

SURFACE AND PHYSICAL PROPERTIES OF POLY(4-VINYLPYRRIDINE)/BARIUM TITANATE NANOCOMPOSITES

Razvan Florin Barzic¹, Iuliana Stoica², Andreea Irina Barzic², Gheorghe Dumitrascu¹

¹*Department of Mechanics, "Gheorghe Asachi" Technical University, Iasi, 700050, Romania
e-mail: barziczrazvan@tuiasi.ro*

²*"Petru Poni" Institute of Macromolecular Chemistry, Iasi, 700487, Romania*

Abstract: *This work reports the preparation of some new nanocomposites using poly(4-vinylpyrrolidone) as matrix in which are incorporated different percents of barium titanate nanoparticles. The synthesis procedure is a traditional one, consisting in solution mixing of the matrix with the nanofiller suspension, stabilized by ultrasonication; subsequently the system is homogenized by stirring. The morphology of the samples is closely examined by atomic force microscopy (AFM), which allows not only identification of both phases, but also offers the opportunity of testing the local mechanical properties. The dielectric and thermal properties of the investigated nanocomposites are determined using Maxwell-Garnett and Lichtenecker approaches. The obtained results indicate that the studied nanocomposites exhibit good mechanical properties and heat transfer – suitable for protecting chips of overheating in power electronics.*

Keywords: *poly(4-vinylpyrrolidone), barium titanate, morphology, dielectric constant, thermal properties.*

1. Introduction

Electrotechnics is a sector in a continuous development, which stimulates the researchers to design new compounds with multifunctional properties. Flexible and conductive substrates offer new possibilities for replacing metal parts in several applications, including power electronics, electric motors and generators or heat exchangers [1]. Polymer composites are the most used materials for such purposes owing to the advantages given by the polymer matrix, such as light weight, corrosion resistance and ease of processing [2-4]. Current interest to improve the thermal conductivity and dielectric constant of polymers is focused on the selective addition of nanofillers with optimal characteristics [5-7]. Barium titanate (BaTiO₃) ceramics have become increasingly important in the electronic industry, because of their ferroelectric, piezoelectric and thermoelectric properties [8-10]. Moreover, its polarization below Curie point is exploited into fabrication of dynamic random access memories. Poly(4-vinylpyrrolidone) (P4VP) is a high-

performance polymer, which exhibits high electrical and thermal conductivity and is widely used on commercial level [11]. This work aims to prepare new nanocomposites based on the above describes compounds and to evaluate some basis thermophysical properties for electronics applications, such as morphology, dielectric constant and thermal conductivity.

2. Experimental

The P4VP, BaTiO₃ nanopowder (with particle size under 100 nm) and dimethylacetamide (DMAc) are used as received from Sigma Aldrich.

The method used for nanocomposites synthesis involves solution processing. First, different amounts of nanofiller are weighted and mixed with 2 ml of DMAc solvent.

The dispersion of the BaTiO₃ is achieved by ultrasonication with Ultrasonic bath model UCI-150 at frequency of 35 kHz and power of 325 W, during 45 min. Then, in the stable BaTiO₃ nanosuspension the same quantity of P4VP is

added and the resulting system is magnetically stirred for 6 h.

Atomic force microscopy (AFM) measurements are performed on a SPM SOLVER Pro-M platform at room temperature.

3. Results and discussion

The morphology of P4VP matrix is analyzed in detail by AFM in tapping mode (Fig. 1).

