ASEAI-622

Thermal Characteristics of Polypropylene Composites Filled with TiO2

Madhusmita Sahu[a],*, Alok Satapathy[b]
[a] Dept. of Mechanical Engg., National Institute of Technology, Rourkela, India
E-mail address: madhusmita_rkl@yahoo.co.in

[b] Dept. of Mechanical Engg., National Institute of Technology, Rourkela, India
E-mail address: satapathy.alok@gmail.com

Abstract

Particulate filled polymer composites with excellent thermal characteristics are highly demanded in electronic industries. In this context, the present work attempts to modify the thermal properties of Polypropylene (PP) by addition of micro-sized titanium dioxide (TiO_2) particles.

The values of the effective thermal conductivities (k_{eff}) of these composites are also estimated using a theoretical model proposed previously. Finally a series of PP-TiO_2 composites with different TiO_2 concentrations (0-25 vol%) are prepared by compression molding technique and their thermal conductivity, glass transition temperature (Tg) and coefficient of thermal (CTE) expansion are measured using the Unitherm™ Model 2022 tester and Perkin-Elmer DSC-7 thermal mechanical analyzer (TMA) respectively. The measured effective thermal conductivity values are then compared with the values obtained from the proposed model. It is seen that the k_{eff} values obtained from theoretical model are in good agreement with the measured values for composites with TiO_2 concentrations up to 15 vol%. This study shows that addition of TiO_2 particles improves the effective thermal conductivity of PP-TiO_2 composites. With addition of 25 vol% of TiO_2, there is an enhancement of about 266% in the k_{eff}. Apart from enhancing thermal conductivity, incorporation of TiO_2 results in improvement of glass transition temperature and reduction in coefficient of thermal expansion of polypropylene resin.

Keywords: Polypropylene, TiO_2, Effective thermal conductivity, T_g, CTE.

1. Introduction

Microelectronic packaging has been playing increasing important role in the rapid progress of the electronic and electric technologies. High density and high frequency as well as high speed have been the representative characteristics of future microelectronic packaging materials, and therefore, development of desirable packaging materials has been more

important subject. It is known that when a microelectronic product with high performance works, more heat is produced, and the heat must be dissipated away in time to avoid over-heat occurrence [G.W. Lee et.al, 2006].
So the packaging material should have good thermal conductivity (k) besides of traditional physico–mechanical properties. On the other hand polymers and polymer composites are appreciated and regularly being used by several electronic industries as encapsulation material, because of their good corrosion resistance, durability, low density, low fabrication cost, easy availability, ease of processability etc. But the requirement for denser and faster microelectronic circuits limits the use of conventional polymeric packaging materials. These polymers set back in the rapid progress of electronics industry because of their very low thermal conductivity and high CTE. The low thermal conductivity of polymer based electronic packaging material becomes an obstacle, because of the overheating caused due to the heat produced in such circuits and not getting dissipated as soon as it is generated. Further, the high CTE of the polymer leads to deformation in the encapsulated material. This problem can be resolved by replacing the polymers by polymer composites filled with particles possessing high thermal conductivity and low CTE. Thermal properties of the polymers can in fact be improved or modified either by molecular orientation or by the addition of conductive fillers. It has been seen that the heat transfer is more in the direction of orientation as compared to the direction perpendicular to the orientation [A. Griesinger et. al. 1997].

Arranging the molecules in the desired direction are often a difficult task, so the addition of conductive fillers is considered to be the more effective method which is being widely used to enhance the thermal conductivity so as to facilitate transferring the excess heat generated due to miniaturization of electronics components.

Lot of experimental work has been reported on thermal conductivity of particulate filled polymer composites in the past. Mamunya et al. in 2002 studied the electrical and thermal conductivity of polymers filled with metal powders like Cu and Ni. Tavman in 1996 reported that the k_{eff} of HDPE increases form 0.543 W/m-K to 3.3 W/m-K as the volume fraction of aluminum filler increases to 30%. More recently, thermal properties like conductivity, diffusivity and specific heat of metal are investigated experimentally [N.M. Sofian, 2001], the investigation shows that up to 16% filler content the k_{eff} measured is matching with existing model. But metals are electrically sensitive, so they cannot be used as fillers in such applications. Some ceramic powders are considered to be better alternative as fillers because of their high thermal conductivity and low dielectric constant. It has been reported that various ceramic fillers such as BN, AlN, Si_3N_4, are already been used to improve thermal and electrical properties of various polymers [W. Zhou et. al., 2007, Y. W. Wong et.al., 2001, W. Zou et.al., 2009]. In a recent research Weidenfeller et al. in 2004 studied the effect of inter-connectivity of the filler particles and its important role in the thermal conductivity of the composites. They prepared polypropylene (PP) samples with different commercially available fillers by extrusion and injection molding using various volume fractions of filler to systematically vary density and thermal properties of these composites.

