

A promising reinforcement for textile composites: Study on the effect of cellulose nanofiber (CNF) content on the mechanical properties of CNF reinforced epoxy resin

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Abstract. The reinforcement effect of volume fraction of CNF on different matrix resin (vinyl-modified epoxy ester resin emulsion; epoxy-modified alkyd emulsion) are investigated in this study. Tensile shear test is carried out following the JIS K 6850:1999 standard, by coating this colloid mixture on substrates. The results show that the maximum shear strength of both waterborne resin increase with the addition amount of CNF at relative humidity 32.78%. It is considered that there exists hydrogen bonding between fiber and matrix, and the stress concentration might be relieved by the 3-D network structure of CNF, thus the maximum stress is increased, and the crack generation and development is suppressed. But it leads to a loss of percentage elongation values. A peak of the deformation energy is found at 10wt.%, which is considered as a force balance point of 3-D network reinforcement and the aggregation of CNF at the interface. The reinforcement of CNF is sensitive to humidity, for epoxy ester matrix is found more easily influenced by humidity than alkyd matrix, which has bigger deformation energy than alkyd matrix in low humidity(32.78%RH), although deformation energy dramatically decreases in high humidity(97.30%RH), it still has compatible humidity as alkyd matrix.

1. Introduction

Fiber reinforced plastic(FRP) is widely used for lightweight structures in aerospace and automotive industry etc. However, as FRP is made by high strength fiber and low strength resin, FRP has high strength in fiber direction, but may weak in transvers direction and out-of-plane direction. Many efforts have been made to improve the transvers and out of plane properties. The bonding between fibers and matrix plays a crucial role in mechanical performance of FRPs. It is considered that to improve the surface condition by removing impurity on the surface or coating, which can improve the mechanical property of fiber and the wettability between fiber and matrix, as a result improve the mechanical property of FRP [1]. Plasma etching, and oxidation are widely used for surface modification. Research on coating functional group of an organic polymer which could reacting with matrix resin is carried out by Hojo M. etc. [2]. Effects of multi-scale modifications by adding nano-particales/ nano-tubes on surface CF on the mechanical property of FRP is studied by many researchers. For example, M. sharma et al. [3][4], interfacial strength has been increased by 113%, and failure was predominantly cohesive matrix failure, in contrast to the untreated fiber.

Epoxy resins are widely used in FRP. The three-dimensional cross-linked thermoset structures gives their high process ability and strength [5-7]. However, higher cross-link density contributes to lower



fracture toughness [8-10]. This drawback can be overcome by modifying epoxy resins with integration of various nanofillers as a second microphase [11-14].

An initial study on the reinforcement effect of CNF on FRP is carried out. To investigate the reinforced effect of CNF on waterborne resin, specimen for dispersion status observation using scanning electron microscopy (SEM) and tensile shear test are prepared separately. Further, the effect of humidity on the reinforcement behavior of CNF is investigated.

2. Experiment

2.1. Materials

The stable suspension of cellulose nanofiber used in this study, is made by high pressure water jet method, which is provided by SUGINO MACHINE Ltd., Uozu, Toyama, Japan. General physical properties of cellulose suspension are shown as below. Concentration: 2 wt. %, viscosity: over 3000 MPa•s, specific surface area: 100~200 m²/g, degree of polymerization: 200~550 and the fiber is shaped in a diameter of about 20 nanometer and a length of a few micrometer. Two different waterborne resins were used as matrix material. (a) vinyl-modified epoxy ester resin emulsion EFD-5560 and (b) epoxy-modified alkyd emulsion WPW-601. Both of the waterborne resins are one-pack type and cure through polycondensation which provided by DIC Corp. . The detailed contents of the matrix waterborne resins are shown in table 1.

Table 1. Content of the matrix waterborne resin.

