Investigation into mechanical, thermal and water absorption behaviors of *Cocos nucifera* shell filler reinforced vinyl ester polymeric composites

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Abstract

Recently, natural filler reinforced polymer composites are important materials for various engineering applications. Hence, this present work focuses on utilization of *Cocos nucifera* shell powder (CNSP) as a filler in vinyl ester (VE) resin to produce particulate composite specimens. The particulate composite plates with various weights or filler contents from 5 to 30 wt.% were fabricated, using compression molding technique. The fabricated composites were subjected to tensile, flexural, impact, hardness, heat deflection and swelling behavior tests to obtain their corresponding material properties. Energy dispersive X-ray (EDX) analysis was carried out on the *Cocos nucifera* shell powder/vinyl ester (CNSP/VE) composite specimens to investigate into the presence of their elements, in addition to the aforementioned tests. From the experimental results obtained, it was observed that the optimum mechanical properties of CNSP/VE composites were obtained at 15 wt.% of filler content, having tensile, flexural and impact strengths of 38.70, 105.13 MPa and 33.04 kJ/m^2, respectively. Also, the heat deflection temperature (HDT) results varied from 158 (0 wt%, neat VE resin) to 171 ^{o}C along various percentages of filler contents. Lastly, the morphological study/analysis of the fractured CNSP/VE composite specimens was conducted by using a scanning electron microscope (SEM) to confirm the experimental data/results obtained. It was evident that CNSP/VE composite structures could be potential substitutes for some synthetic composites. Also, they are suitable for various engineering applications in aerospace, electrical/electronics and automobile industries, based on their properties.

Keywords: *Cocos nucifera* shell powder (CNSP); vinyl ester (VE); mechanical properties; thermal property; fracture mode; swelling behavior.

Introduction

Considering the current increasing application of various engineering materials, natural fiber reinforced polymer (NFRP) composites have attracted attention of research community. This trend has led to emergence of many renewable products, not only for diomestic, but also for industrial uses, including automobile and aeerospace. Application of NFRP composite products is cost-effective and eco-friendly [1–4]. Man-made products are readily available, but people tend to use natural-based products that are environmentally friendly, sustainable and biodegradable. Generally, NFRP composite products require processing and treatment in order to modify their properties as well as to achieve desired strengths [5,6]. Subsequently, these tasks seem to be a long process, but it is eco-friendly. They can be used repeatedly and finally discarded without harming environments. Whereas, these cannot achieved with several synthetic or conventional fiber reinforced polymer (FRP) composite products [7]. Therefore, the main objectives of the present research are to fabricate composites with various percentages of *Cocos nucifera* shell powder (CNSP) as a filler material combined with vinyl ester (VE) resin and test their suitability for engineering applications, based on their mechanical, water absorption and heat deflection behaviors, among others.

Based on compendious review conducted, previous relevant and similar studies are subsequently elucidated. Leaves of pineapple, sisal and abaca have been treated by retting and chemical processing to produce an eco-friendly product [8–11]. The natural fibers have a great potential to replace man-made fibers in numerous ways. Products which are manufactured from natural fibers are biodegradable and can be disposed off easily. Natural fibers are relatively fragile, they can be easily damaged [12,13]. Therefore, they must be processed by various chemical treatments to improve and increase their strengths and durability, respectively [14,15]. Gradually, natural fillers are replacing natural fibers. Natural fillers, such as wood dust, tamarind seed filler, date palm seed filler, fly ash, rice husk and red mud are reinforced

with resins to produce eco-friendly products [16]. For instance, when tamarind seed powder was reinforced with vinyl ester resin, the optimal mechanical properties were obtained at 15 wt.% of tamarind seed filler, as a volume fraction.

Furthermore, the fillers can also be used to improve the quality of eco-friendly adhesives [17–24]. When egg shell powder was combined with calcium and phenylphosphonic acid or with natural rubber latex foam, high strength composites were formed [25,26]. Also, when CNSP was reinforced in resins and chemically treated, reliable composites were produced, as confirmed from mechanical property tests, included tensile, flexural, impact and hardness, among others [27–31]. Heriyanto et al. used different waste powders: Quartz off-cut, sand, waste sea shell, dolomite, limestone aggregates, concentrate waste and limestone dust to prepare a mixture. The mixture was then treated chemically with an amino silane coupling agent to produce high quality structural slabs [32]. A composite with high tensile strength was obtained, when it was prepared with fly ash and fossil fuels [33–35]. When rice husk was combined with natural rubber/wood dust, a composite with the highest mechanical property and high thermal stability was obtained. However, its property was affected with influence of moisture content [36–41]. Abdul Khalil et al. developed a hybrid composite with high stability and thermal properties by using three types of carbon black from bamboo stem, *Cocos nucifera* shell and oil palm [42]. Ben Daly et al. analyzed water absorption property on polyester glass fiber and clay powder, using sea water and distilled water. It exhibited high water absorption quality, when the composites contain low profile additives [43]. Yusriah et al. investigated into mechanical properties of woven glass filler reinforced vinyl ester composites, it resulted to better flexural and impact strengths, when it was combined with phenolic [44].

Besides, Karthik Babu et al. fabricated coir powder/polyester composites by hand lay-up method to find out their thermo-mechanical behaviors. Best interfacial bond strength occured at maximum of 4 wt.% of filler content, among 1, 2 and 3 wt.% of volume fractions of the

fillers [45]. Navaneethakrishnan et al. used taguchi method to optimize fabrication of roselle fiber with 5 wt.% of CNSP reinforced vinyl ester composites [46].

From the aforementioned literature, it is evident that the addition of natural fillers provided better mechanical, thermal properties and water absorption behaviors. Also, it provided low density, low cost, eco-friendliness, high toughness and higher biodegradability, when used as a filler to fabricate the composites [1]. A few studies stated that CNSP was mixed with natural fillers, such as rice husk, wall nut powder and reinforced with recycled polypropylene, polyethylene, polylactic acid, epoxy and polyester. Further intensive literature review revealed that studies were majorly on use of epoxy and other matrices. In an attempt to make a difference from other reported works, vinyl ester has been taken as matrix, since vinyl ester has distinctive properties: relative better mechanical, thermal, chemical resistance and interfacial strength when compared with some matrices. Also, it is also more easily available and cost-effective [47].

Filler reinforced polymer matrix composites provided better improvements, such as high tensile strength, high stiffness, high fracture toughness, good abrasion resistance, among others. These properties depended on the properties of fillers and matrix as well as the concentration of the fillers in the matrix. Usually, vinyl ester provided highly resistance to water, more stronger than polyesters and more resilient than epoxies. Therefore, CNSP fillers provided better mechanical properties, when reinforced with polyester and epoxies [53]. Hence, the objective of the present work focused on fabrication of composite materials with a newly combination of various percentage weights of CNSP and vinyl ester resin.

Importantly, considering cost effectiveness of CNSP, the present research has been carried out on fabricated composites of waste CNSP and vinyl ester (VE) resin. The composites were made with different weight percentages of CNSP: 0 (neat; no filler), 5, 10, 15, 20, 25 and 30 wt.% and their mechanical properties, such as tensile, flexural, impact and Barcol hardness as

well as heat deflection temperature (HDT) and water absorption behaviors were analyzed. From the test results, the addition of filler provided better mechanical properties, which was observed with a certain suitable or optimal wt.% of CNSP based composites, among the seven different wt.% filler. The sample was obtained to be a potential, sustainable and biobased structural material for domestic and other applications. The elements present in CNSP were examined by using energy dispersive X-ray (EDX) analysis. The fractured surfaces obtained after tensile, flexural, impact tests and morphological behaviors of the CNSP/VE composite specimens were analyzed, using a scanning electron microscope (SEM). The most suitable properties among the various wt.% filler reinforced composites was obtained from the tests conducted.

