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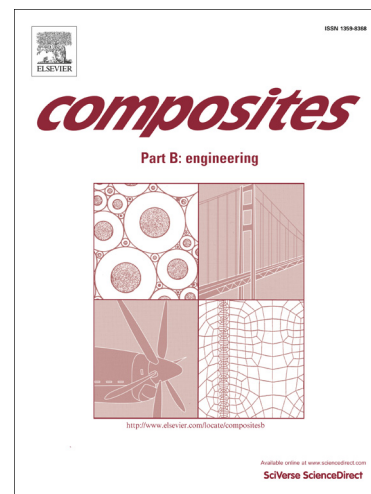
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IMPACT STRENGTH OF COMPOSITES WITH NANO-ENHANCED RESIN AFTER FIRE EXPOSURE

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Abstract: Composite materials have been widely used in several engineering applications. However, there are very few studies about the effects of nanoclays on the impact strength of laminates after exposure to the fire. Therefore, this paper intends to study this subject and the impact performance was analysed by low velocity impact tests carried out at different incident impact energy levels. For better dispersion and interface adhesion matrix/clay, nanoclays were previously subjected to a silane treatment appropriate to the epoxy resin. The exposure to the fire decreases the maximum load and increases the displacement in comparison with the respective values obtained at room temperature. Mathematical relationships are proposed to estimate the maximum impact force and displacement, based on the total impact energy and flexural stiffness. Finally, a decrease of the elastic recuperation can be found, independently of the benefits introduced by the nanoclays.

Key words: A. Polymer-matrix composites (PMCs), A. Nanoclays, B. Impact behavior

1 - Introduction

In recent years, there has been a rapid growth in the use of fibre reinforced composite materials in engineering applications and there is a clear indication that this will be continuing. However, the poor tolerance to accidental low velocity impacts of composite laminates is yet a limitation to their use in many industrial applications. Various types of damages can occur, which are very dangerous because they are not easily detected visually [1-2] and they can affect significantly the residual properties and structural integrity of those materials [3-8].

The literature shows that the adding low concentrations of nanoparticles into polymers are a great solution to improve their mechanical performances without compromising on density, toughness or manufacturing process [9-11]. Clay reinforcements, for example, have been shown to be effective reinforcements in neat polymeric structures [12–17]. In this context, Hosur *et al* [18] showed that the addition of nanoclay in carbon/epoxy composites decreases the impact damage as consequence of the higher stiffness and resistance to damage progression of the nanophased laminates. Iqbal *et al* [19] found significant improvements on the damage tolerance, higher residual strength and higher threshold energy level in CFRPs containing nanoclays. Ávila *et al* [20] showed that the nanoclays presence in fibre glass/epoxy composites led to a more intense formation of delaminated areas after a low-velocity impact test. According to the studies by Reis *et al* [21, 22], on Kevlar/epoxy composites, nanoclays promoted higher maximum impact loads, lower displacements, the best performance in terms of elastic recuperation and the maximum residual tensile strength. The ideal amount of nanoparticles to obtain the best impact performance was investigated and the authors found that the laminates manufactured with resin enhanced by 6 wt.% of nanoclays presented the highest elastic recuperation and penetration threshold [22]. The opposite tendency was observed for the displacement at peak load. However, marginal benefits were found when compared the results obtained for laminates with 3% and 6% of nanoclays. In both studies [21-22], control laminates presented severe damages in the region of the impact point,

which are characterized by a big deformation in the thickness direction. This behaviour was not observed on the laminates with resin enhanced by nanoclays and embrittlement was visible. This phenomenon is consequence of the matrix with nanoclays to present higher stiffness and, consequently, its ductile behaviour decreases [23]. In terms of sandwich composites, Hosur *et al* [24, 25] shows that these materials with nanophased foam sustained higher loads and had lower damage areas compared to neat sandwiches. For Ávila *et al* [26] the addition of 5 wt.% of nanoclays led to more efficient energy absorption and the failure modes were affected by the nanoclays content.

On the other hand, composites can be severely degraded under thermal loading caused by fire [27]. This temperature-dependent behaviour reduces mechanical load carrying capacity and thus can lead to structural failure under operational loads designed without the consideration of fire damage [27]. For example, reductions of more than 80% in flexural strength can be found after exposure to a low-intensity fire (radiating an incident heat flux of 25 kW/m^2) during 20 min [28]. The effect of heat-exposure time on the post-fire tensile and flexural properties was studied detailed by Mouritz and Mathys [28]. All properties dropped rapidly with increasing heat exposure time up to 750-1000 s, particularly the flexural properties. This tendency is consequence mainly to the rapid charring of the composites within this time. After 1000 s the composites were nearly or were completely charred and, therefore, longer heat-exposure times did not cause any further charring [28]. These authors also studied the influence of heat flux on the post-fire tensile and flexural properties. Composite materials were exposed to heat fluxes of 25, 50, 75 or 100 kW/m^2 for 325 s before the properties were measured at room temperature. It was observed that the post-fire properties dropped rapidly with increasing heat flux, particularly to 50 kW/m^2 [28]. In terms of buckling strength, this parameter shows to be proportional to the composite's stiffness. Therefore, the loss in load bearing capability during and after fire exposure depends to a large extent on the thermal stability of the composite matrix resin. Tests have shown strength reduction as much as

