MIXED MODE FRACTURE TOUGHNESS OF CRACKED SPECIMENS MADE OF NANOMODIFIED EPOXY RESIN

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Abstract

In the present work the effects of nanoclay addition on fracture behaviour of an epoxy resin under mixed mode (I plus II) loadings are studied by analysing the results from Single Edge Notch Bending (SENB) specimens. The results allow to conclude that, for weight contents lower than 5 wt.%, nanomodification significantly enhances the fracture toughness of the epoxy resin upon the entire range of mixed mode loadings, the improvements being dependent on the mode mixity ratio.

Experimental results are later compared to the theoretical predictions based on different, well acknowledged, mixed mode fracture criteria. The results from specimens made of pure epoxy are well predicted, almost independently of the approach used for the synthesis. Conversely, as far as the results from specimens made of nanomodified polymer are concerned, the agreement with theoretical predictions is much poorer. This can be thought of as linked to the emergence, of different damaging mechanisms due to nanomodification depending on the mode mixity.

1 Introduction

In the last years, nanocomposites have been given a lot of attention due to their enhanced properties in a wide range of fields from mechanics to physics, from thermal to optical. In particular, great attention has been paid to polymer based nanocomposites in which the higher improvements can be reached with very low nanofiller contents, reducing the problems related to high volume fractions and costs [1].

In the field of structural materials, a smart application of nanotechnology is concerned with the production of composite laminates in which the polymer matrix is loaded with a nanofiller. Unluckily, the research performed to date, aimed at translating resin properties to the fiber reinforced composites, has met with changing fortunes. Quaresimin and Varley [2] reported ‘‘selective’’ improvements in toughness properties of carbon/clay-modified epoxy laminates due to the clay distributions: mode I toughness was slightly decreased while mode II slightly increased with respect to the values for neat epoxy laminates. Rice *et al.* [3] reported a 12% improvement in modulus for aerospace composite materials at 2 wt.% of organosilicate, without improvements in other mechanical properties. Quaresimin *et al.* [4] reported significant enhancements in the fracture toughness and crack propagation threshold of clay modified epoxy. On the other hand, the behaviour of clay-modified laminates was almost comparable to that of the neat epoxy ones.

With the aim to enhance the properties of such laminates, precise studies must be conducted on the biphasic material made up of the polymer matrix and the nanofiller, to exactly comprehend the interactions between the two phases, the damaging mechanisms and the material behaviour under different loading conditions.

In this study, an epoxy resin matrix has been filled with a montmorillonite nanoclay, and the effects of nanomodification have been examined for Single Edge Notch Bending (SENB) specimens, in terms of fracture toughness under mixed mode loadings.

After a brief description of the adopted materials and the production process, the testing methodology will be introduced and the experimental results, obtained on neat epoxy and on nanomodified resin, will be discussed.

2 Materials and specimens preparation

In this study, a DGEBA-based epoxy resin (EC157 with W152LR hardener) from ELANTAS-Camattini has been used as polymer matrix. In addition a montmorillonite clay, Cloisite 30B® from Southern Clay Products, has been used. 30B nanoclays are characterised by 1 nm thick lamellae, lateral dimensions from 70 to 150 nm, and average d-spacing of about 18,5 Å.

The specimens have been manufactured according to a four-step preparation process:

1. dispersion of the filler within the resin;
2. degassing and moulding of the obtained blend;
3. milling and surface polishing;
4. manual tapping and fatigue propagation up to a 10 mm long crack.

Initially, in order to get an as good as possible dispersion and distribution of the filler, nanoclays have been dispersed within the polymer resin through shear mixing followed by sonication. The shear mixing process has been carried out with a DISPERMAT TU shear blender from VMA-Getzmann, at an average rate of 2000 rpm for about 1 hr. The sonication process, instead, has been carried out using a HIELSCHER UP 200s Sonicator, set on 140W (70% of the maximum power) and a Duty Cycle of 50%, for 10 min.

