Enhancement in Adhesive and Thermal Properties of Bio-based Epoxy Resin by Using Eugenol Grafted Cellulose Nanocrystals

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Abstract

Bio-based epoxy resins are being used due to their green chemistry. They have better properties than petroleum-based epoxy resins. Recently, environment friendly nanomaterials have been used for different industrial applications. Cellulose nanocrystals (CNCs) are among the best naturally occurring materials. Therefore, the surface of cellulose nanocrystals are modified by eugenol-based silane coupling agent (EBSCA). Chemical composition and surface morphologies of CNCs were analyzed and characterized by FTIR, AFM, SEM, TEM and ^{1}H-NMR. The SEM and AFM results confirmed eugenol-based silane coupling agent was successfully grafted on cellulose nanocrystals. Modified CNCs demonstrated an excellent tensile strength (2190 MPa) and modulus (16.00 MPa), as well as storage modulus (1622 MPa) exhibited by 1wt% modified cellulose nanocrystals composites. Additionally, modified CNCs displayed hydrophobic behavior (CA=102 ± 2°). The corresponding modified CNCs have significant applications in combination of high stiffness and strength to the epoxy resins. This study lays a foundation towards full bio-based, environment friendly polymers fabrication and consumptions most desirable in adhesive and mechanical industrial fields.

1. Introduction

Epoxy resins have been used on large scale in our daily lives for coating purpose owing to their adhesives and excellent mechanical performance [1, 2]. They have fast curing property and excellent modulus, which assist in fabricating composites having wide variety applications [3]. Epoxy resins, commonly have been used as thermosetting materials, especially in fiber manufacturing materials [4, 5]. However, relatively high content of hydroxyl groups shows high surface energy, attracting their application in some areas, such as anti-fouling coating [6, 7]. Among organic coating; epoxy resins used in large quantity for protective coating due to their high temperature performance [8, 9]. Epoxy resins system have been utilized in high voltages transformers, power apparatus and cable terminations. Epoxy and epoxidized resins can be consumed in preparation of organic-inorganic hybrids owing to their excellent mechanical properties [10–12]. Epoxy resins are the best choice to be used as anti-corrosion and corrosion resistance materials [13]. They have become a favorite choice in term of long-life, and cost effective in various industrial applications [14, 15]. Exploration for an alternative to renewable bisphenol A epoxy resins is a necessary for highly efficient development trend. Environment friendly polymers have gained increasing interest [16, 17]. The development of high-performance biomass-derived epoxy thermosets with excellent flam resistance property is vital i.e., adhesives and coating [18]. Cellulose nanocrystals in combination with polymers owing to their renewable nature and wide variety applications in material science has been attracted an increasing interest of researchers due to their enhanced performances [19–22]. New methods have been introduced to enhance the performance of CNCs [23–25]. Cellulose nanocrystals obtained from natural bio resources are the building blocks to design new biomaterials in nanotechnology [26, 27]. Their widths and lengths vary from 5 to 20 nm and from 100 nm to 1–2 μm respectively [28]. CNCs have been used both in modified and unmodified forms for the development of products for several years, useful in commercial and industrial fields [29–31]. Cellulose nanocrystals

extracted from abundant cellulose nano-fillers having strength-to-weight ratio have been used as reinforcing agent for epoxy composites [32, 33]. Recently, CNCs have been reported as sustainable bio-source material, which serve as a valuable colloidal stabilizer [34, 35]. They have attracted a dynamic attention in developing and high-performance nano-composites due to their mechanical performance [36, 37]. CNCs materials have wide applications due to their unusual properties such as high specific surface area, static mechanical properties and permeability [38, 39]. In several studies, CNCs have been incorporated into polymer matrices as a reinforcing agent due to their hydrophilic and well-dispersion properties [40]. It is also a favorable reinforcing material for production of bio-based composite materials, because of its high strength and stiffness [41]. CNCs are bio-source safe nanomaterials have attracted researchers' interest both in academic and industrial sectors, a leading potential for industrial production [42].

Environmental factors are taken more into consideration. The interest in biomaterials leaves its place to the need. This leads the researchers to search for new materials. The aim of this study is to produce an environment friendly, and sustainable materials of plant's oil origin-based bio-resin. In this study, cellulose nanocrystals are modified by eugenol-based silane coupling agent (EBSCA), reacted with lab-synthesized bio-based epoxy resins. Their adhesive and thermal properties have been evaluated with the help of scanning electronic microscope and thermogravimetric analysis. Epoxy resin is a polymeric material with extensive applications, have been chosen as the model polymer matrix. The modified cellulose nanocrystals are expected to provide a combination of high stiffness and strength to the epoxy resin, which is most desirable for many industrial applications.

2. Materials And Methods

Pure cotton supplied by Guangzhou Liqi textile technology Co., Ltd., for obtaining cellulose nanocrystals. Lab-synthesized eugenol-based silane coupling agent (EBSCA) was used for modification of CNCs. Lab-synthesized bio-based epoxy [43] was used for mechanical properties. Triethylenetetramine (TETA) was used as a curing agent, purchased from Sigma-Aldrich (97.0%). Analytical grade pure reagents including; ethanol, methanol were obtained from the Aladdin reagents Shanghai industry. Thick sulphuric acid: 98%, was received from Tianjin Hengxing Chemical Reagent Co., Ltd. Labs made distilled water were used.

2.1 Preparation of cellulose nanocrystals from cotton

Cellulose nanocrystals (CNCs) were obtained from industrial skimmed cotton as following; 20 g of industrial waste cotton was cut into small pieces and cleaned with hot water to remove the wax and pectin. The washed cotton was dried in hot air oven at 45°C for 8 h. The cleaned cotton in 500 mL of 20% sodium hydroxide was stirred on hot plate at 45°C for 4 h. Alkali was used for hydrolysis to increase the crystallinity of the cellulose. The alkali treated cotton suspension was allowed to cool at room temperature, and then the solution was transferred into 2.5 L of distilled water until the pH reached to neutral state. The neutral suspension was filtered by Buckner filter set-up. The filtrate was heated and stirred in 500 mL of 60% sulfuric acid at 35°C for 10 h. Herein, acid hydrolysis is used for removal of

impurities such as hemi-cellulose and lignin. The cellulose suspension disintegrated rapidly and formed a white slurry. The white slurry was transferred into 2 L of water to become neutral. This suspension was kept aside for 12 h and the slurry was completely settled down. The dilute solution was decanted to the slurry. After decanting process, the white slurry was re-treated with water to remove sodium and sulfate ions residues. The suspension was centrifuged at 8000 round per minute. The chemically purified cellulose nanocrystals were stirred at 40°C having a composition of 45–60% (w/v.%) and H_2SO_4 was strongly agitated through for 30–180 min. After hydrolysis, the solution was cooled down to room temperature and sonicated for 30 mints. The sonicated suspension is centrifuged (Cence TG16-WS) for 15 min at 8000 round per minute for three times until the acid concentration was completely removed from CNCs. The obtained cellulose powder was dried in an oven at 60°C for 10 h and used for further characterization. The schematic diagram is shown in **Figure-1.**