50% at temperatures as low as 121°C for glass reinforced vinyl ester composites [29]. Finally, in terms of low velocity impact, Ulven and Vaidya [30] studied E-glass/VE grooved and non-grooved balsa core sandwich composite panels subjected to a propane flame under different exposure times to obtain the loss of structural integrity. The 'peak load' attained in the flame-side facesheet of the E-glass/VE balsa core sandwich composites decreases as fire exposure time increases. Between the unexposed panel and 50 s exposed panel, a decrease of 26 and 36% in 'peak load' occurred for the grooved and non-grooved sandwich panels, respectively. After 50 s of fire exposure these values dropped significantly. The combustion front causes further thermal degradation of the VE resin matrix producing delaminations and causing embrittlement of the glass fibres in the laminate. This delamination and embrittlement of the glass fibres decreases the structural integrity of the facesheet laminate. The average 'energy to peak load' exhibited a similar trend to the 'peak load' parameter, however, the percentage decrease was less affected by the exposure time. This phenomenon was supported by the authors on the energy absorption mechanisms within the panels change as fire exposure time increases. This phenomenon was associated, by the authors, with the energy absorption mechanisms within the panels and analysed in terms of initial panel stiffness. In fact, a significant reduction of the stiffness in conjunction with the increase in deflection at 'peak load' indicates that energy is progressively dissipated through flexure rather than shear as exposure time increases. After 200 s of exposure, due to loss of integrity in the flame-side facesheet and a portion of the core, the ability to support shear is severely limited. As a result, the impact energy is dissipated primarily through flexure. On the other hand, the low velocity impact parameters are influenced by the boundary conditions [31]. In the fire exposure period of 50 s, a fixed plate boundary condition resulted in 10% higher peak force and 23% higher contact stiffness in comparison to simply supported plate. Beyond 100 s, the peak force and contact stiffness are less influenced by the boundary condition. This can be explained by the reduction on the stiffness that results in higher flexure of the laminate [31].

It is possible to conclude that the composite materials have several application fields but they present safety problems in events of exposure to a fire source. It is possible to find several studies about the degradation of its mechanical properties but there are very few works about the effects of nanoclays on the impact strength of GRP after fire exposure. Therefore, the aim of this work is to study the benefits of a matrix enhanced by nanoclays Cloisite 30B, with a special surface silane treatment, on the low velocity impact response after fire exposure. The results of the present paper are discussed in terms of load-time, load-displacement, energy-time diagrams and damage.

2 - Material and experimental procedure

Six ply laminates, all in the same direction, of woven bi-directional glass fibre 1195P (195 g/m²), were prepared by hand lay-up and the overall dimensions of the plates were 330x330x2.4 [mm]. SR 1500 epoxy resin and a SD 2503 hardener, supplied by Sicomin, were used. The system was placed inside a vacuum bag and a load of 2.5 kN was applied for 24 hours in order to maintain a constant fibre volume fraction and uniform laminate thickness. During the first 10 hours the bag remained attached to a vacuum pump to eliminate any air bubbles existing in the composite. The post-cure was followed according to the manufacturer's datasheet (epoxy resin) in an oven at 40 °C for 24 hours.

Composite laminates with enhanced epoxy matrix by organoclays Cloisite 30B was produced by the same manufacturing process. In order to improve the dispersion and interface adhesion matrix/clay, the nanoclays were subjected to a special treatment appropriate to the epoxy resin. More details about the treatment and the dispersion/exfoliation on the epoxy matrix can be found in [21, 22]. The nanoclays content used in present study is 3 wt.% because, according with studies developed by the authors [22], is the best amount for this epoxy system.

The samples used in the experiments were cut from these plates to square specimens with 100x100x2.4 mm. Low-velocity impact tests were performed using a drop weight-testing machine Instron-Ceast 9340. An impactor with a diameter of 10 mm and mass of 3.4 kg was used. The tests were performed on circular section samples of 70 mm and the impactor stroke at the centre of the samples obtained by centrally supporting the 100x100 mm specimens. The impact energies used were 1, 3, 5, 7 and 9 J, which corresponds to an impact velocity of 0.77, 1.33, 1.71, 2.03 and 2.3 ms⁻¹, respectively. These energies were previously selected in order to enable the measuring of the damage area, but without promote perforation of the specimens. For each condition, five specimens were tested at room temperature.

Fire exposure tests were performed on a propane torch apparatus as shown in Figure 1, which is similar to the equipment used by Ulven and Vaidya [30] on their studies. A BernzOmaticw high temperature torch (60 mm tip diameter) with propane fuel was used to produce a steady flame vertical to the composite laminates. The distance between the torch head and sample determine the flame spread diameter, temperature and heat flux of the flame at the panel surface. A torch distance of 200 mm resulted, at the surface of the panels tested, in the flame characteristics presented on Table 1. The temperature of the flame was measured at the vertical location of the outer surface of the samples and on the vertical axis of symmetry of the system. After correction for the radiation effects, this value was assumed as the reference temperature (T_{ref}) of the hot gas impinging flow. More details about the measurements and corrections of the temperature can be found in [32]. The burn-through characteristics of the composite laminates were studied for a fire exposure time of 30 sec.

3 – Results and discussion

The fire exposure effect on the impact strength of composites with nano-enhanced resin was analysed by impact tests carried out at different incident impact energy levels. Figure 2 shows

typical load and energy versus time curves of control samples and laminates with resin enhanced by 3% of nanoclays tested for an impact energy of 1 J. These curves represent the typical behaviour for each laminate and are in good agreement with the bibliography [21, 22, 33-35].