Along with low thermal conductivity, high CTE of such polymer also become the cause for thermal failure as electronic components are subjected to periodic heating and cooling during their working of the component. So, any reduction in CTE values can improve the performance of such devices. Few works has been reported to resolve the problem of high CTE of polymers.

Benito et al. in 2013 reported on CTE of TiO_2 filled EVA based nanocomposites and the influence of filler particle size on composites. Iyer et al. in 2006 have recently reported significant reduction in CTE as the content of BN is increased in the composite. Dey et al. 2010 studied the dependence of CTE on volume fraction of filler at ambient temperature and Yasmin et al. in 2004 have reported that, as the graphite concentration in epoxy increases to about 2.5 wt %, Tg increases and CTE of the composite decreases. In addition to all these, a number of researchers have also proposed different theoretical models such as ROM, Lewis Nelson model and Maxwell‘s model for estimation of effective thermal conductivity of particulate filled polymer composites [Lewis et.al., 1973, J. Maxwell, 1873].

Against this background, the present work is undertaken to study the effects of addition of micro-sized TiO_2 particles in polypropylene on its heat conduction capability by estimating the effective thermal conductivity values analytically and experimentally. TiO_2 is chosen as the filler material due to its moderate thermal conductivity (about 11.7 W/m-K), high electrical resistivity, no toxicity and a low thermal expansion coefficient (8.6 ppm/˚C). TiO_2 has previously [Nelson et. al. 2004, Siddharth et.al. 2011] been used in polymer composites by many investigators mostly for the purpose of modifying tensile, flexural and dielectric strength of the matrix polymer. But its use for enhancing thermal properties of PP has not so far been reported.

2. Experimental Details

Most widely used thermoplastic polymer, polypropylene also known as propene is another polymer used for the present investigation. Molecular formula for polypropylene is $(C_3H_6)n$, where n is the number of polymerized unit. Polypropylene of homo-polymer M110 grade is chosen for the present research are procured from CIPET, Bhubaneswar. Polypropylene is used for its good mechanical performance, aesthetics, resistance to chemicals, cost effectiveness, stability to heat, recyclability along with low density. Micro-sized Titanium Dioxide (TiO_2) is used as the filler material for the preparation of thermally conductive polymer composites in the present investigation. TiO_2 powders are supplied by Qualikems Ltd with average particle size of 90 -100 micron. TiO_2 is used as filler for its thermally conducting nature. A set of composite of 11 different compositions where filler content ranging from 0 vol % to 25 vol% is fabricated by compression molding technique are prepared. Rheomix 600 batch mixer with chamber volume 90 cm^3 is used to melt and mix PP with TiO_2 by the help of two rotor rotating in opposite direction. The temperature of the mixing chamber is set to 190^oC and time of the mixing is 10 minutes.

The temperature and time differ for different sets of matrix filler combination. As the mixing is over, the material is taken out from the chamber and after cooling, it is cut into small pieces.

These uniformly mixed PP-TiO_2 composite pieces are then kept in a hot air oven for about an hour. These small pieces of materials are then taken out from the hot air oven and kept in compression molding die. The dimension of the die is 3 mm thickness and 60×60 mm^2 area. By using hydraulic press, the material is pressed with a pressure of 150 kg/cm^2 for around three minutes. The temperature of the compression molding die is maintained at 190^oC with the help of heaters. After that it gets water cooled and the sheet is taken out from the die. Later disc type specimens of required dimension are cut from the sheets for experimentation.

