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Effect of Nano Clay Reinforcement on Thermal Conductivity of Epoxy/CNT Composite Material

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Abstract

Epoxy is one of the most important polymers preferred in various technological applications thanks to its good mechanical properties and lightness. However, their low thermal conductivity limits their usage areas. Increasing the thermal conductivity of epoxy is an important research topic. One of the most ideal ways to achieve this is to improve the thermal conductivity of epoxy without increasing its weight, thanks to nanoparticles. Carbon nanotubes (CNT) and clays are among the materials used for this purpose. In this study, the thermal conductivities of hybrid polymer composites reinforced separately and together in an epoxy matrix were investigated. The aim of the study is to find out how CNT and nano clay affect the thermal conductivity of the epoxy matrix, separately and together, and reveal the synergistic effect of these nanoparticles.

Keywords

Epoxy, Carbon Nanotube, Nano Clay, Thermal Conductivity

1. Introduction

A new material formed by combining at least two materials at a macro level in order to obtain better properties is called a composite material. Composite materials are very important for all sectors, especially the automotive, aerospace and defense sectors, as they allow the production of materials with the desired structure and properties according to need. When at least one of the components that make up the composite material is nano-sized, the new material obtained is called nanocomposite. Recent studies have shown that nanoparticle reinforcement improves the electrical, thermal and mechanical properties of composites [1] [2] [3].

However, the key issue in the production phase of nanocomposites is the good distribution of nanoparticles. Especially in the production of polymer nanocomposites, nanoparticles mixed into the viscous polymer matrix tend to aggregate [4]. Epoxy resins, which are frequently used in high-performance polymer composite production, are a highly preferred matrix material in nanocomposite production. Epoxy resins show high adhesion to surfaces and have low residual stress, excellent mechanical properties, and good resistance to heat and chemicals, as well as being used as adhesives for metals, aerospace, and vehicles [5]. However, when reinforced with nanoparticles, the increased viscosity makes production difficult and prevents the desired properties from being obtained. At this point, instead of adding a single type of nanoparticle into the epoxy resin, adding more than one type of nanoparticles to create a synergistic effect and improve dispersion is a frequently used method in recent years. Carbon nanotube and nano clay duo are the reinforcement elements we see most [6] [7] [8]. Thakur *et al.* examined the mechanical properties of an epoxy composite material containing CNT and nano clay using finite element modeling. As a result, they stated that the toughness of composites containing CNT/nano clay improved. They reported that the presence of nano clay could lower the percolation threshold of CNTs [9]. Sanusi *et al.* (2020) and Liu and Grunlan (2007), based on their research, stated that the electrical, thermal and mechanical behaviors of composites obtained by reinforcing CNT and clay into an epoxy matrix are improved, so that this material can be used in sensing, shielding and packaging applications [10] [11]. Thermal conductivity is an important concept for all these applications. Because if the heat generated cannot be removed from the composite, deterioration will occur in the composite material and the parts used will lose their functions. Carbon nanotubes are one of the materials found in nature with the highest thermal conductivity. Therefore, they are frequently used to increase the thermal conductivity of polymers with very low thermal conductivity [12] [13] [14] [15]. However, the complex structure of carbon nanotubes causes different results in the experimental data found in the literature. In addition to studies stating that a fairly good increase in thermal conductivity is achieved with a small amount of CNT reinforcement, there are studies stating that CNT reinforcement reduces thermal conductivity [16] [17] [18].

In this study, it was investigated how nano clay reinforcement affects thermal conductivity in CNT/epoxy polymer composites. Samples containing different ratios of CNT and nano clay were produced and their thermal conductivities were measured, and the results were compared by taking SEM images of the same samples.