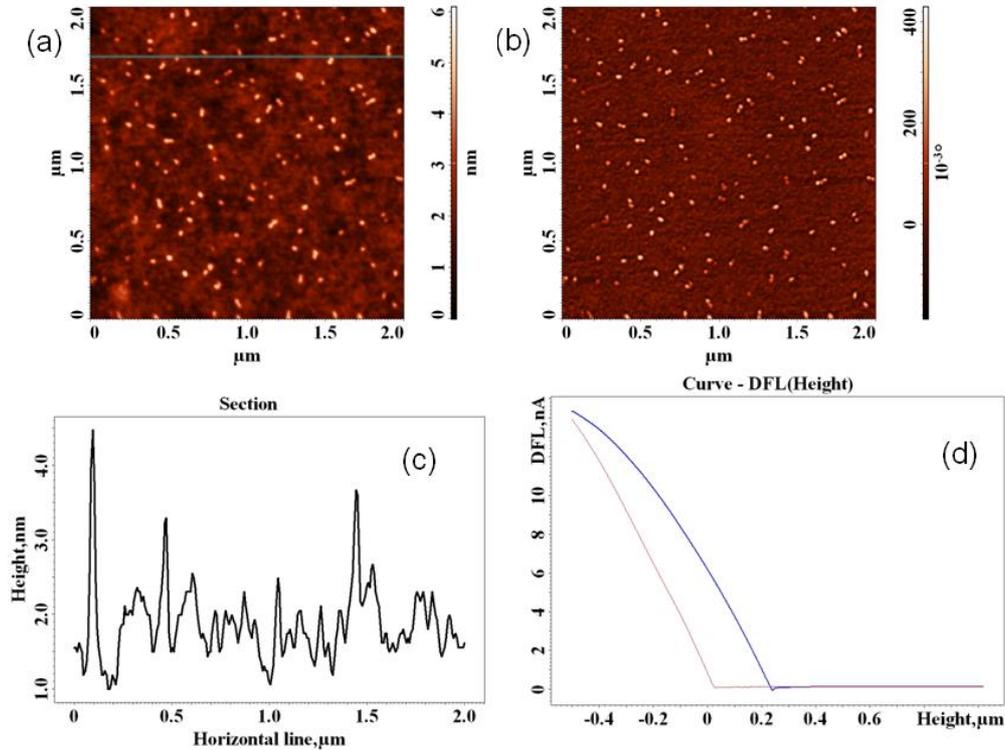


Figure 1: (a) AFM image, (b) phase image, (c) section profile and (d) curve-DFL height for P4VP.

This sample exhibits a flat surface with typical structural formations for this polymer [12]. The size of these aggregates is very small as shown by the low value of the root mean square roughness (Sq), namely 0.6 nm. The section profile, recorded along the line from the corresponding bidimensional AFM image, reveals that the P4VP surface is uniform. The phase images show that the studied film is constituted from a single material.

Introduction of BaTiO_3 nanoparticles in this matrix changes both bulk and surface properties of the polymer. For instance, nanocomposite containing 1 wt%, a slight increase regarding Sq parameter to 4.8 nm, can be noticed. Also, the phase image from Fig. 2 indicates a contrast given by the ceramic inclusions inserted in P4VP.

It is well known that the performance of the composite is dependent on nanofiller characteristics and the state of dispersion. For some properties a perfectly homogeneous dispersion is required, while in other cases a

percolating network is required, which can be achieved by controlled aggregation of the particles.

Figure 3 reflects the effect of nanoparticle dispersion (achieved by ultrasonication) on the surface characteristics in the case of 5 wt% $\text{BaTiO}_3/\text{P4VP}$. It can be observed that without dispersion the BaTiO_3 particles are drawn to each other by van der Waals forces and they remain under the form of aggregates inside the polymer matrix. AFM data indicate that in this case the nanocomposite surface is less uniform and its Sq is higher (32.3 nm), comparatively with the dispersed sample (6.4 nm).

The ultrasonicated film exhibits a uniform and flatter topography, and higher phase contrast. Further addition of BaTiO_3 in P4VP leads to a slight decrease of the Sq to 5.6 nm, which might be due to the fact that the surface tends to be more uniform as the particle-particle interactions are increasing.

