ENHANCEMENT OF INTERLAMINAR FRACTURE TOUGHNESS AND DAMAGE MECHANISMS ANALYSIS IN CFRPS REINFORCED WITH SPRAYED NANO PARTICLES

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ABSTRACT

Three kinds of nano particles were synthesized and prepared, including nano boehmite (AlOOH)、nano Fe_2O_3 and nano montmorillonite. The purity, morphology and size of these nano particles were investigated by the methods of FTIR, XRD, SEM, and TEM, respectively. Instead of dispersing nano particles into epoxy resin, then compounding epoxy resin and carbon fibre, in this paper, those nano particles were sprayed evenly on the surface of every prepregs to enhance interlinear fracture toughness(ILFT) of the laminates, which could improve delamination resistance. In this way, difficulties in dispersing nano particles can be avoided, also, this method need not to change curing process. For comparison, baseline samples with neat prepregs were also prepared. Three groups of carbon fiber reinforced polymers (CFRPs) were fabricated. To verify nano particles sprayed between lamina can toughen CFRPs, and to analyse damage mechanisms, The end-notched flexure (ENF) test was taken at room temperature (RT, 293k) and at low temperature (LT, 77k). Low temperature environments were achieved by immersing the loading apparatus and specimen in liquid nitrogen (77 K). The fracture surfaces were examined by SEM. The results indicated that three kinds of nano particles were pure crystalline and high purity. There were obvious difference on morphology, nano boehmite (AlOOH) was needle-like and sheet, nano Fe_2O_3 was cubic, and nano montmorillonite was lamellar. The ENF test results showed that ILFT of unidirectional CFRPs increased significantly when sprayed nano particles at RT, and at 1wt%, CFRPs sprayed with nano boehmite (AlOOH)、nano montmorillonite achieved max fracture toughness, 931 J/m^2, increased by 29.3%, and 870 J/m^2, increased by 20.8%, compared to that of the CFRPs without nano particles, respectively. But At LT, enchancing CFRPs with sprayed nano particles is not so efficient, because cryogenic toughening mechanisms are different significantly from that at RT.

1. INTRODUCTION

With their excellent modulus and strength, carbon fiber-reinforced epoxy (CFRPs) composites have been increasingly employed for a variety of high-performance applications especially in aerospace industry [1]. CFRPs composites' innovative design possibilities, and advanced manufacturing methods make it easier to improve properties [2]. Over the past few decades, CFRPs' application is changed from secondary bearings to main bearings. For the purpose of light weight in the next-generation reusable launch vehicles (RLVs), One important potential application of CFRPs is in the construction of cryogenic fuel tanks [3]. Reusable fuel tanks are exposed to a wide range of temperatures during service, before fueling, the tank is under room temperature(RT), but if fuelled, the tank would be exposed to extremely low temperature (LT). Under above-mentioned service environment, CFRPs damage may occur, include microcrack and interlinear delamination etc, these damages can extend,

and result in failure in composite structures [4]. More seriously, Undetected subsurface delamination can lead to catastrophic failures without any external signs [5]. Therefore, the weak interlinear mechanical properties of the CFRP laminates limit their applications. Especially for cryogenic composite structures, knowledge of the resistance to interlinear fracture of composite laminates at cryogenic temperatures is essential to establish design allowable and damage tolerance guidelines.

Delamination of the laminates may occur due to high shear and peeling stress concentrations, and the fracture toughness under shear loading is a critical interface property to evaluate the potential crack growth, in order to improve the interlinear mechanical properties of CFRP laminates, increasing the Mode II fracture toughness is a effective method, also, in this paper, Mode II fracture toughness is treated as the evaluation criterion to determin which material performed well on the resistance of delamination. The End-notched flexure (ENF) specimen has been widely used to obtain Mode II interlinear fracture toughness (ILFT) [5].

To achieve high interlinear mechanical properties of CFRP laminates, various method have been proposed [6], such as three-dimensional weaving, interleaving, hybridization, stitching, short fibers and z-pinning. These methods have been proved to be effective in alleviating delamination and subsequent buckling in CFRP laminates, but unfortunately, thoese methods may decrese in-plane mechanical properties to a certain extent [7].

Now, great attention has been paid to the employment of some nanofillers in either the whole matrix or the interlinear interface of CFRPs, with the hope of remedying the relatively low interlinear strength of CFRPs [8]. Nanofillers can be carbon nanotube(CNT), grapheme, etc. CNT can increase the contact area and adhesion to the epoxy matrix and therefore to improve CFRP interlinear fracture toughness. Recently, some researchers reported that inorganic nanoparticles can be good choice, which can provide a number of desirable mechanical and barrier properties for CFRPs, owing to their unique mechanical and tribological properties, and high surface area to mass ratio et al [9]. Reserch indicates that inorganic fillers can affect cure shrinkage, exotherms, thermal and electrical conductivity, machinability, compressive, hardness, flexural, and impact strength of composites. Modifier particle's kinds, size, and shape affect CFRPs' properties a lot.

