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Enhanced Thermal Stability and Thermophysical Properties of High Density Polyethylene Based Polymer Composite Synthesized Through Compression Moulding Route

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Abstract

Polymer composite materials attract researchers as polymers can be filled with different fillers to get desired properties. Thermophysical properties of HDPE-silicon composite is reported in the present study. HDPE-Si composite was synthesized by hot compression and molding technique for different silicon volumetric ratio. Thermal conductivity as well as thermal diffusivity was found to be enhanced significantly on increasing the filler volumetric ratio. Thermal conductivity value for 20 volume % composite was more than twice of the pure HDPE (0.364 W/m-K for pure HDPE and 0.733 W/m-K for 20 volume % composite). Thermal diffusivity value of 20 volume % composite ($0.518\ mm^2/s$) was also more than double than that of the pure HDPE ($0.224\ mm^2/s$). TGA analysis of composite showed a substantial increase in thermal stability from 414°C (for pure HDPE) to 454°C (for 20 volume % silicon). Thermophysical properties were also measured at elevated temperature from 30°C to 80°C for different volumetric ratio of filler. Both thermal conductivity and thermal diffusivity showed a gradual decrement on increasing the temperature. Adding more silicon to the HDPE caused a better adhesion between HDPE and silicon which improved the hardness of the synthesized composite.

Keywords: Compression moulding, Hardness, Polymer composite, Thermal conductivity, Thermal stability

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INTRODUCTION

With the advancement in modern electronic technology, the size of electronic instruments is reducing and at the same time the power of the electronic devices is increased. More number of circuits are being fabricated on the small substrate to decrees the size of the instrument. Higher performance is required from these small sized instruments, which involves fairly high current density for longer time duration [1]. This high current density flowing in a small micro sized circuit for a long time can cause a failure in the circuit which eventually is undesired. In the most of the micro-electronic systems thermal stress is the biggest reason for circuit breakdown. When the heat is allowed to pass through the circuit then there is a thermal stress because of the mismatch between the heat transfer properties between the circuit and the substrate on which the circuit is printed. Mismatch in coefficients of thermal expansion (CTE) causes the device towards

disrupted function. If the heat removal process is efficient these circuits and devices can be escaped from these sorts of issues. Therefore, heat dissipation is a significant and concern in electronic devices [2–5]. It is essential to take into account the thermal management of the electronic devices [6–8]. We need to take care of the amount of the heat which is generating in the circuit and have to find some mechanism which can extract out the excess heat. Heat transfer properties largely depend upon the thermophysical properties of the material. These properties clearly affect the performance of any electronic device [9–11]. Higher the thermal conductivity (TC) of the material, at a faster rate the heat-current can be taken out through it. It implies that materials with high TC and thermal diffusivity (TD) are appropriate for the heat removal process [1, 12].

Highlights
- Thermophysical properties of HDPE-Si at varying Si concentration are studied.
- Thermal conductivity & diffusivity values are doubled for Si volume fraction 0.2.
- Thermal stability improves significantly with rise in silicon volume fraction.
- Thermal conductivity & diffusivity reduces with rise in temperature.
- Thermophysical properties largely depend upon temperature & filler concentration.

In electronic packaging industry, materials with low electrical conductivity but high thermal TC values are in high demand due as the heat removal is a key issue for packaging materials. Polymers based materials nowadays are of very much interest because polymer based materials have the advantages like ease in processing, ease to molding, low cost, and low density [13]. Besides, polymers in general are non-reactive to chemical reagents and are free from corrosion which makes them attractive for many applications. Thermal properties of polymers are not suitable for them to be used as electronic packaging material because TC and TD values of the polymers are very low. However, polymers, if mixed with suitable fillers, give a very good thermal conductivity and thermal diffusivity [14–17]. To obtain material with high TC and low TD values along with poor electrical conductivity researchers have used different fillers like boron nitride, aluminum nitride, silicon carbide and alumina as filler in different polymer matrix [18–22]. Studies have revealed that the thermophysical properties of the polymer composite not only depend upon the properties of filler but these also are a function of shape, size, concentration and orientation of the filler materials. Many research papers have been published reporting the increased thermophysical properties of the polymer composite material with different polymer matrix and filler combination [7, 23–25]. These published researches have shown that the thermophysical properties of a polymer can be increased by adding filler with high thermal conductivity and diffusivity [25–28]. Hafieng Zhang et al. [29] experimentally obtained TC values of different polymer filler combination at room temperature and showed a significant rise in TC value for the synthesized polymer composite on high filler concentration. H.S. Tacke et al. [30] showed that the TD Value of fiber filler is higher than that of the spherical filler or plate shape filler for the low filler concentration. At higher concentration the TD Value of plate shaped fillers were found to be higher than spherical shaped fillers. Kruger and Alam [31] measured TD Value of aligned, vapor grown carbon nano scale fiber reinforced polypropylene composite in longitudinal and transverse directions and reported different values in different directions. Table 1 provides a summary on the thermophysical properties of different polymer composites used for different applications.