Content /wt.%	EE resin (EFD-5560)	EA resin(wPW-601)
Solid content	39.0~41.0	40.0~42.0
Amine	1.6	2.0
Water	58.4	50.0
Organic solvent	0	≤ 6.0 (Methoxybutanol & Dipropylene glycol dimethyl ether)

2.2. Methods

2.2.1. Mixture colloid preparation. Both the specimens for observation of dispersion state and tensile shear test, are prepared with same procedure. All mixture colloid used in this study are prepared using a mechanical mixer, 5min for stirring and degassing each. For shear tensile test, 6 kinds of mixture colloid are made with CNF Mass fraction ration (0, 2.5, 5.0, 10.0 and 20.0) for each type of resin.

2.2.2. Scanning electron microscopy. The dispersion state of CNF in epoxy ester resin with different content are studied using field emission scanning electron microscope JSM-7000F. The acceleration voltage is 10kV. Two specimens with neat CNF and CNF 20% reinforced epoxy ester resin are investigated. The specimens used for SEM observation are cured in the circumstance of 40°C for 2 days until the weight keeps still.

2.2.3. Tensile shear test. Tensile shear tests were performed on an Imada compact tensile/compression testing machine, to clarify the maximum strength of the material. Test pieces are prepared following the JIS K 6850:1999 standard, which is shown in Figure 1. The mixture colloid of CNF and resin were coated onto an aluminium film with a thickness of 2mm. Specimens are made by overlapping two aluminium film at 12.5±0.5mm length. To investigate the effect of humidity on the mechanical property of the coating, specimens are prepared under two environment humidity condition of 32.78RH% and

97.30RH%. According to the study of L. Greenspan [15], $MgCl_2$ and K_2SO_4 are used to control the environment humidity. The chemicals and the specimens are placed in a sealed container with a hydrometer. 8 specimens are prepared for each condition. The concentration and the solidification conditions of specimen are shown in table 2.

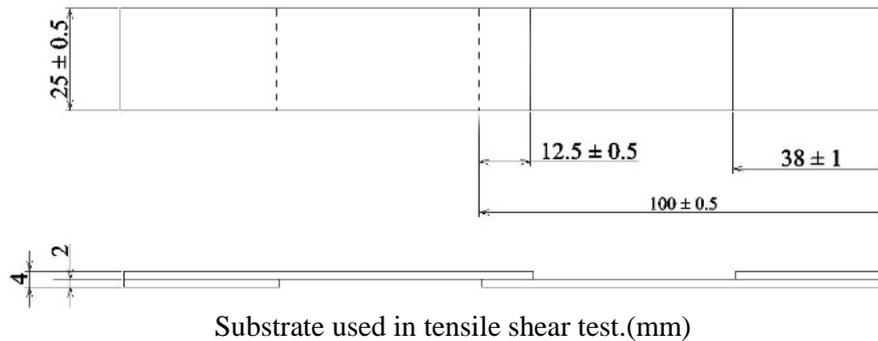


Figure1. Shape of the substrates used in tensile test (a) and tensile shear test (b).

Table 2. Conditions used in the preparation of test pieces.

Matrix	CNF content/ wt.%	Solidification conditions	Quantity of test pieces
Epoxy ester resin/ Alkyd resin	0	45 × 10Day	8 pcs each
	2.5		
	5	+	
	10	25°C/32.78RH% × 10Day	
	20	25°C/97.30RH% × 10Day	

All the tensile shear tests were carried out in the room environment (at a temperature of 20~25 °C and a relative humidity that ranges between 25~40 %) and deformation speed was set to 0.015 mm/s.

