

**HYGROTHERMAL EFFECT ON THE IMPACT RESPONSE
OF CARBON COMPOSITES WITH EPOXY RESIN
ENHANCED BY NANOCCLAYS**

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This paper presents the results of the hygrothermal effect on the impact response of carbon/epoxy composites and the benefits gained from doping the epoxy resin with nanoclays previously subjected to a silane treatment appropriate for the resin. The nanoclay reinforcement increased the maximum load and the elastic recovery of the composites. The thermal degradation caused by exposure to 60°C for 10 days was insignificant, while the immersion in water at 60°C for 30 days led to a continuous reduction in the maximum load and the elastic recovery. Multiple impacts resulted in a continuous and nearly linear degradation of the impact response both of dry and environmentally assisted specimens.

1. Introduction

Composite structures are usually exposed to a range of hygrothermal conditions during their in-service life, which cause their degradation in terms of material properties. According to [1], the material degradation includes chemical changes of matrix materials and debonding at the fiber/matrix interface. If water penetrates into the matrix or the interface region of a composite, it acts as a plasticizer, pushing polymer chains apart, thus significantly decreasing the glass-transition temperature, and the internal stress arising during the process is diminished. This phenomenon makes composites softer, since the matrix becomes pliable due to the presence of the plasticizer. In fact, the glass-transition temperature T_g is a very important parameter of resins, because it determines the service environment for use of the materials. In [2], it is shown that the variation in T_g of an epoxy resin exposed to a hygrothermal environment is rationalized as follows: i) the change in T_g does not depend solely on the water content in the resins, ii) T_g is affected by the hygrothermal history of the materials, and iii) for a given epoxy system,

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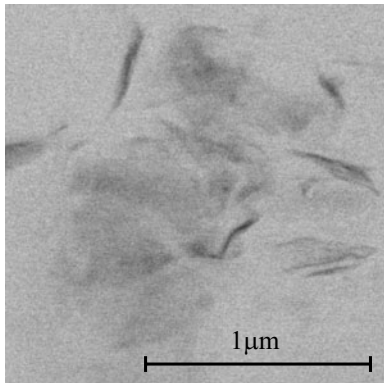


Fig. 1. TEM micrograph. Explanations in the text.

longer time and a higher exposure temperature result in a higher value of T_g . According to [3], there are three absorption modes: (i) bulk dissolution of water in the polymer network, (ii) moisture absorption onto the surface of vacuoles, which define the excess free volume of the glassy structure, and (iii) hydrogen bonding between polymer hydrophilic groups and water. The rate at which water is absorbed by a composite depends on many factors, including the properties of fibers and matrix, temperature, the difference in water concentration within the composite, the environment, and the fact whether the absorbed water reacts chemically with the matrix [4]. However, it was observed in [5] that both the rate of water pickup or the total amount of moisture absorbed depend on the chemical structure of resin, cross-linking agent, temperature, and the relative humidity.

On the other hand, during operational or maintenance activities, there are typical incidents of low velocity, which can affect the strength and stiffness of the composite materials. The impact damage is considered the primary cause of in-service delamination in composites, which can reduce their residual strength [6-9]. However, other types of damages, such as fiber breakage, matrix cracking, and fiber-matrix interfacial debonding, can occur, which are also very dangerous, because they are not easily detected visually and lead to structural failure.

Therefore, the aim of this work was to study the hygrothermal effect on the impact response of carbon composites and the benefits gained, in terms of the impact strength, when an epoxy resin is doped with nanoclays. According to the open literature, nanoclays operate as effective reinforcements in neat polymeric structures [10-12] and also decrease their moisture permeability [13, 14].

2. Materials and Experimental Procedure

Nine ply laminates of woven bidirectional carbon 195-1000P (195 g/m²), all in the same direction, were prepared by hand lay-up. The dimensions of the plates were 330 × 330 × 3 mm. A SR 1500 epoxy resin and an SD 2503 hardener, supplied by Sicomin, were used. The system was placed in a vacuum bag and loaded with 2.5 kN over a period of 24 hours in order to maintain a constant fiber volume fraction and a 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 postcure was carried out, according to manufacturer's datasheet (epoxy resin), in an oven at $T = 40^\circ\text{C}$ during 24 hours.

