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Selvaraj Anidha, Santhosh Mozhuguan Sekar, Elango Natarajan, Manickam Muthukkumar, Kalaimani Markandan, et al.. Preliminary Investigations and Support for the Mechanical and Dynamic Characteristics of a Natural Rubber Reinforcement in E-Glass/CNT/Epoxy Composite. *Journal of Composites Science*, 2024, 8 (4), pp.140. 10.3390/jcs8040140 . hal-04612621

HAL Id: hal-04612621

<https://hal.science/hal-04612621v1>




Submitted on 4 Sep 2024

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Article

Preliminary Investigations and Support for the Mechanical and Dynamic Characteristics of a Natural Rubber Reinforcement in E-Glass/CNT/Epoxy Composite

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Abstract: The present investigation reports the synthesis and mechanical properties of a hybrid polymer composite consisting of E-Glass fiber, epoxy and 2 wt.% carbon nanotubes (CNTs) with a varying percentage of natural rubber (NR). The prepared hybrid polymer composites were examined in terms of their surface morphology, thermal properties as well as mechanical properties. The findings from the present study indicate that natural rubber enhances the mechanical properties of the hybrid polymer composites and, in particular, 10 wt.% is the optimum percentage of NR that yields the highest strength of 88 MPa, while the strength is 52 MPa with 5 wt.% NR. In order to evaluate the damping properties, a dynamic mechanical analysis was carried out on the E-Glass/CNT with NR composites at various frequencies along with a thermogravimetric analysis. It was found that the composite reinforced with 10 wt.% natural rubber exhibited a higher glass transition temperature of 376.86 °C and storage modulus of 2468 MPa when compared to the other composites, which indicates the enhanced cross-linking density and higher polymer modulus of the composite. X-ray diffraction analysis was also conducted and the results are reported to improve the general understanding of crystalline phases.

Keywords: polymer composite; sustainable manufacturing; product innovation; E-Glass; CNT; natural rubber



Citation: Anidha, S.; Mozhuguan Sekar, S.; Natarajan, E.; Muthukkumar, M.; Markandan, K.; Ang, C.K.; Franz, G. Preliminary Investigations and Support for the Mechanical and Dynamic Characteristics of a Natural Rubber Reinforcement in E-Glass/CNT/Epoxy Composite. *J. Compos. Sci.* **2024**, *8*, 140. <https://doi.org/10.3390/jcs8040140>

Academic Editor: Francesco Tornabene

Received: 31 January 2024

Revised: 11 March 2024

Accepted: 26 March 2024

Published: 10 April 2024



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1. Introduction

Epoxy resins, as a predominant thermosetting polymer with a low molecular weight oligomer containing many epoxide groups, have gained significant interest in both research and high-performance applications due to their various properties such as high transfer-ence, good thermal and mechanical properties, low shrinkage upon curing and excellent corrosion resistance. Although epoxy resins have been commonly used as matrix materials in fiber-reinforced composites, as coatings or in structural adhesives, their engineering applications are limited owing to disadvantages arising from matrix-dominated properties such as high brittleness, low load-bearing capacity and vulnerability to extreme temper-ature variations [1,2]. To this end, the addition of reinforcing filler is a common practice to override the individual properties of epoxy resin and significantly enhance its physical properties such as stiffness, hardness, toughness, mold shrinkage and the heat distortion temperature of the final composite.

Fiber-based fillers as reinforcement in composites have remained an interesting research field. In particular, synthetic fibers such as glass fiber have been commonly used in polymer matrices as reinforcing filler owing to their lightweight nature and excellent properties such as high fatigue resistance, high specific strength, corrosion resistance and easy manufacturing [3–6]. For example, in a study by Singh et al., it was reported that the addition of 20 wt.% glass fiber enhanced the tensile strength and flexural strength of pure epoxy by 14.5% and 123.7%, respectively [7]. In another study by Chopra et al., it was reported that the hybridization of filler, i.e., plain weave copper strip meshes with fiberglass (20 wt.%) in epoxy matrix increased the tensile strength, flexural strength and impact energy by 16.4%, 29% and 55.6%, respectively [8]. The enhancement of the mechanical properties were attributed to the inherent properties of the glass fiber, their quantity, distribution and orientation, as well as the excellent interfacial bonds, which improve the interfacial adhesion and load transfer at the interface.

Another example of a commonly used reinforcement in polymer matrices is carbon nanotubes (CNTs) owing to their outstanding electrical, mechanical and thermal properties [9,10]. For example, CNTs have an exceptionally high Young's modulus of around 1 TPa [11] and a tensile strength of up to 63 GPa [12], which makes them a promising material for use in applications such as nano-sensors or atomic transportation. In a study by Guo et al., it was reported that the addition of 8 wt.% CNTs in epoxy increased the strength and fracture strain at break by 11.65% and 127.8%, respectively [13]. In another study by Wang et al., it was reported that the addition of 0.05 wt.% short single-wall CNTs improved the fracture strength of the composite by approximately 160% compared to pure epoxy [14]. When the composite reinforced with CNTs is subjected to loading, the strong interfacial adhesion between the CNTs and polymer matrix will allow for the load to be transferred to the nanotube, since CNTs exhibit high tensile strength; hence, the composite will be capable of withstanding higher loads [15]. Natural rubber (NR) is an abundantly available material in countries such Myanmar, Malaysia, Vietnam and Indonesia. It has been used in domestic and industrial applications for many decades owing to its characteristics such as excellent durability, resistance to abrasion, dampening of vibration as well as high tensile strength and elongation capability. Research pertaining to tough and resilient NR has been performed for various applications: soft actuators [15], roofing membranes and waterproof linings [16], heavy industrial gloves, dipping, casting/molding, foaming, extrusion, and coating [17]. Table 1 presents previous studies on different reinforcements and their effects on the mechanical, wear and thermal properties of E-Glass/epoxy/CNT/NR composites.

Table 1. Epoxy/E-Glass/CNT/NR polymer composites.

