Effect of Synthesized Chitosan Flame Retardant On Flammability, Thermal, And Mechanical Properties of Vinyl Ester/Bamboo Nonwoven Fiber Composites

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Abstract

In this study, chitosan-based bio-flame retardant additive (referred to as NCS) was prepared by altering the chitosan (CS) chemically with silica (S) via ion interchange reaction and studied the effect on flame retardant, thermal and mechanical properties of vinyl ester/bamboo fiber (VE/BF) composites manufactured by the vacuum assisted resin transfer molding (VARTM) process. Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis used to characterize the NCS. The spectral results revealed a new peak at 1560 cm^{-1} corresponding to $\text{NH}_3^+ - \text{O Si}$, bring up the interactive bond between CS and S. SEM, and XRD showed the diverse morphology (coarse surface), and significant decrement in the intensity of diffraction patterns respectively support further the formation of NCS. The heat release rate of NCS decreased significantly by 76%, and residual char increased by 47% compared with chitosan. The flame retardant and thermal behavior of NCS-VE/BF composites were examined by UL-94 standards, micro and cone calorimeter and thermogravimetric analysis. The results showed a delay in burning time in UL-94, enhanced LOI % and decrement of peak heat release rate and total heat release rate compared to pure composites by 32, 14, and 18%, respectively. The residual char increased by 47%. The mechanical properties also improved satisfactorily. Overall, the synthesized NCS could be suitable for the fabrication of sustainable flame-retardant natural fiber composite without deterioration of mechanical properties that are suitable for sub-structural parts in engineering applications.

Introduction

Natural fibers (NFs), similar to a composite, with cellulose, hemicellulose, and lignin as reinforcements act as matrices structurally and present unique properties. Hence, NFs play a vital role in reinforcements for composites for engineering applications (Kuranchie et al. 2021). Automobile and aerospace industries have already started using NF composites for structural and substructural parts because of their low density, good mechanical strength, vibration absorption, and ultraviolet ray blocking (Kumar 2020; Lau et al. 2018). The advancements in NFs toward automobile application has been introduced in the driver and front passenger doors and the rear wing of the new 718 Cayman GT4 Clubsport production vehicles of Porsche's (bioconcept cars). These are formed of an NF composite from economic and energy perspectives (Porsche Newsroom 2019).

The NF cannot withstand fire and are thermally weak. However, although NFs have sufficient mechanical strength and are competitive with synthetic fibers, such as carbon and glass fibers, they cannot control the flammability properties of polymer composites as reinforcements (Elsabbagh et al. 2018). The incorporation of flame retardant (FR) additives are the most common approach for improving the flame retardancy of NF composites and various types of FR additives, including ammonium polyphosphate, magnesium hydroxide, zinc borate, and silicon dioxide, have already been studied (Shukor et al. 2014; Sain et al. 2004; Wu et al. 2020). However, their inclusion predominately interferes with the mechanical properties because of their lack of interfacial chemical bonding with both the matrix and reinforcement,

thereby creating stress concentration points. Hence, improving the fire resistance and strength maintenance are challenging tasks for researchers and industries for the usage of NF composites.

Recently, a few research studies have focused on modifying the chemical interaction of FR with either the NF reinforcement or matrix to enhance the flame resistance of NF composites without significantly affecting their mechanical properties (Khalili et al. 2017; Kim et al. 2020; Jeencham et al. 2014). Research is still required in this area due to the demand of the present market and the necessity to achieve desired properties effectively. Bio-FRs can serve this objective, consisting of biomass that provides dense char during combustion; hence they are drawn attention due to green sources and environmentally friendly characteristics compared with existing FRs showing health and environmental hazards, liberating corrosive gasses, etc [Costes et al. 2017]. However, Bio-FRs did not show high efficiency for polymers and need to be functionalized effectively by chemical modification. Moreover, the selection of a suitable bio-based material for flame retardancy and chemical modification is critical. A few biomaterials are available as waste that can enhance flame retardancy, e.g., chitosan, lignin, bone powder, oyster shell powder, and eggshell powder.

Among, chitosan is an exciting and abundant biowaste polymer that can be easily chemically modified by grafting copolymerization and compounding due to the chemical structure of an amino polysaccharide. The multi hydroxyl and amidogen groups present in chitosan promote flame retardancy behavior. In addition, chitosan has been used as a char-forming agent in intumescent systems. Recently, Prabhakar et al. used chitosan in a thermoplastic starch/flax fabric (TPS/FF) system and effectively improved its thermal and flame retardancy properties to reach those of commercial FRs with satisfactory improvements in its mechanical properties (Prabhakar and Song 2018). In their further studies, a novel FR compound produced by effective modification of chitosan with ammonium polyphosphate could significantly enhance the flame retardancy properties of NF composites (Prabhakar et al. 2019; Prabhakar and Song 2020; Shao et al. 2021). Different FRs are used for the modification of chitosan, as established in the literature (Li et al. 2020).

