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Microhardness and Thermal Resistance of Epoxy Composites Reinforced with Graphene Nanoplatelets doped Carbon Nanotubes

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In this study, the polymer epoxy matrix was reinforced by carbon nanotubes (CNTs) doped with graphene nanoplatelets (Gr). The graphene-doped CNTs were used as received, and doping ratios were 32 wt. % and 52 wt. %, respectively. The purpose of the study was the investigation of the combined effect of graphene and CNTs on an epoxy matrix. The reference (neat epoxy matrix) and 0.5 wt. % filler-added nanocomposites (32Gr-CNT/EP and 52Gr-CNT/EP) were manufactured to characterize the hardness and thermal performance. Vickers microhardness testing method, thermogravimetry analysis (TGA), differential thermal analysis (DTA), and differential scanning calorimetry (DSC) were applied. Approximately 15.63% and 27.50% increments were obtained in the microhardness of the 32Gr-CNT/EP and 52Gr-CNT/EP nanocomposites, respectively. The thermal analyses revealed increased thermal stability, and high enthalpy values were obtained. 32Gr-CNTs addition into the epoxy increased the enthalpy value by about 40%. However, no significant change was found in glass transition temperature values by incorporating 0.5 wt. % CNTs doped with graphene nanoplatelets.

1. Introduction

The epoxy resin sets are widely preferred for manufacturing polymer composites commonly used in adhesives and coatings, biomedical systems, electronics, automotive, aviation, and aerospace industries. But the pure epoxy matrix composites have resulted in poor wear resistance, relatively low mechanical strength and resistance to crack propagation as well as low thermal conductivity. These drawbacks have highly restricted the application fields of the neat epoxy matrix [1-3]. Functionalizing polymer matrix composites with nanoparticles has enhanced the morphological, mechanical, thermal, and electrical characteristics of the structures.

The typical carbon-based nanoparticles are carbon nanotubes, graphene, and fullerene materials. The higher specific surface area of such nanoparticles can promote interfacial adhesion and conduct additional bonding of polymer and reinforcing elements, leading to better stress distribution and mechanical and thermal performance [4, 5]. The carbon nanotube reinforced polymer nanocomposites offer outstanding properties due to their very high strength and stiffness-to-weight ratio, electrical conductivity, and anticorrosion features compared to neat polymers and other filler-doped nanocomposites [6]. Wang et al. [7] compared the effects of carbon-based nanoparticles (carbon nanotubes, graphene, and fullerene) on epoxy composites. They found out that while CNTs had more tendency to aggregate at relatively higher contents, fullerene had the least. The tensile strength values were reported in descending order of fullerene/epoxy > CNT/epoxy > Grp/epoxy. On the other hand, the researchers indicated that the best corrosion resistance was obtained with Grp/epoxy nanocomposites.

Particularly, incorporating of a very low amount of nanoparticles into the epoxy matrix leads to better physical and structural performance. For instance, Li et al. [2] reported that the hardness of the epoxy nanocomposites was increased by the graphene addition up to 0.7 wt. %, whereas Zabet et al. [8] reported a reduction in hardness of the epoxy

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nanocomposites with 2.8 wt. % of CNTs addition. While CNT and graphene have the same allotropes of carbon (sp^2), their structure, morphology, and dimensions differ [9]. Their individual effects were numerously researched for polymer composite applications. Prolong et al. [10] indicated that graphene was more effective for thermal applications, whereas CNTs were better for electrical applications. They also reported that the combined effect of CNTs and graphene provided the hybrid composite with better electrical conductivity and higher thermal decomposition temperatures. To achieve good heat dissipation, obtaining high thermal conductivity for the electrical conductor composites is essential.

In this study, the epoxy matrix was reinforced with multiwalled carbon nanotubes doped with graphene nanoplatelets. It should be noted that the graphene-doped CNTs are commercially available novel nanomaterials and were used as received. The doping ratios of graphene nanoplatelets within the CNTs were 32 wt. % and 52 wt. %, respectively. 0.5 wt. % of graphene-doped CNTs were added into the polymer epoxy matrix. The hardness values were investigated using the Vickers microhardness tester, and thermal properties were investigated via thermogravimetry analysis (TGA), differential thermal analysis (DTA), and differential scanning calorimetry (DSC).

