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Research Article

Effects of Hybrid Graphene Oxide with Multiwalled Carbon Nanotubes and Nanoclay on the Mechanical Properties and Fire Resistance of Epoxy Nanocomposite

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In this study, nanoclay I.30E and multiwalled carbon nanotubes (MWCNT) were hybridized with graphene oxide (GO) on Epikote 240 epoxy resin. Research results show that the hybridization between 0.5 wt.% GO with 1 or 3 wt.% nanoclay and 0.05 wt.% MWCNT has better mechanical properties and flame-retardant properties than the component materials. The combination of epoxy nanocomposite materials with flame-retardant additives such as nanoclay, MWCNT, and GO leads to improving flame-retardant and mechanical properties. Flame-retardant materials have no environmental problems and are nontoxic. Therefore, the flame-retardant additives studied in this work have great potential to become one of the promising flame-retardant hybrid materials. The study also showed that the result of the combination, the hybridization between the three components (nanoclay, MWCNT, and GO) synergized the mechanisms of fire resistance, creating insulating barriers, preventing objects from entering material exposed to heat and oxygen in the air.

1. Introduction

Flame retardants, a large group of polymeric additives, play an important role in improving the fire resistance of polymeric materials. Flame retardants are mainly based on halogens (bromine and chlorine), phosphorus, and inorganic and melamine compounds [1]. To date, many studies have focused on nanoclay, carbon nanotubes [2–4], fly ash [5, 6], graphene oxide [7–11], etc. In addition, a number of works have studied the combination of nanoclay with MWCNTs; nanoclay with fly ash, or MWCNT with fly ash [12]. These works all concluded that the combination of additives provides fire-retardant properties and mechanical properties at a higher threshold when considered separately.

Many studies have been reported on hybrid filler technology in polymers, based on GO and MWCNT [13–16]. The results of this study open up many directions for further research on GO. The results of the studies indicated that very little GO loading also improved the mechanical strength of epoxy composites. Keloth Paduvilan et al. confirmed in their work that the combined effect of graphene oxide and nanoclay can induce a hybrid effect in reducing the air permeability for chlorobutyl-natural rubber blend [16]. The organic hybrid montmorillonite-graphene-filled composite exhibits better thermal stability than pure epoxy. However, if the concentration of hybrid particles is low, the fabricated material has slightly worse properties than the composite material incorporating only graphene oxide [17].

The synergies of graphene nanoplatelets (GP) and montmorillonite nanoclay (MMT) were also reported by Nuruddin et al. The results show that a combination of 3 wt.% MMT and 0.1 wt.% GP leads to increased flexural strength and modulus [18]. A laboratory-synthesized graphene oxide (GO) was used as a dispersant for nanoclay (NC) in epoxy-phenolic. Different weight ratios of GO/NC when granules are mixed are prepared. They are used in concentrations of 1% by weight. Graphene oxide itself is capable of acting as a dispersant for other thin particles such as nanoclay; this combination gives mechanical properties that tend to increase [19]. GO is a material that holds great promise in the future. Gauvin et al. have studied with only 0.5 wt.% GO (<1%); GO significantly increases the mechanical and thermomechanical properties of vinylester polymers [20, 21]. In this study, the presence of nanoclay hybrid with MWCNT and GO at different filler loads was investigated in relation to mechanical properties and flame retardancy. First, the hybrid nanocomposite was prepared by dispersing nanoclay and MWCNT with a solution of mechanical stirring and ultrasonic vibration into the epoxy resin. The hybrid material is then evaluated through the mechanical strength, using the flame-retardant property measurement method (LOI, UL94).

2. Materials and Methods

2.1. Materials. MWCNTs with a diameter of 40-45 nm and a length of around 3 μm were provided by Showa Denko Japan Co. Epikote 240 epoxy (E 240) from bisphenol F was from Shell Chemicals (USA) with 24.6% epoxy content, equivalent of epoxy group 185-196, and viscosity at 25°C: 0.7 ÷ 1.1 Pa·s. Diethylenetriamin (DETA) was from Dow Chemicals (USA); the chemical formula of DETA is as follows: $H_2N(CH_2)NH(CH_2)_2NH_2$, MW: 103 g·mol^{-1}, and specific gravity at 25°C: 0.95 g/cm^3. Nanoclay I.30E was from Nanocor (USA): ivory white powder, specific gravity 1.7 g/cm^3, denatured by octadecyl amine.