Authors	Polymer Matrix	Reinforcement	Fabrication Method	Parameters Investigated and Outcome of the Research
Muchao Qu et al. [18]	Epoxy	E-Glass/carbon nanotube	Hot-pressing processing technique	Mechanical and electrical properties were investigated. Addition of 0.1–0.2 wt.% CNTs decreased the dissipated energy of the specimen by 50%, but it increased the elastic modulus by more than 100%.
N. Gamze Karsli et al. [19]	PolyPropylene (PP)	E-Glass/carbon nanotube	Injection molding technique	Mechanical and electrical properties were investigated. Chemically (Silane) modified carbon nanotubes are more compact and possess better dispersion into the matrix. Also, electrical resistivity decreases when nanotube reinforcement percentage increases from 1 wt.% to 4 wt.%.

Table 1. Cont.

Authors	Polymer Matrix	Reinforcement	Fabrication Method	Parameters Investigated and Outcome of the Research
Abhinav O et al. [20]	Epoxy	E-Glass/ carbon nanotube	Compression molding	Effect of environmental temperature on the flexural properties was investigated. It is reported that higher temperature (110 °C) limits the flexural strength.
Zahra Naghizadeh et al. [21]	Epoxy	E-Glass/ carbon nanotube, silica nanoparticles	Vacuum bag molding	High-velocity impact behavior was investigated. Energy absorption increases up to 1 wt.% silica nanoparticle inclusion and starts shrinking when it increases to more than 1 wt.%.
Yusri H Muhammad et al. [22]	Epoxy	E-Glass, kenaf fiber, natural rubber	Hot-pressing technique	Mechanical properties were investigated. Addition of liquid epoxidized NR contributed to the increment of the impact strength by 40% whilst the flexural strength increased by 13% and flexural modulus increased by 15%.
D. Jayabalakrishnan et al. [23]	Epoxy	Acrylonitrile Butadiene rubber, E-Glass, nanosilica	Hand layup technique	Mechanical, drop load impact and fracture toughness properties were investigated. Penetration strength improved up to 40%.
D. Athith et al. [24]	Epoxy	Jute, sisal, E-glass, natural rubber	Hand layup technique	Mechanical and tribological properties were investigated. Energy absorption and flexural strength improved by 75% and 60% with 10 wt.% filler reinforcements, respectively.
Vu, Cuong Manh et al. [25]	Epoxy	E-Glass, natural rubber	Hot-pressing technique	Mechanical and dielectric properties were investigated. Addition of NR into the epoxy resin increased the fracture toughness up to 80% compared to the unmodified resin.
H. Anuar et al. [26]	Polypropylene (PP), natural rubber	Short glass fiber (GF) and empty fruit bunch (EFB)	Melt blending method	Tensile and impact properties were investigated. Improvement in mechanical properties was observed with the addition of up to 10 wt.% of EFB, while they started to worsen beyond 10 wt.%.
J. M. Prabhudass et al. [27]	Epoxy	MWCNT, bamboo, kenaf	Compression molding	Thermal stability, mechanical properties were investigated. It was reported that storage modulus was increased by 41%.

Researchers [28,29] have utilized graphene and graphene oxide as fillers in carbon fiber-reinforced polymeric composites. Their investigations have revealed that graphene may greatly enhance the electrical, thermal, and mechanical characteristics of polymers and polymer composites, especially when paired with synthetic fibers. Pristine graphene tends to aggregate because of the strong van der Waals interactions among its atoms. Clustering hinders the uniform distribution of particles in the polymer matrix, which is crucial for achieving optimal properties in the composite. The rationale of this current research is to

investigate the effect of hybridization with NR and CNT into an E-glass/epoxy matrix. NR was used in the present study owing to its high flexibility, resilience, tensile strength and elongation. Particularly, NR displays strain-induced crystallization upon stretching since the molecular chains are able to arrange along the stretching direction. This in turn increases the materials' resistance towards cutting, abrasion and tearing as well as improved tensile strength. Studies on the mechanical behavior of hybridized NR-based polymer composites have not been reported in the literature. Hence, NR, a prominent sustainable material and the only biosynthesized rubber was used at a varying amount, while maintaining the inclusion of 2 wt.% of CNTs. To this end, the paper is presented with Sections 2 and 3. Section 2 presents the materials used and method of research. Section 3 presents the mechanical properties, dynamic properties and morphological studies and discusses the effect of hybridization.

2. Materials and Methods

Glass fiber (GF), with density 1.95 g/cm^3 , elastic modulus of 72–77 GPa and maximum service temperature of $380 \text{ }^\circ\text{C}$, was purchased from a local supplier. Meanwhile, epoxy resin (LY 556) with viscosity of 8000–12,000 cPS and hardener (HY 951) with viscosity of 16,000–18,000 cPS were procured from CY Pols, India. NR solution was also purchased from J.K. Rubbers, India. Carbon nanotubes (CNTs) with average diameter of 10 nm, specific surface area of $250 \text{ m}^2/\text{g}$ and carbon purity of more than 90% were purchased from Sigma Aldrich.

2.1. Fabrication of E-Glass/CNTs/Epoxy/NR Composite

The E-glass/CNTs/epoxy/NR (ECEN) composite was fabricated using the hand layup method, similar to that previously reported in [15]. Epoxy resin and hardener were firstly mixed and homogenized in the standard ratio of 3:1 in the pre-processing stage followed by sonication of the mixture with 2 wt.% of CNT for 3 min. At the same time, aqueous ammonia solution was added into varying amounts (5, 10 and 15 wt.%) of natural rubber solution and stirred continuously along with epoxy/CNT rubber for 3 min to avoid natural coagulation process. The epoxy/CNT and natural rubber were then poured into the E-glass fabric mat and gently brushed to spread the material over the E-glass fabric mat. In a similar fashion, multiple layers of materials were deposited one over the other. Once a laminated composite of 3–3.5 mm was fabricated, it was subjected to compression molding at 10 bars for 6 h. The as-compressed composites were then cured at room temperature for 24 h followed by heat treatment in hot air oven at $50 \text{ }^\circ\text{C}$ for 2 h. Samples with varying wt.% of NR rubber were fabricated as shown in Table 2. For readers, designation ECEN15 refers to polymer composite with 15 wt.% natural rubber, 48 wt.% epoxy matrix, 2 wt.% CNT and 35 wt.% E-glass fiber. The cured composites were then cut according to required ASTM standards using water jet machining. Figure 1 shows the infographic chart of the complete step-by-step hybrid composite fabrication procedure.