Experimental details

Materials

Cocos nucifera shells were collected from places surrounding Madurai, Tamil Nadu, India. They were later cleaned by water and dried in open air [27,30]. Then, by using a ball mill apparatus [54], small pieces of *Cocos nucifera* shells were converted into powder and finally dried in a hot air oven at 80 ^{o}C for 24 hrs [27,28]. It was used as filler and VE resin as a matrix material. Accelerator, catalyst and promoters, such as N-dimethylaniline, methyl ethyl ketone peroxide and cobalt naphthenate were procured from Covai Seenu Company, Coimbatore, Tamil Nadu, India.

Fabrication of composites

The process of composite plate fabrication is shown in Figure 1. The compression molding technique [48] was adopted for making composites of CNSP and VE resin. The molds of

dimension of 200 × 200 × 3 mm were prepared to fabricate the composite plates with addition of filler weight percentages from 5 to 30 wt%; at an interval of 5 wt%.

Figure 1. Fabrication of composite plates, showing: (a) collected *Cocos nucifera* shells, (b) ground CNSP, (c) prepared CNSP with vinyl ester resin and curing agents, (d) CNSP/VE poured into 200 × 200 × 3 mm mold, (e) complete set-up of compression molding machine and (f) prepared composite plates with 0 to 30 wt.% of CNSP fillers.

They were used as a random filler for reinforcement. The resin was mixed with the following curing agents: 10 ml of accelerator, 10 ml of catalyst and 15 ml of promotor for each 1000 ml of VE resin. Then, the prepared resin was mixed with already weighted CNSP and poured into the mold cavity. The mold was operated under a pressure of 100 KPa with temperature of 70 ^{o}C, maintained by the electrical heater with holding time of 20 minutes. Afterwards, the composite plates were allowed to dry at room temperature. After drying, the plates were cut into test specimen coupons by electrical board cutting machine in accordance with the ASTM standards for testing composite specimens.

Elemental analysis

EDX analysis of *Cocos nucifera* shell filler was conducted, using BRUKER Nano, GmbH, D-12489, Germany, with accelerating voltage from 0 to 30 KeV, located at Gandhigram Rural Institute, Dindigul, Tamil Nadu, India.

Mechanical testing

Tensile test

The tensile test was carried out on a Tinius Olsen H10KL – Universal testing machine at AC Tech Karaikudi, Tamilnadu, India, having horizon software with accuracy of ±0.05%. The machine has a capacity of 10 kN and crosshead of 1.0 mm/min at operating atmospheric temperature up to 40 ^{o}C. Specimen prepared for a tensile test according to the ASTM D638-10 standard has a dimension of 165 × 10 × 3 mm with gauge length of 60 mm [20]. The horizon software generated the peak load, ultimate tensile strength and load *versus* length graph. Three specimens were tested and their mechanical property test results obtained were averaged and used to present their plots.

Flexural test

Flexural test was carried out on same UTM machine, using three-point flexural test method, a flexural test fixture and load cell of 10 KN. The specimens prepared according to the ASTM D790-10 standard of 127.0 × 12.7 × 3.0 mm with gauge length of 100 mm were used to obtain their flexural properties [19]. The specimens were placed between two supports and load was applied at their centers of gauge length of 100 mm and loading rate of 1.0 mm/min. The peak load, flexural strength and load *versus* length graphs were recorded, using UTM - horizon software.

Impact test

Quantity of the absorbed energy by the CNSP/VE composite specimen was obtained after Izod impact test, using impact testing machine. The specimens were prepared for impact test in accordance with the ASTM D256-10 standard of 65.0 × 12.7 × 3.0 mm [19]. The framing hammer in the tester stroke the upper part of each specimen, when it was released. The impact load applied on the specimen was also recorded.

Barcol hardness test

Hardness test was carried out by using Barcol hardness tester PCE-1000N at OMEGA Inspection and Analytical Laboratory, located at Guindy, Chennai, Tamilnadu. To test the hardness of the composite specimens, they were prepard according to the ASTM D 2583 standard [19]. The specimens were all cleaned without any mechanical damage and their surfaces were polished to eliminate scratches during test. The minimum distance maintained between the pin tip and the edge was not less than 3 mm. To obtain more accuracy, the pin was perpendicular to the surface of the specimen. Barcol hardness number was recorded directly

from the digital meter. From each specimen, three values were taken from different spots and the results of the hardness values were similarly averaged.

Thermal property - Heat deflection test

Heat deflection test was performed. A HDT Tester located at OMEGA testing centre, Chennai, Tamil Nadu was used to measure resistance of distortion under 1.86 MPa at high temperature. The specimens were prepared in accordance with the ASTM D648 standard of 60 × 12 × 3 mm [19]. Silicone oil was used as a heat transfer medium, it did not affect the mechanical properties of the specimens. The oil bath was then heated at a rate of 2 ^{o}C/min until each specimen reached a deflection state, before temperature obtained at this pont was recorded.

Morphological behaviors

Morphological behaviors of tensile, flexural and impact fractured CNSP/VE composite specimens and fractography characteristics were analyzed and compared, using JOEL SEM, located at Gandhigram Rural Institute, Dindigul, Tamil Nadu, India. The fractured portions of the specimens were prepared by coating their surfaces uniformly with gold. This process supported better conductivity. Their SEM micrographs obtained were focused on their interfacial properties, such as CNSP-VE interaction, filler pull-out, crests, troughs and striations formed on the specimens.

Swelling behaviors- Water absorption property

Water absorption behaviors of CNSP/VE composites were calculated at different liquid conditions: normal, hot, cold and sea water. The test specimens were prepared in agreement with the ASTM D570-99 standard of 39 × 10 × 3 mm [19]. The prepared specimens were dried at 105 ^{o}C for 24 hrs in hot air oven [19]. Three composite specimens of same wt.% were tested,

each. The initial weights (W_i) of the specimens were measured using digital weighing scale. These specimens were immersed in normal and sea water with 2.5% of salt content conditions for 24 hrs at room temperature, with exception of hot water condition which was 70 ^oC for 2 hrs in hot water bath instrument (Model: Precision GP 02). The cold water temperature condition was maintained around 4 ^oC in a refrigerator for 24 hrs. These specimens were taken out after above mentioned time (period), wiped with cloth and then, the final weights (W_f) of the specimens were measured. The percentage of water absorption content was determined by Equation (1),

$$\text{Water absorption percentage, } W\% = \frac{W_f}{W_i} \times 100 \quad (1)$$

Where W% = percentage of moisture content, W_f = final weight of the specimen in grams and W_i = initial weight of the specimen in grams.

Results and discussion

Elemental analysis - EDX analysis

EDX image and chemical composition of CNSP are shown in Figures 2(a) and (b), respectively. The test was carried out on SEM with EDX instrument. The results showed that maximum values of 75.98 wt.% of carbon and 24.02 wt.% of oxygen were most dominant elements in the filler particles. When compared with pure *Cocos nucifera* shell particles, an increase of 31.11% of carbon and decrease of 47.78% of oxygen were observed from the composites, as similarly reported [49]. The elemental changes of carbon and oxygen occurred, due to the fiber treatment [55,56].