2.2 Properties of the native CNCs TEM analysis

The microscopic appearance of the CNCs sample produced by a radio lens and from observation chart as we can see, CNCs micro-surface morphology observed as many large mesh formations in transmission electron microscopy, as shown in **Figure-2.** The dimensions of CNCs crystals were also observed having average length 103.47 nm and average width is 12.31 nm. The 88.86% CNCs showed 8.4 nm average diameters. The remaining crystals demonstrated aggregation behavior due to the presence of large numbers of hydroxyl groups on the CNCs surface. [44, 45] The excess amount of CNCs presented aggregation behavior, which can be improved greatly the interface that is reflected in the rough surface layer. However, good dispersion is obtained with low concentrations of CNCs in epoxy resin. The higher concentration of CNCs produce more surface roughness. CNCs form a clear and uniform image. It can be seen that CNCs are rod like in shape. The TEM images of CNCs revealed the presence of compact and uniform nano-sized rod like crystals. [46] It was concluded that the average diameter of the CNCs based nanocomposites depend on the concentration of CNCs in epoxy resin. [46]

2.3 Modification of Cellulose nanocrystals

Modified cellulose nanocrystals were prepared in 150 ml, a single-necked round bottom flask. Firstly, took 80 ml of deionized water with 20 ml of ethanol absolute and 1.5 ml of eugenol-based silane coupling agent (EBSCA) and stirred at room temperature for 2 h, added few drops of acetic acid to maintain the pH 3–4. Subsequently, 1 g of native cellulose nanocrystals were immersed in a single-necked round bottom flask and stirred for the next 3 h, followed by three times wash through centrifugation in deionized water. One round of washing through centrifugation was 10 min at 5000 round per minute (Shanghai Anting scientific instrument factory) to remove any excess of silane from the CNCs. Hereafter, washing the products in centrifuge, then dried open atmosphere in oven at 100°C for 4–5 h. The powder stored in vacuumed oven at 80°C for the next 4–6 h to remove the remaining impurities and then subsequently preserved in sample glass bottle from moisture for further use.

2.4 Preparation of steel plates

A simulating industrial setup for steel plates was designed from Hangzhou iron and steel group Co. Ltd. The steel plates were polished and dried at room temperature, and subsequently, preserved in plastic bags from moisture for further use. According to test methods for adhesive properties of modified cellulose nanocrystals embedded with coated steel plates and polished into three molded standard testing. Bio-based epoxy resin (SIEEP4 and SIEEP2) as shown in **Figure-3** were used. 1 g of bio-based epoxy resin with 1%, 3% and 5% of modified CNCs were taken in the sample glass bottle, and then sonicated at natural temperature for 1 h, followed by stirring at room temperature for next 2 h. After that, 0.2 g of triethylenetetramine (TETA) was added dropwise, and slowly stirred for the next 10–15 mints to achieve complete curing. The corresponding cured composite were kept in vacuum oven at 40℃ for 15–20 mins to eliminate the trapped air from solution. Hereafter, the mixture was poured through glass rod in steel plates with the length of 1.5 cm and width 2.3 cm into three different molds for curing. Curing process was carried out in an oven at 120°C for 1 h. After that, the samples were cooled down naturally to room temperature. These standard testing steel plates were placed at room temperature for 3–4 days before testing.

2.5 Bio-based epoxy used for mechanical property

2.6 Characterizations

The structures of native CNCs and modified CNCs were analyzed by the Fourier transform infrared spectroscopy (FTIR). The infrared spectra recorded on a Nicolet-5700 FTIR spectrophotometer by the KBr-pellet method and scanned from 4000 – 500 cm^{-1} with a resolution superior to 0.5 cm^{-1}. ^{1}H-NMR (Bruker Advanx 600 DMX), spectrometer was used with a solvent D_2O. The images were obtained on Desktop scanning mirror with X-ray energy spectrometer (Model: SU-3500 SEM: Energy spectrometer: Oxford X-max20) Hitachi Japan's, coating of gold surface on the specimen were applied. For AFM Multi-Mode Model: VEECO with sustainable and stable atomic-grade resolution, Company of the United States. For stirring Magnetic stirrer 85 – 1 type zhi wei Shanghai were used. (Cence TG16-WS) Hunan Xiangyi Laboratory Instrumental Development Co. Ltd was used as centrifuged for centrifugation and for mechanical properties, universal material testing machine (Zwick/roell Z020) Germany were used for such properties like tensile strength, bending and impact strength were analyzed.

3 Result And Discussion

3.1 Coupling agent

Eugenol-based silane coupling agent (EBSCA) was synthesized via hydrosilylation. This silane coupling agent enhanced the connection between CNCs and epoxy matrix to achieve sustainable and environment friendly products. Eugenol-based epoxy silane coupling agent with high purity was prepared and used for the surface modification of nano-cellulose crystals. The eugenol epoxy silane-coupling agent, bearing a long chain structure of benzene ring in molecular structure, which could improve the compatibility of

CNCs with different bio-based epoxy, contributing to the dispersion state in the matrix, enhancing the overall performance of epoxy-cured products.

3.2 ^{1}H-NMR of eugenol base silane coupling agent (EBSCA) coupling agent

Figure-4 shows the ^{1}H-NMR spectrum of eugenol base silane coupling agent (EBSCA) in $CDCl_3$. The signals from the allylic group in coupling agent disappeared owing to the complete hydrosilylation reaction, the new signals ($H_{11,12}$) shown in EBSCA assigned at ^{1} H NMR spectrum confirm the synthesis of EBSCA. ^{1}H NMR ($CDCl_3$) δ ppm: H_7 (6.80–6.90); $H_{5,6}$ (6.65–6.72); H_3 (4.13–4.23, 3.92–4.02); $H_{4,11}$ (3.75–3.89); H_2 (3.28–3.39); H_8 (2.80–2.88); H_1 (2.68–2.73, 2.53–2.63); H_9 (1.67–1.82); H_{12} (1.16–1.29); H_{10} (0.60–0.73).