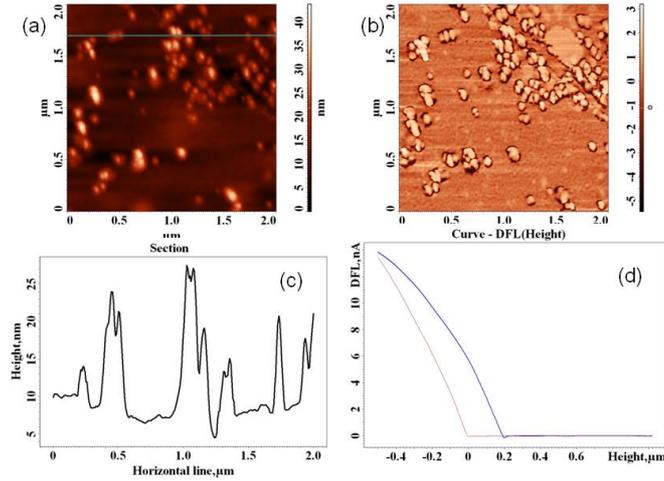


Figure 2: (a) AFM image, (b) phase image, (c) section profile and (d) curve-DFL height for P4VP containing 1wt% BaTiO₃.

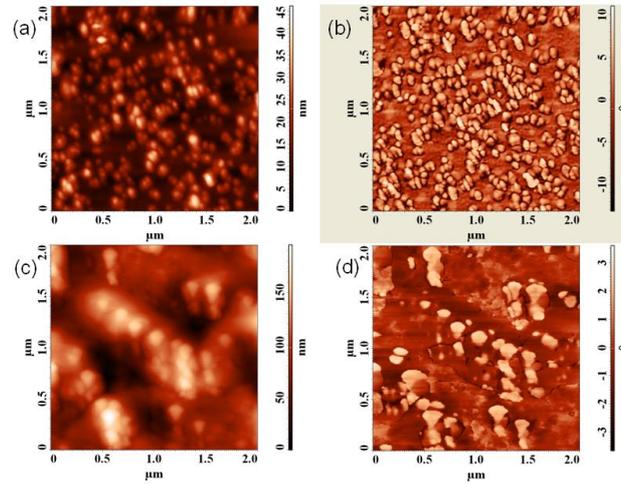


Figure 3: (a) AFM and (b) phase images for P4VP containing 5 wt% BaTiO₃, (c) AFM and (d) phase images for P4VP containing 5 wt% agglomerated BaTiO₃.

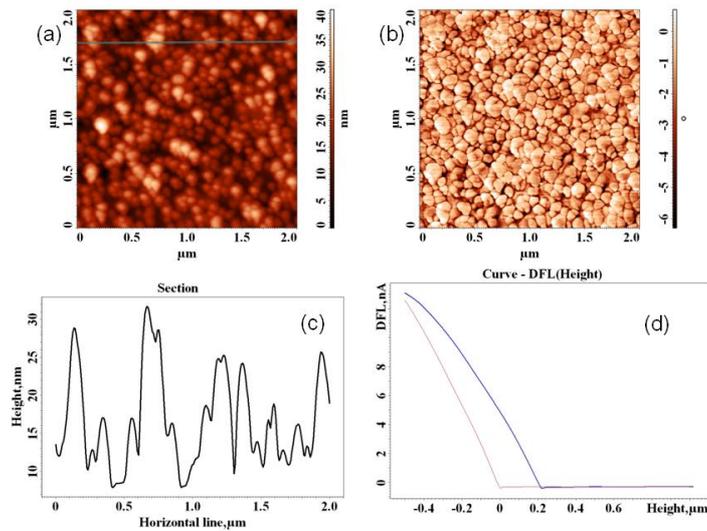


Figure 4: (a) AFM image, (b) phase image, (c) section profile and (d) curve-DFL height for P4VP containing 10 wt% BaTiO₃.

This aspect is supported by phase image from Fig. 4. The regularity of the analyzed nanocomposite surfaces is confirmed by the section profile images (Figs. 2 and 4).

