AN EXPERIMENTAL STUDY ON VIBRATION FREQUENCIES AND DAMPING PARAMETERS OF NANOCOMPOSITES PLATES

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Abstract. *Composite laminates have become widely spread into used in primary structural components in aircrafts, modern vehicles and light-weight structures. 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. 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. This work deals with a fiber glass-epoxy-nanoclay laminate composites with 16 layers and 65% fiber volume fraction is manufactured by vacuum assisted wet lay-up. To understand how the composite overall vibrational behavior is affected by the nanoclay exfoliation into the matrix, a set of nanocomposite with 0%, 1%, 2%, 5% and 10% wt were prepared. These plates were tested and the natural frequencies, damping parameters were determined.*

Keywords*: NanoComposites, Damping Parameters, Natural frequencies, Plates, Vibration*

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 perturbation on media, 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. (2003) 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.

Another issue that must be addressed is how the natural frequency is affected by the stacking sequence and the boundary conditions. One approach for obtain these relations is the finite element method. Ramtekkar and Desai (2002) developed a finite element model based on a six node plane stress mixed element and by applying the Hamilton's energy principle; they were able to obtain the natural frequencies of laminated beams. Their results were in good agreement to data available into the literature. Gubran and Gupta (2005) demonstrated that natural frequencies are directed affected by the angle ply formation and the stacking sequence. Moreover, the bending-twisting effect is more evident for the angle ply configuration and associated to the Poisson effect and the shear-normal coupling. The largest reduction, ≈ 87 %, on the natural frequency when the bending-twisting effect associated to the shear-normal coupling is considered to a 30 degrees angle ply. Moreover, the boundary conditions have also influence into natural frequencies. According to Aydogdu and Timarci (2003), when the boundary conditions from simple supported-clamped-simple supported-clamped changed to simple supported-free-simple supported-free a decrease of approximately 400% on frequencies is observed. As mentioned by Lam and Chun (1994), when impact loading are considered 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.

The objectives of this paper are twofold. On the one hand, a vibration analysis is conducted on the new polymer-nanoclay-fiber glass nanocomposite. This analysis will help us to understand the nanocomposite behavior under impact loadings. 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 Production

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.

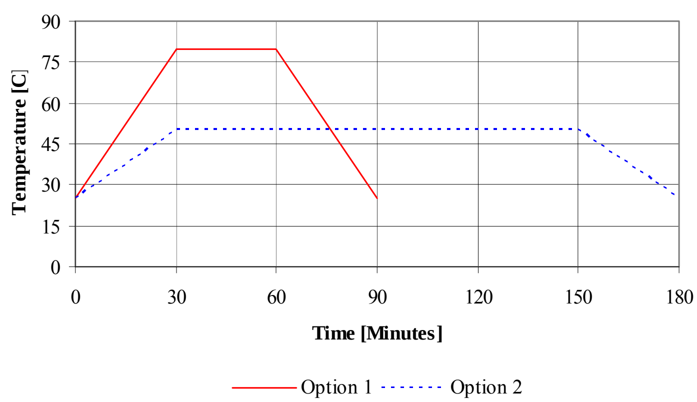


Figure 1: Co-cure procedure from Hunstman (2004).

3. Vibration Experiments

To perform a vibration analysis a set of nanocomposite rectangular plates (150 x 140 mm) with thickness of 2.4 mm are manufactured. The plate dimensions follow the ASTM D 5628-01 standard recommendations for low velocity impact tests (ASTM, 2001). The amounts of nanoparticles used are 0, 1, 2, 5 and 10% in weight of the resin. All plates are manufactured following the procedure described in section two. Once the plates are prepared, each center was marked and placed into the experiment set up shown in Figure 2A. The plate boundary conditions are free in all edges. These conditions can be ensuring by lifting the plates as shown in Figure 2B.

A - Vibration experiment B – Boundary conditions

Figure 2: Vibration experiment set up

A Hewlett Packard 35670A vibration analyzer associated to a power amplifier type 2170 from Bruel & Kjaer was employed in this experiment. The mini shaker type 4810 is also from Bruel & Kjaer, while the vibration transducers are from Piezoeletronics Incorporated.

