DAMAGE TOLERANCE OF NANOCOMPOSITES UNDER IMPACT LOADINGS

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Abstract. *Protection of industrial, military and civil engineering structures against impact loadings have gained a lot of attention, specially after the 9/11 terrorist attacks. The use of composite materials as substitution to conventional materials, e.g. steel, is spreading not only due to their specific properties, i.e. stiffness-to-weight and strength-to-weight, but also due to their toughness. An economical and viable option is the use of fiber glass/epoxy composites, but for impact applications their toughness still has to be enhanced. Studies developed by Yasmin et al. and Isik et al. demonstrated that by adding a small amount of nanoclays into epoxy systems, a sensible increase in mechanical properties can be obtained. To investigate how the impact strength is affected by the presence of nanoclays, a set of glass fiber-epoxy-nanoclay laminate composites with 16 layers and 65% fiber volume fraction is manufactured by vacuum assisted wet lay-up. The fibers have a plain-weave configuration with density of 180 g/m^2, while the epoxy resin system is made of a bisphenol A resin with aliphatic amine as the curing agent. The nanoclay, an organically modified montmorillonite ceramic, is exfoliated into the epoxy system in a 1%, 2%, 5% and 10% in weight. The methodology used for the impact test is based on the ASTM D5628-01 standard. The results have shown that not only the delamination phenomenon is reduced but also the damaged area. To be more specific, for the same energy, a laminated nanocomposite presents a damaged area 20% smaller than the conventional laminated. This is a clear indication of an increase in the impact perforation resistance.*

Keywords: *NanoComposites, Low Velocity Impact tests, Laminated Composites,*

1. Introduction

Composites laminates are a valuable option to conventional materials due to their high specific mechanical properties, i.e. stiffness-to-weight and strength-to-weight. As a result, composite laminates have become widely spread into used in primary structural components in aircrafts, modern vehicles and light-weight structures. These composite structures during their service life undergo various loading conditions. Among them, the most critical condition is the impact loadings due to the laminated nature of these structures. According to Luo et al. (1999), the damage in composite structures resulting from impact events is one of the most important aspects to be considered in the design and applications of composite materials. Impact events, however, can be classified according to the impact velocity, i.e. low and high velocities. As mentioned by Naik and Shrirao (2004), low velocity impact events occur when the contact period of the impactor is longer than the time period of the lowest vibrational mode. In this case, the support conditions are critical as the stress waves generated outward from the impact point have time to reach the edges of the structural element, causing its full-vibrational response. On the other hand, in high velocity impact, the contact period of the impactor is much smaller than the time period of the lowest vibrational mode of the structure. As a consequence, the response of the structural element is governed by the local behavior of the material in the neighborhood of the impacted zone, the impact response of the element being generally independent of its support conditions.

As stated by Hu et al. (1999), low velocity impacts on laminates produce multiple stacked delaminations at a number of interfaces through the thickness of the composite laminates. These delaminations are responsible for a significant reduction in strength and stiffness of the laminates. Hence, understanding the impact damage mechanism is essential to improve the composite materials performance. Experimental studies on low velocity impact developed by Liu et al. (2000) showed that the thickness has a greater influence on impact perforation resistance than on the in-plane dimensions. While in Belingardi and Vadori (2002), the energy absorption was evaluated considering the damage degree and the saturation impact energy which allowed corroborating the relationships between thickness and impact perforation resistance. By performing a finite element analysis associated to experimental data, Moura and Gonçalves (2005) were able to create an accurate progressive damage model and successfully simulate the interaction between crack and delamination into low velocity impact problems. Meanwhile, according to Mines et al. (1999), for high velocity impact, the perforation mechanics depend on the fiber type and volume fraction, the matrix, the stacking sequence, the size and initial kinetic energy of the impactor. Gu (2003), Potti and Sun (1997), and Abrate (1998) are among those researchers that have elaborated perforation models to evaluate the perforation performance. The model created by Gu (2003) took into consideration not only the energy conservation laws but also the absorbed kinetic energy of the projectile. By adding the composite strain energy to his model, Gu (2003) was able to estimate the progressive damage and delaminations caused by the high velocity impact. Potti and Sun (1997), however, considered the use of the dynamic response model along with the critical deflection criterion to analyze the high velocity impact and perforation. They concluded that the delaminated area increases with the velocity up to the penetration ballistic limit, as expected. However, beyond this limit, the delamination area decreases with the increase of velocity. Their model was able to capture this phenomenon with accuracy. Furthermore, Abrate (1998) mentioned that compressive strains in high velocity impact situations are inversely proportional to the stress wave propagation through the composite thickness. Still, in a small area near the impactor, this stress wave reaches the speed of sound, which supports the results presented by Potti and Sun (1997).

