Theoretical Study on Optical and Dielectric Properties of Thermoplastic Polystyrene Containing Nanoinclusions with High Polarizability

ANDREEA IRINA BARZIC[1]*, RAZVAN FLORIN BARZIC[2], CARMEN BEATRICE ZELINSCHI[3]

[1] „Petru Poni" Institute of Macromolecular Chemistry, 41A Grigore Ghica Voda Alley, 700487, Iaşi, Romania

[2] "Gheorghe Asachi" University, Faculty of Mechanics, 43 Dimitrie Mangeron Blv., 700050, Iasi, Romania

[3] "Alexandru Ioan Cuza" University, Faculty of Physics, 11 Carol I Bdv., 700506, Iasi, Romania

The paper aims to evaluate the optical and dielectric properties of the nanocomposites based on polystyrene containing various amounts of barium titanate. The characteristics of the thermoplastic polymer are determined using the connectivity indices formalism, while those corresponding to the nanocomposites are evaluated using the parallel and series models. The variation of the optical and dielectric properties with the volume fraction of the nanofiller is discussed.

Keywords: polystyrene, nanocomposites, optical properties, dielectric constant

Nanocomposites represent a category of hybrid materials in which at least one of the phases exhibits dimensions in the nanometer range. They have emerged as alternatives to overcome the limitations of microcomposites, while raising preparation challenges concerning the control of elemental composition and stoichiometry in the nanocluster phase.

Functional nanocomposites with thermoplastic polymer matrix offer new perspectives in improving the reliability and physical features of both active and passive components in high performance electrical devices [1,2]. The properties of this category of nanocomposites are determined by the size and nature of the nanofiller, and its dispersion degree. Thus, precise control of morphology is an essential factor in production of reinforced polymers with desired physical properties [3,4].

Among the polymer matrix utilized in nanocomposite synthesis, polystyrene is widely investigated owing to its good mechanical resistance and high transparency in some organic solvents. Many studies have been focused on improving the dielectric properties of this macromolecular compound by introduction of various types of nanofillers [5,6]. Barium titanate ($BaTiO_3$) is a ceramic compound with high polarizability, thus its introduction in a polymer matrix is expected to enhance dielectric properties. In order to evaluate and predict the applicability of the reinforced polystyrene in microelectronics, a theoretical assessment of the dielectric features should be performed prior to composite preparation. The evaluation of the reinforced polymer properties requires first the theoretical analysis of the matrix and subsequently the determination of the nanophase characteristics.

This paper describes the evaluation of the optical and dielectric properties of some polystyrene/barium titanate nanocomposites. The optical and dielectric characteristics of the thermoplastic matrix are determined using the connectivity index formalism developed by Bicerano [7], which utilizes connectivity indices defined via graph theoretical concepts as its main structural and topological descriptors. The physical characteristics of the PS-based nanocomposites are evaluated using some mathematical approaches.

Experimental part

Polymer matrix properties

The applied formalism of Bicerano [7] utilizes connectivity indices defined via graph theoretical concepts as its main structural and topological descriptors. The graph theoretical approach of molecular properties relies on the construction of the hydrogen-suppressed graph of the analyzed molecule. The calculations begin by considering the valence bond (Lewis) structure of the molecule, and then omitting hydrogen atoms. Each remaining atom gets a vertex in the graph, whereas each remaining bond becomes an edge. The values of two indices that represent the electronic environment and the bonding configuration of each non-hydrogen atom in the molecule, are next assigned, and listed at the vertices of the hydrogen-suppressed graph. The first atomic index is given by the simple connectivity index, δ, that equals the number of non-hydrogen atoms to which a given non-hydrogen atom is bonded. Expressing this in an equivalent manner one can state that the δ of any vertex in the hydrogen-suppressed graph represents the number of edges emanating from it. The second atomic index refers to the valence connectivity index, δ^V, containing information on the electronic configuration features of each non-hydrogen atom. Bond indices β and β^V can be defined for each bond that does not concern a hydrogen atom, as products of the atomic indices at the two vertices (i and j), which ascertain a given edge or bond [7].

$$\beta_{ij} \equiv \delta_i \delta_j \quad (1)$$

$$\beta^v{}_{ij} \equiv \delta^v{}_i \delta^v{}_j \quad (2)$$

Zero-order (atomic) connectivity indices ($^o\chi$ and $^o\chi^v$) of the entire molecule are related to the summations over vertices of the hydrogen-suppressed graph. First-order (bond) connectivity indices ($^1\chi$ and $^1\chi^v$) for the entire molecule are giving the summations over edges of the hydrogen-suppressed graph [7].