Silicon dioxide is an inorganic material with interesting properties such as low toxicity, good biocompatibility, high versatility, high surface area, uniform porosity, and remarkable chemical and thermal stability (Wang et al. 2020; Huang et al. 2019). In addition, silicon dioxide can act as an effective FR for polymer composites, by condensing the phase and forming an inorganic char, and for wood fiber polymer composites, decreasing the heat release rate (HRR) and total heat release rate (THR) (Pan et al. 2014). Therefore, silicon dioxide gained attention for commercial applications in civil engineering, construction, building, electrical, transportation, aerospace, defense, textile, and cosmetic industries (Hamdani et al. 2009). Moreover, silicon dioxide alone may be able to play a dual role of enhancing the mechanical and flame retardancy properties of NF composites.

Considering the above, this study focused on the preparation of a novel FR additive (referred to as NCS) by a simple chemical approach using chitosan and silicon dioxide. Although the combination of chitosan and silicon dioxide has been studied for other research areas, such as the removal of GO, there is no

information available on the synthesis of a chitosan-based silicon dioxide FR additive (NCS). Therefore, this study further investigated its effect on NF polymer (vinyl ester/bamboo fiber (VE/BF)) composites. The chemical features of the synthesized NCS compounds were characterized via scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), thermogravimetric analysis (TGA), and microcalorimetry. The flammability, thermal, and mechanical properties of the NCS additive-incorporated VE/BF composites were examined via horizontal burn test (HBT), cone calorimetry, TGA, XRD, FTIR, and universal testing machine (UTM). This study aims to introduce a chitosan-based FR additive in NF composites to support flame retardancy and mechanical strength.

Experimental Methods

2.1. Materials

The following chemicals were used in this study without any modifications: VE (viscosity 150 cps and specific gravity 1.03), methyl ethyl ketone peroxide (MEKP), cobalt naphthalate (CN), and Teflon sheets (CCP composites, Korea); bamboo nonwoven fabric (45.1 MPa, reinforced size: 200 × 200 × 0.39 mm (Sungchang Industries, Korea)). Chitosan (molecular weight ~ 600,000, viscosity 50–800 mPa, degree of deacetylation 80–95% (Kwang Jin Chemical Co. Ltd., South Korea); and silicon dioxide (extra pure) (Smachun Chemical Co., Korea).

2.2. Preparation of NCS

First, the required amount of chitosan flakes (10 w/v) was dispersed in 2% acetic acid solution with ultra-pure water under 500 rpm stirring conditions for 4 h at 60°C to obtain a homogenous chitosan solution. Subsequently, added the required amount of silicon dioxide solution (2.5 w/v) to the chitosan solution (equivalent to the molar ratios of SiO₂ in accordance with chitosan), and the stirring was continued at 500 rpm for an h at 80°C. The end of the reaction was determined by the formation of a yellowish-brown thick precipitate, and subsequently, cooled to room temperature and subjected to vacuum filtration. The obtained product was thoroughly washed with deionized water, dried overnight (~ 6 hrs.) in an oven at 70°C, and the obtained flakes finely ground into a powder using a ball mill.

2.3. Manufacture of NCS–VE/BF composites

The VARTM process was used to manufacture the NCS–VE/BF composites, as discussed by Chalapathi et al. (2020). Six bamboo nonwoven fabrics (200 × 200 × 0.39 mm) and 0.4-MPa vacuum pressure were used in the VARTM process. The infused wet composites were subjected to a pre-curing process at room temperature for 5 h, followed by post-curing at 60°C for 3 h in a composite curing oven (Fleta 5, LK LAB Co., Ltd, Republic of Korea). The overall preparation of NCS and the manufacturing process of the NCS–VE/BF composites are demonstrated comprehensively by schematic illustration, as depicted in Scheme 1.

2.4. Testing and Characterization

2.4.1. NCS characterization

The details of the characterization instruments adopted for analyzing the fabricated NCS compound are as follows: a scanning electron microscope with an ion sputter coater (Model: Emcrafts cube 2, EMCRAFTS Co., Korea) was used for microanalysis. A particle size analyzer (Model: Malvern Mastersizer) was used for particle size analysis. FTIR spectrometer (FT-IR-6300, United Kingdom) using the KBr disk method was employed for spectral analysis. X-ray diffractometer (Model: Bruker, D8 Discover) with Ni-filtered Cu Ka radiation at a speed of 50°C/min, current of 30 mA, and range of 0°–50° was used for XRD analysis. A particle size analyzer (Model: Mastersizer 2000, Malvern Panalytical Ltd., United Kingdom) was used to calculate the mean particle size and obtain the particle size distribution. An elemental analyzer (Variable EL, Analyzensusysteme GmbH Co., Ltd., Germany) was employed for detecting the elements. A thermogravimetric analyzer (Model: TGA Q600, TA instruments) was used at a heating rate of 20°C/min under an inert atmosphere with a temperature range of 30°C–700°C for thermal analysis. A microcalorimeter test apparatus (Model: Micro Calorimeter (Federal Aviation Administration, Fire Testing Technology (FTT), United Kingdom)) was utilized to calculate the heat release and THR rates as per ASTM D 7309 standards.

