

Toughening of Carbon Fiber Reinforced Composites with Nanorubber for Advanced Industrial Applications

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ABSTRACT

This paper investigates the effects of nano carboxylated acrylonitrile butadiene rubber (CNBR-NP) and micron sized acrylonitrile butadiene rubber (NBR-NP) on the mechanical properties of carbon fiber reinforced polymer composites (CFRP) with commercial dicyandiamide cured epoxy as matrix. The mechanical characteristics of both systems were systematically studied. Nano-size dispersion of rubber dramatically improved the Mode I delamination fracture toughness (G_{IC}) of the CFRP by 250% and its Mode II fracture toughness (G_{IIc}) by 80% with the addition of rubber.

Keywords: nanorubber, toughening, rheology, mechanical properties

1 INTRODUCTION

Epoxy resins are widely used in many different applications for advanced composites in automotive and aerospace industries due to their outstanding thermal and mechanical properties. However, the drawbacks such as low fracture toughness and notch sensitivity due to their brittle nature limits their application as structural materials.

Due to the brittle nature of highly crosslinked epoxy resins, scientists have been toughening the formulations with nano and micron sized elastomeric particulates for many years. Toughness and impact resistance of fiber reinforced composites can be improved by achieving an even dispersion of elastomeric particles within the matrix and the toughness increment is dependent on the toughener used, its concentration and the size of the particles [1,2,3].

In this research, dicyandiamide-cured epoxy matrices were toughened with micron sized acrylonitrile butadiene rubber (NBR-NP) and nano sized carboxylated acrylonitrile butadiene rubber (CNBR-NP). Solid acrylonitrile butadiene rubber (NBR), with high content of acrylonitrile is a suitable toughener. This is due to the high content of acrylonitrile imparting better compatibility between NBR and the epoxy resin [4,5]. CNBR rubber imparts even better compatibility compared to NBR rubber due to the presence of polar groups on the particle surface [6].

This study constitutes a systematic research on the mechanical properties for two different acrylonitrile butadiene based nanorubber toughened systems.

2 EXPERIMENTAL DETAILS

2.1 Materials

The epoxy resin used was liquid DGEBA resin (Araldite LY1556) with epoxide equivalent weight of 188. Dicyandiamide (DICY) (Dyhard D50EP) was used as the curing agent. A difunctional urone with (Dyhard UR500) was used as the accelerator. The nanorubbers used in this study were acrylonitrile butadiene rubber NBR-NP (VP401) which is a super fine butadiene powdered sulfide rubber, with acrylonitrile content 26% and nano powdered rubber VP501, Carboxylic Nitrile Butadiene UFPR with acrylonitrile content of 26%. Both nanorubbers were received in powder form, mainly in agglomerated form at diameters of 100 μ m from SINOPEC, Beijing Research Institute of Chemical Industry (BRICI). Fumed silica (FS) received from Aerosil ($D_{50} = 1 \mu$ m) was used in some of the formulations to modify the rheological behavior for composite processing. 200 GSM 2 Twill bidirectional carbon plies (Sigmatex UK Ltd) with a fibre volume fraction of 58% were used to produce CFRP laminates. The matrix formulations used are as given in Table 1.

| CODE | NBR-NP | CNBR-NP | FS |
|--------------|--------|---------|----|
| R | - | - | - |
| R/ x FS | - | - | x |
| x CNBR-NP/ R | - | x | - |
| x NBR-NP/ R | x | - | - |

Table 1: Formulations used within experimental work, in phr (parts per hundred of DGEBA), all formulations contain 100 grams of DGEBA, 14 grams of DICY curing agent and 6 grams of accelerator

2.2 Sample preparation

To improve the dispersion of nanoparticles in the matrix, several mixing techniques including mechanical mixing (speed mixing, high shear mixing and triple milling) and ultrasonic dispersion were investigated. The processing facility for both rubber systems are as given in Figure 1.

CNBR-NP modified epoxy resin matrices were prepared by the following procedures. The nanorubber was dispersed in DGEBA matrix and the blend was speed mixed. 0.25 to 1 phr of Aerosil fumed silica was added to epoxy matrix together with the nanorubbers in selected CFRP samples, which considerably increases the viscosity of matrix to prevent the leakage of resins during curing in autoclave under high pressures. The blend was triple milled for 6 times at room temperature (RT).