2. Results and Discussion

2.1. Hardness Test

The Vickers microhardness values were obtained for the neat epoxy composite and hybrid nanocomposites. The results are given in Table 1. As seen, the measurements were obtained with four replications. The average hardness of the neat epoxy composite was obtained 20.22 HV. 0.5 wt.% nanoparticle added composites were resulted in 23.38 HV and 25.78 HV for 32Gr-CNT/EP and 52Gr-CNT/EP nanocomposites, respectively. The comparison of the hardness results is presented in Figure 2. Pizzutto et al. [11] reported approximate results for neat epoxy composite and CNT/EP nanocomposite.

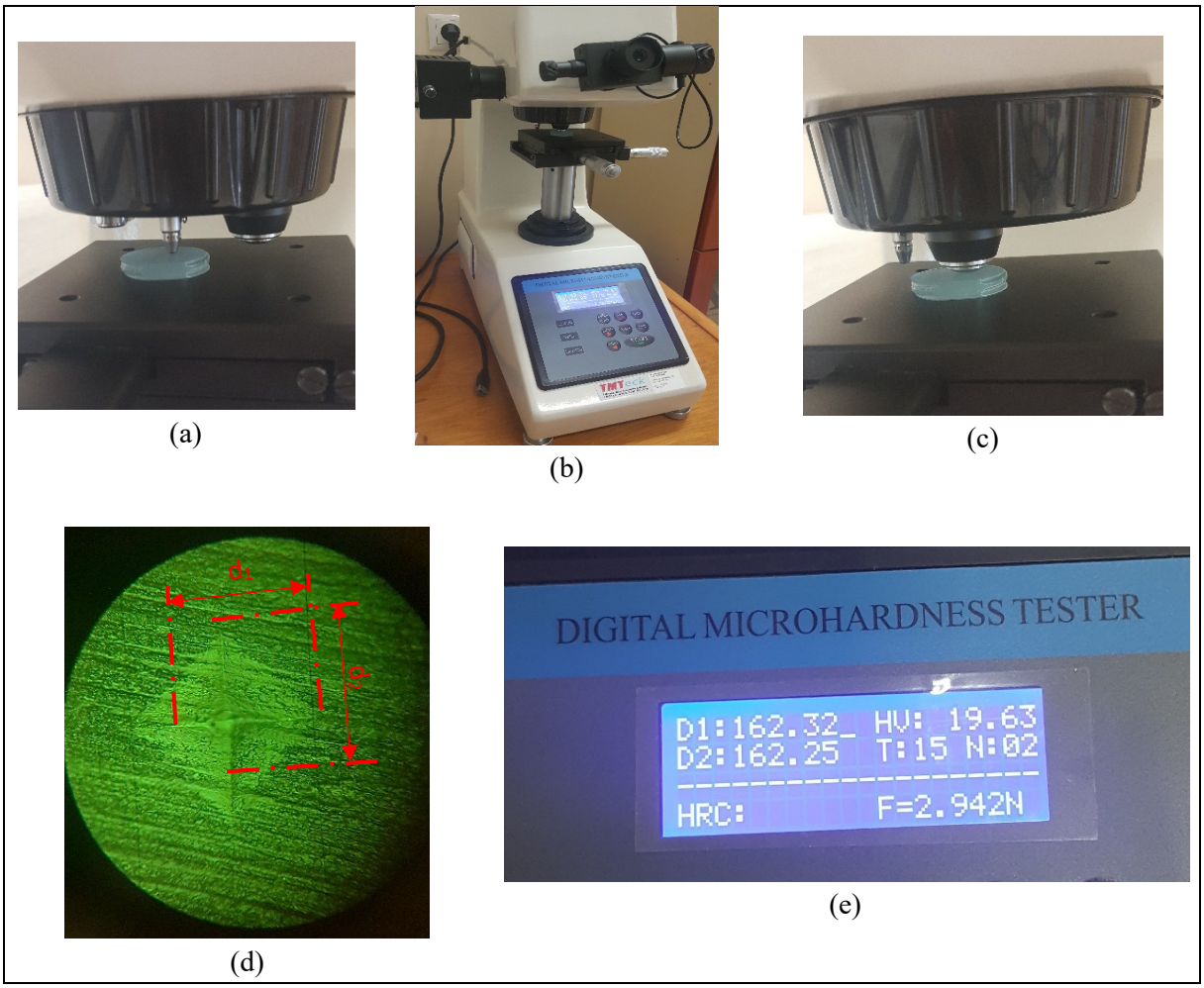

Figure 1. Hardness measurement, a) indentation, b) testing machine, c) monitoring, d) measuring diagonals, and e) test result