After sonication, the hardener has been added and the obtained blend has been mixed at low rate (1000 rpm) for further 5 min.

As a major drawback of the shear mixing, a large amount of air was trapped in the matrix. Thus, in order to prevent void traps and bubbles in the specimens, a degassing process has been carried out. To this end, a low-vacuum pump has been used to induce a very low pressure in the resin pot, promoting bubbles explosion. 1 hr of degassing process was enough to obtain a clear and translucent nanomodified resin, which was later slowly poured into silicone rubber moulds.

In order to match the geometric recommendations by [5], once de-moulded, the specimens have been milled, to cut out the higher surface where inclusions and voids could have been present and polished up to the final thickness.

Using a razor blade the specimens have been later pre-cracked by manual tapping. Finally, 10 mm long cracks (half the specimen width, according to [5]) have been obtained from the artificial short cracks after some zero-to-tension-stressing fatigue cycles.

3 Testing and experimental results

All tests have been carried out by using a MTS 858 servo-hydraulic machine, equipped with a 2.5/25 kN load cell.

3.1 Tensile tests

Tensile tests on dog-bone specimens (dimensions: 2x15x110 mm) have been carried out to determine the failure stress, σ_R, the elastic modulus, E, and the Poisson ratio, ν, of the neat epoxy and nanomodified resin, by using a crosshead speed equal to 2 mm/min. A MTS 632.29F-30 extensometer has been used for accurate strain measurements. At least three specimens were tested for each material configuration. In all the performed tests failure took place in the centre of the specimen.

The effect of the weight content of Cloisite 30B® nano-additives upon the nanocomposite Young Modulus and Strenght is shown in Figure 1. It is noteworthy that the elastic properties of the nanomodified resin show a monotonic increment up to 7.6% for a nanoclay content of 5% wt. Conversely, the nanocomposite strength is decreased from 70.6 MPa (neat resin) to 52.6 MPa (3% wt nanoclay).

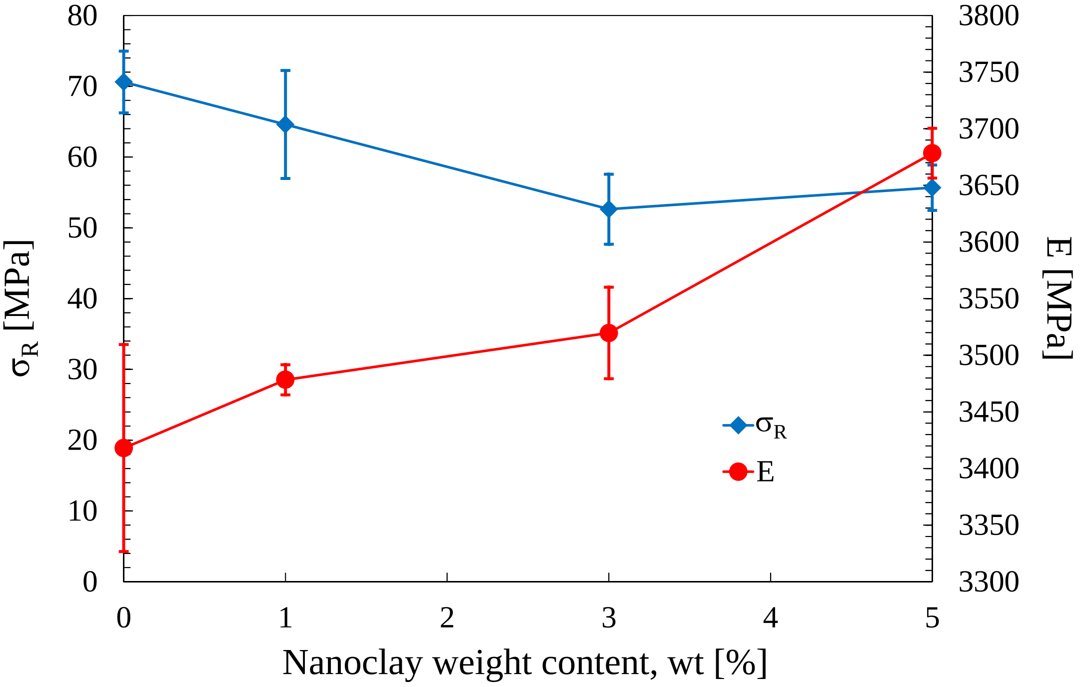

Figure 1. Results of tensile test on neat and nanomodified epoxy resin.