By employing the same manufacturing process, composite laminates based on an epoxy matrix filled with Cloisite 30B organoclays were produced. In order to improve the dispersion and the adhesion at the matrix/clay interface, the nanoclays were previously subjected to a special treatment appropriate for the epoxy resin. The surface-treated clay, which were custom-formulated by CTA Ltd using chemical treatments and high shear mixing techniques subjected to patent applications, may be defined as an organically modified layered silicate with a tetrahedral-octahedral-tetrahedral (T-O-T) basic structure, whose surface layer have been treated additionally to endow it with better dispersive characteristics (in a resin) compared with

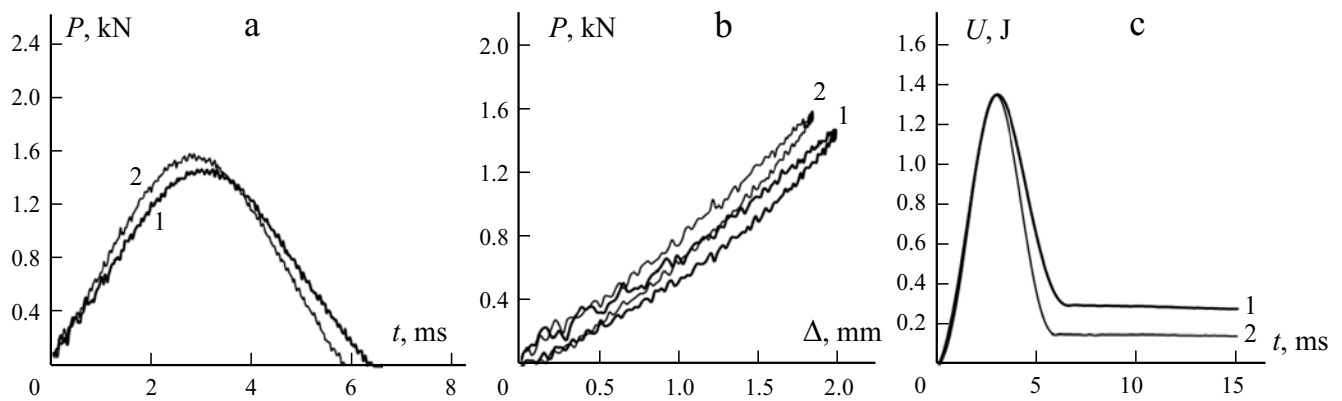


Fig. 2. Typical load vs. time $P-t$ (a), load vs. displacement $P-\Delta$ (b) and energy vs. time $U-t$ (c) curves for laminates with neat (1) and nanoclay-reinforced (2) resin.

those of the traditionally available commercial nanoclay (e.g., with granules of size $< 50 \mu\text{m}$, content of heavy metals < 100 ppm, and content of volatiles $< 1\%$).

The epoxy resin was heated in a glass beaker at 75°C to decrease its viscosity, and then fillers were added. An epoxy system containing 3 wt.% of nanoclays was employed. The mixing was executed at a shear rate of 2500 rpm for one hour by using a high-speed shear mixer, followed by sonication (employing an ultrasonicator) for three hours to further disperse the clay, while maintaining the resin temperature at 75°C by using a bath with hot water. After sonication, the translucent color of the epoxy/clay mixture pointed to a uniform distribution of nanoclays. Figure 1 shows the homogeneous dispersion and the exfoliation of clay. Samples were prepared in an EM FCS (Leica) ultramicrotome for ultrathin sectioning. Morphological analyses were realized by using a NOVA 200 Nano SEM (FEI) ultrahigh-resolution field emission gun scanning electron microscope. A scanning transmission electron microscope and an acceleration voltage between 15 and 18.4 kV were utilized to obtain micrographs.

The square specimens used in experiments, which were cut from the thin plates prepared, had a 100-mm side and 3-mm thickness ($100 \times 100 \times 3$ mm). The specimens were kept in a thermostatic laboratory water bath, Unitronic model S.320-100, at $60 \pm 1^\circ\text{C}$ for 10, 20, and 30 days. The effect of temperature on the impact response of the specimens was also analyzed. For this purpose, the specimens were stored in a muffle furnace (Carbolite Furnaces) for 10 days at $60 \pm 1^\circ\text{C}$, followed by cooling down to room temperature. Low-velocity impact tests were performed using an IMATEK-IM10 drop-weight testing machine. More details of the impact machine can be found in [15]. An impactor with diameter 10 mm and a mass of 2.903 kg was used. The tests were performed on 75×75 mm square samples, and the impactor stroke at the centre of the samples, which were obtained by centrally clamping the 100×100 mm specimens. The impact energy used in the tests was 1.5 J. The specimens were previously removed from the muffle and water and cleaned with tissue paper before tests. For each condition, five specimens were tested at room temperature.