3. Results and Discussion

3.1 Theoretical Model

Based on the one dimensional heat conduction model, a theoretical correlation for estimating effective thermal conductivity of particulate filled polymer composites has recently been developed and proposed by the authors [Agrawal et. al 2012]. This correlation expresses k_{eff} as a function of filler content and intrinsic conductivities of filler and matrix materials. The theoretical analysis of heat transfer across this composite element is made on the basis of following assumptions (1) Locally both the matrix and filler are homogeneous and isotropic (2)

The thermal contact resistance between the filler and the matrix is negligible (3) The composite is free from voids and (4) The temperature distribution along the direction of heat flow is linear.The resulting theoretical correlation for effective thermal conductivity of the particulate filled polymer composite is as follows:

$$K_{eff} = \xi \frac{1}{\frac{1}{k_p} - \frac{1}{k_p}\left(\frac{6\phi_f}{\pi}\right)^{\frac{1}{3}} + \frac{4}{\left(k_p\left(\frac{4\pi}{3\phi_f}\right)^{\frac{2}{3}} + \left(\frac{2\phi_f}{9\pi}\right)^{\frac{1}{3}} 2\pi\left(k_f - k_p\right)\right)}} \qquad (1)$$

Here, k_p, k_f are the thermal conductivities of the polymer and the filler respectively, k_{eff} is the effective thermal conductivity of the composite prepared and Φ_f is the volume fraction of the filler. ξ is correction factor which could be incorporated to account for all the discrepancies associated with the model. In the present work, the value of ξ is tuned to 0.69 so as to achieve a close approximation between the theoretical values and the conductivity test results.

3.2 Effective Thermal Conductivity (Theoretical / Experimental)

The effective thermal conductivity values obtained from various established theoretical models, the proposed theoretical correlation (Equation 1) and the experimental values of the composites under study are presented in Table 1.The variation of k_{eff} as a function of TiO_2 content is illustrated in Figure 1.

Table 1**:** k_{eff} values of PP-TiO_2 composites from various models and experimentation

Filler Content (vol %)	Effective Thermal Conductivity (W/m-K)				
	Rule of Mixture	Maxwell‘s Model	Lewis & Nelson‘s	Proposed Model	Experimental Values
0	0.111	0.111	0.111	0.110	0.111
2.5	0.112	0.118	0.117	0.112	0.127
5.0	0.115	0.126	0.124	0.131	0.148
7.5	0.118	0.136	0.133	0.149	0.167
10.0	0.122	0.145	0.142	0.167	0.188
12.5	0.125	0.155	0.153	0.186	0.211
15.0	0.130	0.166	0.164	0.207	0.230
17.5	0.133	0.177	0.177	0.229	0.369
20.0	0.137	0.189	0.193	0.254	0.394
22.5	0.141	0.202	0.210	0.282	0.401
25.0	0.146	0.216	0.231	0.315	0.407

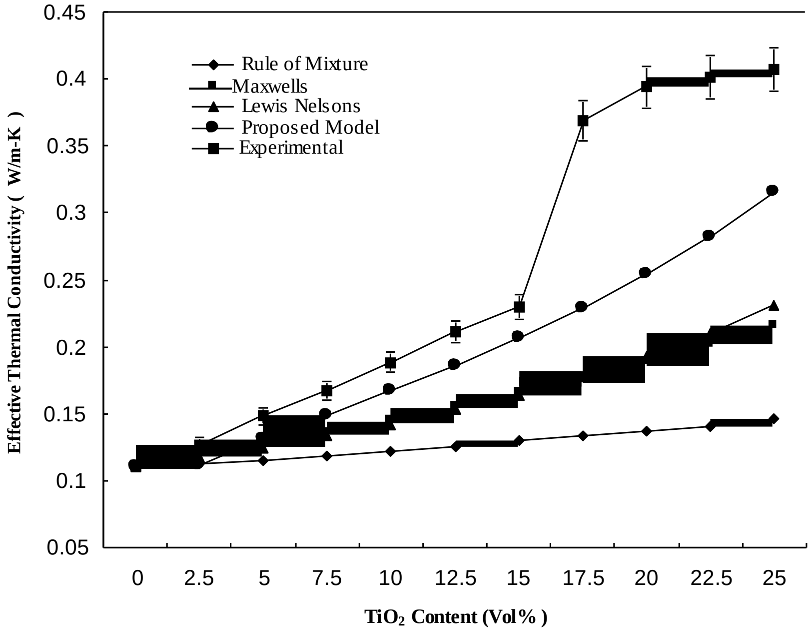

Fig 1: Variation of effective thermal conductivity with TiO_2 content

Figure 1 shows that the theoretically estimated k_{eff} values along with the values calculated from proposed established models are in agreement with the experimental results, but the values from proposed model are in closer approximation to the experimental ones. On comparing, it is noted that there is a reasonably good agreement between the theoretical values with the experimental results up to a TiO_2 concentration of 15vol%. But just beyond this, a sudden jump in the measured value of thermal conductivity of the composites is noticed as seen in Figure 2.