3. Results and discussion

3.1. SEM observations of the dispersion state of CNF

The morphology of neat CNF and CNF reinforced waterborne epoxy ester with CNF content of 20wt.% were examined by SEM under 10kV accelerating voltage. Figure 2 and Figure 3 shows the SEM image of at different magnifications respectively. In Figure 2, severe aggregation of CNF is found and non-aggregated CNF with a diameter of several tens of nm is confirmed. High aspect ratio of CNF is observed, but the length of the fiber cannot be determined from these images. In the case of CNF composites film (20wt.%), fiber like morphology with nearly equal diameter is confirmed, from which CNF is supposed to be well distributed in the resin. The morphology is considered to be a fiber aggregation coated by the resin. As a result, more information could not be obtained above magnification of 2000×.

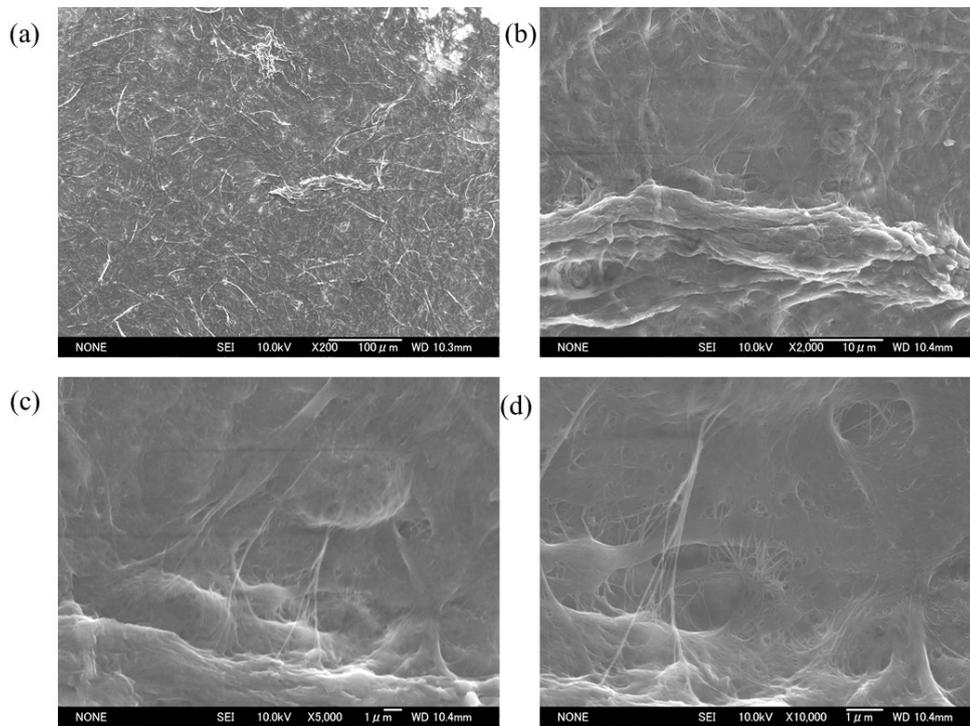


Figure 2. Surfacial SEM photograph of neat CNF at magnifications: (a) 200×, (b) 2000×, (c) 5000×, (d) 10000×.