4. Data Analysis

The first set of this research is to study the co-cure influence into the nanocomposite manufacture. As suggested by the manufacturer, there are two options for co-cure procedures. Preliminary tests have shown that the fast co-cure procedure leads to formation of interlaminar stresses and as consequence delaminations, as it can be observed in Figure 3. This can be due to the formation of “hot spots”, which can lead to an interlaminar stress discontinuity due to the nanoparticle presence. Those interlaminar stress discontinuities can be represented by bubbles inside the composite. A series of smooth results with no delamination was obtained by applying the slow co-cure procedure.

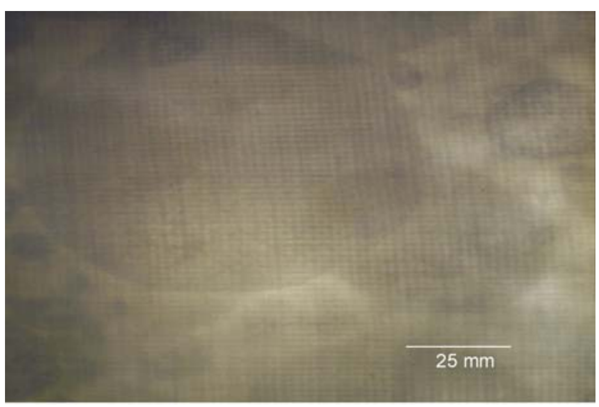


Figure 3: Interlaminar stresses for fast co-cure

The next step is the vibration analysis. The aim here is to study the nanoparticle influence into the plate vibration behavior. To analyze only the nanoparticle influence all manufacturing parameters are kept fixed but the nanoparticle concentration. According to Gibson (2000), a typical frequency/response function for impulse test allows the definition of the natural frequencies. Additionally, the peaks in the frequency/response spectrum are the location of natural frequencies of the specimens. Figure 4 shows these frequency response for the specimens tested, while in Figure 5 the coherence plot is represented. Meanwhile, Tables 2 and 3 summaries not only the natural frequencies but also the damping coefficients associated.

As it can observed in Table 2, there is no significant changes on natural frequencies with the addition nanoparticles up to 2%. The same behavior can be observed with respect to the damping coefficient. No significant variations on natural frequencies, difference around 1.5%, are observed when the nanoparticles content reaches 10%, as it can be seen in Table 3. This can be due to the fiber plain weave configuration, which leads to a “preferential path” for the waive propagation. However, for the 5^{th} vibration mode the damping coefficient experiences an increase close to 32%.

Considering that the stacking sequence is the same the only reason for this increase is the nanoparticle presence. Moreover, Avila et al. (2005) reported an increase on impact toughness close to 100% with the addition of 10% of montmonillonite to epoxy/fiber glass systems. This better performance can be partially explained by the increase on damping coefficient and the increase on stiffness reported by many authors, e.g. Avila et al. (2005), Yasmin et al. (2004) and Subramaniyan et al. (2003).

