EXPERIMENTAL ANALYSIS OF HEAT CONDUCTION IN POLYESTER-ALUMINA NANO-COMPOSITES

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Abstract. *This paper presents an experimental analysis of the thermal conductivity of a nano-composite system composed of an unsaturated polyester resin as matrix and alumina nano-particles as filler. The nano particles used are 30-40 nanometers gamma alumina particles. Samples are fabricated using simple molding and no specialized homogenization equipment is used for mixing the particles with the liquid resin. The thermal conductivity is measured using the Fox-50 device, manufactured by LaserComp. Measurements are taken at different temperatures (from 0° to 50°C) for different batches of samples varying the fraction of nano-particles used in the composite system. The measurements show a small deviation between samples from the same batch, and indicate that there is a minor dependence of the thermal conductivity in temperature. This difference tends to be more notable for batches with a higher nano-particle fraction. Finally, the thermal conductivity measurements are compared with models for predicting the thermal conductivity of composite materials with nano-particles, showing that the obtained results are over the values estimated by these models.*

Keywords: *Composite Materials, Nanoscale, Heat Conduction, Polymers*

1. NOMENCLATURE

k	thermal conductivity
T	temperature
n	parameter in Hamilton-Crosser model
Greek Symbols	
ρ	density or specific mass
ϕ	volume fraction
ϕ_m	mass fraction
ψ	sphericity
Subscripts	
m	matrix
p	nano-particle
nc	nano-composite
Max	Maxwell model
HC	Hamilton-Crosser model
$Brug$	Bruggman model

2. INTRODUCTION

Modern technologies continuously need new materials and there is a crescent tendency to design novel compounds using existing constituents. By doing so, one can engineer new materials that possess user-prescribed properties. Over the last decades, many efforts have been made for obtaining nano-materials with determined functionality. The combination of metal and metal-oxides with polymer are typical examples, leading to nano-composites composed of pure metal or metal oxides as additives in polymer matrices. Nano-sized metals have different properties from bulk metals originating from nano-crystals size. Nano-crystals measure a few nanometers containing few hundred atoms. In this way, nano-materials can show unique properties (thermal, electronic, magnetic, structural, and so on) depending on nano-structure size. Previous studies have shown that the addition of a small fraction of nano-particles to a solution can lead to a noticeable change in the overall thermal conductivity. With the inclusion of nano-particles, the macroscopically observed thermal conductivity of a solution is significantly higher than the predicted value if particles of a large size scale were used. Several studies, both of experimental and theoretical nature, have been conducted with the attempt of investigating and explaining this phenomena. Regardless of the mechanisms that are responsible for this increase, it is known that the addition of nano particles (of higher thermal conductivity, naturally) can effectively augment the thermal conductivity of a material. As observed from the literature, most of these studies are oriented towards thermal intensification of liquids (Eastman, Choi et al., 2001; Eastman, Phillpot et al., 2004; Chen, 2001, 2002; Vadasz, 2006), leading to the so-called nano-fluids. Despite the fact that most previous studies are nano-fluid oriented, the same thermal intensification can occur in solids. Some studies investigate the thermal conductivity of different polymeric matrix composites (Kuriber and Alam, 2002; Putnam, David et al., 2003; Tavman, 1997; Kumlutas, Tavman et al., 2003). In this context, the goal of this study is to experimentally determine how the effective thermal conductivity is influenced by the addition of aluminum oxide (or alumina) nano-particles in an unsaturated polyester matrix composite which has a lower thermal conducting compared to raw alumina. The polymer matrix consists of an unsaturated polyester resin which is used in the production of fiber-reinforced plastics or non-reinforced filled products for various applications and end-markets.

3. MATERIALS AND METHODOLOGY

In order to obtain the nano-composite system, unsaturated polyester resin was used as the matrix and aluminum oxide (Al_2O_3) nano-particles as the filler (dispersed phase). The polymer used in this investigation was Polylite 10316-10 (provided by Reichold), an unsaturated polyester diluted in 44% styrene. The resin system is pre-accelerated by the manufacturer and the initiator used was methyl ethyl ketone peroxide (1.5 phr). The unsaturated polyester resin properties are presented in table 1.