In all cases, low or high impact velocities, the key issue in the design of composite structures is the damage tolerance of each component, i.e. fibers and matrix. According to da Silva Junior et al. (2004), the use of aramid reinforced composites presents one of the best protections to weight ratio for impact applications. However, the high cost of these fibers is a disadvantage. One viable substitute to aramid fibers is the use of carbon fibers. Nevertheless, as mentioned by Davies and Zhang (1995), carbon fibers epoxy composites have an elastic behavior but they are also brittle. Therefore, they suggested the use of fiber glass reinforced as carbon fiber replacement. Yet, fiber glass composite toughness is highly dependent on strain rate damage and the matrix behavior itself. A possible solution for this problem is to enhance the matrix toughness. This goal can be obtained by substituting the net epoxy system by a polymer-clay nanocomposite system.

According to Liu et al. (2003), the use of nanoclays as reinforcement of polymer systems was introduced by the Toyota Research group in the early 90's. By that time, nylon-6 based clay nanocomposites were synthesized. They concluded that nanoclays not only influenced the crystallization process but they were also responsible for morphological changes. Liu et al. (2004) reported that there was an increase in storage elastic modulus of 100% when clay content was up to 8 wt% in comparison with net nylon 11. Yie et al. (2003) demonstrated that for polystyrene-montmorillonite nanocomposites, the glass transition temperature was higher than the virgin polystyrene. In both cases, thermoplastics were used as matrices. Different researchers, however, decided to study the influence of nanoparticles in epoxy systems due to their large use by the composite structures industry.

Yasmin et al. (2004) were among those researchers who studied the effect of nanoparticles (organically modified montmorillonite - Cloisite 30B) into epoxy systems. By varying the amount of Cloisite 30B, in weight from 1% up to 10%, they found an increase in the elastic moduli to a maximum of 80%. A more interesting result using nanoparticles into epoxy system was reported by Isik et al. (2003). They concluded both stiffness and toughness were enhanced by nanoparticles. However, for their binary system, resin - diglycidyl ether of bisphenol *A* and cure agent - triethylenetetramine, the maximum impact strength was obtained at 1% in weight of montmorillonite content. The difference between Yasmin et al. (2003) and Isik et al. (2003) results can be attributed to the mixing process, shear mixing in Yasmin's case and direct mixing for Isik's conditions. A more comprehensive study on clay-epoxy nanocomposites was performed by Haque and Shamsuzzoha (2003), since not only mechanical properties but also thermal properties were evaluated. Their main conclusions were that thermo-mechanical properties mostly increase at low clay loadings (~ 1-2% in weight) but decrease at higher clay loadings (≥ 5% in weight). In addition, the uses of nanoclays also decrease the coefficient of thermal expansion (CTE). They also observed a degradation of properties at higher clay loadings. This phenomenon can be due to the phase-separated structures and defects in cross-linked structures. Furthermore, these problems can be caused by the heating step during the manufacturing process. It is important to mention that in all the references mentioned previously, heating was present during the nanocomposite synthesis procedure.

The objectives of this paper are twofold. On the one hand, low velocity impact tests are conducted to investigate the penetration mechanism on the new polymer-nanoclay-fiber glass nanocomposite. On the other hand, the co-cure procedure of this new nanocomposite is investigated. This new type of polymer-nanoclay-fiber glass nanocomposite is synthesized using a new procedure where no heating is applied.

2. NanoComposites: Synthesis and Experiment Set up

The nanocomposite prepared for this investigation is a S2-glass/epoxy-clay. The resin system was chosen owing to its low viscosity and long gel time (60 minutes) at room temperature. The epoxy formulation is based on two parts, part A (*diglycidyl ether of bisphenol A*) and part B - hardener aliphatic amine- (*triethylenetetramine*). The weight mixing ratio suggested by the manufacturer is 100A:20B, and the average viscosity is around 900 cps (Hunstsman, 2004). The nanoclay particles used in this study are organically modified montmorillonite in a platelet form, while the S-2glass fiber has a plain-weave woven fabric configuration with density of 180 g/m^2 from Texiglass. The S2-glass/epoxy-nanoclay composite is a laminate with 16 layers and 65% fiber volume fraction. This type of laminate configuration is prepared using a vacuum assisted lay-up which leads to an average thickness of 2.4 mm. The amount of nanoclay exfoliated into the epoxy system, in weight, is 1% and 2%, respectively. The nanoclay properties listed in Table 1 are from Subramaniyan et al. (2003). Moreover, a set of S2-glass/epoxy laminated composite without nanoclay is prepared to serve as comparative basis. For each group at least five specimens is prepared and tested.