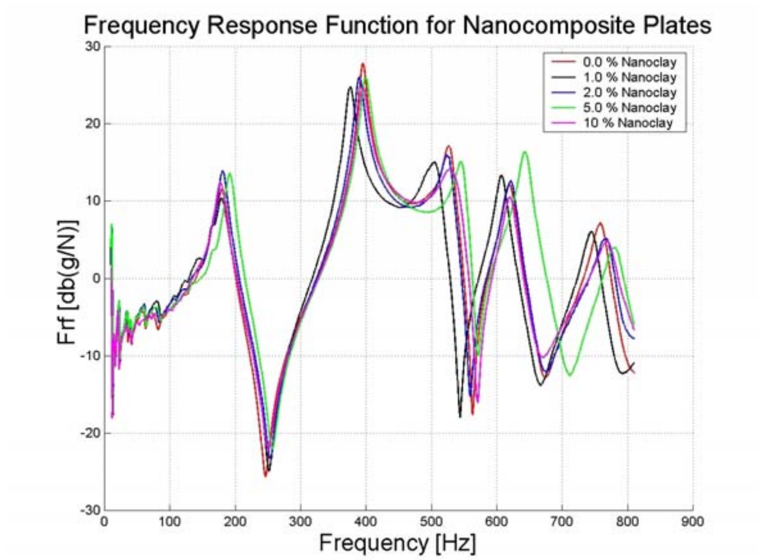


Figure 4. Frequency/response function for impulse

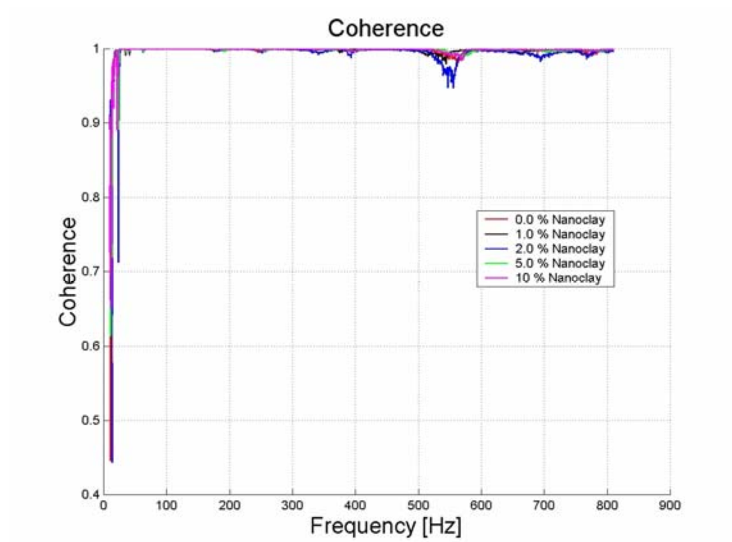


Figure 5. Coherence plots

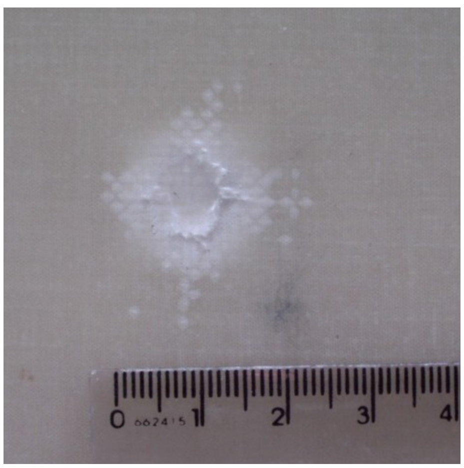
Table 2. Vibration parameters – 0 through 2% nanoparticle content

Nanoparticles Content 0%		Nanoparticles Content 1%		Nanoparticles Content 2%	
Natural Frequency [Hz]	Damping Coefficient 10^{-3}	Natural Frequency [Hz]	Damping Coefficient 10^{-3}	Natural Frequency [Hz]	Damping Coefficient 10^{-3}
181.50	38.72	180.50	36.41	181.00	35.10
386.00	14.86	375.50	17.91	389.50	14.44
528.50	13.70	508.00	24.12	526.00	15.39
619.50	15.40	607.50	12.65	622.00	14.27
759.50	13.68	745.50	14.41	768.50	15.84

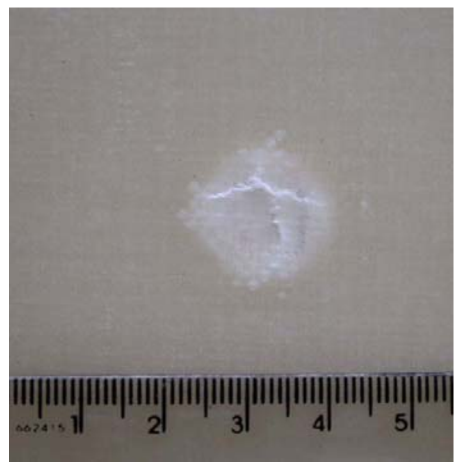
Table 3. Vibration parameters – 5 through 10% nanoparticle content