3.2 Single Edge Notch Bending tests

Pure mode I, pure mode II and mixed mode loadings tests have been carried out using a crosshead speed equal to 10 mm/min, as suggested in [5]. Single Edge Notch Bending (SENB) specimens have been used (see figure 2); at least three specimens for every loading condition and every filler fraction were tested.

The testing device consists of two steel plates, 18 mm thick, one fixed on the load cell, the other attached to a vertical moving ram. One or two pin supports can be mounted on each plate, so that the specimen can be loaded on precise points.

The pure Mode I loading tests have been carried out using the three point bending configuration shown in Fig. 3.a, with $L_3 = L_4 = 40$ mm. Accordingly, along the crack plane the bending moment is the maximum while the shear force is equals to zero, so that $K_{II} = K_{II}/K_I = 0$.

The pure mode II loading tests have been carried out using a four point bending configuration with span lengths $L_1 = L_4 = 30$ mm and $L_2 = L_3 = 40$ mm (see figure 3.b). This resulted in a skew-symmetric loading configuration, according to which the bending moment vanished along the crack plane, so that $K_{II}/K_I = \infty$.

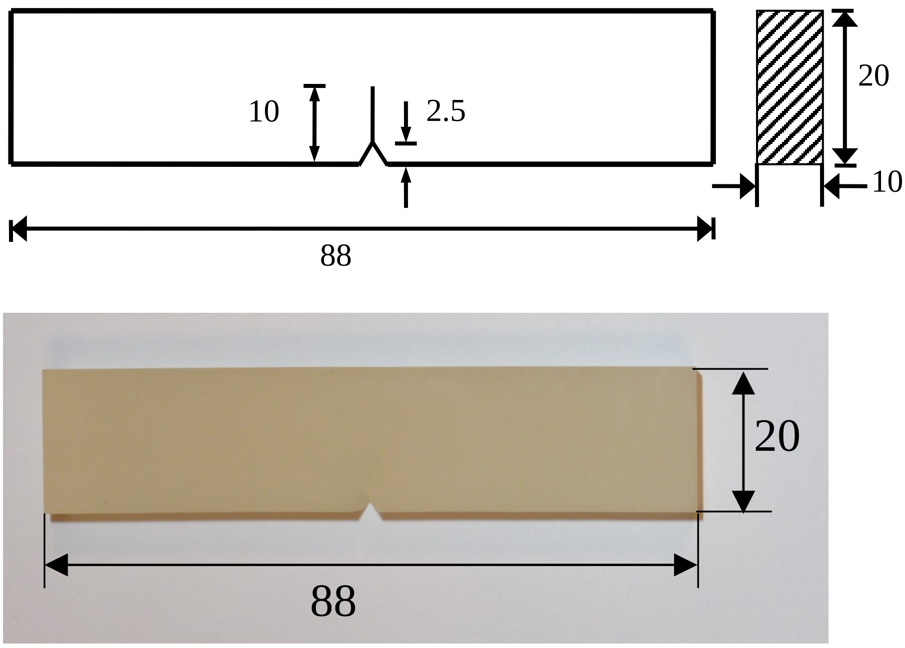

Figure 2. Single Edge Notch Bending (SENB) specimens used in the tests. Size in mm.