Table 2. Various weight fraction of E-Glass/CNTs/epoxy/NR configurations reported in the present study.

Designation	Epoxy Matrix	CNT	E-Glass Fiber	Natural Rubber
ECEN15	48	2	35	15
ECEN10	53	2	35	10
ECEN5	58	2	35	5

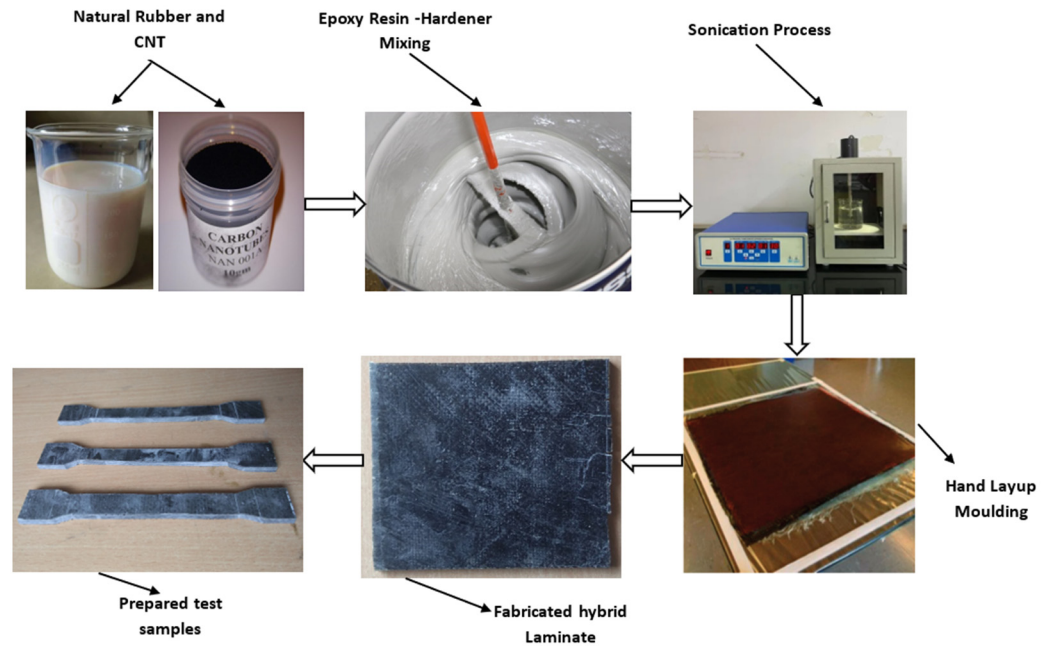


Figure 1. Fabrication procedure of hybrid composites.

2.2. Method of Research

Functional groups of the fabricated composites were investigated using FTIR spectra that were acquired using a Bruker IFS 28 spectrophotometer at room temperature ranging from 4000 cm^{-1} to 400 cm^{-1} . Microstructural characterizations were performed using Field Emission Scanning Electron Microscopy (FE-SEM) on the as-fabricated samples and fractured samples to analyze the failure mechanism as the natural rubber content was varied in the composite. A wide-angle X-ray diffractometry (XRD) analysis was conducted using a rotating anode and $\text{CuK}\alpha$ radiation source ($\lambda = 0.15418\text{ nm}$) with a reflection–transmission spinner (PW3064/60) on modified E-Glass/epoxy composites containing different percentages of NR (5, 10 and 15 wt.%), using the XRD Model XPERT-3. XRD patterns were obtained at a rate of 2 degrees per minute throughout the scan range of 5 to 90 degrees. A Thermogravimetric analysis was performed at a maximum temperature of $650\text{ }^{\circ}\text{C}$ to measure the sample's changes in mass as the temperature increased. TGA analysis was performed using a PerkinElmer TGA 4000 instrument, USA, optimized via Pyris Software. Tensile and flexural characteristics were evaluated according to ASTM D3039 and ASTM D7264, respectively, using a Servo controlled universal testing machine at a speed rate of 30 mm/min . Impact strength was obtained with Izod test as per ASTM D256, and was conducted using an AIT-300N impact tester with 600 mm of pendulum swing and 18.7 kg striking hammer weight. Dynamic mechanical analyses to investigate the viscoelastic properties were performed using DMA Q800 (TA Instruments, New Castle, DE, USA) with a 3-point bending clamp setup from room temperature to $200\text{ }^{\circ}\text{C}$.

3. Results and Discussion

3.1. FTIR Analysis

FTIR is primarily used to rapidly and conclusively detect substances such as formulated plastics, mixes, additives, pigments, rubber compounds, protective coatings, chemicals and glues in the developed hybrid composites [30]. Figure 2 shows the FTIR spectra of NR and ECEN composites. In the NR spectra, the peak at 3345 cm^{-1} was attributed to the $-\text{OH}$ group, while the peak at 2922 cm^{-1} was assigned to the $-\text{CH}_3$ symmetric stretching vibration. The peaks at 1401 cm^{-1} , 1249 cm^{-1} and 1063 cm^{-1} represent the isoprene unit of the C-H bond stretching, C=C stretching and C-C stretching, respectively. The appearance of degradation also occurs, as shown by the peaks forming and increasing with transmittance [31]. Similar peaks were observed in the ECEN composites, which

indicates the presence of NR in the composite formation. The disappearance of the peak at 3345 cm^{-1} indicates that the composite was not in viscous form. Some new stretching vibration peaks were formed in the polymer composite spectrum such as that at 1722 cm^{-1} , which corresponds to the C=O vibration frequency, and $876\text{--}693\text{ cm}^{-1}$, which represents the bending of the C-O bond and aromatic C-H bonds; all of these indicate strong bond formation of NR with the other composite compounds.