These curves are characterized by an increase in the load up to a maximum value, P_{\max} , followed by a drop after the peak load. In all tests the impactor deforms the specimens and always rebound, which means that the maximum impact energy was not high enough to produce full penetration. In all cases the maximum time of contact, between impactor and plates, occurred for control laminates increased with the increases of the impact energy. For laminates tested at room temperature and manufactured with resin enhanced by nanoclays, impacted with energy of 1 J, the average time was 5.8 ms, which represent around 6.5 % less than that occurred for laminates with neat resin (6.2 ms). Relatively to the samples that were under fire exposure, the average time for control samples was approximately 7.2 ms while for samples with nanoclays was around 6.8 ms. Comparing these values, it is possible to conclude that the exposure to the fire promotes higher contact times, 15.4% for control samples and 18.6% for samples with nano-enhanced resin, compared with the values obtained at room temperature. From the curves that represent the evolution of the energy with time, it is possible to observe that the highest values of energy relate to smaller elastic recovery and, consequently, higher level of damage. The beginning of the plateau of the curve coincides with the loss of contact between the striker and the specimen, so this energy coincides with that absorbed by the specimen [21, 22, 36].

The value of P_{\max} is very dependent on the impact energy. Some authors found that the maximum load increases with increasing impact energy [21, 22, 37] and similar tendency was observed in this work for both materials as shown in Figure 3. Increases, between 1 to 9 J, were observed around 250.7% and 211.2% for, respectively, control samples and specimens with epoxy resin enhanced by nanoclays tested at room temperature. However, the addition of nanoclays promoted major maximum impact loads with values, relatively to the control samples, around 29%

higher for 1 J and 14.4% for 9 J. These results agree with the studies developed by Reis *et al* [21] where, for example, the addition of clays promoted maximum loads around 16.1% highest than occurred in Kevlar with pure epoxy resin. Similar tendency was observed for both laminates after exposure to the fire and, for the same energy range (1-9 J), increases around 212.6% and 230.1% were observed, respectively, for control samples and laminates with nanoclays. On the other hand, it is possible to conclude that the exposure to the fire decreases the maximum average load around 18.5% and 27.3% for control samples but around 29.7% and 25.4% for laminates with nanocalys, respectively, for the impact energies of 1 J and 9 J. Found and Howard [38] proposed an estimation of the maximum impact force based on the following equation:

$$F_{\max} = \sqrt{2 \cdot U \cdot k} \quad (1)$$

where U is the total impact energy and k is the flexural stiffness of the laminates. For this purpose, static tests were performed in three point bending (3PB) in order to collect the load and flexural displacement in the linear elastic region of the load-displacement plot. Therefore, the flexural stiffness was obtained by linear regression of the load-displacement curves considering the linear segment from zero loading. However, this equation doesn't fit the experimental results for the constant "2". In this context, a new relationship is proposed based on the following mathematical equation:

$$F_{\max} = \sqrt{c \cdot U \cdot k} \quad (2)$$

where U is the total impact energy, k is the flexural stiffness and c a constant that is dependent of the material. In this case the values were selected for each laminate, with a correlation factor greater than 95%, and are presented in Table 2.

Figure 4 shows the displacement observed during the impact loads. Independently of the impact energy, the largest values occur with laminates manufactured exclusively with pure epoxy resin. One more time, these results agree with the studies developed by Reis *et al* [21, 22] and can

be interesting because some systems must absorb the energy of the projectile, but cannot be allowed to deform so extensively that the wearer of the armour is crushed in the process. For the energy range studied, between 1-9 J, the displacements increased around 190.6% and 201.9% for control samples and laminates with resin enhanced by nanoclays, respectively. However, comparing the displacements for 1 J, it is possible to observe that the control samples present values around 1.6 mm, which are 18.6% higher than that occurred for laminates with nanoclays (1.3 mm). Similar comparison for 9 J presents values around 14.1% higher for control samples. In fact, the presence of nanoclays into the epoxy resin decreases its ductile behaviour [23]. Consequently, the laminates present lower displacement but the opposite tendency occurs for the impact loads. On the other hand, the exposure to the fire promotes higher displacements in comparison with the values obtained at room temperature. For example, control samples present increases around 17.9% for 1 J and 13.6% for 9 J, while these values are, respectively, 31.9% and 21.6% for laminates with nanoclays. In order to estimate the maximum displacement, a new mathematical relationship is proposed by the following equation:

$$\delta_{\max} = \sqrt{d \cdot \frac{U}{k}} \quad (3)$$

where U is the total impact energy, k is the flexural stiffness of the laminates and d a constant that is dependent of the material. Once again these values were selected, for each laminate, with a correlation factor greater than 95%. In this context, the smooth curves showed in Figure 4 represents an estimation of the maximum displacement in function of the impact energy, determined from the equation 3, and fits very well to the experimental data for the values presented in Table 2.

Figure 5 compares the elastic recuperation for each laminate. The elastic energy was calculated as the difference between the absorbed energy and the energy at peak load from the diagrams presented in Figure 2. The average values represented, in percentage, show that higher

energies present lower elastic recuperation and, consequently, major damages. For laminates with neat resin, tested at room temperature, it is possible to observe a decrease in the elastic recuperation around 31.1%, between 1 and 9 J, and the data can be fitted by a linear curve with a correlation coefficient around 0.997. On the other hand, when the nanoclays were added better results can be found. For impact energies of 1 J, nanoclays improve the elastic recuperation around 5.1% while for 9 J this value increase to 14.2%. One more time, the data can be fitted, by a linear curve with a correlation coefficient around 0.995. The same tendency was observed by Reis *et al* [21, 22], where the laminates manufactured with epoxy resin enhanced by nanoclays presented the best performance in terms of elastic recuperation and penetration threshold compared to the neat laminates.