In order to reseach enhancement of CFRPs' interlinear toughness and analysis damage mechanisis, in this paper, three kinds of nano particles were synthesized and prepared, including nano boehmite (AlOOH)、nanoFe_2O_3 and nano montmorillonite, instead of dispersing nano particles in the whole matrix, an alternative approach has been developed, which employed solvent spraying to achieve a uniform dispersion of nano particles, this method has many advantages. Nano particles were sprayed between two prepregs, then multi-scale reinforcement of composite laminates were achieved, and it won't change curing process, improving interlinear properties directionally. This paper focus on delamination behavior of CFRPs laminates modified by nano particles at RT and LT, and ENF tests were taken, fracture morphology of all samples was also studied.

2. EXPERIMENTAL

2.1 Materials

T700 Polyacrylonitrile (PAN) carbon fibers made by TORAY in Japan were used as reinforcement of composite materials, The resin and fiber densities are 1.2 and 1.80g/cm3, respectively and the nominal fiber volume was 56.8%. Absolute ethanol (99.7%), 4,4'-diaminodiphenyl methane (DDM) were obtained from Sinopharm Chemical Reagent Co, Al(NO3)3•9H2O and urea were obtained from Tianjin Damao Chemical Reagent in China. Nano montmorillonite was purchased from USA NANO TEC.

2.2 Preparation of nano particles

Three kinds of nano particles were synthesized and prepared, including nano boehmite (AlOOH)、nano Fe_2O_3 and nano montmorillonite. For nano montmorillonite, we get it from USA NANO TEC, so in this paper, only two kinds of nano particles were synthesized.

In a typical synthesis procedure, 30g of Al(NO3)3•9H2O was firstly dissolved in 60mL of deionized water. After 9.1g of urea was added, the mixture was stirring mildly at 50C° for 1h. The obtained transparent solution was then transferred into a Teflon-lined autoclave of 150 mL and heated at 160C° for 24h. After being cooled to room temperature naturally, the sample was filtered and washed with distilled water until its pH was neutral. The synthetic boehmite (AlOOH) nanosheets obtained above was dissolved in ethanol.

Fe_2O_3 NPs were prepared using a modified procedure firstly, in a typical synthesis, 3.6 g PVP and 2.424g $Fe(NO_3)_3 9H_2O$ were dissolved in 108 mL of DMF, then the obtained solution was transferred into an Teflon-lined autoclave of 150 mL and heated at 180 ℃ for 30 h. After reaction, the autoclave was cooled to room temperature naturally. The resulting Fe2O3 particles were collected by centrifugation (12,000 rpm, 20min), and washed several times with deionized water and absolute ethanol to remove impurities. 40 mg of Fe_2O_3 NPs was mixed with 0.2 mL APTES and 40 mL absolute ethanol in a round-bottom 100 mL glass flask with a Teflon-coated magnetic stirrer bar, followed by vigorous stirring for 24 h at 25 ℃ [10]. The colloids were washed with absolute ethanol to remove excess APTES.

2.3 Fabrication of CFRPs toughened by nano particles

Nano particles were firstly mixed with ethanol respectively, and mass ratio were 1:500, The reason for choosing ethanol as dispersive medium based on the analysis of surface wetting, since prepregs are made up of polymer matrices, which have low energy surfaces. Studies showed that, ethanol drop have smaller contact angle, which means better dispersion, also, ethanol is non-poisonous, and volatile, toghter these factors determine the choice. However, some one may argue that the solvent could interact with the resin, affecting its curing behavior, and possibly resulting in a detrimental effect on interlinear fracture properties. The work by Mujika et al. [11] interestingly showed that such degradation was absent when using ethanol, since they get similar mode II fracture toughness when comparing neat samples with those obtained by spraying ethanol only on the prepreg layers.

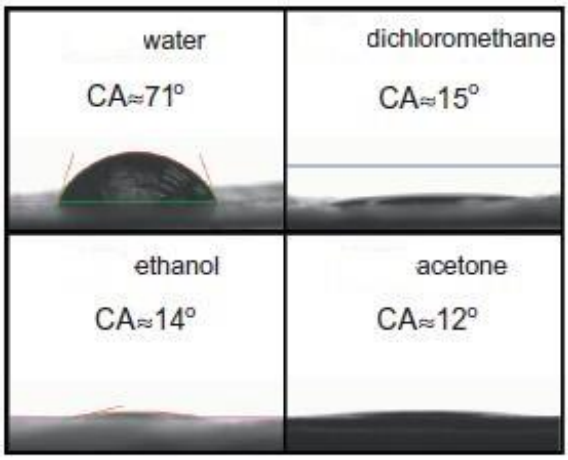

Figure 1: Contact angle of different solvent on prepreg surface.