Table 1. Properties of Unsaturated Polyester Resin

Property	value
Viscosity at 25°C μ (cP)	250 to 350
Density ρ (kg/m^3)	1090
Heat Distortion Temperature HDT (°C)	85
Modulus od Elasticity E (GPa)	3.3
Flexural Strength (MPa)	45
Tensile Strength (MPa)	40
Maximum Elongation (%)	1

The nano-particles are aluminum oxide (Al_2O_3), provided by NanoAmor, constituted of mainly alpha alumina (containing 5-10% theta) with 99.99% purity. The average particle size, as provided by the manufacturer is 30-40 nm, and its properties are presented in table 2 (provided by the nano-particles manufacturer).

The nano-composite specimens were manufactured by adding a mass fraction of mass to about 250 ml of liquid (pre-cured) unsaturated polyester resin, leading to mixtures having 5%, 10% and 15% mass fraction of alumina nano-particles. However, the catalyzer is added to the mixed solution after mixing the nano-particles into the resin in amount that corresponds to 1.5% of the resin mass. Samples of size is about 50 mm in diameter and 13 mm in thickness were manufactured using simple molding. The mold is composed of a central metal frame between two glass plates. The frame was

Table 2. Thermophysical properties of alumina particles.

Property	value
thermal conductivity ($W\,m^{-1}\,K^{-1}$)	30 to 40
density (kg/m^3)	3500 to 3900

built from a tin plate that was machined with the samples holes and a flow channel for introducing the liquid resin, as displayed in figure 1. The nano-particles and resin mixtures were homogenized

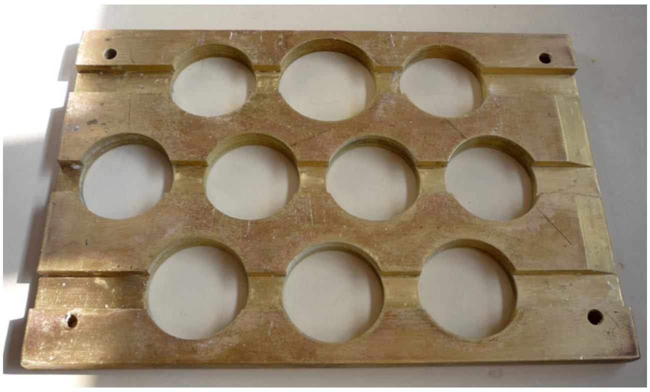

Figure 1. Tin frame used in molding the samples.

simply by manual mixing, and the catalyzer was added just prior to pouring into the mold. Also, pure unsaturated polyester resin specimens with no filler were made as reference. Figure 2 also shows two used polyester samples.

Figure 2. Samples, with (left) and without (right) alumina particles.

The experiments were conducted using thermal conductivity measurement device manufactured by LaserComp, Fox-50, which is capable of measuring samples from $-10°C$ to $110°C$. Figure 3 shows the equipment used for the measurements. The test parameters, as specified to the Fox-50 device, are displayed in table 3. The calibration curve must be selected, and a material that has a thermal conductivity closer to the measured samples must be selected. The chosen calibration curve was based on Perspex, whose thermal conductivity values are displayed in table 4.

4. THERMAL CONDUCTIVITY MODELS

In order to comparatively analyze the experimental results obtained in this study, models for determining the effective thermal conductivity of a two-phase system involving a dispersed phase sur-

Figure 3. Thermal conductivity measuring device (Lasercomp Fox-50).

