ISSN 2176-5480

22nd International Congress of Mechanical Engineering (COBEM 2013)
November 3-7, 2013, Ribeirão Preto, SP, Brazil

EXPERIMENTAL INVESTIGATION OF DENSITY AND THERMAL CONDUCTIVITY IN POLYMER NANOCOMPOSITES

Nelson Rodrigues Braga Jr
Debora Carneiro Moreira
Leandro A. Sphaier
Universidade Federal Fluminense - Passo da Pátria, 156 Bl. E sala 216, Niterói, Rio de Janeiro, Brasil
nelsonbraga@id.uff.br
dcmoreira@id.uff.br
lasphaier@id.uff.br

Abstract. *The present paper shows an experimental analysis of density and thermal conductivity of polymer nanocomposites. The polymers used for continuum phase were the unsaturated polyester resin (UPR) and the epoxy resin (ER), while aluminum oxide (Al_2O_3) and copper oxide (CuO) nanoparticles were employed as the dispersed phase. The samples were fabricated through simple molding using different amounts of nanoparticles. Different sizes of aluminum oxide particles were used in order to analyze the effects of size variation on the nanocomposites properties. The Thermal conductivity of each sample was measured at three different temperatures, the measurement method is in accordance with ASTM C 518 and ISO 8301. The results showed that higher nanoparticle concentrations were responsible for an increase in both properties, moreover it was observed that larger nanoparticles were responsible for a higher variation in the thermal conductivity.*

Keywords: *Nanocomposite, density, termal conductivity, polymer*

1. INTRODUCTION

Polymeric resins have been used extensively as a continuous phase in composite materials in several parts of industry. Studies have shown that addition of a small fraction of nanoparticles can lead to a perceptible change in the overall thermal conductivity. Fan *et al.* (2004) reported effects of nanoadditives in electrical and thermal conductivity in polymer composites. Moreira *et al.* (2011) examined thermal conductivity of polymeric nanocomposites manufactured by the same process as samples studied in this paper. As observed from the literature, many of these studies are oriented towards thermal intensification of liquids (Eastman *et al.*, 2001; Zhang *et al.*, 2007; Tavman *et al.*, 2008), leading to the so-called nano fluids

In this study AL_2O_3 (alumina) and CuO (tenorite) nanoparticles were mixed and manufactured through simple molding with epoxy and polyester resin, in order to investigate the thermal conductivity and density variation for different volume fractions.

2. MATERIALS AND METHODS

2.1 Materials

Polymers used as continuum phase were the unsaturated polyester resin (UPR) Polylite 10316-10 (provide by Reichold), and the epoxy resin (ER). The hardener used for the polyester resin was the methyll ethyl ketone peroxide (MEKP), and an aliphatic amine hardener for the epoxy resin. The nanoparticles, provided by NANOAMOR, were aluminum oxide (Al_2O_3) and copper oxide (CuO). The average particle size and other nanoparticles information, as provided by the manufacturer, are presented in Table 1

Table 1. Thermophysical properties of nanoparticles.

Property	Al_2O_3	Al_2O_3	CuO
Termal conductivity (W m^{-1} K^{-1})	36	36	32.9
True density ρ (kg/m^3)	3500 a 3900	3500 a 3900	6300 a 6490
Morphology	Nearly spherical	Spherical	Nearly spherical
Particle size (nm)	30 - 40	200	30 - 50
Purity	99.99%	99.9%	99%

ISSN 2176-5480

2.2 Nanocomposite fabrication

Before fabrication, the nanoparticles are placed in a oven for 24 hours at a temperature of 120 °C to remove the moisture. This is an important process since some metal oxide particles can uptake significant amounts of water vapor from atmospheric air. The polymer and the nanoparticles are mixed using the planetary ball mill, and this homogenization is carried out for an average period of 1h at 200rpm. After mixing, the hardener is added, and the liquid nanocomposite is poured into the mold. The mold is composed of a metal frame with circular holes and a flow channel, which is secured between two glass plates. The last stage in fabrication consists of demolding followed by surface finishing. In final form, the samples are circular cylinders with dimensions of 50mm diameter by 13mm thickness.