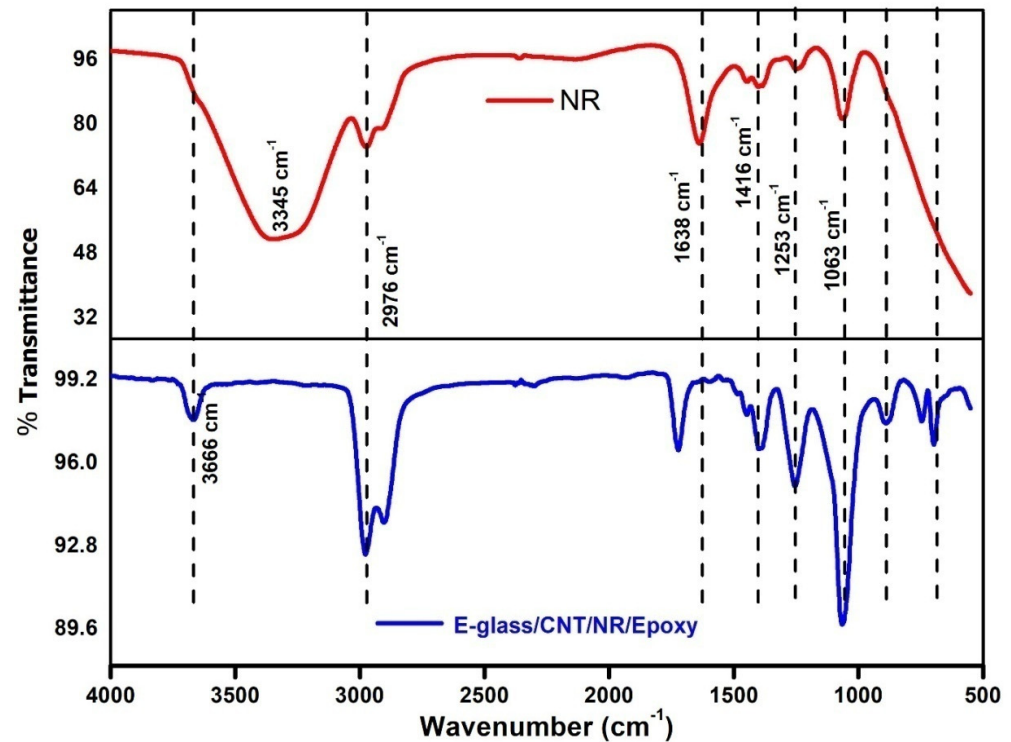


Figure 2. FTIR spectrum of E-Glass/CNTs/epoxy/NR blended samples.

3.2. XRD Analysis

The XRD plots shown in Figure 3 display the diffraction peaks of the solid solution phase in the hybrid composites containing 5 wt.%, 10 wt.% and 15 wt.% NR content. It is also noted that the XRD spectrum shows a graphite diffraction peak rather than a peak representing the carbon nanotubes, as the sintering mold is composed of graphite. The CNT particles are amorphous, and the diffraction peak is wide, similar to results in previous studies [32]. The reinforcing characteristics of the carbon nanotubes (CNTs) are primarily influenced by their uniform dispersion and interaction with the polymer matrix. In addition, Figure 3 shows the deconvoluted peaks for the samples developed with natural rubber; here, a larger proportion of amorphous material leads to a greater widening of the diffraction peaks. The sample containing 15 wt.% NR-filled E-Glass/CNT/NR exhibits the smallest broadening effect, indicating a higher level of crystallinity in this instance. Similarly, the XRD pattern of E-Glass/CNTs/epoxy/NR displays integrated peaks for the CNTs and NR at 24° , 23° and 22° for ECEN5, ECEN10 and ECEN15, respectively. The peaks of CNT/NR were broader following the development of NR due to the disturbance of the crystal structure in the epoxy matrix, indicating the production of CNTs by tip growth.