2. Material and Method

In the experimental study, hybrid CNT/Nano clay/epoxy composite materials with different weight ratios were produced. The produced samples and their contents are given in **Table 1**. MGS LR285 brand epoxy was used as matrix material. Multi-walled carbon nanotubes functionalized with -COOH and clay particles processed at the nanoscale level were used as reinforcement materials. This nano clay is a Montmorillonite mineral that contains cations such as sodium and calcium. To prepare samples containing CNTs and nano clay, carbon nanotubes were first added to isopropyl alcohol and mixed in an ultrasonic mixer for 20 minutes. The aim here is to disperse the clumped CNTs thoroughly before mixing them into the epoxy. Then, clay and epoxy were added to the mixture, which was mixed for 5 seconds and then waited for 5 seconds in an ultrasonic mixer for 40 minutes. The reason for this is to prevent the matrix and reinforcement material from being damaged and degraded by the heat generated in the ultrasonic mixer. The mixture obtained as a result of ultrasonic mixing processes was taken into a magnetic stirrer. Here it was mixed at 1000 rpm at 40˚C - 50˚C. The aim is to completely remove IPA from the system with the effect of temperature and mixing. At this stage, after checking the weight and making sure that IPA was completely removed from the system, hardener was added and the mixture was poured into silicone molds. The curing process was waited for 24 hours and after curing, the samples were removed from the molds. The samples were sanded with 800, 1200, 2000 sandpapers and polished with alumina to remove burrs and dirt on the surface. To determine their thermal conductivity, the thermal conductivity coefficients of the samples were determined with a C-THERM/TCi brand thermal conductivity device at room temperature. After the surfaces of the samples to be measured were prepared, measurements were made by contacting them with the sensor of the device. Then, SEM analysis was performed on the same samples and carbon nanotube distributions were tried to be observed.

3. Experiment Results and Discussion

The contents and thermal conductivity results of the samples produced are given in **Table 1**. First of all, pure epoxy, samples containing only CNTs and samples containing only clay were produced. Then, in the first group of hybrid experiment set, the nano clay ratio was kept constant at 0.5%, and the CNT ratio was changed to 0.1%, 0.5% and 1%. In the second hybrid group of samples, the CNT ratio was kept constant at 0.5%, and clay ratio was changed to 0.1%, 0.5% and 1%. In the third group of samples, the CNT ratio was kept constant at 1%, and the clay ratio was changed to 0.1%, 0.5% and 1%. The main purpose of selecting these sample groups is to find the best CNT-Nano clay ratios for thermal conductivity and determine whether CNTs or nano clays have a more important role in the thermal conductivity system.

Experimental results show that in composite samples produced with a single type of nanoparticle, both CNT and nano clay caused an increase in the thermal conductivity of the epoxy matrix. However, when CNT and nano clay were compared, the same amount of CNT caused a greater increase in thermal conductivity. **Figure 1** and **Figure 2** are also seen.

Table 1. Produced samples and their contents.

	% CNT	% Nano Clay	Thermal Conductivity (W/mK)
Pure Epoxy	-	-	0.42
1	0.1	-	0.48
2	0.5	-	0.55
3	1	-	0.62
4	-	0.1	0.45
5	-	0.5	0.47
6	-	1	0.51
7	0.1	0.5	0.34
8	0.5	0.5	0.41
9	1	0.5	0.45
10	0.5	0.1	0.52
11	0.5	0.5	0.43
12	0.5	1	0.41
13	1	0.1	0.5
14	1	0.5	0.54
15	1	1	0.61

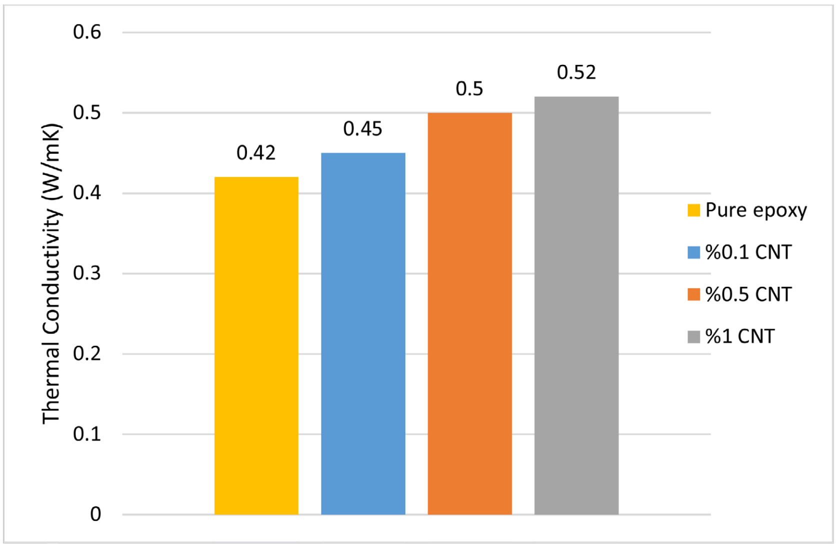

Figure 1. Effect of CNT reinforcement on thermal conductivity.