3. Results and Discussion

The impact tests were carried out considering different environmental conditions. Figure 2 shows the load versus time (Fig. 2a), load versus displacement (Fig. 2b), and energy versus time curves (Fig. 2c) of control samples and laminates with 3% of nanoclays. These diagrams represent the typical behavior for each laminate at room temperature. They agree with those given in [16-18] and are also similar to the diagrams obtained for the different environmental conditions considered.

The load–time (Fig. 2a) and load–displacement (Fig. 2b) curves reveal small oscillations, which, according to [19], result from elastic waves and are created by vibrations of the samples. They depend on the stiffness and mass of the specimen and impactor [20]. In all tests, the maximum impact energy was not high enough to reach full penetration. This phenomenon

TABLE 1. Temperature and Hygrothermal Effects on the Impact Response

Exposure conditions	P_{max} , kN		Δ_{max} , mm		δ , %	
	Average value	SD	Average value	SD	Average value	SD
Neat laminate						
Room temperature	1.53	0.04	2.39	0.19	90.8	0.8
10 days*	1.49	0.08	2.28	0.25	86.4	0.9
10 days**	1.46	0.09	2.22	0.26	81.9	1.1
20 days**	1.44	0.09	2.02	0.3	77.3	1.3
30 days**	1.39	0.1	1.91	0.31	70.2	1.4
Nanoenhanced resin						
Room temperature	1.56	0.02	2.14	0.14	93.1	0.7
10 days*	1.54	0.06	2.01	0.18	91.9	0.8
10 days**	1.51	0.07	1.91	0.21	88.3	0.9
20 days**	1.48	0.08	1.84	0.22	85.8	1.2
30 days**	1.44	0.1	1.60	0.25	80.9	1.3

*Temperature effect (60°C for 10 days, followed by cooling down to room temperature).

**Hygrothermal effect (immersion in water at 60°C).

can be observed on the Fig. 2c, where the beginning of the plateau coincides with the loss of contact between the striker and specimen. This energy is equal to that absorbed by the specimen [21], but the elastic energy (elastic recovery) is calculated as the difference between the absorbed energy and the energy at the peak load, which can be found from the diagram presented in Fig. 2c.

Table 1 presents the average values and standard deviations (SDs) of the peak load P_{max} , the maximum displacement Δ_{max} , and the elastic recovery δ for each laminate. At room temperature, the average maximum load P_{max} of the control samples was about 1.53 kN. With nanoclays added to the resin, this value increased to 1.56 kN, which is by 2% higher. A similar tendency was observed for the elastic recovery, whose values were about 90.8% and 93.1%, respectively, for control samples and the laminates with nanoclays. According to [18], their damage mechanisms are different and explain the better impact strength of the hybrid laminates with nanoclays. In fact, the stiffness of the matrix filled with clays is higher, and its ductility decreased. Finally, for the maximum displacement observed during impact loads, the highest values, equal to about 2.39 mm, were observed for laminates manufactured with a pure epoxy resin, while for the laminates with a resin filled with nanoclays, this value was about 2.14 mm (by 10.5% lower). In fact, this behavior may be of utility, because some system must absorb the impact energy, but cannot be allowed to deform so excessively.

Concerning the effect of temperature, it was observed that 10 days of exposure to 60°C affected the impact strength. The elastic recovery, for example, was about 4.8% for the laminates with neat resin, while for laminates with a resin filled with nanoclays, this value was only about 1.3%. This reduction can be explained by degradation of the fiber/matrix interface [22-26]. The structure and properties of the interface largely determines the mechanical and physical properties of composite materials [22]. For example, different thermal expansion coefficients of fibers and polymer lead to residual stresses at the interface, which can result in microvoids or cracks [27]. However, the introduction of nanoclays is beneficial, as show the results and data available the literature. In several studies, it is found that the addition of nanoclays reduces the thermal expansion coefficient [28-30].

When the water was combined with the temperature effect, the values of P_{max} , displacement Δ , and elastic recovery δ decreased significantly, as shown in Table 1. In terms of the elastic recovery, the hygrothermal action led to about a 10% reduction for laminates with a neat resin, while for laminates with a resin filled with nanoclays, this value was only about 5%.

