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 impor-

tant. 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 $4 \times 10^{-6}/°C$, while that of polymer is about $50–100 \times 10^{-6}/°C$. 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-

Table 1
Model predictions for the effective thermal conductivity of particle filled polymers.

Model	Prediction	
Maxwell [15]	$k_c = k_m \dfrac{k_f + 2k_m + 2\phi(k_f - k_m)}{k_f + 2k_m - \phi(k_f - k_m)}$	(1)
Bruggeman [16]	$(1-\phi) = \dfrac{(k_f - k_c)(k_m/k_c)^{1/3}}{(k_f - k_m)}$	(2)
Hamilton and Crosser [18]	$k_c = \dfrac{k_f + (n-1)k_m + (n-1)(k_f - k_m)\phi}{k_f + (n-1)k_m - (k_f - k_m)\phi} k_m$	(3)
Meridth and Tobias [19]	$\dfrac{k_c}{k_m} = \dfrac{2(2+k_f/k_m) - 2(1 - k_f/k_m)\phi}{2(2+k_f/k_m) + (1 - k_f/k_m)\phi} \times \dfrac{(2-\phi)(2+k_f/k_m) - 2(1-k_f/k_m)\phi}{(2-\phi)(2+k_f/k_m) + (1-k_f/k_m)\phi}$	(4)
Cheng and Vashon [21]	$\dfrac{1}{k_c} = \dfrac{1}{\sqrt{C(k_f - k_m)}(B(k_f - k_m))} \ln \dfrac{\sqrt{k_m + B(k_f - k_m)} + B/2\sqrt{C(k_f - k_m)}}{\sqrt{k_m + B(k_f - k_m)} - B/2\sqrt{C(k_f - k_m)}} + \dfrac{1 - B}{k_m}$ where, $B = \sqrt{\dfrac{3\phi}{2}}$ and, $C = -4\sqrt{\dfrac{2}{3\phi}}$	(5)
Lewis and Nielsen [22]	$k_c = k_m \dfrac{1 + A\beta\phi}{1 - \beta\psi\phi}$, where $\beta = \dfrac{k_f/k_m - 1}{k_f/k_m + A}$ and $\psi = 1 + \dfrac{1 - \phi_m}{\phi_m^2}\phi$	(6)
Agari and Uno [25]	$\log k_c = \phi C_2 \log k_f + (1 - \phi) \log(C_1 k_m)$	(7)

k_c, k_m and k_f are the thermal conductivity of the composites, polymer and filler, respectively. φ is the concentration of the added filler; ϕ_m is the maximum packing fraction of the dispersed particles, A is a constant depends on the shape and orientation of the dispersed particles, C_1 is a factor influencing the effect of crystallinity of the polymer; C_2 represents ease in formation of the conductive chains of the filler particles.
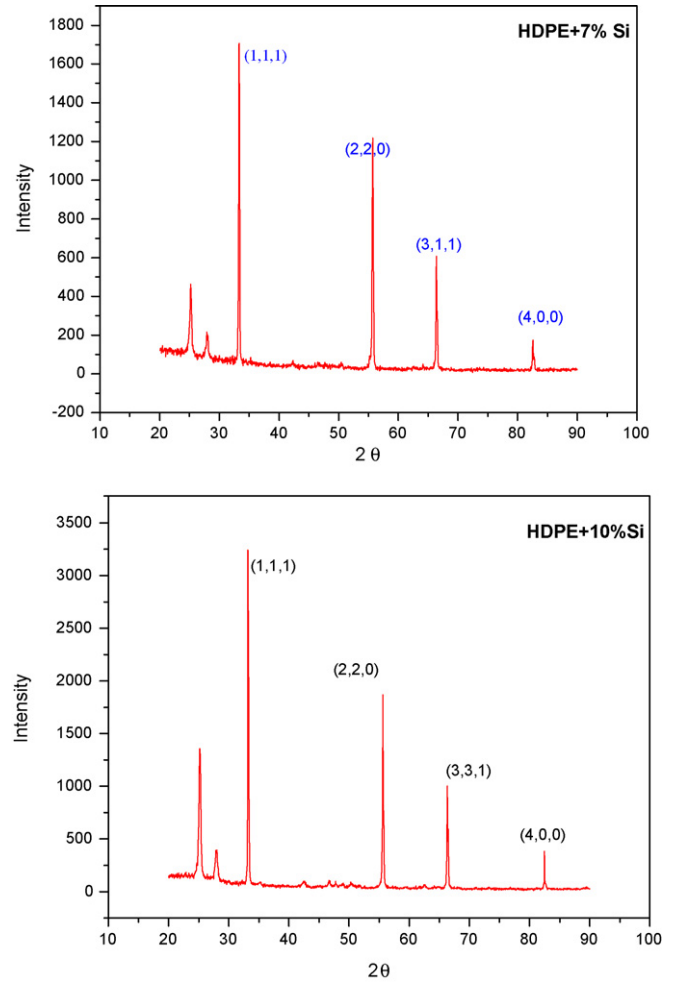