3.3 Chemical modification of cellulose nanocrystals with silane coupling agent

Cellulose nanocrystals modified with eugenol-based silane coupling agent **(**EBSCA) are shown in the **Figure-5.** The broad peak appeared at 1540 cm^{-1} is due to C = C stretching vibration. The peak appeared at 780 cm^{-1} attributed to ~ CH bending vibration. This confirmed the successful modification of cellulose nanocrystals, modified by eugenol-based silane coupling agent **(**EBSCA) [47].

3.4 Scanning electron microscope of native and modified CNCs

The Scanning electron microscope images were obtained on field emission scanning electron microscope (SEM, SU-3500). After sputter coating of gold on the specimen's surface. The morphologies of the surface of native and modified cellulose nanocrystals images were obtained and clearly showed the surfaces morphologies, reacted with aforementioned epoxies. The native CNCs surface is much rougher than the modified CNCs. In general, their combination has a favorable effect on the performance of composites, which results an increase in the adhesive properties [48]. In **Figure-6 (A**) shows surface of native CNCs. **Figure-6 (B).** SEM of cellulose nanocrystals matrix appeared with bio-based epoxy resin, but their diameter decreased after spreading to varying degrees in the epoxy.

However, as additional CNCs aggregation occurred, which prevented the formation of a homogeneous mixture. In general, their combination has a favorable effect on the performance of composites. However, better dispersion was obtained using a modified epoxy resin with low CNCs content. Low concentrations of CNCs are more appropriate than higher, and aggregation resulted with increasing concentrations. Another factor contributing to the uneven distribution is residual epoxy evaporation. Dispersion of CNCs in liquid feed is affected by liquid phase ratio. The presence of multiple break lines in the bio-based epoxy

surface indicates the hardness of the material. The modified bio-based epoxy resin particles exhibited bumps and collapsed morphology.

3.5 Surface analysis of modified CNCs

Surface roughness measurements were used as criteria to evaluate the dispersion quality of modified CNCs. Images obtained by atomic force microscopy (AFM) are presented in **Figure-7.** Qualitatively comparing the micrographs revealed that the addition of modified CNCs have increased the surface roughness, irrespective of the surface modification method. Moreover, the higher loading level, associated with rougher surface. The modified CNCs showed high roughness on surface. Quantitative measurements of roughness had small values, showing that modified CNCs had a smooth surface showed Rq 0.14 μm.

Therefore, it was confirmed that the roughness increased proportionally with modified CNCs loading level. Strong van der Waals forces between modified CNCs could explain the need for higher shear rate. The observed increase in roughness and especially, if the viscosity of the epoxy coating was considered. These roughness measurements demonstrated that modified CNCs were used as a reinforcing agent had relatively good compatibility.

3.6 Adhesive properties of native and modified CNCs

Here, we have also evaluated the adhesives strength of native and modified CNCs, because they have an assured strength and toughness. The average adhesive strength is mentioned in **Table-1 and Table-2**, using eugenol-based silane coupling agent with the CNCs content, while triethylenetetramine used as a curing agent. The bio-based epoxy resins containing native and modified CNCs at 1, 3 and 5 weight percent (wt%) to evaluate the effect of enhancement potential. With the introduction of tensile modulus and strength at maximum load using steel plates. Modified CNCs has an obvious enhancement effect with 1 wt% and 3 wt% on tensile modulus, but after adding 5 wt% caused agglomeration in the epoxy medium [49, 50]. The maximum value observed for nanocomposites reinforced with 1 wt%. [51]. The tensile data shows that all the modified CNCs samples had a higher tensile strength than the standard one. The results of modified CNCs binding themselves through -OH, creating a high strength linkage, with potentially interaction among them, increasing the adhesive properties. The increasing of modified CNCs loading result in agglomeration between particles, which produce weakness in the material, explaining the comparative decrease in adhesive with individual loading.

Table 1
Adhesive properties of bio-based epoxy with native and modified CNCs

Formulation SIEEP4 bio-based epoxy	Tensile strength MPa	Tensile modulus MPa	Elongation at Break dl%
1% modified	2190	13.50	0.6
3% modified	2100	13.20	0.5
5% modified	2150	15.70	0.6
1% unmodified	2160	10.50	0.7
3% unmodified	2040	10.50	0.7
5% unmodified	2090	11.00	1.1

Table 2
Adhesive properties of bio-based epoxy with native and modified CNCs

Formulation SIEEP2 bio-based epoxy	Tensile strength MPa	Tensile modulus MPa	Elongation at Break dl%
1% modified	1940	14.70	1.3
3% modified	2000	16.00	1.6
5% modified	2410	15.30	1.9
1% unmodified	1840	14.16	1.3
3% unmodified	1870	15.60	1.2
5% unmodified	2000	16.00	0.9

3.7 Bio-based epoxy with native and modified CNCs mechanical properties

The main challenges encountered to use bio-based epoxy resins and their composites; including the design of high processability (low-viscosity) epoxy resins and cured epoxy resins with high stress-strength and toughness that can be recycled and reused. Here, we have also tried our best to study different types of bio-based epoxy for mechanical properties. We have found good mechanical properties in our synthesized bio-based epoxy. The results are much better, because the remaining bio-based epoxy (SIEEP4 and SIEEP2) are hyper-branched epoxy resins. This is an important epoxy resin that belongs to one sub-class of dendrimers and contain highly branched topological structures with a high content of functional groups. The deformable topological structure, good solubility with other matrixes, high chemical stability and low viscosity makes them more important. Triethylenetetramine (TETA) is used as

curing and toughening agent for thermoset materials for bio-based epoxy resins. In recent years, scientists have made significant progress in synthetic methods of low viscosity. The synthetic approaches of hyper-branched that includes esterification, etherification, polymerization and oxidation of double bonds, and hydrosilylatin reaction. The low viscosity of curing agent can improve the mechanical properties of SIEEP4 and SIEEP2 (bio-based epoxy codes) by separating the entangled molecular chains of bio-based epoxy. Among the wide applications of TETA, one of the important use in the industrial field is their simultaneous reinforcing and toughening function on epoxy. Existing methods of simultaneous reinforcing and toughening of bio-based epoxy includes the use of nanomaterials, block polymers and hyper-branched epoxy resins. The homogeneous dispersion and size of nanoparticles, as well as good adhesion between these bio-based epoxies and nanoparticles are critical factors, influencing the degree of improvement of strength and toughness.

To cope with aforementioned challenges, which includes highly efficient recycling, improving our understanding of the homogeneous reinforcing and toughening mechanism. We have prepared degradable hyper-branched bio-based epoxy resins by esterification and thiol-ene reaction for high-performance. The cured bio-based epoxy composites demonstrated good mechanical properties and degradability, high tensile strength and toughness.