When hybrid composites are considered, the results clearly show that as the amount of CNT increases, there is an increase in thermal conductivity. The coexistence of CNT and clay in the system created positive effects at low rates. In Figure 3, we see that the ratio of CNT increases while the nano clay ratio is constant at 0.5%. The highest thermal conductivity is obtained with 1% CNT

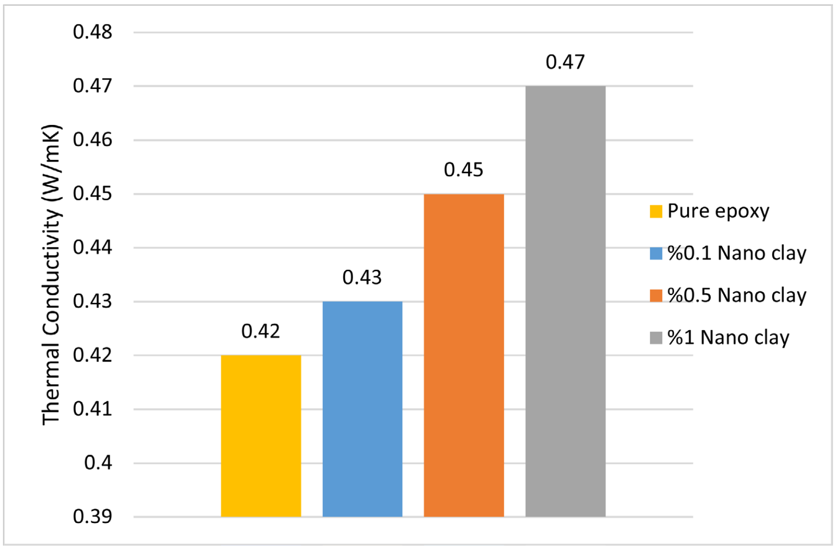

Figure 2. Effect of nano clay reinforcement on thermal conductivity.

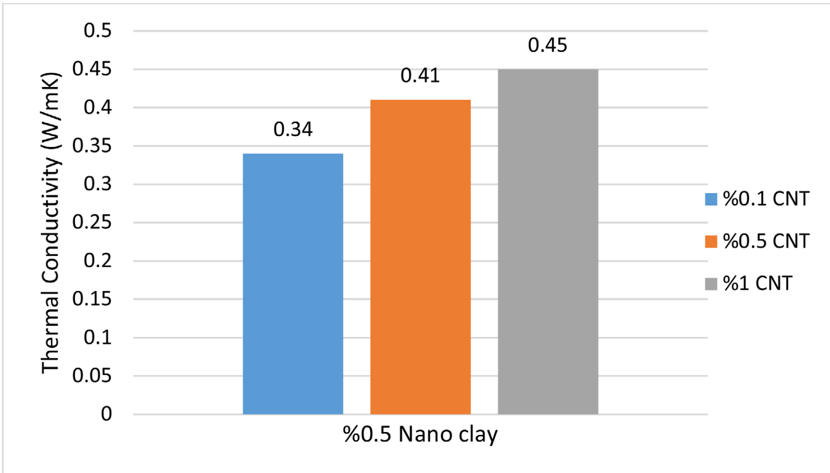

Figure 3. Thermal conductivity results of samples containing %0.5 nano clay and different ratios of CNT.

content. The thermal conductivity obtained from the sample containing 0.5% nano clay and 0.1% CNT was even lower than pure epoxy. Figure 4 shows the sample results in which the amount of clay varied while the CNT ratio was constant at 0.5%. Here is the highest. The thermal conductivity was seen in the sample with the lowest amount of particles. Figure 5 also shows a supporting result, showing that increasing the amount of particles decreased the thermal conductivity.