Then ultrasonicat those three kinds of mixtures for 1.5 hour to ensure good dispersion, after that, cut prepregs in 300 × 300 mm, and lay 16 pieces, a stacking of 16 prepreg sheets in the 0° direction was made. Note that, An airbrush was used to spray the nano particles dispersion between the plies, in addition, nonadhesive polytetrafluoroethylen (PTFE) film was put in the center plane to create an initial pre-crack. Before the curing process, the laminates were heated at 85℃ for 1 h to allow the ethanol to evaporate, then cured at 100C° for 2h, 160C° for 4h to get the CFRPs. The mass percent of nano particles is 0, 0.5, 1, 1.5, 2 wt%.

Figure 2: Process of CFRPs manufacture

2.4 ENF tests

According to ASTM D7905/D7905M-14, CFRPs specimens for the ENF test were prepared. The specifications of the ENF specimens are shown in Fig.1. The specimen width (20 mm), thickness (2H= 2 mm), and span to precrack length ratio (2L/a0≈3.75) were held constant, and the specimen length and span were l=100mm, 2L=75mm, respectively. To create a starter delamination crack, a 50 μm thick nonadhesive polytetrafluoroethylen (PTFE) film was inserted along one edge of the mid-plane prior to processing to provide the initial midplane delamination crack during the filament winding process. Insertion of the 50 μm thick PTFE film created a resin-rich region ahead of the insert. The resin-rich region will affect the measured initiation value of Mode II interlinear fracture toughness. In this study, a precrack was propagated ahead of the insert beyond the resin-rich region. The precracking was performed by pushing a wedged razor blade into a clamped ENF specimen [12].

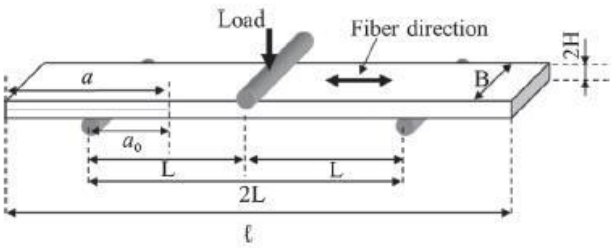

Figure 3: Schematic illustration of specimen for ENF tests.

Figure 4: Experimentl setup for RT/LT ENF tset

2.5 Characterizations

Fourier transform infrared (FTIR) spectrum for AlOOH nanosheets and nano Fe_2O_3 was obtained using an EQUINOX55 FTIR spectrometer. The crystal structure was identified by X-ray diffraction (XRD, Panalytical X'Pert Pro MPD, Netherlands, Cu Ka radiation, I=1.54 Å), TEM were performed using a Tecnai G220 S-Twin transmission electron microscope to research the morphology of the prepared AlOOH nanosheets and nano Fe_2O_3.

A testing machine (Comten Industries, model 945KRC0300; loading unit, PSB5000; digit controller, DMC 026S) with C-Tap 3.0 software is used to test interlinear fracture toughness of modified CFRPs. Low temperature environments were achieved by immersing the loading apparatus and specimen in liquid nitrogen (77 K). The ENF specimens were loaded in a three-point bend –test fixture, Stroke control mode was used with a crosshead speed of 1.0 mm/min. Displacement of the crosshead was measured with a linear voltage differential transducer, and the instantaneous load (P) and displacement (δ) were recorded by a computerized data acquisition system. The values were taken from an average of five specimens. After bending test, all specimens were split open in order to examine the fracture surfaces by scanning electron microscopy (SEM).

3. RESULTS AND DISCUSSION

3.1 Analysis of synthesized nano particles

In order to obtain information about synthesized nano particles' purity, morphology, size and composition, FTIR, XRD, SEM, TEM analysis were used respectively. In our laboratory, nano boehmite (AlOOH)、nano Fe_2O_3 were synthesized, and nano montmorillonite was purchased, it's purity and other parameters can be found from manufacturer, so in this paper, we focus on nano boehmite (AlOOH) and nano Fe_2O_3.

FTIR spectrum Analysis

To measure purity of the synthesized nano AlOOH and nano Fe_2O_3, An EQUINOX55 FTIR spectrometer was used.