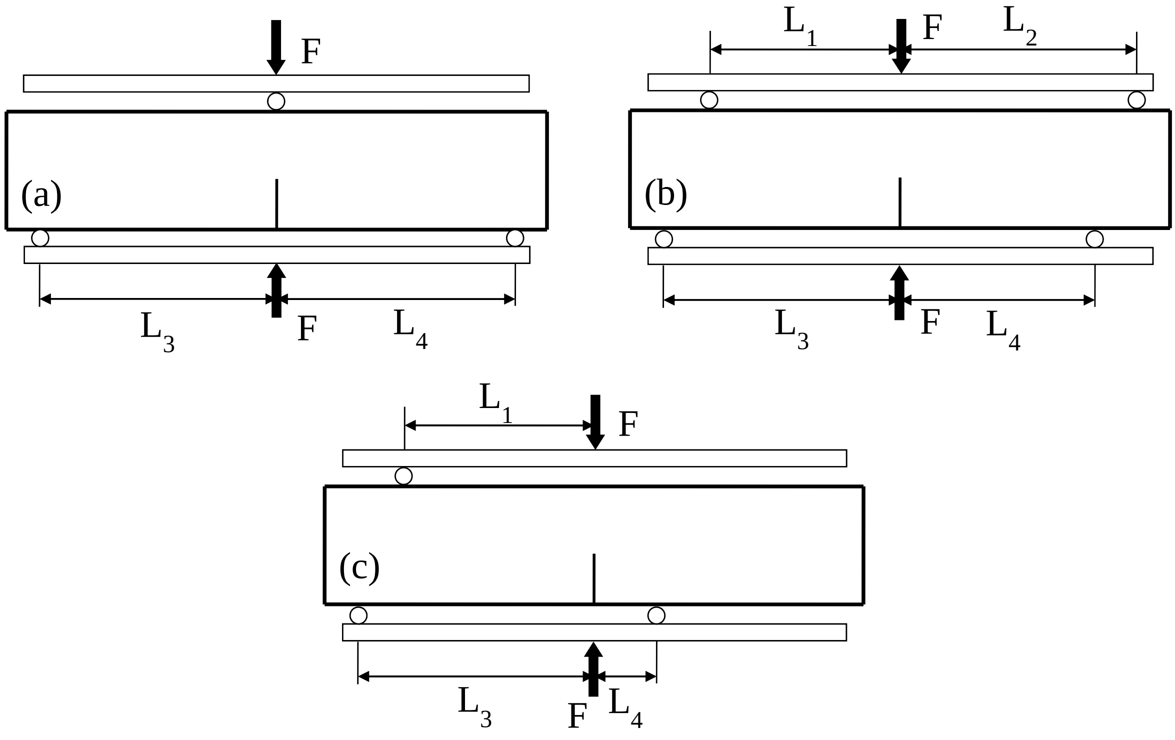

Figure 3. Three different loading configuration, which generate different loading conditions: (a) pure Mode I $K_{II}/K_I = 0$; (b) pure Mode II, $K_{II}/K_I = \infty$; (c) mixed mode, $K_{II}/K_I = 0.33$.

Finally mixed mode loading tests have been carried out with $K_{II}/K_I = 0.33$, using a three point bending configuration with span lengths $L_1 = 30$ mm, $L_3 = 40$ mm and $L_4 = 10$ mm (Fig. 3.c). This resulted in a K_{II}/K_I ratio equal to 0.33.

During all the tests the material exhibited a pure linear elastic behavior, the force - displacement plots being linear up to the fracture load. The fracture load considered was the peak load of every specimen.

The average value and the scatter band of all the experimental data obtained in this work are shown in Figure 4. It is evident that nanomodification results in a higher fracture toughness, independently of the loading mode. Moreover, based on the obtained results, the following relevant conclusions can be drawn:

- the highest fracture toughness improvements can be obtained under pure Mode I loading condition, with a maximum increment of 48.7% for 1% wt. content of nanofiller;
- the lower fracture toughness have been obtained for Mode II loading condition, with a maximum improvement of 22.5% for 3% wt. content of nanofiller;
- the mixed mode loading conditions $K_{II}/K_I = 0.33$ provides result similar to those of the pure mode I loading conditions, with a maximum improvement in terms of mode I and II fracture toughness, K_{IC} and K_{IIC}, for 1% wt. content of nanofiller.

