delta = 2/d \tag{5}$$

$I_z(h)$ is the intensity of light extracted by the nanolayer of thickness *h*, and d is the penetration depth from eqn. (2) .

Experimentally, we can evaluate the deposited thickness nanoprofile from the Integrated Optical Density (IOD) which is proportional approximately to the "effective mass" of the investigated layer :

$$IOD = \iint_S D(x,y) \cdot ds = \int_0^\infty D \cdot H(D) dD \tag{6}$$

IOD is obtained from measuring the light intensity emanating from the waveguide with a microscope equipped with a CCD camera. In (6) *D(x,y)* is the pixel image density at *(x,y)* and *H(D)* is the intensity histogram of the local defined area.

We showed in [10] that the IOD is proportional to the η and for the case $\delta \cdot h << 1$ from eqn.(5) we obtain the

following linear approximation between any two IOD, $\eta$ and $h$

$$\frac{IOD_1}{IOD_2} = \frac{\eta_1}{\eta_2} = \frac{(1-e^{-\delta h_1})}{(1-e^{-\delta h_2})} \approx \frac{h_1}{h_2} \qquad (7)$$

Thus given the value of $h_2$ and measuring the IOD 's one can calculate other thicknesses $h_1$ of the nanoprofile by :

$$h_1 \cong \frac{IOD_1}{IOD_2} h_2 \qquad (8)$$

If $h_2$ can be measured by independent techniques such as Spectrometric, SEM , AFM or other nano profiling technique the DELI profiles can also be calibrated absolutely, not only displayed relatively.

## 4. Morphological characterization of the dielectric materials nano profiles by DELI

To observe the morphology at a higher resolution and closer to the substrate level, we captured DELI images at several zooming powers of the microscope, down to the range of well resolved x-y areas of 16x16 μm, as shown in Fig.1. As can be observed, the morphology at this resolving power gives for the PP based materials a typical surface structure of isolated spherical particles or dimmers and only a few higher number of interconnected spheroids. However, for the PE based materials one observes a higher connectivity and touching between the spheroids. It can also be seen that the PP-cellofiber and PE-Amidon compounds are more surface homogenous than the PP and PE undoped materials.

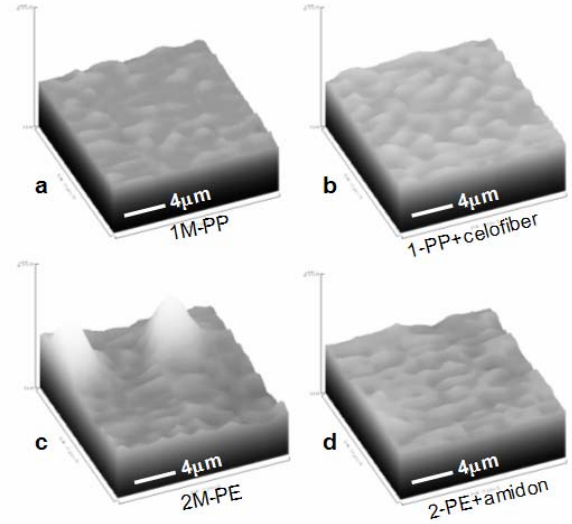


*Fig.1. DELI 3D zoomed images of 4 samples areas : a.) PP, b.) PP with 20% Celofiber, c.) PE and d.) PE with Amidon in magnified zone areas of size ~ 16 x 16 μm.*

To observe the absolute and relative surface nanoprofiles of the 4 materials types in the z-direction we evaluated the mean Integrated Optical Density (IOD) in the deposited zones as shown in Fig.2. In the insets above the IOD curves, the 2D captured images of the samples shown in Fig.1 are given. We observe that besides their higher mean profile, the PP materials are also of a smoother profile as compared to the PE materials.