In the FTIR spectrum of the synthesized AlOOH nanosheet shown in Figure 5, all the absorption bands at 478, 629,752, 885, 1157, 1635, 3099 and 3392 cm-1 are in good agreement with the values of those reported in the literatures, which prove that AlOOH is prepared. The intensive bands at 3099 cm-1 can be described to the νs O-H stretching vibration of AlOOH nanosheet. The strong, broad band at 3329 cm-1 is assigned to stretching vibration of -OH group in the hydroxide structure as well as in physically absorbed water. The band at 1157cm-1 is believed to be δas Al-O-H mode, and the shoulder at 1639 cm-1 is taken for the bending mode of absorbed water. The other bands located in 478, 629, 752 cm-1 belong to AlO6 vibration mode. From the FTIR spectrum, no absorption bands from the other phase are observed, which indicate the high purity of the synthesized AlOOH nanosheet samples.

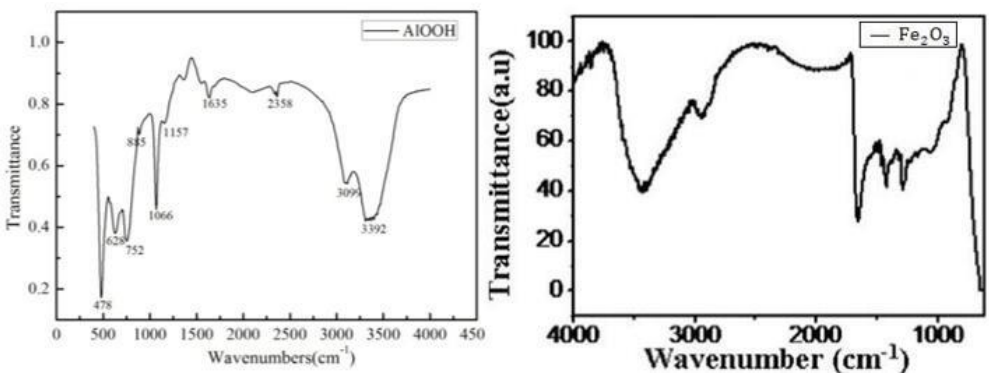

Figure 5: The FTIR spectra of the synthesized AlOOH and Fe_2O_3 samples.

In the FTIR spectrum of the synthesized nano Fe_2O_3, a strong but rather broad band and a weak band were observed at 3450 cm-1 and at 1600 cm-1. They arise from the vibration stretching of O–H groups. The adsorption band at 2900 cm-1 can be assigned to C–H groups. The bands at 1651 cm-1, 1464 cm-1, 1424 cm-1 and 1292 cm-1 are respectively related to C=O, C–N, –CH– and $-CH_2-$ groups of the backbone of PVP. The result of FTIR spectra confirms the formation of the PVP stabilizing Fe_2O_3 NPs.

XRD Analysis

By XRD measurement, the crystalline phase of synthesized AlOOH nanosheets was examined. The result shown in Figure 6 revealed that the diffraction peaks of the prepared product can be perfect in good agreement with the standard value of orthorhombic γ-AlOOH, which indicates the prepared product is high purity AlOOH. The sharp peaks (020, 120, 031, and 200) in the XRD spectrogram indicate the obtain γ-AlOOH is high crystalline.

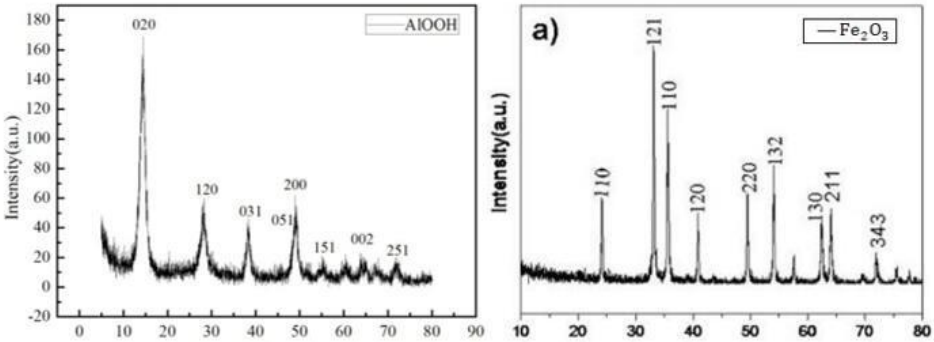

Figure 6: XRD spectrum of synthesized AlOOH and Fe_2O_3 samples.

The XRD pattern of the prepared nano Fe_2O_3 is shown in Figure 6, where all the diffraction peaks in the patterns are readily indexed to a pure rhombohedral phase of α-Fe_2O_3. The result indicates the high purity of our products, and the well-resolved diffraction peaks reveal the good crystallinity of the α- Fe_2O_3.