Some pictures of fractured specimens are shown in figure 5. As it can be seen, Mode I loaded specimens fractured all along the initial crack plane (θ=0). Differently, the presence of mode II loadings gives rise to a crack tilting: for specimens under mixed mode loadings, $K_{II}/K_I = 0.33$, the fracture took place at an angle θ= 36-38° with respect to the crack line, while for Mode II loaded specimens the crack tilted at about 63-65 degrees.

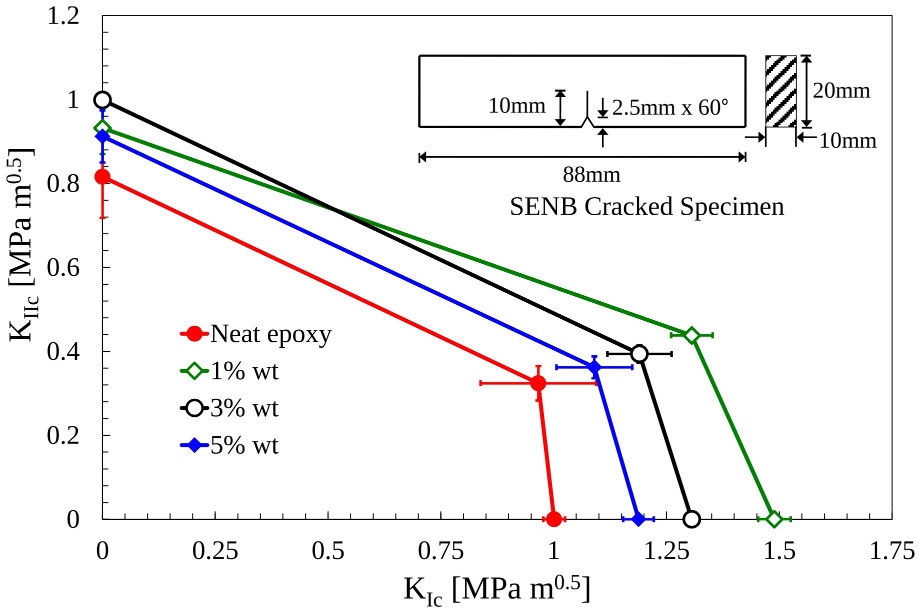

Figure 4. Comparison of fracture toughness results for different nanoclay contents and for different loading conditions.

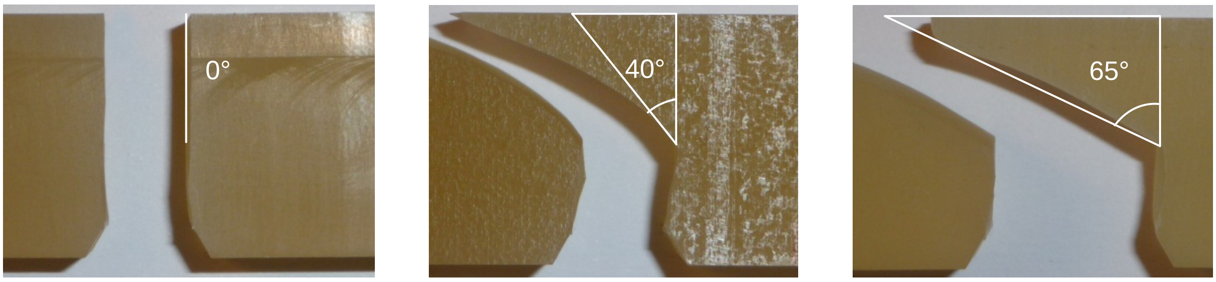

Figure 5. Fracture angles for Mode I, mixed mode and Mode II loading conditions, respectively.

Finally, the values of fracture toughness obtained in the present work were compared to four mixed mode fracture criteria: MTS [6], S-criterion [7], G criterion [8] and ASED criterion [9]. Figure 6-9 show a comparison between the experimental results and different fracture criteria.