* *email: irina_cosutchi@yahoo.com; Tel: +40232 217 454*

$$^0\chi \equiv \sum_{vertices}(1/\sqrt{\delta}) \quad (3)$$

$$^0\chi^v \equiv \sum_{vertices}(1/\sqrt{\delta^v}) \quad (4)$$

$$^1\chi \equiv \sum_{edges}(1/\sqrt{\beta}) \quad (5)$$

$$^1\chi^v \equiv \sum_{edges}(1/\sqrt{\beta^v}) \quad (6)$$

The refractive index, n, is calculated with the relation proposed by Bicerano [7]:

$$n = 1.885312 + 0.024558 \cdot \cdot (17 \cdot {}^0\chi^v - 20 \cdot {}^0\chi - 12 \cdot {}^1\chi^v - 9N_{rot} + N_{ref}) / N \quad (7)$$

where N_{rot} is the number of rotational degree of freedom and N_{ref} is the correction index, and N is a structural parameter defined by Bicerano [7] as being 0.125 for polystyrene.

$$N_{ref} = -11N_F - 3N_{(Cl\ bonded\ to\ aromatic\ rings)} + +18N_S + 9N_{fused} + 12N_{HB} + +32N_{(Si-Si)} \quad (8)$$

The dielectric constant, ε, of PS is determined with the relation developed by Bicerano [7]:

$$\varepsilon = \frac{1.412014 + (0.001887 \cdot E_{coh})}{2.286940 \cdot {}^0\chi + 17.140570 \cdot {}^1\chi^v + 1.368231} \quad (9)$$

where the cohesion energy is E_{coh} = 39197 J/mole for polystyrene.

Polymer nanocomposite properties

Many theoretical approaches have been proposed for describing the physical properties of reinforced thermoplastics, particularly the dielectric ones. These approaches involve the knowledge of the properties of the matrix and of the nanoparticles, but also the amount of the introduced filler.

In the parallel model, each phase is presumed to contribute independently to the overall property, proportionally to its volume fraction (noted with V). Thus, it is maximized the influence of the high polarizable phase and implicitly it is considered a perfect contact between particles in a fully percolating network. Equation (10) describes the parallel model:

$$Property_{(composite)} = Property_{(matrix)} \cdot V_{(matrix)} + Property_{(filler)} \cdot V_{(filler)} \quad (10)$$

On the other hand, the basic series model starts from the idea that there is no contact between particles and their contribution is confined to the region of matrix. Equation (11) denotes the series model:

$$Property_{(composite)} = \frac{1}{(V_{(matrix)} / Property_{(matrix)}) + (V_{(filler)} / Property_{(filler)})} \quad (11)$$

Results and discussions

Organic–inorganic nanocomposites with high refractive index are typically constructed by integrating high refractive index inorganic nanoparticles building blocks into a processable, transparent organic matrix. These nanocomposites combine the numerous advantages of organic and inorganic components, and have many promising applications in design of advanced opto-electronic devices. The interactions of polymers with electromagnetic radiations are described by their optical and dielectric properties. The refractive index of a medium medium is a measure of the reduction of speed of light inside the medium. The evaluation of this fundamental is essential since it is directly related to other optical, electrical, and magnetic properties. The addition of nanosized inorganic dopants, like barium titanate, to thermoplastic matrix allows the modification of the polymers' physical properties enabling the preparation of functionalized polymers with extended application possibilities.

