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Thermal properties of silicon powder filled high-density polyethylene composites

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ABSTRACT

Thermal conductivity and coefficient of thermal expansion (CTE) of silicon particulates reinforced high-density polyethylene (HDPE) composites are reported. Composite samples were fabricated by mixing the components in proper volumetric ratio, molding and hot pressing. Incorporation of Si powder in HDPE enhances both the thermal stability and the effective thermal conductivity of the composites. CTE of the composites display substantial reduction with increasing Si content in HDPE, while with increasing temperature CTE increases linearly. Effective thermal conductivity for HDPE containing 20-volume fraction (%) Si becomes double than that for unfilled HDPE. Results on both the effective thermal conductivity and CTE of the composites have been discussed in light of various theoretical models. Our analysis confirms that the effective thermal conductivity of HDPE/Si composites is predicted extremely well by the model proposed by Agari et al. and conductive channels are not easily formed in HDPE/Si composites. We also show that CTE data could be successfully explained taking into account the role of the interphase volume and the strength of the polymer–filler interactions.

1. Introduction

With miniaturization of microelectronics and associated increase in power densities, thermal management has become a critical issue to achieve sustained device performance and their lifetime [1]. Polymer filled with appropriate fillers having improved thermal conductivity offers possibilities of its applications as heat sinks in electronic packaging [2]. In addition, thermally conductive polymer composites are advantageous due to their enhanced chemical resistance, processability and non-corrosive nature. Polymer composites can offer a varied combination of properties, which cannot be achieved by a single element. Investigations on the thermophysical and mechanical properties of polymers containing various kinds of fillers have been widely reported [3–7] and it is now known that the thermal properties of particles filled polymers is a complex function of their geometry, thermal conductivity of different phases, distribution in the matrix and contact between the particles. Further, the physical properties of polymer composites can be tailored according to the need by reinforcing the polymer with different kind of fillers and their amount in polymeric matrix. Though, many theoretical and empirical models have been proposed to predict the thermophysical properties of particulate composites, the accurate prediction of the effective thermal conductivity still remains a challenge and consequently measurement of thermal conductivity of the composites is important. The metal–polymer and/or, ceramic–polymer composites are widely used in electronic packaging of integrated circuits, in which polymer films act as the interlayer dielectrics. Heat dissipation problems are very critical now a days due to the miniaturization and the increase in power density of integrated circuits. Consequently, the CTE mismatch in materials adjacent to each other tends to become a major source of failure in microelectronic devices [8]. Typically, thermal expansion coefficient of an electronic device composed of silicon is about $4 \times 10^{-6}/{}^\circ\mathrm{C}$, while that of polymer is about $50\text{–}100 \times 10^{-6}/{}^\circ\mathrm{C}$. One of the most effective approaches to improve the CTE of a polymer is the addition of particulate inorganic filler material with low CTE. Usually, higher loading of fillers is required to decrease the CTE of the polymer. Fillers generally incorporated for control of CTE of elastomers, include mica, chalk, kaolin, carbon black and glass fibers [9,10]. Iyer et al. [11] recently reported significant reductions in CTE for boron nitride elastomeric composites as compared to pure elastomers. High-density polyethylene (HDPE) is one of the most widely used commercial polymers, because of its superior mechanical and physical properties. However, its toughness, weather resistance, and environmental stress cracking resistance are not good enough which limited its application in many high-technology areas. Reinforcing HDPE with fillers (viz., aluminum and copper particles, short carbon fibers, carbon, graphite, aluminum nitrides and magnetic particles) has been found to improve its properties. Tavman and co-worker [12] reported a significant improvement of thermal conductivity of HDPE containing 33% by volume of aluminum particles and more recently, Sofian et al. [13] and Kuriber and Alam [14] also observed a moderate enhancement in the effective thermal

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conductivity of metal powder and aligned carbon nanoscale fibers filled in HDPE and polypropylene, respectively.

Silicon being the primary material used in microelectronic devices, use of Si-based polymer composite as material for electronic packaging material is expected to reduce appreciably the problems associated with thermal mismatch in the device. It may be noted that relatively large thermal conductivity (~140 W/mK) and very low CTE of silicon are favorable for the above applications. In the present communication, we report our results on the use of silicon powder as a filler material to enhance the effective thermal conductivity and to reduce the coefficient of thermal expansion of high-density polyethylene (HDPE). Results obtained have been discussed and analyzed in light of various theoretical models.