Similar tendency can be observed for laminates that were subjected to the fire exposure. However, in the energy range studied, a decrease of the elastic recuperation around 15.2% can be found for control samples, between 1 and 5 J, but this value drops to 34.4% between 5 and 9 J. The same tendency occurs for laminates with nanoclays, independently of the benefits introduced by the nano-enhanced resin, where these values are, respectively, around 13.7% (between 1-5 J) and 24.8% (between 5-9 J). In this case, for both laminates, the data can be fitted by a polynomial curve (type $y = ax^2+bx+c$) with a correlation coefficients of 0.999 for both laminates.

These results are consequence of the stiffness reduction, during fire exposure, which is associated a significant loss of load bearing capability from melting or devitrification of the matrix resin at elevated temperatures [29]. Figure 6 shows pictures of the specimens after fire exposure. It is possible to conclude that the heat fluxes used in the fire tests generate high enough surface temperature to degrade the matrix and, according to Mouritz and Mathys [28], it is hot enough (≈ 1200 °C) to cause damage of the glass fibres (that occurs at 1065-1120 °C [28]). In fact, epoxy resins starts to decompose at 295 °C in two major steps with maximum rate at 297 and 336 °C followed by a slow weight loss in the temperature region 360–600 °C [39, 40]. In the present

study, for example, the fire tests promoted weight loss around 17.8% and 9.9% for control samples and laminates with nanoclays, respectively. In addition to char formation the radiant heating also causes delaminations, as shown Figure 6a) for the control samples. In some cases, these delaminations cause complete separation of the char from the unburnt portion of the composite, which agrees with Mouritz and Mathys [28]. On the other hand, in Figure 6b) the char formation and the delaminations are not so evident because the clays improve the fire performance of the polymers. Jang and Wilkie [41], for example, found that the peak heat release rate of polyamide 6/clay nanocomposite could be reduced by 60% during combustion measured by cone calorimeter, compared to the virgin polymer, at levels of only 5 wt.%. Other studies reported that even when the fraction of clay was as low as 0.1%, the peak heat release rate was lowered by 40% [42, 43]. According with Kashiwagi *et al* [44] the reduction of peak heat release rate is attributed to the formation of protective floccules on the sample surface which shield the polymer from the external thermal radiation and heat feedback from the flame, thus acting as a thermal insulation barrier.

4 – Conclusions

The fire exposure effect on the impact strength of a glass fibre/epoxy composite enhanced by nanoclays Cloisite 30B especially modified was analyzed for different impact energies. The maximum load, maximum displacement and elastic recuperation were shown to be highly dependent of the impact energy. The introduction of nanoclays promoted significant benefits especially in terms of displacement and elastic recuperation. For 9 J the elastic recuperation of nanoclay filled composite was around 14.2% higher than occurred for control material, but, in terms of displacement, the values obtained for the control samples are 14.1% higher.

The exposure to the fire decreases the maximum load and elastic recuperation, while the displacement increases in comparison with the respective values obtained at room temperature.

Between 1 and 5 J a decrease of the elastic recuperation around 15.2% was found for control samples and 13.7% for laminates with nano-enhanced resin. Based on the total impact energy and flexural stiffness it was suggested a mathematical relationship to estimate the maximum impact force and displacement.

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ACCEPTED MANUSCRIPT

REFERENCES

- [1] Adams RD, Cawley PD. A Review of Defects Types and Non-Destructive Testing Techniques for Composites and Bonded Joints. *NDT Int* 1998; 21: 208-222.
- [2] Amaro AM, Reis PNB, de Moura MFSF, Santos JB. Damage Detection on Laminated Composite Materials Using Several NDT Techniques. *Insight* 2012; 54: 14-20.
- [3] Caprino G. Residual Strength Prediction of Impacted CFRP Laminates. *J Compos Mater* 1984; 18: 508-518.
- [4] Davies GAO, Hitchings D, Zhou G. Impact damage and residual strengths of woven fabric glass/polyester laminates. *Compos Part A-Appl S* 1996; 27: 1147-1156.
- [5] de Moura MFSF, Marques AT. Prediction of low velocity impact damage in carbon-epoxy laminates. *Compos Part A-Appl S* 2002; 33: 361-368.
- [6] Amaro AM, de Moura MFSF, Reis PNB. Residual strength after low velocity impact in carbon-epoxy laminates. *Mater Sci Forum* 2006; 514-516: 624-628.
- [7] Amaro AM, Reis PNB, de Moura MFSF. Delamination effect on bending behaviour in carbon-epoxy composites. *Strain* 2011; 47: 203-208.
- [8] Reis PNB, Ferreira JAM, Antunes FV, Richardson MOW. Effect of Interlayer Delamination on Mechanical Behavior of Carbon/Epoxy Laminates. *J Compos Mater* 2009; 43: 2609- 2621.
- [9] Luo, J-J, Daniel IM. Characterization and modeling of mechanical behaviour of polymer/clay nanocomposites. *Compos Sci Technol* 2003; 63: 1607-1616.
- [10] Giannelis EP. Polymer Layered Silicate Nanocomposites. *Adv Mater* 1996; 8: 29-35.
- [11] Saber-Samandari S., Khatibi AA, Basic D. An experimental study on clay/epoxy nanocomposites produced in a centrifuge. *Compos Part B-Eng* 2007; 38: 102-107.
- [12] Ke Y, Long C, Qi Z. Crystallization, properties, and crystal and nanoscale morphology of PET-clay nanocomposites. *J Appl Polym Sci* 1999; 71: 1139-1146.
- [13] Liu W, Hoa SV, Pugh M. Organoclay-modified high performance epoxy nanocomposites. *Compos Sci Technol* 2005; 65: 307-316.
- [14] Liu W, Hoa SV, Pugh M. Fracture toughness and water uptake of high-performance epoxy/nanoclay nanocomposites. *Compos Sci Technol* 2005; 65: 2364-2373.
- [15] Ho M-W, Lam C-K, Lau K-T, Ng DHL, Hui D. Mechanical properties of epoxy-based composites using nanoclays. *Compos Struct* 2006; 75: 415-421.