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Table 1. Hardness measurement results

Measurement	neat EP	32Gr-CNT/EP	52Gr-CNT/EP
1	19.63	23.56	26.24
2	20.77	23.73	26.08
3	20.70	23.50	25.73
4	19.77	22.72	25.06
Average	**20.22**	**23.38**	**25.78**
Std.Dev.	0.521	0.389	0.453

The increase in nanocomposites' microhardness can be attributed to the unique properties and combined effects of graphene and carbon nanotubes.

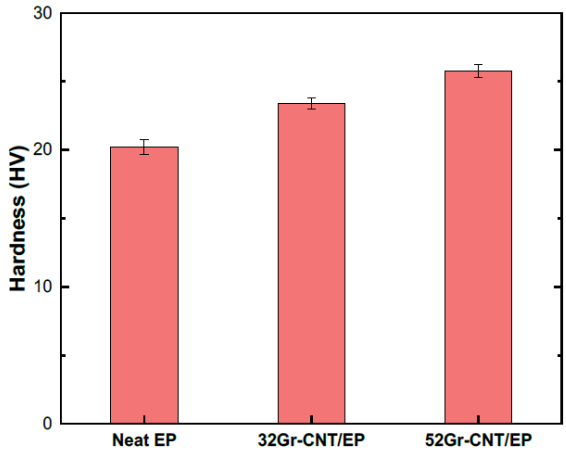

Figure 2. The comparison of the neat EP composite and Gr-CNTs/EP nanocomposites.

Hsu et al. [12] also indicated that CNTs have high resilience, and hence they contributed to the structural rigidity. In the present study, it is evident that the graphene doping effect contributed to the hardness of the polymer nanocomposites since 52 wt. % graphene added CNTs provided 10.27% higher hardness than 32 wt. % graphene addition within the CNTs. In the literature, Bisht et al. [13] compared the hardness of Grp/EP and CNT/EP, and obtained higher hardness values with Gr reinforcements, especially at lower contents (till 0.2 wt. %). It was explained by the two-dimensional structure of Gr nanoparticles that add a sheet form within the matrix.

2.2. Thermal Properties

Thermal stabilities of the prepared neat epoxy and nanoparticle-doped nanocomposite materials were investigated with thermal analyses. Figure 3 shows the DTA curves of neat EP, 32Gr-CNT/EP, and 52Gr-CNT/EP composites. As seen from the DTA curves in Figure 3, there is an endothermic peak between 68 °C and 71 °C. In the DTA curves, crystallization is seen by a broad endothermic peak neat EP, 32Gr-CNT/EP, and 52Gr-CNT/EP composites of 322 °C, 330 °C, and 334 °C respectively. The enthalpy was experimentally determined using a DTA. The enthalpy values are given in Table 2. 32Gr-CNTs increased the enthalpy value of the epoxy by about 40%. In the literature, similar results were reported by Ren et al. [14].

Figure 4 shows the TGA curves of neat epoxy, 32Gr-CNT/EP, and 52Gr-CNT/EP composites. The degradation starts above 340 °C. TGA curve shows weight loss in primary steps. At the same time, all the samples are stable up to 340 °C. This suggests that adding graphene-doped CNTs within the epoxy and cross-linking between them would thermally reinforce the base epoxy matrix. Investigations on nanoparticle studies in epoxy composite materials confirm these results [15, 16]. Such a shift indicates an increase in thermal stability and the participation of both fillers and epoxy resin in forming a cross-linked network.

