The Effect of Nanoclay on Damaged Areas of Composite and Nanocomposite Laminates

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Abstract:
The influence of nanoclay on the impact damage resistance of glass fiber–epoxy composites has been investigated using high-velocity repeated ice impact tests. The incorporation of nanoclay into epoxy enhances the impact resistance of the composites. The impact of ice is a realistic scenario for composite structures such as aircraft fuselages, wing skins and fan blades and it is not a completely understood threat. Repeated ice impact events, such as the ones during a hailstorm, can cause significant damage. This work focuses on repeated ice impact experiments and damage in composite and nanocomposite materials. X-ray diffraction analysis confirmed the exfoliation and intercalation of the nanoclay in the studied epoxy resin system. The result shows that plates with a fiber orientation of [45°/45°]s in the composite produce the minimum delamination and that a small amount of nanoclay is enough to improve the mechanical properties of the nanoclay-polymer nanocomposites.
Keywords: *Nanocomposites, Ice impact, Damage assessment, Nanoclay, Damaged areas.*

1. INTRODUCTION

Recent researches have studied solid body impacts on composite materials [1,2]. However, the major part of an ice impact event cannot be studied as a solid body impact [3, 4, 5] because the fracture threshold of ice is low. Understanding the failure of composite structures due to ice impact will help engineers predict the conditions for which a structure may undamaged and estimate the damage that would occur when the structure does not survive. A large body of work on low velocity impacts, exists in the field of impact on composite structures [1,6].

Composites are typical advanced engineering materials that show high strength-weight and modulus-weight ratios and are used in the aerospace, military and automobile industries.

There are a number of factors that determine the fracture processes, such as material variables, loading and environmental conditions and impactor geometries [7]. Among the material variables, the mechanical properties of the fiber and matrix, the failure strains, the interface properties and the fibre shape play important roles in determining the impact damage resistance[8].

Epoxy resins are a class of polymer that possess high strength, high temperature resistance and excellent process ability, but pure epoxy resins are brittle when subject to impact loading, thus requiring the development of tougher resin systems. Nanoclays that have a layered structure have been considered for roles as reinforcements in epoxy systems. These layers are bonded together by van der Waal's forces. The dispersion state of the nano platelets plays an important role in determining the mechanical and

physical properties of the composite, such as the fracture behavior and toughening mechanisms [9]. Many previous studies [10,11] have suggested that intercalation is fundamental for improving fracture toughness and that complete exfoliation improves the strength and stiffness of the nanocomposites. A balance an intercalation and exfoliation may be beneficial for improving both the modulus and toughness without giving strength in epoxy resin matrices [12].

Dispersed nanoclay particles led to improvements in viscoelastic and thermo-mechanical properties and stiffness [13, 14], which were shown to enhance adhesion and constrain the polymer chain movements. The nanocomposites containing nanoclay have been employed as the matrix material used to produce hybrid nanoclay-fiber reinforced polymer composites that possess improved mechanical and fracture properties [15,16].

More research is required on the properties that have not been evaluated to demonstrate the applications of the hybrid composites [18-22]. This paper is a continuation of our previous studies on composites and nanocomposite laminates [17, 18]. Repeated ice impact tests were carried out to evaluate the impact damage resistance of composite laminates made from neat epoxy and nanoclay-modified epoxy.

2. EXPERIMENTAL

2.1. Materials

The nanoclay chosen for the study was Cloisite30B with density of 1.98 kg/m^3 and particle size of less than 13 µm that was a natural montmorillonite modified with methyl, tallow, bis-2-hydroxyethyl; quaternary ammonium chloride used as organically modified clay. Cloisite30B was obtained from Southern Clay, Texas USA. The nanoclay particles were surface modified for their dispersion and exfoliation within the epoxy matrix. All of the samples were made by E-glass fibre unidirectional (UD) of 450 g/m^2 that were obtained from Camelyaf Turkey. Epoxy resin CO-207 was used as the matrix material, and Amine based hardener HA-11 was used with the selected epoxy resin; both are manufactured by Mokarrar Engineering Materials Company (Iran). The ratio of epoxy to hardener was 100:15 in all samples.