- [16] Ferreira JAM, Reis PNB, Costa JDM, Richardson BCH, Richardson MOW. A study of the mechanical properties on polypropylene enhanced by surface treated nanoclays. *Compos Part B-Eng* 2011; 42: 1366-1372.
- [17] Ferreira JAM, Reis PNB, Costa JDM, Richardson MOW. A study of the mechanical behaviour on injection moulded nanoclay enhanced polypropylene composites. *J Thermoplast Compos* 2011 doi: 10.1177/0892705711428658.
- [18] Hosur MV, Chowdhury F, Jeelani S. Low-velocity impact response and ultrasonic NDE of woven carbon/epoxy–nanoclay nanocomposites. *J Compos Mater* 2007; 41: 2195- 2212.
- [19] Iqbal K, Khan S-U, Munir A, Kim J-K. Impact damage resistance of CFRP with nanoclay-filled epoxy matrix. *Compos Sci Technol* 2009; 69: 1949–1957.
- [20] Ávila AF, Soares MI, Neto AS. A study on nanostructured laminated plates behavior under low-velocity impact loadings. *Int J Impact Eng* 2007; 34: 28–41.
- [21] Reis PNB, Ferreira JAM, Santos P, Richardson MOW, Santos JB. Impact response of Kevlar composites with filled epoxy matrix. *Compos Struct* 2012; 94: 3520-3528.
- [22] Reis PNB, Ferreira JAM, Zhang ZY, Benameur T, Richardson MOW. Impact Response of Kevlar Composites with Nanoclay Enhanced Epoxy Matrix. *Compos Part B-Eng* 2013; 46: 7-14.
- [23] Ferreira JAM, Reis PNB, Costa JDM, Richardson MOW. Fatigue behaviour of Kevlar composites with nanoclay-filled epoxy resin. *J Compos Mater* 2013; 45: 1885-1895.
- [24] Hosur MV, Mohammed AA, Zainuddin S, Jeelani S. Impact performance of nanophased foam core sandwich composites. *Mater Sci Eng A* 2008; 498: 100–109.
- [25] Hosur MV, Mohammed AA, Zainuddin S, Jeelani S. Processing of nanoclay filled sandwich composites and their response to low velocity impact loading. *Compos Struct* 2008; 82: 101–116.
- [26] Ávila AF, Carvalho MGR, Dias EC, da Cruz DTL. Nano-structured sandwich composites response to low-velocity impact. *Compos Struct* 2010; 92: 745–751.
- [27] Gu P, Dao M, Asaro RJ. Structural stability of polymer matrix composite panels in fire. *Mar Struct* 2009; 22: 354-372.
- [28] Mouritz AP, Mathys Z. Post-fire mechanical properties of marine polymer composites. *Compos Struct* 1999; 47: 643-653.
- [29] Sorathia U, Lyon R, Gann R, Gritz L. Materials and fire threat. *SAMPE J* 1996; 32: 8-15.
- [30] Ulven CA, Vaidya UK. Post-fire low velocity impact response of marine grade sandwich composites. *Compos Part A-Appl S* 2006; 37: 997-1004.

- [31] Ulven CA, Vaidya UK. Impact response of fire damaged polymer-based composite materials. *Compos Part B-Eng* 2008; 39: 92-107.
- [32] Figueiredo AR, Costa JJ. Experimental analysis of the use of wet porous media for thermal protection against high intensity heat fluxes. *Heat Mass Transfer* 2004; 47: 11-19.
- [33] Aslan Z, Karakuzu R, Okutan B. The response of laminated composite plates under low-velocity impact loading. *Compos Struct* 2003; 59: 119-127.
- [34] Hosur MV, Adbullah M, Jeelani S. Studies on the low-velocity impact response of woven hybrid composites. *Compos Struct* 2005; 67: 253-262.
- [35] Reis PNB, Ferreira JAM, Rodrigues NFS. Impact behaviour of panels for automotive applications. *Strain* 2011; 47 (Suppl. 2): 79-86.
- [36] Ríó TG, Zaera R, Barbero E, Navarro C. Damage in CFRPs due to low velocity impact at low temperature. *Compos Part B-Eng* 2005; 36: 41-50.
- [37] Iqbal K, Khan S-U, Munir A, Kim J-K. Impact damage resistance of CFRP with nanoclay-filled epoxy matrix. *Compos Sci Technol* 2009; 69: 1949-1957.
- [38] Found MS, Howard LC. Single and multiple impact behaviour of a CFRP laminate. *Compos Struct* 1993; 32: 159-163.
- [39] Luda MP, Balabanovich AI, Camino G. Thermal decomposition of fire retardant brominated epoxy resins. *J Anal Appl Pyrol* 2002; 65: 25-40.
- [40] Levchik SV, Weil ED. Thermal decomposition, combustion and flame-retardancy of epoxy resins - a review of the recent literature. *Polym Int* 2004; 53: 1901-1929.
- [41] Jang BN, Wilkie CA. The effect of clay on the thermal degradation of polyamide 6 in polyamide 6/clay nanocomposites. *Polymer* 2005; 46: 3264-3274.
- [42] Zhu J, Wilkie CA. Thermal and fire studies on polystyrene-clay nanocomposites. *Polym Int* 2000; 49: 1158-1163.
- [43] Jash P, Wilkie CA. Effects of surfactants on the thermal and fire properties of poly(methyl methacrylate)/clay nanocomposites. *Polym Degrad Stabil* 2005; 88: 401-406.
- [44] Kashiwagi T, Harris RH, Zhang X, Briber RM, Cipriano BH, Raghavan SR, Awad WH, Shields JR. Flame retardant mechanism of polyamide 6-clay nanocomposites. *Polymer* 2004; 45: 881-891.

