EVALUATION OF MECHANICAL, DIELECTRIC AND THERMAL PROPERTIES OF POLYSTYRENE/ ALUMINUM NITRIDE NANOCOMPOSITES

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Abstract. The paper is focused on evaluation of mechanical, dielectric and thermal properties of some new nanocomposites based on polystyrene containing various amounts of aluminum nitride. The characteristics of the 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 thermophysical properties with the volume fraction of the nanofiller is discussed.
Keywords: polymer nanocomposites, mechanical properties, thermal properties.

1. INTRODUCTION

Nanocomposites are composites in which at least one of the phases shows dimensions in the nanometre range. They have emerged as suitable alternatives to overcome limitations of microcomposites and monolithics, while posing preparation challenges related to the control of elemental composition and stoichiometry in the nanocluster phase.

Functional nanocomposites with polymer matrix have the potential to improve the reliability and physical characteristics of both active and passive components in high performance electrical devices [1]. The properties of such materials depend on the size and nature of the nanofiller, and its dispersion degree. Thus, precise control of morphology is one of the most important factors in production of nanocomposites with desired properties [2]. Among the used dispersion techniques, the ultrasonication leads to good results. Also, to incorporate nanofillers in polymer matrix, several methods have been reported, but solution processing is a low cost and a fast procedure.

Most reported studied invlove carcon based nanofillers, however they require an additional stept for processing, namely the alignmment [3]. The utilization of spheric nanoparticles eliminates this problem. Aluminum nitride (AlN) a semiconducting compound with relative high thermal conductivity and oxidative resistance, thus its introduction in a polymer matrix is expected to enhance both thermal conductivity and dielectric properties. On the other hand, polystyrene is a commercial polymer with good mechanical properties [4].

This paper describes the evaluation of some mechanical and thermal properties of some polystyrene/AlN nanocomposites. The characteristics of the matrix are determined using the conectivity index formalism. The dielectric constant of the nanocomposites is estimated from the Maxwell relationship, while the mechanical and thermal properties are evaluated using the paralel and series approaches.

2. THEORETICAL APPROACH

The applied formalism of Bicerano [5] utilizes connectivity indices defined via graph theoretical concepts as its main structural and topological descriptors. Connectivity indices have been widely used for simple molecules. The graph theoretical treatment of molecular properties starts by the construction of the hydrogen-suppressed graph of the molecule. Starting with the valence bond (Lewis) structure of the molecule, hydrogen atoms are omitted. Each remaining atom becomes a vertex in the graph, while each remaining bond becomes an edge. The values of two indices, which describe 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 the simple connectivity index, δ, equals the number of non-hydrogen atoms to

which a given non-hydrogen atom is bonded. Equivalently, the δ of any vertex in the hydrogen-suppressed graph is the number of edges emanating from it. The second atomic index is the valence connectivity index, δ^V, containing information on details of the electronic configuration of each non-hydrogen atom.

Bond indices β and β^V can be defined for each bond not involving a hydrogen atom, as products of the atomic indices at the two vertices (i and j) which define a given edge or bond. Zeroth-order (atomic) connectivity indices ${}^0\chi$ and ${}^0\chi^v$ for the entire molecule are defined in terms of summations over vertices of the hydrogen-suppressed graph. First-order (bond) connectivity indices ${}^1\chi$ and ${}^1\chi^v$ for the entire molecule are defined in terms of summations over edges of the hydrogen-suppressed graph.

$$\beta_{ij} \equiv \delta_i \cdot \delta_j \tag{1}$$

$$\beta^v{}_{ij} \equiv \delta^v{}_i \cdot \delta^v{}_j \tag{2}$$

$${}^0\chi \equiv \sum_{\text{vertices}} \left(\frac{1}{\sqrt{\delta}} \right) \tag{3}$$

$${}^0\chi^v \equiv \sum_{\text{vertices}} \left(\frac{1}{\sqrt{\delta^v}} \right) \tag{4}$$

$${}^1\chi \equiv \sum_{\text{edges}} \left(\frac{1}{\sqrt{\beta}} \right) \tag{5}$$

$${}^1\chi^v \equiv \sum_{\text{edges}} \left(\frac{1}{\sqrt{\beta^v}} \right) \tag{6}$$

Certain physical properties of materials, such as the cohesive energy, molar volume, molecular weight per repeat unit, molar heat capacity, molar enthalpy and molar entropy, are extensive properties. An extensive property depends upon the size of the system. Its value increases in direct proportion to the amount of material present. On the other hand, many important properties of materials are intensive properties, which can usually be expressed in terms of the quotient of a pair of extensive properties. Intensive properties should not be directly correlated with an extensive property such as χ. It is much more reasonable to scale the values of the χ indices in an appropriate manner and convert them to a set of intensive indices to be used in developing correlations for intensive properties.