2.2. Preparation of Composite and Nanocomposite Samples

The composite samples were prepared in four different fiber orientations. To prepare the samples with 45º fiber orientation, plain [90º/90º] was laid-up at 45º angles. All of the samples were cured for 24 h at room temperature and post-cured for 8 h at 80ºC. The samples were cut to 150×150 mm to fit in a steel frame-type holder that constrained the panel edges from rotation.

The nanocomposite samples were prepared by placing a specified amount of Cloisite30B in an oven for 1 h at 150°C to remove any moisture, and then adding to the epoxy resin, followed by mixing using a high speed shear mixer at 2000 rpm for 1 h at room temperature. The mixture was sonicated using an ultra-sonicator for 30 min, and the resin temperature was kept low using a cold water bath until a homogenous mixture was obtained. HA-11 was then added, and thoroughly; the mixture was then placed in an oven under vacuum conditions to remove air bubbles. All samples were cured for 24 h at room temperature and post-cured for 8 h at 80°C. Table 1 summarizes the details of the samples and their lay-ups.

Table 1: *A matrix showing the sample variables.*

Wt.% Nanoclay	Panel thickness (mm)	Number of layers	Lay-Up	Type of glass fiber
0	2.1	4	[90°/90°/90°/90°]	Unidirectional
0	2.1	4	[45°/90°/90°/45°]	Unidirectional
0	2.1	4	[90°/45°/45°/90°]	Unidirectional
0	2.1	4	[45°/45°/45°/45°]	Unidirectional
1.5	2.1	4	[45°/45°/45°/45°]	Unidirectional

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2.3. Characterization

Transmission electron microscopy (TEM) was employed to study the morphology of the nanocomposites. TEM was performed on ultra-microtomed samples that were prepared using a LEICA microtome equipped with a glass knife and were mounted on 200-mesh copper grids.

Bragg's law, $\lambda=2d\sin\theta$, was used to calculate the crystallographic spacing (d-spacing), to show the intercalation and exfoliation of the nanoclay in the epoxy resin. XRD patterns were obtained using a Philips XPERT XRD system equipped with a CuKa radiation source at a generator voltage of 40 kV and generator current of 40 mA ($\lambda=1.5405$ Å).

2.4. High velocity impact

A single stage gas gun, designed and constructed at the Iran Polymer and Petrochemical Institute, was used to conduct the high velocity impact tests. A schematic of the gas gun is presented in Figure. 1. The projectile used for the impact tests was cylindrical ice that was 40 mm in length, 20.5 mm in diameter and 11.7 g in weight. Helium gas was selected as the propellant. High-velocity impact tests were performed on all of the samples in the velocity range of 130-140 m/s. The gas gun was first calibrated, and the velocity of the projectile (before impact) was measured for various gas pressures of the helium gas using the depicted chronograph (F-1 model from Shooting Chrony Canada).

After repeated ice impact tests, the damaged area for all of the samples was determined using back light marking and a whitening phenomenon associated with the delamination and brittle fractures of composite laminates. The damaged areas were measured using Image J software [19].

3. RESULTS AND DISCUSSION

3.1. X-ray diffraction analysis

Figure 2 shows the XRD patterns for the epoxy resin-Cloisite30B nanocomposites at 1.5wt% compared to pure Cloisite30B. The figure shows a reduction in the intensity of the peak. The characteristic peak for the nanoclay is absent in the XRD pattern for the epoxy resin-nanoclay (1.5wt%), suggesting the disordering and loss of the structural regularity of the clay layers and hence the possible formation of an exfoliated nanocomposite structure [20].