Table 1. Nanoclay properties from Subramaniyan et al. (2003)

Mean dry particle size [μm]	Average platelet thickness [nm]	Mineral Purity [% min]	Moisture [%max]	Specific density [g/cm^3]
8-10	49	98	3	1.71

The nanocomposite synthesis involves two different steps, i.e. the nanoclay exfoliation procedure and the lamination practice. As stated by Yasmin et al. (2004), the exfoliation process can be done by direct mixing, sonication mixing, shear mixing or a combination of sonication and shear mixing. Additionally, they affirm that shear mixing is more appropriate to the exfoliation of expanded graphite, while direct mixing is more suitable for ceramic nanoparticles. In our case, the nanoclay exfoliation process is performed by stepwise direct mixing, in other words, the nanoclay particles are mixed to acetone and later on the solution, acetone/nanoclay, is blended into the uncatalized resin. In the first step, the stirred procedure is performed up to the formation of a homogeneous mixture. During the second step of our stepwise direct mixing procedure, a rather foamy solution is formed. After degassing for at least two hours, the solution (resin+acetone+nanoclay) becomes clear of any particle agglomeration and bubbles. However, the addition of nanoclays turns a usually translucent resin into an opaque one. A longer degassing guarantees not only the elimination of all bubbles but it also allows the acetone evaporation. The next step is a conventional stacking sequence and vacuum assisted wet lay-up lamination. After twenty-four hours of cure under vacuum at room temperature, a co-cure procedure is applied. Following the manufacturing recommendations, there are two options for co-curing shown in Figure 1. According to Kim and Daniel (2002), residual strains and stresses can be induced by the cure/co-cure procedures. Likewise, for the present case, the cure kinetic is highly dependent on peak temperature, increase/decrease rates, and the components mixed, i.e. resin, hardener, nanoclay and acetone.

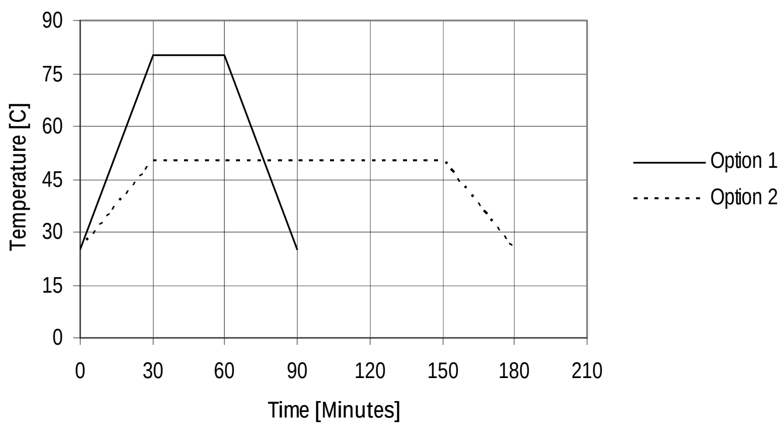


Figure 1: Co-cure procedure from Hunstman (2004).

Once the S2-glass/epoxy-clay is prepared, the impact resistance test by falling dart can be performed. Following the ASTM D 5628-01 (2001), the dart has a hemispherical nose with a radius of 10.0±0.1 mm. The testing machine is described by the schematic diagram represented in Figure 2, while the specimen clamp is a two-piece rectangular specimen with a central circular cutout of 100.0±0.1 mm. The dart has a weight of 246 grams and six additional steel circular plates with a diameter of 75.0±0.1 mm and a thickness of 15.0±0.1 mm. They can be placed into the rod linked to the dart. The average weight of each circular plate is 528 grams. As stated by Belingardi and Vadori (2002), the velocity in a low velocity impact test, such as the one described in ASTM D 5628-01 standard (ASTM, 2002), can be calculated by the expression:

$$v = \sqrt{2g\Delta h} \qquad (1)$$

where v is the velocity, g is the gravity acceleration and Δh is the difference in height.

