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Investigation of Morphology and Interface in Polymer Composite Thin Films

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ABSTRACT

Laser scanning confocal microscopy (LSCM) has been applied to examine the filler particles and their distribution in $BaTiO_3$-polymer composite films. We have measured thin-slice images of the composite films at various depths from the film surface and visualized the submicron size particles and the polymer between them nondestructively. We have found that, although $BaTiO_3$ particles appear to be uniformly dispersed in the composite films when observed under conventional microscope, the particles form clusters at low $BaTiO_3$ concentrations. The lower the concentration the larger the cluster size. The particles appear to be better dispersed in the high concentration composites than at low concentrations.

INTRODUCTION

High dielectric constant (High-K) ferroelectric ceramic-polymer composite are important electronic materials. Detailed understanding of this class of materials will help electronic industry in planning, design and processing of these materials. Previously, we have synthesized a series of $BaTiO_3$-polymer composite films and measured their dielectric properties over a wide volume fraction of $BaTiO_3$ filler [1]. $BaTiO_3$ was used, because it is the best-known ferroelectric ceramics.

In this paper, we report the morphology of the polymer composite films as observed by laser scanning confocal microscopy (LSCM). LSCM. is known for visualization of micron-size particles in detail.[2,3] The LSCM affords imaging of smaller features than the conventional microscopy and with a better depth resolution. We applied LSCM to examine the distribution of the filler particles in the $BaTiO_3$ ceramic-polymer composites, the particles size, and, the cluster shapes.

EXPERIMENTAL

Trimethylolpropane triacrylate (TMPTA monomer) was purchased from Monomer Polymer & Dajac Labs. Barium titanate powder ($BaTiO_3$ filler) and 2,2-dimethoxy-2-phenylacetophenone (photoinitiator) were obtained from Aldrich. All materials were used as received.[4]

First, 1 % solution of the photoinitiator in the monomer was prepared. Next, barium titanate powder was mixed into the solution to form liquid formulations of various filler concentrations. The formulations were cured by exposure of a few drops of each formulation squeezed between microscope slides to UV-light. During the exposure, the slides were kept at a constant distance using self-adhesive labels in the role of spacers. The cured composites did not adhere strongly to the glass and were carefully separated from the slides in the form of thin films of the thickness of the order of 50 - 200 µm. In this way, we prepared a series of $BaTiO_3$-polymer composite films with $BaTiO_3$ volume fraction of 5%, 10%, 15%, 20%, 25%, 30%, and 35%. The films were examined directly by the laser scanning confocal microscopy.

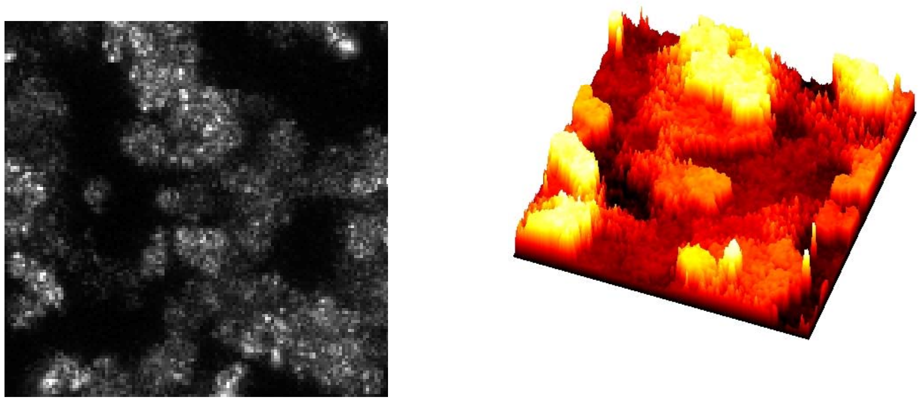
A Zeiss Laser Scanning Confocal Microscope Model LSM510a was applied to characterize the microstructure of the composites. The wavelength of the laser was 543 nm with the bandwidth of 10 nm. Each confocal micrograph covered the scanning area of about 18.4 × 18.4 µm. An oil immerge objective (100/1.3) was used for the refractive index matching with the polymer matrix. The objective numerical aperture was 1.3, which provided the transverse and depth resolutions of 155 nm and 286 nm respectively at the laser wavelength applied. Several LSCM optical slices at various focal plane distances from the sample surface were collected for each composition. The LSCM images shown in this paper are either 2D intensity profile presentations of overlapping optical slices (i.e., stacks of several z-scan images in 2D projection with z = 1 µm per z-step), or, 3D presentations composed from the slices, unless specified otherwise.