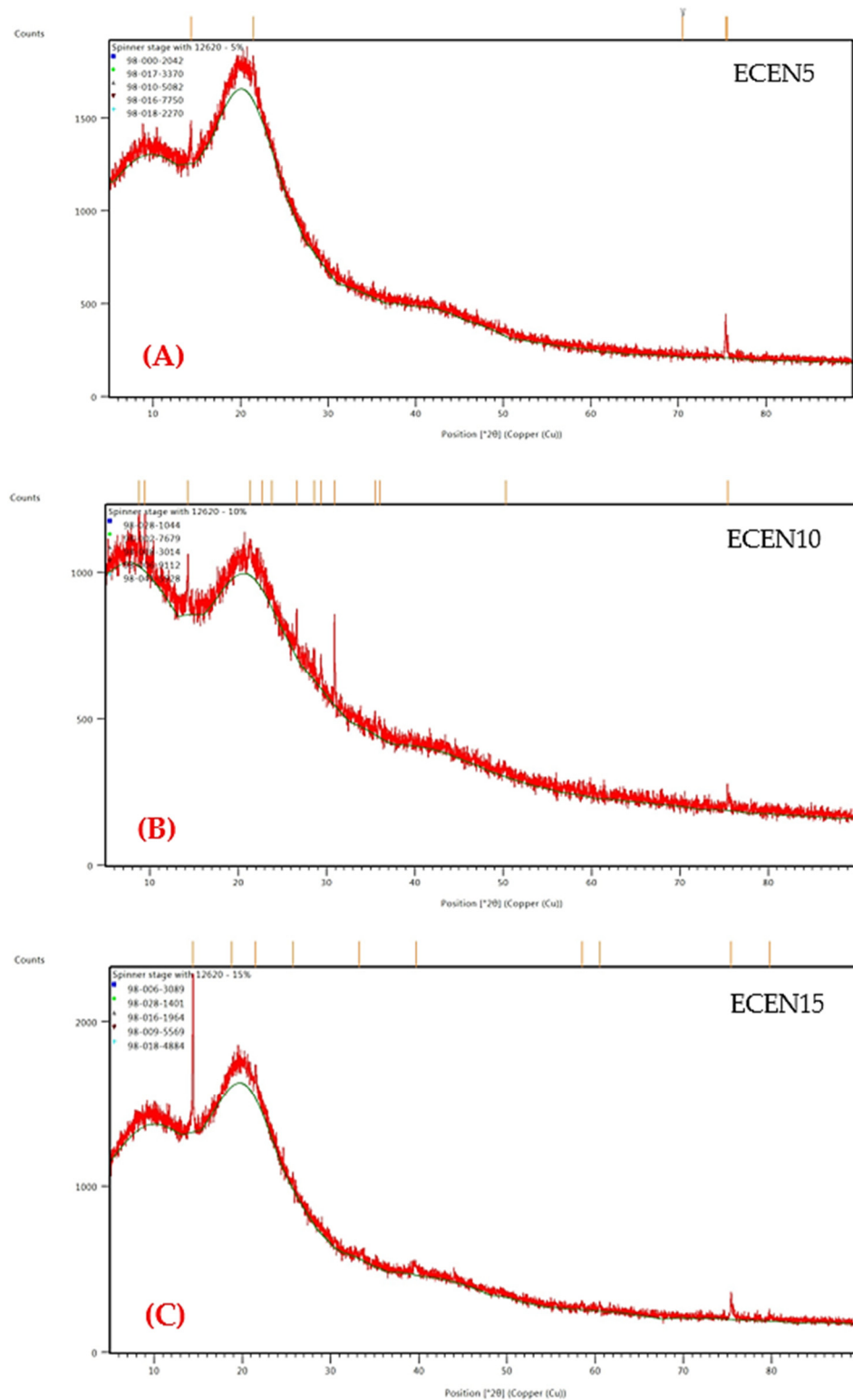
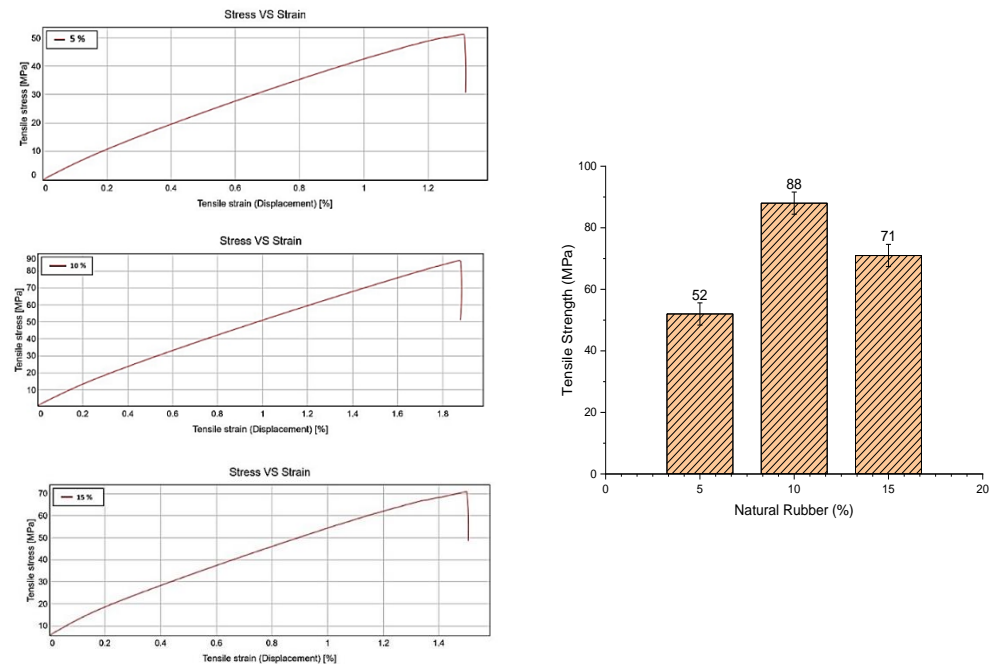


Figure 3. XRD patterns of (A) 5 wt.%, (B) 10 wt.% and (C) 15 wt.% NR-filled E-Glass/CNTs/epoxy/NR blends.

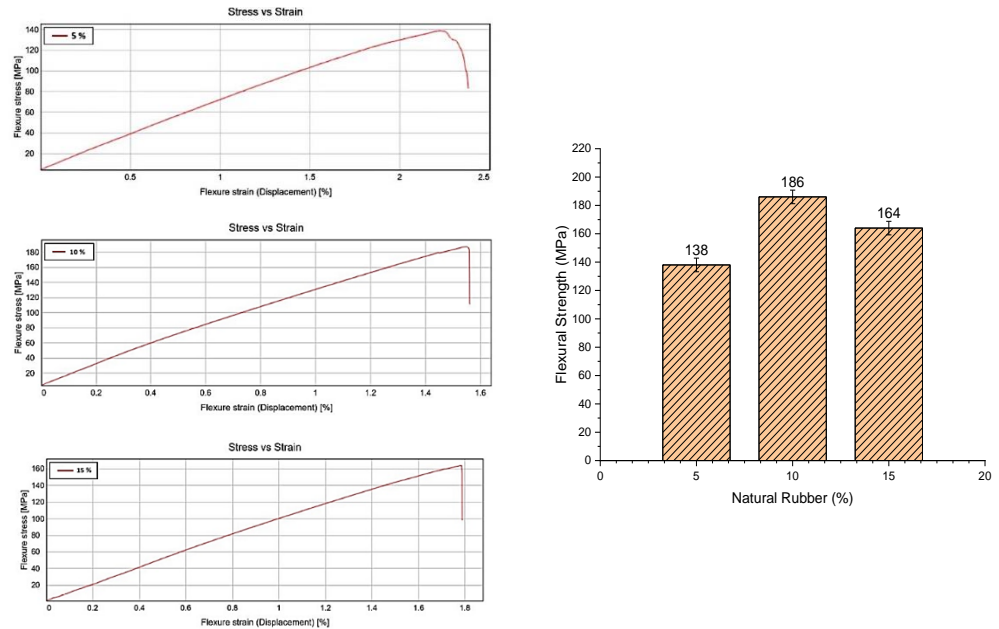
3.3. Mechanical Properties of ECEN Composite