Table 1. Thermophysical properties of different polymer composites used for different applications

Polymer Matrix	Filler	Thermal Conductivity (W/m-K)	Applications	References
Epoxy	Boron Nitrate	6.07	Electronic Industry	[14]
Epoxy	Boron Nitrate Nanosheet	5.86	Electronic packaging	[15]
Rubber	AlN + CNT	0.502	Improve heat transfer network	[22]
Phenolic resin	M-Al_2O_3	4.01	Electronic devices	[32]
LDPE	Graphite	19.6	Electromagnetic Interference Shielding	[33]

Polydimethylsiloxane	Carbon fibers	6.04	high power devices	[34]
Oil Palm Shell	Copper	0.408	Electronic Packaging	[17]
Epoxy resin	Boron Nitrate	4.42	Electronic Packaging	[24]
Polyester	Graphene	2.5	Conductive Polymer	[35]

Mechanical strength of the material is also a significant parameter and it should be large if it the material is considered for the industrial application. Hardness basically determines the stiffness of a material [36–39]. The hardness is the measure of the material to resist the plastic deformation. Lower hardness implies that the material is prone to undergo the plastic deformation while higher hardness value is suggestive of a stronger material. Hardness is a local phenomenon as it generally explains the defiance towards the indentation of the particles within the material. Low values of hardness, however, are also advantageous as the low hardness of the materials (especially polymers) makes them flexible. This flexibility supports the molding of the materials into the desired shape. Hence hardness of a polymer should not be very high but it should carry an optimum value which provides a balance between the strength and the ease of synthesis and molding [40, 41]. Greater the hardness of the material, the greater resistance it has to deformation. Senol Sahin et al. [42] reported an improvement in the hardness of the polypropylene by addition of the filler to it.

Thermophysical properties of the synthesized HDPE-Si composite provided us the information related the heat flow. The rapidity of the heat flow i.e. thermal diffusivity and thermal conductivity both are will be helpful in selecting the electronic packaging materials. Other than this the data obtained from the present study can also be used in understanding the heat transfer mechanism in the polymer composites. The information and data collected in the present study may also be a help for the development of an empirical model to explain and realize the thermophysical properties and the heat transfer in polymer composites. This information may lead to the other constructive utilization of HDPE-Si composite too.

In the present work, we have synthesized the HDPE-Si composite using the hot compression technique. Volume filler fractions 0.01, 0.03, 0.07, 0.10, 0.15 and 0.20 are doped with HDPE matrix. Thermal stability, thermophysical properties and the hardness of the synthesized composite are measured and are discussed. High density polyethylene (HDPE) is a widely used in a number of applications. It is one of the most popular polymers. Due to its unique thermal, mechanical characteristics HDPE finds its applicability in many industrial applications. HDPE enjoys high ductility, toughness, large chemical-resistance, low permeability of water-vapor, very low water absorption and non-corrosive nature. Other than these characteristics higher flexibility as well as high strength makes it easy to process and mould [43–45]. These properties of HDPE make it a very attractive and useful for industries like, manufacturing, electronic packaging, construction, insulation etc. Most of the studies discussing the thermophysical properties of polymer-based composites usually use metals are metal based fillers (refer to Table 1), while the current study utilizes silicon as a filler. study on the thermophysical properties of HDPE-Si composite is the novelty of the current work. Use of silicon as filler will not only improve the thermophysical properties of composite but also it will produce a good match of coefficient of thermal expansion (CTE) between the circuit substrate and the circuit. This matching of CTE will reduce the thermal stress. The lowering of thermal stress will eventually lower the chance of equipment failure. This study further discuses thermal stability of HDPE mixed silicon composite. Moreover, silicon has larger thermal conductivity, mechanical strength, thermal stability and high electrical conductivity compared to HDPPE. These properties are favorable for the electronic packaging material. This study is focused on determination the suitability of HDPE-Si composite as an electronic packaging material.

EXPERIMENTAL METHOD
Sample Preparation
HDPE-Si composite for this investigation was prepared by using the commercial grade high density polyethylene in the powder form having the density 0.94 gm/cm^3 and powder of silicon supplied by

Chemica Loba (India) having the density 2.38 gm/cm^3. The silicon particles used were spherical in shape and were having the size of around 5–10 µm. Calculated amount of HDPE and silicon powder for different volumetric ratio was mixed mechanically for about 30 minutes. Appropriate amount of xylene was added to it and was heat treated at 70°C. The volume fraction of filler silicon was calculated using the formula provided in Eqn. 1. Table 2 provides the masses of the matrix and filler used for the preparation of these composites.

$$M_f = \frac{\rho_f}{\rho_m} M_m \, f \tag{1}$$

Where, M_f = Mass of filler (mass of silicon in the present case)

          M_m = Mass of matrix (mass of HDPE in the present case)

          ρ_f = Density of filler (density of silicon in the present case)

          ρ_m = Density of matrix (density of HDPE in the present case)

          f = Volume fraction of filler (volume fraction of silicon in the present case)

Table 2. Composition of HDPE and silicon in the samples

Filler fraction of silicon	Mass of HDPOE (g)	Mass of silicon (g)	Total mass of the composite (g)
0.01	50	1.266	51.266
0.03	50	3.798	53.798
0.07	50	8.862	58.862
0.1	50	12.660	62.660
0.15	50	18.989	68.989
0.2	50	25.319	75.319

During the heat treatment consistent and brisk stirring was ensured. This vigorous stirring was conducted to ensure a proper mixing of silicon particles in HDPE matrix. Heating was done until all the xylene evaporated out of the mixture which took about 2 hours. This Viscous gel was then cooled up to the room temperature slowly. The cooling should always be done slowly. The slow cooling provides proper settlement of all the particles within the matrix and chances of bubble formation are lowered. Once the samples were cooled it gets solidified. This solidified HDPE-silicon mixture was cut into small pieces and was fed to a cylindrical die. This mixture was then undergone through compression molding at 120°C at high pressure for 45 min. After cooling the mixture got solidified and was removed from the die carefully. The shape of the obtained composite sample was cylindrical. Its diameter was 24 mm. These samples were cut so as to make its height of 32 mm.

Sample Characterization
Elemental and Morphological Analysis
The instrument used for X-ray diffraction was a microprocessor controlled X-Ray Powder Diffractometer (PHILIPS Model PW1840) with Co K-alpha radiation (λ = 1.542Å) with a rate of 3°/minute between angles from 20° to 90°.