2.3 Methods

The experiments were conducted using a thermal conductivity measurement device (LaserComp, Fox-50) capable of measuring samples at different temperatures. The measurable conductivity range is from 0.1 to 10 W m^{-1} K^{-1}, and the measurement method conforms to the standards ASTM C518-04 and E1530-06, the results for the thermal conductivity can be seen in Moreira (2011).

The density of the composite materials was determined using Archimedes principle.Where the mass of the sample was measured immersed in a fluid with known density (apparent mass). For the measurement of mass and apparent mass it was used the precision balance Shimadzu AW220 along with the Specific Gravity Measurement Kit. Water was chosen as fluid.

Using the experimental values for the density of the matrix, it is possible to calculate a theoretical density for the nanocomposite according to the experimental volume fraction (ϕ), by the equation:

$$\rho_{nc} = \rho_p \, \phi + (1 - \phi)\rho_r \tag{1}$$

$$\frac{\rho_{nc}}{\rho_r} = 1 + \left(\frac{\rho_p}{\rho_r} - 1\right) \phi \tag{2}$$

where $\rho_{nc}, \rho_p, \rho_r$ are, respectively, the density of nanocomposite, nanoparticle and the density of the matrix. The same can be done as function of mass fraction (ϕ_m) , by the equation:

$$\frac{\rho_{nc}}{\rho_r} = \frac{\rho_p}{\rho_r \, \phi_m + (1 - \phi_m) \, \rho_p} \tag{3}$$

Particle density values were taken from Table 1. Since the manufacturer provided a density range for the nanoparticles, upper and lower limits for the nanocomposites densities were calculated.

It is know that the volume can be calculated as a ratio between the mass and the density:

$$V = \frac{M}{\rho} \tag{4}$$

and the mass of the matrix in a composite material can be calculated as a function of mass fraction:

$$M_r = M_{nc}(1 - \phi_m) \tag{5}$$

where M_r and M_{nc} are, respectively, the mass of the matrix and the mass of the nanocomposite. With equations (4) and (5) it can be found the value for the volume of the matrix (V_r) and the volume of the nanocomposite (V_{nc}). Considering that the nanocomposite manufactured just have two phases the volume of nanoparticles in nanocomposite also can be calculated:

$$V_p = V_{nc} - V_p \tag{6}$$

and with equation (6) it can be estimated a experimental volume fraction (ϕ_e):

$$\phi_e = \frac{V_p}{V_{nc}} \tag{7}$$

We must emphasize that the possible existence of air bubbles inside the samples will make that the values for experimental volume fraction change, because of the air volume that will decrease the nanoparticle volume.

3. RESULTS AND DISCUSSION

The first samples were manufactured without nanoparticles, in order to analyze the properties of the resin with hardener. This results are showed in Table 2, where ρ is the density of the liquid resin and ρ_r is the density of the matrix (resin

ISSN 2176-5480

Table 2. Properties of unsaturated polyester resin and epoxy resin.

Properties	UPR	ER
ρ_r measured (kg/m^3)	1196.4 ± 0.25	1157.4 ± 0.24
k_r measured (W/mK)	0.1578 ± 0.0021	0.2014 ± 0.0020
ρ by the manufacturer (kg/m^3)	1090	1160

with hardener). k_r is the thermal conductivity of the resin with hardener, the result for the samples without nanoparticles were necessary to measure the variation of the properties when it was added the nanoparticles .

As it can be seen in Table 2, the density value provided by the manufacturer is very close to the measured density of the epoxy resin, while experimental results for polyester resin density is clearly higher than the value provided by the manufacturer. This increase can be explained by a contraction of the polyester resin during the hardening process.

Figures 1, 2 and 3 show a comparison between experimental results of increased density as a functions of mass and volume fractions, respectively. It is important to mention that volume fraction values were recalculated, based on experimental density values obtained from pure resin samples measurements.

The manufacturing process can be evaluated taking into account the comparison between these results. The value obtained for the two types of Al_2O_3, 30-40nm and 200nm, are in the expected range, with only one exception in Figure 1, that has a sample outside of this range, manufactured with 7.5% in volume fraction of Al_2O_3 nanoparticles 30-40nm. For the copper oxide, figure 3, we can observe that the value with volume fraction above 10% suffered a slight deviation from the theoretical model curve.