Table 3. Test parameters

description	value
Number of consecutive equilibrium stages	12
Temperature equilibrium condition	1°C
Between block HFM equilibrium	200 μV
Heat flow meter (HFM) percent change	2%
Calculation blocks	3
Calibration material	Perspex

Table 4. Perspex calibration curve

T (°C)	k (W m^{-1}K^{-1})
-10	0.184800
20	0.188500
40	0.190900
60	0.193300
70	0.194550

rounded by a continuous phase. Denoting k_p the thermal conductivity of the particles and k_m as the thermal conductivity of the surrounding phase, the following ratio is defined:

$$k^* = \frac{k_p}{k_m}, \tag{1}$$

The Maxwell model (Trisaksri and Wongwises, 2007) is a traditional method for calculating the effective thermal conductivity of suspensions with relatively large (applicable to micro-particles) spherical particles.

$$k_{nc,Max} = \frac{k^* + 2 + 2\,(k^* - 1)\,\phi}{k^* + 2 - (k^* - 1)\,\phi}\,k_m. \tag{2}$$

The Hamilton-Crosser model (Trisaksri and Wongwises, 2007) is an improvement on to Maxwell model for taking into account the particle shape. The thermal conductivity of mixture of a disperse phase mixed within a surrounding phase is given by:

$$k_{nc,HC} = \frac{k^* + (n-1) - (n-1)\,(1-k^*)\,\phi}{k^* + (n-1) + (1-k^*)\,\phi}\,k_m \tag{3}$$

where n is an empirical form factor given by

$$n = \frac{3}{\psi}, \tag{4}$$

and ψ is the sphericity, defined as the ratio of the surface area of a sphere having a volume equal to that of the particle, to the surface area of the particle. Naturally, for spherical particles, $\psi = 1$ and $n = 3$, which leads to the Maxwell model.

The Bruggeman model (Murshed, Leong et al., 2005) is based on the following relation:

$$k_{nc,Brug} = k_m \left[\frac{1}{4}\,[(3\,\phi - 1)\,k^* + (2 - 3\,\phi)] + \frac{\sqrt{\Delta}}{4}\right] \tag{5}$$

where the parameter Δ is given by:

$$\Delta = \left[(3\,\phi - 1)^2\,(k^*)^2 + (2 - 3\,\phi)^2 + 2\,(2 + 9\,\phi - 9\,\phi^2)\,k^*\right]. \tag{6}$$

Since all of the previous models are based on the volume fraction of particles (ϕ), and the experiments performed in this study are based on a mass fraction basis (ϕ_m), the volumetric and mass fractions are related, based on the following equation:

$$\rho_{nc} = \rho_m\,[(1 - \phi) + \phi\,\rho^*] \tag{7}$$

In order to calculate the thermal conductivity according the to previously presented models, values for the properties of the polymeric matrix and particles must be used. While the properties of the polymer were measured in this study, the nano-particle properties were taken from literature data, as presented in table 2.

5. RESULTS AND DISCUSSION

Results of pure polyester resin samples, and other samples loaded with 5%, 10% and 15% (calculated without the catalizer) in mass fraction of nano-particles were experimentally obtained and are presented in the following tables Table 5 presents the values obtained for pure resin samples. As can be seen, there is a minor variation in thermal conductivity with temperature. Based on the mea-

Table 5. Thermal conductivity measurements of pure polyester sample (no nano-particles)

	k (W m^{-1}K^{-1})							
T (°C)	A1	A2	A3	A4	A5	A6	Av.	St.Dev.
0	0.1535	0.1523	0.1538	0.1529	0.1551	0.1532	0.1535	0.000952
25	0.1557	0.1548	0.1556	0.1547	0.1568	0.1550	0.1554	0.000787
50	0.1560	0.1558	0.1563	0.1550	0.1567	0.1555	0.1559	0.000598

surements for these pure resin samples, an average value (at each temperature) is calculated and is also presented on table 5. These values will be used for calculating thermal conductivity estimates at different temperatures, using the models presented in the previous section.

Next, tables 6 and 7, present values of the measured thermal conductivity for samples loaded with different concentration of alumina nano-particles. As seen for the pure resin samples, there is little variation with temperature; nevertheless, for this dependency seems to be unrelated to the fraction of nano-particles in the samples.

