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RESEARCH ARTICLE

The investigation of reinforcement properties of nano-CaCO$_3$ synthesized from *Achatina fulica* snail shell through mechanochemical methods on epoxy nanocomposites

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ABSTRACT

The current study investigates the reinforcement properties of novel nano-calcium carbonate (nano-CaCO$_3$) synthesized from *Achatina fulica* snail shell. The shell was wet-milled to nano-particle sizes using mechanochemical procedures. Epoxy nanocomposites prepared with nanofiller content ranges of 1–7 wt.% were fabricated using a conventional resin casting method. Thermal stability and degradation with mechanical properties such as tensile strength, impact strength, and the hardness properties of prepared nanocomposites were determined. It was observed that the reinforcement by the synthesized nano-CaCO$_3$ improved the thermal stability and mechanical properties of neat epoxy irrespective of the filler content. Significantly, the inclusion of 1 w.% *Achatina fulica* snail shell nanoparticles increased the neat epoxy tensile strength by 75%, stiffness by over 25%, impact strength by 25%, and hardness 35%. These improved properties indicate that nano-CaCO$_3$ synthesized from *A. fulica* snail shell possesses suitable reinforcement properties that can be used for nanocomposite fabrication.
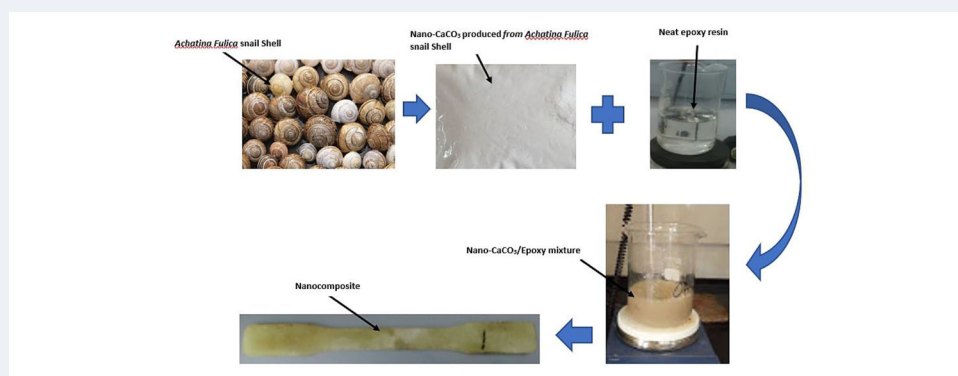
1. Introduction

Reinforcements, both organic or inorganic, play a significant role in modifying specific characteristics of polymeric materials [1–4]. These filler materials are incorporated into matrix materials to increase strength, conductivity, thermal stability, or resistance to indentation. According to Katritzky et al. [5,6] and Fu et al. [5,6], filler or fillers are used to improve thermal, physical, and chemical properties and enhance the bonding properties of the composite, which often result in the improvement of the mechanical properties. Even though the inclusion of fillers helps reduce the cost of polymeric matrix and binders used to produce composite materials [7–11], their reinforcement properties need to be validated.

According to Shao-Yun et al. [6], polymer nanocomposites with a small filler ratio are essential for polymer composites but are neglected. The review study provided detailed information on particle size, particle/matrix interface adhesion, and particle loading on mechanical strength, stiffness, and toughness of polymer composite. Similarly, Azeez et al. [12] provided information on how the physical and chemical properties of the epoxy systems are influenced by the processing techniques, loading of clay modifier, and curing agents used for the preparation

of nanocomposites. This review confirmed that incorporating nanoclay into the epoxy system is a viable way of improving the mechanical and thermal properties of epoxy/clay nanocomposite. These discoveries generated rigorous studies on the reinforcement effect of different filler materials on polymeric material properties.

Several fillers have been explored as reinforcement in polymer composites to improve the properties of polymeric materials. Fillers such as SiO_2, TiO_2, and carbon-based fillers include, but are not limited to, carbon nanotubes, graphite nanopowder, and calcium carbonate ($CaCO_3$). These fillers have been found to be most suitable as reinforcements and are commonly used. Their reinforcement potentials have been investigated in some studies [13–15]. The abovementioned fillers are extensively used based on their excellent reinforcement properties, availability, and low cost [11,16–19]. Furthermore, the influence of particle sizes and the effect of reinforcement ratio of filler materials on polymer composite properties have been investigated extensively. Reports from these investigations show that the reinforcements by fillers at different particle sizes and volumes proved to have different effects on the composites, improving one property and negatively affecting another in some cases [5,20,21].