Fig. 1. Typical XRD patterns for HDPE/7 vol.% Si and HDPE/10 vol.% Si composites.

tion corresponding to the most intense peak, the average crystallite sizes of the filler are estimated to be ~10 μm. Fig. 2a and b is two typical scanning electron micrographs of the prepared composites. SEM photographs show that the Si fillers are mostly spherical in shape and are distributed fairly uniformly in the HDPE matrix.

Thermo-gravimetric analysis of the prepared composites is performed in nitrogen atmosphere using PerkinElmer Pyris Diamond DTA/TGA Analyzer between 45 and 650 °C, with a heating rate of ~10 °C/min. TGA curves of pure HDPE and HDPE composites with different silicon loadings are shown in Fig. 3. The temperature at which sample looses 35% of its weight of given composites (T_{35}) is taken as measure of thermal stability of the composites. It may be seen that the thermal decomposition of all the composites occurs mostly between 300 and 500 °C. It is apparent from Fig. 3 that Si loading in HDPE enhances the thermal stability of the composites. Observed increase in thermal stability is thought to be due to the restriction of mobility of segmental movement of HDPE, due to the enhanced interaction between Si and the polymer matrix.

3.2. Measurement of thermal conductivity

Effective thermal conductivity of HDPE–Si composites is measured by a 30 mm long duel needle sensor (SH-1), which is coupled to the thermal properties analyzer (model KD2 Pro, Decagon Device, Inc). KD2 Pro thermal analyzer is based on transient hot wire method, which has the advantages of convenience, ease of construction, accuracy and short measurement time. The duel nee-
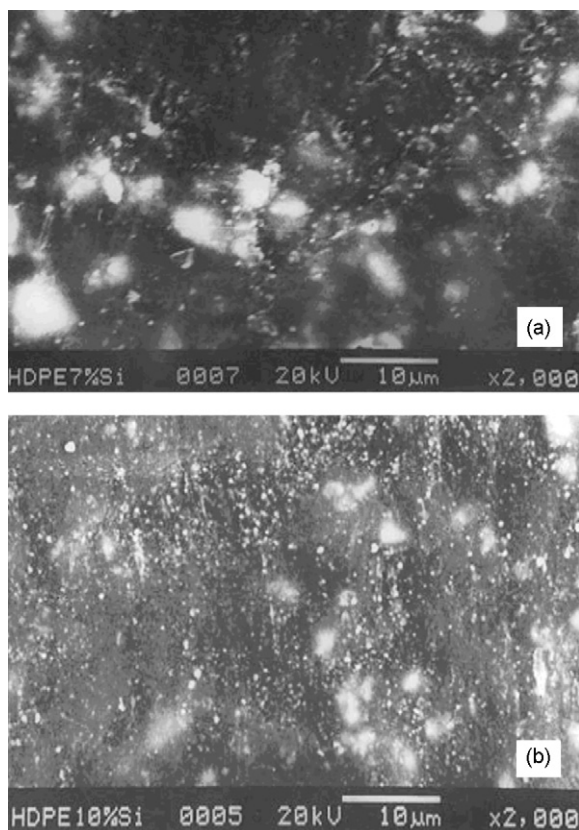
Fig. 2. Typical SEM micrographs for HDPE/7 vol.% Si and HDPE/10 vol.% Si composites.

dle probe (SH-1) consists of two parallel needles spaced 6 mm apart. One needle contains a line heat source and the other a thermocouple. The probe (SH-1) is buried in the homogeneous material (sample) and the heater is excited to produce a constant heat output per unit length. Temperature distribution in the material depends on the thermal properties of the material. Rise in temperature with time is recorded by the temperature sensor located 6 mm away from the heat source. When a quantity of constant heat flux per unit wire length q (w/m) is applied to the line heat source over a period of time, the temperature rise at distance, r from the heat

Fig. 3. TGA curves of HDPE/Si composites.