2.4.2. NCS–VE/BF composites characterization

The details of the testing instruments for analyzing the fabricated NCS–VE/BF composites are as follows: a universal testing machine (Model: R&R, Inc., Korea) was used for conducting tensile (250 × 25 × 3 mm) and flexural (support span 64 mm (16 times the thickness)) tests according to ASTM D638 and ASTM D 790-03 standards, respectively. An Izod impact instrument (QC-639F, Cometech Testing Machine Co., Ltd., China) with an 11-J impact hammer was used for conducting impact tests. A cone calorimeter (Fire Testing Technology, United Kingdom) was employed according to ASTM E 1354/ISO 5660 standard (100 × 100 × 3 mm) at 50 kW/m² to obtain, the external heat flux for examining the flammability and smoke properties.

Results And Discussion

3.1. Experimental results for NCS

3.1.1. Spectral analysis

The spectral peaks of NCS and the related raw materials, chitosan and silicon dioxide additives, are shown in Fig. 1. In the chitosan spectrum, the spectral peaks appear at 3500–3300, 1620, 1430, 1378, 1160, 1079, and 1032 cm⁻¹, corresponding to -OH and -NH₂, C = O, O–H, C–N(amide), C–O (bridge oxygen), (C–O–C assym), and (C–O–C sym) (Lustriane et al. 2018). Besides the silicon dioxide spectrum, the peaks appearing at 1051 and 781 and 1600–1700 cm⁻¹ correspond to the bending vibrations of Si–O and –OH, respectively. In contrast, the synthesized NCS compound exhibits the spectral peaks of both raw compounds, chitosan, and silicon dioxide, at 3427 and 1079, 776, and 683 cm⁻¹. Most importantly,

new peaks appeared at 1628 and 1560 cm^{-1} , suggested a chemical bond may be formed between chitosan and silicon dioxide by $\text{NH}_3^+-\text{O Si}$ (Hassan et al. 2019; Budnyak et al. 2014). It is evident that the spectral peaks disappeared at 891 and 762 cm^{-1} , revealing a combined interaction of silica and chitosan (Yeh et al. 2007). In addition, the broad peaks of chitosan at 2917 and 2849 cm^{-1} become sharp, and at 1382 cm^{-1} shifts to 1406 cm^{-1} . Notably, the intense bond at 1079 cm^{-1} may be associated with Si-O-Si and Si-O-C , suggesting interaction bond formation. Overall, the FTIR spectrum suggested the ion exchange reaction between chitosan and silicon dioxide to form NCS compound and further strengthened by XRD and SEM analysis discussed in the following sections.

3.1.2. XRD analysis

The XRD patterns of NCS and the corresponding raw materials chitosan and silicon dioxide are shown in Fig. 2(A). Silicon dioxide exhibits well-defined sharp diffraction peaks at 20.8° , 26.6° , 36.5° , 42.4° , 45.5° , and 49.9° , clearly indicating a crystalline structure (Kumar and Koh 2012). Chitosan presented typical semi-crystalline peaks at approximately 10° and 20° (Zang, Yan, Shen, Fang, Zhang, Wang, & Zhang, 2014). Conversely, the NCS compound totally diverse from CS and exhibited sharp crystalline diffraction peaks at 20.8 , 26.6 , 36.5 , 39.4 , 40.2 , 42.4 , and 45.8° , almost similar to silicon dioxide. Moreover, the intensities of the main two peaks of silicon dioxide at 20.8° and 26.6° are having 20978 and 106065, which are drastically decreased in the NCS compound to 16345 and 66383. Further, the calculated crystalline diameter (inserted table in Fig. 2(A)) of NCS showed 47 nm, but CS and SiO_2 having 2.27 and 55.75 nm, respectively. Overall, the obtained diffraction patterns of NCS may conclude the structure difference by the chemical reaction between CS and S to form the NCS compound.

3.1.3. Microanalysis

Micro images of NCS and the corresponding raw materials chitosan and silicon dioxide additives are shown in Fig. 2(B). Silicon dioxide particles showed smooth metallic surface morphology without any voids. The particles varied the size, majorly two types of particle sizes are observed in the micrograph, i.e., $\sim 2\text{--}10\text{ }\mu\text{m}$ and $\sim 10\text{--}20\text{ }\mu\text{m}$. Chitosan exhibited a rough and continuous morphology without voids. However, in NCS, the micrograph showed an entirely different morphology than CS, and S compound confirms the reaction between them. The shape of the particles seems slightly in between the trend of CS and S, but the course surface with continuous morphology without voids could be observed. In addition, $2\text{--}5\text{ }\mu\text{m}$ sized particles are stick to the surfaces of larger-sized particles and form lumps in between them. The NCS particles are also of two types of sizes, similar to silicon dioxide particles. In conclusion, the morphology of NCS showed a clear difference in morphology than CS and S might help to understand further and support the aforementioned FTIR and XRD analysis.