Table 2. DTA enthalpy values of neat EP, 32Gr-CNT/EP, and 52Gr-CNT/EP composites

Peak No	Temperature (°C)	Enthalpy (J/g)
1	68.73	-2.1254
2	71.98	-2.0426
3	68.72	-2,9562
4	322.47	48.5084
5	330.32	83.2583
6	334.76	32.0278

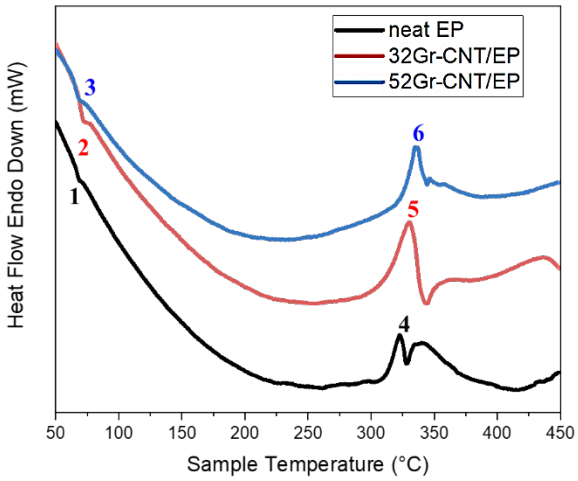

Figure 3. DTA curves of neat EP, 32Gr-CNT/EP, and 52Gr-CNT/EP composites.

The heat-flow DSC evaluates the difference in temperature between the sample and reference as a function of time. Figure 5 shows the DSC curves of neat epoxy, 32Gr-CNT/EP, and 52Gr-CNT/EP

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composites. The enthalpy was experimentally determined using a DSC. The enthalpy values are

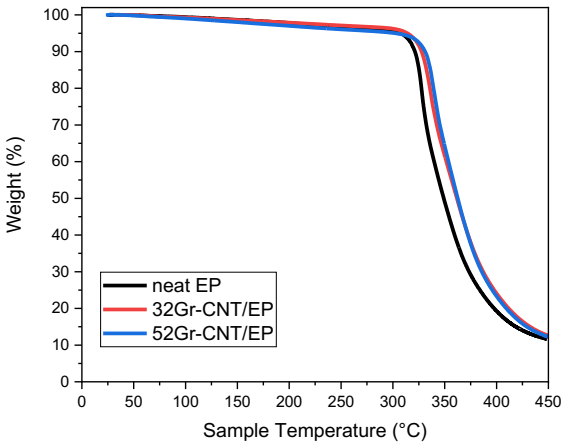

Figure 4. TGA curves of neat EP, 32Gr-CNT/EP, and 52Gr-CNT/EP composites

given in Table 3. The 0.5 wt. % nanoparticle addition did not create a noticeable effect on the glass transition temperature of the epoxy. An exothermic crystallization peak between 335 and 350 was determined. The enthalpy values were determined by calculating the areas formed by the exothermic peaks [17], and the incorporation of nanoparticles increased the enthalpy values.

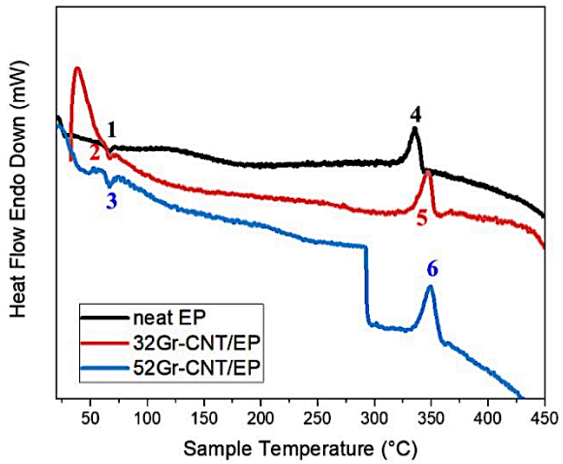

Figure 5. DSC enthalpy values of neat EP, 32Gr-CNT/EP, and 52Gr-CNT/EP composites

Table 3. DSC enthalpy values of neat EP, 32Gr-CNT/EP, and 52Gr-CNT/EP composites

Peak No	Temperature (°C)	Enthalpy (J/g)
1	66.37	-0.8600
2	66.67	-0.9202
3	66.77	-1.6645
4	335.39	11.7493
5	346.98	15.0792
6	349.48	19.4727