Morphological Analysis
PHILIPS XL-30/ESEM microscope was used to perform scanning electron microscopy (SEM) of the composite samples. The composite samples were exposed to a highly energetic beam with the operating voltage of 200 kV.

Thermogravimetric Measurements
Thermogravimetric analysis was carried out of the prepared samples to determine the thermal degradation behavior of the samples. Thermal degradation behavior is highly important especially when the sample is expected to be used in under elevated temperature conditions. If the thermal

degradation is very high, then thermal stability will be low and the material may not be suitable for the application at higher temperatures. Generally the volatiles, moisture and low molecular gasses present in the material vaporize with the rise in temperature and thus results in the thermal degradation. Perkin Elmer Pyris Diamond DTA/TGA Analyzer instrument was used to perform the Thermogravimetric analysis in the current study. All the samples were studied within the temperature range of 45°C to 650°C. Heating rate during the investigation was set to 10°C/min. Experiment was performed under N_2 atmosphere and N_2 flow rate was 100 ml/min.

Measurement of Thermal Conductivity and Diffusivity

The thermal conductivity and diffusivity measurement of the samples was performed by KD2 Pro (SH-1) dual needle TD Value analyzer, based on the transient hot wire (THW) technique. This THW method is proffered over the other methods for the thermophysical [properties determination as it is quick and more reliable. Moreover, the THW technique is more accurate as compared to other techniques.

This instrument consists of dual needle probe containing two needles of 30 mm length and separated by 6 mm. One of these two needles acts as a heat source and the other as a temperature sensor. This dual needle probe is inserted into the sample. A heat pulse is then given to the sample under investigation with the help of the heating probe. Temperature rise in the sample is measured by the sensing probe situated at 6 mm away from the heat source. The rise in the sample temperature will be a function of the thermophysical properties of the sample. The time vs. temperature profile within the sample is recorded in the instrument and then it is further processed to attain the thermal conductivity, thermal diffusivity and the heat capacity of the test sample. Figure 1 gives a schematic diagram for the principle of the measurement of thermophysical properties using THW technique.
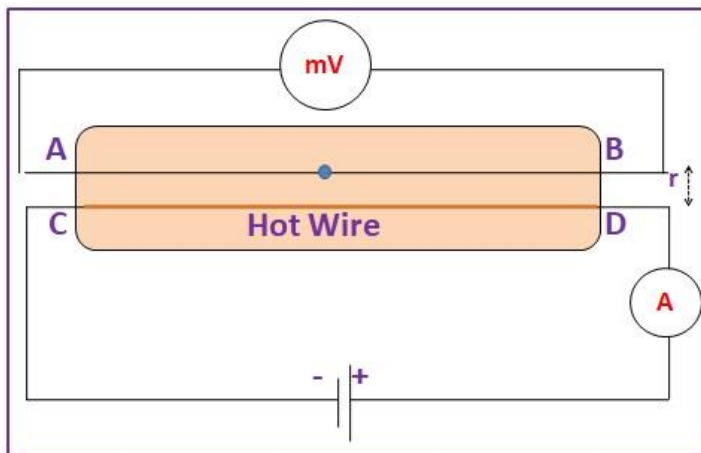

Figure 1. Schematic of principle of transient hot wire technique.

If q (in W/m) is amount of the heat is supplied to the sample in a definite time, then the enhancement in temperature (ΔT) at a distance r (in m) may be given by the Eqn. 2 [39].

$$\Delta T(r,t) = \frac{q}{4\pi\kappa} Ei(\frac{r^2}{4at}) \text{ for } 0 < t \le t_1 \tag{2}$$

Where,

κ is thermal diffusivity of the sample.

α is thermal conductivity of the sample.

Ei is the exponential integral.

t_1 is the heating time.

Further, the decrement in the temperature of the sample after the heat is turned off is given by Eqn. 3 [39]:

$$\Delta T = -\frac{q}{4\pi.k}[-Ei(\frac{-r^2}{4at}) + Ei(\frac{-r^2}{4a(t-t_1)})] \text{ for } t > t_1 \tag{3}$$

The time-temperature profile of the sample obtained from the experiment is fitted into the Eqn. 2 for the heating duration. The data obtained from the time-temperature profile during the cooling of the sample is fitted into the Eqn. 3. From these fittings thermal conductivity and thermal diffusivity of the sample was determined. It is important to bring into the notice that each sample was monitored three times to ensure the consistency and reliability of the data. Here the average values of those three values are reported here. Figure 2 represents a schematic of the device and the thermophysical properties measurement technique in the current study.
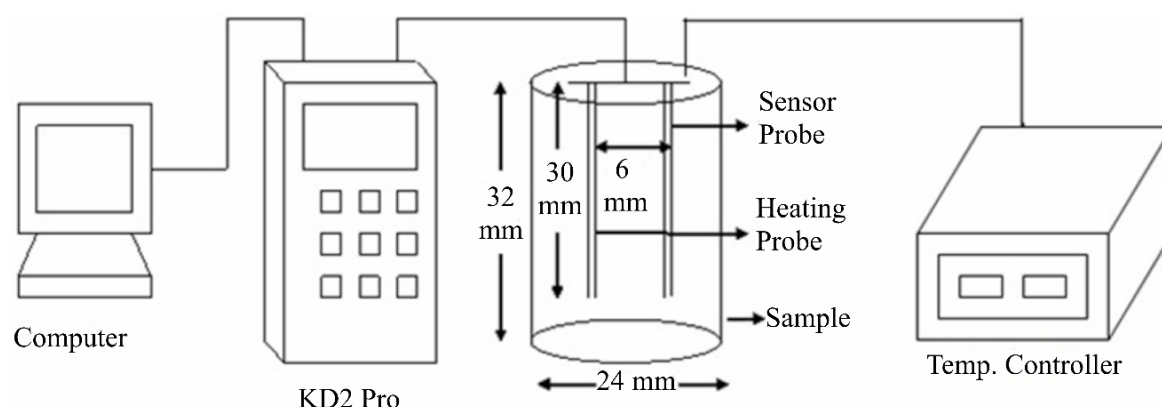

Figure 2. Schematic of the measurement set up for Thermophysical properties.