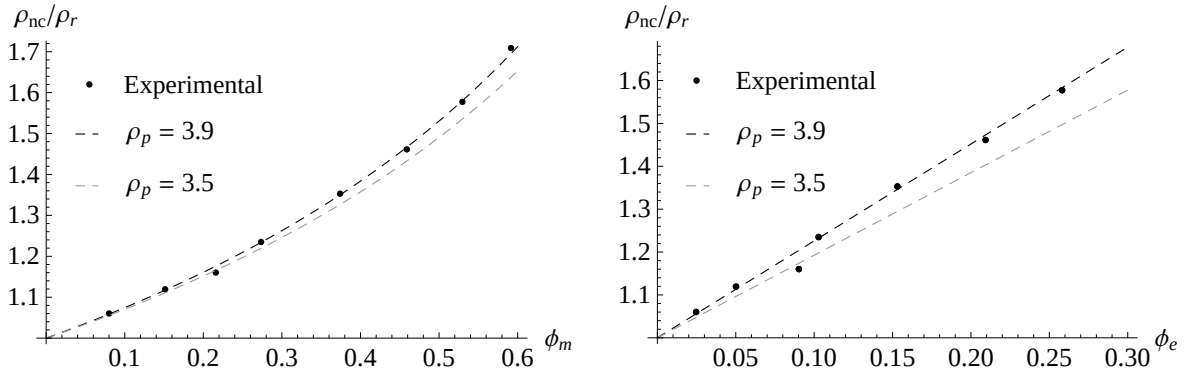

Figure 1. Variation in density as a function of mass fraction and experimental volume fraction of UPR nanocomposites with 30-40nm Al_2O_3 nanoparticles.

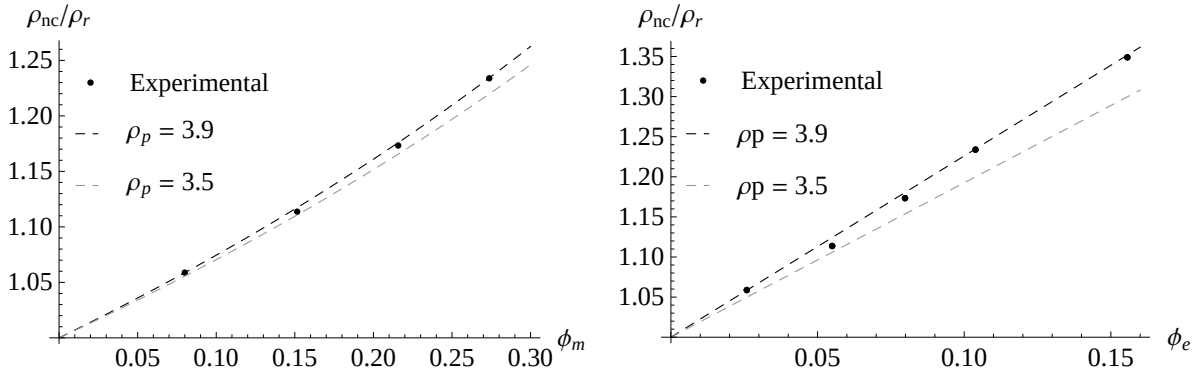

Figure 2. Variation in density as a function of mass fraction and experimental volume fraction of UPR nanocomposites with 200nm Al_2O_3 nanoparticles.

Through the analysis of figures 1 and 2, we can assign 3900kg/m^3 as the value of the density of Al_2O_3 nanoparticles. With the results obtained for the CuO nanocomposites it is not possible to find a standard value for the nanoparticle density due to the deviation above 10%.