The TEM micrographs taken of the epoxy resin-nanoclay (1.5wt %) are shown in Figure 3. The quality of the dispersion of nanoclays in the liquid resin was evaluated using morphology tests and due to the intercalation and exfoliation of the nanoclay
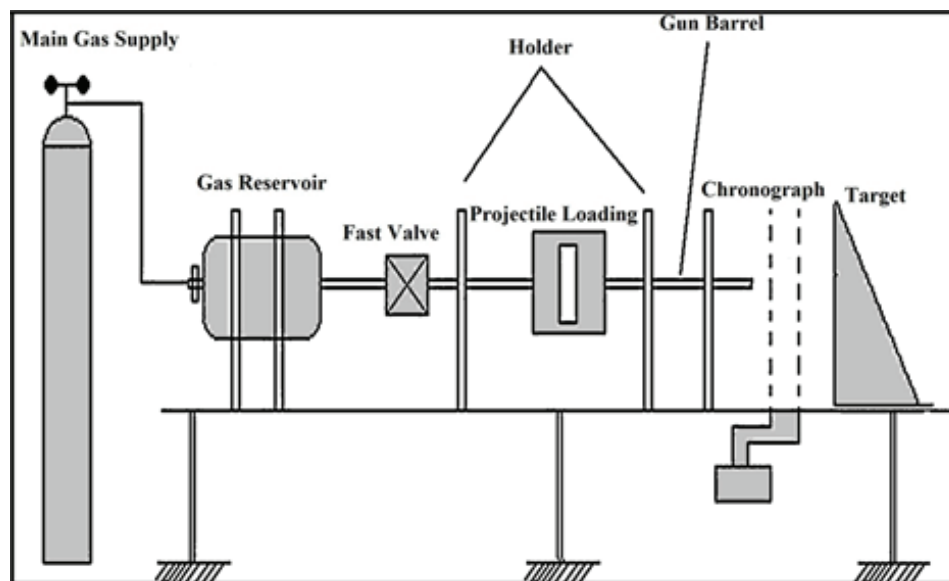