Yue et al. [21] have established that the amount of filler reinforcement in polymer has a strong effect on the thermal properties of the composite. Similarly, Mohan and Kanny [22] confirmed that reinforcing using nanoparticles is a viable way of improving the mechanical, thermal, and tribological properties of the composite. However, these studies reported only the reinforcements using synthetic fillers (nanoclay and nano-silica), which may have some toxic elements that can cause harm to human health and the environment [23]. The increasing use of synthetic filler/fillers reinforced composites raised some concerns about environmental and sustainability issues. These issues are related but not limited to the energy-intensive and unsustainable production processes of the reinforcing synthetic fibers and plastics [24,25]. Limited recyclability and end-of-life disposal options of synthetic fillers reinforced composites were also identified as potential issues [26,27].

Consequently, materials from renewable resources were considered replacement components for composites to lighten the challenges mentioned above. Filler materials such as cellulose, chitin, and bone particles are currently extracted from animal and plant stems and used as reinforcement for improving the properties of composite materials [13,28–32]. The experimental results reported on the reinforcement potential of these materials obtained from agricultural waste show that these naturally sourced fillers effectively improve the properties of polymer composites. However, these studies are limited to reinforcements such as using eggshell particles at microparticle sizes [13,33,34].

Furthermore, there is limited literature where filler material is synthesized through a mechanochemical procedure (Ball milling) as most are produced either using a blender or a multipurpose grinding machine. In the present study, nano-$CaCO_3$ is synthesized from *Achatina fulica* snail shell using mechanochemical methods. The nano-$CaCO_3$ is used to reinforce the polymer composite, and reinforcement properties of the synthesized nano-$CaCO_3$ at a different loading percentage on the epoxy resin are investigated. This study claimed that a relatively low smaller percentage loading of natural sourced nano-$CaCO_3$ could increase the mechanical properties of epoxy matrices. It also proved that an increase in the loading of natural sourced nano-$CaCO_3$ might improve polymer material thermal stability and degradability.

2. Experimental details

2.1. Raw materials collection

Epoxy resin and catalyst supplied with LR 30 and LH 30 (medium) trade were commercially purchased from AMT composite, Durban.

2.2. Preparation of nano-$CaCO_3$

The nano-$CaCO_3$ was synthesized from *A. fulica* snail shells using a mechanochemical milling procedure. Both dry and wet milling processes were adopted to produce nano-$CaCO_3$. In the first sage, 30 g of dried *A. fulica* snail shell powder was measured and dry-milled in a planetary ball mill (Retsch ® PM 100, Germany) to obtain a fine particle [35]. The milling set-up comprises 50 stainless steel balls of 10 mm diameter and a 500 mL stainless steel jar (inner diameter of 100 mm). The snail shells were milling at 450 rpm for 30 min in a clockwise direction. After the milling process, shell particles were sieved using a mechanical sieving shaker (Retsch, AS 200 basics, Germany) to the particle size of $\leq 50 \mu m$ [13]. Snail-shells powder collected was wet-milled to achieve nanoparticles. Then, 30 g of snail-shells particle size of $\leq 50 \mu m$ was measured into the 500 mL stainless steel jar; Then, 100 mL of solvent was added and wet-milled at 450 rpm for 258 min in a clockwise direction. Subsequently, the mixture of fine particles and solvent was separated by removing the fluid layer, free of a precipitate using the decantation method. Then, particles were dried in the oven at 35 °C for 72 h. The fine powders obtain thereafter were used as fillers for nanocomposite fabrication.