Evaluation of mechanical properties of the bio-based epoxy was investigated by performing normal stress tests, as shown in **Figure-8 and Figure-9.** The inelastic deformation was observed with increase in applied stress as shown in the curvature portion of the curves. Eventually, fracture strength resulting in breakage. Modified CNCs exhibited a yielding behavior. Such a yielding phenomenon was not observed by composite samples having native CNCs matrix. This reinforcing effect was attributed to the high rigidity and the increased crystallinity of modified CNCs. It should be pointed out that the loss of the ductility was accompanied. Furthermore, the observed reinforcing effect maintained at high temperature condition. The storage modulus was 1622 MPa for 1wt% modified CNCs composites, which was considerably higher than 1429 MPa value of the native CNCs. In a sharp contrast, the composites exhibited higher storage modulus since the existence of CNCs within polymeric matrix, which restricted the molecular motion. For semi-crystalline polymer like modified CNCs, its strength is usually proportional to its crystallinity. Thus, the increased crystallinity played a key role in reinforcement of composite's properties. On the other hand, the high rigidity nature of CNCs also contributed to reinforcement.

3.8 Contact angle of native CNCs with bio-based epoxy

The contact angle is an angle, which is conventionally measured through the liquid, where a liquid vapor interface meets a solid surface. The contact angle of water on native and modified CNCs with bio-based epoxies were carried out to demonstrate the wettability of native and modified CNCs as shown in the **Figure-10.**

The abundant –OH groups of native CNCs are responsible for hydrogen bonding with the water molecules (CA = 55 ± 2°). The native CNCs lost their hydrophilicity after modification with bio-based

epoxy. The modified CNCs showed hydrophobic behavior (CA = 102 ± 2°) due to the presence of eugenol based-silane coupling agent (EBSCA).

Conclusion

Surface morphology of cellulose nanocrystals obtained from industrial skimmed cotton have observed large mesh formations with average length of 103.47 nm and average width 12.31 nm in transmission electron microscopy. The excess amount of CNCs presented aggregation behavior having highly rough surface, however, good dispersion observed in low concentrations of CNCs in bio-based epoxy resins. The TEM images of CNCs revealed the presence of compact, uniform and rod-shape nano-sized crystals. It was concluded that the average diameter of the CNCs based nanocomposites depend on the concentration of cellulose nanocrystals in bio-based epoxy resin. Eugenol-based silane coupling agent was synthesized via hydro-sialylation. The corresponding coupling agent bears a long chain structure of benzene ring in molecular structure, granting compatibility to CNCs with different bio-based epoxy, contributing to the dispersion state in the matrix. In addition, higher loading of modified CNCs have increased the surface roughness, irrespective of the surface modification method. The surface modification has been confirmed through different techniques; the FTIR broad peak appeared at 1540 cm^{-1} is due to C = C stretching vibration and the peak appeared at 780 cm^{-1} attributed to ~ CH bending vibration, which confirmed successfully modification of cellulose nanocrystals by eugenol based-silane coupling agent. Modified CNCs have obvious enhancement effect with 1 wt% and 3 wt% on tensile modulus, but addition of 5 wt% caused agglomeration in the epoxy medium. Our reported bio-based epoxy (SIEEP4 and SIEEP2) have a good mechanical. The modified CNCs with EBSCA composites demonstrated good mechanical properties and degradability, high tensile strength (2190 MPa) and modulus (16.00 MPa), as well storage modulus (1622 MPa) for 1wt% modified CNCs composites. maintained obviously good tensile strength. Additionally, the modified CNCs showed hydrophobic behavior (CA = 102 ± 2°). The increased crystallinity played a key role in mechanical reinforcement of modified CNCs than native CNCs composite. AFM demonstrated qualitatively comparing of micrographs revealing that the addition of modified CNCs decreased the surface roughness. The effects of EBSCA on the adhesive and mechanical properties with bio-based epoxy systems indicated that silane-coupling agent could effectively improve the toughness of the epoxy system.

Declarations

Statement

We have no conflict of interest.