As the drop weight tower has a maximum height of 3.0 meters, the limiting velocity for the device is 7.67 m/s. The dart weight is made of AISI 4330 steel. Moreover, the six steel disks can be assembled individually into the dart leading to a mass variation from 246 to 3414 grams. As mentioned by Lam and Chun (1994), the target boundary conditions have direct influence on the materials response to low velocity impact tests. Furthermore, Tan et al. (2003) verified that clamped laminate plates undergo deflection and stretching during the impact process, while for simply supported conditions stretching does not occur. In other words, when the stress wave produced outward from the impact region reaches the clamped edges, it results in stretching. Therefore, this investigation considers not only the clamped condition, but also the simply supported one. The clamped condition is guaranteed by the usage of four bolts as shown in Fig 2.

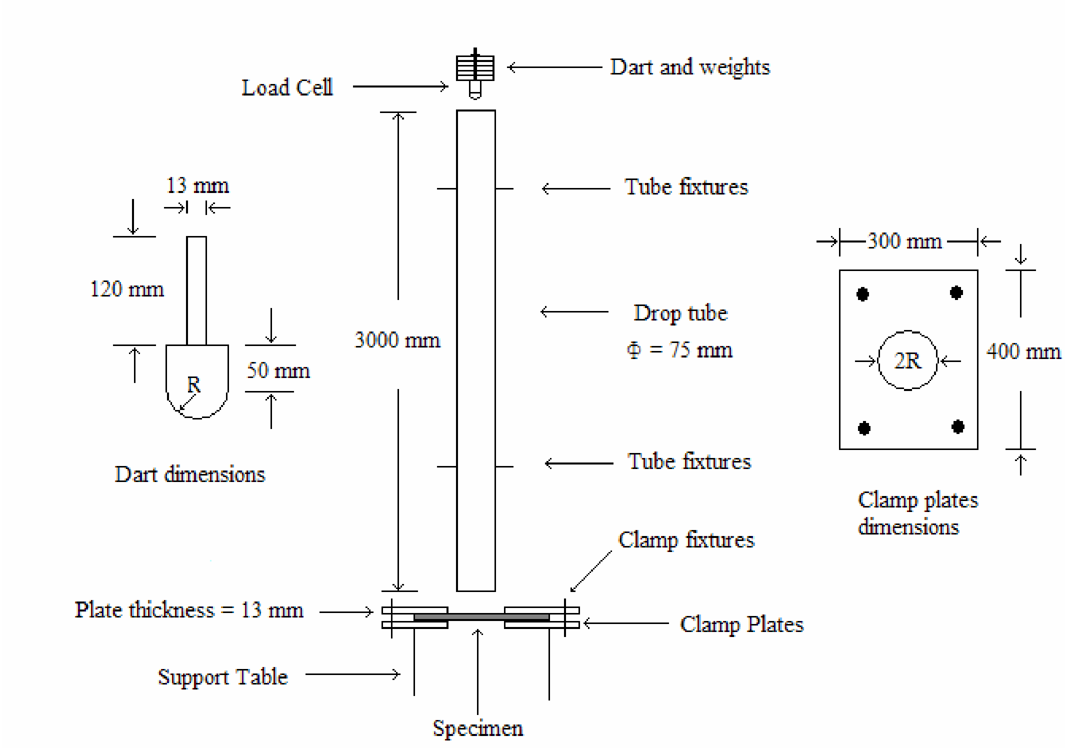


Figure 2: Falling mass impact tester - schematic diagram

3. Results and Analysis

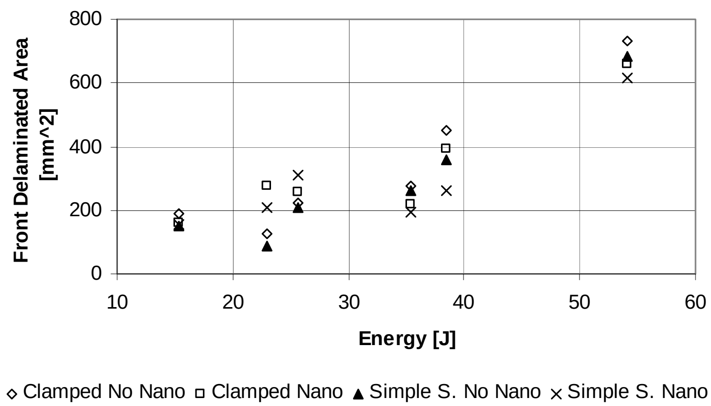
In this study two boundary conditions are considered, i.e. clamped and simply supported, two different heights and two masses. These conditions lead to six levels of impact energy and a total of twelve distinct conditions. Table 2 summarizes all conditions.