RESULT AND DISCUSSION

XRD Analysis

XRD pattern of 10 volume % and 20 volume % silicon samples are shown in the Figure 3 (a) and in Figure 3 (b). Both the RXD patterns are analogous in nature. The peak matching was carried out using the available data and a detailed analysis of these peaks was carried out. Most intense peak in the XRD pattern was observed for the 2θ value 33.3⁰. Other peaks after the most intense peak were observed for the 2θ values corresponding to 25.3⁰, 28.2⁰, 55.65⁰, 66.35⁰ and 82.55⁰. The peaks corresponding to 2θ = 25–30⁰ correspond to the oxides formed within the material. Silicon present in the composite may react with the oxygen and it may produce silica. The peaks observed at 25.3⁰ and 28.4⁰ correspond to the silica present in the material [46, 47].
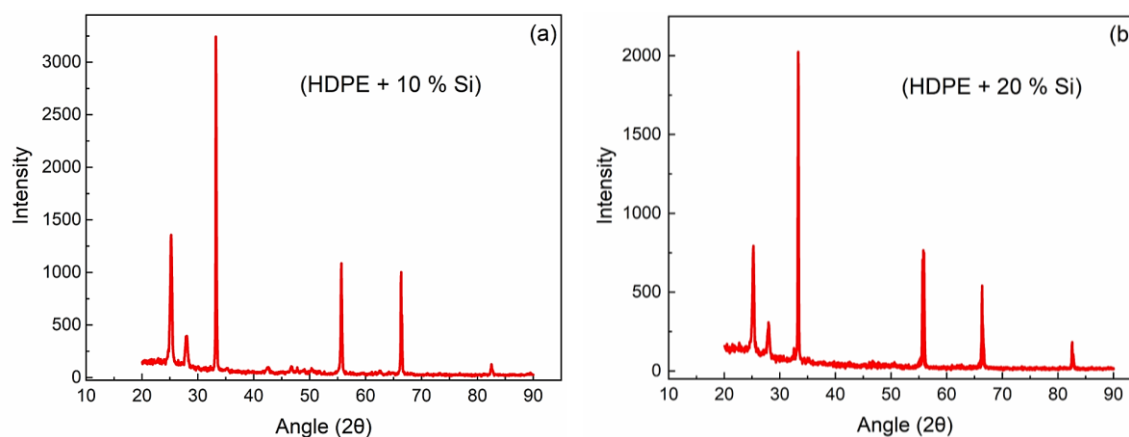

Figure 3. XRD pattern of (a) 10% and (b) 20% filler fraction HDPE –Si composite.

The analysis showed that the peak at θ=33.3º corresponds to the plane with miller indices (111). While the peaks corresponding to θ =55.65º, 66.35º and 82.55º are representing the planes with miller indices (2,2,0), (3,3,1) and (4,0,0) respectively. Here it is observed that all the planes are having the miller indices in such a way that the value of h, k and l are either all odd or all even. This kind of behavior is shown by face centered cubic (fcc) structure. Hence the analysis implies that the silicon which is used as a filler material has an fcc structure.

Debye Schereer formula is the most commonly used method to calculate the particle size using the XRD of material. Debye Schereer formula is given by Eqn. 4 n it can be written as [48, 49]

$$D_{hkl} = \frac{K\lambda}{\beta_{hkl}\cos\theta} \hspace{3cm} (4)$$

Where, K is the particle shape factor (0.9), λ is the X-ray wavelength (1.542Å), βhkl is the half width of the most intense peak and θ is the diffracted angle for the most intense peak. Analysis based upon the Debye-Scherer Formula implies that the crystalline size of the silicon particle is about 10 μm. XRD pattern of the samples negate any impurity in the samples also.

It should be noted that the XRD of all the samples were carried out and there is no significant change in the peak positioning in XRD pattern of these samples. The same can be seen in Figure 3 where the peak position of 10% and 20% samples are almost same. It should be noted that the XRD of all the samples were carried out and there is no significant change in the peak positioning in XRD pattern of these samples. The same can be seen in Figure 3 where the peak position of 10% and 20% samples are almost same. Therefore, the XRD pattern of only two samples is provided here.