2.2. Methods

2.2.1. Sample Preparation. The content of substances used is as shown in Table 1.

The fabrication of hybrid nanocomposites has been carried out as follows. Initially, Epikote 240 epoxy resin was heated in an oven at 80 degrees C for 60 minutes; nanoclay I.30E was dried in an oven at 80°C for 3 hours. The content of nanoclay I.30E used was 1%, 3%, and 5 wt.% of the mixture; MWCNT used was 0.05% mass of the mixture. In that gas, the amount of GO used was 0.5 wt.% of the mixture. The mixture was mechanically stirred at 1000 rpm at 80 degrees Celsius for 3 hours on mechanical stirrer HS-T SET (WiseStir, Korea). Then, the mixture was sonicated in an Elmasonic S300H (Elma company, Germany) ultrasonic bath (ultrasonic frequency 37 kHz, ultrasonic power 300 W) at room temperature for 6 hours. Samples were allowed to cool at room temperature; then, DETA curing agent was added, stirred at 150 rpm for 10 minutes, then defoamed for 30 minutes, and samples were poured to determine mechanical properties and anticorrosion properties, burned on stainless steel molds, and, after 24 hours, dried at 80 degrees Celsius for 3 hours, for 7 days to stabilize; mechanical properties and fire retardant were tested.

2.2.2. Analysis. The fire-retardant evaluation methods are as follows:

(i) Limiting Oxygen Index (LOI) according to JIS K720 standard (Japan): the sample bars used for the test were $150 \times 6.5 \times 3$ mm^3

TABLE 1: Hybrid nanocomposite label according to nanocontent.

Label	Nanoclay % (wt.%)	MWCNT % (wt.%)	GO % (wt.%)
Neat epoxy	0	0	0
1NM0.005MT0.5GO	1	0.05	0.5
3NM0.005MT0.5GO	3	0.05	0.5
5NM0.005MT0.5GO	5	0.05	0.5

(ii) The horizontal burning tests (UL-94HB): standard bar specimens are to be 125 ± 5 mm long by 13.0 ± 0.5 mm wide and provided in the minimum thickness and 3.0 $(-0.0 + 0.2)$ mm thick. (ASTM D635-12)

(iii) Vertical burning test: UL 94 V, the standard bar samples shall be 125 ± 5 mm long $\times$ 13.0 ± 0.5 mm wide and supplied in the minimum and maximum thicknesses. The maximum thickness does not exceed 13 mm (ASTM D635-12)

The UL 94 flame-retardant and oxygen limit tests are conducted at the Polymer Materials Research Center, Hanoi University of Technology, Vietnam.

The methods for determining mechanical properties are as follows:

(i) Tensile strength was determined according to ISO 527-1993 standard on INSTRON 5582-100 kN machine (USA) with tensile speed 5 mm/min, temperature 25°C, and humidity 75%

(ii) Bending strength was determined according to ISO 178-1993 standard on INSTRON 5582-100 kN machine (USA) with bending speed 5 mm/min, temperature 25°C, and humidity 75%

(iii) Compressive strength was determined according to ISO 604-1993 standard on INSTRON 5582-100 kN machine (USA), compression speed 5 mm/min, and temperature 25°C

(iv) Izod impact strength was determined according to ASTM D265 standard on Tinius Olsen machine (USA). Measured at Research Center for Polymer Materials, Hanoi University of Science and Technology

(v) The morphology of the samples was carried out by a scanning electron microscope (SEM, S4800, Japan).