2.3. Nanocomposite preparation

Epoxy-filled nanocomposites were prepared using the conventional resin casting method. To reduce matrix viscosity and facilitate shell particle dispersion, 100 wt.% of epoxy resin was measured into a beaker using a Snowrex digital electronic scale with 0.1 g, placed on an electric stove heated up to 65 °C. Subsequently, 1–7 wt.% of nano-CaCO$_3$ synthesized from *A. fulica* snail shell was slowly incorporated into the resin and mixed using a mechanical stirrer at 500 rpm for one hour to ensure homogeneous dispersion of shell particles. Afterward, the nanocomposite was taken off the stirrer and allowed to cool down to room temperature. The catalyst was added to the nanocomposite at the mixing ratio of 100 to 30 wt% to facilitate the curing process. After that, the blend was mix using spatular for 5 min and poured to have a composite panel. The panel was allowed to cure for two days. However, the wax was applied to the inner surface of the plastic mold before pouring to facilitate demolding. The mechanical strength, thermal stability, and material degradation of $250 \times 250 \times 3$ mm nanocomposite panel obtained was investigated after 15 days of curing at room temperature.

2.4. Mechanical testing

Mechanical tests such as tensile, hardness, and impact tests were performed on fully cured composite panel samples obtained after fifteen casting days.

2.4.1. Tensile

The tensile strength and Young's modulus of the nanocomposite were measured according to ASTM 3039 test standard. Dog bone test samples were cut from a developed nanocomposite panel using a CNC machine. The test was carried out on samples using a Lloyd universal testing machine (Model 43) fitted with a 30 kN load cell. Five samples were tested at ambient temperature, and a constant cross-head speed was 1.3 mm/min. The mean value and standard deviation of the five samples were reported [35].

2.4.2. Hardness

Nanocomposite hardness property was determined according to ASTM D 2583 test standard using a Barcol hardness tester manufactured by Shenyang TX Testing instrument, China. The investigation was conducted at ambient temperature by placing the Barcol intenter on the nanocomposite sample panel's surface, and a uniform downward pressure was applied by hand for the dial indicator to generate readings. Subsequently, readings generated were collected directly from the dial indicator.

Twenty-five indentation readings were randomly collected on the sample, and the mean values were used for results and discussions.

2.4.3. Impact

According to ASTM D6110-10 at room temperature, the Charpy test was performed using an Unnotched Izod impact machine manufactured by Tensiometer Ltd., Croydon, England. Five test specimens were investigated, and the mean value was considered for results and discussions. This investigation was conducted to determine the impact resistance of biocomposite.

2.5. Thermal properties

Thermal stability and degradation of unfilled and nano-CaCO$_3$ filled composites were determined using a thermal gravimetric analyzer (TGA) (Thermal Universal V 4.5 A). The investigation was conducted under a dry nitrogen gas flow at 100 mL/min from 0 to 1000 °C at a 10 °C/min heating rate.

3. Results and discussion

3.1. Effect of nano-CaCO$_3$ reinforcement on tensile strength and stiffness of nanocomposites

3.1.1. Tensile strength and stiffness

Tensile strength and stiffness values of neat and nano-CaCO$_3$ reinforced composites determined using Lloyd universal testing machine as per ASTM 3039 test standard are presented in Figures 1 and 2, respectively. It is noted that the trends of the graphs representing the tensile strength in Figure 1 and the tensile modulus in Figure 2 are pretty similar. This result indicates that the incorporation of nano-CaCO$_3$ increased the strength and stiffness of the epoxy matrix [31,36]. This enhancement could be due to the uniform dispersion of nanoparticles with uniform size and shape in the matrix at low filler content. These results are similar to those observed in the literature where reinforcement of 1 and 2 wt% nano-CaCO$_3$ synthesized from naturally sourced resources increases the strength and stiffness of the matrix [13,31,37–39]. The addition of 1 wt.% enhanced the strength of nanocomposite by 70%, and a drop-in strength was observed afterward. The nanocomposite strength enhancement can be attributed to the high surface area of nano-CaCO$_3$ and its adhesion to the matrix [40].