Figure 4A,B shows the tensile and flexural strength of various ECEN composites when reinforced with varying amounts of natural rubber, i.e., 5, 10 and 15 wt.%. The findings in Figure 4A indicate that the amount of natural rubber in the composite affects the tensile behavior of the composite. For instance, the composite with 10 wt.% natural rubber

exhibited optimal tensile properties compared to that with 5 wt.% natural rubber, which could be related to the increased ductility of the ECEN composite. This is ascertained by the higher strain at break of the composite when reinforced with 10 wt.% natural rubber, i.e., 1.8% at 88 MPa compared to 1.2% when reinforced with 5 wt.% natural rubber. When the ECEN composite reinforced with the optimum amount of natural rubber was subjected to tensile testing, the natural rubber assisted in transferring the load uniformly to the E-glass fiber, CNTs and throughout the polymer matrix, which enhanced the strength of the composite.



(A)



(B)

Figure 4. (A) Stress vs. strain relationship and tensile strength comparison of hybrid samples. (B) Stress vs. strain relationship and flexural strength comparison of hybrid samples.

Figure 4B shows the flexural behavior of the ECEN composite when reinforced with varying amounts of natural rubber, i.e., 5, 10 and 15 wt.%. From Figure 4B, it can be seen that the composite reinforced with 10 wt.% natural rubber exhibited the optimal flexural strength. Above 10 wt.%, the flexural strength started decreasing, since a higher amount of natural rubber may lead to agglomeration, which in turn restricts the flexural ability of the ECEN composite [32].

Figure 5A,B shows the FE-SEM images of the composite (10 wt.% natural rubber) fabricated in the present study, while Figure 5C,D shows the microstructure of the composite upon fracture. From Figure 5, it can be seen that the natural rubber exhibited good interfacial adhesion with the polymer matrix, while the E-glass fiber and CNTs were successfully incorporated within the polymer matrix. The good interfacial adhesion between the natural rubber, E-glass fiber and CNTs with the epoxy matrix is important for enhancing the effective stress transfer to strengthen the composite [33,34]. It was observed from the mechanical and thermal studies that up to 10 wt.% of NR inclusion, there is a gradual improvement in the strength, then over this amount, it starts shrinking. To improve the wettability of fillers and matrices, the fillers are supposed to be modified or pretreated [35]. Toughening mechanisms such as CNT pull-out, fiber breakage as well as crack deviation observed in the present study will lead to enhanced energy absorption when a load is applied; thus, this increases the toughness as well as the strength of the composite, as reported in the previous section of this study.

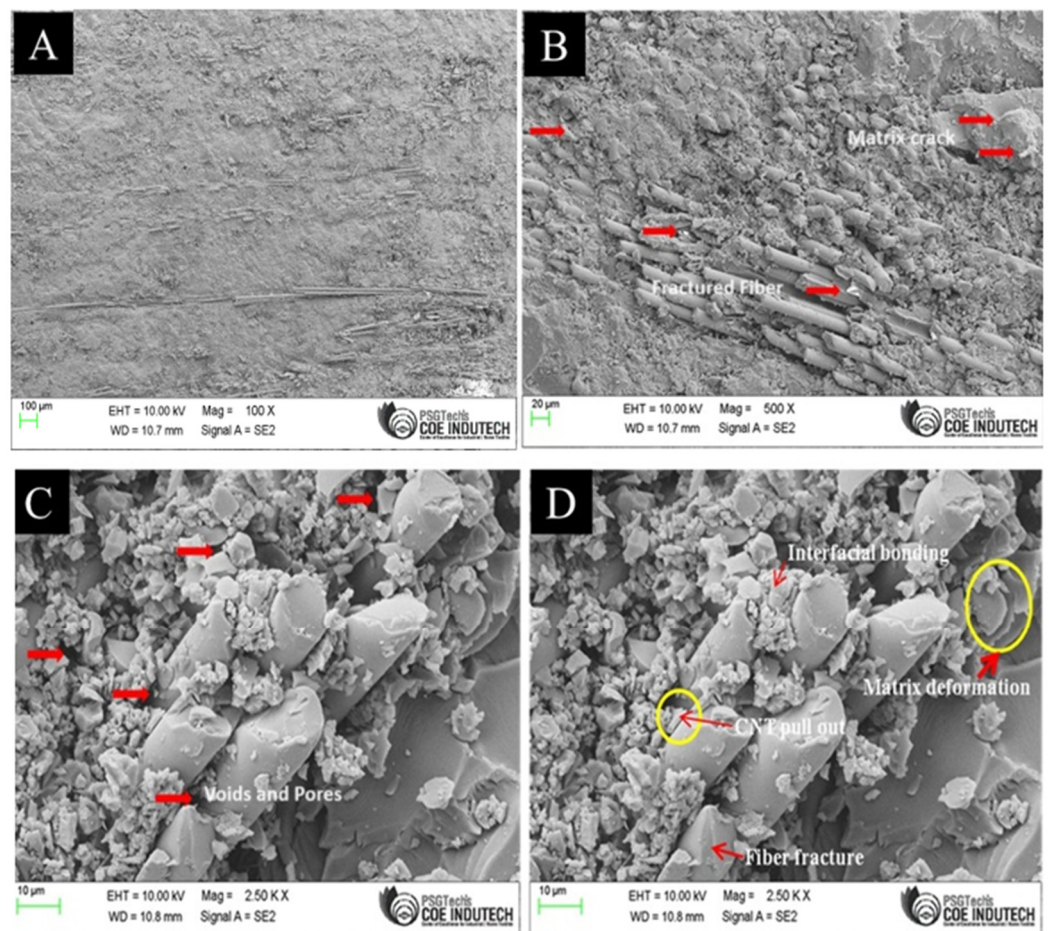


Figure 5. (A,B) FE-SEM images of the composite (10 wt.% natural rubber) fabricated in the present study; (C,D) microstructure of the composite upon fracture.