3.1.4. Particle size analysis

The particle size distribution of the NCS additive is shown in Fig. 2(C). Two average particle sizes of NCS were approximately 100 and $1000\text{ }\mu\text{m}$, with volume percentages of 2 and 24, respectively. The mechano ball mill process interestingly produced a precise NCS particle size of about $1258\text{ }\mu\text{m}$ at 22% volume.

3.1.5. Elemental analysis

The composition of chitosan and the NCS compound elements include carbon, hydrogen, nitrogen, and sulfur, tabulated in Fig. 2(D). From the table, chitosan has the main elements of C, H, and N with 42%, 6.88%, and 8.17% content, respectively. Besides, the synthesized NCS compound showed similar to chitosan elements, i.e., C, H, and N; however, a significant reduction could be observed in the values, 22.33%, 5.12%, and 3.38%, respectively. In addition, 0.46% of silicon element can be seen in the table representing silicon moiety obtained by the chemical reaction with SiO_2 . Hence, the elemental analysis further strengthens the spectral and diffraction analysis to form the NCS compound.

3.1.6. Thermal analysis

The thermograms of chitosan and NCS additive are shown in Fig. 3(A). Chitosan exhibited a two-step degradation process in the thermogram; the initial step at $< 100^\circ\text{C}$ was due to the exclusion of the absorbed water. The prominent pyrolytic degradation of the chitosan molecule was observed at 350°C and continued to 700°C owing to dehydration of saccharide rings and decomposition of the acetylate and deacetylate units. The multihydroxyl group present in chitosan formed a dense char of almost 30% at 700°C . Besides, the NCS compound showed a very different trend in thermograms, and the thermal degradation progressed as a single-step process. Initial decomposition temperatures at around 100°C maintained constant weight without degradation, and the weight loss occurred after 100°C , and the degradation proceeded with a marginal decrement in the weight loss. The maximum degradation occurred above 300°C with weight loss of around 20%; in chitosan, the % was almost 60, which clearly refers to the significant slowdown of the thermal degradation process due to the synergistic effect of the silicon and chitosan. It may be understood, in the thermal degradation process, the silicon moiety present in the NCS protects the material from thermal degradation. In addition, NCS produced nearly 56% char residue at 700°C showing substantial thermal stability. The chitosan and silica moieties present in NCS probably produce a carbonaceous and silica-based char residue.

The oxidative thermal degradation of NCS is shown in Fig. 3(A₁). As can be observed from the figure, the thermal oxidation of NCS occurs in two steps in the $30\text{--}400^\circ\text{C}$ temperature range. Almost 20% of weight loss occurred at initial degradation temperature $> 240^\circ\text{C}$ without decline so drastic. After that, a drastic thermal degradation occurred, directly resembling chitosan in the nitrogen atmosphere, which refers to the degradation of saccharide rings. However, after 400°C , the slowdown of thermal degradation could be seen; almost 15% of weight loss occurred until 580°C . Interestingly even at elevated temperatures from 580 to 700°C around the thermal degradation stopped, no further weight loss occurred and formed almost 37% char residue showed significant thermal stability under air atmosphere.

3.1.7. HRR analysis

The HRR peaks of chitosan and the NCS additive are shown in Fig. 3(B). From the figure, it can be observed that both CS and NCS produced two pHRR peaks during the combustion analysis. Chitosan burned rapidly during microcalorimetry analysis refers to the sensitivity with the fire and produced the

highest pHRR with a value of 61.9 kW/g at 321°C. The second pHRR peak was also generated with the value of 18 kW/g at 538°C due to thermal stresses. Remarkably, NCS showed changed flammability behavior than CS. The synergistic effect of CS and SiO₂ effectively decreased by showing the pHRR value 14.9 kW/g, which refers to the severe decrement of pHRR about 75% compared with CS with an equal amount of flame retardant [Shao 2014]. Moreover, the delayed temperature of about 10°C could be observed for the generated pHRR peak, further supporting the flammability property of the NCS compound. Crack formation due to thermal stress also happened in NCS due to dense char, although it is almost 90 C later than CS. Overall, a significant improvement is achieved in the flammability property of the NCS compound owing to the production of the dense char from the synergistic effect of the silicon dioxide and chitosan moieties through the condensed phase.