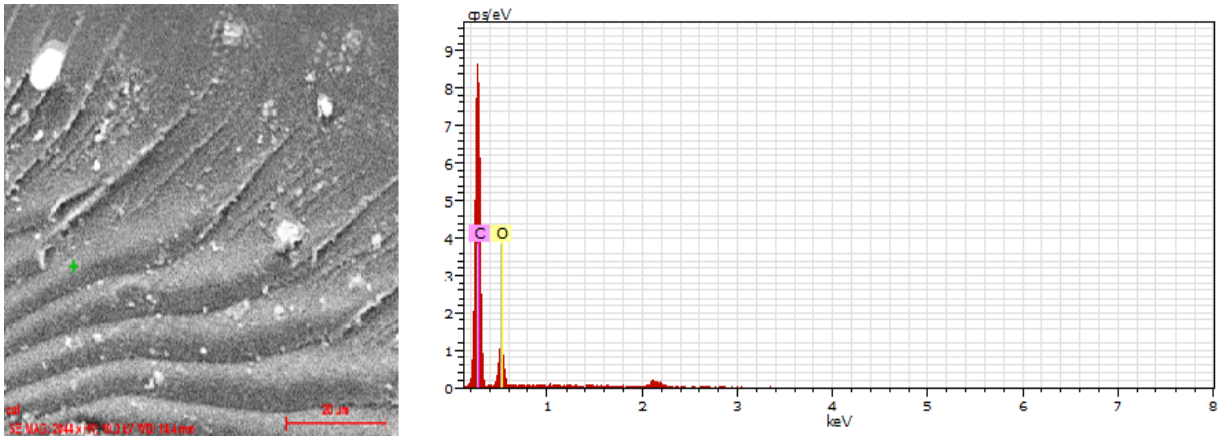

Figure 2. (a) EDX image and (b) chemical composition of *Cocos nucifera* shell filler of CNSP/VE composite specimens.

Mechanical properties

Tensile strength

Tensile strengths *versus* different wt.% of CNSP filler in VE resin are shown in Figure 3. The tensile strength of pure vinyl ester resin exhibited 27.6 MPa. By adding 5 wt.% of CNSP filler content into VE resin, the tensile strength became 28.7 MPa, which was more than the pure vinyl ester resin. The percentage of improvement between the pure resin and 5 wt.% CNSP/VE specimen was 3.83%. It showed that less filler was added to the VE resin. This minimum weight percentages of the filler caused a less interaction between the filler and the matrix, because the minimum amount of filler could not fully occupy the matrix in the entire mould [41,44]. The tensile strength of the composite specimen was increased by 22.22% from 5 to 10 wt.% CNSP/VE. The value of tensile strength increased up to 36.9 MPa at 10 wt%. This result showed that increment of filler in the composites made an enormous rise in tensile strength [26].

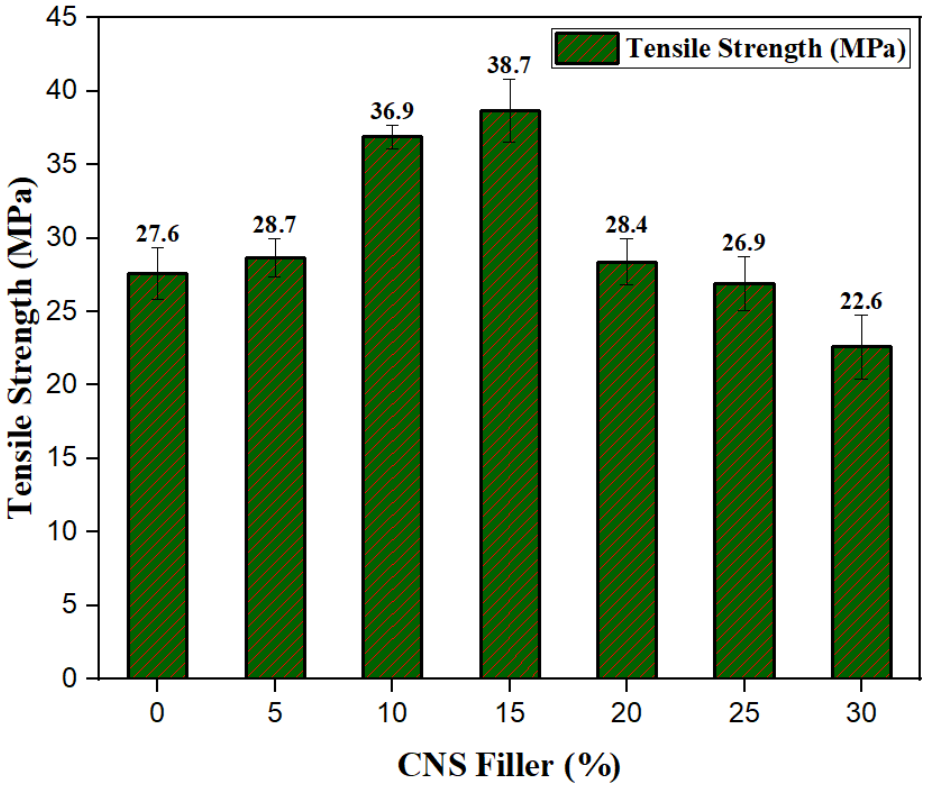

Figure 3. Effects of filler loadings on tensile strengths of the various CNSP/VE composite samples.

By adding 15 wt.% of the filler, the highest tensile strength of the composite was about 38.7 MPa, since the composite filler was equally distributed throughout the composite [20]. It can be evidently observed from the SEM images obtained, as later presented. Here, the improvement of strength from 0 to 15 wt.% was 28.68%. The tensile strength abruptly decreased up to 36.26% at 20 wt.% filler content. Similarly, the tensile strength further decreased at 25 and 30 wt.% of filler contents and their values were 26.9 and 22.6 MPa, respectively. By adding more wt.% of filler, it occupied much space in the mould, thus led to lower strength properties of the composites [26]. The tensile moduli *versus* different wt.% of CNSP filler in VE resin are shown in Figure 4.

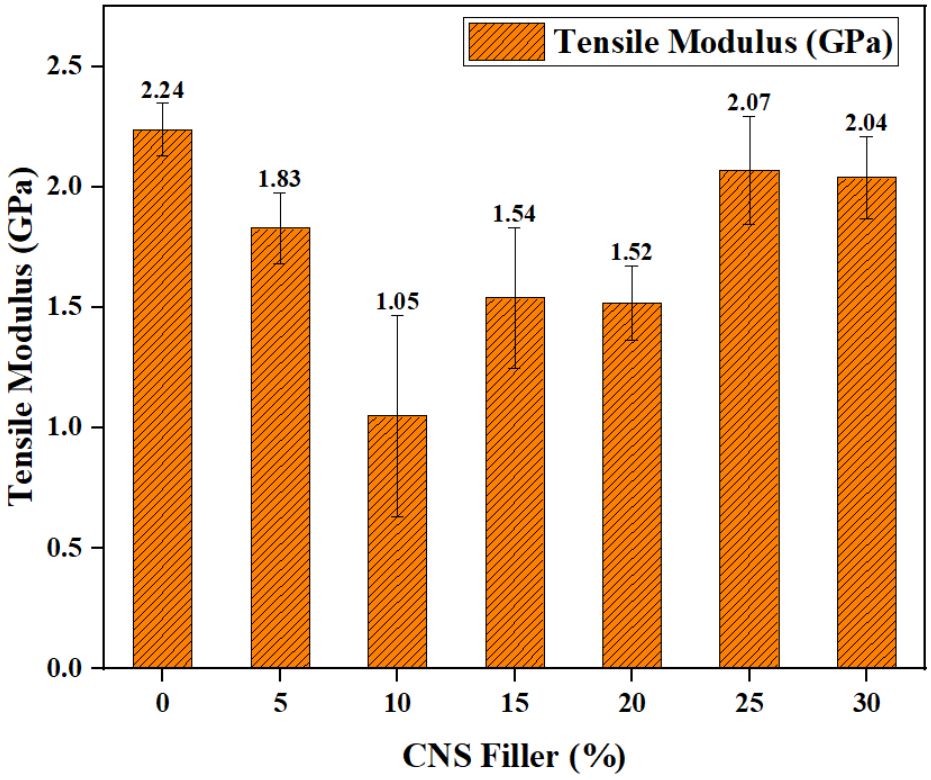

Figure 4. Effects of filler loadings on tensile moduli of the various CNSP/VE composite samples.