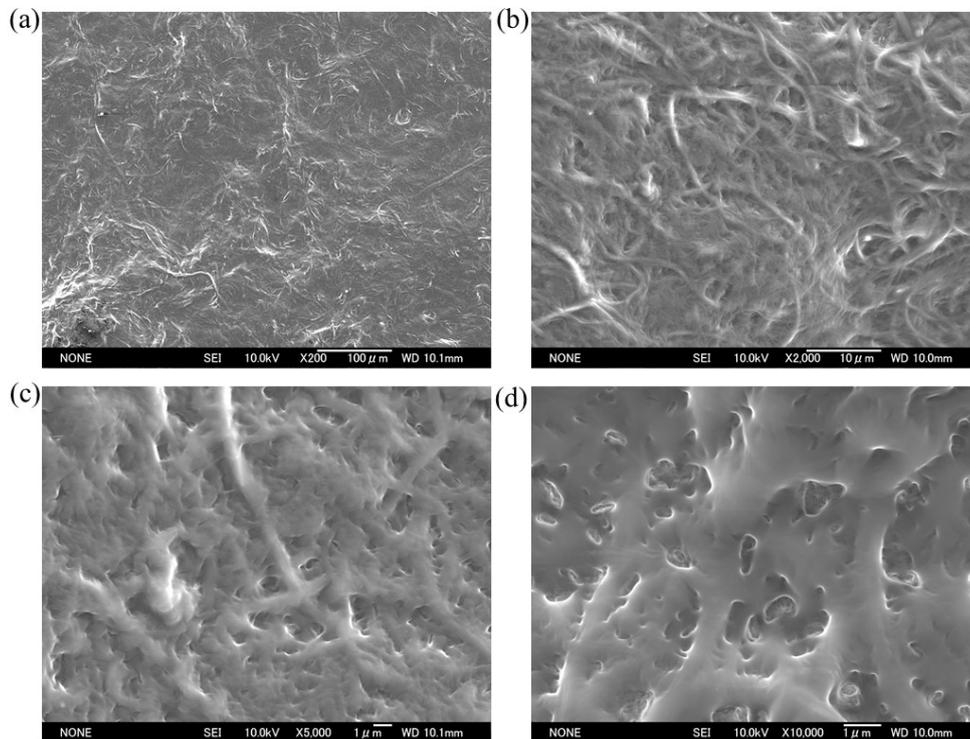


Figure 3. Surfacial SEM photograph of 20wt.% CNF reinforced epoxy ester at magnifications: (a) 200×, (b) 2000×, (c) 5000×, (d) 10000×.

3.2. Result of Shear tensile test

3.2.1. Stress-strain curve. Representative curves of shear stress-strain curve of Epoxy ester matrix and Alkyd matrix specimen at relative humidity 32.78%, are shown in Figure 4. In order to make further investigation, Maximum stress, strain at Max. stress and deformation energy are sort out in Figure 5 and 6 separately. The maximum stress in both kinds of matrix increase with the CNF addition level, and the effect on epoxy ester matrix seems is bigger than alkyd matrix. As regards to strain at Max. stress in epoxy ester, it is bigger than neat resin when CNF content is lower than 20wt.%. On the other hand, a monotonous decrease with the CNF content is found in alkyd matrix.

The CNFs are expected to be well compatible with epoxy ester matrix than alkyd matrix due to the fact that both the resin and the CNF surface contain hydroxyl functional groups and the hydrogen bonding between phases can occur. This interaction might induce an effective stress transfer from the matrix to CNF. But the stress improvement is at the expense of the elongation values. Tensile shear test of neat resin is very unstable at high humidity, which result in a boost in energy caused by irregular strain. Epoxy ester matrix has bigger deformation energy than alkyd matrix in low humidity, although deformation energy dramatically decreases in high humidity, also has compatible humidity as alkyd matrix. Deformation energy of epoxy ester matrix increases with CNF content, when CNF content is not more than 10wt.% at relative humidity 32.78% but decreases or not change very much at relative humidity 97.30%. In the case of alkyd matrix, CNF content 5wt.% shows the highest deformation energy without reference to humidity.

3.2.2. Observation of fracture surface. Example of fracture surface in tensile shear test bounded with CNF reinforced waterborne epoxy ester, is shown in Figure 7 in ascending order of CNF content (2.5, 5, 10, 20 wt.%). As the content is very small a relatively smooth resin like fracture was seen in CNF 2.5wt.%. At CNF content 5wt.%, CNF became in dominant, inside failure was observed due to the increase of the CNF. When CNF content increase further, there is more chance that CNF present in the interface of coating and the substrate, which result in interface failure and fiber pull out. This is consistent with the relation between deformation energy vs. CNF content in Figure 6 that deformation energy reaches peak when fiber pull out appeared at CNF10wt%.