The high surface area of fillers is often beneficial, and reinforcement leads to effective stress from matrix to filler, increasing the strength of the nanocomposite. This trend is consistent with the results in the literature, where the effectiveness of reinforcing a polymer composite with nanoparticles at a low weight percentage is noted for improving the mechanical properties [5,8,41]. A significant improvement in strength was observed at 1 wt.% loading, and this can be attributed to the reinforcing effect of nano-
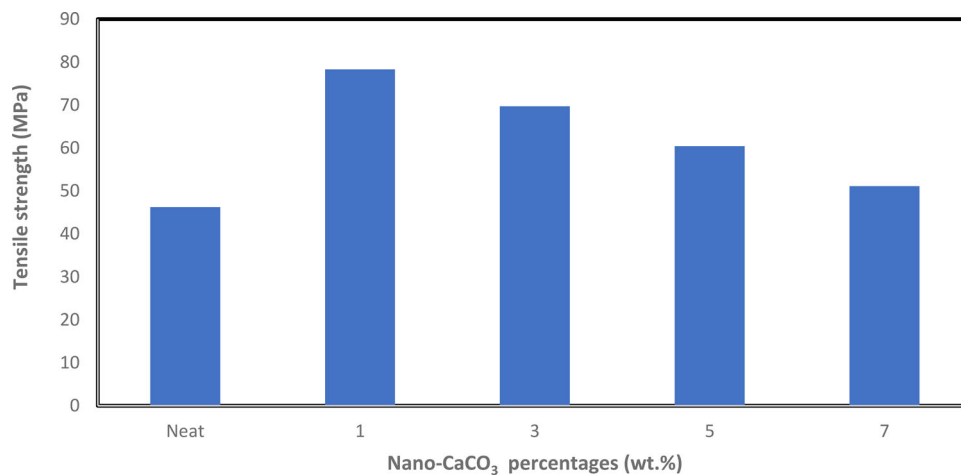
Figure 1. Tensile strength of neat and nano-CaCO$_3$ reinforced epoxy nanocomposites.
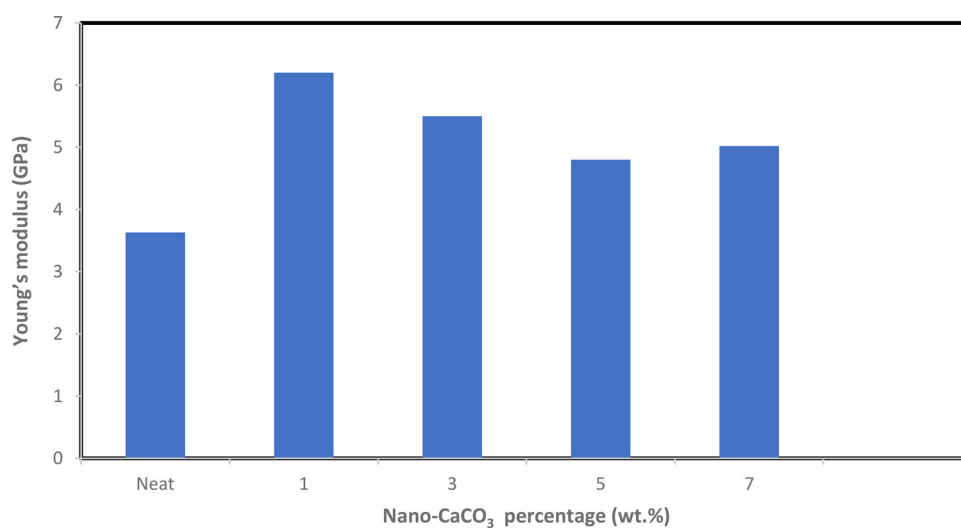

Figure 2. Tensile stiffness of nano-CaCO$_3$ reinforced nanocomposite.

CaCO$_3$ and homogeneous dispersion of the incorporated nanoparticles. This trend aligns with the available literature, where loading of low nano-filler content improves tensile strength [31,35,42]. The chemical treatment of the nanoparticles could be another reason for the observed enhancement in strength as the treatment removes impurities from the nano-CaCO$_3$ surface area, which, in turn, helps to provide strong adhesion between the nanoparticles and the matrix.

A slight drop in strength as seen when loading is above 1 wt.% may result from agglomeration of the particles in the matrix. It is noted that a large volume of particles often leads to a weakening of the bonds between the particles and the epoxy matrix. This weak structure is due to the availability of a limited amount of matrix at the interface of the filler surfaces, leading to a reduced stress transfer and lower strength for the nanocomposite. The high weight ratios of nanoparticles also create stress concentrations that induce crack propagation when the component is subjected to external tensile stress. This crack

projection leads to reduced toughness and stiffness, which, in turn, affects the tensile strength of the composite as observed with a composite reinforced with 7 wt. % nano-CaCO$_3$ [31,35,42].