In addition, ultimate tensile modulus of 2.24 GPa was obtained with the pure resin composite plate and the corresponding percentage elongation at break was 1.23. The next highest value occured at 25 and 30 wt.% of filler contents and their tensile modulus values were 2.07 and 2.04 GPa, respectively. The corresponding percentages of elongation values were 1.03 and 1.11, respectively. An increase in filler percentage caused a decrease in elongation at break [26]. The minimum value of tensile modulus occured at 10 wt.% of filler content and the corresponding percentage of elongation at break was 3.35. It significantly showed that the tensile modulus was directly proportional to the elongation at break. When the elongation at break was minimum, the modulus value was maximum, *vice versa*. The elongation at break increased from pure resin to 10 wt.% CNSP/VE composites. The elongation at break suddenly decreased from 15 to 30 wt%, as CNSP was increased. The composite chain mobility caused composite failure after certain level of elongation [28]. The strain percentage

of 15 wt.% CNSP/VE composite specimen was 2.51%. The mechanical and thermal properties of CNSP/VE composites were compared with various natural filler reinforced VE polymer composites, as shown in Table 1. The fracture behavior of the tensile test recorded an optimum result with 15 wt.% of CNSP/VE composites. Analysis of the morphological changes in the 15 wt.% CNSP added before testing the specimen, was carried out by using SEM with different magnitudes.

Table 1.

Comparison of mechanical properties and HDT of wt.% CNSP/VE composites with various natural filler reinforced VE polymer composites.

Reinforcement	Tensile strength (MPa)	Flexural strength (MPa)	Impact strength (kJ/m^2)	Hardness	HDT (^oC)	References
5 - 30 wt.% of *Cocos nucifera* shell filler/VE composites.	22.60 - 38.70	46.15-105.13	15.84-33.04	20.00-29.67	160-171	Present work
5 - 50 wt.% of tamarind seed filler (TSF)/VE composites.	9.0-34.1	47-121	7-14	23.00-42.33	71	[19]
5 - 50 wt.% of date seed filler/VE composites.	40.30	149.00	17.03	51.00	84	[50]
5 – 50 wt.% of *Polyalthia longifolia* seed filler /VE composites.	9.0-32.5	44-125	10.00 - 31.09	23.00 - 36.50	53-66	[51]

Flexural strength

Flexural test results of pure VE and various weight percentages of filler loaded CNSP/VE composite are shown in Figure 5. CNSP/VE composite with highest flexural strength occurred with 15 wt%. The percentage improvement of 56.44% occured between the pure resin and 15

wt.% CNSP/VE composite specimen. The incremental strength can be attributed to the presence of good interfacial bonding between CNSP and VE resin [42]. The flexural strength of pure resin poorly increased by 2.07% with addition of 5% wt of filler content, because of the absence of filler over the entire composite and absence of effective stress transfer rate between the filler and the matrix [52]. There was an increase in flexural strength of 5 wt.% CNSP/VE composite specimen when it was increased to 10 wt%, varied from 46.75 to 86.15 MPa, respectively. The percentage increase between them was 45.73%, due to a better arrangement between 10 wt.% CNSP filler and VE matrix, when compared with 5 wt.% counterpart.

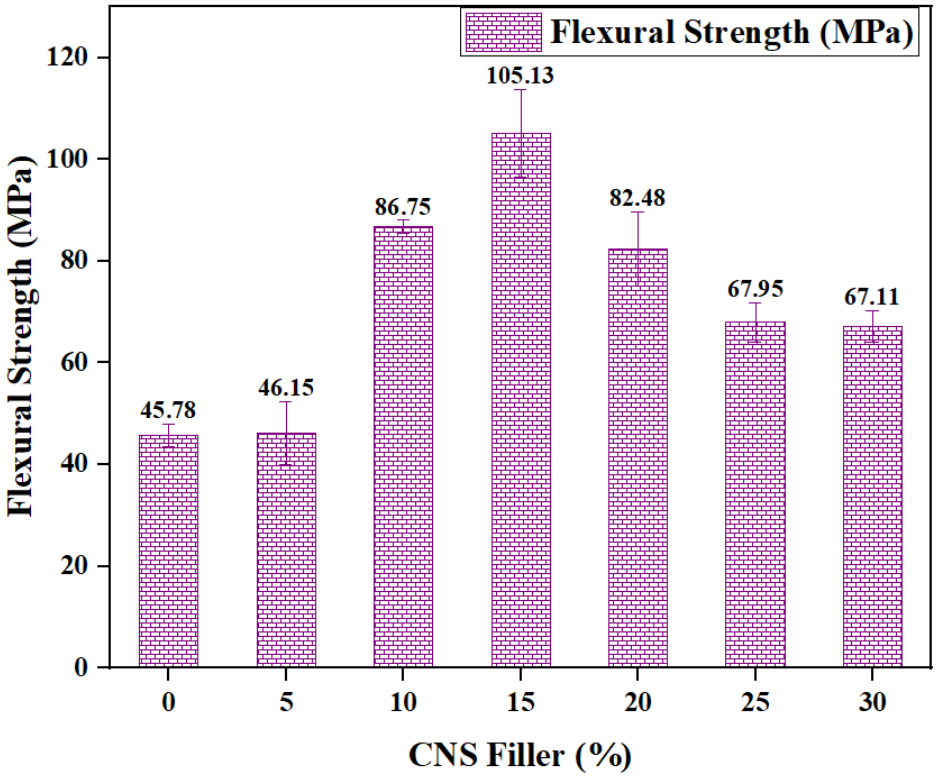

Figure 5. Effects of filler loadings on flexural strengths of the various CNSP/VE composite samples.

Besides, optimal flexural strength of the composite occurred at 15 wt.% filler and it produced nearly 105.13 MPa. The reason for obtaining optimal composite at 15 wt.% can be

attributed to uniform distribution of 15 wt.% CNSP filler and presence of better wettability of CNSP filler with VE resin, when compared with other filler loaded composites [19,20]. From 15 to 30 wt.% composites, low flexural strength was observed, because of the increase of filler loading in the mold. Since higher percentage of filler content fully occupied the composites. Hence, it produced coarse structured and rough composite. Also, it obstructed possible increase in flexural strength as well as created poor adhesion between CNSP filler and VE matrix [52]. The highest flexural modulus value of 6.87 GPa was obtained with 15 wt.% composite, as summarily shown in Figure 6.

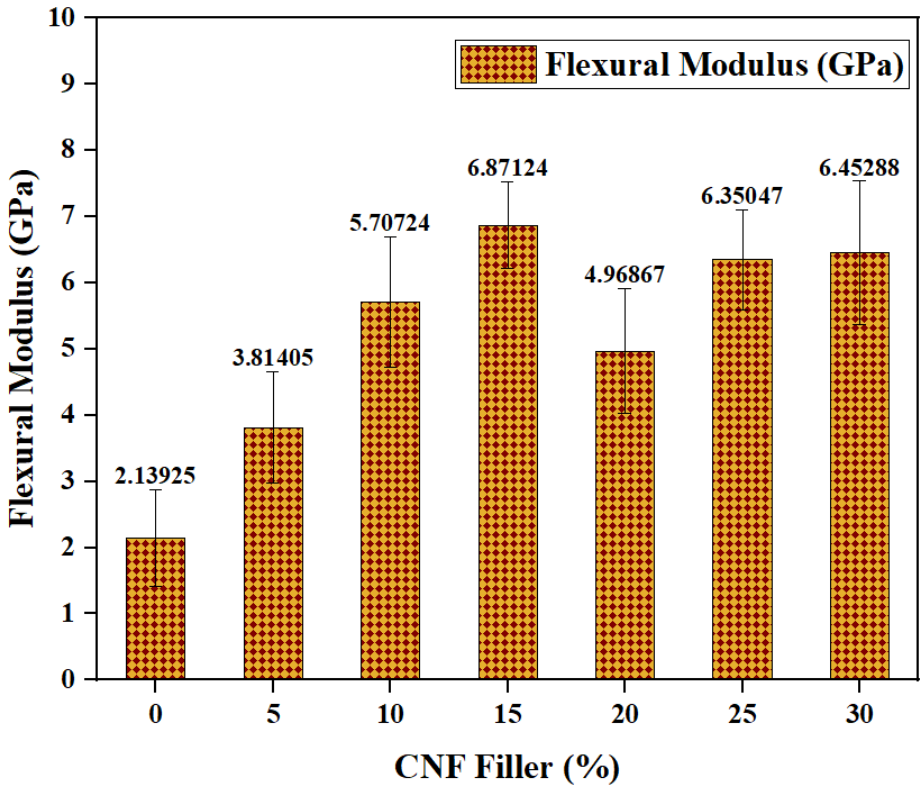

Figure 6. Effects of filler loadings on flexural moduli of the various CNSP/VE composite samples.