Morphological Analysis

The SEM images obtained for the samples are shown in Figure 4. Figure 4 carries a scale which can help to determine the particle size of silicon in the matrix. The scale implies that the silicon particles have a size approximately 10 μm. It is worth noting that the calculation made by the XRD analysis of the HDPE-Si composite (provided in Figure 3) also predicts the particle size of silicon particles to be around 10 μm. Thus, the SEM images shown in Figure 4 verify the predictions made by the Debye-Scherer Formula.
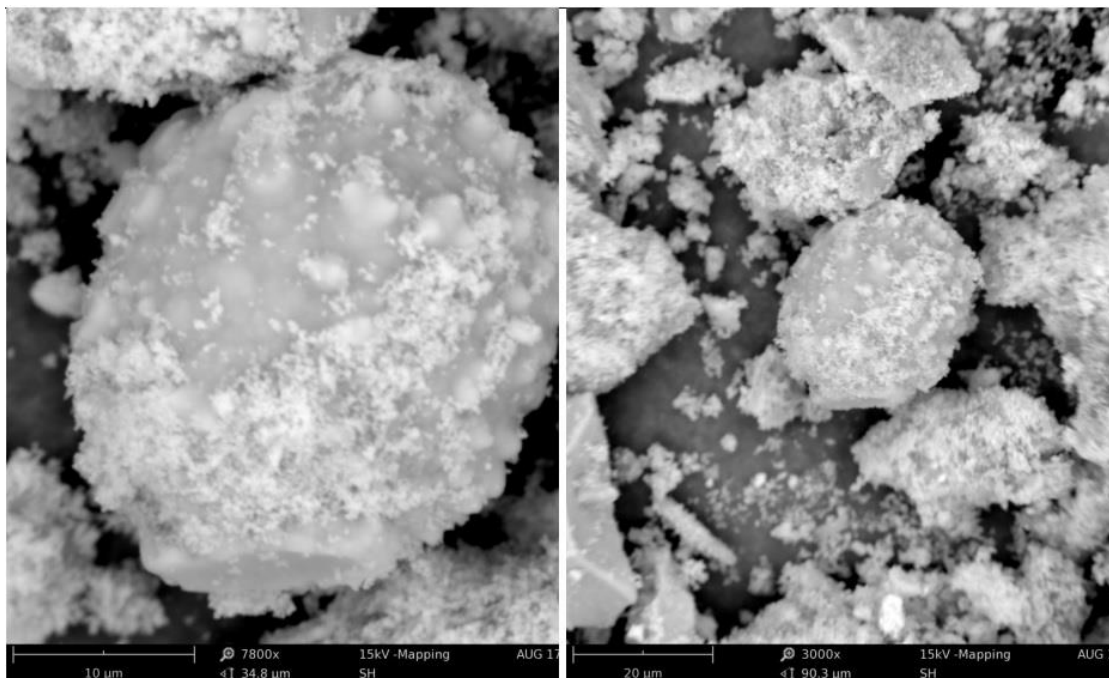

Figure 4. SEM Photographs of 10% and 20% filler fraction HDPE-Silicon composite.

Hardness Test

Hardness as mentioned earlier is an important parameter to know the strength of the material. It is a measure of the resistance of the indentation of the material. Generally, the soft materials like polymers need to go for the indentation tests (i. e. tests) to ensure their suitability in many applications. Shore-D test is the most widely technique to determine the hardness of the polymer-based materials. In Shore-D test the sample is indented through a needle like probe. A fixed load is applied on the sample and the indentation depth of the probe needle within the sample is noted. This load and indented depth data provides the hardness of the sample under investigation. The Shore-D hardness of the sample is a dimensionless number and it does not have any unit. The hardness of the sample is determined at a scale of 1 to 100. If the probe is completely inserted within the sample, then the hardness is said to be 0. If the probe does not get indented within the sample at all, the hardness vale is said to be 100.

In this work, hardness test for all specimens were performed by using a Shore-D hardness tester SHR-MARK III, D-676 at room temperature (27°C). All specimens were tested for at least three times in each case and the average values were recorded. Figure 5 represents the hardness of the prepared samples as a function of volume fraction at room temperature.

Figure 5 implies that the hardness value of the samples increases with the increase in silicon loading in the composite. The hardness value of the 20% volumetric ratio of the Si powder loaded composite is approximately 35% higher than that of pure HDPE. So we conclude that the addition of the silicon in HDPE matrix converts it into a strengthen material. The increase in hardness of the composites can be explained by considering the better adhesion between silicon and HDPE molecules. As the silicon volume fraction in the composite increases, an improved interaction between the silicon and HDPE molecules is expected. Larger interaction between the molecules may result in improved hardness.
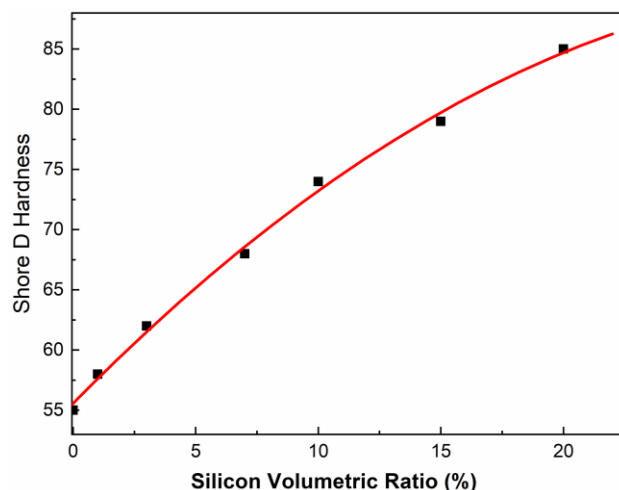

Figure 5. Hardness of HDPE-Si composites for different filler concentration.

Thermogravimetric Analysis

Thermogravimetric analysis was conducted to analyze the thermal degradation behavior and the thermal stability of the prepared HDPE-Si composite samples. The information related to these can be extracted by carefully monitoring the weight-loss of the composites during its heating. The weight-loss of the samples during heating is also a measure of the low molecular weight volatiles present within the sample. The weight-loss of the samples during heating is due to the evaporation of moisture and low molecular weight volatiles present within the sample. On heating the samples, oxidation of the carbon into carbon dioxides and other gasses occurs. Also this heating causes the oxidation of residual metal catalysts into solid oxides. The net weight-loss of the sample during the heating is the resultant of the all these processes discussed above. Figure 6 represents the TGA of prepared HDPE-

Si composite samples. This TGA curve is plotted between the weight losses of the samples against the temperature of the sample within 35°C–650°C.