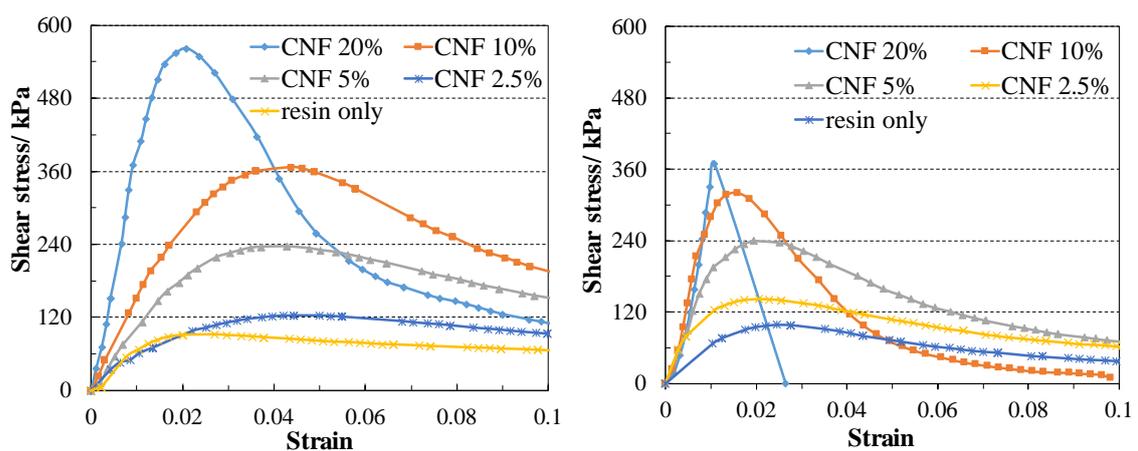


Figure 4. Stress-strain curve of shear tensile test (a) Epoxy ester matrix; (b) Alkyd matrix.