4. Conclusion

In this study, the combined effects of graphene and carbon nanotubes on the epoxy matrix composites were investigated by using commercially available as-received CNTs doped with graphene nanoplatelets. While the nanoparticle addition was 0.5 wt. % with respect to the epoxy matrix, the doping ratios of graphene within the CNTs were 32 wt. % and 52 wt. %, respectively. Using such hybrid nanoparticles provides simplicity for manufacturing additive polymer composites and can be attractive for obtaining synergistic effects on the characteristics of polymer composites. The neat EP matrix composite resulted in 20.22 HV, whereas 32Gr-CNT/EP and 52Gr-CNT/EP nanocomposites provided 15.63% and 27.50% higher hardness, respectively. The thermal stability of the nanocomposites was also improved due to the higher decomposition temperatures and increased enthalpy values. However, the 0.5 wt. % nanoparticle addition did not significantly change the glass transition temperature of the modified epoxy matrix composites.

Method

The polymer nanocomposites were manufactured by using an epoxy resin set and 0.5 wt. % multiwalled carbon nanotubes (CNTs) doped with graphene (Gr) nanoplatelets. The doping ratios were 32 wt. % and 52 wt. % within the CNTs. The Gr nanoparticle doped CNTs were commercially available and used as received. The constituents of neat polymer matrix were supplied from Dost Kimya Inc. (Turkey), and the nanoparticles were supplied from Nanografi Nano Teknoloji Inc. (Turkey). The neat polymer matrix has a density of 1190 kg/m^3, and its tensile and compressive strength values were 75 MPa and 90 MPa, respectively. The multiwalled CNTs have more than 97 wt. % purity, 15-25 μm length, a true density of 2400 kg/m^3, the average outside and inside diameters are greater than 50 nm and 5 nm, respectively. Two-dimensional Gr nanoparticle has a purity of 99%, and its thickness and diameter values are 5 nm and 1-12 μm, respectively. The specific surface area of Gr nanoparticles is 500-1200 m^2/g. The aforementioned properties of the constituents of polymer nanocomposites are based on the suppliers' technical data sheets.

In the present study, a total of 50 g of polymer nanocomposite was produced. The commercial epoxy polymer resin consists of two components, named Hexion MGS L160 (resin) and H160 (hardener). The curing process is started by mixing these components at a ratio of 4:1 by weight. When the curing process starts, the casting of the product

should be completed within approximately one hour. In order to prevent early curing, L160 and nanoparticle material should be mixed in the first stage while producing polymer nanocomposites. Thus, 39.8 gr L160 and 0.25 gr multiwalled CNT were mixed using an ultrasonic homogenizer. The mixture was cooled with an ice bath to prevent the resin from overheating during the process. In the next step of production, the L160 - CNT mixture was mixed with H160 using a mechanical stirrer. At the last stage, the prepared mixture was poured into the mold and waited for 24 hours for the curing process.

After the curing was completed, the neat epoxy composite and hybrid nanocomposites were removed from the molds. Then the surfaces were grounded with emery papers to succeed a good surface finish for hardness and thermal characterizations.

Hardness values were determined by applying the Vickers microhardness testing method. The tester penetrates an indenter having a pyramid-form tip into the nanocomposites and applies a load of 2.942 N. The load was applied for 15 seconds, and then the pyramid form was monitored by a microscope attached to the testing machine and measured from its diagonals. Figure 1 shows a hardness measurement of the neat epoxy matrix composite on the testing machine.

The thermal behavior of the neat epoxy composite and the graphene-doped CNT/epoxy nanocomposites was studied using thermogravimetric analysis (TGA), differential thermal analysis (DTA), and differential scanning calorimetry (DSC) Perkin-Elmer Diamond TG/DTA and Perkin-Elmer DSC-7 Sapphire (DSC) instrument. The thermal analyses were carried out at a heating rate of 10 °C/min with temperatures ranging from 30 to 450 °C. Also, 2–5 mg of the composite sample was used for analysis under a continuous nitrogen gas flow of 200 mL min^{-1}.

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Authors' contributions

Ç.U.: Conceptualization, investigation, hardness experiments, writing- original draft, reviewing and editing; H.Y.: Investigation, thermal experiments, writing-original draft, D.C.A.: composite manufacturing, writing-original draft.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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