Figures

Figure 1 - Propane torch apparatus used on the fire tests.

Figure 2 - Load and energy versus time curves obtained from the impact tests carried out for 1 J and: a) room temperature; b) after exposition to the fire.

Figure 3 – Evolution of the maximum average load with the impact energy (CS = Control Samples; LN = Laminates with nanoclays).

Figure 4 – Evolution of the maximum average displacement with the impact energy (CS = Control Samples; LN = Laminates with nanoclays).

Figure 5 – Evolution of the average elastic recuperation with the impact energy (CS = Control Samples; LN = Laminates with nanoclays).

Figure 6 Pictures of the samples after fire exposure: a) Control samples; b) Laminates with nanoclays.

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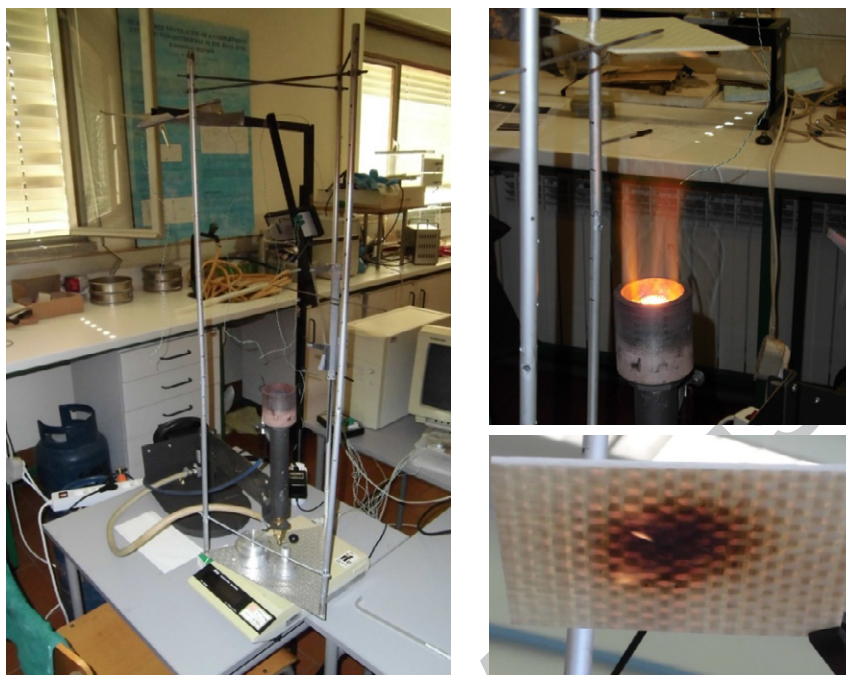
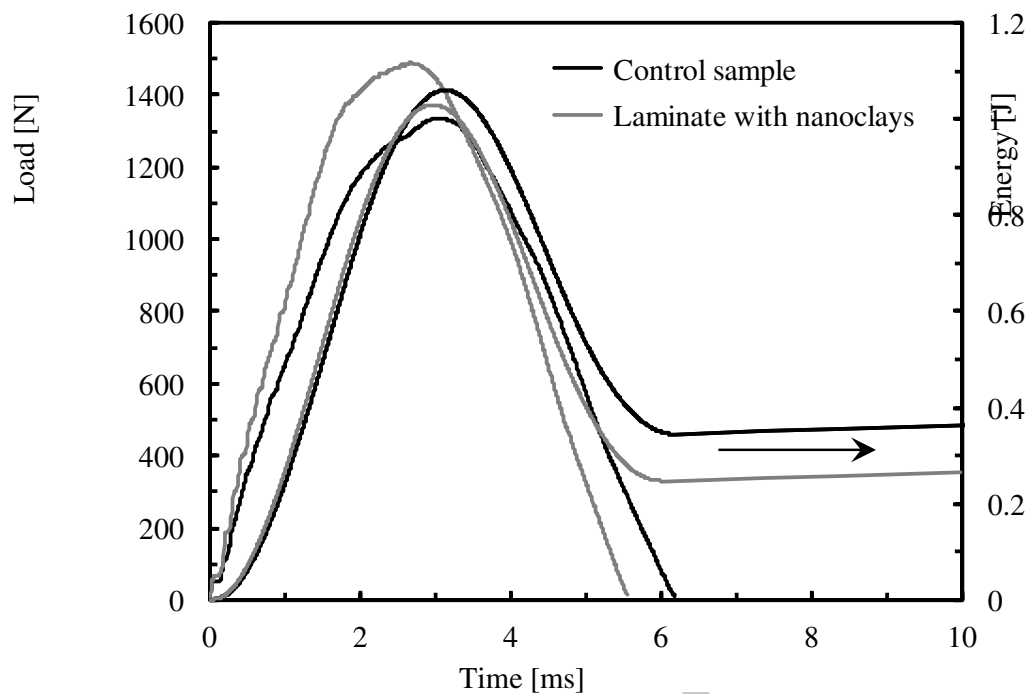
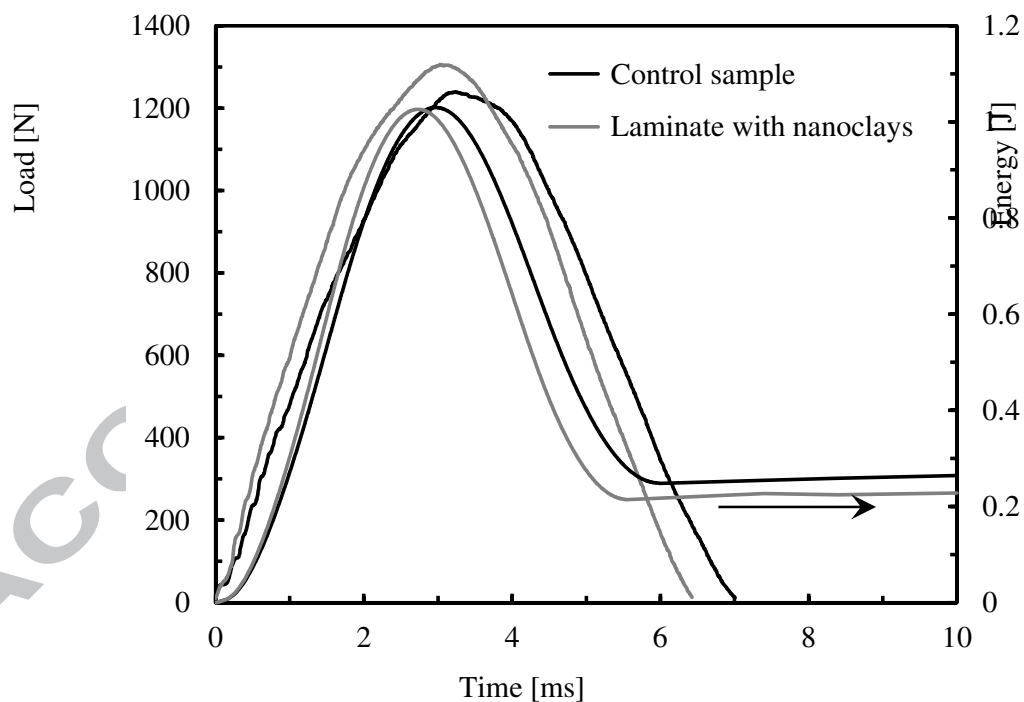