Figure 2 shows Young's modulus versus reinforcement percentage curve. It is observed that Young's modulus reaches a maximum at around 1 wt.% of the reinforcement and decreases at higher levels of the reinforcement. Although the improvement varies with the amount of nano-CaCO$_3$ incorporating into the matrix improves stiffness regardless of the filler concentration. The increase in stiffness could be attributed to the homogeneous dispersion of grain in the matrix. Reduction in stiffness observed at loading above 1 wt.% may be due to agglomeration.

The higher percentage of particles often induces brittle failure due to high-stress concentrations around agglomerated particles, ultimately reducing plastic deformation [42,43]. Meanwhile, homogeneous dispersion of nano-CaCO$_3$ and more durable matrix-filler interface at a reduced amount of nano-
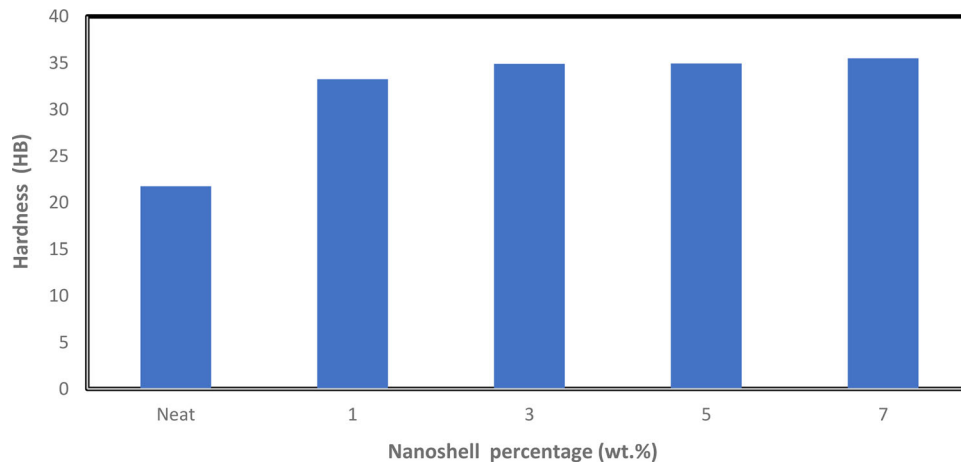
Figure 3. Hardness properties of neat and reinforced nanocomposite.

$CaCO_3$ might have prevented crack initiation at the initial stage, which prevents the propagation of cracks and, in turn, results in improved stiffness.

Significantly, reinforcement by 1 wt.% nano-$CaCO_3$ improved the stiffness of epoxy nanocomposite by 72%, and a sharp drop in stiffness is observed after that. The composites with 3 wt.%, 5 wt.%, and 7 wt.% nano-$CaCO_3$ reinforcement increased the stiffness by 53%, 33%, and 38%, respectively. Although all amounts of nano-$CaCO_3$ improved the stiffness, epoxy composite filled with 1 wt.% nano-$CaCO_3$ offered the highest stiffness. This trend is consistent with results elsewhere, where loading of 1 wt.% and wt.% nano-$CaCO_3$ synthesized from naturally sourced resources increases the strength and stiffness of the matrix [13,31,37–39].

3.2. Hardness

The hardness properties of reinforced and unreinforced epoxy nanocomposites are presented in Figure 3. It is observed that reinforcing with nano-$CaCO_3$ enhances the indentation resistance of the epoxy nanocomposite irrespective of the reinforcement percentages. It is noteworthy that the incorporation of 1 wt.% nano-$CaCO_3$ improved the hardness by 53%. A slight linear increase in the hardness with an increase of nano-$CaCO_3$ reinforcement was observed after this point. The enhancement in hardness can be attributed to the interlocking structure formed through an adhesive bond forming between the filler and the matrix, resulting in a stronger surface that resists indentation. These results confirm the effectiveness of nanoparticle reinforcement at low concentrations [8,22,42,44].

Despite the linear increase in hardness as the percentage of nanoparticles increases, a slight improvement was observed after 1 wt.% nano-$CaCO_3$. This result could be due to a concentrated stress area caused by a high percentage of the nanoparticles resulting in a weak resistance to indentation.