ISSN 2176-5480

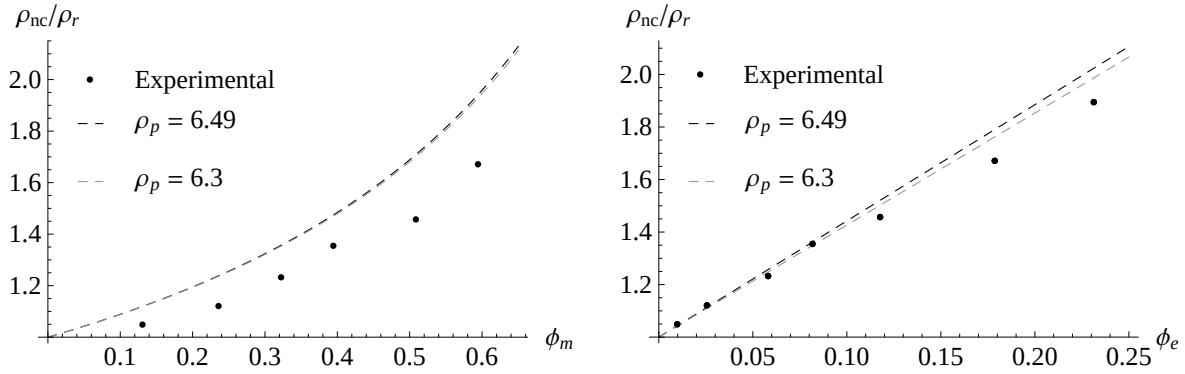

Figure 3. Variation in density as a function of mass fraction and experimental volume fraction of UPR nanocomposites with CuO nanoparticles.

Results of density augmentation with particle content were also obtained for epoxy matrix nanocomposites, and may be seen in Figures 4, 5 and 6.

Unlike the results from polyester matrix, epoxy nanocomposites present a great variation in density, if compared with theoretical prediction. These discrepancies between experimental and theoretical results can be explained by the possible existence of air bubbles inside the samples. In fact, epoxy resin has a high viscosity, about four times higher than that of polyester resin, such that epoxy nanocomposites may have retained significant amounts of air, while polyester nanocomposites haven't.

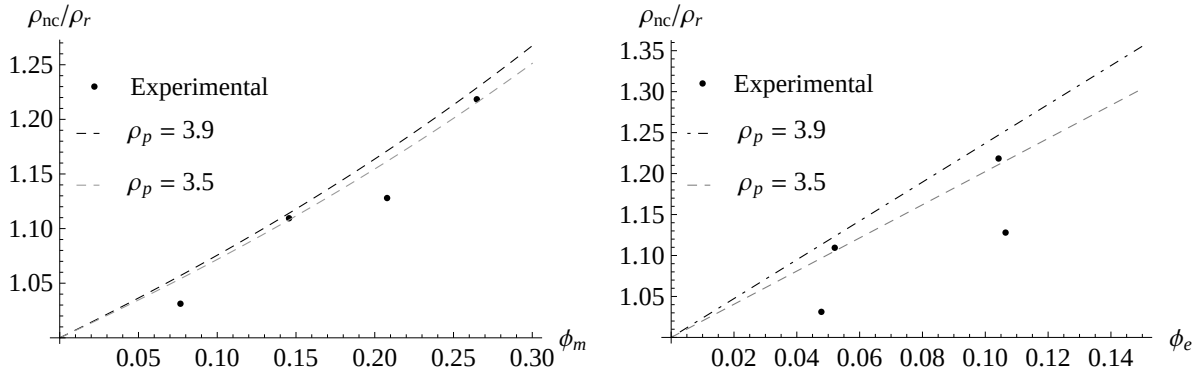

Figure 4. Variation in density as a function of mass fraction and experimental volume fraction of ER nanocomposites with 30-40nm Al_2O_3 nanoparticles.

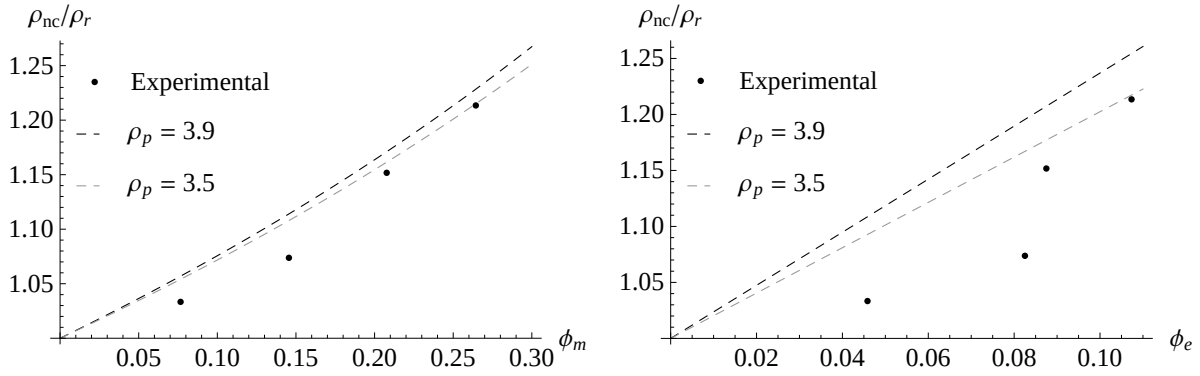

Figure 5. Variation in density as a function of mass fraction and experimental volume fraction of ER nanocomposites with 200nm Al_2O_3 nanoparticles.