Figure 1: *A schematic of the high-velocity ice impact testing device (Gas Gun).*
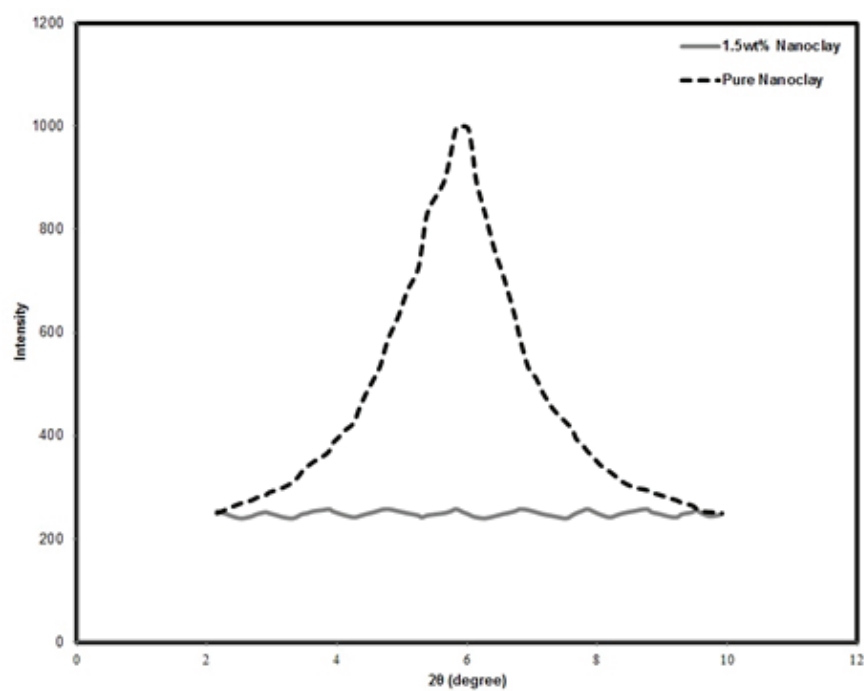
Figure 2: XRD patterns of epoxy resin-Cloisite30B nanocomposites (solid line) and pure Cloisite30B (dashed line).
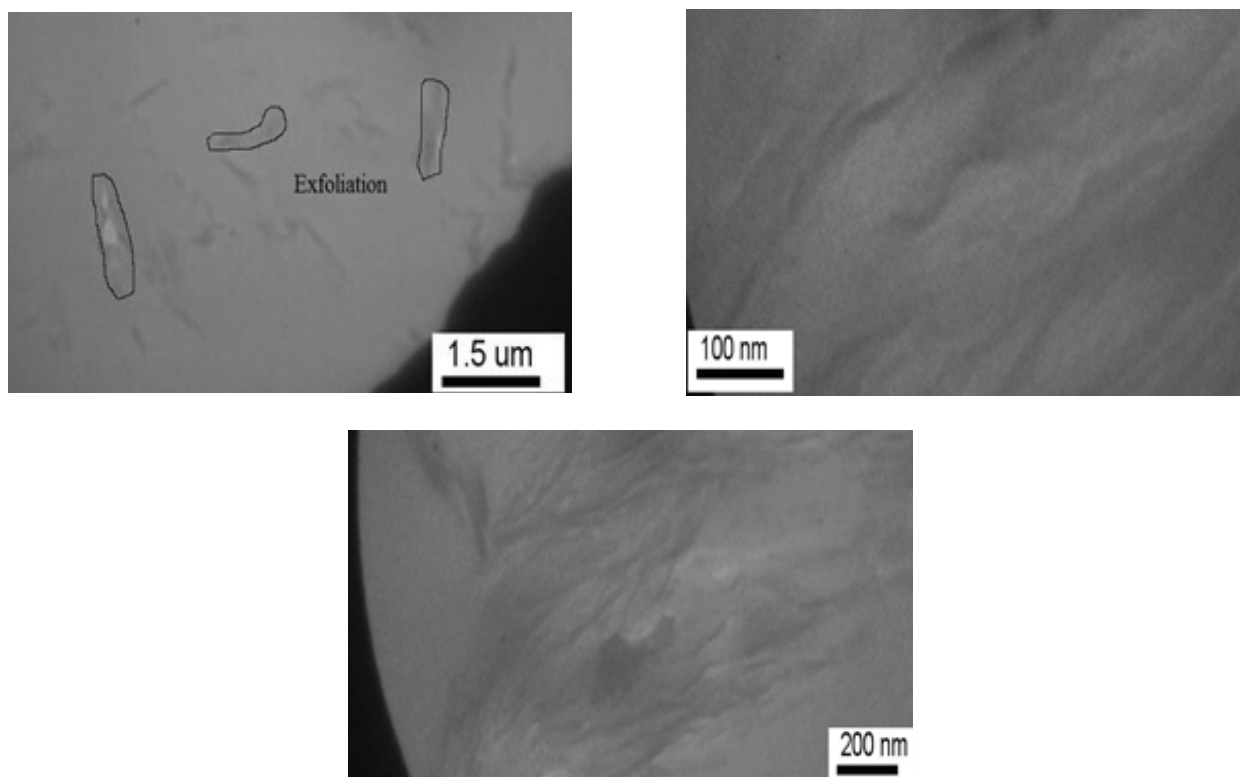

Figure 3: TEM micrographs of the nanoclay–epoxy nanocomposites at various magnifications. Scale bars show (a) 1.5 μm, (b) 100 nm, (c) 200 nm.

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platelets. This morphological behavior shows the properties of the nanoclays with the polymer matrix and its surface treatment and indicates its affinity with the polymeric matrix [21].