Impact strength

Impact strength values of the various CNSP/VE composite specimens with different filler loadings are shown in Figure 7. The impact energy of particulate composites mainly depend

on adhesion between their fillers and matrices [52]. For the pure resin, the impact energy observed was up to 19.5 kJ/m^2. 5 wt.% of CNSP produced an impact energy value of 20.380 kJ/m^2. The impact energy increased up to 2.64%, when 5 wt.% of CNSP filler was added to the pure resin. Initially, a very poor dispersion of CNSP filler within the matrix did not exhibit a significant difference in their impact properties [19, 20]. When 10 and 15 wt.% CNSP fillers were added, the corresponding or respective values of impact strengths were 30.13 and 33.04 kJ/m^2.

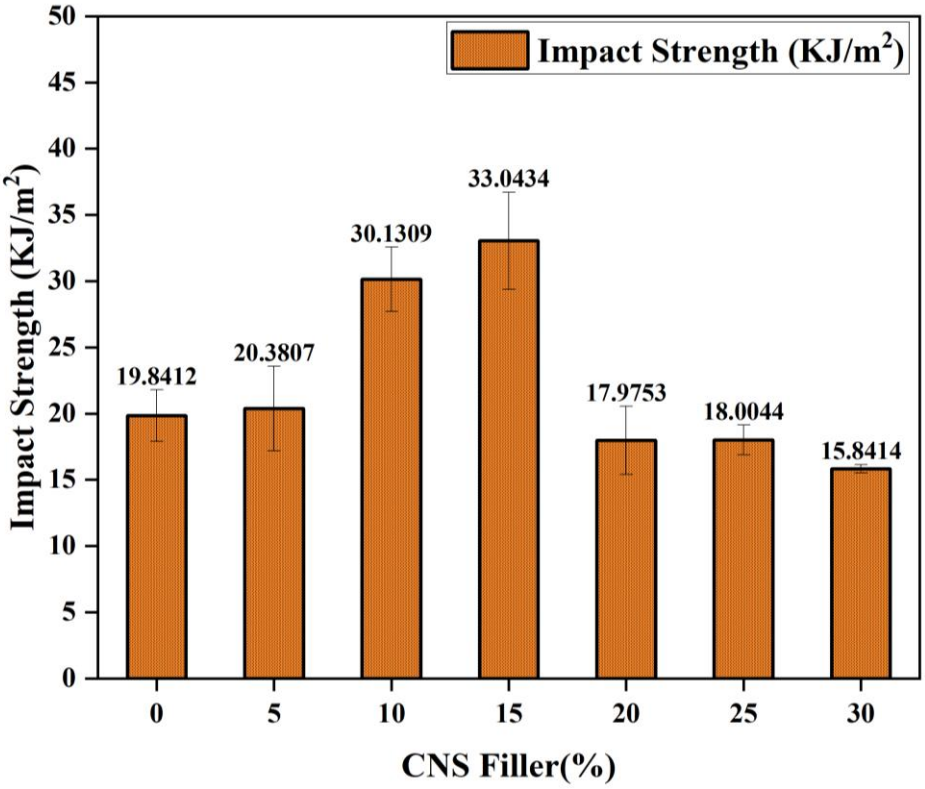

Figure 7. Effects of filler loadings on impact strengths of the various CNSP/VE composite samples.

Moreover, 15 wt.% CNSP filler reinforced composites provided 39.95% increase in impact strength, when compared with pure resin. Similarly, from 5 to 15 wt%, the value was 38.31%. It was evidently shown that the filler accommodated matrix vigorously, when it was added and fine structure of the fillers possessed better wettability. In addition, the matrix provided good bonding, which supported more stress transfer between the matrix and the filler [20, 52].

Therefore, the 15 wt.% absorbed more energy and this caused the recorded increment of impact strength of the speciment. By adding more fillers to the composites with various compositions of 20, 25 and 30 wt%, the corresponding impact energies of the materials were 17.97, 18.00 and 15.84 kJ/m^2. These values showed that the energy gradually decreased, because addition of fillers reduced the absorbing characteristics and subsequenty, the binding between the matrix and the filler was decreased or very low [36]. When compared with both 15 and 30 wt%, the energy was reduced to 52.05%. Evidently, optimal impact strength was obtained with 15 wt.% CNSP/VE composite specimen.

Barcol hardness properties

Barcol hardness values were taken from three different spots of each of the specimens, before their average results were obtained. The Barcol hardness values of the pure VE resin and various CNSP/VE composites are shown in Figure 8. It was observed that the hardness value of the pure resin was 19.67. When 30 wt.% of CNSP filler was added, the hardness value slightly increased to 20. Significantly, the pure VE resin and 30 wt.% filler reinforced composite exhibited approximately the same lowest Barcol hardness value of 20, because of their compositions. This implied that addition of 30 wt.% of the filler created improper bonding, due to insufficient matrix. It also increased the flexibility of the composites and hence, the Barcol hardness number was reduced [52]. At 5 wt.% of filler content, the hardness increased by 15.68% and the corresponding value was 23.33. The 5 wt% filler reinforced composites consisted voids and improper wetting, which also reduced their Barcol hardness number [52]. When 10 wt.% filler was added, the value slightly decreased by 2.9%. When compared these two hardness values, 5 wt.% CNSP/VE composite has less demobilizing effect than 10 wt.% CNSP/VE counterpart [17]. This denoted that the distribution of filler was very low, since the percentage of filler content was minimum and the strength of the matrix was very high.

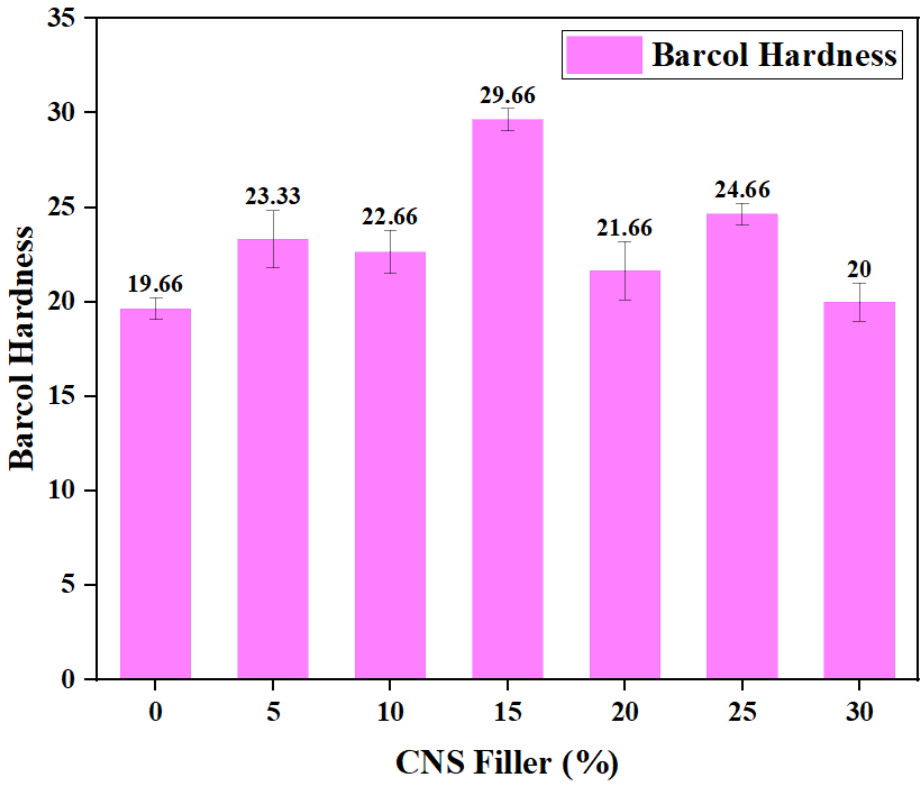

Figure 8. Effects of filler loadings on Barcol hardness of the various CNSP/VE composite samples.