Table 2: Experiment conditions

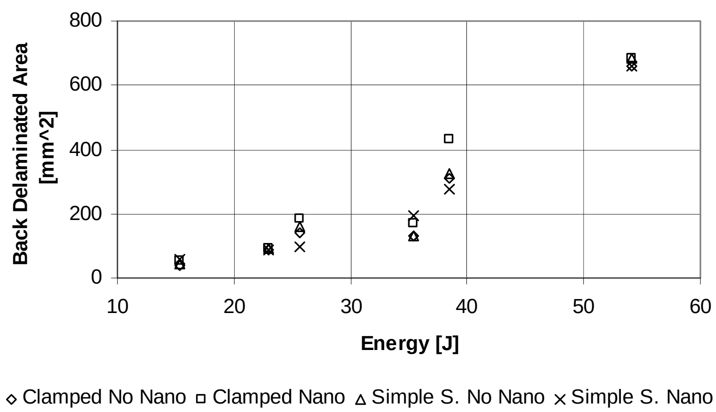
	Clamped and simple supported			Clamped and simple supported		
Specimen ID	#1	#2	#3	#4	#5	#6
Height [m]	2.00	2.00	2.00	3.00	3.00	3.00
Velocity [m/s]	6.26	6.26	6.26	7.67	7.67	7.67
Mass [g]	780	1308	1840	780	1308	1840
Energy [J]	15.30	25.67	36.10	22.96	38.49	54.15

As this research deals with a new type of composite, the co-cure procedure has to be investigated. From the resin manufacturing, two co-cures are applied to the S2-glass/epoxy-nanoclay nanocomposite with 1%, and 2% wt. The time for co-cure in the first option is much smaller than in the second one, as shown in Figure 1. However, as the peak temperature is much higher, bubbles are formed between the layers. This phenomenon can be explained by the possible humidity entrapment between the layers during the lamination procedure. The point is that when the temperature reaches around 80 ^{o}C, it triggers the formation of “hot spots”, leading to a local temperature higher than a 100 ^{o}C and, as a result, to water vapor formation. These vapors generate internal stresses and strains resulting in delaminations and bubbles.

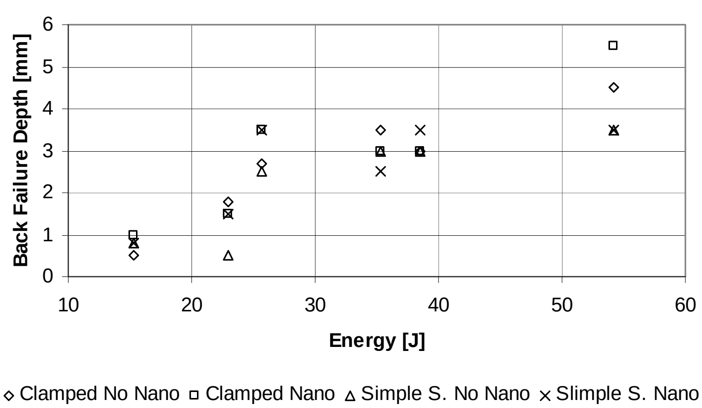
The nanocomposite performance is evaluated by three parameters, i.e. the front area delaminated, the back area failure and its depth. The front area delaminated is calculated considering the average diameter of a circular area, while the back area failure is computed either by a rectangular or circular shape area. Notice that for all cases the occurrence of dart rebounding has to be investigated. Figures 3A-3C show the three parameters studied as a function of the impact energy. As expected the front areas delaminated are higher for the clamped condition than the ones from the simply supported. For the same impact energy, the front side delamination area is reduced by approximately 22% with the addition of 1 %wt of nanoclay to the epoxy system for both cases, i.e. clamped and simply supported conditions. However, the front area delamination increases when the dart rebound phenomenon is noticed. The dart rebound, however, is only observed when nanoclays are present. Nanoclays are associated with the molecular links creating a matrix less brittle than the original one, which can lead to a rebound without a critical failure. Figures 4A-4B show the rebound marks for two levels of impact energy, 15.30 and 25.67 J, respectively. In some cases the rebound is observed during the impact but the marks are too close to be perceived as shown in Figure 4C.