SEM and TEM Analysis

The morphology of the prepared nano boehmite (AlOOH)、nano Fe_2O_3 and nano montmorillonite were investigated by scanning electron microscope (SEM) and Transmission electron microscopy (TEM). The SEM picture shown that the prepared AlOOH nanosheets had overlapped lamellar morphology and unambiguous boundaries between lamellar, AlOOH nanosheet samples can be distinguished. According to the measuring results from the TEM as shown in Figure 7, the thickness of the AlOOH sample is about 22 nm.

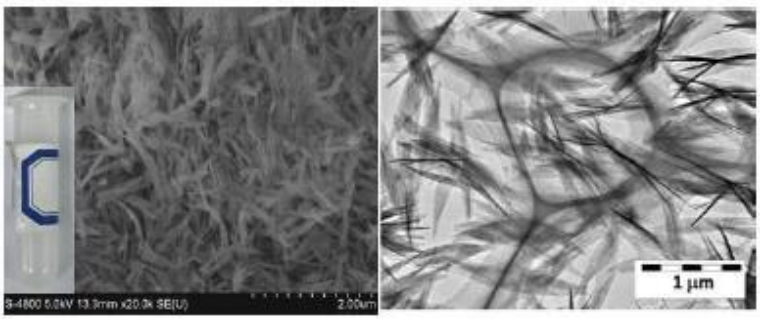

Figure 7: SEM and TEM images of synthesized AlOOH nanosheet

SEM image (as shown in Figure 8) reveals that the obtained Fe_2O_3 is cubic and their size is about 40 nm. TEM image of the obtained Fe_2O_3 shows that these Fe_2O_3 are monodisperse. The dispersed solution of the Fe_2O_3 is very stable, and it can exist at least for one month.

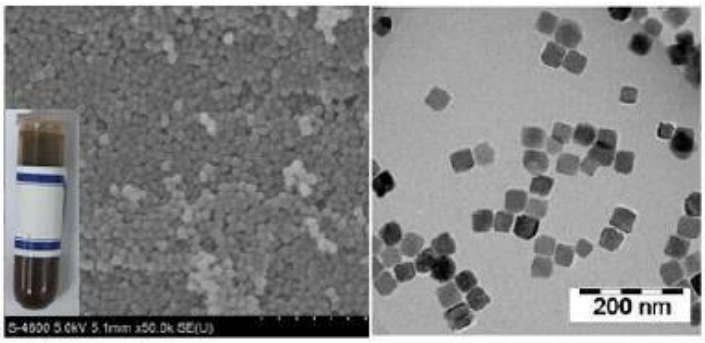

Figure 8: SEM and TEM images of synthesized nano Fe_2O_3

SEM image (as shown in Figure 9) reveals that nano montmorillonite have lamellar structure, after ultrasonic in alcohol, we can obtain well dispersed lamellar montmorillonite.

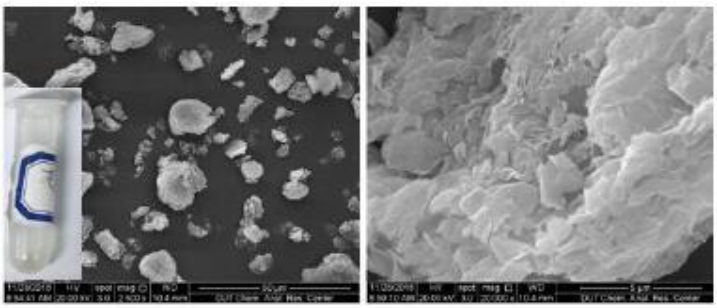

Figure 9: SEM images of nano montmorillonite

3.2 Mode II interlinear fracture toughness of CFRP sprayed with nano particles at room temperature

The ENF test specimens were prepared, and performed with the aid of a three-point bending apparatus fixed on a universal test machine at a testing rate of 1.0 mm/min according to the ASTM D7905/D7905M-14. The instantaneous load (P) and displacement (δ) were recorded by a computerized data acquisition system as shown in Figure 10. In the part (I) of Figure 10, the first inflection point represented that the precrack has begun to propagate and the part (II) represented that the specimen has been broken completely. The load value on the first inflection point was used to calculate mode II interlaminar fracture toughness by formula (1). The expression for the mode II interlaminar fracture toughness for ENF beam can be given as

$$G_{\mathrm{II}c} = \frac{9P_c\delta a^2}{2W(2L^3+3a^3)} \times 10^3 \quad \textbf{(1)}$$

where, GIIC--mode II interlaminar fracture toughness, J/m^2; Pc--critical force for mode II fracture, N; δ--displacement of loading roller during testing perpendicular to the plane of the specimen, mm; a--visually determined crack length after precrack toughness test, mm; W--specimen width, mm; L--specimen half-span, mm.

