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Thermal Properties of Polymer Blend Reinforced Nano – Sic Nanocomposite

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ABSTRACT

Thermal conductivity plays an important role on the thermal withstand capability of the insulatingmaterials. It has been observed that the use of nano composites in the matrix of polymeric materials can greatly improve the thermal, mechanical and electrical properties of polymeric nano composites. A nano composite (Sic + UFG) with blend (EP / UPE) has been tested as nano filler. These nano composites were mixed withhelp of ultrasonic vibrator.The Nano – Sicvolume percentage filled in blend matrix (0%, 5%, 10%, 15%) with 5% UFG (ultra fine graphite). In this studywas measured thermal conductivity, diffusion, Eiffusiyity, heat capacity and thermal Resistance by Mathis TC i Analyzer. the thermal conductivity improvement with increase filled materials. as will as thermal diffusion and thermal Eiffusiyity.The Heat capacity descries with increase percentage Nano – Sic, but the thermal Resistance increased with increase percentage Nano – Sic.

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INTRODUCTION

Since 1930's, polymers have made significant advances in the markets of metals, wood glass, paper, leather, and vulcanized rubber that were conventionally used in most household goods and industrial components as well as creating new markets of their own. The main reason behind the widespread use of polymers is their unique set of properties such as toughness, light weight, low cost, and ease of processing and fabrication. Even though polymers are not the panacea of industry's material problems, their unique set of properties have made them one of the important classes of materials finding their way into widespread use in the electronic industries (Harper, C.A., 2004). The combination of two different materials, for instance polymeric, is a simple route for combining the attractive features of different materials in order to enhance the deficient characteristics of a particular material (Di Lorenzo, M.L., M. Frigione, 1997). Many common examples of composite materials can be found in the world around us. Wood and bone are examples of natural composites (Lionetto, F., M. Frigione, 2009). Recent and successful examples of improved properties that can be achieved by using these procedures are offered by adding to a polymeric phase of organic and inorganic filler, for instance hyper branched polymers (Frigione, M., E. Calò, 2008; Esposito Corcione, C., M. Frigione, 2009) and inorganic nanofillers. In particular, polymer composites reinforced with inorganic fillers of dimensions in the nanometer range, known as nanocomposites, have attracted great interest from researchers, due to unexpected synergistic properties derived from the two components. The most studied polymer nanocomposites(PN) are composed of thermoplastic or thermosetting matrix.Polymer materials show a weak thermal conductivity. Thermal conductivities of insulating polymer materials are usually 1-3 orders lower than those of ceramics and metals due to the chain-like structure of polymers, the heat capacity consists of the contribution of two mechanisms: (a) lattice vibrations and (b) characteristic vibrations, which originate from internal motions of the repeating unit. The lattice (skeleton) vibrations are acoustic vibrations, which give the main contribution to the thermal conductivity at low temperatures. The characteristic vibrations of the side groups of the polymer chains are optical vibrations, which become visible at temperatures above 100 K generally, the thermal conductivity of amorphous polymers increases with increasing temperature, if the temperature is in the glassy region and decreases slowly or remains constant in the rubbery region. Numerous applications in the field of electrical engineering require high thermal conductivity, such as insulating materials for power equipment, electronic packaging and encapsulations, computer chips, satellite devices and other areas where good heat dissipation is needed. For polymers reinforced with different types of fillers this is even more important. Improved thermal

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conductivity in polymers may be achieved either by molecular orientation or by the addition of highly heat conductive fillers (Tekce, H.S., 2007). Temperature, pressure, density of the polymer, orientation of chain segments, crystal structure, the degree of crystallinity and many other factors may affect the thermal conductivity of polymers (Yang, Y., 2007). It has been shown that the thermal conductivity is highly sensitive to the degree of crystallinity and the polymer chain segment orientation (Kurabayashi, K., 2001). K. Fukushima *et al.* (Fukushima, K., 2004). have developed a novel material design to improve the thermal conductivity, where polymer chains align themselves, by controlling the higher crystalline ordering.

The thermal conductivity values of the new developed resin were up to 5 times higher than those of conventional epoxy resins, because the mesogens form highly ordered crystal-like structures, which suppress phonon scattering. To improve the thermal conductivity of the polymer composites, E-kstrand and co-authors (2005) proposed:
(a) decreasing the number of thermally resistant junctions;
(b) forming conducting networks by suitable packing; and
(c) minimize filler-matrix interfacial defects.