In electronic packaging, the substrate material must withstand a temperature up to 400 °C and maintain their properties for a given period of time. Therefore, the degradation temperature for the composite must be higher than 400°C. The TGA curves of HDPE and its silicon composites show interesting trends. For pure HDPE the degradation of the composite starts at temperature close to 350°C but for the composite with 20% volumetric ratio of silicon the thermal degradation starts at about 400°C.
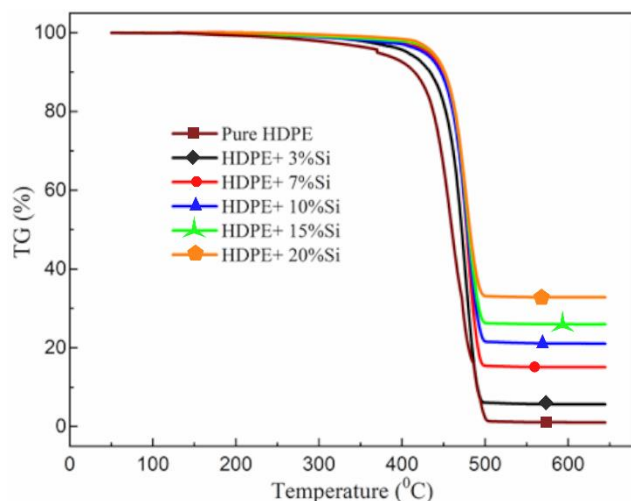

Figure 6. TGA profile of HDPE and HDPE-Si.

As seen from the TGA curve, thermal degradation of the pure HDPE sample occurs very sharply after 400°C and as we reach up to a temperature of 490°C nearly 90% of the weight has been lost. But for the 20% volumetric ratio composite the weight loss is 65% showing a clear increase in the stability. This may be explained through the higher specific heat capacity of silicon (0.39 J K^{-1} g^{-1}) as compared to specific heat capacity of HDPE (0.18 J K^{-1} g^{-1}). As the specific heat of the silicon is high, on increasing the loading of the silicon in HDPE-Si composite the composite will be able to absorb more heat and thus resulting in rise in specific heat capacity.

Figure 7 is a graphical representation of the residue remained as a function of filler concentration. It is very clearly seen from Figure 7 that as the filler volume fraction increase, the amount of residue remained also goes up. This is an expected result as with the rise in silicon filler fraction more and more non-volatile components are added up to the material. Similar kinds of observations have also been by made few studies in which the addition of the metal fillers have been observed to enhance the thermal stability of the composite samples [2, 40, 41]. The rise in the thermal stability with the increased filler volume fraction is also an indicative of the appropriateness of these composites for the electronic packaging applications.

From the weight loss data for different filler volumetric ratio of HDPE-Si composite we can have an idea of the temperature at which a fix amount of residue will be lost. The thermal decomposition temperatures of the HDPE-Si composite with different silicon volumetric ratio are shown in the Table 3. In this table we have used T_{10}, T_{20}, T_{30}, and T_{40} as the temperatures at which sample loses 10%, 20%, 30% and 40% of its weight respectively. The temperature which corresponds to the 10% weight-loss is considered to the quantitative representative of the thermal stability. This temperature has been denoted by T_{10}. Similarly, T_{20}, T_{30} … can be determined which will correspond to the temperatures at which the samples lose its 20%, 30% … weight respectively. Same benchmarking foe the determination of thermal stability has been observed in previous studies as well [2]. Table 3 provides

the thermal stability values (T_{10}, T_{20}, T_{30} …) based upon the 10%, 20%, 30% … reduction in their weights. The values showed in Table 2 indicate that as the filler volume fraction increases in the composites, Thermal stability of the composite increases. The increment in the thermal stability is associated with the evaporation of non-volatile fraction in the sample. With the rise in of silicon volume fraction in the composite non-volatile fraction lowers and thus the thermal stability is enhanced.
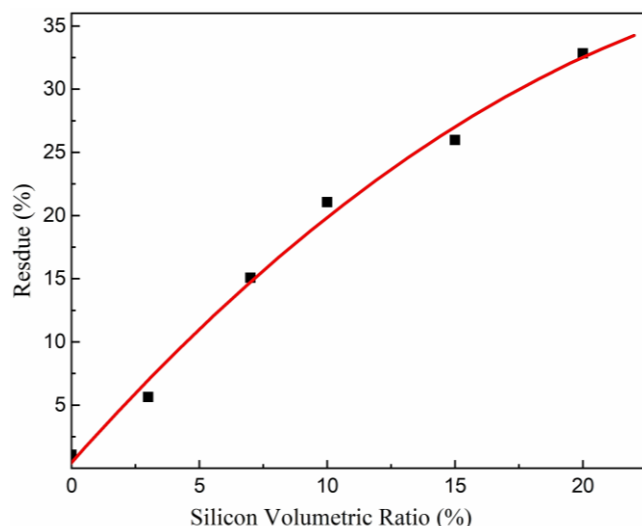

Figure 7. Residue after decomposition.

Table 3. Table showing decomposition temperature for various weight losses

Weight loss (%)	HDPE Pure	HDPE+3 % Si	HDPE+7% Si	HDPE+10 % Si	HDPE+15 % Si	HDPE+20 % Si
T_{10}	414	433	446	449	451	451
T_{20}	437	452	461	461	463	464
T_{30}	447	461	463	468	470	471
T_{40}	453	467	473	473	475	476

T_{10} value which represents the thermal decomposition temperatures of prepared DPE-Si composites having silicon volume fraction 3%, 7%, 10%, 15& and 20% are 433°C, 446°C, 449°C, 451°C and 451°C respectively. These values are 19°C, 32°C, 35°C, 37°C and 37°C larger than that of the pure HDPE sample ($T_{10}$for pure HDPE is 414°C). It clearly implies that the incorporation of the silicon filler in the HDPE matrix improves the thermal stability of the composite. It is a well-known that the rise in the filler concentration in the composite, improves the filler matrix interaction in composite. Thus, the addition of silicon in HDPE enhances the interaction between these. This improved interaction may be the reason for the improvement in thermal stability with the rise in silicon volume fraction of the composites. Similar observations were made while studying the thermal stability of HDPE be materials [50–53]. Table 4 provides a comparison of the thermal stability of HDPE be materials.