In a solid material, there are two main mechanisms of heat conduction: through elastic waves called phonons and by free electrons. Polymer materials generally do not have freely moving electrons. Therefore, heat transfer is carried out only by elastic waves, that is, phonons. For one-dimensional and linear heat flow, steady-state heat transfer in solid materials can be described by Fourier's law [19].

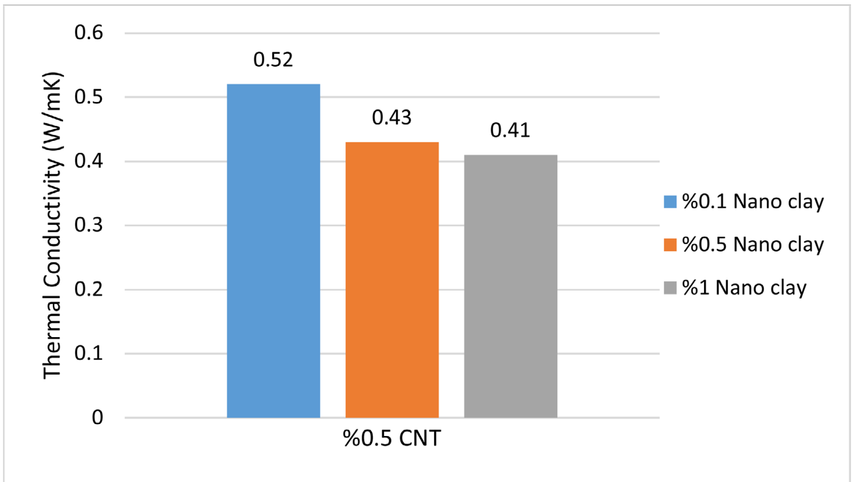

Figure 4. Thermal conductivity results of samples containing %0.5 CNT and different ratios of nano clay.

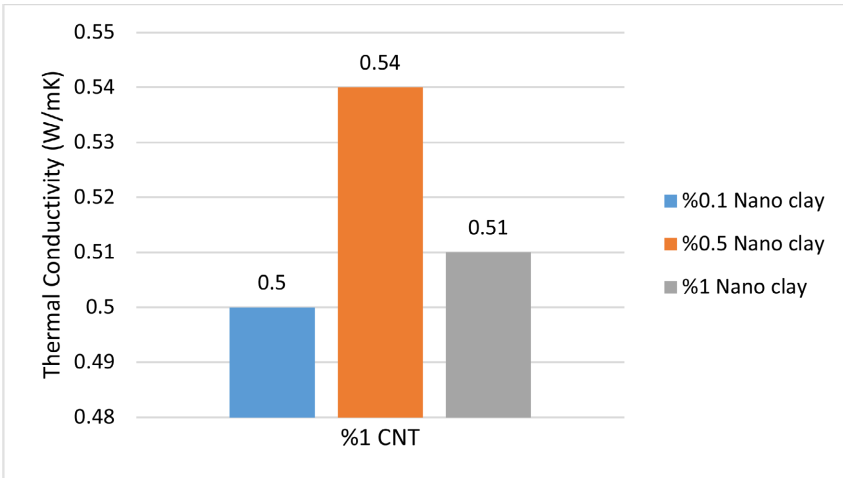

Figure 5. Thermal conductivity results of samples containing %1 CNT and different ratios of nano clay.

$$Q = -\lambda \, \mathrm{d}T/\mathrm{d}x$$

Here, Q is the heat flux, x is the material thickness, $\mathrm{d}T/\mathrm{d}x$ is the temperature gradient for unit temperature range and the constant of proportionality λ is known as the thermal conductivity coefficient. Thermal conductivity, often written λ, is the most commonly used property that helps measure the transport of heat through a material. The Debye Equation is also used to theoretically calculate the thermal conductivity of polymer materials where phonons dominate the conduction mechanism [20] [21] [22] [23].

$$\lambda = \frac{1}{3} C_p v l$$

Here, C_p is specific heat, v is average molecular speed, and l is the average free oscillation of molecules. The value of l is an extremely small constant (a few angstroms) due to phonon dispersion, which is one of the numerous defects for amorphous polymers, causing the polymers to have a very low thermal conductivity [24].