3.2. Experimental results for NCS–VE/BF composites

3.2.1. Spectral (FTIR) analysis

A spectral (FTIR) analysis is performed to verify the interaction (chemical or physical) between NCS and the VE/BF composites. The spectral analysis data of VE/BF and various % of NCS–VE/BF composites are shown in Fig. 4(A) and **Supplementary section SI** Fig. 1. The VE/BF composite spectrum consists of the combined spectral peaks of VE and BF at 1713, 2920, and 1032 cm⁻¹ corresponding to the carboxyl group of ester, methyl groups (C–H), and glucopyranose rings (C–O). Notably, the spectral peak intensity at 1713 cm⁻¹ is increased, clearly signifying the presence and interaction of BF with VE (Sefadi and Luyt 2012). On the addition of the NCS additive to the VE/BF composites, no apparent chemical changes occur in the composites, as shown in the spectrum (Fig. 3B). The combined spectral peaks of VE and BF in the VE/BF composite persists in NCS-VE/BF composites. In fact, several apparent changes occurred in the spectrum of VE/BF composites after the addition of NCS. For instance, the disappearance of spectral peaks at 910 and 1644 cm⁻¹, the spectral peak at approximately 3400 cm⁻¹ corresponding to the –OH groups slightly shifted to higher wavenumbers with the percentage increase in NCS and the formation of a new peak at 797 cm⁻¹. Hence, these spectral alternations might be evidence for the interaction effect of NCS on the VE/BF composites.

3.2.2. XRD analysis

The XRD patterns of the VE/BF and NCS–VE/BF composites are shown in Fig. 4(B). The VE/BF composite shows a broad peak at approximately 19.9° with an intensity of 6215 counts. It suggests the non-crystallinity of the VE/BF composite with an amorphous structure. Whereas, the addition of the NCS additive significantly influences the structural behavior of the VE/BF composites. It can be observed that sharp XRD peaks appear at 20.8, 26.6 (predominate), 36.5, 39.4, and 42.4° for the 2 wt.% NCS-loaded VE/BF composite, which gradually becomes predominant with increasing percentage of NCS. These sharp peaks exhibit the induced effect of the NCS crystalline structure and the intensity of the peaks could be clearly observed in the figure at 6% NCS-VE/BF composite spectrum. The appearance of the NCS crystalline peaks also indicates that the powder particles are distributed homogeneously throughout the

VE/BF composite. Overall, the XRD results further strengthen the spectral analysis for the interaction of NCS with VE/BF composites.

3.2.3. Microanalysis

The surface and tensile fracture surfaces of the VE/BF and NCS–VE/BF composites were examined by microanalysis, and the micrographs are shown in Fig. 5. The surface SEM images clearly present the differences in the structural morphology of the VE/BF and NCS–VE/BF composites. The VE/BF composites are almost smooth, with some impurities are found to be present everywhere on the surface while cutting the specimen. In comparison, the surface of the 2 wt.% NCS-loaded VE/BF composites seems coarse, and some of NCS particles covered by the VE resin are observed on the surface. This rough behavior gradually predominates, and even the number of particles on the surface increases with increasing wt.% of NCS in VE/BF composites. Furthermore, the EDX and EDX mapping support the microanalysis by exhibiting additives and their distribution, as shown in Fig. 5. From the EDX graphs, the presence of 'silicon element in the NCS inclusion and its increment with increasing percentage can be observed, absent in those of the VE/BF composites. These observations strongly support the EDX mapping results shown in the figure.

3.2.4. Thermal analysis

The TGA curves of the VE/BF and NCS–VE/BF composites under pyrolytic and oxidative atmospheres are shown in Fig. 6 and important data is tabulated in **Table 1**. In the pyrolytic atmosphere, the trends of the thermograms are almost similar, with marginal differences in the initial degradation process. An approximately 1% weight loss occurs below 150°C, corresponding to the degradation of the sample by the evaporation of free water. The major degradation process under the effect of constituents (zeolites) present in the bamboo fibers, a slight degradation step observed at approximately 350–400°C, more predominant in the case of the VE/BF composites and marginal for the NCS–VE/BF composites. At the end of the maximum degradation process, the char's mass residue at 700°C for the VE/BF and 2, 4, and 6 wt.% NCS–VE/BF composites are 4.7, 6.8, 8.2, and 9.0% corresponding. Therefore, the introduction of NCS can accelerate the decomposition of the VE/BF composites by forming about 47% char residue compared with pure VE/BF that can suppress the release of combustible gases.

In the oxidative atmosphere, the trends of the thermograms are almost similar, and no apparent changes are observed between the VE/BF and NCS–VE/BF composites. However, the VE/BF composites (~ 350°C) start major degradation process slightly earlier than that of the NCS–VE/BF composites (~ 359°C). This behavior of the VE/BF composites progressively continues at the end of the maximum degradation. In addition, the inclusion of NCS shows an impact, even in small quantities, on maintaining a marginal dominance throughout the degradation process. The VE/BF composites completely combust without leaving any char residue at 700°C. However, in the case of a high percentage of NCS loading, the VE/BF composites are not combustible and left behind at approximately 1.5 wt.% stable residues indicating the enhancing thermal stability of the composites even under an oxidative atmosphere.