Table 4. Comparison of thermal stability of HPE be materials.

Filler	Thermal stability	Reference
HDPE-C_{60}	459°C	[50]
HDPE-LDPE	290°C	[51]
HDPE-Clay	350°C	[52]
HDPE-Birch	360°C	[53]
HDPE	230°C	[54]

Thermal Diffusivity and Thermal Conductivity of HDPE-Si Composite

Experiments were carried out to calculate the thermophysical properties of the HDPE-Si composite. These properties were measured for the different filler content at the room temperature. Table 5 shows the variation of the thermal conductivity, thermal diffusivity and specific heat capacity of prepared HDPE-Si composites at room temperature. These experimental results imply that the increase in the volumetric ratio of silicon in the HDPE-Si composite enhances its thermal conductivity. Also, at the room temperature, thermal conductivity of the composite with silicon volume fraction 0.2 is 0.733 W/m-K. This value is more than twice the thermal conductivity of pure HDPE. Thermal conductivity of silicon is much larger than that of HDPE. Therefore, generally any increment in the silicon volume fraction will improve the thermal conductivity value. However, there is another effect which may be the cause of the rapid rise the thermal conductivity value of composites. When the silicon content the HDPE matrix is large, then the formation of the conductive chain may occur within the composite. These thermally conductive chains may provide an easy passage for the heat to pass through and thus the heat can travel faster within the composite. For the larger silicon volume fraction composites, transfer of heat in that situation may be enhanced by the interaction of lattice phonons through lattice vibrations as well. The rate of thermal propagation depends on the intensity of coupling between the movements of atoms and with their adjacent atoms. Therefore, it can be concluded that the higher thermal conductivity value of silicon, formation of conductive chains by filler particles and the phonon interaction are the main cause of this rapid increase of thermal conductivity value [42].

Table 5 also shows the variation of thermal diffusivity of the composite with silicon volume fraction room temperature. Thermal diffusivity determines how fast the thermal flow will occur within the material. It may be considered as the rate of thermal propagation also. This makes the thermal diffusivity an important parameter for almost all the applications related to the heat flow in material. In electronic packaging applications too, thermal diffusivity plays a significant role. Table 5 shows that the thermal diffusivity of the prepared composites raises with the rise in the silicon volume fraction within it. Thermal diffusivity of composite with silicon volume fraction 0.2 is seen to be 0.518 mm^2/s while for pure HDPE thermal diffusivity is 0.224 mm^2/s. This rise of 131.25% in thermal diffusivity is a significant increase and may affect the thermal transport drastically. It means that the thermal response of the composite material is increased by the incorporation of the silicon within the HDPE matrix.

Table 5. Thermophysical properties of HDPE-Si composite as a function of filler concentration at room temperature

Filler Concentration (%)	Thermal Conductivity (W/mK)	Thermal Diffusivity (mm^2/sec)	Specific Heat J/(g-K)
0.00	0.362	0.224	1.719
0.01	0.364	0.226	1.688
0.03	0.385	0.238	1.649
0.07	0.481	0.293	1.585
0.10	0.562	0.355	1.438
0.15	0.672	0.436	1.347
0.20	0.733	0.518	1.167

Specific heat capacity is defined as the heat capacity per unit mass. It is a measure of the heat required to raise the temperature of a material by 1º. The specific heat capacity in a way determines the energy consumed by the material while heating it. Specific heat of the composite is decreasing on increasing the filler concentration. This decrease in the specific heat indicates that as the filler volumetric ratio is increased the temperature of the composite can be enhanced by smaller amount of heat energy. Specific heat capacity of the composites is seen to lower with the increment in the volume fraction of silicon in the composite. For pure HDPE this value is 1.719 J/(g-k) while for 0.2

volume fraction of silicon the specific hear capacity value is 1.167 J/(g-k). Hence, there is drop of 32.11% in the specific heat capacity value. This drop may not be considered as significant as for thermal conductivity (increment of more than 100%) and for thermal diffusivity (increment of 131.25%), but it is also a noticeable change.

The lowering in the specific heat capacity indicates that lesser amount of heat will be now required to increase the temperature of the material. The lowering in specific heat capacity means that the smaller heat will now increase the temperature of the sample. This is not advantageous as with the lower specific heat capacity the sample will not be able to maintain the temperature and the device temperature may increase more quickly. But since magnitude of rise thermal conductivity and thermal diffusivity of the composites is much more as compared to the lowering in specific heat capacity. Therefore, the lowering in the specific heat capacity may be taken care by the enhanced thermal conductivity and thermal diffusivity.

Effect of Temperature on Thermal Conductivity and Thermal Diffusivity
The effect of the temperature on the thermal conductivity of the prepared HDPE-Si composites is also studied in the present work. The temperature range selected for the present study was selected between 30°C to 80°C. This temperature range is selected as in most of the applications related to the electronic packaging the temperate remains within this and generally the temperature of the device does not go up beyond 80°C. The results obtained in the study are represented graphically in Figure 8. Thermal conductivity value of all the samples is lowered as the temperature of the sample is increased. The lowering in the thermal conductivity with rise in temperature indicates that on elevate temperatures the heat transfer will be affected and the thermal transport within the composites obstructed. The main reason of lowering in the thermal conductivity of the composites with the rise in temperature is the increased lattice vibrations at the elevated temperatures. The increase in temperature causes the increment in the lattice vibrations. The lattice-phonon interactions get enhanced because of this increased lattice vibration. Thus, the mean free path of the phonons gets reduced. These phonons with smaller mean free path are responsible for the slower heat conduction process within the composites.