NBR-NP modified epoxy resin matrices were prepared by the following procedures. After drying the nanorubber and speed mixing with the DGEBA matrix, the blend was stirred using a Silverson high shear mixer in an ultrasonic bath for 4 hours at RT. This processing method is more suitable for micron-sized particles, which was proved by microstructural analysis.

For both rubbers after the mixing stage, the blends were magnetically stirred and degassed at 70°C inside a glass flask under vacuum. After degassing the curing agent and accelerator were added and the final mixture was speed mixed. Hand lay-up technique was used to produce the CFRP laminates. The CFRP laminates were heated to 120°C at a heating rate of 0.5°C/min and hold for 1 hour at this temperature before cooling down to room temperature in an autoclave under 6 atm pressure. Specimens for mechanical testing were cut using a water jet and were carefully polished.

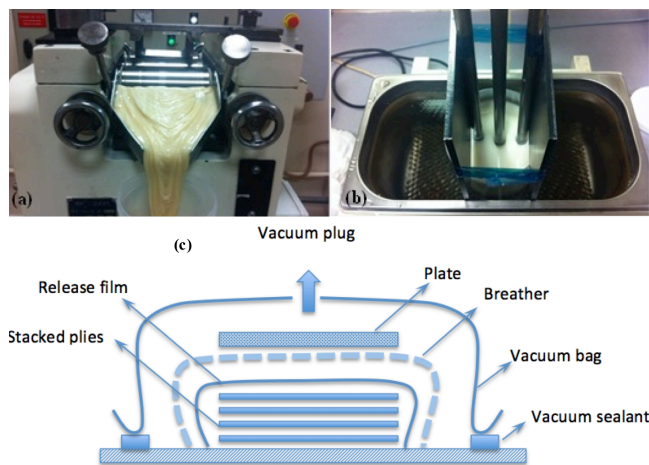


Figure 1: (a) Triple milling of CNBR-NP blend, (b) High shear mixing and ultra-sonication of NBR-NP blend, (c) Vacuum bagged hand laid carbon fiber plies ready to be autoclaved

3 CHARACTERIZATION

3.1 Double cantilever beam (DCB) fracture toughness (Mode I)

Mode I delamination toughness, G_{IC} test of CFRP laminates was performed following the EN6033 standard with Zwick Z50 machine at a crosshead speed of 10mm/min perpendicular to the delamination surfaces.

A strand of release film was placed on the mid carbon ply during hand lay-up process to create a 30mms long pre-crack. 3 DCB specimens with dimensions of 250-25-3 mms were cut from the demolded CFRP laminates with a water jet. Screw able grips were bonded onto the two sides of the specimen end having the pre-crack as in Figure 2. The edges of the testing samples were coated with correction fluid and marked for a clear reading of the crack length. The pre-cracked sample was loaded continuously by peel forces until a total propagated crack length of approximately 100 mm was achieved. The interlaminar fracture toughness energy was calculated from the propagated crack length and the applied energy determined from load-cross head displacement diagram. Data is based on the average of 5 test samples.

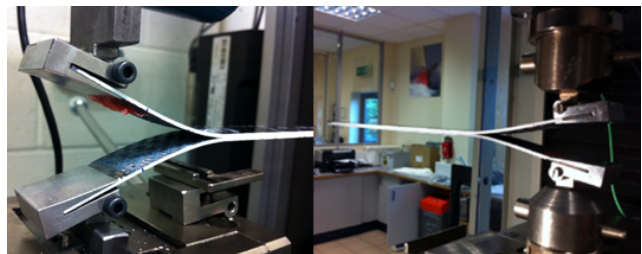


Figure 2: Experimental Apparatus of G_{IC} Test

For calculation of the interlaminar fracture toughness energy, the following formula was used:

$$G_{IC} = [A/(aw)]10^6 \quad (1)$$

Where:

G_{IC} is the fracture toughness energy, in J/m^2

A is the energy to achieve the total propagated crack length, in Joules (Integration of the area under the load-cross head displacement diagram)

α is the propagated crack length, in mms (final crack length minus initial crack length), w is the width of the specimen, in mms

3.2 Mode II interlaminar fracture toughness (end notch flexure test)

The effect of nanorubber on the interlaminar shear fracture toughness (G_{IIC}) of CFRP was studied by end notch flexure tests following the AITM 1-0006 standard with Zwick Z50 machine at a crosshead speed of 1mm/min. The samples were positioned on a three-point bend fixture with a total span of 100 mm, so that an initial crack length of 34-35 mm was achieved. Figure 3 shows the dimensions and the geometry of the ENF sample. The width of the specimens is 25 ± 0.2 mm and the total length is greater than 110 mm.

The load and crosshead movement were recorded continuously. After the maximum load was observed, the sample was unloaded. G_{IIC} values were calculated as the fracture toughness energy at the initial maximum load sustained by the laminate.

G_{IIC} was calculated according to the protocol [7,8] by:

$$G_{IIC} = \frac{9Pa^2 \delta 1000}{2B[\frac{1}{4}L^3 + 3a^3]} \quad (2)$$

where G_{IIC} is the Mode II fracture toughness energy in J/m^2 , P is the load (N), δ is the crosshead displacement at the crack growth onset (mm), B the specimen width (mm), a the initial crack length (mm), L the span length (mm). 5 samples were tested for each formulation and the data is based on the average value.

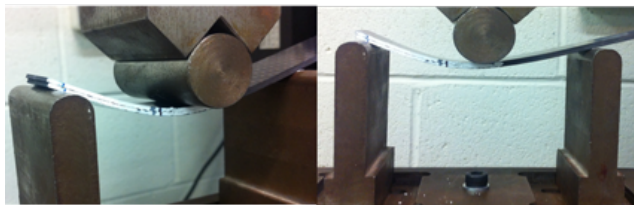
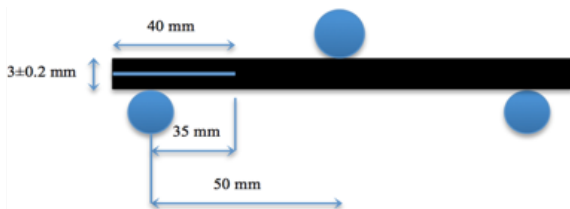


Figure 3: Experimental apparatus of G_{IIC} test

4 RESULTS AND DISCUSSION

4.1 Double cantilever beam (DCB) fracture toughness (Mode I)

The Mode I fracture toughness data of CFRP with neat epoxy resin matrix and CFRP with rubber modified resin matrix are as given in Table 2. There is a great increase in G_{IC} values with nanorubber addition for both rubber systems. NBR-NP and CNBR-NP have almost the same toughening effect on the matrix.

Figure 4 represents the load vs. crosshead displacement curves of the CFRP laminates. Maximum load and crosshead displacement attained before fracture increases constantly with CNBR-NP rubber addition to the structure. Figure 4 also shows that the force linearly increases until it reaches the maximum force value, and then gradually decreases with zigzag shape in the propagation stages. This could be due to the variations of resin-rich regions or fiber-rich regions along the longitudinal directions, misalignment of the fibers and voids within the structure [9,10].

| Sample | G_{IC} (J/m^2) | σ (J/m^2) | % Increase |
|--------------|----------------------|----------------------|------------|
| R/ 1FS | 392 | 32 | - |
| 5CNBR-NP/ R | 517 | 24 | 32 |
| 10NBR-NP/ R | 803 | 29 | 100 |
| 10CNBR-NP/ R | 809 | 15 | 100 |
| 15CNBR-NP/ R | 950 | 102 | 142 |
| 20CNBR-NP/ R | 1305 | 105 | 250 |