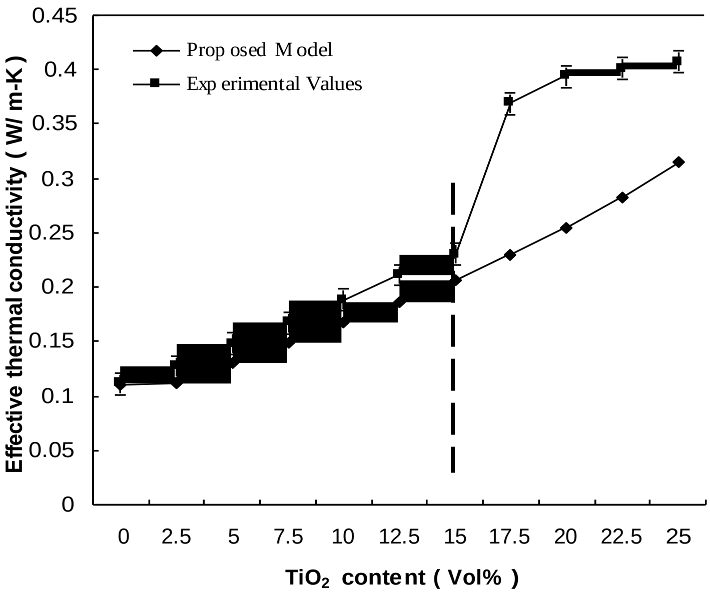

Fig 2: Variation of k_{eff} with TiO_2 content (Proposed model / Experimental)

This feature of sudden rise in k_{eff} is not obtained while using the proposed correlation which indicates only a monotonic and almost linear increase in k_{eff} with increase in filler content. It reveals that TiO_2 particulates exhibit a percolation behavior in PP resin at a volume fraction of 15 %. This stage is called the percolation threshold. It can be observed from Figure 2 that below this percolation threshold, enhancement of thermal conductivity is negligible and the threshold conductivity of the composites is almost equal or slightly higher than that of the matrix polymer, but just after 15 vol% of TiO_2 concentration, the unexpected rise occurs. This is the critical concentration at which TiO_2 particles start contacting with each other and hence the actual size of the agglomerates becomes larger. Consequently, the heat conduction performance of PP composites incorporating TiO_2 exceeds expectations. With addition of 25 vol% of TiO_2, the thermal conductivity of PP composite improves by about 266 %. In filled polymer composites, fillers are connected and conduction networks are formed in the case of high filler content whereas these particles are isolated by the matrix in the case of low filler content [Zhang et.al. 2010].

As already mentioned, effective thermal conductivity of the composite is usually the same as that of the polymer as long as the filler concentration is zero or is little higher than zero. When the polymer is filled with any conductive filler (having conductivity higher than that of polymer) like TiO_2, the effective conductivity of the composite increases making the polymer more conductive. This trend is observed in case of all the polypropylene-TiO_2 composites considered in this study. The percolation threshold point is actually the point at which a network first spans the system. This is the first appearance of long-range connectivity. According to experimental findings, as already mentioned, the effective thermal conductivity increases rapidly when the filler volume fraction exceeds the percolation threshold. Furthermore, the effective thermal conductivity increases non-linearly with the increase in filler content due to the gradual development of density of the network. The precise location of the percolation threshold is affected by many factors, including the size, aspect ratio and distributions of the conductive particles within the matrix body. Immediately after the percolation threshold, even a slight increase in the concentration of conductive TiO_2 particles are found to greatly increase in the conducting network leading to a substantial improvement in k_{eff} of the composites.