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Figures

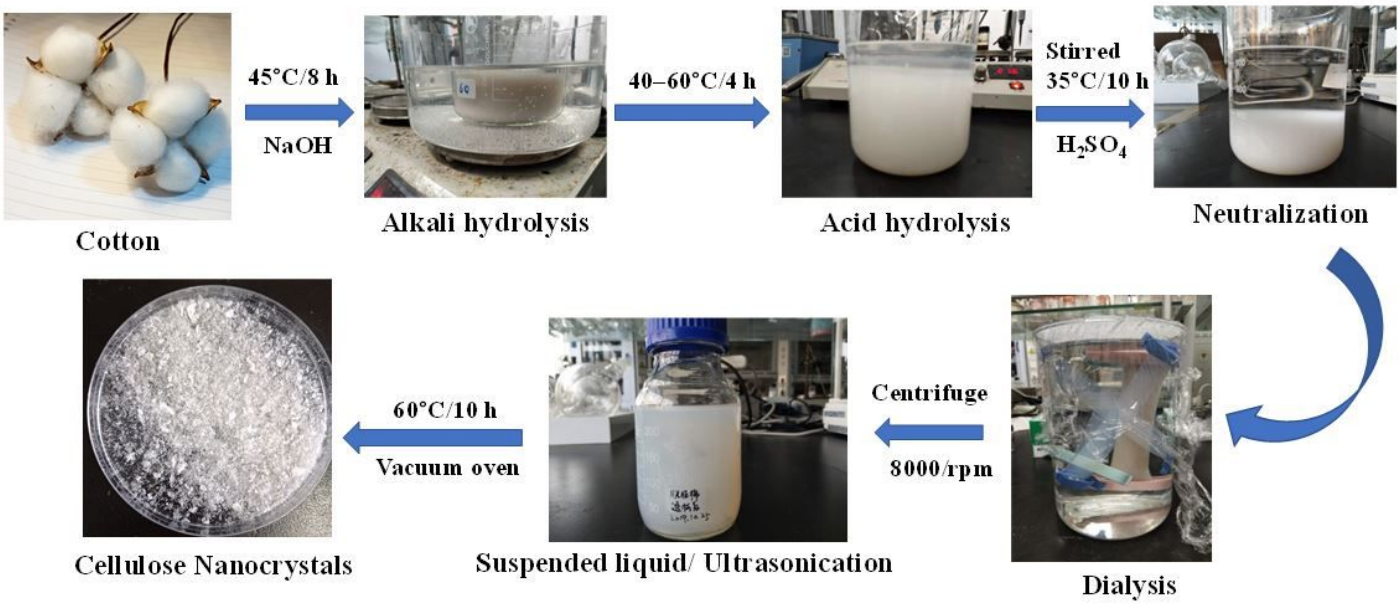

Figure 1

Extraction of Cellulose nanocrystals from cotton

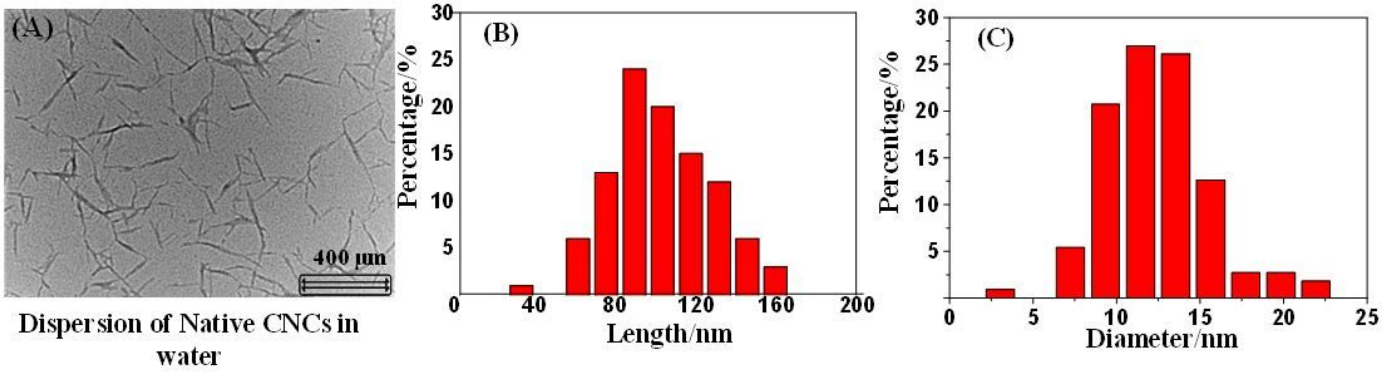

Figure 2