3.3. Impact strength

Figure 4 presents the results for the impact resistance of neat and nano-$CaCO_3$ reinforced nanocomposites. It is observed that reinforcement by nano-$CaCO_3$ increased the impact resistance of the neat epoxy composite. The loading of 1 wt.% nano-$CaCO_3$ slightly increase the impact strength by 25%, and a drop in the impact strength was observed afterward. The increase in impact strength can be attributed to even dispersion of shell particles forming an interconnecting bond which improves the energy-absorbing capacity of the nanocomposite. The decrease in the impact resistance as the percentage of the reinforcement increases could be due to agglomeration resulting from higher nano-$CaCO_3$ content leading effectively to defects. According to Mohsenzadeh et al. [45], the increase in $CaCO_3$ content often reduces plastic zone size, eventually reduces nanocomposite impact resistance. This performance corresponds with studies elsewhere, where a low concentration of nano-$CaCO_3$ improves impact resistance [35,42,45].

The improvement of impact strength with 1 wt.% nano-$CaCO_3$ is similar to what was observed in Figures 1, 2, and 3. This trend implies that reinforcing by novel nano-$CaCO_3$ synthesized from *A. fulica* snail shell at the lowest concentration is a viable way of improving the mechanical properties of polymer composites.

3.4. Thermal properties

Thermal properties in terms of thermal stability and degradation of neat and nano-$CaCO_3$ reinforced composites are shown in Figure 5. It is observed that reinforcing by nano-$CaCO_3$ improved the thermal stability and degradation temperature of the neat epoxy. An insignificant weight loss (0.057) of neat epoxy up to 100^0C corresponds to the heat evaporation of water. Significantly, reinforcing by nano-$CaCO_3$ increased the nanocomposite thermal stability by approximately 34%. Significantly, the
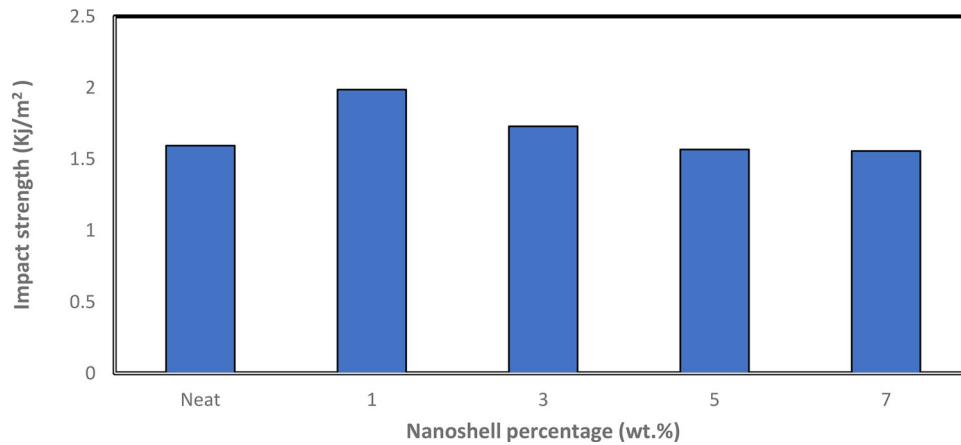
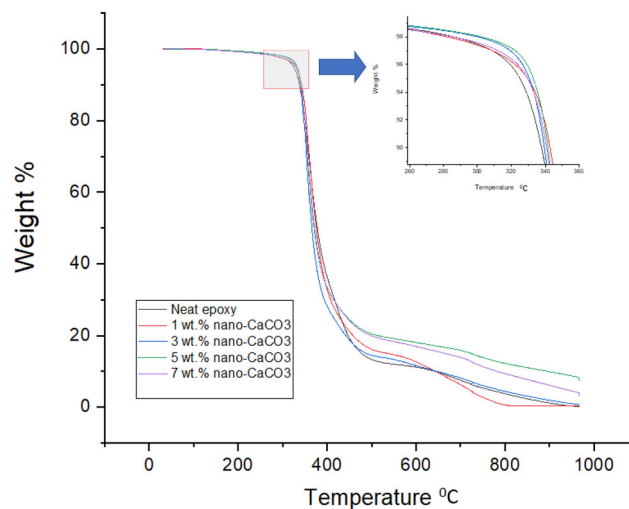**Figure 4.** Impact strength of neat and reinforced nanocomposite.