2. Theoretical models

2.1. Models on thermal conductivity of composites

The effective thermal conductivity of a composite material is dependent on several factors, viz., filler concentration, particle size and shape, and homogeneity of the dispersed phase in the matrix, the thermal conductivity of different phases and contact between the filler particles, etc. The review and derivation of these models are out of the scope of the present study and only a brief summary for the background of the equations is given. Over the years, numerous theoretical models have been reported to predict the precise value of the thermal conductivity of two phase and multiphase composites. By solving Laplace's equation and assuming absence of any interactions between the filler particles, Maxwell [15] calculated the effective thermal conductivity of a random distribution of spheres in a continuous medium which worked well for low filler concentrations. Starting with Maxwell model, Bruggeman [16] derived another exact model for the effective thermal conductivity, under different assumptions for permeability and field strength. However, the model failed to predict the measured data on AlN filled epoxy system [17]. Hamilton and Crosser [18] extended Maxwell's model to include an empirical factor n to account for the shape of the particles ($n = 3$ for spheres and $n = 6$ for cylinders). It may be noted that both Maxwell, nor, the Hamilton and Crosser model contains any dependence on particle size, and they also imply that the temperature dependence of the thermal conductivity is approximately the same as that of the base fluid. A useful theoretical model for high filler-loaded composites was first suggested by Meredith and Tobias [19], with a reasonable success [20]. Cheng and Vachon [21] assumed a parabolic distribution of the discontinuous phase in a continuous medium and determined the parabolic distribution constants by analysis, which was related to the discontinuous phase volume fraction. The effective thermal conductivity was then derived for the two-phase solid mixture. A semi-empirical model was reported by Lewis and Neilson [22], which was based on modification of the Halpin–Tsai equation [23,24]. Their proposition takes into account the effect of the shape and the orientation of the particle or, the type of packing for a two-phase system. The constant A, in their equation, takes care of the particle shape and how they are oriented with respect to the direction of the heat flow, while the type of packing is accounted by the term ϕ_m, For example, for randomly packed spherical particles, $A = 1.5$ and $\phi_m = 0.637$; where as for randomly packed aggregates of sphere or for randomly packed irregularly shaped particles, $A = 3$ and $\phi_m = 0.637$. This model has been reported to be more successful for low and medium filler-loaded composites (<20%). Agari and Uno [25] also proposed another semi-empirical model, which is based on the argument that the enhanced thermal conductivity of high filler-loaded composites originates from forming conductive channels or, chains of fillers. Their expression contains two parameters, C_1 and C_2, which respectively accounts for the effect of the crystallinity of the polymer and the ease in formation of conductive chains of fillers. The equations used in the present study to describe the effective thermal conductivity of polymer composites are given in Table 1.

2.2. Models on CTE of composite

Several theoretical or, empirical equations exist in the literatures to predict the thermal expansion coefficient of composites. Some of them are based on the theory of elasticity, some others uses mechanics of materials approach or, express a law of mixtures, and some try to match theoretical expressions to the experimental data by suitably defining the existing constants in these expressions. Amongst them, most widely used ones are, the rule of mixtures (ROM). In the absence of the interaction between the matrix and the fillers, the rule of mixtures [26] serves as the first-order approximation to estimate the CTE of composites. The rule of mixtures model was modified by Turner [27] to take into account of the mechanical interactions between materials in the composite [28]. Turner et al. derived the final equation (11) assuming the same dimensional changes with temperature for all the constituents present in the composite. Kerner [29] and Schapery [30] derived the CTE equations (12) and (13), respectively, considering simple spherical shape of the second phase. Schapery model, modified by Hashim [31] derived the bounds on effective thermal expansion coefficients of isotropic and anisotropic composites consisting of isotropic phases by employing extremum principles of thermoelasticity. Among these bounds for elastic constants, H–S bounds could cover most of the experimental data on elastic modulas [32,33]. Based on the experimental data, Thomas [34] and by Chen et al. [35] suggested purely empirical equations (16) and (17), respectively. Recently, Vo et al. [36] proposed a novel microscopic model for predicting the effective CTE of underfills and other polymeric composites by considering the effect of an interface zone surrounding the filler particles in a polymer matrix. The model appears to resolve several conflicts associated with the effect of filler concentration, filler size and shape, and the filler–polymer interaction on the effective CTE of polymeric composite materials.

3. Experimental

3.1. Composites preparation and characterization

HDPE/Si composite for the present studies are prepared using commercial grade high-density polyethylene (HDPE) powder (density of 0.94 g/cm^3) and fine Si powder (density 2.3 g/cm^3) obtained from Loba Chemicals (India). Si powder used in the present investigation is approximately spherical in shape and particle size between 5 and 10 μm. Various volume concentration of Si powder is mechanically mixed with appropriate amount of HDPE powder for 30 min. Calculated amount of xylene is then added and the mixture is slowly heated to about 70 °C for about 2 h. The heating is accompanied with vigorous stirring of the viscous fluid mixture to ensure a homogeneous distribution of Si powder. Heating and stirring is continued till xylene is completely evaporated. The resultant homogeneous mixture of HDPE and Si is then slowly cooled to room temperature. Pieces cut from the solidified HDPE–Si mixture is transferred to a stainless steel die and subjected to hot compression molding at 120 °C. After cooling and complete solidification under pressure, the HDPE/Si composite sample is carefully taken out of the die. Typical size of the HDPE/Si composite prepared for the thermal conductivity measurements was 35 mm long and 25 mm diameter.

Typical XRD patterns of HDPE composites containing 7 and 10 vol.% Si are shown in Fig. 1a and b. Using Debye–Scherer equa-