(A), TEM image of native CNCs in water (B) CNCs length and (C) CNCs diameter

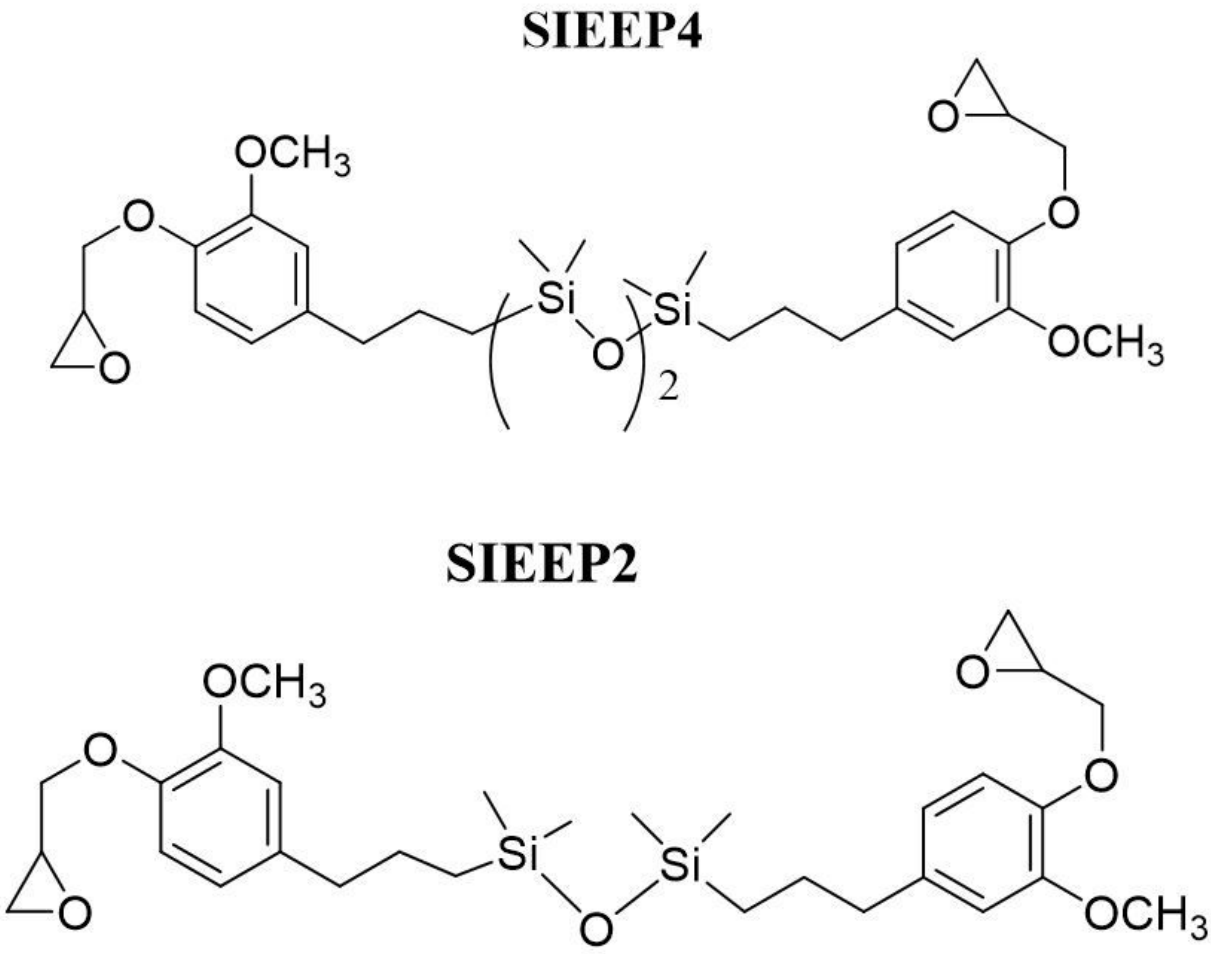

Figure 3

Bio-based epoxy SIEEP4 and SIEEP2

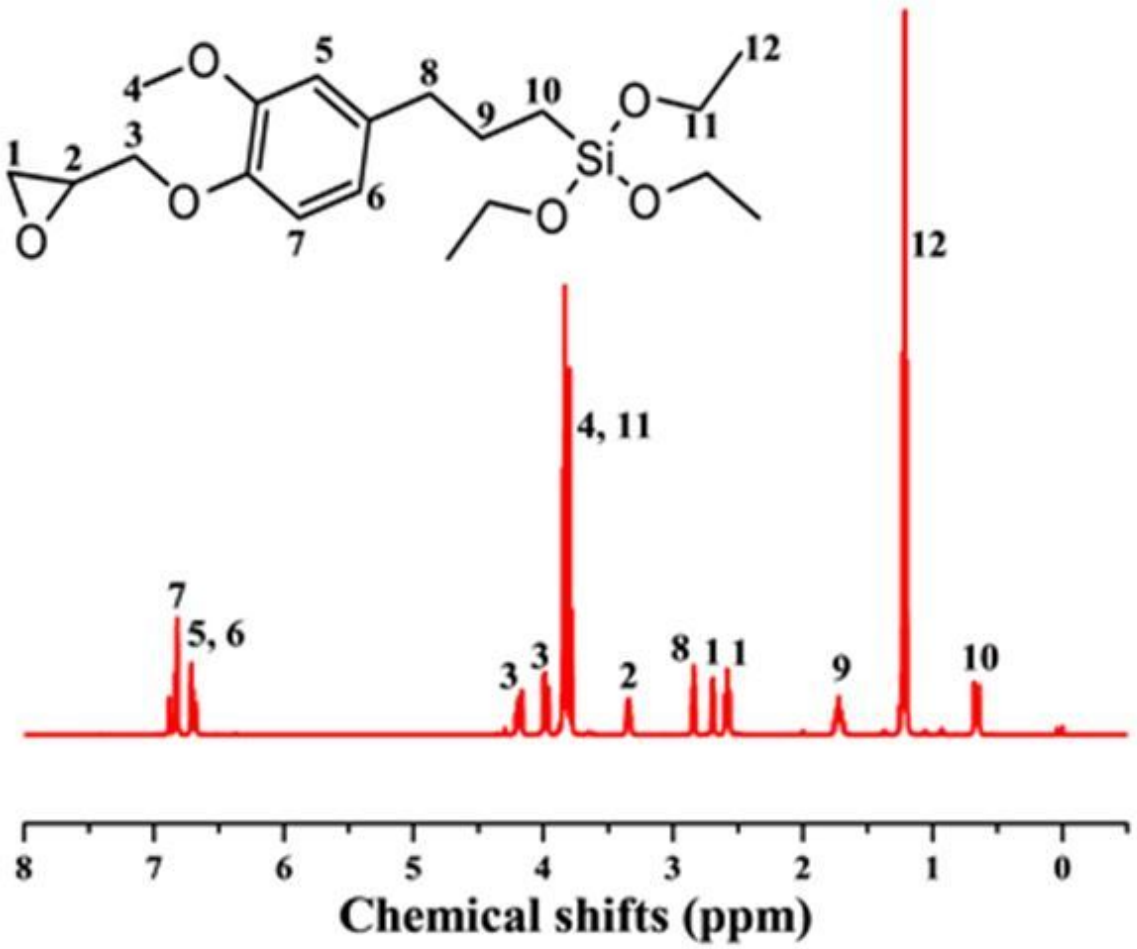

Figure 4

1H-NMR spectrum of EBSCA coupling agent in CDCl3.