Table 6. Thermal conductivity measurements of samples with $\phi_m = 5\%$.

	k (W m^{-1}K^{-1})					
T (°C)	A1	A2	A3	A4	Av.	St.Dev.
0	0.1679	0.1690	0.1676	0.1681	0.1682	0.000603
25	0.1696	0.1704	0.1691	0.1694	0.1696	0.000556
50	0.1725	0.1734	0.1720	0.1716	0.1724	0.000776

Table 7. Thermal conductivity measurements of samples with $\phi_m = 10\%$.

	k (W m^{-1}K^{-1})							
T (°C)	A1	A2	A3	A4	A5	A6	Av.	St.Dev.
0	0.1808	0.1821	0.1824	0.1822	0.1826	0.1816	0.1820	0.000657
25	0.1828	0.1836	0.1835	0.1848	0.1842	0.1834	0.1837	0.000694
50	0.1865	0.1857	0.1848	0.1859	0.1853	0.1844	0.1854	0.000763

Table 8. Thermal conductivity measurements of samples with $\phi_m = 15\%$.

	k (W m^{-1}K^{-1})				
T (°C)	A1	A2	A3	Av.	St.Dev.
0	0.2016	0.2009	0.2021	0.2015	0.000603
25	0.2037	0.2030	0.2030	0.2032	0.000404
50	0.2050	0.2072	0.2035	0.2052	0.001861

Table 9, provides the average values obtained from the previous tables. As naturally expected, the conductivity increases with the fraction of nano-particles. Then in order to compare the measured results with data obtained from thermal conductivity models, the averaged values presented in table 9

Table 9. Thermal conductivity measurements (average of samples) for different nano-particle fractions.

	ϕ_m			
T (°C)	0.00%	5%	10%	15%
0	0.1535	0.1682	0.1820	0.2015
25	0.1554	0.1696	0.1837	0.2032
50	0.1559	0.1724	0.1854	0.2052

are plotted together with estimates from three different thermal conductivity models. Figure 6 displays this comparative results. As can be seen, the estimates from the three models employed underestimate the measured values. The Hamilton-Crosser model represents better the experimental data; however,

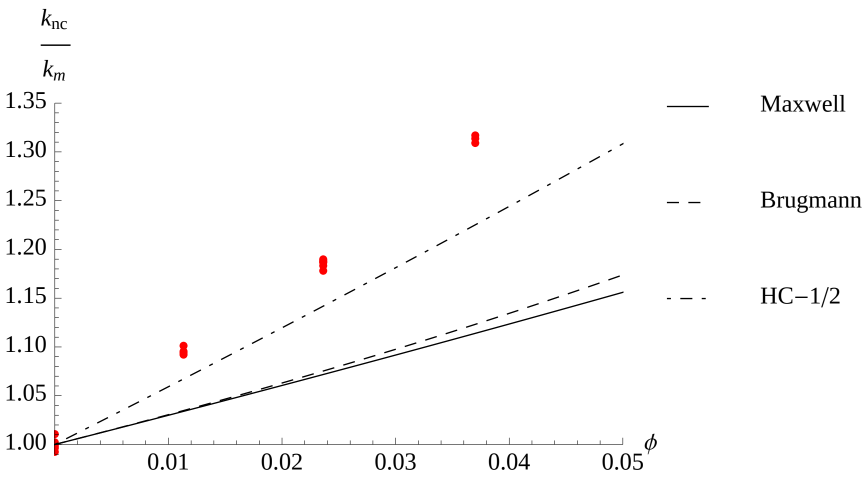

Figure 4. Comparisons of experimental data (in red) with thermal conductivity models at 0°C.

it was plotted with an sphericity value of $1/2$, which would occur for particles that have a greater specific surface area, while compared to a sphere. At this point is worth noting, that the manufacturer data sheet indicates that the supplied nano-particles are nearly spherical. This confirms observations seen for nano-fluids in which additional thermal effects associated to the nano-scale can lead to a thermal intensification over traditionally expected values for particles in a larger length scale.

Finally, in order to provide more accurate data on the measured thermal conductivity, the last table (tab. 10) provides the average percentual aumentation in k compared to that of the pure resin.

Table 10. Thermal conductivity aumentation for different nano-particle fractions.