3.4. Dynamic Mechanical Analysis (DMA) of ECEN Composite

Figure 6A shows the storage of the composite when reinforced with various percentages of natural rubber. As a thermoset polymer, the composite in the present study exhibits both crystalline and amorphous forms and the composite transforms from the glassy to the rubbery state, which indicates the enhanced cross-linking density and higher polymer modulus of the composite. The composite reinforced with 10 wt.% natural rubber exhibited the highest storage modulus of 2468 MPa, while the composite reinforced with 15 wt.% exhibited the lowest storage modulus of 1492 MPa. The natural fiber exhibited excellent interfacial bonding and cross-linking between the materials in the epoxy matrix with the epoxy resin, CNTs and E-glass fiber, which enhanced the storage modulus of the composite. The findings also show that the $\tan \delta$ of the 10 wt.% natural rubber composites is around 1.319, which is greater than that of the other configurations, indicating the highest amount of molecular mobility of the fillers inside the polymer matrix. This effect occurs because of the stiff and elastic nature of materials at lower temperatures, leading to a low $\tan \delta$ value.

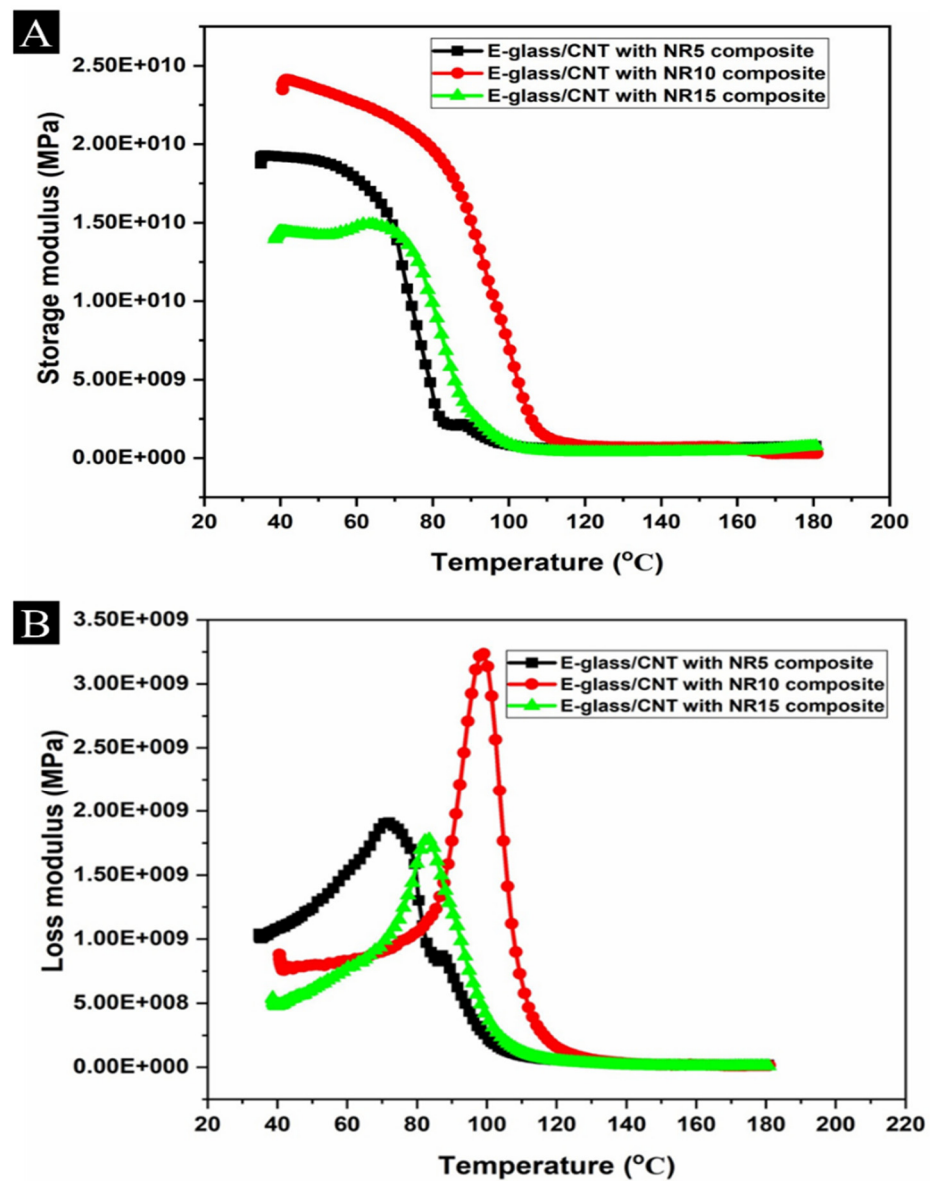


Figure 6. (A) Storage modulus and (B) loss modulus of ECEN hybrid composite.

Figure 6B shows the loss modulus of the composite when reinforced with various percentages of natural rubber, which indicates the quantity of energy released as heat.

Similar trends were observed for all the composites, where the molecular moment was activated as the temperature increased and reached the glass transition region. From Figure 6B, it can be seen that the composite reinforced with 10 wt.% natural rubber exhibited the highest loss modulus of 3256 MPa compared to the composites reinforced with 5 and 15 wt.% natural rubber at the similar temperature. The higher loss modulus of the composite reinforced with 10 wt.% natural rubber indicates the higher viscous nature of the material, which exhibits better damping properties. In a previous study by Saba et al., it was reported that highly cross-linked thermoset polymers will exhibit a tighter and stiffer network structure, which in turn leads to enhanced storage and a greater loss modulus [17]. When reinforcing the epoxy matrix with glass, flax or pineapple fibers, Prabhu et al. [36] found similar trends. Hybrid composite materials with nano filler/fiber added to a hybrid Lannea Coromandelica Blender (LCE) matrix are more rigid in ductile and brittle areas. The material becomes more liquid-like, with a gradual decrease in $\tan \delta$ due to less hindered molecular motion.