A – Front area delaminated versus impact energy



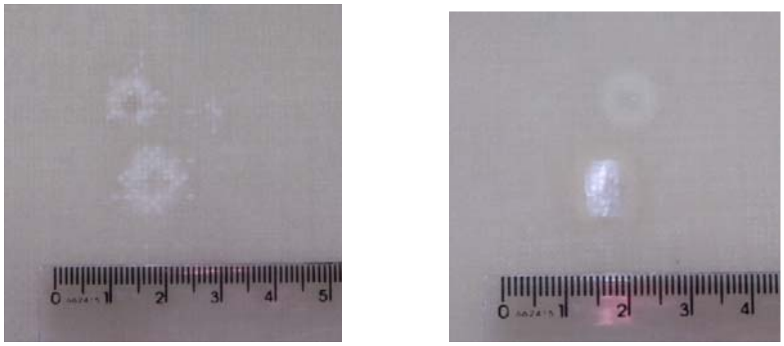
B- Back area failure versus impact energy



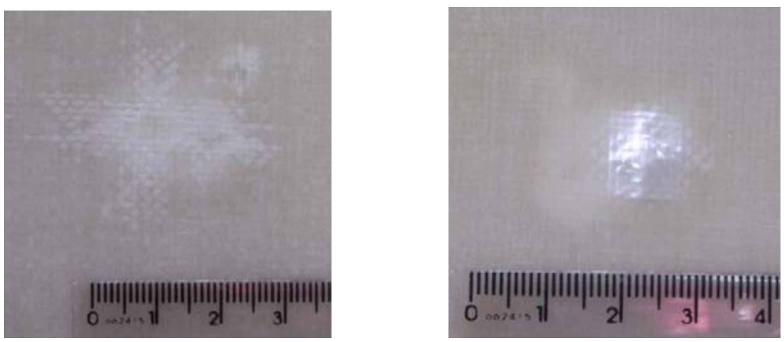
C – Failure depth versus impact energy

Figure 3: Comparative study – Conventional versus Nanocomposites

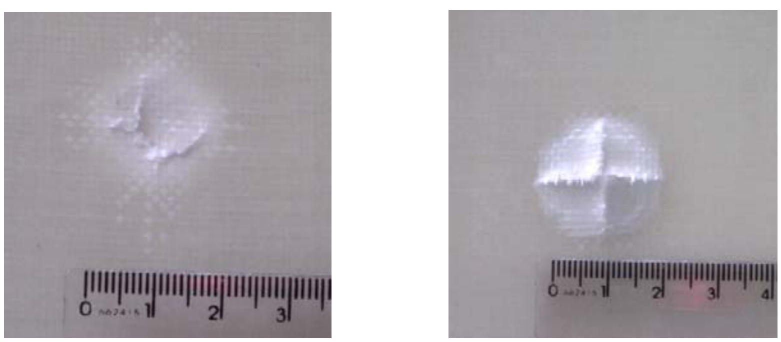
The back area failures and its depth are much smaller in those composites with nanoclays. For low impact energy levels, i.e. 15-22 J, the area reduction is around 10 % while the depth reduction is close to 45%. In middle range impact energy, i.e. 25-36J, the back area failure reduction is kept close to 21%, while its depth reduction approaches 20%. Finally, in high range impact energy level, i.e. 38-54 J, a small decrease close to 10 % on back damaged area is observed, while its depth is reduced to about 20%. This behavior, an increase in toughness, can be explained because of the addition of nanoclays.