Furthermore, at 15 wt.% of filler content, the value of the hardness was 29.67 and the increased percentage was 23.59% from 10 to 15 wt%. From pure resin to 15 wt.% CNSP/VE composite, the increase was 33.70%. For the increment from 5 to 15 wt.% filler in CNSP/VE composite, the hardness value was 21.36%. These values vividly showed that hardness increased with an increase in filler content. The filler was uniformly distributed, because it was mixed in a proper proportion. When sufficient filler was loaded, it provided good bonding between matrix and filler [36]. Proper distribution of filler on the entire composites occurred at 15 wt.% CNSP/VE composite and it exhibited an optimal or best hardness value, among other various wt.% CNSP filler reinforced VE composites. When 20, 25 and 30 wt.% of fillers were loaded, they provided hardness values of 21.67, 24.67 and 20, respectively.

SEM analysis - Fracture behaviors

SEM images of fractured surfaces of 15 wt.% CNSP/VE composites; optimum specimens were taken at higher and lower magnitudes, before and after their mechanical tests. With these specimens, filler was distributed evenly. Figure 9(a) shows smooth surfaces of the composites and their proper filler distribution. The average size of CNSP of nearly 2.3- 2.5 µm was obtained from Figure 9(b). Figures 10(a) and (b) illustrate 15 wt.% of tensile test fractured specimen of CNSP/VE composites. Figure 10(a) presents wavy pattern on their tensile fractured surface. The wavy pattern was formed by the distributed filler, which discontinued the resistance and formed crests and troughs on the fractured specimen [35]. Figure 10(b) depicts that the filler stopped fast propagation of cracks. Hence, the filler material was removed, due to the applied load.

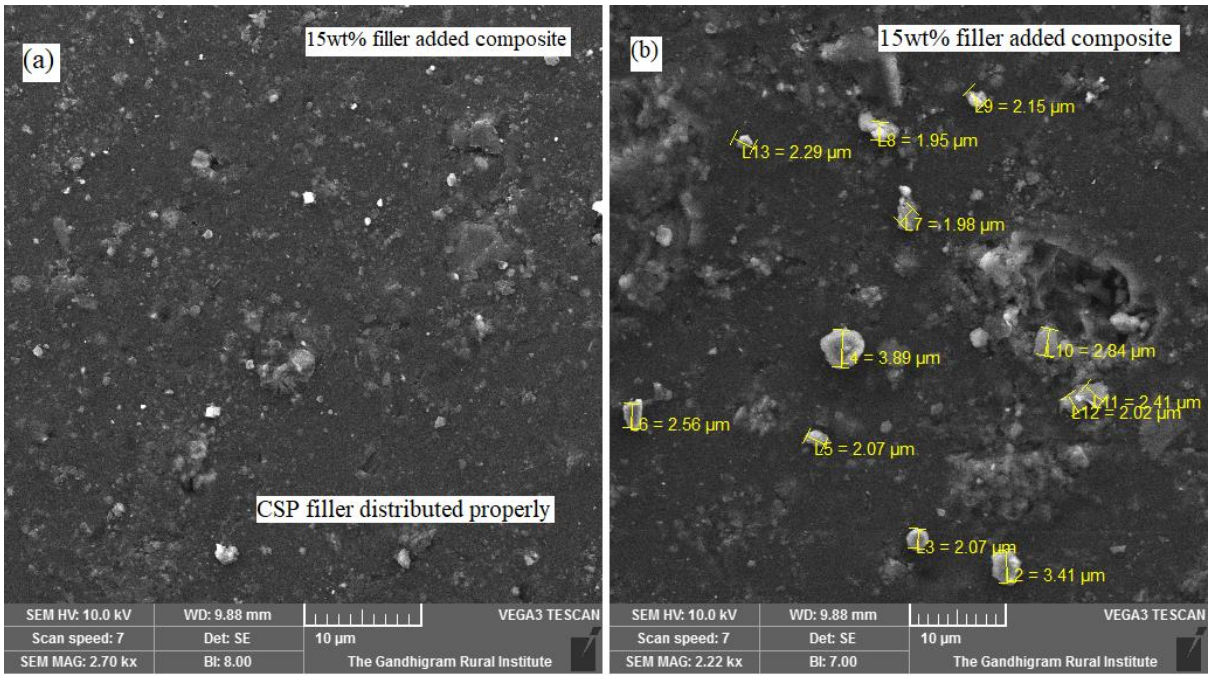

Figure 9. (a) Proper/uniform filler distribution occurred within 15 wt.% CNSP/VE composites and (b) different CNSP filler sizes, measured in micron (µm) on 15 wt.% CNSP/VE composites.

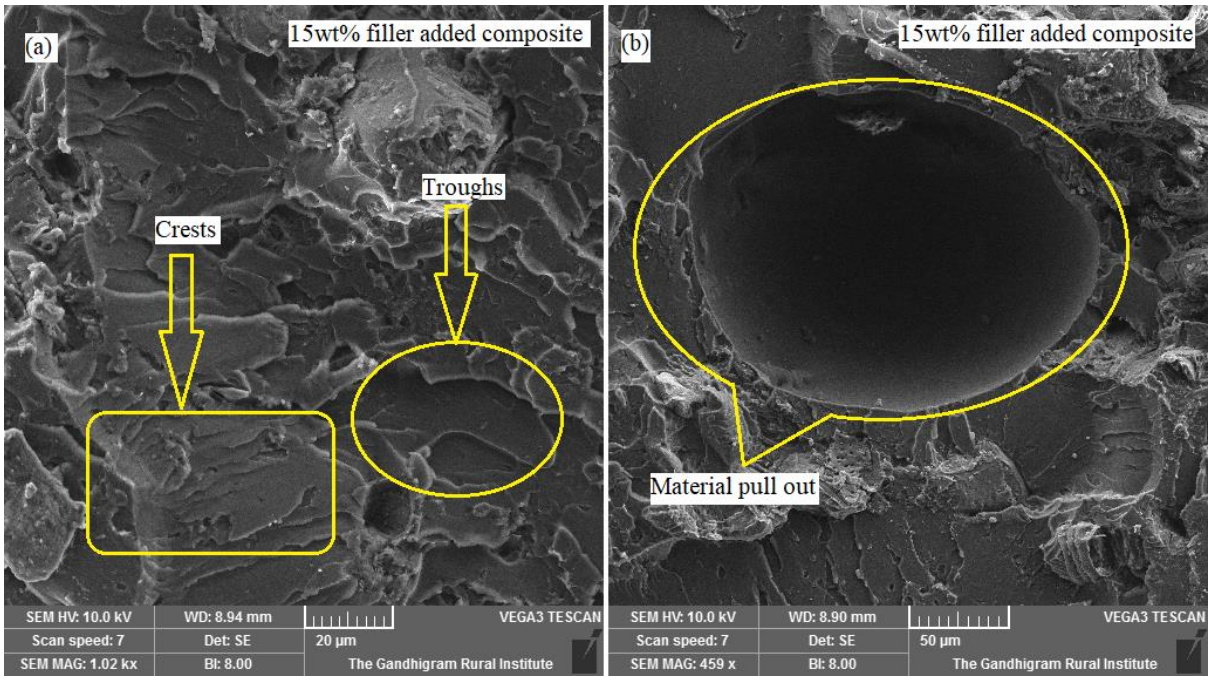

Figure 10. (a) Crests and troughs observed from 15 wt.% CNSP/VE composites and (b) large hole created by CNSP filler/material pull-out on 15 wt.% CNSP/VE composites, after tensile test.