(vi) Fourier transform infrared spectrum (FTIR) is recorded using FTS 2000 FTIR (Varian) using KBr tablets which are created by compressing KBr powder mixed with a small amount of sample GO

3. Results and Discussion

3.1. Mechanical Properties. The results of studying the mechanical properties (tensile strength, flexural strength, compressive strength, and impact strength) of hybrid materials by nanoclay/MWCNT/GO on epoxy resin are

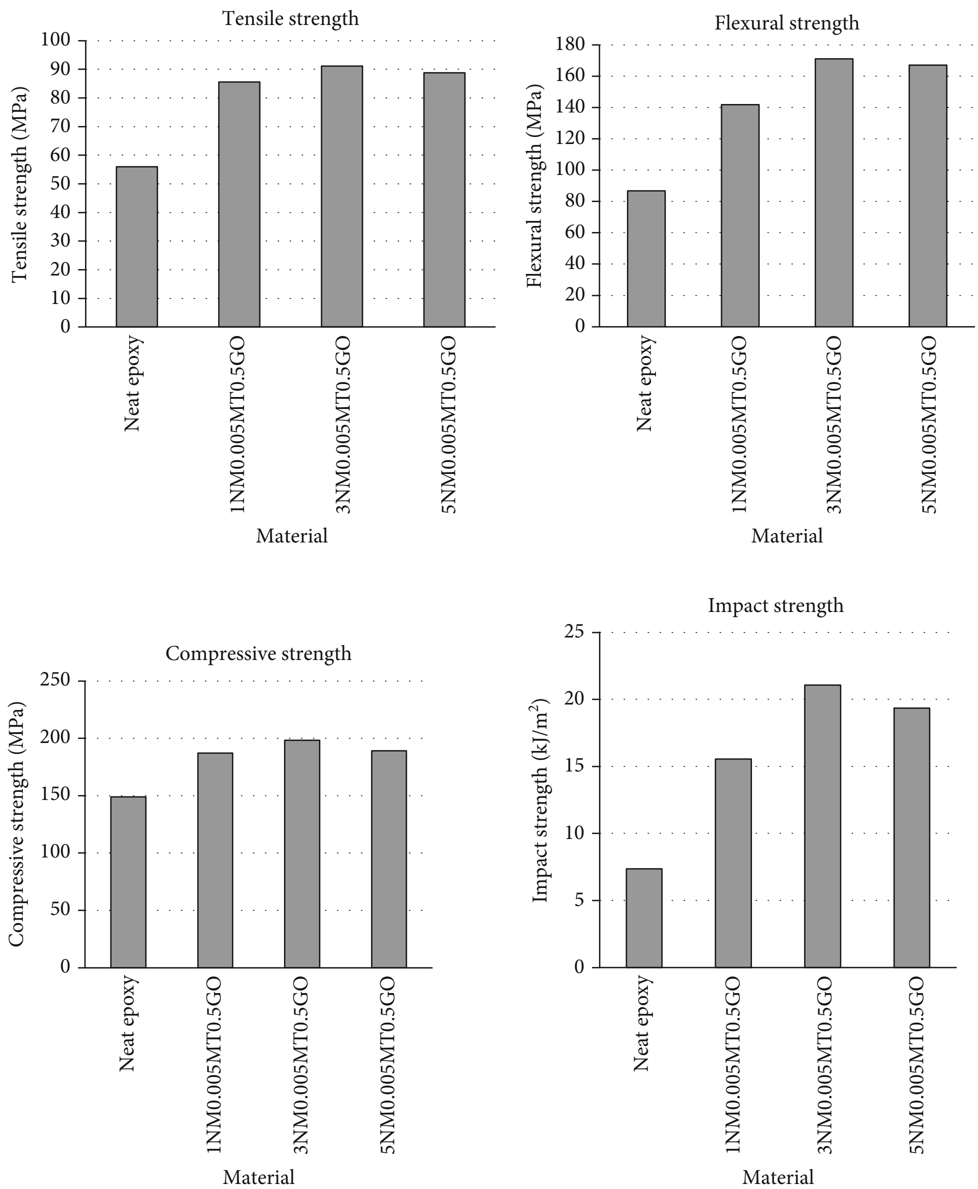


Figure 1: Mechanical properties of epoxy composite materials.

presented in Figure 1. From the results of Figure 1, it can be seen that the cross between 3 wt.% nanoclay, 0.05 wt.% MWCNT, and 0.5 wt.% GO gives the best results compared to other combinations.