Some studies in the literature have reported that the phonon mismatch occurring at the polymer/CNT interface causes interfacial thermal resistance. The mechanism of polymer composites whose thermal conductivity decreases even though CNTs are added is explained in this way. Accordingly, in this study, the extra new surfaces created by nano clays as well as CNTs mixed into the resin caused an increase in thermal resistance and phonon scattering, thus decreasing the thermal conductivity. In addition, considering the Debye Equation, there are opinions that discontinuities within the polymer may reduce the average free oscillation of polymer molecules and, accordingly, reduce the thermal conductivity [21] [24]. As a result of this study, thermal conductivity is high in samples containing small amounts of nanoparticles, while nanoparticles have been observed that as the amount of particles increases, especially the amount of nano clay increases, the thermal conductivity decreases. When clay and CNT were added separately into epoxy, thermal conductivity increased. When added together, the recipe with a lower clay amount and higher CNT amount (0.5% nano and 1% CNT) gave the best results.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

[1] Srivastava, V.K., Gries, T., Veit, D., Quadflieg, T., Mohr, B. and Kolloch, M. (2017) Effect of Nanomaterial on Mode I and Mode II Interlaminar Fracture Toughness of Woven Carbon Fabric Reinforced Polymer Composites. *Engineering Fracture Mechanics*, **180**, 73-86. https://doi.org/10.1016/j.engfracmech.2017.05.030

[2] Liu, L., Yan, F., Li, M., Zhang, M., Xiao, L., Shang, L. and Ao, Y. (2018) Improving Interfacial Properties of Hierarchical Reinforcement Carbon Fibers Modified by Graphene Oxide with Different Bonding Types. *Composites Part A*: *Applied Science and Manufacturing*, **107**, 616-625. https://doi.org/10.1016/j.compositesa.2018.02.009

[3] Zhang, X., Fan, X., Yan, C., Li, H., Zhu, Y., Li, X. and Yu, L. (2012) Interfacial Microstructure and Properties of Carbon Fiber Composites Modified with Graphene Oxide. *ACS Applied Materials & Interfaces*, **4**, 1543-1552. https://doi.org/10.1021/am201757v

[4] Eguílaz, M., Gutiérrez, A., Gutierrez, F., González-Domínguez, J.M., Ansón-Casaos, A., Hernández-Ferrer, J., Ferreyra, N.F., Martínez, M.T. and Rivas, G. (2016) Covalent Functionalization of Single-Walled Carbon Nanotubes with Polytyrosine: Characterization and Analytical Applications for the Sensitive Quantification of Polyphenols. *Analytica Chimica Acta*, **909**, 51-59. https://doi.org/10.1016/j.aca.2015.12.031

[5] Wei, H., Xia, J., Zhou, W., Zhou, L., Hussain, G., Li, Q. and Ken, K. (2020) Adhesion and Cohesion of Epoxy-Based Industrial Composite Coatings. *Composites Part B*, **193**, Article ID: 108035. https://doi.org/10.1016/j.compositesb.2020.108035

[6] Pielichowska, K. and Nowicka, K. (2019) Analysis of Nanomaterials and Nanocompo-

sites by Thermoanalytical Methods. *Thermochimica Acta*, **675**, 140-163. https://doi.org/10.1016/j.tca.2019.03.014

[7] Pielichowska, K. and Nowick, K. (2023) Polymer-Based Nanocomposites as Defence Material. *Bulletin of Materials Science*, **46**, Article No. 79. https://doi.org/10.1007/s12034-023-02932-4

[8] Al-Saleh, M.H. (2017) Clay/Carbon Nanotube Hybrid Mixture to Reduce the Electrical Percolation Threshold of Polymer Nanocomposites. *Composites Science and Technology*, **149**, 34-40. https://doi.org/10.1016/j.compscitech.2017.06.009

[9] Thakur, A.K., Kumar, P. and Srinivas, J. (2016) Studies on Effective Elastic Properties of CNT/Nano-Clay Reinforced Polymer Hybrid Composite. *IOP Conference Series: Materials Science and Engineering*, **115**, Article ID: 012007. https://doi.org/10.1088/1757-899X/115/1/012007