3.2.5. Flame retardancy

3.2.5.1. UL-94 (HBT and VBT) and LOI test

The horizontal burn time and rate data of the VE/BF and NCS–VE/BF composites obtained by the HBT test are tabulated in **Table 2**. The weak flammability properties of both VE and BFs induce rapid burning of the VE/BF composites with a burn time of 1.53 min. However, the burning time meaningfully increased with the incorporation of NCS into VE/BF composites. Addition of 2 wt.% NCS delays the burn time to 2.32 min, an approximately 34% delay compared to that of the VE/BF composites. This trend gradually increases for 4 and 6 wt.% NCS addition, with delays of 2.35 and 2.54 min, respectively, mainly due to the formation of the char residue, particularly the carbonaceous silicate char, which slow down the propagation of the fire and protected the underlying material (Shen et al. 2014). In addition, the inclusion of NCS into the composites effectively improved the modulus of the composites as discussed in Sect. 3.2.6. The high stiffness leads to heat resistance, which is one of the factors in the fire triangle, and hence, results in a low burning rate (Atta ur Rehman et al. 2018). Besides, the flammability ratings of NCS-VE/BF composites obtained by vertical burn test and LOI results are tabulated in Table 2. The incorporation of NCS could not make the VE/BF composites reach VB levels; all the composites burnt completely. However, as shown in (supplementary information) SI. Figure 1, the digital images during the vertical burn test exhibited the rate of burning time decreased after incorporation of NCS than VE/BF composites. In addition, the oxygen percentage decently increased with the increasing amount of NCS in VE/BF composites. The O₂ % reasonably increased for 2, 4, and 6% of NCS in VE/BF composites by 28, 31, and 33%, respectively.

3.2.5.2. Micro and cone calorimetry analysis

The microcalorimetry analysis was carried out to obtain the HRR and THR data for further understand the flammability behavior of the NCS–VE/BF composites. The HRR and THR data of the VE/BF and various NCS-loaded VE/BF composites are shown in Fig. 6(B) and tabulated in **Table 1**. It can be observed from the figure that the attained data are in agreement with the HBT results. The pHRRs of the VE/BF and 2–6% NCS–VE/BF composites are 422.7, 381.5, 373.6, and 361.9 W/g, respectively. The inclusion of NCS into the VE/BF composites significantly suppressed the pHRR by approximately 14%, and the reduction gradually continues with an increasing percentage of NCS. Correspondingly, the THR data follow the pHRR trend, showing values of 25.5, 24.7, 23.3, and 20.7 kJ/g for the VE/BF and 2–6% NCS–VE/BF composites. The inclusion of NCS lowers the THR by approximately 18%. In the same way, the fire growth index (FIGRA) (**Table 2**) indicated the growth profile respectively reduced by 28, 31, and 33% with the addition of 2, 4, and 6% of NCS to VE/BF composites. Besides, as shown in **SI** Fig. 2, the CO₂, CO and SPR of the NCS-VE/BF composites also reduced slightly around 20%. The reduction in the smoke production rate responsible for the condensed phase could be attributed to the control exerted on the VE/BF composites by the inclusion of NCS. (Song et al. 2014). Hence, the UL-94 test, LOI, micro and cone calorimeter results concluded that, the NCS additive can serve as a flame retardancy for natural fiber polymer composites by a condensed phase arising from carbonaceous char. The plausible flame retardant mechanism of NCS-VE/FF composite during the combustion process as shown in Scheme 2.

3.2.5.3. Char analysis

The SEM images of the residual char surfaces of VE/BF, 2%NCS-VE/BF, 4%NCS-VE/BF, and 6%NCS-VE/BF composites after horizontal burn test are shown in Fig. 7. It can be observed that the VE/BF composites showed a thin and loose flakes kind of brittle scarred char produced through quick evaporation of the condensed phase. As a result, the intensity of the fire propagation increased by allowing the two factors in the fire triangle, oxygen and heat. However, the introduction of NCS into VE/BF composites exhibited the dense and continual char formation, which may not allow flammable gases and resist the propagation of the combustion. The gradual improvement of the compact char formation could be observed with higher loadings of NCS additive. In addition, the SEM-EDX analysis presented the major elements present in the char residue of VE/BF and NCS-VE/BF composites. The VE/BF exhibited the major elements C and O refers the carbonaceous char. However, inclusion of NCS into VE/BF composites showed the Si element in the char along with C and O. The % of Si and O increased and decreased the % of C in the char residue in 4 and 6 wt.% of NCS-VE/BF composites which means the crystalline silica was presented in the char residue.