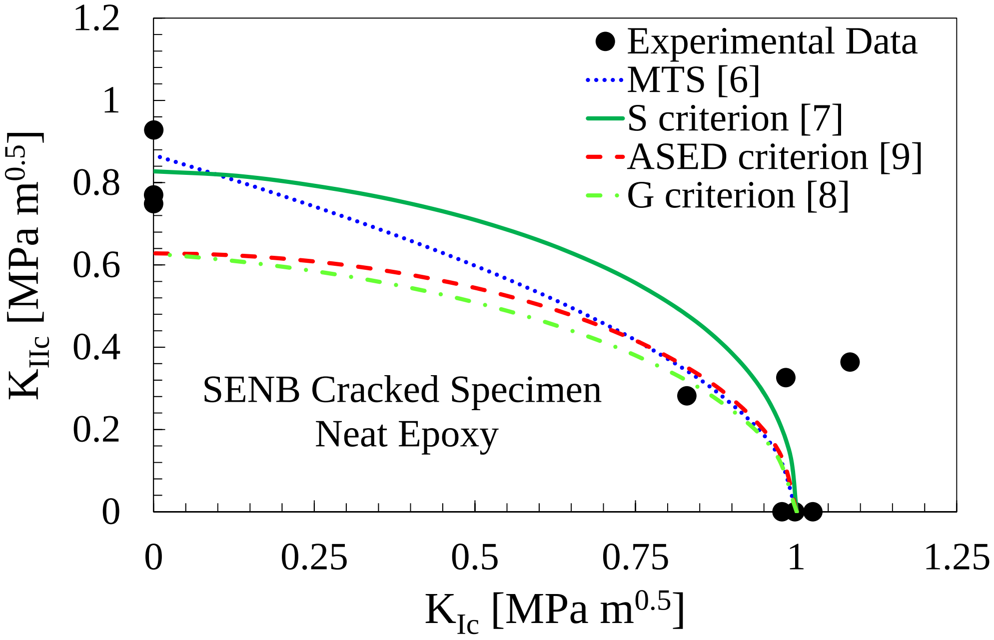

Figure 6. Comparison of fracture toughness predicted by different fracture criteria and test results for cracked specimens made of neat epoxy.

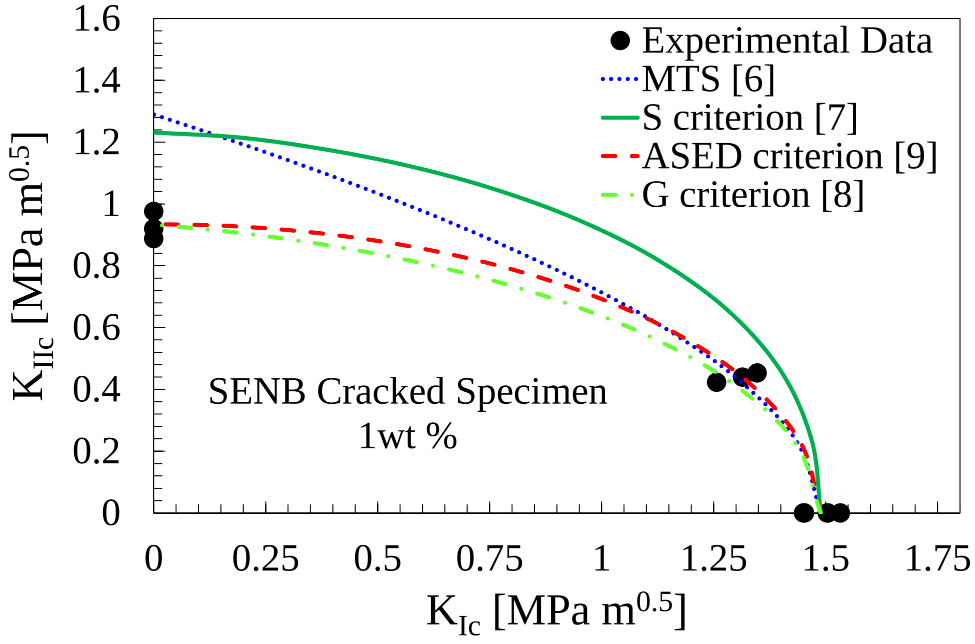

Figure 7. Comparison of fracture toughness predicted by different fracture criteria and test results for cracked specimens made of epoxy resin filled with 1% wt of nanoclays.