RESULTS AND DISCUSSION

The $BaTiO_3$-polymer composites were two-component systems, where $BaTiO_3$ particles were distributed at random in the TMPTA polymer matrix. Figures 1 and 2 show typical LSCM images of the 2D projections, and the 3-D stereo-views of $BaTiO_3$-polymer composites containing 5 % and 25 % of $BaTiO_3$ filler by volume, respectively. When we used a traditional microscopy for the same composites, the film with 5 % $BaTiO_3$ content appeared to be uniform under transmission light. The LSCM images provide clear difference in the particle distribution. This is result from the fact that a conventional microscope usually covers much thicker layer than that imaged by LSCM. The LSCM uses coherent light to illuminate the specimen and collects the light exclusively from a single plane (i.e., a pinhole slit conjugated to the focal plane) while rejecting the light out of focal plane. Thus, by moving the focal plane location along z-axis, optical slices up to certain depth from a sample surface can be visualized separately. As there is a large contrast in light scattering cross-section between the $BaTiO_3$ particles and the polymer matrix, LSCM has provided a non-destructive, powerful visual aid for characterizing particles distribution in the $BaTiO_3$-polymer composites.

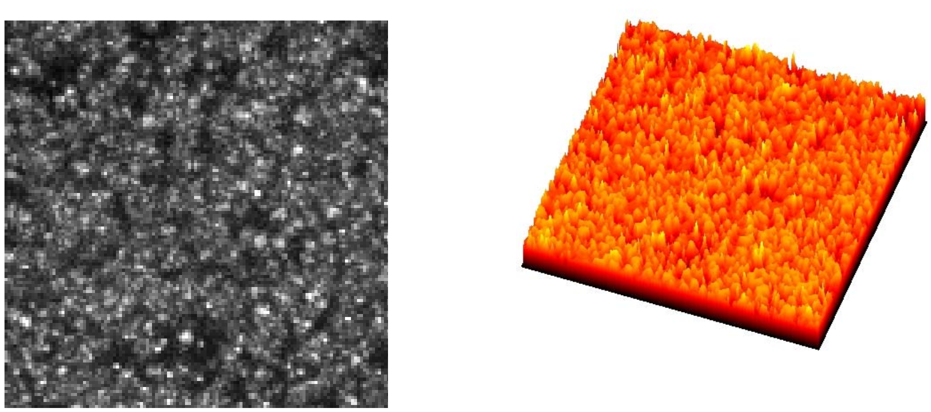
Using LSCM, we observe that $BaTiO_3$ particles have tendency to form clusters, which are the most pronounced feature of the composite microstructure at small concentrations. As the concentration increases, the clusters coalesce into more uniform structures. Consequently, $BaTiO_3$ particles appear to be better dispersed in the high concentration composites than at low concentrations. In the 25 % film the filler appears to be uniform and there is no significant change in the particles distribution at higher concentrations.

Figure 3 shows a single-slice image of $BaTiO_3$-polymer composite containing 25 % volume fraction of $BaTiO_3$ filler. Single focal plane usually crosses only several particles across the area imaged. The intensity variation along a line provides information about vertical distance of the points on the reflecting particle surface relative to the focal plane. We used this technique to examine the size of $BaTiO_3$ particles in the composites studied. Graph in Figure 3 shows the vertical distribution of $BaTiO_3$ particles along a 4 µm line marked on the adjacent image.



(a) (b)

Figure 1. LSCM 2D-projection image (a) and 3D micro-topography image (b) of the particle distribution at 5 % volume fraction of $BaTiO_3$ in TMPTA polymer matrix.



(a) (b)

Figure 2. LSCM 2D-projection image (a) and 3D micro-topography image (b) of the particle distribution at 25 % volume fraction of $BaTiO_3$ in TMPTA polymer matrix.

From these data we found that the size of $BaTiO_3$ particles was in the range of 0.5 - 1 µm with a relatively narrow size distribution. At high concentration, the closeness of these clusters let the material appears to be more uniform..

Figure 4 illustrates the shape analysis of a few clusters observed at low $BaTiO_3$ concentration. The clusters have irregular shape. This indicates that the clusters were formed by random encounters of individual particles in the liquid TMPTA phase and were kept together at the contact position by direct short-range particle-particle interactions without significant involvement of the surface tension forces at the particle-monomer interface. Otherwise, the clusters would form spherical (or ellipsoidal) rather than the irregular shapes. When the monomer was photo-polymerized the originally formed cluster shapes were preserved.