ISSN 2176-5480

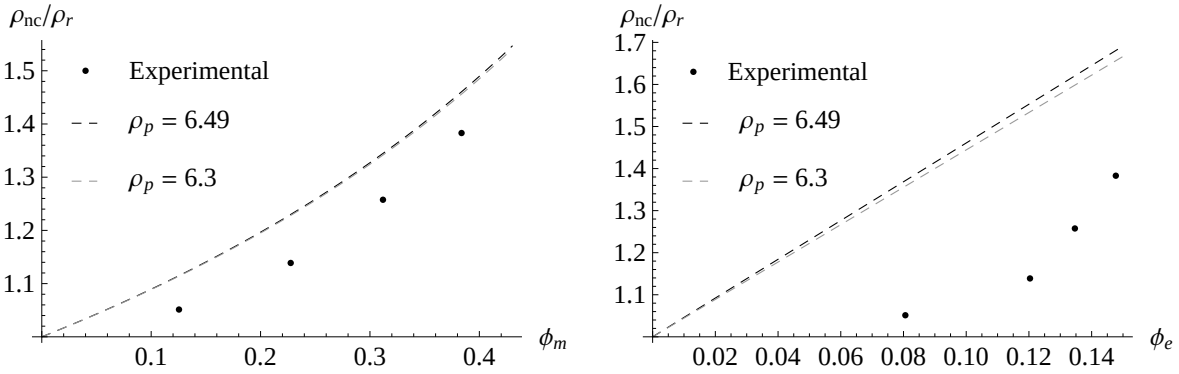

Figure 6. Variation in density as a function of mass fraction and experimental volume fraction of ER nanocomposites with CuO nanoparticles.

An effectiveness of thermal intensification can be defined as the ratio between the increase in thermal conductivity and increased density:

$$\epsilon = \frac{k_{nc}/k_r}{\rho_{nc}/\rho_r} \tag{8}$$

where k_{nc} and ρ_{nc} are, respectively, the thermal conductivity and the density of the nanocomposite. Experimental results for k_r and ρ_r were shown in table 2. This parameter could be used to evaluate this new material, as we seek material with higher improve in thermal conductivity maintaining lower densities. Figure 7 shows the comparison of effectiveness in function of volume fraction for the three types of nanocomposites, for polyester and epoxy resin.

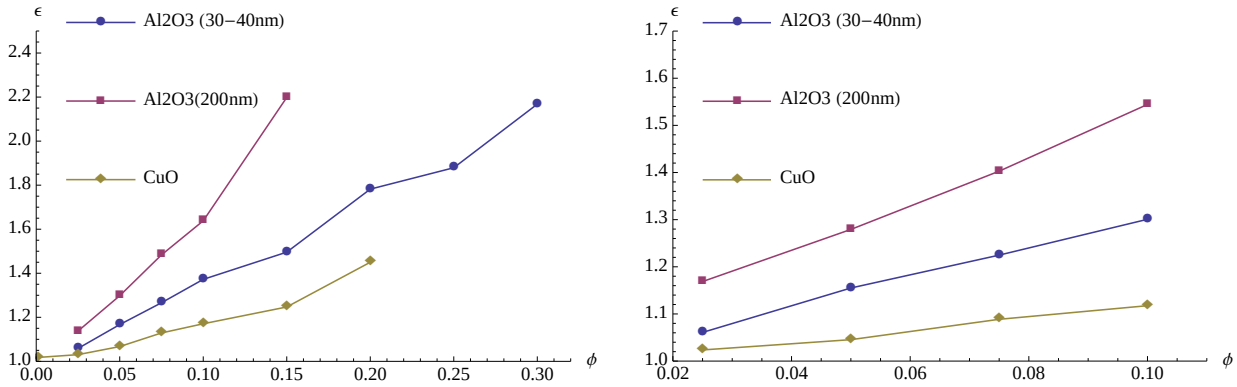

Figure 7. Effectiveness as a function of volume fraction of UPR and ER resin, respectively.