Figure 3 show that well-bonded and rather uniformly distributed nanoclays were responsible for the enhanced damage resistance. Visible interfacial debonds were observed between the nanoclay and the epoxy matrix, indicating a strong interfacial adhesion for all of the samples studied. For better observation of the dispersion of the nanoclays, the TEM micrographs were taken at three different magnifications.

3.2. Damage assessment

All of the samples were subjected to impact kinetic energies of 114.36 J. After performing the calibrations, two consecutive ice impact tests were performed on each of the composite and nanocomposite laminates.

All of the samples were investigated for various damage modes, including delamination, fiber splitting and fiber fracture. Delamination was identified as the major failure mode in all samples. The effect of the fiber orientation on the damage extension for all samples under repeated ice impact was studied. Figure 4 show that because the major
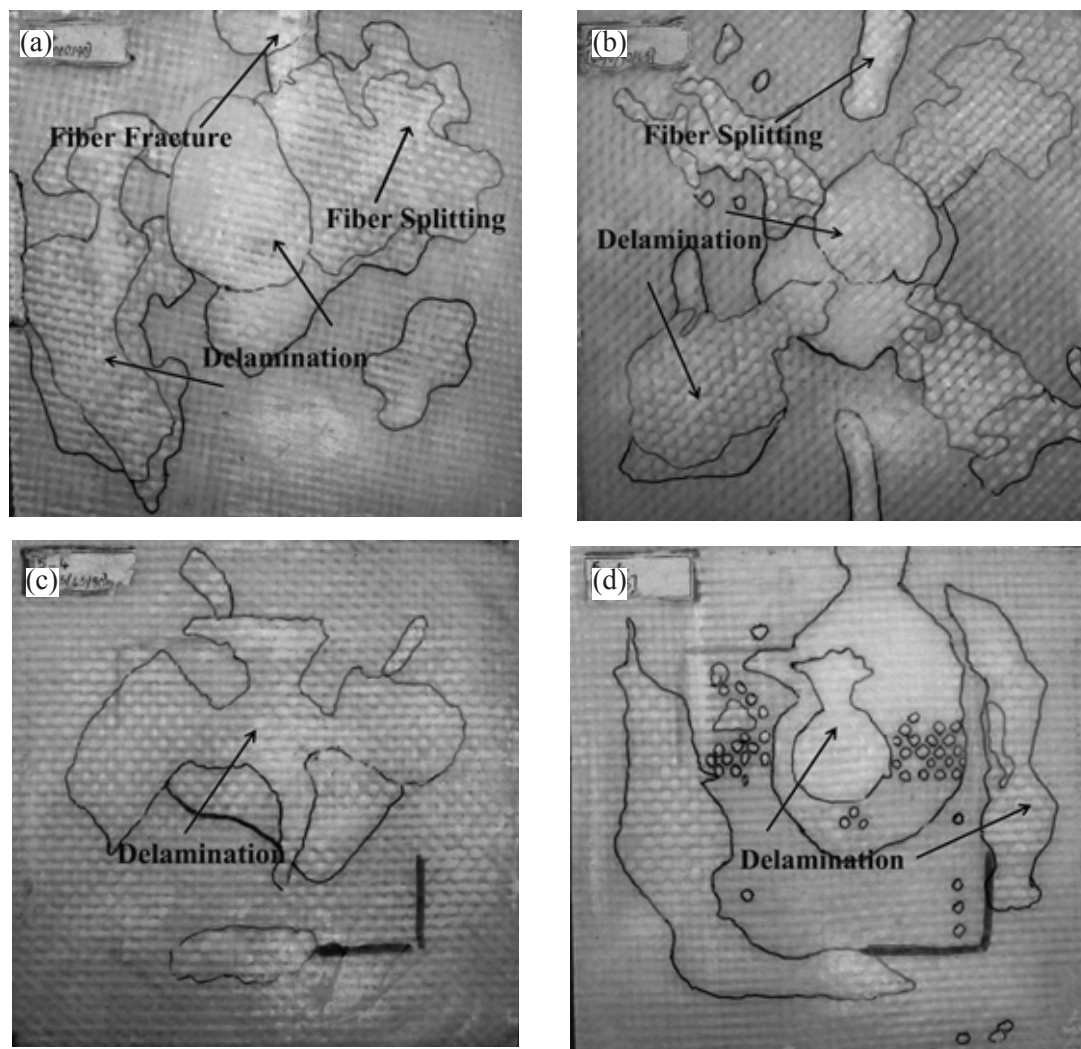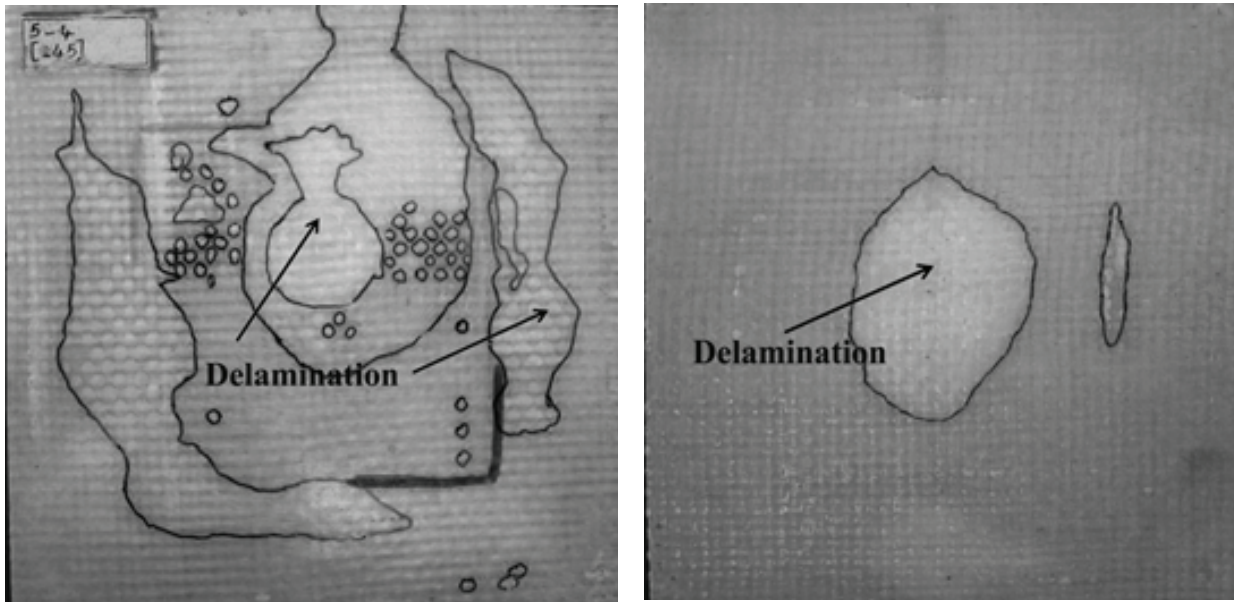