Additionally, Figure 11(a) evidently shows the flexural fractured surface. It depicts that plastic deformation of the matrix occurred, which caused formation of striations, as observed on their fractured surfaces. In this region, the deformation of the resin was clear. The filler was not clearly visible [35]. Figure 11(b) shows the wavy nature of the surface formed by means of breaking, due to the strong adhesion present between the filler and the matrix. It also produced crests and troughs on the entire region. Figures 12(a) and (b) depict the fractured surfaces of the impacted specimen. Figure 12(a) shows the evidence of rich resin zone at a certain region. Small holes, crests and troughs were observed, as depicted in Figure 12(b). These damage responses were attributed to sudden filler material removal under the applied load [35].

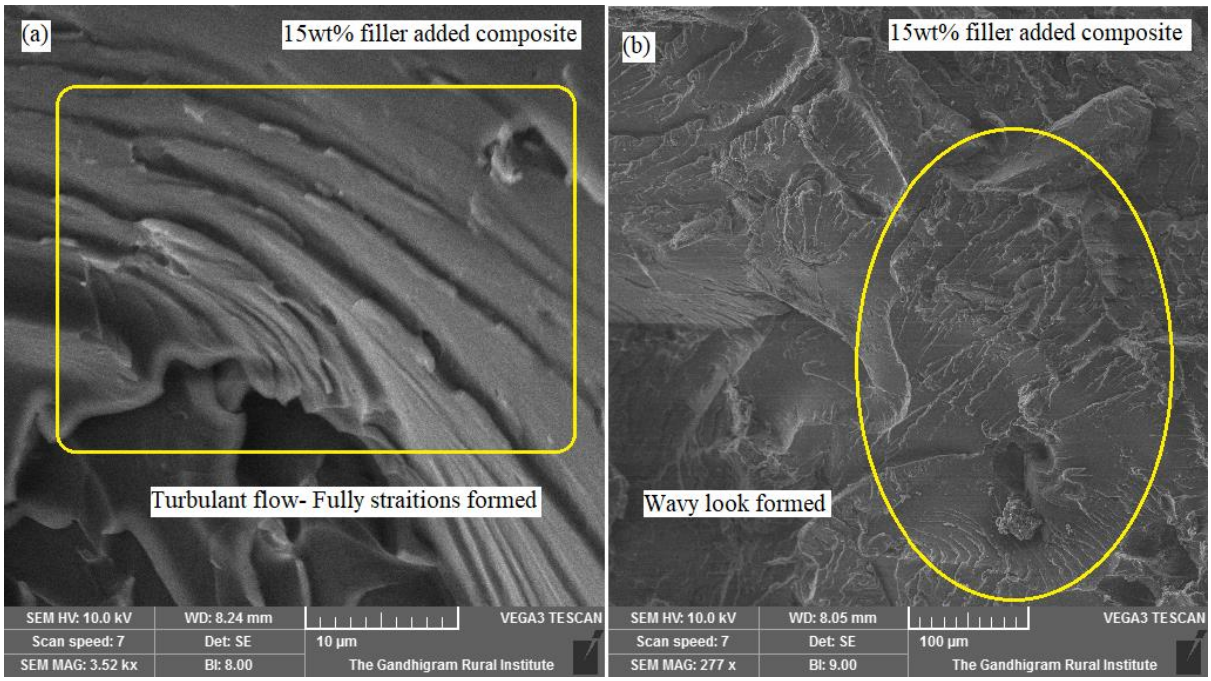

Figure 11. (a) Fully striations formed by a unsteady flow pattern during flexural test and (b) wavy nature of the flexural fractured specimen observed from 15 wt.% CNSP/VE composites.

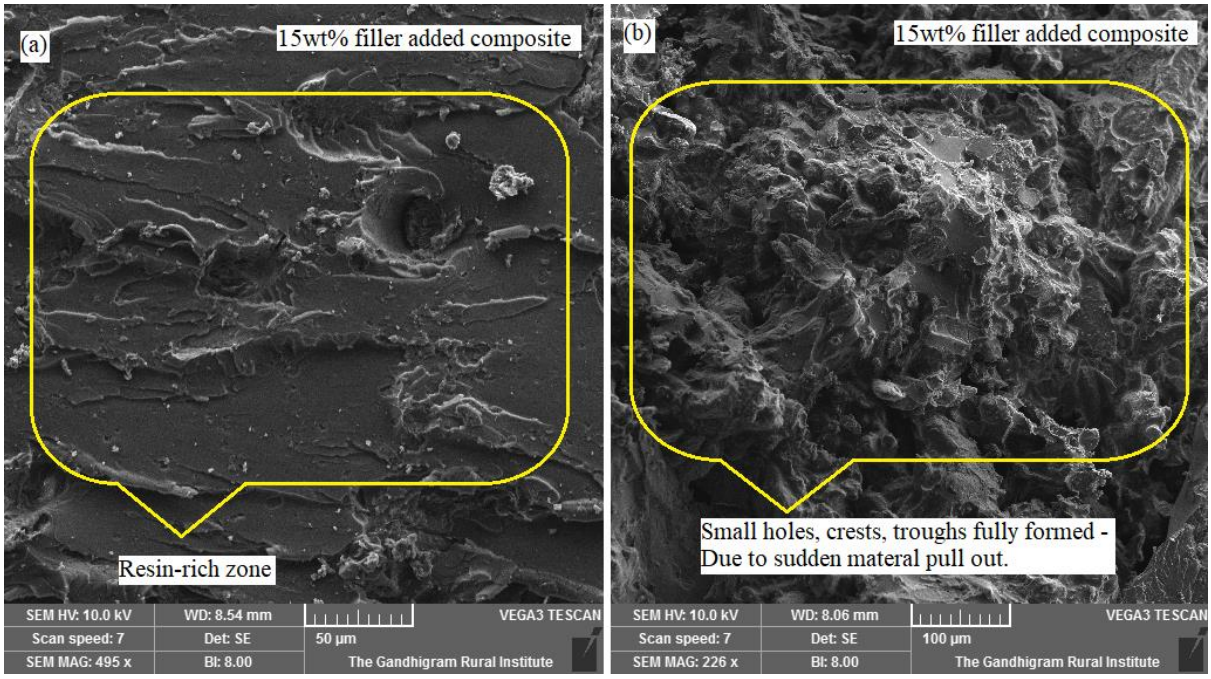

Figure 12. (a) The resin-rich zones, as showed on 15 wt.% CNSP/VE composites and (b) small holes, crests and troughs formed, due to sudden CNSP filler/material pull-out, after impact test.

Thermal properties - HDT

HDT is the temperature at which a polymer deforms under a particular load. The HDT of the pure resin and CNSP/VE composites with different weight percentages are shown in Figure 13. The results showed that pure resin has HDT value of 158 ^{o}C. The addition of filler contents by different weight percentages gradually increased HDT values. Importantly, the average HDT value of 15 wt.% CNSP/VE composites was 165.5 ^{o}C, considering from 5 to 30 wt.% filler contents. This value was more than twice that of TSF/VE composites and other similar composites, as previously presented in Table 1. The increased manner of HDT value clearly implied that it increased with addition of filler content. It was understood that more addition of CNSP filler withstood temperature up to 171 ^{o}C at 30 wt%. These results evidently established that CNSP filler has better thermal characteristics, among various natural fillers.