This behavior of decrement in the thermal conductivity with temperature follows an almost linear trend. The magnitude of the slope of this linear trend is however slightly increased with increase in the silicon volume fraction within the composite. It indicates that the composites with higher silicon content offer a larger drop in the thermal conductivity value a compared to the composites with lower silicon content.
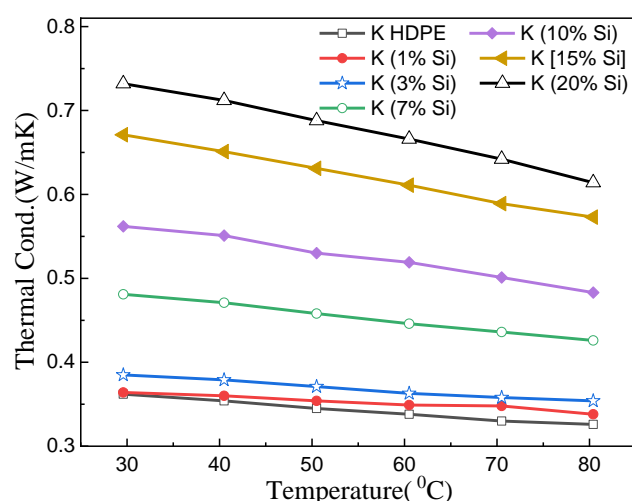

Figure 8. Thermal conductivity and of HDPE-Si composite as a function or temperature for the different filler fraction.

The effect of thermal diffusivity is also investigated as a function of temperature within the temperature ranges of 30°C to 80°C. Figure 9 shows the thermal diffusivity vs. temperature profile for the prepared composites within the investigated temperature range. Thermal diffusivity like the thermal conductivity also lowers as the temperature started increasing. Thermal diffusivity of the prepared composites reduces almost linearly wit temperature similar to the thermal conductivity trend. However, the drop in thermal diffusivity value is larger than that of the thermal conductivity value. Increased lattice vibrations at higher temperatures may be the reason for lowering in thermal diffusivity of these HDPE-Si composites with increase in temperature. As the temperature increases lattice-phonon interaction also gets increased. Increased lattice phonon interaction produces hurdle in the movement of the phonons and thus the rate through which the heat is transferred gets decreased and consequently thermal diffusivity gets lowered
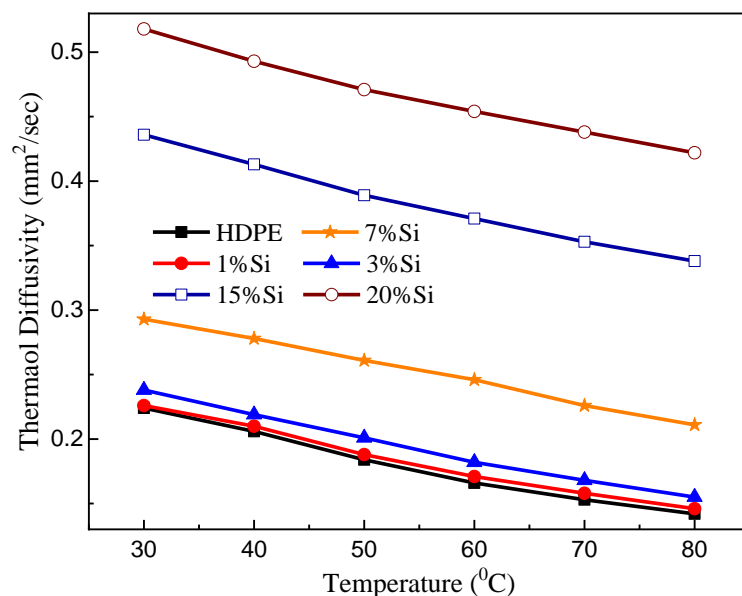

Figure 9. Thermal Diffusivity of HDPE-Si composite as a function or temperature for the different filler fraction.

CONCLUSIONS

In the present work, HDPE-Si composite was prepared using mixing, molding and hot compression technique. Structural characterization of the composite showed that silicon particles were spherical; with size approximately 10 µm. TGA revealed that the maximum decomposition of the composites occurs between 350°C–500°C. It is observed that thermal stability of the composites with 0.2 volume fraction of silicon was 451°C while that of pure HDPE was 414°C. Shore D hardness test indicated that addition of the silicon in HDPE matrix increased the hardness of the HDPE-Si composites significantly.

Thermophysical properties of the prepared composites were studied as function of silicon volume fraction in the HDPE-Si composite. The Study showed that the HDPE-Si composite with silicon volume fraction 0.2 offered thermal conductivity 0.733 W/m-K which is more than twice to the thermal conductivity of pure HDPE (0.362 W/m-K). Thermal diffusivity value increased by 131.25% (from 0.224 mm^2/s to 0.518 mm^2/s) on increasing the volume fraction of silicon from 0.0 to 0.2. Increase in the thermal conductivity and thermal diffusivity can be explained by considering the formation of the conductive chain between HDPE and silicon.

Thermal conductivity and thermal diffusivity both lowered almost linearly with the rise in temperature. Composites with higher silicon volume fraction offered higher drop in the thermal conductivity values as compared to those with lower.

Declaration Funding
    NA

Conflicts Interest/Competing Interests
    No conflict of interest is involved

Data Availability
    Data is available with the corresponding author and can be produced if required.

Authors' Contributions
- Manoj Tripathi and Avita Agarwal performed the experimental work including sample preparation and thermophysical measurement of the prepared samples.
- Mona Bhavnagar compiled all the results and analyzed it.
- Mubarak Mujawar and Krishna Kumar Pandey performed the characterization and wrote the manuscript.

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