Figure 5. TGA thermogram curves of neat and nano-CaCO$_3$ reinforced epoxy nanocomposites.

nanocomposite decomposition temperature and thermal stability varied at different percentages of nano-CaCO$_3$. This performance may be associated with the inherent thermal properties of the filler incorporated [46]. This trend is consistent with the results available in the literature, where reinforcing by nano-CaCO$_3$ synthesized from naturally sourced materials was also shown to improve the composite material's thermal properties [31,47].

Generally, the curves show three phases within the temperature range of 0–1000 °C. The first phase (310–373 °C) is exothermic. This performance was attributed to the breakdown of organic substances and depolymerization of the biocomposite [48], which eventually caused a small weight loss (up to 4.72%). The second phase (370–398 °C) is endothermic and is linked to the decomposition of calcium carbonate into carbon dioxide. This weight loss equated to 62%. The third phase (398–950 °C) is a further endothermic decomposition of carbon dioxide to calcium oxide (ashes), which amounts to about 34% weight loss. At the second phase of decomposition temperature, the weight loss of the unreinforced composite was 86%. Nano-CaCO$_3$ filled composites with different loading percentages of 1, 3, 5, and 7 wt.%, showed a mass loss of 64.3%, 62.2%, 60.7%,

and 52.1%. This output indicates that nano-CaCO$_3$ reinforcement reduces the mass loss of the neat composite. To be specific, the maximum amount of 7 wt.% of nano-CaCO$_3$ reduced the mass loss of the neat composite by 40%. This result agrees with the results reported by Mohan and Kanny [31], where it was reported that nano-CaCO$_3$ reinforcement improved the thermal properties of unfilled epoxy.

4. Conclusions

The reinforcement effect of different filler loading (1–7 wt.%) of novel nano-CaCO$_3$ synthesized from *A. fulica* snail shell on polymer composites properties has been investigated. The nano-CaCO$_3$ was synthesized from *A. fulica* snail shell using ball milling mechanochemical technique, and composites with different amounts of nano-CaCO$_3$ ranging from 1 to 7 wt.% were produced using mixing and resin casting procedures. Thermal and mechanical properties of neat and nano-CaCO$_3$ filled nanocomposites were investigated. An increase in the tensile strength, stiffness, hardness, and impact strength of nano-CaCO$_3$ filled nanocomposites was observed at 1 wt.% filler content. This performance is attributed to a

homogeneous dispersion and the high surface area of nano-CaCO₃ particles that enable effective stress transfer to the reinforcement and excellent adhesion between the nanofiller and the epoxy matrix, forming a material with improved mechanical properties. A decrease in the mechanical properties was observed for nano-CaCO₃ contents above 1 wt.%. The decrease in performance was attributed to particle agglomeration, which induces brittle failure due to defect structure and stress concentrations around agglomerated particles. This factor often hampers the strength and stiffness of nanocomposites.

Thermal stability and degradation of the nanocomposites increased with a corresponding increase in the nano-CaCO₃ content. The decomposition temperature and thermal stability of the nanocomposites varied with the nano-CaCO₃ content. Thermal stability and degradation of the nanocomposites improved with increasing nano-CaCO₃ content. However, nanocomposite filled with 7 wt.% nano-CaCO₃ offered superior thermal properties. This performance was attributed to the inherent thermal properties of the nano-CaCO₃. The outcome of the present study indicates that reinforcing with nano-CaCO₃ improves the mechanical properties of nanocomposites, enhances thermal stability, and reduces the mass loss of neat composite. It also confirms the nano-CaCO₃ synthesized from *A. fulica* snail shell as an alternative to commercial nano-CaCO₃.

Acknowledgements

Authors' contributions

O. J. Gbadeyan conceived this idea that translates to this publication, designed an experiment plan, conducted the experiments, analyzed the experiment, and developed the manuscript. Prof. S. Adali, Prof. G. Bright, and Professor B. Sithole provided material and equipment for experimenting, supervised all processes, and proofread the manuscript.

Disclosure statement

The authors declare that they have no conflict of interest as all authors are affiliated with the institution as academic staff members and students.

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