Another factor that is modified by the presence of the ceramic nano-inclusions is represented by the local mechanical properties. The surface adhesion of the prepared films is evaluated by means of the adhesive forces between the nanocomposite and the AFM tip. These adhesion forces can be calculated directly from the force-distance curves, more precisely from the retraction curves (blue curves from Figs. 1(d), 2(d) and 4(d)). When the AFM tip withdraws, it loses contact to the sample surface upon overcoming of the adhesion forces (at level 0). Therefore, the surface hardness can be investigated through the force-distance curves, offering information on flexibility and toughness of the analyzed material. The withdraw force is equal with the adhesion force and can be determined from Hooke's law:

$$F = K_e \Delta x. \quad (1)$$

where Δx is the cantilever shift in rapport with sample film surface.

The adhesion forces for P4VP/BaTiO₃ films, determined from expression (1), are 134 nN for the matrix, 112 nN for 1 wt% and 68 nN for 10 wt% BaTiO₃, respectively. A decrease in adhesion properties is noticed when the inserted nanofiller percent is higher. This observation is indicative that the structural organization slightly changes in the presence of a possible nanoparticle network. Thus, the mechanical toughness of the surface is easily improved by the presence of the BaTiO₃.

The studied nanocomposites can be used as embedded capacitors. They represent the primary way of further miniaturizing electronic systems because the ratio of capacitors to total passive components can be as high as 60%. However, for these applications the relative dielectric constant must be enhanced. In order to evaluate this property the Maxwell-Garnett and Lichtenecker approaches are applied [13, 14]:

$$\varepsilon_{composite} = \varepsilon_p \frac{2\varepsilon_p + \varepsilon_c + 2V_c(\varepsilon_c - \varepsilon_p)}{2\varepsilon_p + \varepsilon_c - V_c(\varepsilon_c - \varepsilon_p)}. \quad (2)$$

$$\ln \varepsilon_{composite} = V_p \ln \varepsilon_p + V_c \ln \varepsilon_c. \quad (3)$$

where ε_p is the dielectric constant of the polymer, ε_c is the dielectric constant of the ceramic filler, V_p and V_c is the volume fractions of the matrix and ceramic, respectively.

The dielectric constant (ε) and the thermal conductivity (λ) of P4VP are determined using relations (4) and (5):

$$\varepsilon = 1.412014 + (0.001887 \cdot E_{cohl} + N_{dc})/V_w. \quad (4)$$

$$\lambda = 0.135614 + 0.126611 \cdot {}^1\chi^{BB}/N + 0.108563 (N_N + N_O - 0.125 N_H)/N. \quad (5)$$

where E_{cohl} is the cohesive energy, V_w is the van der Waals volume, ${}^1\chi^{BB}$ is a connectivity index, and N_{dc} , N_N , N_O , N_H , N are some structural parameters described by Bicerano [15].

The theory based on connectivity indices gives a dielectric constant for P4VP matrix of 3.15 and a thermal conductivity of 0.16 W/mK. Knowing that BaTiO₃ is characterized by a ε of 2000 and λ of 2.65 W/mK, the corresponding values of the investigated composites are evaluated and plotted in Fig. 5 as a function of the filler loading. The resulted data concerning the thermal conductivity of the samples is estimated by considering that it is a function of composition, as follows:

$$\lambda_{composite} = \lambda_p \cdot V_p + \lambda_f \cdot V_f. \quad (6)$$

where λ_p and λ_f are the thermal conductivities of the P4VP and nanofiller.

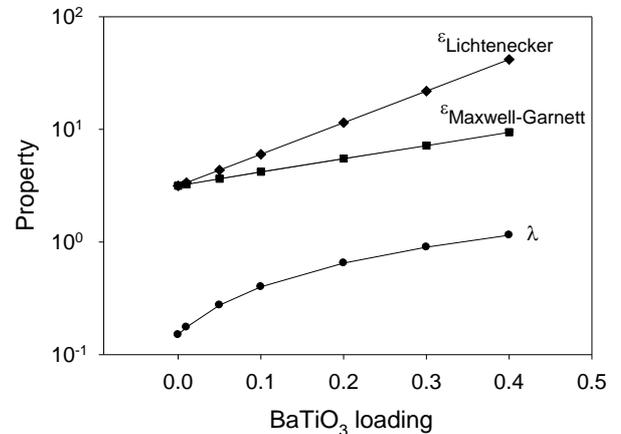


Figure 5: Variation of dielectric constant and thermal conductivities with filler loading

The data depicted in Fig. 5 show that there are some differences regarding the dielectric constant obtained from the two approaches, but literature [16] indicates a better fitting with experimental values, when the Lichtenecker relation is used. Also, the thermal conductivity of P4VP is increased with one magnitude order at high nanoparticle loadings.