Z. Han *et al.* (2008) discovered that an epoxy-filler composite with agglomerates of particles is more efficient in enhancing the thermal conductivity than a nanocomposite with well dispersed nanoparticles. This is presumably due to the formation of percolated pathways or networks. The main approach to an effective improvement of the low thermal conductivity of polymers is to fill them with particles with high thermal conductivity. Industrial companies, which are specialized in the production of polymer-based insulating materials, use a fill grade up to 60 wt.% of silica or alumina. The thermal conductivity of these materials is not significantly high but the price is low (Hsieh, C.Y., S.L. Chung, 2006). Lieutenant. J. Ganesan1, D. Edison Selvaraj (2013) study Thermal conductivity plays an important role on the thermal withstand capability of the insulating materials. It has been observed that the use of nanocomposites in the matrix of polymeric materials can greatly improve the thermal, mechanical and electrical properties of polymeric nanocomposites. A nanocomposite (TiO2+SiO2) has been tested as nano filler. Bu-Ahn Kim 1 and Chang-Kwon Moon(2013), studyThe improve the properties of epoxy resin using titanium oxide nanoparticles. The effects of particle weight fraction, dispersion agent, curing agent with different molecularweights on the thermal and mechanical properties in titanium oxide reinforced epoxy resin has been investigated. In addition, the effect of particle dispersion situation on the mechanical properties of nanocomposites has been studied.

2.Theory:

Thermal Conductivity Analyzer byMathis TCi:

Thermal conductivity can be measured using several different instrumental techniques. One of these is based on differential scanning calorimetry (DSC). DSC is a thermal analysis technique which measures heat flow into or out of a material as a function of temperature or time. DSC is primarily used to measure transition temperatures and associated heats of reaction in materials, particularly polymers. Measurement of glass transition temperature, melting point, % crystallinity, degree of cure, decomposition temperature, and oxidative stability are specific examples of some of the more common DSC measurements. The most widely used approach for making DSC measurements is the.heat flux. DSC, in which the sample and reference materials (usually contained in metal pans) are placed on a thermoelectric disk inside a temperature programmed environment. Heat flow in this approach is measured using the thermal equivalent of Ohm'sLaw (Marcus, S.M. and R.L. Blaine, 2013). Where dQ/dt = dT/R (Q = heat, t = time, T = temperature, R = thermal resistance of thermoelectric disk. have modified heat flux DSC.s to measure the thermal conductivity of insulating materials such as thermoplastic solids, elastomers, thermoplastic melts and pyrotechnics, respectively. In their work, a test specimen is placed in the DSC cell in contact with the sample platform. The DSC sensor measures both the temperature of one side of the specimen and the heat flow into it. A heat sink of known temperature is constructed to contact the opposite side of the test specimen. From the recorded heat flow and the temperature difference between the DSC cell and the heat sink (along with the test specimen dimensions), thermal conductivity can be calculated using the equation (Callister, D., 2003).

$$\frac{dH}{dt} = -\frac{\lambda A dT}{dx} \quad (1)$$

where:
H = Heat (J)
t = Time (sec)
λ = Thermal Conductivity (W/K. m)
T = Temperature (K)
x = Height of test specimen (m)
A = Cross Sectional Area of test specimen (m2)
The thermal diffusion equation (m^2/ s):

$$\delta = \frac{\lambda}{Cp.\rho} \quad (2)$$

where:
C_p: Specific heat capacity by (J/km. k)
ρ: Density of sample (km / m^3)
The Eiffuisivity by ($Ws^{½}$ / m^2. k)

$$\varepsilon = \sqrt{\lambda . \rho . Cp} \quad (3)$$

The thermal Resistance by(km. k / J)

$$R = \frac{1}{Cp} \quad (4)$$

This DSC measurement of thermal conductivity works well but requires modification of the commercially available DSC cell, as well as very careful attention to experimental detail.

Principles of Operation of Mathis TCi:
(Thermal Conductivity Analyzer):

The Mathis TC i is based on the modified transient plane source technique. It uses a one-sided, interfacial, heat reflectance sensor that applies a momentary, constant heat source to the sample. Both thermal conductivity and effusivity are measured directly and rapidly, providing a detailed overview of the thermal characteristics of the sample material.Sample material can be a solid, liquid, paste or powder (E1952, 2013).