source is given by [37]:

$$\Delta T(r, t) = -\frac{q}{4\pi\kappa} Ei\left(\frac{-r^2}{4at}\right) \quad 0 < t \le t_1 \tag{8}$$

where, k and a is the thermal conductivity and diffusivity of the medium, respectively, t_1 is the heating time and Ei is the exponential integral. The decrease in temperature after the heat is turned off is given by:

$$\Delta T = -\frac{q}{4\pi k}\left[-Ei\left(\frac{-r^2}{4at}\right) + Ei\left(\frac{-r^2}{4a(t - t_1)}\right)\right] \quad t > t_1 \tag{9}$$

Thermal conductivity (K) of the composite is determined by fitting the time-temperature data during heating to Eq. (8), and to Eq. (9) during cooling. Thermal conductivity at 300 K for each sample is measured at least five times and the mean value is recorded. Overall uncertainty in the measurement of thermal conductivity is ~3%.

3.3. Measurement of coefficient of thermal expansion (CTE)

CTE measurement on the prepared samples were performed between 30 and 100 °C at 5 °C/min using Thermo Mechanical Analyzer (TMA) (M/S, PerkinElmer, Diamond TMA). The average dimension of the sample used for TMA was 5 mm × 5 mm × 5 mm. TMA measures linear or volumetric changes in the dimension of the material as a function of time, temperature, or force. The coefficient of thermal expansion was determined from the slope of the plot between thermal expansion and temperature by using TMA data analysis software.

4. Results and discussions

4.1. Thermal conductivity of HDPE–Si composite

Thermal conductivity of HDPE/Si composites at room temperature as a function of filler (Si) concentration is shown in Fig. 4a. It is seen that with the increase in filler loading, the effective thermal conductivity of the composite increases. Effective thermal conductivity of 0.833 W/mK is achieved for HDPE containing 20-vol.% Si, which is more than double of pure HDPE. The enhancement in the effective thermal conductivity of HDPE/Si composites is expected, as the thermal conductivity of the filler (Si) is significantly higher ($K_{Si} = 140$ W/mK) than that of HDPE ($K_{HDPE} = 0.362$ W/mK). With the increase in volume content of silicon in HDPE, the interaction between Si particles increases and they come in contact with each other, resulting in the ease in transfer of heat and consequent enhancement of thermal conductivity. Fig. 4b shows the temperature dependence of the thermal conductivity of the composites. For all the filler contents in HDPE/Si composites, only a marginal decrease in thermal conductivity is observed between room temperature and 80 °C. The decrease observed in thermal conductivity with increased in temperature is expected due to the dominance of both phonon–phonon and phonon–electron scattering.