Nanoparticles Content 5%		Nanoparticles Content 10%	
Natural Frequency [Hz]	Damping Coefficient 10^{-3}	Natural Frequency [Hz]	Damping Coefficient 10^{-3}
192.00	33.30	177.50	36.84
399.00	15.18	395.00	16.51
547.50	13.27	533.50	27.40
643.50	12.46	620.50	14.19
781.00	16.78	771.00	18.17

Assuming that there is no significant variation on wave propagation velocity with the amount of nanoparticles inside the nanocomposite, the failure mechanism during the impact tests must be associated not only to the damping coefficient but also stiffness and toughness variations. From the data shown by Avila et. al. (2005), the amount of nanoparticles is responsible to the impact strength increase, as it can be observed in Figures 6A-6B. As we are dealing with two different levels of reinforcement, one at nanoscale, nanoparticles inside the matrix/resin, and another at microscale, fiber reinforcement with plain weave configuration, it is possible to conclude that coupling between nano and micro effects can be a key issue in this problem.



A – Front damage (0% of nanoparticles)



B – Front damage (2% of nanoparticles)

Figure 6. Front impact marks from Avila et al. (2005)

5. Closing Comments

The co-cure process was also studied and the fast co-cure procedure suggested by Hunstman (2004) seems not be appropriate for nanocomposites. The reason is the intense interlaminar stresses developed that could be the cause of bubbles formation and delaminations experimented during the process. The slow co-cure procedure leads to more uniform laminate without the presence of delaminated areas.

The natural frequencies and the damping coefficient were experimentally determined for the new laminated nanocomposite. A small variation on natural frequencies was observed when the amount of nanoparticles are exfoliated into the matrix. The damping coefficient is practically constant, the only variation observed was for the 781 Hz frequency (5^{th} vibration mode for nanocomposite with 10% nanoparticle content) shows and increase around 30% with respect to the nanocomposite without nanoparticles. As the impact toughness is increased by the exfoliated nanoparticles it is reasonably to suppose that a more complex phenomenon is present. This work is a working in progress is based to the results presented a more comprehensive study is under development.

6. Acknowlegments

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7. References

Abrate, S., 1998, “Impact on composite structures”, Cambridge University Press; Cambridge UK, Chapters 1-3.

ASTM D 5628-01, 2001 "Standard test method for impact resistance of flat, rigid plastic specimens by means of a falling dart (tup or falling mass)", Annual Book of ASTM Standards, Vol. 08, No. 02, pp. 628-637.

Avila, A.F., Soares M.I., Silva Neto, A., 2005, "An experimental investigation on nanocomposites under impact loading", Impact Loading of Lightweight Structures, Ed. WIT Press, Southampton, UK, M. Alves and N. Jones (editors), pp.89-102.

Aydogdu, M., Timarci, T., 2003, "Vibration analysis of cross-ply laminated square plates with general boundary conditions", Composites Science and Technology, Vol. 63, No 5, pp. 1061-1070.

Belingardi, G., Vadori, R., 2002, "Low velocity impact tests of laminate glass-fiber-epoxy matrix composite material plates", International Journal of Impact Engineering, Vol. 27, No. 2, pp. 213-229.

Davies, G.A.O., Zhang, Z., 1995, "Impact damage prediction in carbon composite structures", International Journal of Impact Engineering, Vol. 16, No. 1, pp. 149-170.

da Silva Junior, J.E.L., Paciornik, S., d'Almeida, J.R.M., 2004, "Evaluation of effect of ballistic damaged area on the residual impact strength and tensile stiffness of glass-fabric composite materials", Composite Structures, Vol. 64, No. 1, pp. 123-127.

Gibson, R.F., 2000, "Modal vibration response measurements for characterization of composite materials and structures", Composites Science and Technology, Vol. 60, No 10, pp. 2769-2780.

Gu, B., 2003, "Analytical modeling for ballistic perforation of planar plain-woven fabric target by projectile", Composites Part B, Vol. 34, No. 3, pp. 361-371.

Gubran, H.B.H., Gupta, K., 2005, "The effect of stacking sequence and coupling mechanisms on natural frequencies of composite shafts", Journal of Sound and Vibrations, Vol. 282, No 2, pp. 231-248.