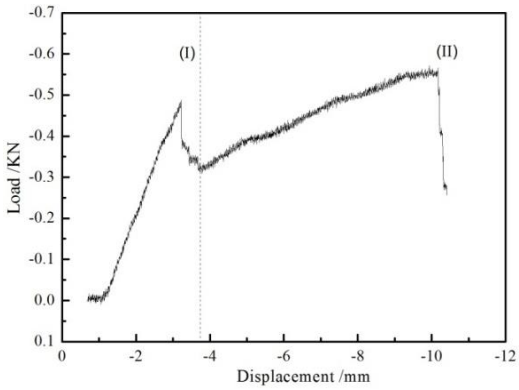

Figure 10: Typical load-displacement curves from ENF test

The delamination fracture of specimens after three-point bending test was observed as shown in Fig.7 (a) and (b), which load-displacement relationship corresponded to Figure 10 (I) and (II), respectively. From Figure 11 (a), no fiber breakage was been observed, but only the precrack propagation. The delamination fracture and fiber breakage have appeared distinctly in Fig.7 (b).

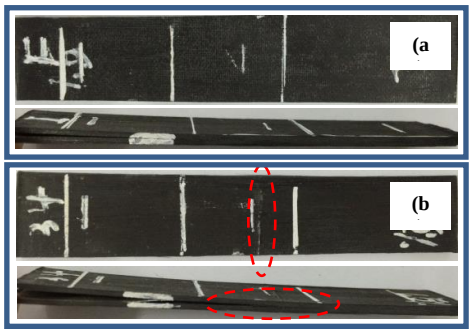

Figure 11: The photograph of top and side of a fractured ENF test specimens; (a) beginning of the precrack propagation; (b) the broken specimen.

To analysis enhancement effects of CFRPs' Mode II interlaminar fracture toughness at RT, three groups specimens were prepared, and conducted for ENF test, every group corresponding to a kind of CFRPs sprayed with nano particles, which have five sub-groups, and sub-groups corresponding to 0, 0.5, 1, 1.5, 2 wt% nano particles (calculated by areal density). Results were shown in Figure.

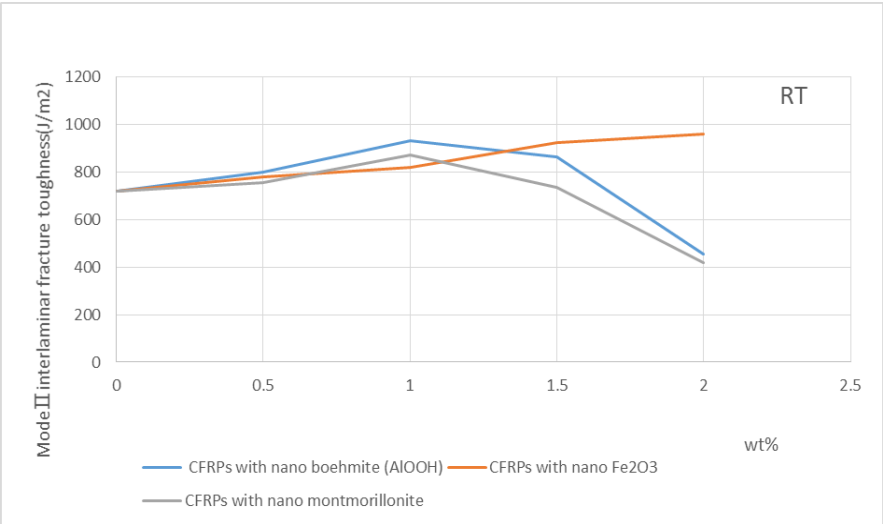

Figure 12: Mode II interlaminar fracture toughness of CFRPs sprayed with different content nano particles at RT

Figure 12 indicates that the mode II interlaminar fracture toughness value increased between 0-1wt% (we called them stage Ⅰ), in this stage, the trend of CFRPs sprayed with nano particles is same. CFRPs sprayed with nano boehmite (AlOOH)、nano montmorillonite achieved max fracture toughness, 931 J/m^2, increase by 29.3%, and 870 J/m^2, increase by 20.8% compared to that of the CFRPs without nano particles, respectively. For CFRPs sprayed with nano Fe_2O_3, it also achieved relatively high fracture toughness, 820 J/m^2, increase by 13.9%. This benefit from nano particles' special morphology. Nano particles were embed into interlayer' epoxy resin, or attach themselves to carbon fibre, these behaviors can form bridge, join-sheet and other reinforcing structures, which enhance interface strength and increase mode II interlaminar fracture toughness, Another effect factor is microcracks deflecting, in the existing manufacturing process, micro defects are unavoidable, including inclusion、void and resin enrichment. These defects may induce microcracks, nano particles' introduce can largely restrain microcracks, and deflect crack propagation. But on the other hand, from Fig 8 we can see, with same content, enhancement of nano boehmite (AlOOH) is more efficient than nano montmorillonite. The reason is that nano boehmite (AlOOH)' needle-like structure and sheet structure is better than nano montmorillonite' lamellar structure. Both needle-like structure and sheet structure can play a bridging role, they fit adjacent layers together, so, during the process of delamination, pulling out or breaking may absorb some energy, and this is against delamination, so CFRPs sprayed with nano boehmite (AlOOH) performed better than CFRPs sprayed with nano montmorillonite.