[10] Sanusi, O.M., Benelfellah, A. and Hocine, N.A. (2020) Clays and Carbon Nanotubes as Hybrid Nanofillers in Thermoplastic-Based Nanocomposites—A Review. *Applied Clay Science*, **185**, Article ID: 105408. https://doi.org/10.1016/j.clay.2019.105408

[11] Liu, L. and Grunlan, J.C. (2007) Clay Assisted Dispersion of Carbon Nanotubes in Conductive Epoxy Nanocomposites. *Advanced Functional Materials*, **17**, 2343-2348. https://doi.org/10.1002/adfm.200600785

[12] Yang, Z., Choi, D., Kerisit, S., Rosso, K.M., Wang, D., Zhang, J., *et al.* (2009) Nanostructures and Lithium Electrochemical Reactivity of Lithium Titanites and Titanium Oxides: A Review. *Journal of Power Sources*, **192**, 588-598. https://doi.org/10.1016/j.jpowsour.2009.02.038

[13] Zhang, X., Wen, R., Huang, Z., Tang, C., Huang, Y., Liu, Y., *et al.* (2017) Enhancement of Thermal Conductivity by the Introduction of Carbon Nanotubes as a Filler in Paraffin/Expanded Perlite Form-Stable Phase-Change Materials. *Energy and Buildings*, **149**, 463-470. https://doi.org/10.1016/j.enbuild.2017.05.037

[14] Yu, A., Itkis, M.E., Bekyarova, E. and Haddon, R.C. (2006) Effect of Single-Walled Carbon Nanotube Purity on the Thermal Conductivity of Carbon Nanotube-Based Composites. *Applied Physics Letters*, **89**, Article ID: 133102. https://doi.org/10.1063/1.2357580

[15] Martin-Gallego, M., Verdejo, R., Khayet, M., de Zarate, J.M.O., Essalhi, M. and LopezManchado, M.A. (2011) Thermal Conductivity of Carbon Nanotubes and Graphene in Epoxy Nanofluids and Nanocomposites. *Nanoscale Research Letters*, **6**, Article No. 610. https://doi.org/10.1186/1556-276X-6-610

[16] Shen, Z., Bateman, S., Wu, D.Y., McMahon, P., Dell'Olio, M. and Gotama, J. (2009) The Effects of Carbon Nanotubes on Mechanical and Thermal Properties of Woven Glass Fibre Reinforced Polyamide-6 Nanocomposites. *Composites Science and Technology*, **69**, 239-244. https://doi.org/10.1016/j.compscitech.2008.10.017

[17] Biercuk, M., Llaguno, M., Radosavljevic, M., Hyun, J., Johnson, A. and Fischer, J. (2002) Carbon Nanotube Composites for Thermal Management. *Applied Physics Letters*, **80**, 2767-2769. https://doi.org/10.1063/1.1469696

[18] Moisala, A., Li, Q., Kinloch, I.A. and Windle, A.H. (2006) Thermal and Electrical Conductivity of Single- and Multi-Walled Carbon Nanotube-Epoxy Composites. *Composites Science and Technology*, **66**, 1285-1288. https://doi.org/10.1016/j.compscitech.2005.10.016

[19] Hashim, A. (2012) Smart Nanoparticles Technology. Intechopen, Rijeka. https://doi.org/10.5772/1969

[20] Osswald, T.A. and Menges, G. (1995) Material Science of Polymers for Engineers. Hanser Publishers, Munich.

[21] Rohsenow, W.M.R. (1998) Handbook of Heat Transfer. McGraw-Hill, New York.

[22] Sun, L. (2008) Phonon Transport in Confined Structures and at Interfaces. Ph.D. Thesis, Purdue Üniversitesi, West Lafayette.

[23] Han, Z. and Fina, A. (2013) Thermal Conductivity of Carbon Nanotubes and Their Polymer Nanocomposites: A Review. *Progress in Polymer Science*, **36**, 914-944. https://doi.org/10.1016/j.progpolymsci.2010.11.004

[24] Henry, A. (2014) Thermal Transport in Polymers. Begell House, Danbury. https://doi.org/10.1615/AnnualRevHeatTransfer.2013006949