It is evident that, for the pure epoxy (figure 6), the S-criterion exhibits the best agreement with the experimental data. This is not true for nanomodified specimens, for which the difference between the predictions of S-criterion and the experimental results are higher, especially under pure mode II loading. Under mixed mode loadings, $K_{II}/K_I = 0.33$, the best agreement with the experimental data can be achieved by using, equivalently, the G-criterion or the ASED criterion, which provide very good predictions for 1% wt nanoclays filled specimens, rather independently of the mode mixity.

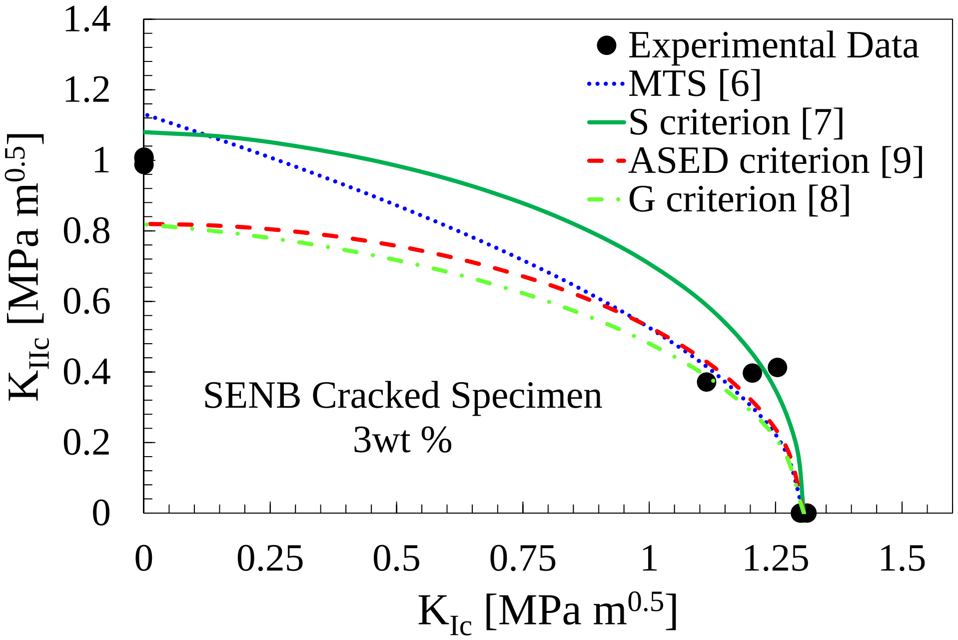

Figure 8. Comparison of fracture toughness predicted by different fracture criteria and test results for cracked specimens made of epoxy resin filled with 3% wt of nanoclays.