3.2.6. Mechanical performance

3.2.6.1. Tensile Properties

An evident increase in the tensile properties of the VE/BF composite was observed as a result of the NCS addition. The tensile test results are presented in Fig. 8 and **Table 3**, along with error bars. The tensile strength of VE/BF is enhanced by 29.5 % after the inclusion of 6% NCS. The tensile strength values of the composites are in the order of 6% NCS–VE/BF (36.24 MPa) > 2% NCS–VE/BF (30.73 MPa) > 4% NCS–VE/BF (30.42 MPa) > VE/BF (27.95 MPa). The inclusion of FR particles in BF-based polymer composites generally reduces their tensile strength and interfacial bonding due to the particles non compatibility with the fibers and polymers; this has been frequently reported in the literature (Fang et al. 2020; Liu et al. 2012). However, in this study, the NCS particles enhance the interfacial bonding of the BFs with VE, and hence, increase the tensile strength of the composites. This increase in the tensile strength supports -OH interactions between the NCS particles and VE/BF composites, as revealed in the FTIR analysis. These results also verify the fine dispersion of the NCS particles in the composites, as evident from the SEM images of the composite surfaces. The deposition of the NCS particles on the BF surfaces enhances the interfacial bonding with the VE matrix, which results in a reduced number of fiber pull-outs during the tensile fracture, as is evident from the SEM fractographs in Fig. 5. The decrease in the fiber pull-out spots in the NCS-filled VE/BF composites indicates enhanced interfacial bonding between the fibers and the matrix. The friction at the interfaces between the fibers and the matrix in the presence of NCS facilitates the transfer of load from the matrix to the fibers, thereby causing a dominant fiber breakout failure instead of fiber pull-outs.

The higher stiffness of the NCS particles compared to those of BFs and VE also shows its effect in the form of the higher tensile modulus of the NCS-filled VE/BF composites. The results indicate that the tensile modulus of the VE/BF composite increases after the incorporation of the NCS particles. The tensile moduli of the composites are in the order of 6% NCS–VE/BF (2.38 GPa) > 4% NCS–VE/BF (1.76

GPa) > 2% NCS–VE/BF (1.68 GPa) > VE/BF (1.57 GPa). The increase in the tensile modulus is as before attributed to the enhanced interfacial bonding between the fibers and the matrix in the presence of NCS particles. In the NCS-filled VE/BF composites, the load is largely transferred to the BFs, which has a higher tensile modulus than that of the VE matrix, causing the tensile moduli of these composites to increase. A similar trend is reported in the literature regarding the tensile moduli of other particulate-filled NF composite materials (Chee et al. 2021; Beigloo et al. 2020).

3.2.6.2. Flexural Properties

An increase in the flexural properties was observed after incorporating NCS particles into the VE/BF composite. The results of the three-point bending test are summarized in Fig. 8 and **Table 3**. The maximum flexural strength is observed after incorporating 4% NCS particles into the VE/BF composite. The increase in the flexural strength of the 4% NCS–VE/BF composite is 15.5 % of that of the VE/BF composite. The flexural strengths of the composites follow the order 4% NCS–VE/BF (135.9 MPa) > 2% NCS–VE/BF (122.89 MPa) > VE/BF (117.53 MPa) > 6% NCS–VE/BF (63.32 MPa). The same reason explains the increase in the flexural strength of the composites as that for the increase in the tensile strength. The compatibility of NCS particles, their interaction with BFs, and the fine distribution of the particles in the VE resin enhance the interfacial bonding between the resin and the reinforcement. The distribution of NCS particles in the VE/BF composite can be seen in the SEM images of composite surfaces in Fig. 4. The interaction of NCS with the VE/BF composite is explained based on the FTIR analysis results. A decrease in the flexural strength of the VE/BF composite is observed after NCS loading exceeds 4 wt%. The 6% NCS–VE/BF composite has the lowest flexural strength. The low flexural strength at a high loading of NCS particles in the VE/BF composite may be attributed to the agglomeration of the particles, causing a higher stress concentration.

The flexural modulus of the composites also increases after loading the NCS particles in the VE/BF composite. The 4 wt% NCS-incorporated VE/BF composite displays the highest flexural modulus, which is 2.33 times that of the basic VE/BF composite. The flexural modulus of the composites follow the order 4% NCS–VE/BF (18.01 GPa) > 2% NCS–VE/BF (14.68 GPa) > VE/BF (7.7 GPa) > 6% NCS–VE/BF (2.2 GPa). The increase in the flexural modulus of the VE/BF composite after the incorporation of NCS is attributed to the compatibility and enhanced interfacial bonding. The higher flexural and tensile moduli also ensure higher thermal stability of the VE/BF composites in the presence of NCS particles.

3.2.6.2. Impact Properties

The ability of the VE/BF composites to absorb energy before impact failure was observed to increase after the incorporation of NCS particles. The results of the Izod impact test are summarized in Fig. 8 and **Table 3**. The VE/BF composite with 4 wt% NCS particles absorbs the highest amount of energy in the impact test, which is 53% of that of the VE/BF composite. The composites absorb the impact energy in the following order: 4% NCS–VE/BF (0.0314 J/mm) > 2% NCS–VE/BF (0.0306 J/mm) > 6% NCS–VE/BF (0.026 J/mm) > VE/BF (0.0205 J/mm). The impact properties of the composites decrease after NCS loading exceeds 4 wt%. The 6% NCS–VE/BF composite absorbs lower impact energy than the other NCS-

filled VE/BF composites; may be due to the agglomeration of particles, which causes stress concentration, hence, rapid failure. The rigidity of the NCS particles as compared to the VE resin also enhances the impact properties of the VE/BF composites. A similar trend regarding the enhancement in the impact properties of NF-based polymer composites caused by FR particles is reported in the literature (Raghul et al. 2020; Bozkurt et al. 2017).