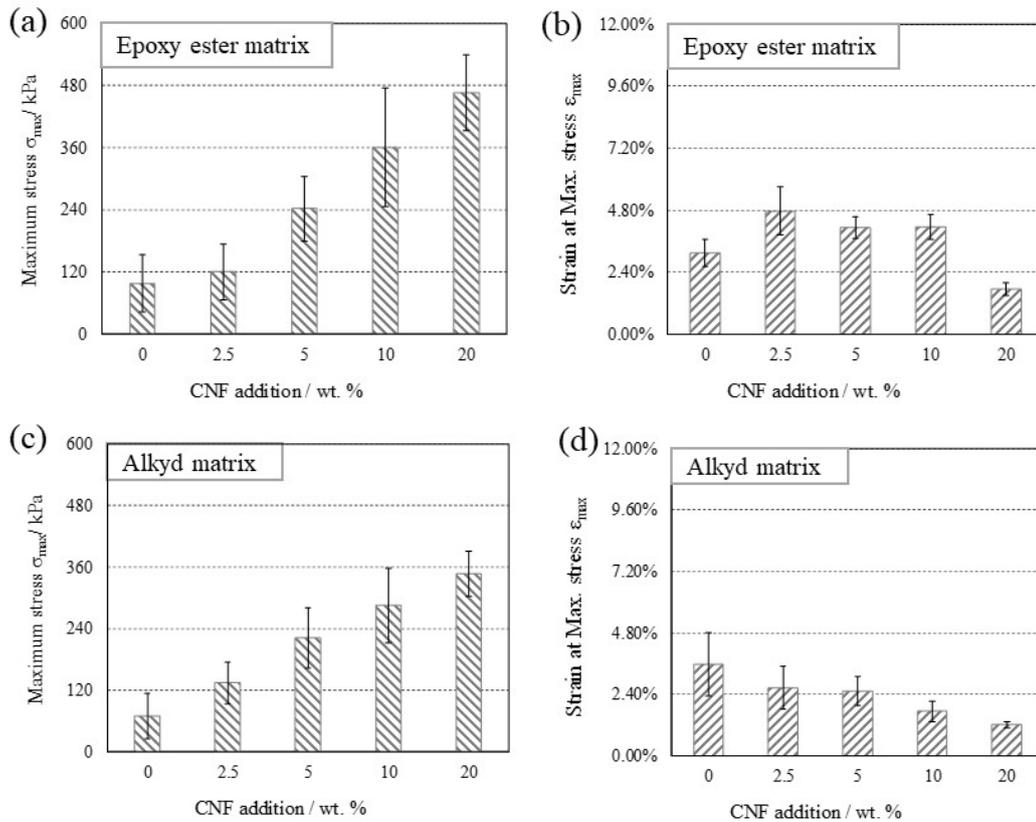


Figure 5. (a), (b) and (c), (d) are Max. strength and Strains at max. strength of Epoxy ester matrix and Alkyd matrix specimen at with various CNF respectively.

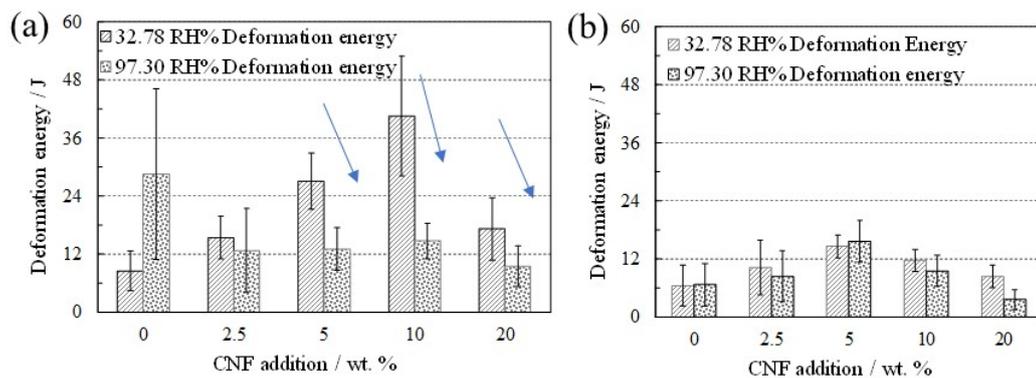


Figure 6. Deformation energy vs. CNF content of (a) Epoxy ester matrix; (b) Alkyd matrix at relative humidity 32.78% and 90%.