Figure 1 - Propane torch apparatus used on the fire tests.



a)



b)

Figure 2 - Load and energy versus time curves obtained from the impact tests carried out for 1 J and: a) room temperature; b) after exposition to the fire.

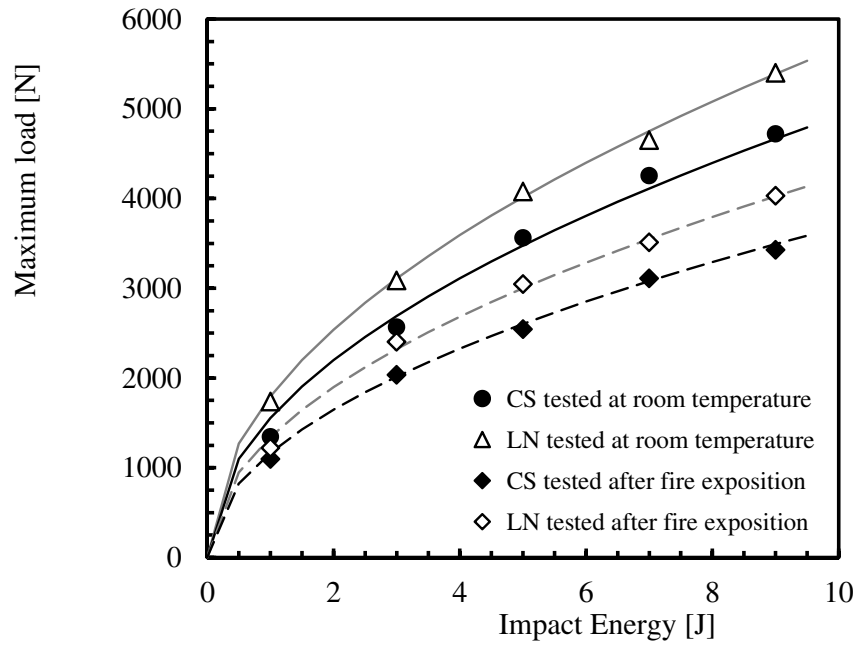


Figure 3 – Evolution of the maximum average load with the impact energy (CS = Control Samples; LN = Laminates with nanoclays).