The Mathis TCi features multiple graphical and tabular display options, and provides direct, indirect* (calculated), and user input** capabilities for a number of thermal testing properties, including:
• Thermal Effusivity • Thermal Diffusivity* • Density**
• Thermal Conductivity • Heat Capacity* Thermal Resistance

3. Experimental:

3.1 Materials:

The Nano-silicon carbide (Nano- Sic) and ultra fine graphite (UFG) used for reinforced the blend matrix , the physical properties for (Handbook Goodfellow 2012):

Nano – SicandUFG:

Physical Properties	
Density	3.2 g cm-^{3}
Volume resistivity	103-105 at 25C^{0}Ohm - cm
Dielectric constant40	
Coefficient of thermal expansion	4.5 at 20- 1000C x10^{-6} K^{-1}
Melting point2650-2950 C^0	
Specific heat	670-710 at 25CJ K-1 kg-1
Thermal conductivity	90-160 at 20CW m^{-1} K^{-1}
Compressive strength	1000-1700 MPa
Hardness – Vickers	2500 kgf mm^{-2}
Tensile modulus	200-500GPa
Morphology Color Average particle size	Nearly spherical Green 50nm

UFG ultra fine graphite powder is a high-purity synthetic graphite that can improve the thermal and electrical conductivity of a wide variety of materials including paints, coatings, plastics, rubber and adhesives**.** UFG ultra fine graphite powder is a product of Show Denko KK, Tokyo.

Crystal structureHexagonal , Diamond	
Boiling point	5000 C
Density2.25 at 20C g cm-3	
Melting point	3650 C^0
Coefficient of thermal expansion	0.6-4.3 at 0-100C^0 x 10^{-6} K^-
Specific heat712 at 25C J K^{-1} kg^{-1}	
Thermal conductivity80-240 at 0-100C^0	

Blend Resin:

All two component polymer blends synthesized in this work are prepared by simultaneous polymerization and cross – linking of the constituent polymers. Epoxy resin and unsaturated polyester resin is the blend composition selected for investigation. The epoxy resin and unsaturated polyester resin were added together and thoroughly prepared mixed to obtain the polymer blend required. The mixture is stirred for 40 sec, than casting Teflon mold and finally left overnight at room temperature for complete curing.

3.2. Nanocomposite preparationand Standards:

Nanocomposites are prepared by dispersing (Nan –SIC / ULG) kinetically by ultrasonication. To achieve better state of dispersion first the nanoparticales were treated with alcoholicmedium (ethanol or acetone) for the deagglomeration of the particlebundles. The treated particles are then added to the blends resin and sonicated for 2 h at room temperature. Then themixture is cured under vacuum at (363K) for 10 h followedby hardener addition by using simultaneousmagnetic stirring (100 rpm), for an hour to homogenization. The prepared samplesare treated at (353K) for 6 h in the oven to remove themoisture contents of the samples. The samples are placed between two metal plates under pressure to reduce porosity forming during hardening, before mechanical and thermal measurements, the surfaces of the specimens are mechanically polished to minimize the influence of surface flaws, mainly the porosity**.** To prepare the nano composite samples, molds are made from Teflon. The mold smeared by wax before the mixture is poured into the moldafter homogeneity. To calculation the weight of blends resin and [Nano – SIC / ULG] used Sensitive Electronic Balance.

3.3Testing Equipment and Techniques:

Thermal conductivity analyzer (Mathis TC I) test:

The third generation of Mathis technology expands the capabilities of this rapid, non-destructive thermal conductivity and effusivity testing instrument to a whole new level. Designed to provide simple, highly accurate thermal characterization for lab, quality control and production environments, the Mathis TCi Thermal Property Analyzer requires no calibration or sample preparation. The system has broad testing capabilities (0.0 to 100 W/m.K) in a wide range of temperatures (–50˚ to 200˚C). The TCi can be equipped with one or two sensors for increased capacity, and provides accurate thermal analysis of solids, liquids, powders and pastes in less time than any other instrument – only 5 seconds. And because the procedure is non-destructive, samples remain intact undisturbed and reusable after testing.

The Mathis TCi is based on the modified transient plane source technique. It uses a one-sided, interfacial, heat reflectance sensor that applies a momentary, constant heat source to the sample. Both thermal conductivity and effusivity are measured directly and rapidly, providing a detailed overview of the thermal characteristics of the sample material.