Measured effective thermal conductivity of the HDPE/Si composite and those predicted by the various models (Table 1) are plotted (Fig. 5a) over a wide range of filler content between 0 and 20%. Most of the models fail to predict the measured effective thermal conductivity of HDPE/Si composites over the entire range of filler concentration used in the present study. It may be noted that Maxwell, Bruggeman and Russell equations largely over estimate the experimental data over the entire range of filler concentration, while Hamilton Crosser model (with $n = 3$, spherical shape of fillers) severely under estimates the effective thermal conductivity. Geometric mean model as well as Meredith equation predicts fairly well the effective thermal conductivity only for very low concentration of Si in HDPE. Meredith and Tobias model [19], which is based on the
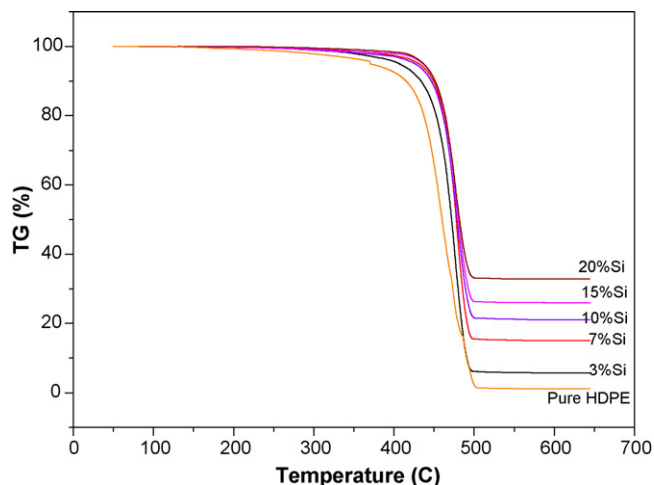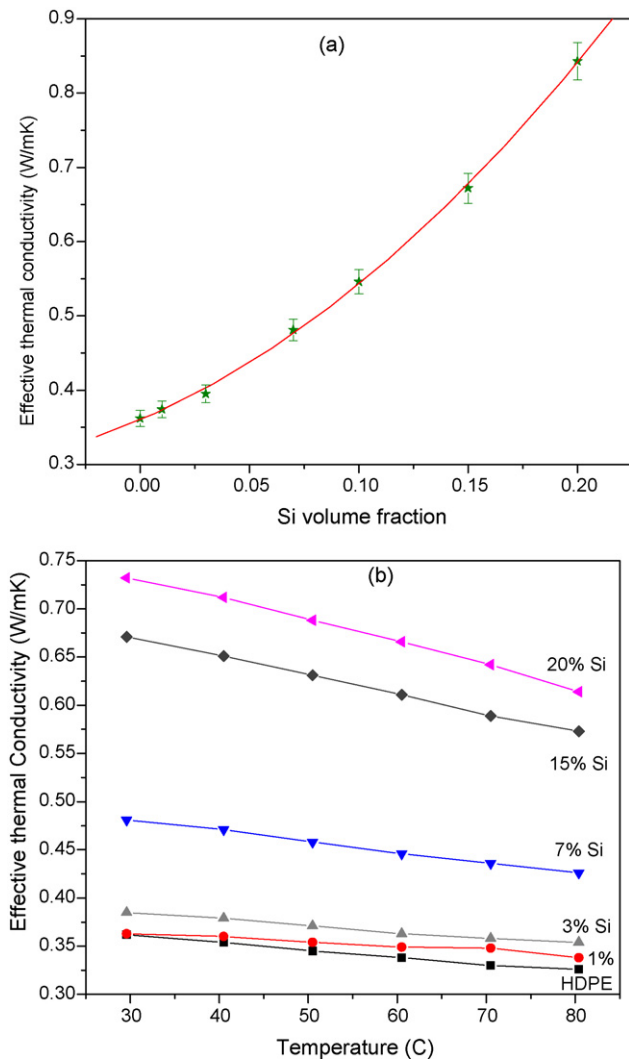
Fig. 4. (a) Room temperature effective thermal conductivity of HDPE/Si composites as a function of Si content. (b) Temperature dependence of the effective thermal conductivity of HDPE/Si composites.