It can be concluded that the hybridization of the three components (nanoclay, MWCNT, and GO) promoted the interaction between the polymer and the filler. The ratio of hybridization on the elements achieved the best compatibility that was found in this work. Simultaneous addition of three reinforcers enhanced the interface between the dispersed phases and the epoxy resin, thereby promoting transfer from the resin matrix to the reinforcements. Hybrid 3 wt.% nanoclay with 0.05 wt.% MWCNT and 0.5 wt.% GO has 63% increase in tensile strength, 97.19% increase in flexural strength, 33.23% increase in compressive strength, and 163.12% increase in impact strength compared to epoxy polymers. These results indicate that at the simultaneous addition of nanoclay, MWCNT, and GO at suitable hybridization rates, the material achieves a special structure with a compatibility on the interface between the matrix resin phase and the reinforcements at low level and senior level. It is recognized that when nanoparticles are added, the functional groups present on their surface interact with the epoxy polymer molecules to form strong covalent bonds that enhance their properties such as tensile strength, flexural strength, and hardness. The increase in tensile, flexural, and impact strength is higher as a result of the limitations in molecular chain motion caused by the increased cross-linking of polymers, this increase being moderate enough to prevent the material from hardening to lead to embrittlement. This also causes a reduction in deformation leading to failure [14].

3.2. Fire-Retardant Property. The effects of GO and MWCNTs/nanoclay on LOI values are shown in Figure 2.

From the results of Figure 2, it shows that the hybrid materials at different combination ratios give good fire resistance (limited oxygen index reaches from 27.6 to 31% of the minimum oxygen for the material to ignite). The flame-retardant mechanism of the hybrid material here can be proposed as the nanoclays, MWCNT, and GO synergistically create thicker-than-normal shields (walls) that prevent the material from coming into contact with source of heat and oxygen in the air.

The flame-retardant mechanism of the hybrid material here can be proposed as follows: the nanolayers, MWCNT, and GO synergistically create thicker-than-normal shields (walls) to prevent the material from being exposed to heat and oxygen sources in the air.

On the other hand, in the presence of GO, GO increases the density, reducing the ability of gas to penetrate from the outside and vice versa or in other words, making the path of gas from the outside to the inside of the material longer due to the road which is longer and more complicated [17].

However, when increasing the nanoclay content to 5 wt.%, the degree of flame retardancy tends to decrease where it can be explained that when the content increased to 5 wt.% increased defects, the surface interface between reinforcements and epoxy was not the same as before.

Flame-retardant properties were further evaluated by the UL 94 V method; the results are presented in Table 2. From the results in Table 2, it is again confirmed that the hybrid material by 3 wt.% nanoclay and 0.05 wt.% MWCNT with 0.5 wt.% GO gives the best results, reaching V0.

These results confirm that the hybridization of GO, MWCNT, and nanoclay gives not only high mechanical properties but also good flame-retardant properties. This result will promise in the future a potential hybrid material with high fire resistance and good mechanical properties. However, in order to be able to apply it in industry, it is necessary to continue to research on different plastic substrates at different combination ratios to increase the application level in a wide range.

The surface SEM images of the materials after the UL 94 V combustion test are shown in Figure 3. As shown in Figures 3(a)–3(c), the surface structure of the material after burning did not appear to have cracks. Structural damage is not observed. Nanoadmixtures (nanoclay, MWCNT) formed a nanocoating on the surface of GO to effectively block oxygen transport and thereby reduce the decomposition reactions that occurred. GO shows excellent flame resistance in nanohybrid coatings. The flame-retardant coal produced by the nanoadmixture covered on the GO surface can prevent flammable volatiles from diffusing to the surface flame and thus shield the polymer chains from heat and oxygen effectively. Figures 3(a)–3(b) show spherical porous structures on the surface after burning. Unfortunately, such a porous structure after combustion will not limit heat and oxygen attack in internal molecules thereby causing structural damage. A nanoclay/MWCNT/GO coating is formed to protect combustible materials from flame penetration. This coating acts as an effective barrier to effectively inhibit