3.2.6.3. Fracture morphology

No noticeable changes were observed among the composites in the fracture micrographs, except for the resin's coarse surface responsible for the filler addition and the nonwoven fabric fracture behavior. The interfacial bonding between the fibers and the matrix was marginally weak, and few fiber pullouts were observed in the VE/BF composites. However, the filler-loaded resin improved the interfacial bonding in the composites and tightly adhered to the fibers. Thus, the fiber breakage is preponderated over the fiber and matrix interfacial failure described in the FTIR and mechanical section.

Conclusions

In this study, chitosan was successfully modified to a superior FR and thermally stable form (NCS) by a simple chemical method. Characterization techniques such as SEM, elemental analysis, FTIR, XRD, TGA, and microcalorimetry proved the chemical formation of NCS and its thermal and FR properties. NCS–VE/BF composites showed satisfactory flame retardancy and thermal stability compared to VE/BF composites: delay burn time of approximately 40%, enhanced LOI about 33% and HRR decrease of roughly 14%, and TGA data showed 9 wt.% at 700°C. Interestingly, incorporating the NCS additive significantly improved the tensile, flexural, and impact properties of the VE/BF composites. Furthermore, SEM analysis demonstrated a homogeneous distribution of the additives, which was the main factor responsible for changing the properties of the composites. In summary, the above results confirmed that NCS could be used as an FR in NFs composites with improved mechanical strength and thermal stability.

Declarations

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Ethics declarations

Conflict of interest

The authors declare no conflict of interest.

Animal Studies

The authors carried out no animal or human studies.

Consent to participate

All the authors give explicit consent to participate and submit the article.

Consent for publication

The authors obtained consent for publication from the responsible authorities at the institute where the work has been carried out.

Ethics approval

All the authors agree with the content of the article.

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Tables

Table 1. TGA results of VE/BF and NCS–VE/BF composites

Sample	Thermogravimetric analysis					
	Nitrogen			Air		
	T _{onset} 10% [°C]	T _{max} 75% [°C]	Residue wt.% @ 700°C	T _{onset} 10% [°C]	T _{max} 75% [°C]	Residue wt.% @ 700°C
VE/BF	341	454	4.7	317	393	0
2%NCS-VE/BF	341	457	6.8	317	409	0
4%NCS-VE/BF	341	456	8.2	324	421	1.2
6%NCS-VE/BF	336	454	9.0	306	417	1.3

Table 2. UL-94, LOI, micro and calorimetry results of VE/BF and NCS–VE/BF composites

Sample	Horizontal Burn Test		VB Test		LOI	Calorimeter		
	Air					O ₂ + N ₂		
	Burn time [sec]	Burn rate [mm/sec]	Dripping	Rating	(%)	pHRR [W/g]	THR [kJ/g]	FIGRA W/g. s ⁻¹
VE/BF	1.53	0.66	N	NR	18.9	422.7	25.5	0.92
2%NCS-VE/BF	2.32	0.49	N	HB	26.4	381.5	24.7	0.86
4%NCS-VE/BF	2.35	0.48	N	HB	27.6	373.6	23.3	0.84
6%NCS-VE/BF	2.54	0.43	N	HB	28.3	361.9	20.7	0.83

Table 3. Mechanical data of VE/BF and NCS-VE/BF composites

	Tensile strength (MPa)	Tensile Modulus (GPa)	Flexural strength (MPa)	Flexural Modulus (GPa)	Impact strength (J/mm)
VE/BF	27.95	1.57	117.53	7.70	0.0205
2%NCS-VE/BF	30.73	1.68	122.89	14.68	0.0306
4%NCS-VE/BF	30.42	1.76	151.65	18.01	0.0314
6%NCS-VE/BF	26.29	2.36	63.32	2.66	0.0260

Figures

Figure 1

Spectral analysis results of NCS compounds.

Figure 2

(A) Powder XRD analysis, (B) SEM micrographs, (C) Particle size analysis, and (D) Elemental analysis results of chitosan and NCS compounds.

Figure 3

(A) TGA (N₂), (A₁) TGA (Air), and (B) Microcalorimeter profiles of NCS compounds.

Figure 4

(A) FTIR spectra and (B) Powder XRD spectra of VE/BF and NCS-VE/BF composites.

Figure 5

SEM micrographs of surfaces and tensile fracture surfaces of VE/BF and NCS–VE/BF composites.

Figure 6

TGA profiles of VE/BF and NCS-VE/BF composites under N₂ and air atmosphere.

Figure 7

Char micro and EDX analysis results of VE/BF and NCS-VE/BF composites.

Figure 8

Char micro and EDX analysis results of VE/BF and NCS-VE/BF composites.

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