generalization of models for parallel and series conduction in composites usually, predicts the thermal conductivity of composites with high conductivity fillers and for high filler content. However, in the present case, thermal conductivity calculated by Geometric mean and Meredith equations for composites with high filler concentration (>5 vol.%) of Si gives ∼40% higher and ∼30% lower effective thermal conductivity compared to the measured values, respectively. It may be pointed out that Cheng-Vashon model [21] is derived for composites with $k_f/k_m > 100$. However, our analysis shows that even with $k_f/k_m \sim 380$ (for HDPE/Si), satisfactory agreement with the measured data is achieved only up to ∼15 vol.% Si and at higher filler concentration it largely over estimates the effective thermal conductivity. As is evident from Fig. 5b, models proposed by both Neilson and co-worker [22] and Agari and co-worker [25] predicts well the effective thermal conductivity of the present composite over the studied range of filler concentration. Neilsen equation (6), which takes into account the shape and orientation of the dispersed medium, predicts our data more closely for $A = 3$ and $\varphi = 0.74$. This indicates that the dispersed phase in the composite are randomly oriented aggregates of spherical particles with hexagonal close/face centered cubic type of packing. It is interesting to note from Fig. 5b that Agari and Uno model [25] also predicts extremely well ($\chi^2 = 8 \times 10^{-5}$), the effective thermal
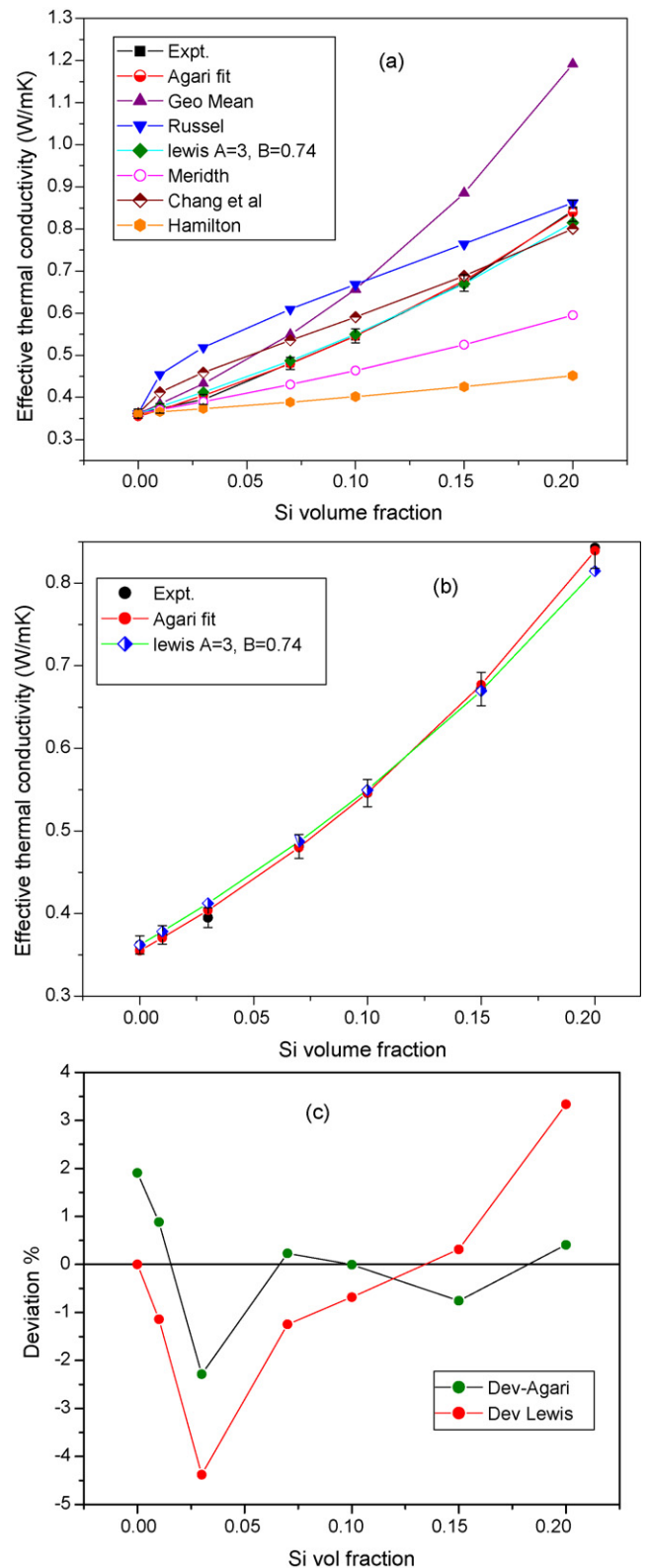

Fig. 5. (a) Comparison between the measured and predicted values of effective thermal conductivity in terms of various models. (b) Effective thermal conductivity of HDPE/Si plotted with the predicted values using Eqs. (6) and (7). (c) Deviation (%) ($= ((k_{measured} - k_{calculated})/k_{measured}) \times 100$) vs. Si volume fraction.

conductivity of the HDPE/Si composite in the whole range of Si concentration (0–20 vol.%). The situation becomes clear from Fig. 5c, where deviation (%) from the measured thermal conductivity has been compared for both Neilson and Agari models. As seen from Fig. 5c, thermal conductivity of HDPE/Si composites calculated from Agari et al. model [25] fits the measured data to better than 2% both for lower and higher concentration range. The values of the parameters C_1 and C_2 obtained from the best fit of Eq. (7) are 0.98092 and 0.66116, respectively. According to Agari and Uno, the parameters C_1 and C_2 should be in between 0 and 1. The parameter C_1 obtained from the fit is close to 1, which indicates that the introduction of Si into HDPE does not have any effect on the crystallinity of the polymer. Further, the closure C_2 values are to 1; more easily the conductive chains/channels are formed in composites. It may be noted that, depending on the dispersion state of the particulates, the thermal conductivity of the composites may be different, even if the composition of the composites is same. Zhou et al. [38] reported that composites with smaller particle size of the filler give higher value of C_2. This is because a better state of filler dispersion can be achieved in smaller particles reinforced composites compared to the larger particles and formation of conductive channels in smaller particles filled composites is more likely [39,40]. However, in the present composite, the average filler size is ~10 μm and the value of C_2 (viz., 0.66116) obtained from the fit indicates that the conductive channels/chains are not easily formed in HDPE/Si composites. This is in agreement with the observations of Zhou et al. [38] on HDPE/BN composites, prepared with filler (BN) of various sizes.