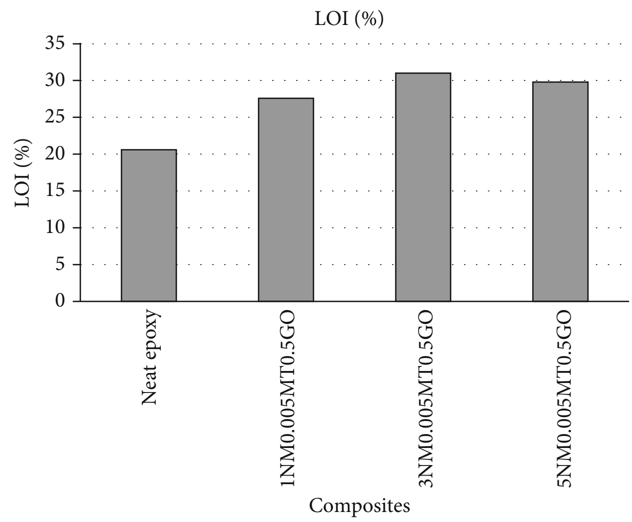


FIGURE 2: LOI values of epoxy composite.

TABLE 2: Combustion parameters of epoxy nanocomposites.

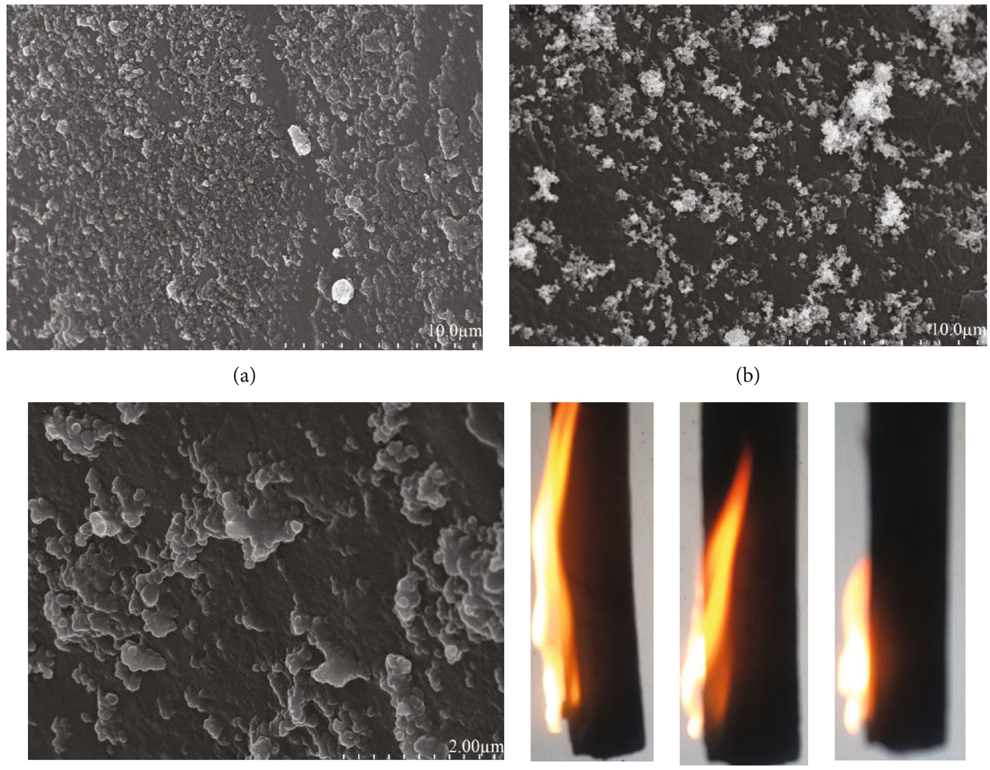
Samples			UL 94 V	
	t_1 (s)	t_2 (s)	Burning grade	Dripping
Neat epoxy	—	—	—	—
1NM0.005MT0.5GO	18	16	V-1	No
3NM0.005MT0.5GO	8.7	7.5	V0	No
5NM0.005MT0.5GO	15	12	V1	No

heat and oxygen; and, therefore, the flame resistance is greatly improved when complete. Figure 3(c) shows that the surface of the material after combustion is smooth; the alignment on the interface between the porous structure and the rest of the material is showing the solid structure, after burning confirm that the topology can be kept well. The addition of nanoclay, MWCNT, and GO to the epoxy resin matrix improved the fire resistance of the material. The best flame retardancy was at 3 wt.% nanoclay, 0.05 wt.% MWCNT, and 0.5 wt.% GO.