A – Front and back sides, delamination marks – Specimen #1



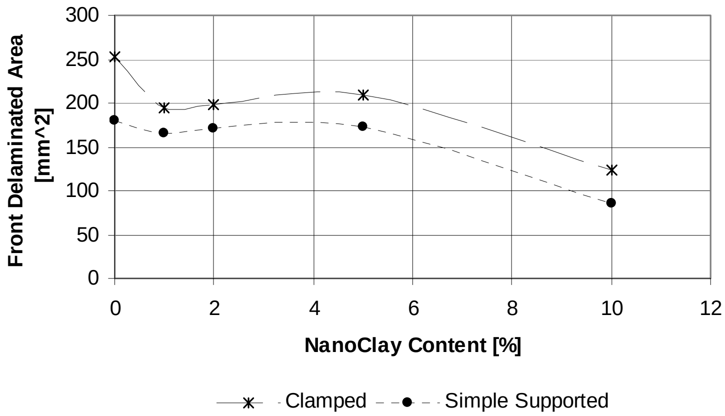
B – Front and back sides, delamination marks – Specimen #2



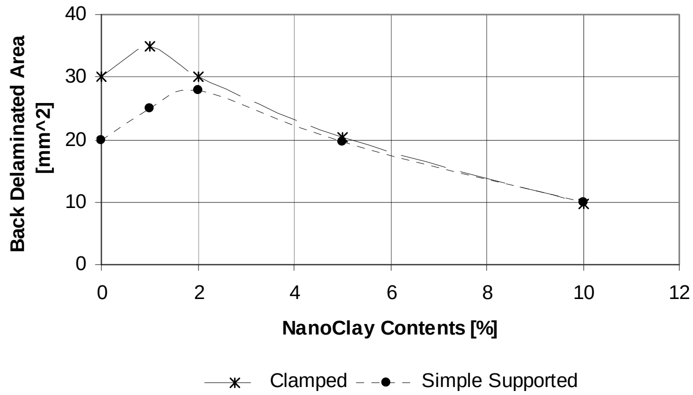
C – Front and back side, delamination marks – Specimen #5

Figure 4. Impact marks at front and back sides

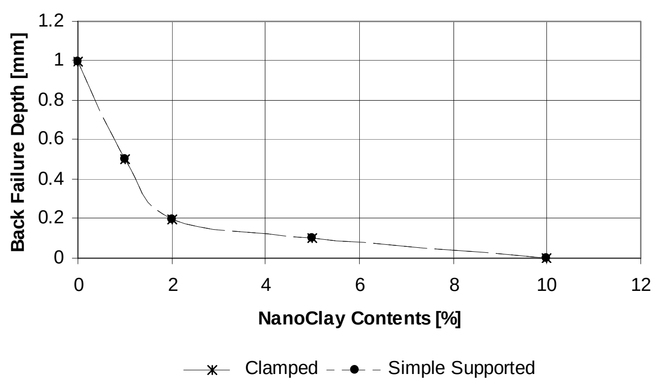
A final analysis will not be complete without an investigation of the nanoclay effects on impact strength. As mentioned by Haque and Shamsuzzoha (2003), mechanical properties increase with low concentrations of nanoparticles. Therefore, a new set of nanocomposites nanoclay up to 10 %in weight is prepared and tested. Figures 5A-5C show the three parameters studied. It is important to mention that for this comparative study a moderate impact energy level, around 20J, is selected. A clear pattern is observed, the impact strength increases with the nanoclay presence. However, the impact strength seems to increase gradually with the nanoclay content. When the nanoclay content reaches 10% the delaminated area drops drastically. Moreover, not only the back delaminated area decreases but also the failure depth. In fact, for the 10% nanoclay content although delamination phenomenon is present, no back failure is observed. When a comparison is done considering the composite's front delaminated area with net resin and 10 % nanoclay content the conclusion is that a decrease of 50% can be observed. The presence of nanoclays increases the matrix toughness due to stronger molecular crosslink.



A- Front side delaminated



B – Back side failure area



C- Failure area depth

Figure 5: Comparative study as a function of nanoclay content

4. Closing Comments

The effect of the exfoliation of nano-sized organically modified montmorillonite into glass fiber/epoxy composites impact strength was investigated. The nanoclay presence into the epoxy system affected the co-cure procedure. The fast co-cure procedure suggested by the manufacturer, i.e. 80 ^{o}C for one hour, is not acceptable, as it induces the formation of interlaminar stresses and strains. On the other hand, the slow cure leads to much better results without bubbles formation. The exfoliation of nano-sized clays increases the composite impact strength, as the damaged area is decreased by approximately 20% for small amounts of nanoclay contents. However, when the concentration reaches around 10% the increase on impact strength is close to 50%. Moreover, the rebound/spring effect is also noticed in all cases where the nano-sized clay is applied with superior performance when compared against conventional composites.

5. Acknowlegments

The authors would like to acknowledge the financial support provided by the Brazilian Research Council (CNPq).

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