4.2. CTE of HDPE–Si composites

Coefficient of thermal expansion (CTE) of HDPE/Si composites have been measured both as function of volume fraction of the filler concentration and temperature. Fig. 6a shows the variation of (CTE) of the composites with various filler loading at different temperatures between 40 and 100 °C. It is seen that for all compositions CTE steadily decreases with Si volume fraction (%). The temperature dependence of CTE for composites with different filler concentration is shown in Fig. 6b. CTE of all the studied composites increases linearly with temperature. However, the slope of the dimensional change versus temperature becomes shallower for the entire temperature interval as the reinforcement volume fraction increases from 3% to 20%. As is expected, the composite with higher filler loading shows consistently lower CTE values than the composites with lower filler concentration. Compared to the CPE of pure HDPE, CTE of HDPE composite with 0.2 Si concentrations decreases by more than an order of magnitude at around room temperature. The decrease in CTE of the composites depends on the difference between the CTE of the polymer matrix and the filler particles. In the present case, the filler (Si) particle has a very low CTE value (4.1×10^{-6}/°C) as compared to HDPE (~100×10^{-6}/°C). The reduction of CTE is, however, also influenced by the strength of the interfacial adhesion between the matrix and the filler.

Fig. 7 shows the comparison of the experimental CTE with the values calculated by various models (Table 2). It is seen that most of the models display significant deviations from the measured data. The primary reason for the observed deviation lies on the fact that thermal expansion of the composite is influenced by several factors that could not be fulfilled by any single model. The rule of mixtures (ROM), which is widely used for the calculation of the effective CTE of the composite, fails to predict the measured CTE in the present case. It may be noted that estimation of CTE based on Turner model [27] significantly under-predicts the measured CTE values of the HDPE/Si composites. Turner model [27] predicts fairly well the CTE of composites, only when bulk modulus of both filler and the matrix are of comparable magnitude. In the present

Table 2
Model predictions for the coefficient of thermal expansion of particle filled polymers.

Model	Prediction	
Rule of mixture (ROM) [26]	$\alpha_c = \alpha_m(1-\phi) + \alpha_f\phi$	(10)
Turner model [27]	$\alpha_c = \dfrac{(1-\phi)K_m\alpha_m + \phi K_f\alpha_f}{(1-\phi)K_m + \phi K_f}$	(11)
Kerner model [29]	$\alpha_c = \alpha_m(1-\phi) + \alpha_f\phi + [\phi(1-\phi)(\alpha_f-\alpha_m)] \times \dfrac{K_f - K_m}{(1-\phi)K_m + \phi K_f + (3K_f K_m/4G_m)}$	(12)
Schapery's model [30]	$\alpha_c = \alpha_f + (\alpha_m - \alpha_f)\dfrac{1/K_c - 1/K_f}{1/K_m - 1/K_f}$	(13)
	$K_c^{(-)} = K_m + \dfrac{(1/(K_f-K_m)) - ((1-\phi)/(K_m+(4/3)G_m))}{\phi}$ (lower bounds)	(14)
	$K_c^{(+)} = K_f + \dfrac{(1/(K_m-K_f)) - (\phi/(K_f+(4/3)G_f))}{1-\phi}$ (upper bounds)	(15)
Thomas model [34]	$\alpha_c^a = \alpha_m^a\phi + \alpha_f^a(1-\phi)$, exponent 'a' may vary from +1 to −1	(16)
Chen et al. model [35]	$\alpha_c = a\alpha_m \exp\left(-\dfrac{\phi}{b}\right) + (1-a)\alpha_m$; a and b are constants	(17)
Vo et al. model [36]	$\alpha_c = \dfrac{1}{1 + k_0\phi(1-\phi)}[\phi\alpha_f + (1-\phi)\alpha_m + k_0\phi(1-\phi)(\alpha_f + \alpha_m) + k_0\phi(1-\phi)k_1]$	(18)

