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Micromorphological characterization of polymer-oxide nanocomposite thin films by atomic force microscopy and fractal geometry analysis

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ABSTRACT

The purpose of this study was to evaluate the 3-D surface micromorphology of polymer-oxide thin films spin-coated from a composite of poly-methyl-methacrylate as the matrix and elongated titania nanorods as the filler particles. The surfaces of these composite films were investigated by atomic force microscopy and characterized by fractal geometry analysis. The effect of increasing loading of the fillers between 0 and 30% by weigth relative to the matrix was assessed. An increasing roughness was observed, with typical emergence of protruding ripples progressively extending into larger stripes. The amplitude parameters of the surfaces were determined by analysis of the height distributions. The fractal analysis of roughness revealed that the films have fractal geometry. Triangulation method based on the linear interpolation type was applied to determine the fractal dimension. A connection was observed between the surface morphology and the physical properties of the coatings as assessed in previous works.

1. Introduction

The progress in control of polymeric materials and their hybrid composites with inorganic particles during the last twenty years has led to their use in a number of applications [1–3]. Composites of organic matrix and nanoparticles as the fillers are used in many devices, from OLED$_s$ to photovoltaic solar cells and gas sensors [4], as well as in structural materials [5] for aeronautics, automotive, biomedical [6] and dental restoration [7]. The nanocomposites are used in bulk or as coatings. In both cases, but particularly for the thin coatings, homogeneous distribution of the filler particles inside the matrix is required, even at high loading, without appearance of large aggregates, which are often accompanied by phase segregation [1–3,5]. Phase segregation is particularly detrimental not only for the expected bulk properties of the composite, which are the result of careful design of the matrix-filler mixture [8,9], but also for their surface. In fact, may the composite be a coating or a bulky piece, the surface roughness is one of the most important properties to be controlled, affecting e.g. the lifetime of lubricating surfaces or the wetting properties of self-cleaning materials [10]. In most cases a high roughness is undesirable (e.g. for optical components or surfaces exposed to environmental bacteria that should not adhere [11,12]), but in some cases controlled roughness can be of help (e.g. for orthopedical and dental implants, where new tissue on-growth is fostered by tuned height and spacing of surface features [13]).

A common polymer used often as the model matrix in experimental nanocomposites is poly-methyl-methacrylate (PMMA) [3,4,6]. An interesting candidate as the filler nanoparticle material is the semiconducting oxide of titanium, TiO_2, namely titania. This is of interest for applications in photonics and photoelectronics, thanks to its light-guiding high refractive index (n = 2–2.3 in the visible) [14]. Additionally, the photo-chemical properties of titania make it useful for catalytic degradation of pollutants [15] and for controlled wetting on UV irradiation [16], which suggest using its composites for lithographic fabrication of microfluidic biomedical devices. We studied nanocomposite thin films of titania nanorods (NRs) dispersed in PMMA by means of atomic force microscopy (AFM).

Fractal geometry is an advanced mathematical tool that has been used for quantifying the irregular complex structures and patterns across many spatial or temporal scales, relevant to

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applications in surface engineering research [17–20]. Whereas to our best knowledge no multifractal geometry study of the 3-D surface micromorphology of polymer-oxide nanocomposite coatings exists in the available literature, we think that this analysis can give deeper insight in the complexity of the topographical patterns emerging in similar materials. Therefore, the purpose of this study was to investigate the 3-D surface micromorphology of our polymer-oxide nanocomposite thin films.

2. Materials and methods

2.1. Materials

The fillers were prolate titania NRs, of crystalline character (anatase in phase), synthesized in toluene as described elsewhere [21]. The typical dimensions were 30 nm in length and 4 nm in diameter. The NRs presented a coating of oleic acid, working as a surfactant, to prevent aggregation. The suspension of NRs was mixed with PMMA (Aldrich, Italy) of $\langle M_w \rangle = 120$ kDa, at different relative concentration by weight ϕ, from 0 (bare polymer) up to 30%. The absolute concentration of PMMA was changed such as to maintain approximately the same thickness of the resulting film, which was always ~100 nm. The mixture was spin coated on glass at fixed conditions of 2000 RPM for 1 min and let to dry in ambient air.

2.2. Methods

2.2.1. AFM measurements

All AFM images of the samples were acquired in ambient conditions ($21 \pm 1\,^{\circ}C$) and ($44 \pm 2\%$ RH) with an MFP-3D Bio (Asylum Research, USA) working in contact mode. The probes used were CSG10 (NT-MDT, Russia), with nominal spring constant and tip apex diameter of ~0.1 N/m and ~10 nm, respectively. The scans were performed on areas of $10 \times 10\,\mu m^2$, collecting images with 512×512 pixels. The measurements were repeated for four times for each sample on different reference areas to validate the reproducibility of the typical features. All images have been modified only with plane fitting for background subtraction, and with no filter or other non-linear treatment (such as e.g. line-by-line flattening).