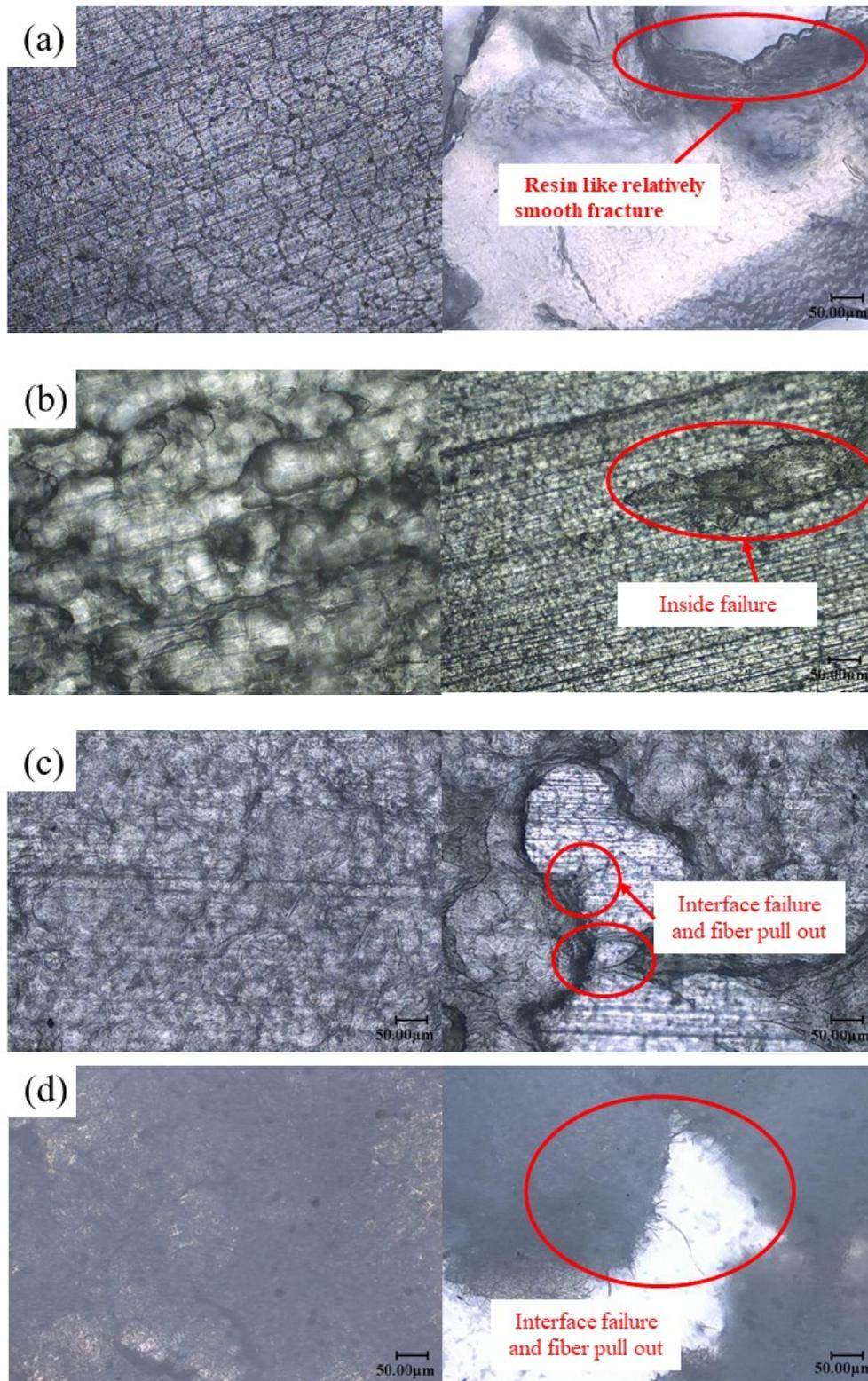


Figure 7. Fracture in tensile shear test pieces made at relative humidity 32.78% with various CNF content (2, 5, 10, 20 wt.%). Left column shows the flat part of the fracture while the right shows the part with intense deformation.

4. Conclusions

The aim of this study is to investigate the effect of CNF on different matrix resin (vinyl-modified epoxy ester resin emulsion and epoxy-modified alkyd emulsion). The study ends with the following observations and conclusions: (1). The maximum stress in both kinds of matrix increase with the CNF content at the expense of their percentage elongation values; (2). Deformation energy reach to the maximum at the content of CNF 10wt.% and 5wt.% for epoxy ester matrix and alkyd matrix respectively. The CNFs are expected to be well compatible with epoxy ester matrix than alkyd matrix due to the fact that it has more hydroxyl functional groups, thus has more hydrogen bonding between phases. This interaction might induce an effective stress transfer from the matrix to CNF respectively. On the other hand, more content of CNF increases the risk of exposure to the interface or sever aggregation occurred, which result in a strength decrease. With the increase of content of CNF, resin like failure, inside failure and interface failure mode are observed in sequence. (3). Relative humidity has considerable influence on the reinforcement effect of CNF in Epoxy ester matrix, but insignificant effect on alkyd matrix. Epoxy ester matrix has bigger deformation energy than alkyd matrix in low humidity, although deformation energy dramatically decreases in high humidity, also have compatible humidity as alkyd matrix.

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