Figure 4: *Photographs show the front face damage extension for (a) Sample [90°/90°]s, (b) Sample [45°/90°]s, (c) Sample [90°/45°]s, (d) Sample [45°/45°]s.*

(a) **(b)**

Figure 5: *Photographs show the front face damage extension for (a) Sample [45°/45°]s without nanoclay, (b) Sample [45°/45°]s with nanoclay.*
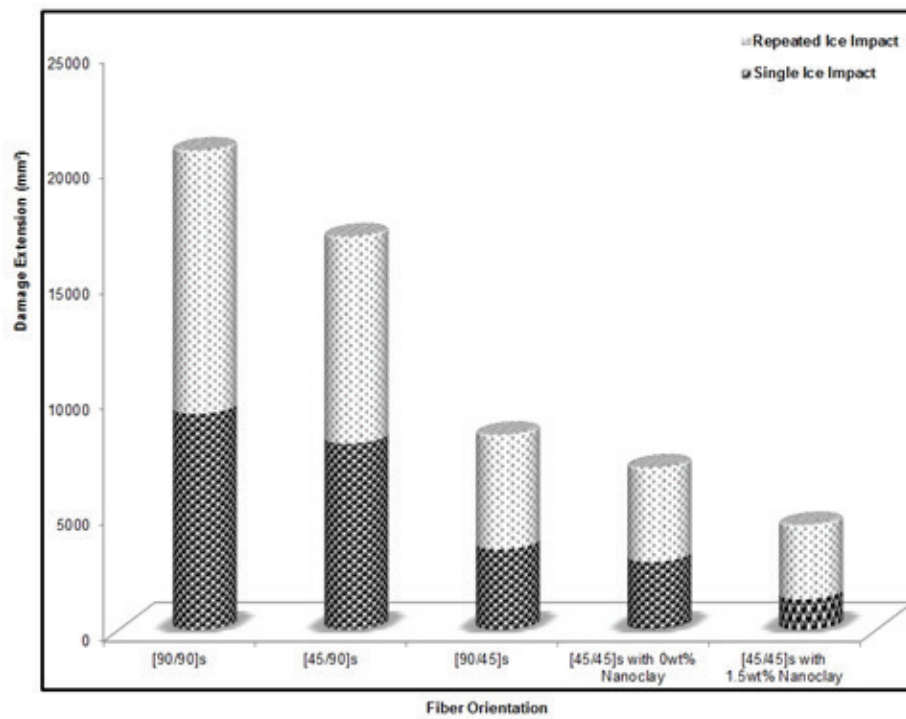

Figure 6: *Damage extension vs. different fiber orientations for the four layeres under repeated ice impact for the composite and nanocomposite laminates.*

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damage type was delamination, the most resistant sample had the 45° fiber orientation. Therefore, as shown in Figure 5, by adding nanoclay to the optimum composite sample (with 45º fiber orientation), the damage area was decreased. Furthermore, because of gaps in the nanoclay sheets, the micro-cracks in polymer matrix were reduced and the matrix and nanoclay stickiness phase increased.

3.3. High-velocity repeated ice impact

The results from the repeated ice impacts on all of the samples are shown in Figure 6. Investigating the composite and nanocomposite results shows that the damaged area resulting from repeated ice impacts in comparison with single ice impact in the samples with stacks arranged as [90°/90°]s, [45°/90°]s and [90°/45°]s increased by 25.15%, 21.5% and 30.67%, respectively.
In the [45°/45°]s without nanoclay and [45°/45°]s with nanoclay samples, the increase in the damaged area was 68.1% and 58.7%, respectively. As noticed, the percentage increase in the damaged area in samples [90°/90°]s, [45°/90°]s and [90°/45°]s was less than for samples [45°/45°]s without nanoclay and [45°/45°]s with nanoclay. The former samples sustained more serious, visible and non-repairable damages in comparison with the optimum sample and the sample with nanoclay. In other words, the damage in the optimum sample and the sample with nanoclay is repairable and from delamination.

4. CONCLUSION

This study documented the impact damage resistance of epoxy resin reinforced with nanoclay particles, paying particular attention to the effects of high-velocity repeated ice impact on these materials. The following closing comments are highlighted from the obtained experimental results.

- The XRD and TEM analyses confirmed the exfoliation and intercalation of the nanocaly particles and the dispersion of nanoclay in the epoxy resin system for samples containing 0wt% and 1.5wt% nanoclay.

- The result of investigating sample without nanoclay showed that placing the layers at an angle of 45º in the fiber orientations, resulted in improvement with respect to the impact.

- Adding a few nanoclay particles to optimum sample will result in an improvement in the impact qualities.

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