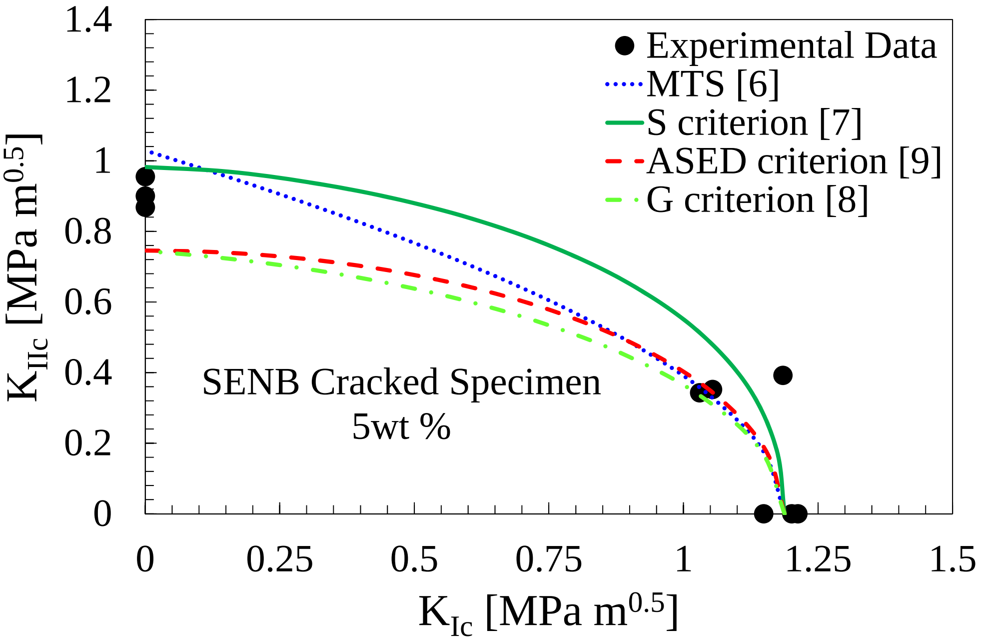

Figure 9. Comparison of fracture toughness predicted by different fracture criteria and test results for cracked specimens made of epoxy resin filled with 5% wt of nanoclays.

It is further evident that, in some cases, fracture toughness of nanocomposites does not comply with the LEFM based mixed mode fracture criteria. This can be due to the fact that the classical mixed mode fracture criteria do not take into account some extra fracture mechanisms which might arise in nanocomposites and which require an “ad hoc” insightful investigation.

4 Conclusion

In the present work the effects of nanoclay addition on fracture behaviour of an epoxy resin under mixed mode (I plus II) loadings have been studied by analysing the results from Single Edge Notch Bending (SENB) tests. The results allow to conclude that, for weight contents lower than 5wt%, nanomodification significantly enhances the fracture toughness of the epoxy resin upon the entire range of mixed mode loadings, the improvements being dependent on the mode mixity ratio.

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References

[1] Fischer H. Polymer nanocomposites: from fundamental research to specific applications. *Mater Sci Eng C*, **23**, 763–72 (2003).

[2] Quaresimin M, Varley RJ. Understanding the effect of nanomodifier addition upon the properties of fibre reinforced laminates. *Compos Sci Technol*, **68**, pp. 718-26 (2008).

[3] Rice BP, Chen C, Cloos L, Curliss D. Carbon fibre composites: organoclay–aerospace epoxy nanocomposites, Part I. *SAMPE J*, **37**, pp. 7-9 (2001).

[4] Quaresimin M, Salviato M, Zappalorto M. Fracture and interlaminar properties of clay-modified epoxies and their glass reinforced laminates. *Eng Fract Mech*, **81**, pp. 80-93 (2012).

[5] ASTM D 5045. *Standard Test Methods for Plane-Strain Fracture Toughness and Strain Energy Release Rate of Plastic Materials* (1999).

[6] Erdogan F, Sih GC. On the crack extension in plates under plane loading and transverse shear. *Trans ASME, J Basic Eng*., **85**, pp. 519–27 (1963).

[7] Sih GC. Strain-energy-density factor applied to mixed mode crack problems. *Int J Fracture*, **10**, pp. 305-21 (1974).

[8] Hussain MA, Pu SL, Underwood J. Strain energy release rate for a crack under combined mode I and Mode II. Fracture Analysis, ASTM STP 560 American Society for Testing and Materials, Philadelphia 2-28 (1974).

[9] Lazzarin P, Zambardi R. A finite-volume-energy based approach to predict the static and fatigue behaviour of components with sharp V-shaped notches. *Int J Fract*, **112**, pp. 275-298 (2001).