EXPERIMENTAL ANALYSIS ON THE THERMAL INTENSIFICATION OF POLYMERS BY THE ADDITION OF NANOPARTICLES

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Abstract. *This work comprises an experimental investigation of the thermal intensification in polymeric nanocomposites. Two thermoset polymers were employed as continuous phases and different sizes of alumina nanoparticles were used as fillers. The thermal conductivities of the fabricated samples were directly measured using a guarded heat flow meter and the influence of filler size was investigated. Results show that larger particles are responsible for greater thermal intensification of the polymeric matrices and indicate that interfacial properties may play a significant role in the effective thermal conductivity of nanocomposites.*

Keywords: *Thermal conductivity, Nanocomposites, Polymer, Guarded Heat Flow Meter, Alumina nanoparticles.*

1. INTRODUCTION

The thermal conductivity augmentation of polymeric materials caused by the addition of particles has been investigated over decades and several studies have been conducted with the attempt of investigating this phenomenon. Theoretical and experimental studies were developed with the objective of understanding and predicting changes in macroscopical properties of polymers with particle content and the mechanisms of heat conduction in a composite media are partially understood. It is known that the effective thermal conductivity of a composite material depends not only on the thermal conductivity of the different phases, but also on the geometry, morphology, distribution and interaction between the particles (Kumlutaş *et al.*, 2003). Changes in physical properties of compounds loaded with nanoadditives have been intensely investigated, since it has been shown that enhancements in physical properties could be obtained with little increase in weight.

Some works investigate the influence of nanoparticles in mechanical properties of polymers (Fu *et al.*, 2008; Moreira *et al.*, 2012), other are related to the thermal intensification of polymer matrices (Putnam *et al.*, 2003; Fu *et al.*, 2010; Moreira *et al.*, 2011). Most of these investigations show that nanocomposites present unpredicted enhancement in properties, if compared to larger scale composites. Such enhancement may be attributed to the high aspect ratio of nanofillers. Due to nanoparticle dimensions, large fractions of atoms may reside on its surface and interfacial interaction of the filler with polymer matrix is strengthened, giving greater importance to interfacial properties (Rong *et al.*, 2006; Kim *et al.*, 2007). Thus, aggregation of particles and interfacial thermal resistance between the dispersed and continuous phases play a significant role in thermal transport (Evans *et al.*, 2008) and results obtained by different works, be experimental or theoretical, may often disagree between themselves.

In this context, the main goal of this study is to fabricate polymeric nanocomposites and experimentally analyze variations in the effective thermal conductivity of the fabricated samples. Two different thermoset polymers were employed as the continuous phase of the nanocomposites, which were loaded with alumina nanoparticles. Three types of alumina nanoparticles were used, in order to investigate the influence of the nanoparticles size in the effective thermal conductivity of the nanocomposites. The thermal intensification of the two matrices are also compared.

2. MATERIALS AND METHODS

2.1 Nanocomposites Fabrication

The unsaturated polyester resin (UPR) Polylite 10316-10, provided by Reichold, and the epoxy resin (ER) RR515 from SILAEX were employed as matrices for the nanocomposites. The polymerization occurred by the addition of catalyst agents: methyl-ethyl-ketone peroxide (MEKP) in a proportion of 1.5 phr by weight for polyester resin and an aliphatic amine hardener for the epoxy resin, in a proportion of 25 phr by weight. Alpha-alumina (Al_2O_3) spherical nanoparticles were used as dispersed phase in the nanocomposite systems. The nanoparticles were provided by NanoAmor and were available in three different sizes: 30-40 nm, 27-43 nm, and 200 nm. Samples of pure polyester and pure epoxy resins were manufactured to be used as references, and nanocomposites specimens containing different volume fractions of nanoparticles (varying from 2.5% to 10%) were fabricated.