4. Conclusions

New nanocomposites are prepared by solution mixture of P4VP with BaTiO₃ nanoparticles, which are dispersed in the polymer matrix by ultrasonication. The AFM data indicate a low Sq (<10 nm) for the uniform distributed nanofiller, comparatively with the sample containing agglomerated BaTiO₃, which presents Sq of 32.3 nm. The adhesion force decreases with increasing the nanoparticle percent in the system indicating that the structural organization is slightly changes by the presence of the formed BaTiO₃ network. This aspect is useful in enhancing the elastic shear modulus, the dielectric constant and thermal conductivity as required in microelectronic applications.

Acknowledgement: This paper was realized with the support of POSDRU CUANTUMDOC "Doctoral Studies for European Performances in Research and Innovation", ID79407, project funded by the European Social Fund and Romanian Government.

References

- [1] Hirano, K., Nakatani, S., Handa, H. and Takehara, H., *IEMT/IMC Symposium*, 1998.
- [2] Barber, P., Balasubramanian, S., Anguchamy, Y., Gong, S., Wibowo, A., Gao, H., Ploehn, H.J. and zur Loye H.-C., *Materials*, 2, 1697, 2009.
- [3] Lewis, N.S., *Electron Devices Meeting*, 2002. IEDM '02. International, 485, 2002.
- [4] Aman, A., Yaacob, M.M., Alsaedi, M.A. and Ibrahim, K.A., *International Journal of Electrical Power & Energy Systems*, 45, 346, 2013.
- [5] Lee, G.W., Park, M., Kim, J. and Lee, J.I., *Composites Part A: Applied Science and Manufacturing*, 37, 727, 2006.
- [6] Shi, Z., Radwan, M., Kirihara, S., Miyamoto, Y. and Jin, Z., *Appl. Phys. Lett.*, 95, 224104, 2009.
- [7] Weber, E.H., *Development and Modeling of Thermally Conductive Polymer/Carbon Composites*, Michigan, 1999.
- [8] Yogo, T., Kikuta, K.I., Yamada, S. and Hirano, S.I., *Journal of Sol-Gel Science and Technology*, 2, 175, 1994.
- [9] Gorzkowski, E.P. and Pan, M.J., *IEEE Transactions on Ultrasonics, Ferroelectrics, and Frequency Control*, 56, 1613, 2009.
- [10] Biswas, A., Bayer, I. S., Karulkar, P. C., Tripathi, A., Avasthi, D. K., Norton, M. G. and Szczech, J. B., *Appl. Phys. Lett.*, 91, 212902, 2007.
- [11] Shi, S. P., Zhang, L. F., Zhu, J., Zhang, W., Cheng, Z.P. and Zhu, X. L., *eXPRESS Polymer Letters*, 3, 401, 2009.
- [12] Chen, D., Handa, H., Wan, L. and Mao, G., *Macromol. Rapid Commun.*, 28, 1619, 2007.
- [13] Maxwell-Garnett, J. C., *Philos. Trans. R. Soc., London, Ser. A*, 203, 385, 1904.
- [14] Lichtenecker, K., *Phys. Z.*, 27, 115, 1926.
- [15] Bicerano, J., *Prediction of the properties of Polymers from their structures*, J.M.S. – Rev. Macromol. Chem. Phys. C36, pp. 161-196, 1996.
- [16] Lee, D.H., Lee, J.H., Kim, D.W., Kim, B.K. and Je H.J., *Journal of the Ceramic Society of Japan*, 118, 62, 2010.