When content of nano particles increased beyond 1wt%(we called them stage II), From the Figure 12, fracture toughness of CFRPs sprayed with nano boehmite (AlOOH) and nano montmorillonite decreased, the reason is that, nano particles are poorly dispersed in the epoxy resin, and the aggregate of nano particles would lead to stress concentrations or defects in the composites and bring about the decrease of fracture toughness value. Note that, nano Fe_2O_3 is different from the other two, even on the stage II , nano Fe_2O_3 content's increase make the CFRPs perform better instead of the decrease of fracture toughness. As explained above, three kinds of nano particles have different morphology, which not only influence interface strength, but also have different dispersibility. Nano Fe_2O_3 have special cubic morphology, smaller size, and have the best dispersibility (as shown in Figure 13). So, with nano Fe_2O_3 content increasing, fracture toughness increased, too. Besides, the SEM images of fracture interface (as showen in Figure 14) indicates that CFRPs sprayed with AlOOH is anomalous, while CFRPs sprayed with nano Fe_2O_3 is in alignment, which means uniform interfacial strength, and benefits for improving ILFT. But this doesn't mean the more the better, overmuch nano Fe_2O_3 also results in aggregate. In fact , for nano Fe_2O_3, more experiment is needed.

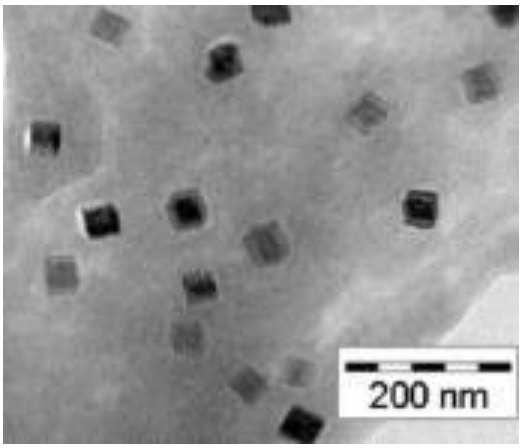

Figure 13: Well dispersed nano Fe_2O_3

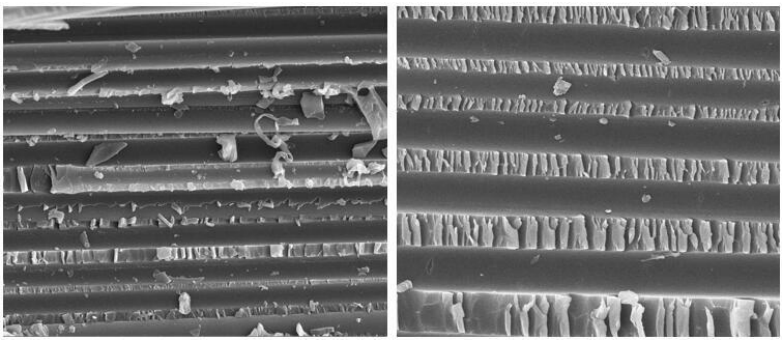

Figure 14: The fracture interface of the CFRPs sprayed with nano AlOOH and CFRPs sprayed with nano Fe_2O_3

3.3 Mode II interlinear fracture toughness of CFRP sprayed with nano particles at low temperature

Mode II interlaminar fracture toughness of CFRPs with the nano AlOOH at low temperature was also been investigated by immersing the loading apparatus and specimen in liquid nitrogen (77 K) and the results were shown in Figure 15.