3.5. Thermogravimetric Analysis

Figure 7A displays the weight loss curves of the three composites that were fabricated in the present study. Figure 7A shows that ECEN5 begins to lose weight earlier compared to the other composites. The change is caused by the moisture content of the matrix and the presence of natural rubber in the sample. When the temperature surpasses 30 °C, the moisture in the samples begins to evaporate. At an elevated temperature of 650 °C, the quantity of residues left after composite deterioration was documented. Epoxy matrix often has the least number of residues compared to other thermoset matrices because of its low char-forming attribute. The graph indicates that the produced hybrid samples exhibit a high thermal stability with very little differences in weight losses across the samples. The most significant deterioration and reduction in weight of the samples happened between 300 °C and 400 °C. Samples with 15 wt.% natural rubber reinforcements exhibit a higher glass transition temperature (T_g). The observed effect is due to the adherence of carbon nanotube particles with the matrix and natural rubber reinforcements, which limit deterioration at high temperatures. ECEN10 (10 wt.% NR) has a glass transition temperature (T_g) of 376.86 °C, whereas ECEN15 (15 wt.% NR) has a T_g of 358.51 °C due to stable fibers and the production of reasonable char. ECEN15 seems to have superior thermal stability in this investigation. The usage of carbon nanotubes (CNTs) and nanorods (NRs) greatly improves the heat resistance.

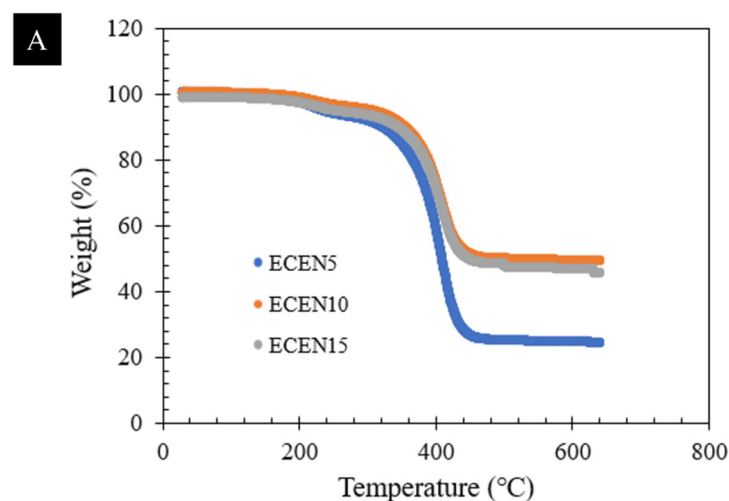


Figure 7. Cont.

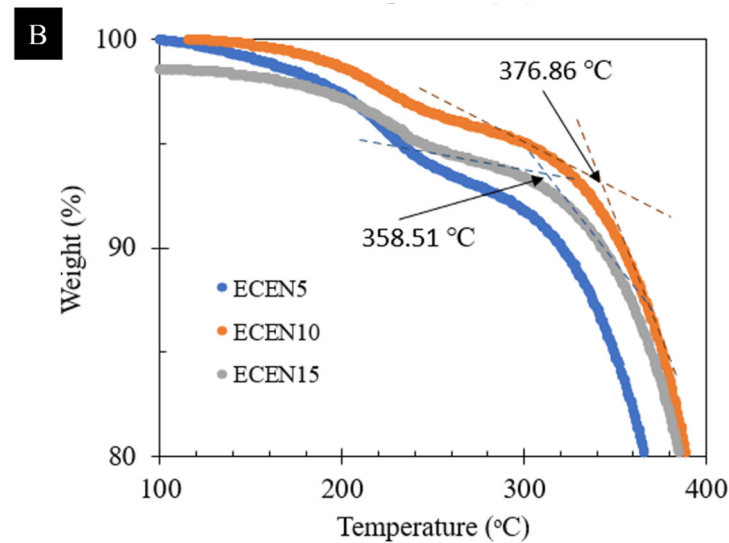


Figure 7. (A) Thermal Gravimetric Analysis (TGA) of E-Glass/CNTs/epoxy/NR blends, (B) magnified version of TGA curve to show significant weight loss from 300 °C to 400 °C.

4. Conclusions

The present research investigated the wettability behavior of natural rubber and carbon nanotubes inside a epoxy matrix when it was reinforced with E-Glass fiber. In conclusion, hybrid polymer composites consisting of E-Glass fiber, epoxy and 2 wt.% carbon nanotubes (CNTs) with varying percentages of natural rubber were successfully fabricated. It was found that 10 wt.% of NR significantly enhanced the strength, storage modulus as well as the glass transition temperature of the composite. It exhibits a higher glass transition temperature of 376.86 °C and a storage modulus of 2468 MPa when compared to the other composites. The SEM images displayed the good interfacial adhesion between the natural rubber and epoxy while the E-Glass fiber and CNTs were shown to be successfully incorporated within the matrix. Similarly, the XRD diffraction peaks represented the solid solution phase in the hybrid composites. It was also observed that integrated peaks for CNT and NR occurred at 24°, 23° and 22° for ECEN5, ECEN10 and ECEN15, respectively. The preliminary findings reported in the current study will be useful for further research in the field of natural rubber-based nanocomposites as well as for fabricating sustainable composite materials with a high strength to weight ratio that could be used in a range of applications, such as the production of conveyor belts or tires, automotive structural components and aircraft structures.

Author Contributions: Conceptualization, S.A., C.K.A. and G.F.; Methodology, E.N. and K.M.; Software, S.M.S.; Validation, E.N.; Formal analysis, M.M.; Resources, M.M. and G.F.; Data curation, E.N., C.K.A. and G.F.; Writing—original draft, S.A. and M.M.; Writing—review & editing, S.M.S., C.K.A., G.F. and K.M.; Supervision, C.K.A.; Project administration, E.N. and G.F.; Funding acquisition, G.F. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: The data presented in this study are available within the article.

Conflicts of Interest: The authors declare no conflict of interest.

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