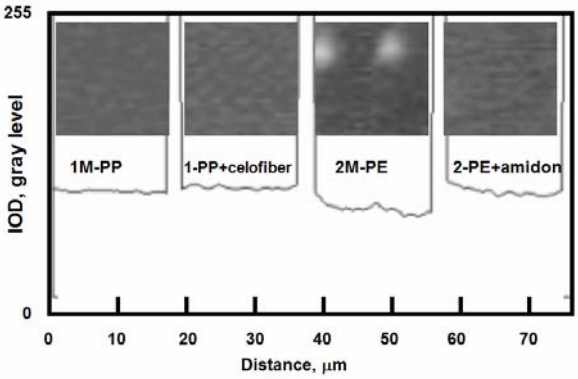


*Fig. 2. IOD profiles for the typical samples of PP, PP with 20% Celofiber, PE and PE with Amidon in magnified zone areas of size ~ 16 x 16 μm.*

To quantify these properties we define below relations of $h_{rel}$ and $RMS_{rel}$ presented in Table 1

$$h_{rel} = \frac{h}{h_{\max}} \approx \frac{IOD}{IOD_{\max}} \qquad (1)$$

Where h are absolute values of the height of the particles and IOD their corresponding values for the various materials.

$$RMS_{rel} = \sqrt{\frac{1}{t} \cdot \iint (\Delta IOD(x,y))^2 \cdot dxdy} = \frac{\langle \Delta h \rangle_{rms}}{h} \cong \frac{\Delta h_{\max}}{h} \qquad (2)$$

and *ΔIOD* is the fluctuation of *IOD(x,y)* in a typical t=20 μm distance on the surface.

*Table-1. Relative Thickness and RMS of the dielectric samples profile from the IOD curves*

| *Material* | $h_{rel}$ | $RMS_{rel}$ |
|---|---|---|
| *1M-PP* | 0.88 | 0.29 |
| *1-PP+celofiber* | 1 | 0.33 |
| *2M-PE* | 0.80 | 1.10 |
| *2-PE+amidon* | 0.91 | 0.82 |

Thus we can see quantitatively from the $RMS_{rel}$ column in Table-1 that the PP and PP-cellofiber surface profiles are more homogenous than the PE based materials although the height profiles are about the same magnitude. We were also interested to characterize the structure of the individual spheroids composing the materials.

For this end we performed accurate DELI images profiling for a few particles observed directly resting on the substrate level.

In Fig. 3 typical DELI profiling plots are given which show the details of the spheroids for the 4 dielectric materials types investigated.

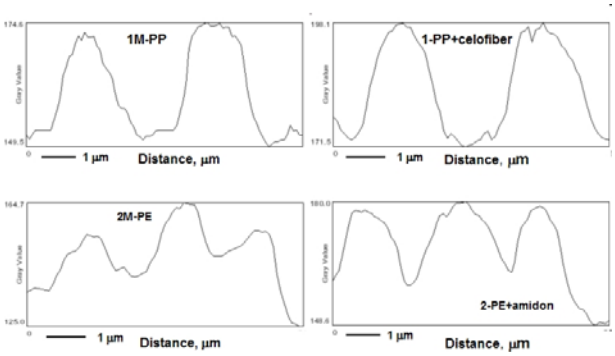


*Fig. 3. Typical detailed profile plots for single particles details of the 4 dielectric materials types investigated The 1-PP-celofiber sample particles were calibrated by SEM images to give an approximate height of 250 nm for the spheroids.*

The results are very interesting since they show a difference in the structures of the PP and PE based materials. That is, while for the PP based materials the profiles go down to the substrate level, in the PE based materials the nanospheroids rest on a layer of compact material above the substrate level, with thickness of the order of the spheroids diameter. This hints that the compact layer below the PE dielectric particles was created by the same particles which merged into a higher level deposit.

Finally, we used image processing algorithms to find further resolution details in the z-direction of the spheroids shown in Fig.4. The main image processing tools used were Irfan program [11] and imageJ [12] of NIST. The diameters of the tiny particles composing the spheroids, as seen in Fig.4 are 37.5nm, 75nm, 187.5nm and 133.3nm for the 1M-PP, 1-PP+ 2M-PE, 2-PE+Amidon respectively.

Thus the DELI optical technique is capable due to its sensitive local spatial differential properties to provide us with profile details information down to about 40 nm.