3.3. Morphology. The hybrid efficiency of nanoclay and MWCNT and GO is basically determined by the degree of dispersion as well as the interaction and interface binding with the epoxy-based resin. Therefore, morphometric analysis is very important to determine the dispersion and interaction of nanoadmixtures and epoxy matrix.

The results of the structural morphology analysis (SEM) of the hybrid materials are presented in Figures 4 and 5. As discussed previously, the mechanical and flame-retardant properties of the hybrid materials, especially the hybrid materials, were at the combined ratio: 0.5 wt.% GO and 0.05 wt.% MWCNT with 3 wt.% nanoclay.

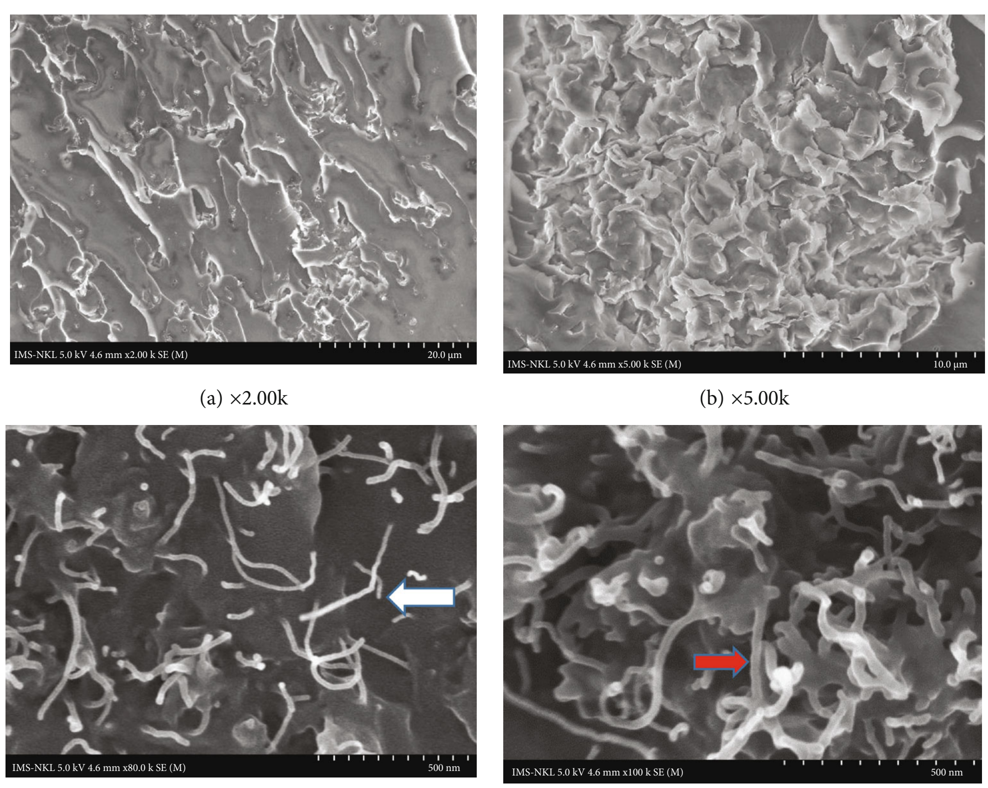
From the results of Figure 4, it can be observed that at the material fracture surface, individual MWCNT nanoreinforced materials are protruding from the interface between nanoclay, GO, and epoxy (white and red arrows, see Figure 4). Thus, there was a synergistic effect of the



(a) (b)

(c) (d) (e) (f)

Figure 3: Flame-retardant mechanism analysis. SEM image of material surface after burning according to the UL 94 V method: (a, d) 1NM0.005MT0.5GO, (b, e) 5NM0.005MT0.5GO, and (c, f) 3NM0.005MT0.5GO.