α_c, α_m and α_f are respectively the CTE of the composite, polymer and the filler. ϕ: the filler volume fraction. K and G are the bulk and shear moduli; respectively and the subscripts m and f stands for matrix and filler, respectively. $K = E/(3(3 - E/G))$. K_0 reflects the matrix–filler interaction strength: K_1 is a measure of the temperature dependence of K_0. The shear modulus is calculated using the standard relationship.
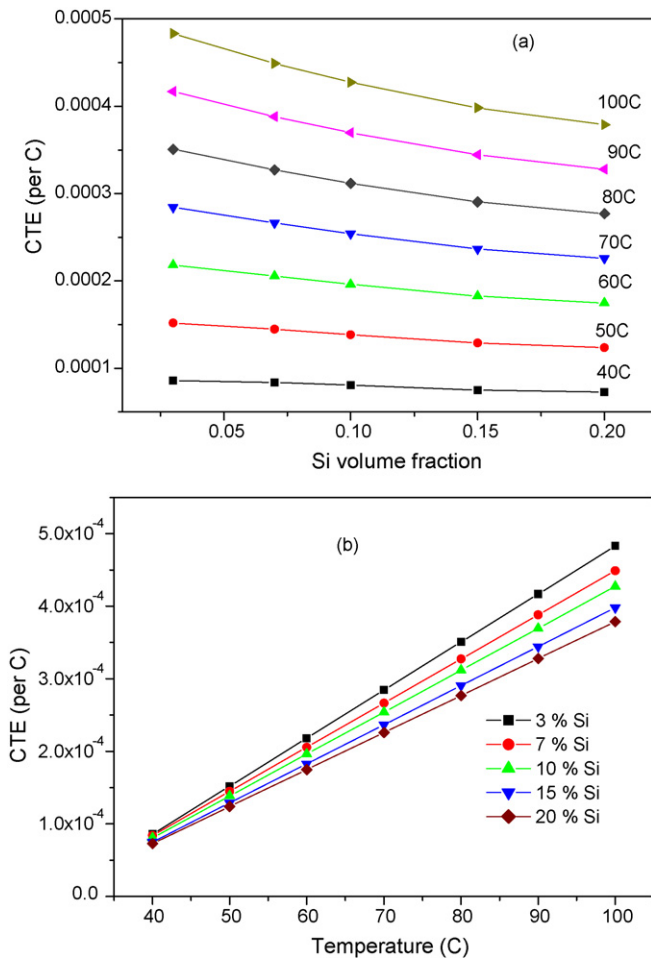
Fig. 6. (a) Effect of filler (Si) addition on the CTE of HDPE at various temperatures. (b) Temperature dependence of CTE of the HDPE/Si composites.

Fig. 7. (a) Comparison of measured CTE of HDPE/Si composites with. The predicted values in terms of various theoretical models. (b) CTE of the interphase ($\alpha_{\mathrm{interphase}}$) as a function of Si volume fraction calculated from Eq. (19).