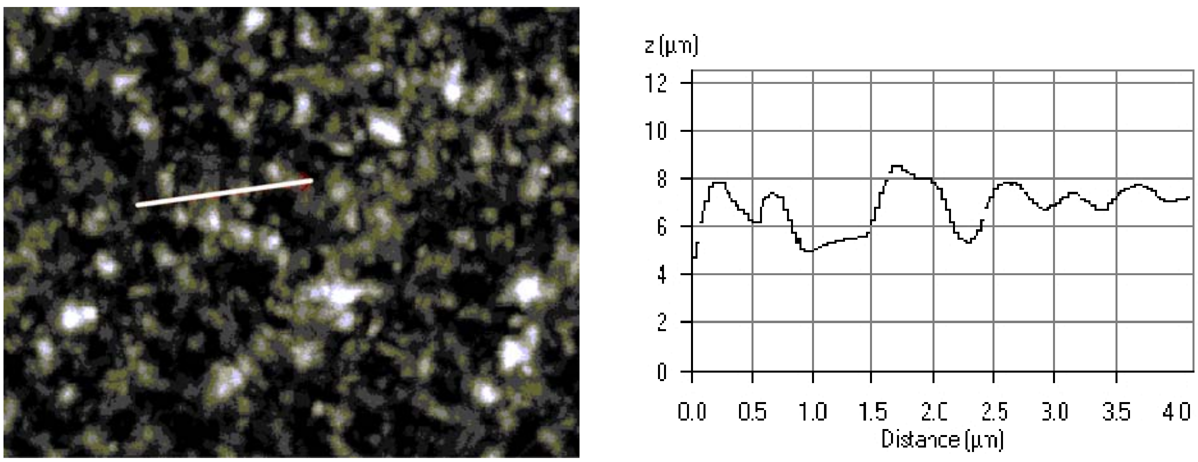


Figure 3. Analysis of particle size in the $BaTiO_3$-polymer composites by LSCM. The data on the right correspond to the vertical particle distribution along the white line on the left image, based on digital intensity analysis.

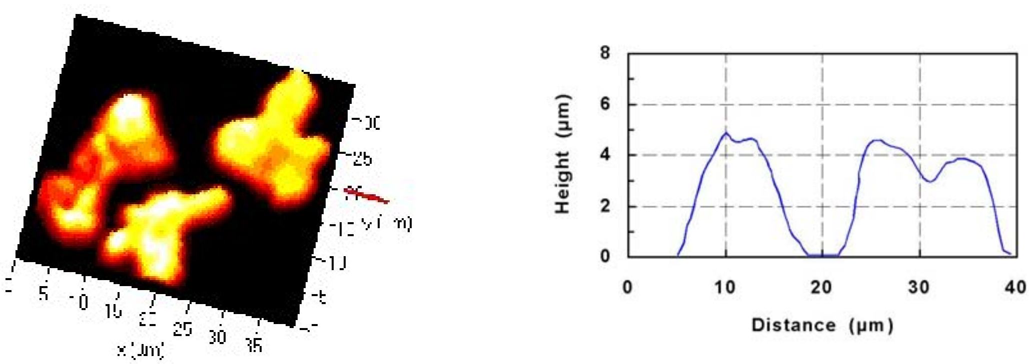


Figure 4. Analysis of the shape and size of $BaTiO_3$ clusters.

CONCLUSIONS

LSCM has been found to be a very useful technique to study microstructure of the $BaTiO_3$-polymer composites. We obtained micro-topography images of $BaTiO_3$ particles distribution in the films. From the images we have determined the particles size and the other features of the composites morphology. LSCM images have revealed that $BaTiO_3$ particles form clusters at low particle concentrations. The average diameter of the clusters was up to 10 μm at 5 % volume fraction of $BaTiO_3$. The cluster size decreases with increase of the particle concentration. Above 25 % the particle distribution appears to be uniform due to the closeness of those clusters.

REFERENCES

1. R. Popielarz C. K. Chiang, R.Nozaki, J. Obrzut. Mater. Res. Soc. Symp. Proc.: Organic/Inorganic Hybrid Materials-2000, 628, CC11-5, (2001).
2. T.R. Corle, and G.S.Kino, "Confocal Scanning Optical Microscopy and Related Imaging Systems," Academic Press, 1996.
3. L.Sung, M.E Nadal, P Stutzman, M.E. McKnight. "Characterization of coating microstructure using laser scanning confocal microscopy," PMSE Preprint, **83**, 343 (2000).
4. Certain instruments and materials identified in this paper are to adequately specify experimental details. In no case does it imply endorsement by NIST or that those are necessarily the best for the purposes specified.