(a) ×2.00k (b) ×5.00k

(c) ×80.0k (d) ×100k

Figure 4: SEM images of the hybrid GO (0.05 wt.%), MWCNT (0.05 wt.%), and nanoclay (3 wt.%) at different resolutions.

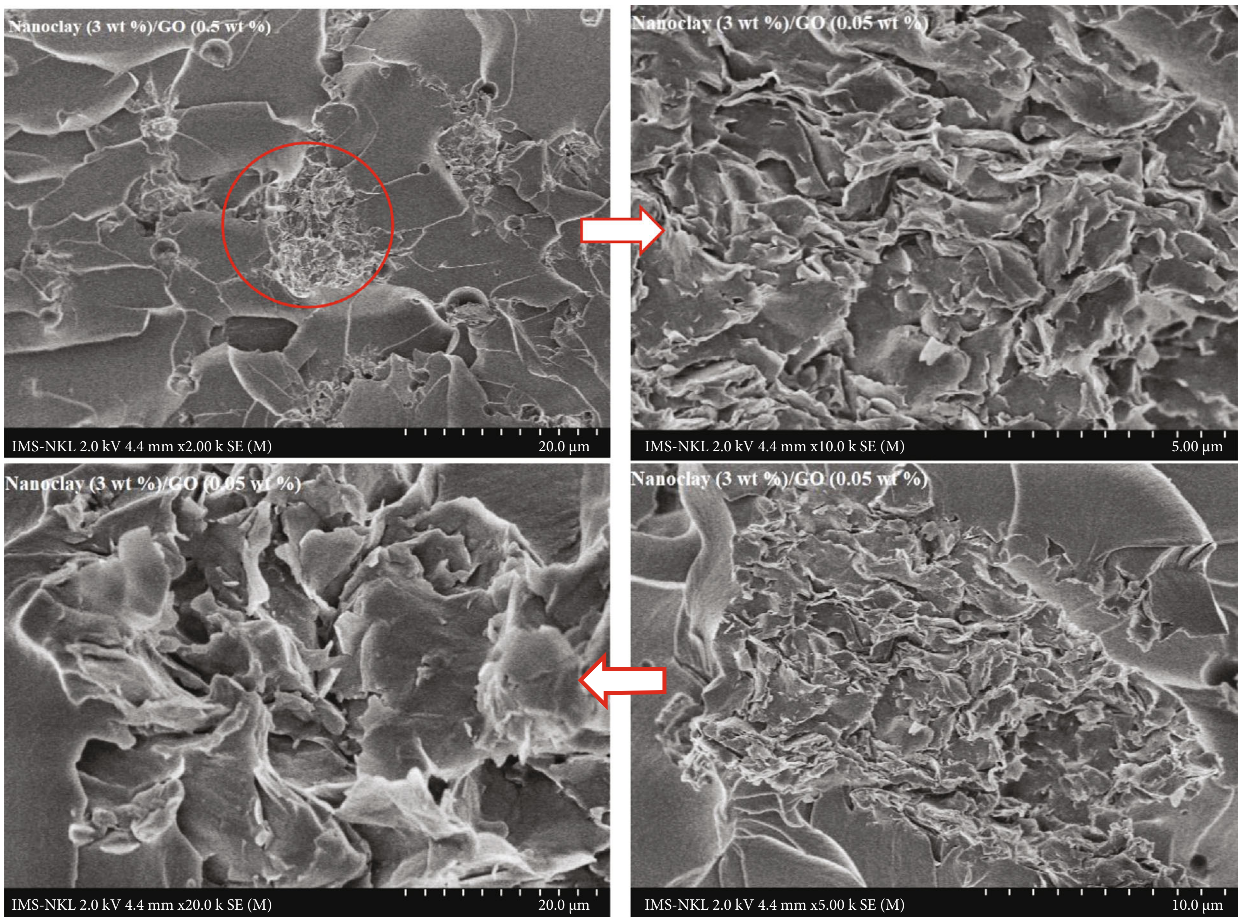


Figure 5: SEM images of the hybrid GO (0.05 wt.%) and nanoclay (3 wt.%) at different resolutions, with different resolutions: 2.00k, 5.00k, 10.0k, and 20.0k.

nanoparticles. This finding supports the results obtained from the mechanical strength and flammability testing discussed before.