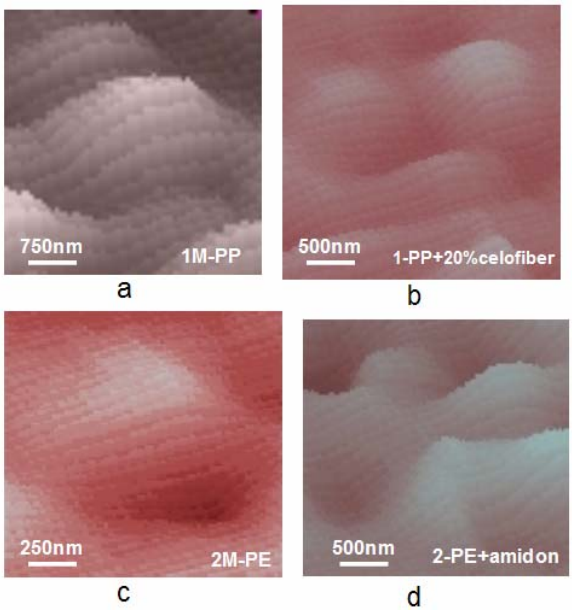


*Fig. 4. DELI processed micrographs by Image Processing, giving 3D perspective of the nano-structural details at the highest magnification: a) for 1M-PP; b) for 1-PP+Celofiber; c) for 2M-PE; d) for 2-PE+Amidon.*

## 5. Discussion

The morphological investigation of this work shows that the polymers observed on the glass substrates have structures with spheroids diameters typically in the range of 100-300 nm as obtained by DELI and SEM microscopies alike.

Previous SEM microscopy investigations for these materials in the literature have shown only flat surfaces with no clear features of the nanometric 3D perspective details. However, the morphology of the nano-structures of polymers observed by DELI in this work shows a convoluted array of individual particles merged partially on the surface at high magnification, see Fig.4.

We compared also the DELI images with SEM morphological investigation for the 4 dielectric materials used. The comparison gives indeed very similar features at the same magnifications. In fact we saw in some cases a better contrast of the features obtained by the DELI technique vs. SEM.

Comparing the DELI technique with SEM morphological investigation for the polymeric materials used as insulators, we realize the following merits and disadvantages of the various techniques:

| *Technique* | *Area* | *z-resolution* | *Ease of use* | *Measuring time* | *Ambient* |
|---|---|---|---|---|---|
| *DELI* | $cm^2$ | *30nm* | *high* | *minutes* | *air* |
| *SEM* | $cm^2$ | *100nm* | *low* | *hours* | *vacuum* |

We realized in particular, that the highest merits of the DELI technique are the operation in air, fast and ease of measurements, better z-resolution than SEM and large areas profiling capability and mean thickness evaluation, suitable to almost any lab equipped with a good optical microscope.

## 6. Conclusions

The morphological investigation shows that the polymers spheroids observed on the glass substrates have diameters typically in the range of 100-300 nm as obtained by both DELI and SEM nanoprofiles microscopies.

The morphology of the nano-structures of polymers observed at high magnification by DELI shows a convoluted array of individual spheroids merged partially on the surface. To observe the morphology at a higher resolution and closer to the substrate level, we captured DELI images at the highest zooming power of the microscope 40x. It was observed, at 40x resolving power that PP based materials had a typical structure of isolated spherical particles or dimmers and only a few higher number of interconnected spheroids. For the PE based materials we observed a much higher connectivity and merging between the spheroids.

In this work the DELI technique was used to obtain the nanostructural morphology of thin films of dielectric materials based on PE and PP compounds for large areas.The method gave profile details down to a resolution of about 40 nm in the z direction. It is shown thus that the DELI technique is suitable for observing nanostructural details of various materials deposited on optical waveguides using the evanescent phenomenon in conjunction with image processing methods.

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[11] IrfanView program downloadable from : http://www.irfanview.com/ This program allows various image enhancing filtering operations such as Gamma, Brightness, Contrast, Saturation and Color balance.

[12] imageJ program of NIST downloadable from : http://rsb.info.nih.gov/ij/ This program allows various image processing operators such as: Plot Profile, Surface Plot.

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