Table 2: G_{IC} Test data, σ = Standard Deviation

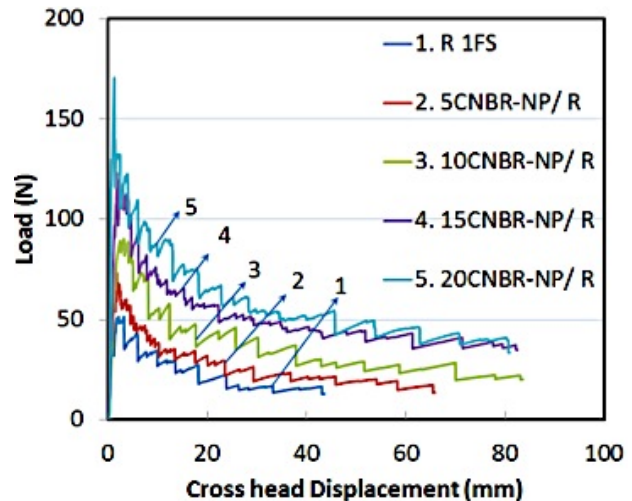


Figure 4: Load vs. displacement graph of CFRP with CNBR-NP modified matrix

4.2 Mode II interlaminar fracture toughness (end notch flexure test)

The Mode II fracture toughness data of CFRP with neat epoxy resin matrix and CFRP with rubber modified epoxy resin are as given in Table 3. 10 phr of CNBR-NP addition increases the G_{IIC} toughness of neat epoxy resin laminates for about 37% whereas 10 phr of NBR-NP addition to the matrix increases the G_{IIC} toughness for about 60%. Mode II interlaminar energy values are higher than Mode I values due to fibers resisting the crack growth better since they are perpendicular to the crack opening. Figure 5 shows the corresponding force vs. crosshead displacement curves of the samples. The force increases until the crack initiates and propagates, which then results in a decrease in force. Once the decrease in force was observed, the test was stopped. It is obvious that with an increase in rubber concentration both the maximum load attained before fracture and the crosshead displacement till crack propagation increase.

| Sample | G_{IIC} (J/m^2) | σ (J/m^2) | % Increase |
|--------------|--------------------------|-------------------------|------------|
| R/ 1FS | 1090 | 103 | - |
| 5CNBR-NP/ R | 1156 | 56 | 6 |
| 10NBR-NP/ R | 1739 | 69 | 60 |
| 10CNBR-NP/ R | 1489 | 89 | 37 |
| 15CNBR-NP/ R | 1823 | 122 | 67 |
| 20CNBR-NP/ R | 1976 | 46 | 81 |

Table 3: G_{IIC} Test data, σ = Standard Deviation

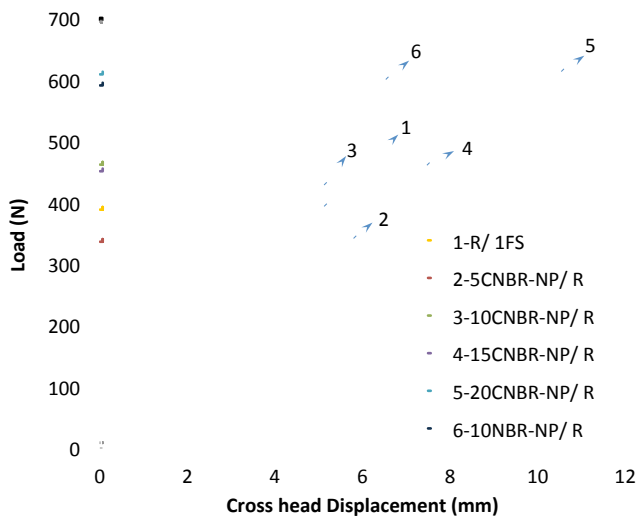


Figure 5: Load vs. crosshead displacement graph for CFRP with CNBR-NP/ R and NBR-NP/ R matrices

5 CONCLUSIONS

In the present study, two different acrylonitrile based nanorubber modified resin structures are introduced from the mechanical aspects. G_{IC} and G_{IIC} toughness increased steadily for about 250% and 80% respectively with rubber loading for both systems, with no significant effect of single particle size being observed.

This study constitutes a comparison of two novel nanorubber modified CFRP systems. The most efficient dispersion technique was identified for each rubber system and the mechanical properties of the carbon fiber laminates processed with these nano-modified matrices were studied in detail.

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