composite, the bulk modulus of HDPE and Si are widely different (viz., HDPE = 1.46 GPa and Si = 113.33 GPa). Further, Turner model assumes homogeneous strain throughout the composite and each constituent is assumed to change dimensions with the temperature at the same rate as the composite; which may be not be the real situation for the present composite. Similarly, the expression derived by Kerner [29] fails completely to predict the measured CTE for HDPE/Si composites. It is seen that the measured CTE of HDPE/Si composites lies in between the lower and upper bounds predicted by Schapery model [30]. Hashim and Shtrikman [31] noted that when the bulk modulus, shear modulus and CTE of filler and matrix material are of comparable magnitudes, then only the upper and lower bound curves tend towards each other and they coincide if the above mentioned properties of filler and matrix are same. Since the moduli of Si are very large compared to those of HDPE, the bounds are far apart from each other and the experimental value lies in between the upper and lower bounds. Fig. 7 shows the measured effective CTE of HDPE/Si composite along with that calculated using the expression derived by Vo et al. [36]. It is also evident from Fig. 7 that the equation derived by Vo et al. is in excellent agreement ($\chi^2 = 5.7697\mathrm{E}{-}12$) with the experimental data. Vo et al. [36] modeled the effective CTE of a composite, taking into account the existence of interphase zone surrounding the filler particles in a polymer matrix. The parameter K_0 in Eq. (18) reflects strength of the filler–matrix interaction. For negligible interaction between matrix and filler K_0 tends to zero and a large positive value of K_0 indicates a strong polymer–filler interaction. The parameter K_0 is also sensitive to both the filler size, shape and the preparation conditions. It
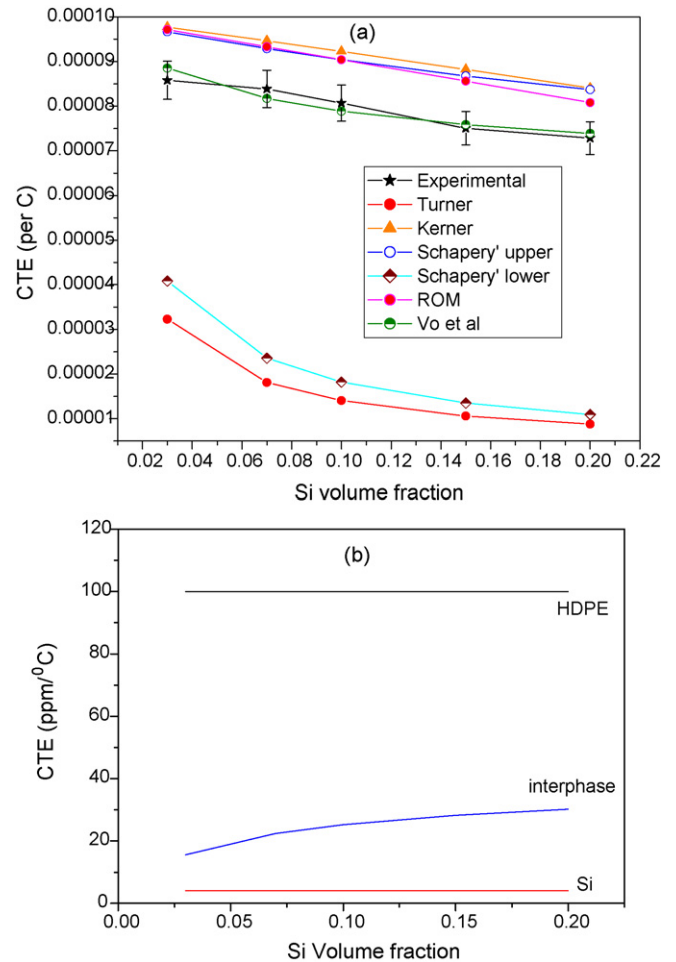
may be noted that for a given fraction of filler, a smaller filler particle size will have a larger fraction of interphase volume. The fitted parameters K_0 and K_1 obtained in the present case are 17.22561 and −0.00003, respectively. Positive and large K_0 obtained for the present composite indicates strong filler–matrix interactions, as well as, better interfacial adhesion between the filler and matrix. Using the fitted parameter K_1 and knowing the CTE of the filler, matrix and the composite, one can also estimate CTE value of the interphase as [36]:

$$\alpha_{\mathrm{interphase}} = k_1 + \alpha_m + \alpha_f - \alpha_c \tag{19}$$

Fig. 7b shows the CTE value of the interphase as a function the filler volume fraction in the present composites calculated from Eq. (19). Thus, compared to all other models, the model proposed by Vo et al. [36], achieves an excellent agreement to the experimental data and thereby confirms the importance of the role of the interphase volume and the strength of the matrix–filler interactions for successful prediction of CTE of polymer composites.

5. Conclusions

Effective thermal conductivity and coefficient of thermal expansion (CTE) of HDPE/Si composites are reported as a function of Si content between 0 and 20 vol.%. Composite samples were prepared by mixing, molding and hot pressing. The prepared composites show fairly uniform distribution of the nearly spherical particles of Si in the polymer matrix. TGA analysis confirms that incorpora-

tion of Si in HDPE increases the thermal stability of the composite. Thermal conductivity of HDPE is found to be a sensitive function of Si content. Effective thermal conductivity of HDPE/Si composite increases with increasing Si content and at 20 vol.% of Si effective thermal conductivity becomes more than twice than that for pure HDPE. Analysis of the thermal conductivity of HDPE/Si composites confirms that some of the models proposed to predict the effective thermal conductivity of a composite in a two-phase system could not be applied to HDPE/Si composites, such as, Geometric mean, Maxwell, Bruggeman, Russell, Meridth, Cheng-Vashon and Lewis–Neilson equations. We find that only the model proposed by Agari et al. predicts correctly, the measured effective thermal conductivity of the composites over a wide range from 0% to 20% volume content of Si. Analysis further indicates that the conductive channels/chains are not easily formed in HDPE/Si composites. The coefficient of thermal expansion of the composites shows strong dependence on both the filler loading and temperature. Comparison of the CTE computed with various models confirms that only the model proposed by Vo et al. [36], which considers the influence of interphase volume within the polymeric composite and also the strength of matrix–filler interactions, predicts very well the measured data. Summing up, improved thermal stability, enhanced effective thermal conductivity and significant reduction in CTE shown by HDPE/Si composites should be attractive for electronic packaging applications.

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