	$(k_{nc} - k_m)/k_m$		
T (°C)	5%	10%	15%
0	9.57%	18.6%	31.3%
25	9.13%	18.2%	30.8%
50	10.6%	19.0%	31.7%

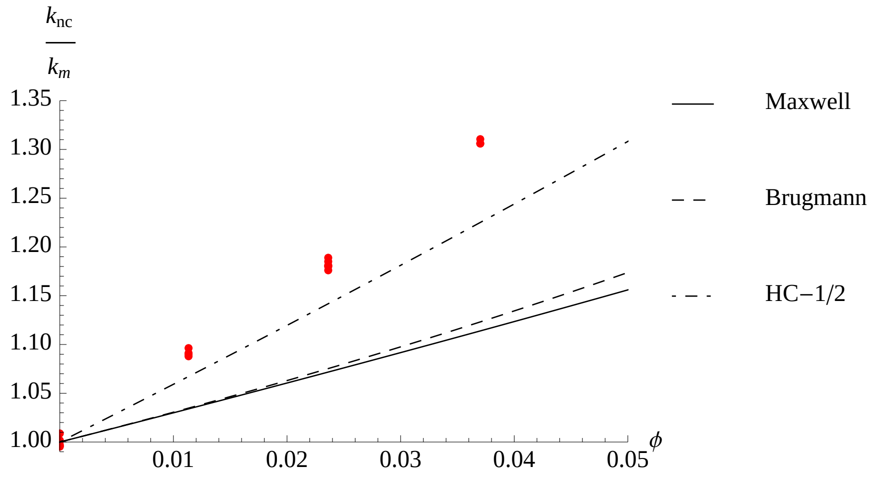

Figure 5. Comparisons of experimental data (in red) with thermal conductivity models at 25°C.

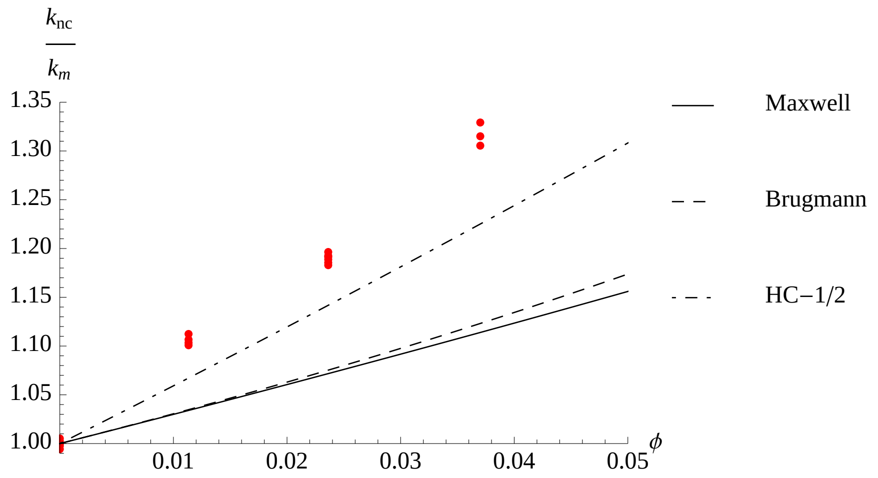

Figure 6. Comparisons of experimental data (in red) with thermal conductivity models at 50°C.

6. CONCLUSIONS

This paper presented an experimental investigation of heat conduction in nano-composites. Polymer samples with different concentrations of Alumina nano particles were manufactured and experimentally analyzed using a thermal conductivity measuring device. Predictions from different thermal conductivity models were used for comparing the experimental results with the measured data. The results showed that the thermal conductivity increases with nano-particle concentration, as expected. Nevertheless, the measured values exceed the prevision from traditional models for estimating the effective conductivity of composite materials. As a final comment one should mention that, in spite of the relevance of the presented findings, these results are preliminary measurements and a more extensive investigation will follow this work. The effects of homogenization using specialized equipment for mixing the resin-nano-particles solution must be investigated. Furthermore, other effects such as analyzing the effects of nano-particle size and material should be carried-out.

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