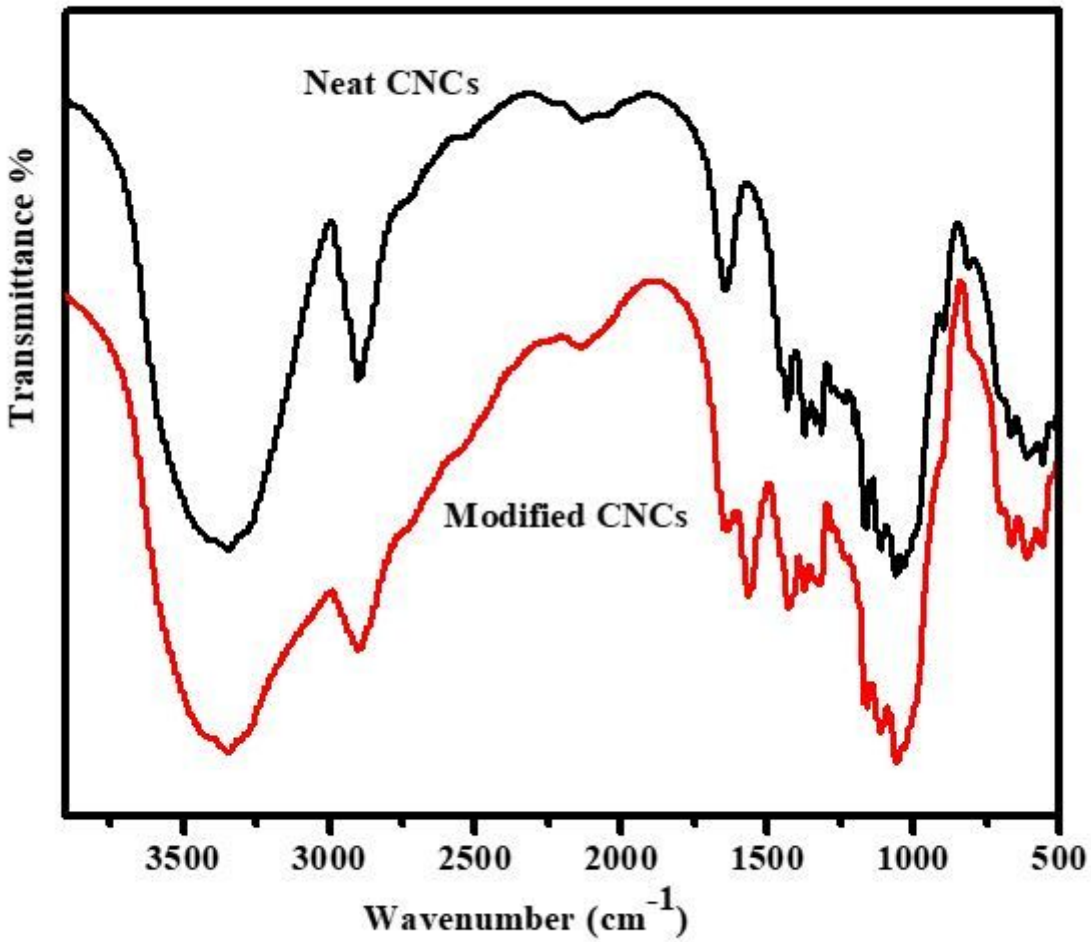

Figure 5

FTIR Spectra of neat and Modified CNCs

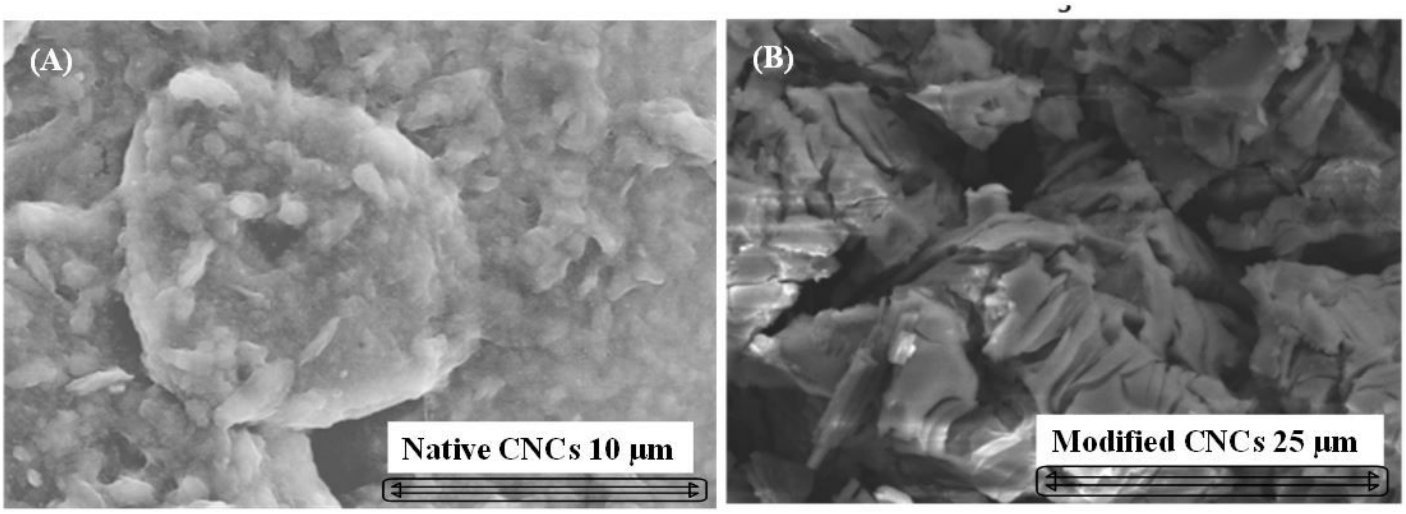

Figure 6

SEM images of (A) Native CNCs and (B) Modified CNCs

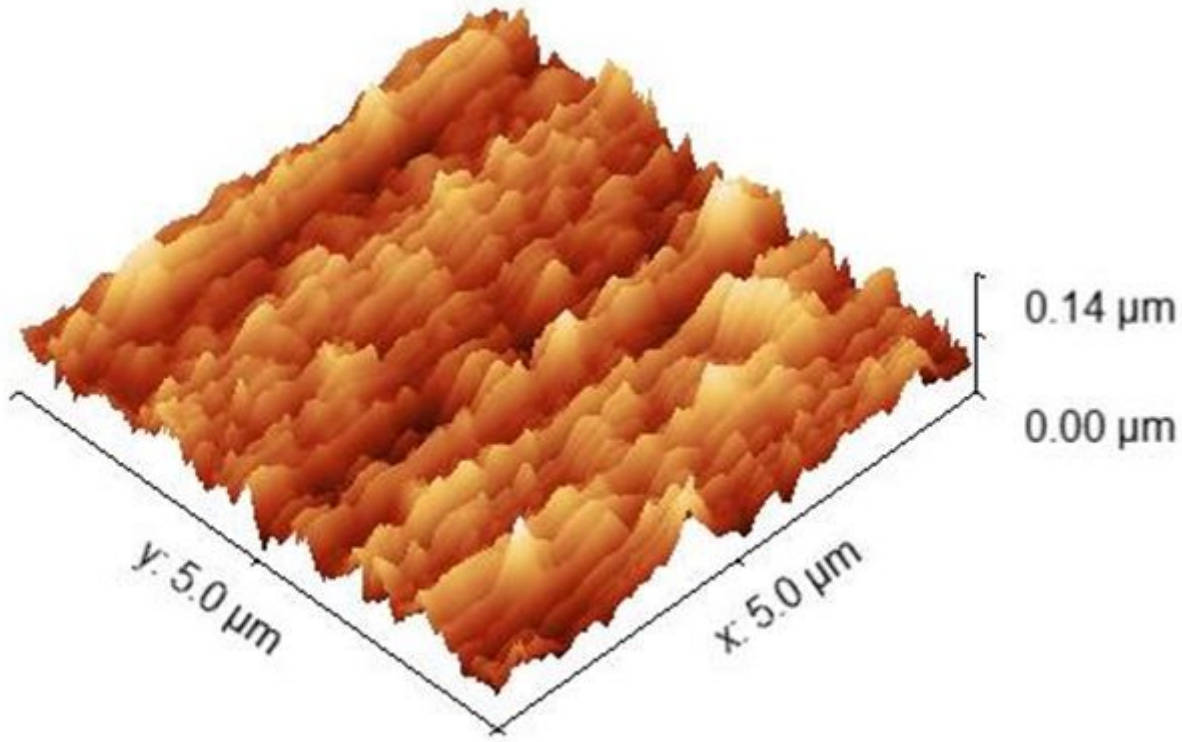

Figure 7

Atomic Force Microscopy (AFM) image of modified CNCs

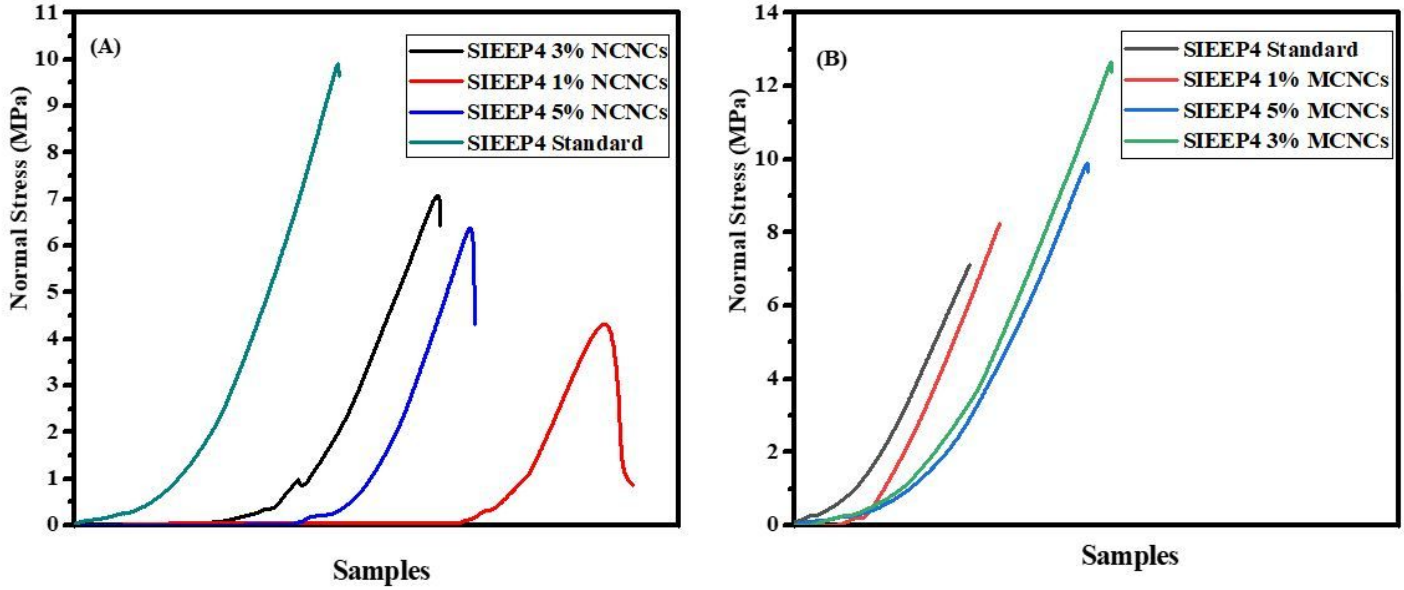

Figure 8