How It Works:

1- Sample material can be a solid, liquid, paste or powder.
2- A known current is applied to the sensor's heating element providing a small amount of heat.
3- The heat provided results in a rise in temperature at the interface between the sensor and the sample - typically less than 2º C.
4- This temperature rise at the interface induces a change in the voltage drop of the sensor element.
5- The rate of increase in the sensor voltage is used to determine the thermo-physical properties of the sample material.

Thermal conductivity can be calculated using the equation (1), the thermal diffusion using the equation (2), the Effusivity equation by (3),and the thermal Resistance equation by(4). all measurements of these parameters obtained from [Mathis TC i]. see in figure (1).

$$Effusivity = \sqrt{k\rho c_p}$$

Where :

$k = thermal\ conductivity\ (W/m \cdot K)$

$\rho = density\ (kg/m^3)$

$c_p = heat\ capacity\ (J/kg \cdot K)$

Fig. 1: (Mathis TC i) test.

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RESULTS AND DISCUSEIONS

The thermal conductivity of the different samples was measured by Mathis TCi method [90]. four different conductive blend resins are investigated. Heat capacity of a thick sample is measured with Mathis TCi and the thermal analyzer is calculated using equations (1,2,3,and 4). The results are summarized in Table [1]. The influence of different modulation is illustrated in Figures (2,3,4,5and 6)The thick samples are placed directly on the wetted sensor, without using an aluminum foil in between. In reference aluminum foil is recommended to distribute the heat more evenly over the sample area, since the sample diameter is somewhat larger than the sensor diameter. In the present study, where better conducting samples areinvestigated, it is found that the use of the aluminum disk is superfluous. Table showedthe results ofEiffiusivity thermal increasing with increase percentage of load Nano- Sic, the improving may be can to UFG and Nano – Sic particles Reinforced in matrix Figure (2), as well as improving in thermal conductivity from 0.288 for blend matrix to 0.65(w /m.k) for 15% Nano – Sic, because good distributions of nanoparticales of Nano – Sic and good thermal conductivity of materials reinforced in blend[19].showed that in figure (3). thethermal diffusion too increase with increase percentage load**,** in figure (5). the heat capacity is drop from 1354 in blend to 1089 J/ kg. k in 15% Nano – Sic, because low heat capacity of Naon – Sic and UFG see Figure (4).while the thermal Resistance is increase from ($0.74 *10^{-3}$) for blend to ($0.913 *10^{-3}$) kg.k / J , because the thermal Resistance is inverse of heat capacity. The increase of thermal Resistance values back to Nano – Sic and UFG reinforced ,resulted charge carries (electrons and holes) to find in materials reinforced.

Table 1: Thermal analyzer by Mathis TC I Values.

No. Sample	Sample Name	λ (w / m. k)	Ɛ $ws^{½}/m^2.k$	δ m^2 / s $*10^{-6}$	C_p (J/kg.k)	R (kg..k/ J) $*10^{-3}$
1	Neat	0.288	655	0.193	1354	0.738
2	Blend	0.266	630	0.180	1275	0.784
3	5% Sic	0.465	838	0.310	1170	0.854
4	10% Sic	0.489	860.6	0.336	1099	0.909
5	15% Sic	0.650	1020	0.400	1089	0.913

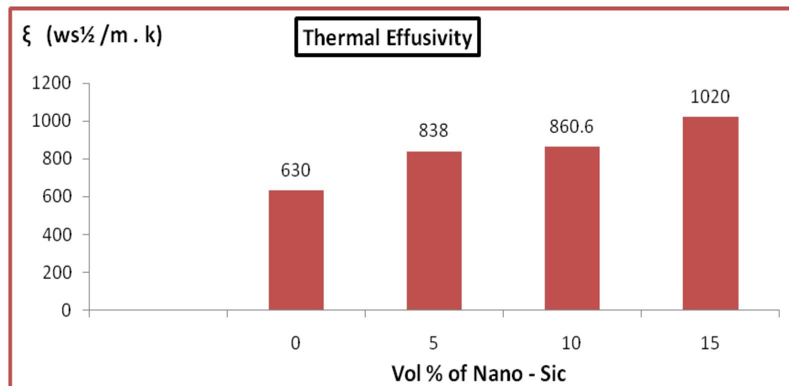

Fig. 2: Thermal Effusivity Values.