On the other hand, Figures 4 and 5 show a clean fault surface with sharp edges. Figure 5 shows the dispersion of nanoclay (red circle in Figure 5) and GO (colored arrow in white Figure 5). Figure 4(d) at ×100k magnification shows the adhesion between MWCNT/nanoclay/GO and the epoxy matrix as all nanotubes including the agglomerated MWCNTs which are well covered by the polymeric substrate, resulting in mechanical outstanding efficiency.

3.4. Results of Infrared Spectroscopy (IR) Measurement. The results of the infrared spectra of the materials are shown in Figure 6. The valency of the O-H group from 3507.92 cm^{-1} is shifted down to 3376.73 cm^{-1}, respectively, 3395.09. The legs of the absorption fringes, in turn, tend to be wider and less intense. The C-H valence oscillation of the CH_2 group and the aromatic ring of the absorption band are narrowed and shortened.

On the FTIR spectrum, it was found that the analysis was obtained from the infrared spectrum of epoxy/-GO/MWCNT/nanoclay films with a wavelength range of 400-4000 cm^{-1}. On the infrared spectrum, the absorption band is characteristic for the following: the valence oscilla-

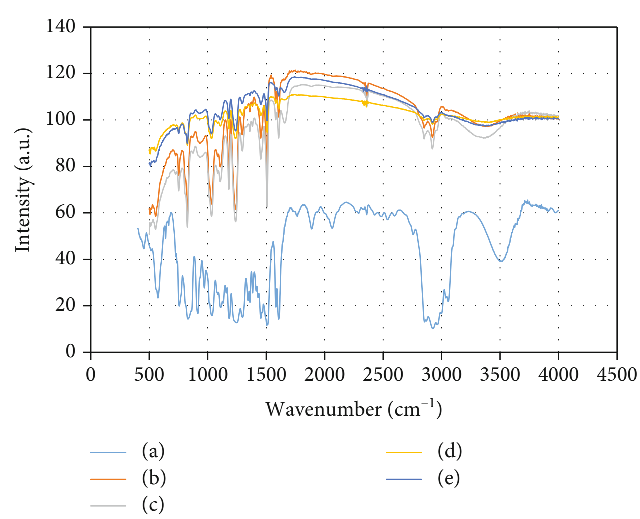


Figure 6: Infrared spectrum of epoxy resin, epoxy/0.5 wt.%GO, epoxy/0.5 wt.%, and GO/0.05 wt.% MWCNT/nanoclay composite: (a) neat epoxy, (b) MWCNT/nanoclay/GO/epoxy, (c) nanoclay/GO/epoxy, (d) MWCNT/GO/epoxy, and (e) GO/epoxy.

tion of the –OH group is at about 3395 cm^{-1}, the C=C group is at about 1606 cm^{-1}, and the C-O bond is at 1032 cm^{-1}. Besides, there is an absorption band characteristic for the

CH_2 group which is asymmetric and symmetrical at about 2921.39 and 2850.07 cm^{-1}. Angular strain oscillation of Si-O-Si bond is at about 554.72 cm^{-1}.

4. Conclusions

This study investigates how the combination and hybridization of nanoclay, MWCNT, and graphene oxide (GO) affect the mechanical properties and flame retardancy on epoxy resins. It can be concluded that the hybridization between 3 wt.% nanoclay and 0.05 wt.% MWCNT and 0.5 wt.% graphene oxide on epoxy resin substrate produces a hybrid material with outstanding mechanical and flame-retardant properties. The mechanical properties and fire resistance results demonstrated that the combined use of MWCNT, nanoclay, and GO at an appropriate ratio will produce an enhanced effect, synergizing good properties.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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