3.3 Glass Transition Temperature (T_g)

Figure 3 shows the glass transition temperature of the polypropylene -TiO_2 composites with different filler loading. It is observed that T_g of polypropylene increases from -14.9˚C to 9.04˚C with incorporation of 25 vol% of TiO_2. The increase in T_g of the polypropylene -TiO_2 composites can be due to the strong interaction between the TiO_2 and polypropylene matrix. The interaction between the filler particles and the polymer restricts the mobility of the polymer chain. Similar observations have also been reported by previous investigators [Ash et.al. 2002].

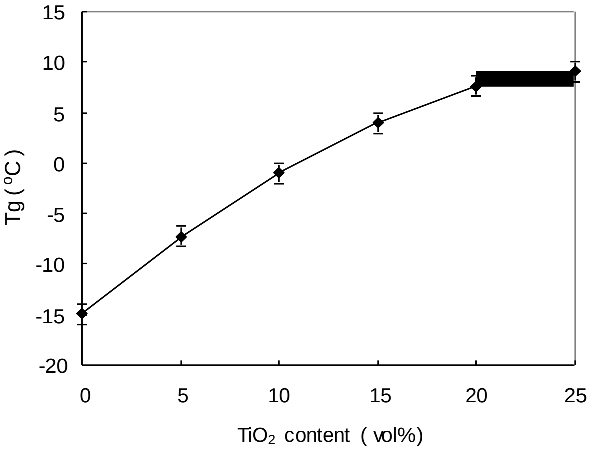

Fig 3: Variation of glass transition temperature with TiO_2 content

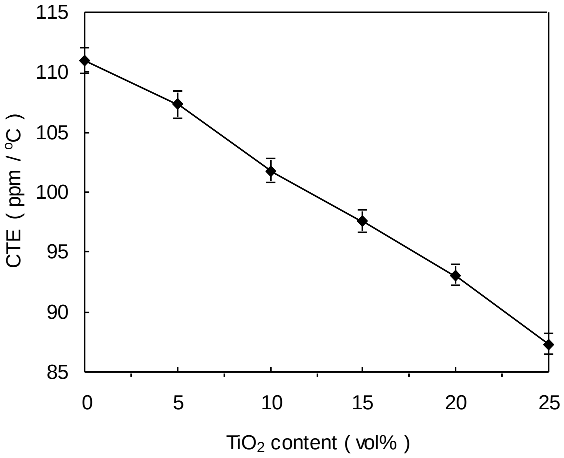

Fig 4: Variation of coefficient of thermal expansion with TiO_2 content

3.4 Coefficient of Thermal Expansion (CTE)

A low CTE is desirable for applications like micro-electronics encapsulation to maintain the dimensional stability of the material, and can be obtained by dispersing fillers with low CTE within the matrix. TiO_2 is known to have low CTE [Bejito et.al. 2013], hence it is expected that its addition would reduce considerably this property of the polypropylene matrix. The variation of CTE of polypropylene -TiO_2 composites is shown in Figure 4. It is observed that CTE of neat polypropylene which is 111 ppm/˚C gradually decreases to 87.3 ppm/˚C with addition of 25 vol % of TiO_2. The low CTE of TiO_2 (about 8.6 ppm/℃) and the constraint of deformation of the polypropylene-matrix due to the interaction of TiO_2 and polypropylene are responsible for the reduction in CTE of the TiO_2–polypropylene composites. A maximum decrease of 21.35 % in CTE is observed for 25 vol% loading of TiO_2. This results suggest that CTEs can be tailored by tuning the amount of TiO_2 added, and such composites may find applications as smart materials and in thermal management of electronics applications.

4. Conclusions

The results of analytical effort are validated by experimental determination of k_{eff} for a set of fabricated PP composites filled with TiO_2. The values of k_{eff} obtained for composites using the proposed theoretical model are in reasonable agreement with the experimental values for filler content within the percolation limit. Addition of 25 vol% of TiO_2 results in 266% of increase in thermal conductivity. The k_{eff} of the composite increases as the TiO_2 content increases and the rate of increase of thermal conductivity is rapid beyond the percolation threshold which occurs at 15 vol%. With incorporation of $TiO_{2\,,}$ Tg of the composite increases and CTE decreases making the composite a more suitable material for electronic packaging and encapsulations.

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