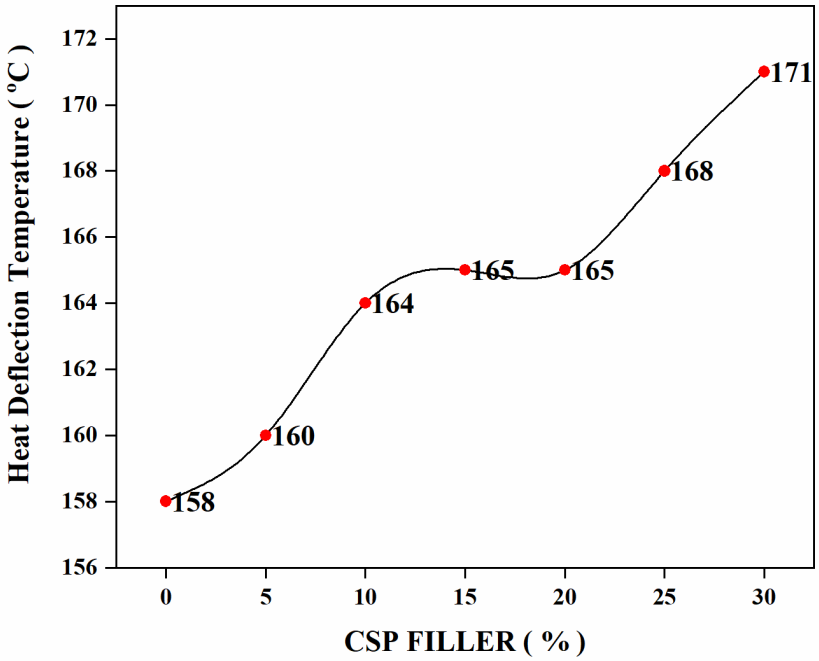

Figure 13. Effects of filler loadings on HDT of the various CNSP/VE composite samples.

Swelling behaviors - Water absorbtion properties

Water absorption behaviors were experimented for various aqueous conditions: normal, salt, cold and hot water. The values of absorption behaviors of the four different conditions are shown in Figure 14. From Figure 14, it was understood that with 0 wt.% (neat VE resin), there was no response, because of its hydrophobic nature. Whereas, water absorption was more in all conditions at 5 wt%, due to the presence of higher microvoids in 5 wt.% CNSP/VE composite specimens, which accommodated more water. From 10 to 20 wt%, the water absorption behaviors decreased, because CNSP filler percentage increased and hence, the presence of voids was very less. It showed that absorption behaviors decreased with increase of CNSP fillers, due to dense microstructure with few pores and gaps up to 20 wt%.

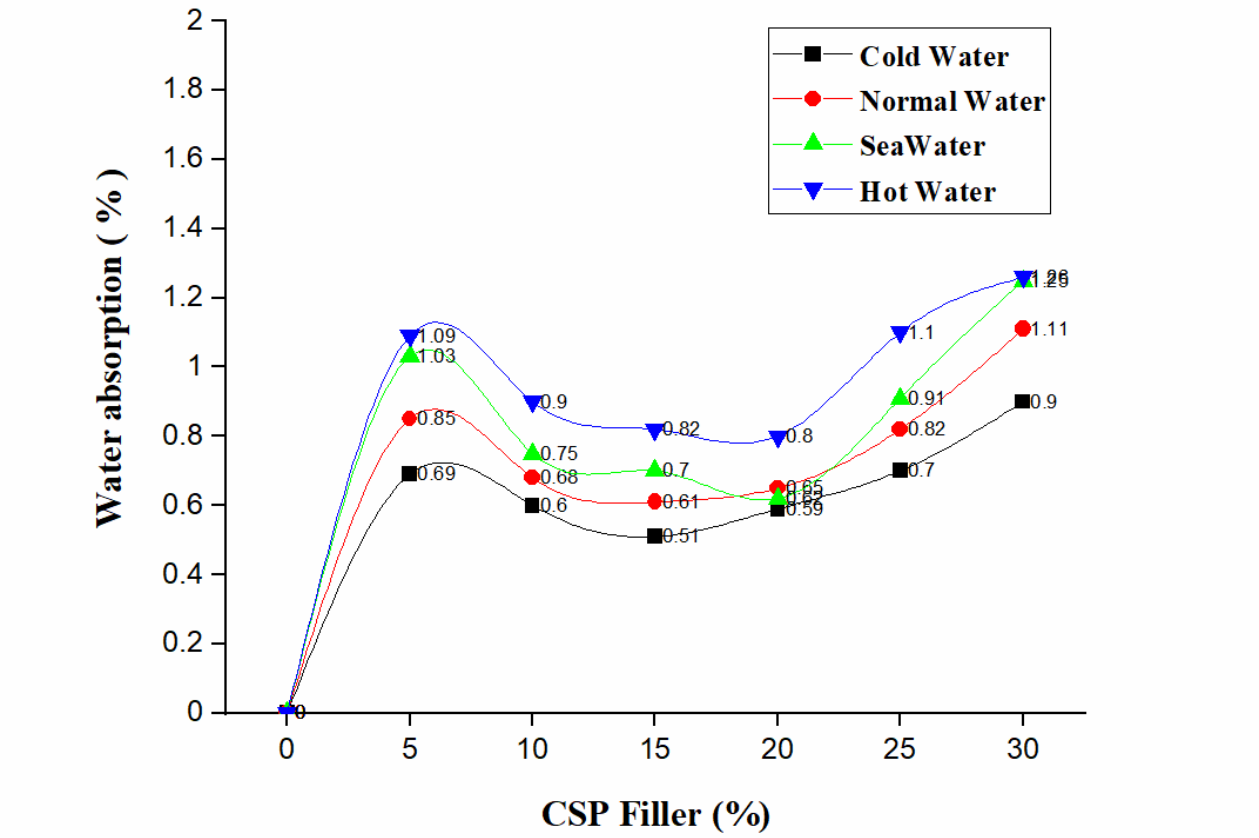

Figure 14. Effects of filler loadings on water absorption behaviors of the various CNSP/VE composite samples under different aqueous conditions.

After increasing CNSP particles to 25 and 30 wt%, the absorption behaviors increased. This can be attributed to remarkable water absorption of natural filler polymer composites [43]. With cold water condition, absorption behaviors were lowest when compared with other three conditions. This was because CNSP filler and VE resin structured could not absorb cold water. Usually, cold water is not suitable for plants as well as its fiber components, as naturally evident during winter season. Normal water absorption percentages were lower when compared with both hot and sea water, but they were higher than that of cold water. This can be attributed to the lower salt content present in normal water when specially compared with sea water.

During sea water condition, the water absorption behaviors of various CNSP filler reinforced VE composite specimens were higher than that of normal water, because of more salt content in sea water. Hot water absorption percentages were highest, when compared with other three different aqueous or water conditions. Since heat was applied on the composite specimens, more micro voids were formed on the various CNSP/VE composite specimens and more water was absorbed during immersion. The highest kinetic energy gained by molecules of hot water also supported its fast penetration into the CNSP filler. Consequently, it produced highest water absoption percentages at all various wt.% CNSP filler contents. Hence, weakest filler-matrix interfacial adhesion would be probably obtained with hot water condition [51].

Conclusions

Study on compression molded CNSP/VE composite specimens with different weight percentages of filler loadings has been elucidated. The most dominant elements in CNSP filler were 24.02 and 75.98 wt.% of oxygen and carbon respectively, as obtained from the EDX analysis.

The maximum Barcol hardness, impact, tensile and flexural strengths were 29.67, 33.04 kJ/m^2, 38.70 and 105.13 MPa at 15 wt.% of CNSP filler content, which were comparatively

higher than a few similar composites available in literature. The highest HDT of CNSP/VE composite was achieved at 171 ^{o}C with 30 wt.% of filler content. These results were further confirmed, using SEM to examine the fractured surfaces of the specimens, after mechanical tests. Optimal mechanical properties including Barcol hardness, impact, tensile and flexural strengths of the specimens were obtained at 15 wt.% of filler content.

The response of the specimens to swelling behavior was highest in hot water condition, followed by salt, normal and lastly cold water conditions. Summarily, it was evident that optimum eco-friendly 15 wt.% CNSP/VE composite materials can be suitable for fabrication of domestic appliances, such as fan blades, cover/casings, panels, among other various applications by using compression molding technique.

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Conflicts of interest

The authors declare that they have no conflict of interest.

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