Haque, A., Shamsuzzoha, M., 2003, "S2-glass/epoxy polymer nanocomposites: manufacturing, structures, thermal and mechanical properties", Journal of Composite Materials, Vol. 37, No. 20, pp. 1821-1837.

Hu, N, Sekine, H., Fukunaga, H., Yao, H.Z., 1999, "Impact analysis of composite laminates with multiple delaminations", International Journal of Impact Engineering, Vol. 22, No. 7, pp. 633-648.

Huntsman Chemical Co, 2004, "Araldite Data Sheet", Huntsman Chemical Company; New York, pp. 1-18.

Isik, I., Yilmazer, U., Bayram, G., 2003, "Impact modified epoxy/montmorillonite nanocomposites: synthesis and characterization", Polymer, Vol. 44, No. 25, pp. 6371-6377.

Kim, Y.K., Daniel, I.M., 2002, "Cure cycle effect on composite structures manufactured by resin transfer molding", Journal of Composite Materials, Vol. 36, No. 14, pp. 1725-1743.

Lam, K.Y., Chun, L., 1994, "Analysis of clamped laminated plates subjected to conventional blast", Composite Structures, Vol. 29, No. 2, pp. 311-321.

Liu, D., Raju, B.B., Dang, X., 2000, "Impact perforation resistance of laminated and assembled composite plates", International Journal of Impact Engineering, Vol. 24, No.8, pp. 733-748.

Liu, T., Lim, K.P., Tjiu, W.C., Pramoda, K.P., Chen, Z-K., 2003, "Preparation and characterization of nylon 11/organoclay nanocomposites", Polymer, Vol. 44, No. 27, pp. 3529-3535.

Luo, R.K, Green, E.R, Morrison, C.J, 1999, "Impact damage analysis of composite plates", International Journal of Impact Engineering, Vol. 22, No. 5, pp. 435-447.

Mines, R.A.W., Roach, A.M., Jones, N., 1999, "High velocity perforation behavior of polymer composite laminates", International Journal of Impact Engineering, Vol. 22, No 6, pp. 561-588.

Moura, M.F.S.F., Gonçalves, J.P.M., 2005, "Modeling the interaction between matrix cracking and delamination in carbon-epoxy laminates under low velocity impact", Composites Science and Technology, to appear.

Naik, N.K, Shrirao, P, 2004, "Composite structures under ballistic impact", Composite Structures, Vol. 66, No. 8, pp. 578-590.

Potti, S.V., Sun, C.T., 1997, "Prediction of impact induced penetration and delamination in thick composite laminates", International Journal of Impact Engineering, Vol. 19, No. 1, pp. 31-48.

Ramtekkar, G.S., Desai, Y.M., 2002, "Natural vibrations of laminated composite beams by using mixed finite element method", Journal of Sound and Vibration, Vol. 257, No 4, pp. 635-651.

Subramaniyan, A.K., Bing, Q., Nakaima, D., Sun, C.T., 2003, "Effect of nanoclay on compressive strength of glass fiber composites", Proceedings of the 18th ASC/ASTM Joint Technical Conference; Edited by B.V. Sankar; University of Florida; Gainesville; CDROM.

Tan, V.B.C., Shim, V.P.W., Tay, T.E., 2003, "Experimental and numerical study on response of flexible laminates to impact loadings", International Journal of Solids and Structures, Vol. 40, No. 22, pp. 6245-6266.

Yasmin, A., Abot, J.L., Daniel, I.M., 2003, "Processing of clay-epoxy nanocomposites by shear mixing", Scripta Materialia, Vol. 49, No. 1, pp. 81-86.

Yasmin, A., Luo, J-J., Daniel, I.M., 2004, "Processing of graphite nanosheet reinforced polymer nanocomposites", Proceedings of the 19th ASC/ASTM Joint Technical Conference; Edited by E. Armeiros; Georgia Institute of Technology; Atlanta; CDROM.

Yei, D-R., Kuo, S-W., Su, Y-C., Chang, F-C., 2004, "Enhanced thermal properties of PS nanocomposites formed from inorganic POSS-treated montmorillonite", Polymer, Vol. 45, No. 22, pp. 2633-2640.

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