The nanoparticles were dried at 120°C for 24 h and then were added to the liquid resin. The amount of nanoparticles was added to the resin according to the desired volume fraction (ϕ). After the addition of nanoparticles, the mixtures were homogenized by a planetary ball mill for 1 h at 200 RPM. The hardener was added, then, manually mixed. Finally, the resulting blends were poured into the mold, which was composed of a central metal frame with 4 circular holes and a flow channel secured between two glass plates. All samples were demolded after 24h and the upper and lower surfaces were carefully finished, because surface imperfections lead to a greater thermal contact resistance with the surfaces of the conductivity meter, which leads to underestimated values for the thermal conductivity of the samples. Batches containing 4 samples of each mixture were made and the specimens final dimensions were 51 mm in diameter and 12.5 mm in height.

2.2 Experimental Methods

The thermal conductivities of the samples were directly measured with the guarded heat flow meter technique, modified to take into account the thermal contact resistance. The experiments were conducted using the Fox-50 device, a commercially available instrument manufactured by LaserComp. To perform a test, a sample with flat-parallel surfaces must be placed between the plates of the equipment and the temperatures of upper and lower plates are set up. The upper plate was set up to be in a higher temperature than the lower plate, so that the heat flowed down. Measurements of thermal conductivity are assumed to be taken at the mean temperature between the plates of the equipment and the thermal contact resistance is assumed to be the same as in the calibration archive. Different calibration materials are offered by the instrument and the user should select one with the closer expected thermal conductivity value. The experiments were conducted with heat flowing down at three different temperature setpoints (0, 25 and 50°C), with a temperature difference of 20°C between upper and lower plates.

3. RESULTS AND DISCUSSION

Results of pure polyester and epoxy resin samples were obtained to be used as references. Table 1 presents the average values of thermal conductivity obtained for the pure resins at 0, 25 and 50°C. These values were used for calculating the thermal conductivity augmentation of the nanocomposites at each temperature.

Table 1. Average thermal conductivity of polyester and epoxy resins, measured at 0, 25, and 50°C.

Resin	k_r (W m^{-1} K^{-1})		
	0°C	25°C	50°C
UPR	0.1550	0.1574	0.1578
ER	0.1966	0.2011	0.1995

Figures 1 and 2 show the thermal intensification of polyester and epoxy resins obtained by the addition of the three different kinds of alumina nanoparticles. Results taken at 25°C are not shown because it was not observed any significant

variation in thermal conductivity with temperature. As one can observe, the thermal intensification of the polyester resin was higher than that of the epoxy resin, but the behavior presented by polyester and epoxy nanocomposites are very much alike. It can also be noticed that larger nanoparticles (200 nm) produced higher thermal intensification of both polymers and, even though 27-43 nm and 30-40 nm nanoparticles are in the same size range, these two types of nanoparticles were responsible for different augmentation in thermal conductivity.

(a) 0°C

(b) 50°C
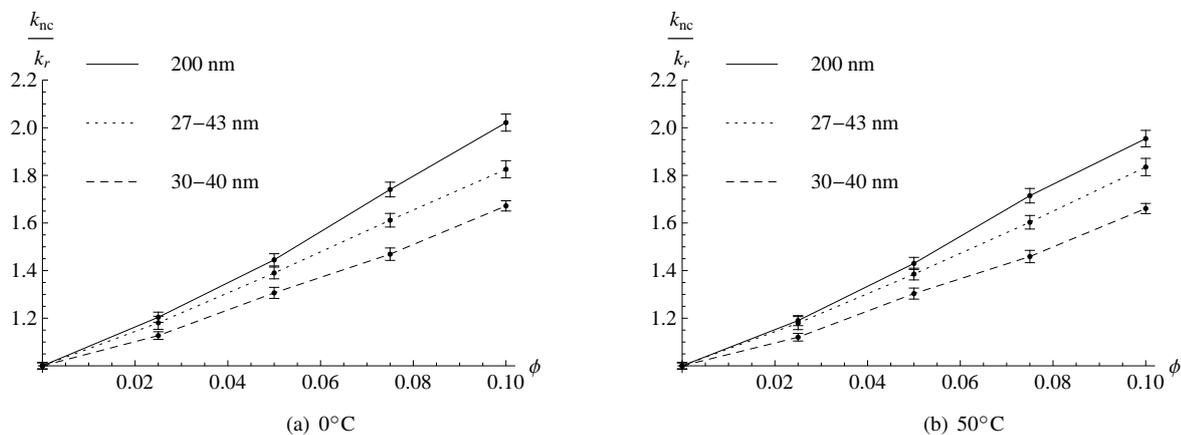
Figure 1. Thermal intensification of polyester resin.