Graphical representation of Normal Stress (MPa) of Native CNCs and modified CNCs with SIEEP4 bio-based epoxy

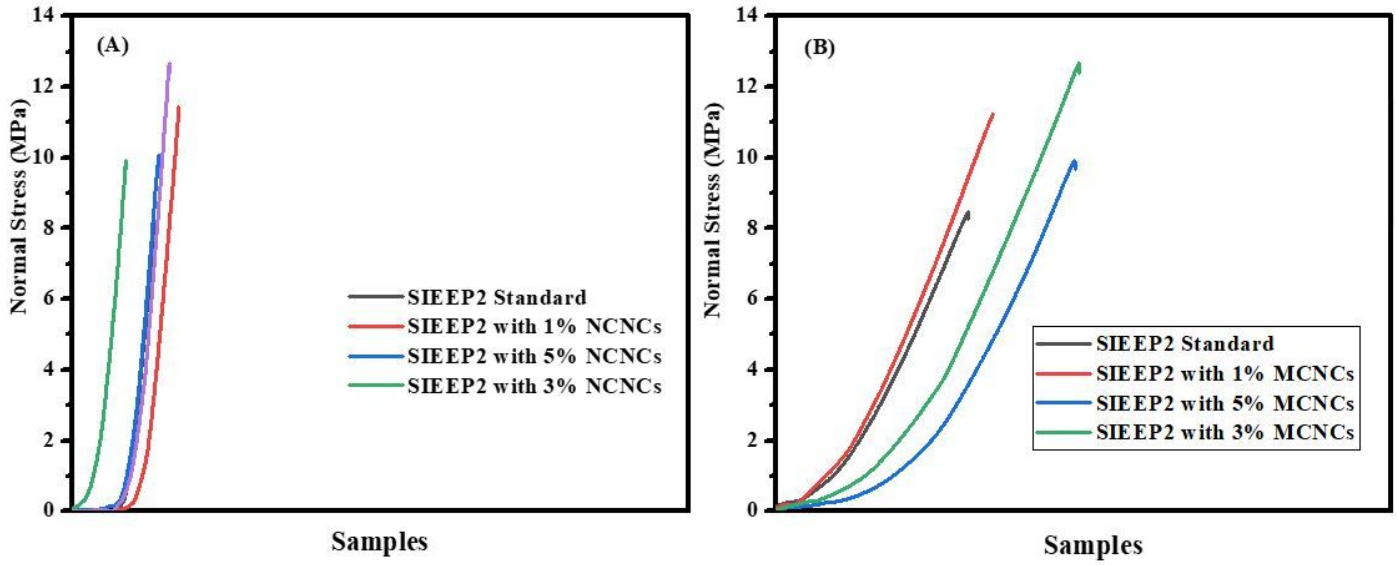

Figure 9

Graphical representation of Normal Stress (MPa) of Native CNCs and modified CNCs with SIEEP2 bio-based epoxy

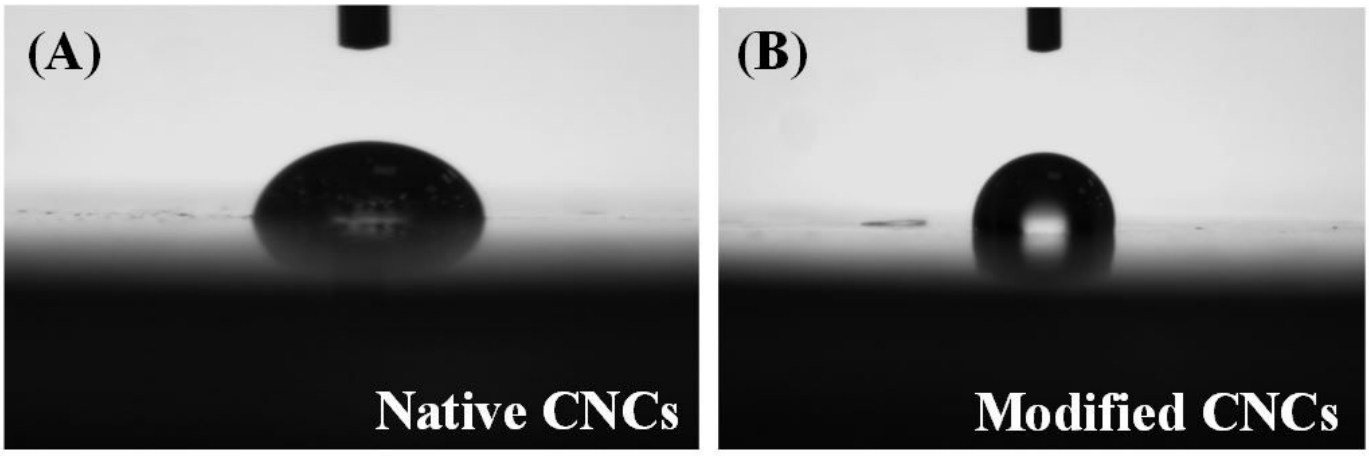

Figure 10

(A) Native CNCs (B) Modified CNCs with bio-based epoxy