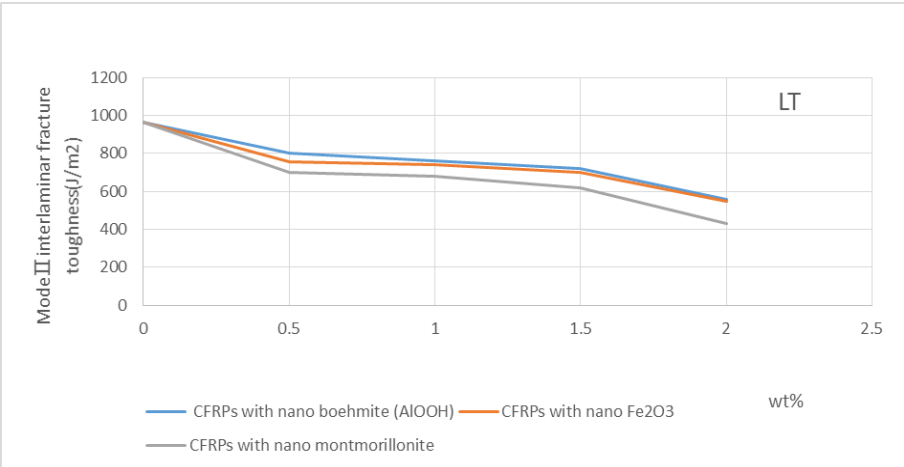

Figure 15: Mode II interlaminar fracture toughness of CFRPs sprayed with different content nano particles at LT

As Fig indicates, at LT, Mode II interlaminar fracture toughness without nano particles is 33.75% higher than it at RT, the introduce of nano particles decreased fracture toughness, further more, the more content of nano particles, the worse CFRPs performed. It is because that the ILFT is determined by morphology and temperature, especially cryogenics. Cryogenic toughening mechanisms are different significantly from that at RT. At RT, CFRPs sprayed with nano particles benefit from these particles' special morphology, but at LT, thermal residual stress, polymeric matrix' properties and material defects were main influencing factors. The thermal contraction of epoxy resin is about an order of magnitude greater than for carbon fiber, when exposed at 77 K, thermal contraction' mismatching induced thermal residual stress, and thermal residual stress in the radial direction at fiber-matrix interface may contribute to the increase of the interfacial strength and higher interface resistance, which results in higher ILFT than RT. But the fiber-matrix interfacial adhesion strength was decreased when the nano particles were included, which resulted in the lower ILFT of CFRP. Besides, nano particles can lead to the formation of defects, which decreased the cryogenic ILFT of CFRP. So, the introduce of nano particles decreased fracture toughness at LT. The Fig also indicates that nano boehmite (AlOOH) performed best and nano montmorillonite performed worst.

4. CONCLUSION

Three kinds of nano particles were synthesized and prepared, including nano boehmite (AlOOH)、nano and nano montmorillonite. The purity, morphology, size and composition of those nano particles were investigated by the methods of XRD, SEM, TEM and FTIR, respectively. The results indicated that synthesized nano particles are high pure. Those nano particles were sprayed evenly on the surface of every prepregs to enhance interlinear fracture toughness(ILFT) of the laminates. At RT, ENF tset results indicated that ILFT of CFRPs increase firstly, and at 1wt% CFRPs sprayed with nano boehmite (AlOOH)、nano montmorillonite achieved max fracture toughness, 931 J/m^2, increase by 29.3%, and 870 J/m^2, increase by 20.8%, compared to that of the CFRPs without nano particles, respectively.Then, with content of nano particles increasing beyond 1wt%, ILFT of these two kinds of CFRPs decreased, the reason is that, nano particles are poorly dispersed in the epoxy resin, and the aggregate of nano particles would lead to stress concentrations or defects in the composites and bring about the decrease of fracture toughness value, while nano Fe_2O_3 is different from the other two, nano Fe_2O_3 content's increase make the CFRPs perform better, because nano Fe_2O_3 have special cubic morphology, smaller size, and have the better dispersibility.. But this doesn't mean the more the better, overmuch nano Fe_2O_3 also results in aggregate. At LT, ILFT of CFRPs without nano particles is 33.75% higher than it at RT, the introduce of nano particles decreased fracture toughness. It is because that the ILFT is determined by morphology and temperature, especially cryogenics. Cryogenic toughening mechanisms are different significantly from that at RT. At LT, thermal residual stress, polymeric matrix' properties and material defects were main influencing factors. Thermal contraction' mismatching induced thermal residual stress, and thermal residual stress in the radial direction at fiber-matrix interface may contribute to the increase of the interfacial strength and higher interface resistance, which results in higher ILFT than RT. But the fiber-matrix interfacial adhesion strength was decreased when the nano particles were included, which resulted in the lower ILFT of CFRP. Besides, nano particles can lead to the formation of defects, which decreased the cryogenic ILFT of CFRP. So, the introduce of nano particles decreased fracture toughness at LT. Consequently the introduction of nano particles at a proper content can significantly enhance the ILFT at RT, nano boehmite (AlOOH) and nano Fe_2O_3 are good choices, but at LT, enchancing CFRPs with sprayed nano particles is not so efficient.

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