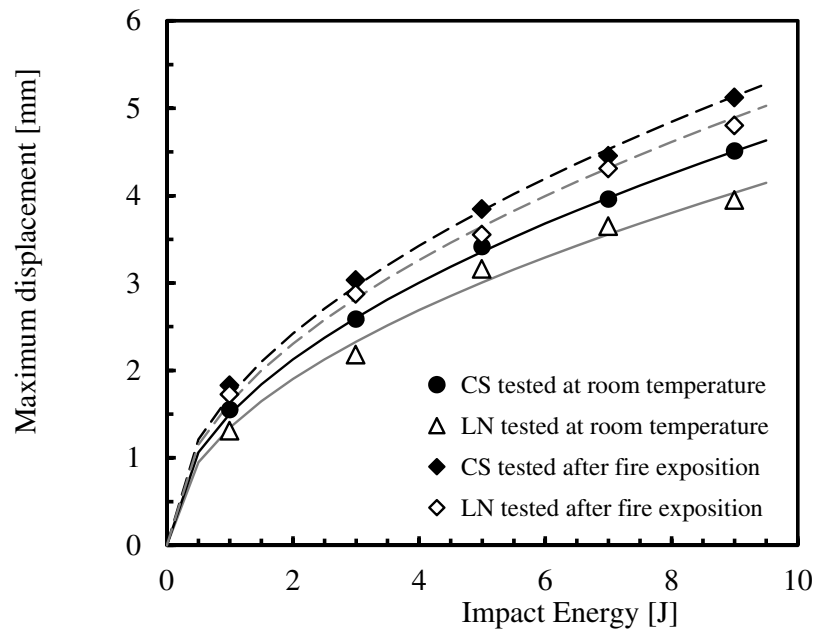


Figure 4 – Evolution of the maximum average displacement with the impact energy (CS = Control Samples; LN = Laminates with nanoclays).

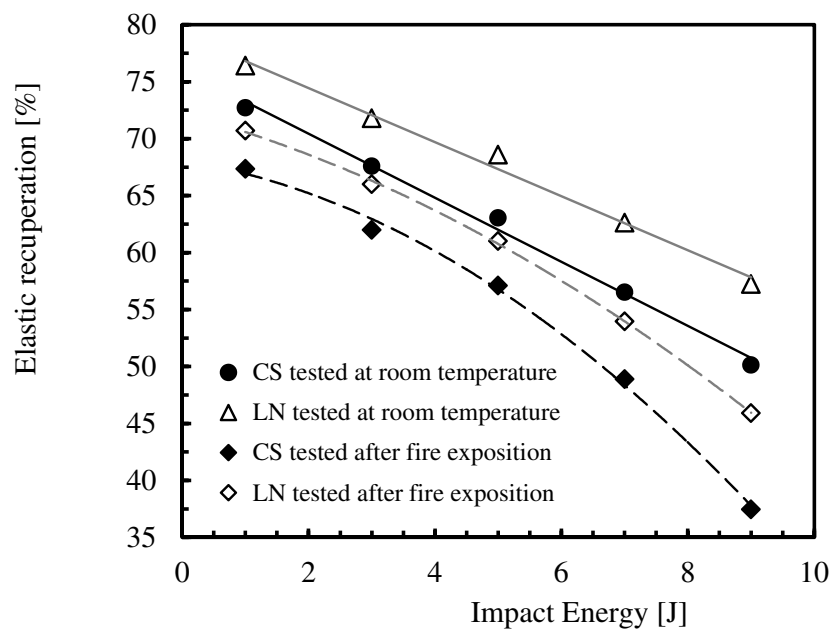
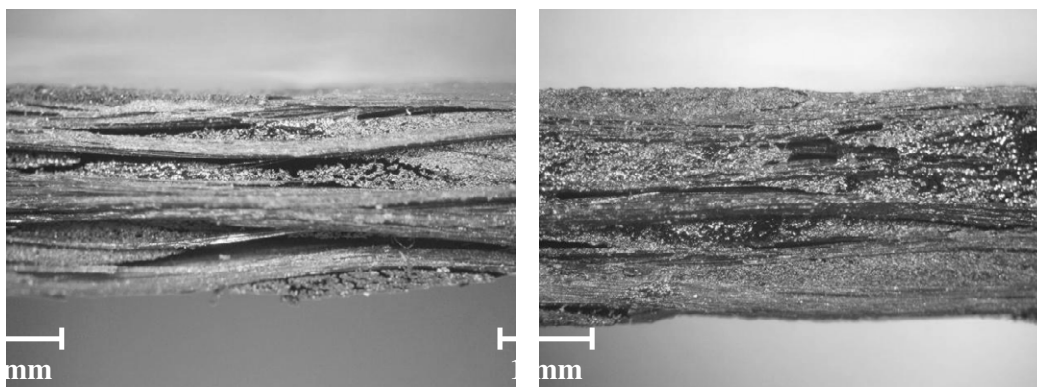


Figure 5 – Evolution of the average elastic recuperation with the impact energy (CS = Control Samples; LN = Laminates with nanoclays).



a) b)

Figure 6 – Pictures of the samples after fire exposure: a) Control samples;
b) Laminates with nanoclays.

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Table 1 – Flame characteristics at the surface of the panels.

Flame Spread Diameter [mm]	Flame Temperature [°C]	Heat Flux [kW/m²]	Convective heat transfer [W/m²°C]
80	1200±56	24	21.8±1.4

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Table 2 – Flexural stiffness and constant values.

Laminates		Flexural stiffness		Constants	
		Average value [kN/m]	Std Dev [kN/m]	c	d
Neat resin	Room temperature	210.1	2.4	11.5	380
	After fire exposure	180.6	17.7	7.5	530
Resin enhanced by nanoclays	Room temperature	230.3	1.9	14	520
	After fire exposition	199.9	10.2	9	532

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