The Greek letter ξ will be used for intensive values of connectivity indices. It is desirable, for consistency, to remain within the framework of graph theory, by only using quantities defined in terms of the hydrogen-suppressed graph. The number N of non-hydrogen atoms in the system (the number of vertices in the hydrogen-suppressed graph of the system) will therefore be used as the scaling factor in defining the ξ indices in terms of the χ indices ($\xi = \chi / N$). Each ξ, index has the same subscripts and superscripts as the corresponding χ index. The general form of the linear regression correlating an extensive property with χ-type indices is given by Equation (7), while Equation (8) shows the general form of the correlation for an intensive property with ξ-type indices.

$$\text{(Extensive property)} \approx \Sigma(a\chi) + \text{(extensive structural parameters, and atomic or group correction terms)} \tag{7}$$

$$\text{(Intensive property)} \approx \Sigma(b\xi) + \text{(intensive structural parameters, and atomic or group correction terms)} + c \tag{8}$$

3. RESULTS AND DISCUSSION

The interactions of materials with electromagnetic fields are described by their optical and electrical properties. The complex dielectric constant, ε^*, complex refractive index, n^*, refractive index n, absorption index K, and real (storage) and imaginary (loss) components ε' and ε'' of ε^* are interrelated as follows:

$$\varepsilon^* = \left(n^* \right)^2 \tag{9}$$

$$n^* = n \cdot \left(1 - i \cdot K \right) \tag{10}$$

$$\varepsilon' = n^2 \cdot \left(1 - K^2 \right) \tag{11}$$

$$\varepsilon'' = 2n^2 \cdot K \tag{12}$$

The refractive index at room temperature (298 K) can be evaluated as follows:

$$n(298K) \approx 1.885312 + 0.024558 \cdot \cdot \left(17 \cdot {}^0\chi^v - 20 \cdot {}^0\chi - 12 \cdot {}^1\chi^v \cdot 9 \cdot N_{rot} + N_{ref} \right) / N \tag{13}$$

where: N_{rot} is the number of rotational degree of freedom; N_{ref} – the correction index.

$$N_{ref} \equiv -11N_F - 3N_{(\text{Cl bonded to aromatic ring atoms})} + 18N_S + \\ +9N_{fused} + 12N_{HB} + 32N_{(\text{Si-Si bonds})} \quad (14)$$

The refractive index of the polystyrene matrix determined using equation (13) is 1.604 and its dielectric constant (as results from Maxwell equation (9)) is 2.57.

The Young modulus (E(T)) and shear modulus (G(T)) are determined from expression (15):

$$E(T) = 2G(T)\cdot\left[1+\upsilon(T)\right] = 3B(T)\cdot\left[1-2\upsilon(T)\right] \quad (15)$$

where $B(T)$ is the bulk modulus and $\upsilon(T)$ is Poisson's ratio. For polystyrene at room temperature $\upsilon(T)$ is 0.360, $B(T)$ is 3.572 GPa and $G(T)$ is 1100 MPa.

The thermal conductivity of polystyrene, λ, is calculated using relation (16), resulting a value of 0.135 W/mK:

$$\lambda = 0.135614 + 0.126611\cdot{}^1\chi^{BB}/N + \\ +0.108563\cdot(N_N + N_0 - 0.125\cdot N_H)/N \quad (16)$$

where the subscripts refer to the chemical elements.

For the determination of the physical characteristics of polystyrene/AlN nanocomposites the series and parallel approaches are applied. The two basic models representing the upper bound and the lower bound for some properties of composites are the rule of mixture and the so-called series model, respectively. In the rule of mixture model, also referred to as the parallel model, each phase is assumed to contribute independently to the overall conductivity, proportionally to its volume fraction. The parallel model maximizes the contribution of the conductive phase and implicitly assumes perfect contact between particles in a fully percolating network.

$$\text{Property}_{(\text{composite})} = \text{Property}_{(\text{matrix})}\cdot V_{(\text{matrix})} + \\ + \text{Property}_{(\text{filler})}\cdot V_{(\text{filler})} \quad (17)$$

where V represents the volume fraction.

On the other hand, the basic series model assumes no contact between particles and thus the contribution of particles is confined to the region of matrix embedding the particle. The conductivity of composites accordingly with the series model is predicted by equation (18):

$$\text{Property}_{(\text{composite})} = \\ = \frac{1}{(V_{(\text{matrix})}/\text{Property}_{(\text{matrix})}) + (V_{(\text{filler})}/\text{Property}_{(\text{filler})})} \quad (18)$$

Knowing that the dielectric constant of AlN is 9, the elastic modulus is 330 GPa and the thermal conductivity is 285 W/mK the corresponding properties are determined using the above approaches. As observed in Figure 1 the parallel model leads to higher values of estimated properties comparatively with the series one.

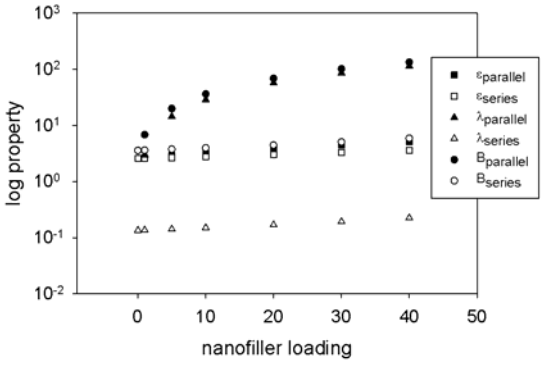

Fig.1. Dependence of some properties of nanocomposites on the AlN content as determined from the parallel and series models.

4. CONCLUSIONS

The physical properties of polystyrene/aluminum nitride nanocomposites are determined using different approaches: connectivity indices formalism for the matrix and parallel and series models for the reinforced polymer. The addition of AlN leads to the enhancement of thermal conductivity and mechanical modulus, recommending the studied samples for high power electronic applications.

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