In figure 7 it can be concluded that nanocomposite with 200nm Al_2O_3 nanoparticles would be the best material to be used in applications where it is necessary a high thermal conductivity, since it achieves greater intensification thermal with a smaller mass increase, although nanocomposite with 30-40nm Al_2O_3 nanoparticles are the only that could be fabricated with higher concentrations of nanoparticles.

4. CONCLUSIONS

This paper presented an experimental investigation of density and thermal conductivity in nanocomposites materials, composed of epoxy resin (ER) and unsaturated polyester resin (UPR) with three different metallic oxides as dispersed phase. Nanocomposites were manufactured with different concentrations of aluminum oxide (Al_2O_3) and copper oxide (CuO), different size of aluminum oxide particles were used, 200nm and 30-40nm.

The results obtained for the density of the nanocomposites were possible to evaluate the method of manufacturing used. While the polyester resin present similar results to the expected according theoretical results. Nanocomposites made with epoxy resin showed lower results according to theoretical, due to the greater presence of bubbles and possible variations of mass fraction in fabrication. Results showed that higher nanoparticle concentrations were responsible for an increase

ISSN 2176-5480

in both properties, moreover it was observed that larger size of nanoparticles were responsible for a higher variation in the thermal conductivity, hence the aluminum oxide with diameter of 200nm present greater thermal intensification.

In order to evaluate nanocomposites properties was defined a parameter, as the ratio between the increase in thermal conductivity and increased density, results showed that nanocomposites of Al_2O_3 200nm would be the best material to be used in applications where it is necessary high thermal intensification with a small mass increase, although the results for Al_2O_3 200nm present a greater thermal intensification, it was not possible to manufacture nanocomposites with volume fractions above 15% while nanocomposites with 30-40nm Al_2O_3 nanoparticles was manufacture with volume fractions up to 30%, thus achieving higher values of thermal conductivity but also increasing the density of the sample.

5. ACKNOWLEDGEMENTS

The authors would like to acknowledge the financial support provided by, CNPq, FAPERJ and Universidade Federal Fluminense.

6. REFERENCES

C518-04, 2004. "Standard test method for steady-state thermal transmission pro- perties by means of the heat flow meter apparatus." *ASTM, West Conshohocken, Pennsylvania.*

E1530-06, 2006. "Standard test method for evaluating the resistance to thermal transmission of materials by the guarded heat flow meter technique." *ASTM, West Conshohocken, Pennsylvania.*

Eastman, J., Choi, S.U.S., Li, S., Wu, W. and Thompson, L., 2001. "Anomalously increased effective thermal conductivities of ethylene glycol-based nanofluids containing copper nanoparticles". *Applied Physics Letters*.

Fan, L., Su, B., Qu, J. and Wong, C.P., 2004. "Effeccts of nano-sized particles on electrical and thermal conductivities of polymer composites". *9th International Symposium on Advanced Packaging Materials*.

Moreira, D.C., 2011. "Análise experimental de propriedades termomecanicas em nanocompositos polimericos." Universidade Federal Fluminense.

Moreira, D.C., Sphaier, L.A., Reis, J.M.L. and Nunes, L.C.S., 2011. "Experimental investigation of heat conduction in polyester Al_2O_3 and polyester CuO nanocomposites". *Experimental Thermal and Fluid Science*, Vol. 35, pp. 1458–1462.

Tavman, I., Turgut, A., Chirtoc, M., Schuchmann, H. and Tavman, S., 2008. "Experimental investigation of viscosity and thermal conductivity of suspensions containing nanosized ceramic particles,". *Archives of Materials Science*, Vol. 100, No. 100.

Zhang, X., Gu, H. and Fujii, M., 2007. "Effective thermal conductivity and thermal diffusivity of nanofluids containing spherical and cylindrical nanoparticles". *Experimental Thermal and Fluid Science*, Vol. 31, No. 593–599.

7. RESPONSIBILITY NOTICE

The authors are the only responsible for the printed material included in this paper.