In the case of the composite system, here under analysis, we calculated the refractive index by using the relation (7). First, the connectivity indices were introduced. Starting from the chemical structure of polystyrene we have determined the connectivity indices resulting: $^0\chi$=5.3973, $^1\chi$ =3.9663, $^0\chi^\varpi$=4.6712 and $^1\chi^\varpi$=3.0139. Then, we have inserted the obtained values in equation (7) together with the values of N_{rot} and N_{ref}, which for polystyrene are 3 and 0, respectively. The resulted value of refractive index at 589 nm for the polystyrene is 1.604. This value is in agreement with the experimental value reported in [8,9].

The control of refractive index of polymers also means the control of dielectric constant. This property is a material characteristic that expresses the force between two point charges inside it. The dielectric constant of the polystyrene matrix was determined (9). The obtained permittivity value of the analyzed matrix is found to be 2.57.

Theoretical evaluation of the physical properties of the reinforced polystyrene also requires the knowledge of the nanophase properties. In the case of the barium titanate nanofiller the refractive index and dielectric constant were taken from literature [10], being 2.59 and 665 at 10 kHz at room temperature, respectively. Furthermore, the series and parallel models are employed in calculation of the optical and dielectric features of polystyrene/barium titanate system by considering different reinforcement amounts. The utilized approaches represent the upper bound and the lower bound for some physical properties of composites.

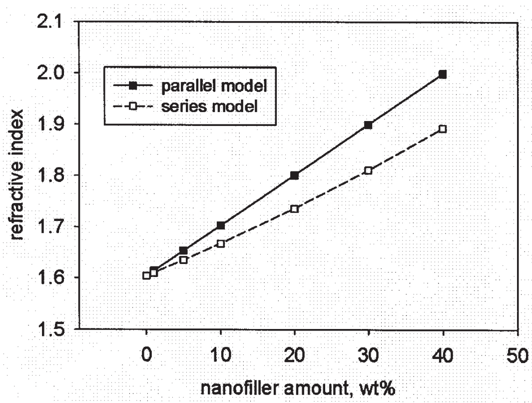

Fig. 1. Dependence of refractive index of polystyrene/barium titanate nanocomposites on the filler content determined from the parallel and series models

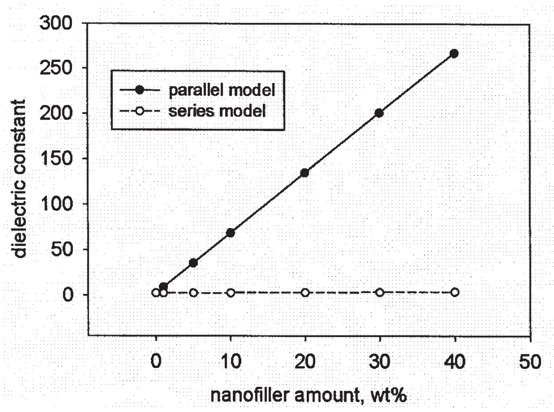

Fig. 2. Dependence of dielectric constant of polystyrene/barium titanate nanocomposites on the filler content determined from the parallel and series models

The individual optical and dielectric properties constant of the each phase constituent of the nanocomposite system were introduced in equations (10) and (11) and the pursued characteristics are determined. As observed in figures 1 and 2, the parallel model leads to higher values of estimated properties comparatively with the series one.

The data displayed in figures 1 and 2 shows that introduction of barium titanate in the polystyrene matrix increases its refractive index and dielectric constant values. The enhancement of the sample polarizability caused by the presence of the ceramic nanoparticles leads to the augmentation of the dielectric constant upto 270 at 40 wt%. The obtained result is useful in designing high dielectrics for capacitor construction.

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Conclusions

The physical properties of polystyrene/ barium titanate nanocomposites are determined. The refractive index and the dielectric constant of the polymer matrix were evaluated using the connectivity indices formalism, resulting a value of 1.604 and 2.570, respectively. The optical and dielectric features of the reinforced thermoplastic polymer were investigated using the parallel and series models. The addition of barium titanate into polystyrene leads to the enhancement of dielectric constant upto 270 at 40 wt%, recommending the studied nanocomposites for construction of capacitors.

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