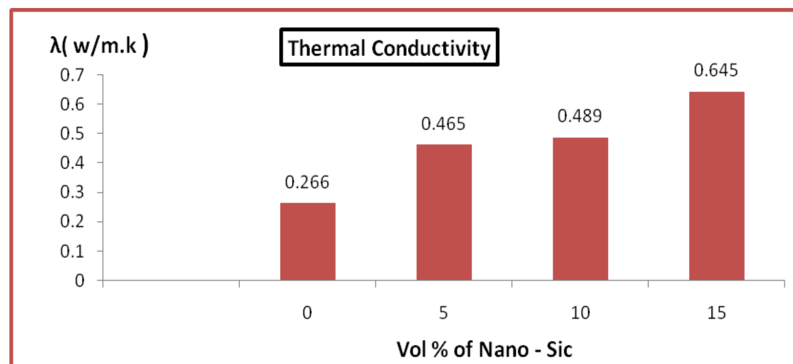

Fig. 3: Thermal conductivity Values.

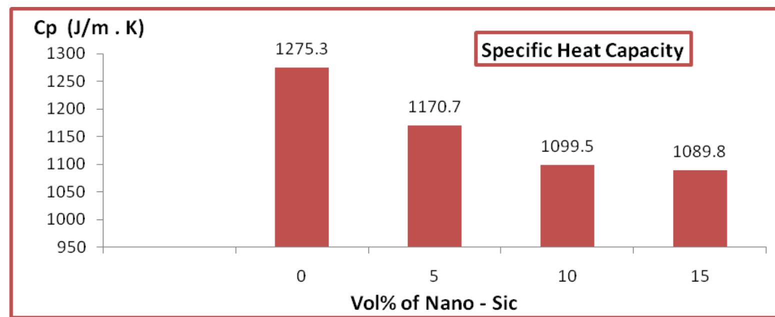

Fig. 4: Specific heat capacity Values.

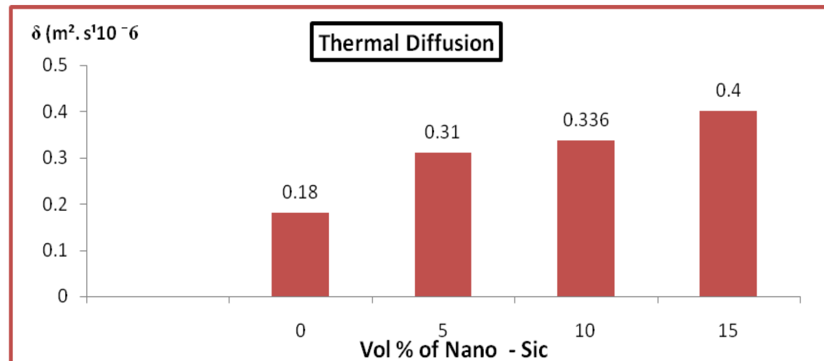

Fig. 5: Thermal diffusion Values.

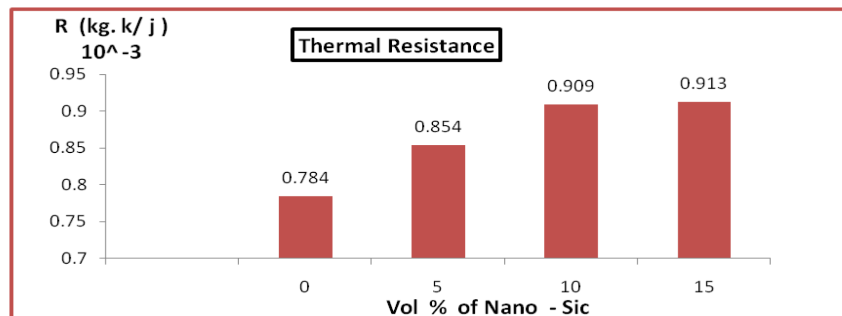

Fig. 6: Thermal Resistance Values.

Conclusion:

1- Thermal Effusivity, conductivity, diffusion and Resistance increase with increase percentage of Nano – Sic values.
2- The heat capacity decrease with increase percentage of Nano – Sic values.
3- The values of thermal Resistance at range (10^{-3}).

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