2.2.2. Analysis of the AFM images

For parametric description of the 3-D surface, the images have been analyzed with dedicated AFM software Gwyddion [22]. Detailed information on the quantitative parameters extracted from the AFM images of topography can be obtained by the respective definitions, according to published standards [23].

The fractal analysis was applied to the AFM images also by means of the above-mentioned freeware program Gwyddion. The triangulation method was used, with a linear interpolation type. In this method the fractal dimension D_s is obtained directly from box-counting of the surface with triangles. At each step i a grid of linear size units l_i is placed on the surface, which defines the position of the vertices of triangles, tiling the surface texture and presenting different angles of inclination with respect to the xy base-plane. The areas of all triangles are calculated and summed to obtain an approximation of the surface area $S(l_i)$. The initial grid size is $l_1 = L$, same as the whole image scan size (in our case $L = 10$ μm). l_i is progressively decreased by a factor 2, so that $l_i = l_1/2^{i-1}$, and the process continues until l_i corresponds to the single pixel size p (in our case $p = L/512 \approx 20$ nm). Thus, the number of l_i values is n such that $p = L/2^{n-1}$, which means $n = 10$. In the used program the $S(l_i)$ is then plotted versus $\ln(p/l_i)$ and the slope of this curve identifies $D_s - 2$.

Statistical analysis between D_s values from different images ($N = 5$) was performed using the SPSS 14 for Windows (Chicago, Illinois, USA). One-way ANOVA was used to test the differences between the two groups with Scheffé post-hoc tests for multiple comparisons, considering statistically significant the differences with a P value <0.05.

3. Results and discussion

A set of 3-D topographic AFM images selected to be representative of the nanocomposite films with different NR filler loading ϕ is shown in Fig. 1, with $\phi = 0$, 5, 10, 20 and 30 wt%, for panels (a)–(e), respectively. The surfaces are rendered in 3-D perspective view, with the vertical (height) scale displayed in color coding, according to the palette presented on the respective right hand side, and the scale chosen to stress the surface texture on each image. Clearly, the bare PMMA film ($\phi = 0$) looks quite flat and smooth, while in the nanocomposite films features appear in the form of round grains ($\phi = 5\%$), progressively coalescing into connected ridges of increasing width.

In Fig. 2 the peculiar type of plots used for the analysis carried out in this work are shown, for the single case of the representative AFM images presented in Fig. 1. In the different rows, the plots corresponding to the images Fig. 1a–d with increasing NRs filler loading $\phi = 0$–30% are shown. In the two columns, on the left the distributions of heights appear, whereas on the right the plots used for calculating the respective fractal dimensions D_s appear. These latter plots report the data points, and the respective linear fits, of the approximated surface area $S(l_i)$ resulting from the triangulation method, versus a parameter describing the finesse of the grid used for triangulation, in pixel size units and logarithmic scale, namely $\ln(p/l_i)$.

From the height distributions as in Fig. 2a, c, e, g and i, the values of height range (i.e. maximum–minimum), median, average roughness S_a, root mean square roughness S_q, skewness S_{sk} and kurtosis S_{ku} have been calculated. After repeating this calculation for all the different sets of AFM images ($N = 5$), the resulting values have been listed in Table 1, in the form of mean ± one standard deviation.

In Fig. 3 these results are presented in the form of plots versus the NRs loading ϕ. It can be seen from Fig. 3a that all the height parameters (height range, median, S_a and S_q) increase monotonically with ϕ, and in particular the roughness parameters S_a and S_q increase along an almost straight line with a weak tendency to saturation and only slightly higher slope for S_q (~1.8 vs ~1.5 nm/%). The linear increase in roughness with ϕ observed here is consistent with previous reports on similar samples with NRs of both anatase [24] and brookite [25]. In this work, in addition to the width S_q we also observed the higher moments of height distribution of our samples. The skewness qualifies the symmetry, as negative values indicate predominant valleys and positive ones indicate predominant peaks. From Fig. 3b it appears that, while the starting surface (bare PMMA) is balanced in peaks and valleys, the type of roughness emerging on NRs loading is more of peak–type, with strongest peakedness for the 5% sample. Kurtosis instead qualifies the type of protruding features providing the roughness, since for spiky (bumpy) surfaces it is >(<) 3. Again the 5% surface is clearly different from the others, and it qualifies as spiky. This is the sample where roughness starts to arise as the result of the presence of single NRs or small aggregates. On the contrary, all the other surfaces present rather bumpy-type peaks.

As compared to the standard quantities reported in Table 1 and Fig. 3, fractal geometry analysis may offer new parameters for characterizing the morphology of complex objects [17–20]. In particular, the surface area S of a surface fractal object increases with its size (equivalent radius) r according to $S \propto r^{D_s}$, with D_s surface