(a) 0°C

(b) 50°C
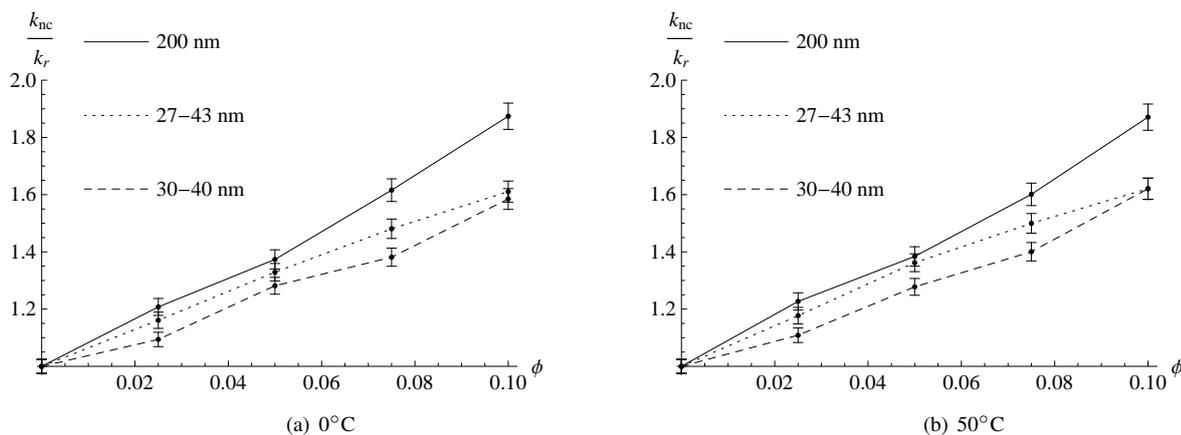
Figure 2. Thermal intensification of epoxy resin.

The difference between the thermal conductivities of nanocomposites containing the same amount of alumina nanoparticles may be explained by different properties of nanoparticles/resin interfaces. Although the manufacturer is the same, 30-40 nm alumina nanoparticles are white, while 27-43 nm are pale pink, and blends containing 10% in volume of 27-43 nm alumina were much more viscous than blends containing 10% in volume of 30-40 nm alumina. Besides, according to the manufacturer, the nanoparticles are nearly spherical, so that 30-40 nm and 27-43 nm nanoparticles may present different aspect ratios, which could also explain the difference between the observed thermal intensification.

Moreover, 200 nm nanoparticles have lower specific surface area than smaller nanoparticles. This could lead to less interactions between the filler and the matrix, however, if the contact between the dispersed and the continuous phases is not perfect, there may exist an interfacial thermal contact resistance. So, by diminishing the interfacial area this resistance would decrease, and the effective thermal conductivity of the nanocomposite would be higher for larger particles.

4. CONCLUSIONS

This work presented an experimental investigation of heat conduction in polymeric nanocomposites. The samples were composed of polyester or epoxy resins as matrices, loaded with different types of alumina nanoparticles. The

thermal conductivities of the nanocomposites were measured with the guarded heat flow meter method by a commercially available heat flow meter instrument. According to the results, the effective thermal conductivity of the nanocomposites is increased by the addition of alumina nanoparticles. Also, it was possible to observe that the 200 nm alumina nanoparticles were responsible for a greater thermal intensification than that produced by 27-43 nm or 30-40 nm particles, which could be attributed to the existence of an interfacial thermal resistance between the matrix and the filler. Although 27-43 nm and 30-40 nm nanoparticles are in the same size range, these particles produced different results of thermal intensification. This fact may indicate that the properties of these particles surfaces are different. It could lead to a stronger interaction between 27-43 nm nanoparticles and the polymers, if compared to the interaction between 30-40 nm nanoparticles and the matrices. It is important to mention that these results are preliminary, and a more extensive investigation concerning the interactions between dispersed and continuous phases should be carried out.

5. ACKNOWLEDGEMENTS

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