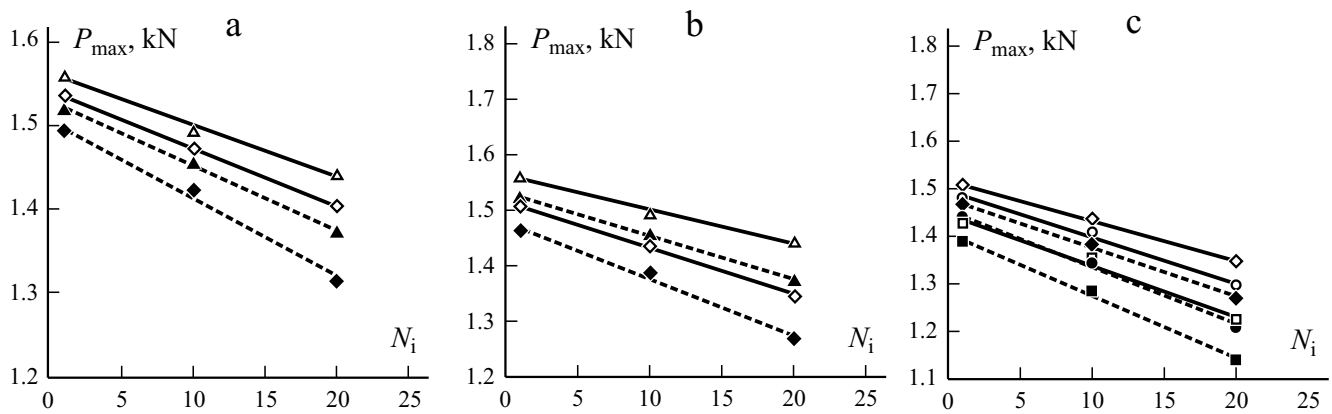


Fig. 3. Maximum load P_{max} vs. the number of impacts N_i for neat (filled symbols) and nanoclay-filled (open symbols) resins: a) the effect of temperature (Δ , \blacktriangle — room temperature; \diamond , \blacklozenge — 60 °C/10 days), b) water and temperature (Δ , \blacktriangle — room temperature; \diamond , \blacklozenge — 60 °C/10 days), and c) water, temperature and exposure time (\diamond , \blacklozenge — 10 days; \circ , \bullet — 20 days; \square , \blacksquare — 30 days).

According to [27], moisture may penetrate into polymeric composite materials by diffusive/capillary processes, and the mechanical degradation is a function of the matrix swelling strain. Moisture can cause debonding at the fiber/matrix interface not only through a chemical attack and reaction, but also through mechanochemical effects, such as the osmotic pressure. In [23], it is shown that the presence of water in an epoxy-based matrix plasticizes the network and lowers the elastic modulus by increasing in the free volume and facilitating the segmental motion when a load is applied to the composite. As moisture is absorbed in specimens, it creates a hydrostatic pressure at crack tips and hastens crack propagation and damage in the matrix. According to [31], moisture is absorbed mainly by the resin, and the temperature affects the moisture absorption in various ways. As diffusion is a thermally activated process, a growth in temperature accelerates the short-term diffusion and increases the diffusion coefficient. However, the nanoclays bring benefits in terms of the impact strength, because they decrease the permeability of composites [13, 14]. This phenomenon can be attributed to the high aspect ratio of clay platelets, which increase the tortuous path of gas or water molecules as it diffuses into nanoclay composites. On the contrary, the results obtained in [32] showed that the incorporation of impenetrable clay nanoparticles with high mechanical characteristics did not reduce the negative effect of absorbed moisture. In this context, the coupling agent used reduced the degradation of mechanical properties and contributed to a higher adhesion between the resin and particles, which is in agreement with literature data [33, 34].

Finally, the effect of exposure time in a hygrothermal environment shows that the nanoenhanced resin brings benefits in terms of the impact strength. For laminates with a neat resin immersed in water at 60°C for 30 days, the elastic recovery was by 22.7% lower than for those tested at room temperature. Under the same conditions, the value found for laminates with a clay-filled resin was about 13%. Thus, we can conclude that the exposure time also affects the impact strength significantly, which agrees with literature data [22].

The effect of repeated impacts was also analyzed, and Fig. 3 shows the evolution of the maximum load P_{max} with the number of impacts. As seen from Table 1, the maximum load decreases with temperature, and this tendency continues with the number of impacts. For example, after 20 impacts, P_{max} decreased by 9.7 and 7.5% for control laminates and laminates with nanoclays tested at room temperature, respectively. The effect of temperature T is displayed in Fig. 3a, and these values are 11.9 and 8.6, respectively. Finally the effect of combined action of water and temperature is illustrated on Fig. 3b. As seen, the value of P_{max} decreased by about 13.2 and 10.6%, respectively. The experimental results presented in [35] show that the maximum contact force decreases and the energy absorbed by the composite increases with increasing number of impacts. Figure 3c depicts the effect of exposure time, and the same phenomenon is seen. However, the drop in the maximum load is greater when the immersion time is increased.

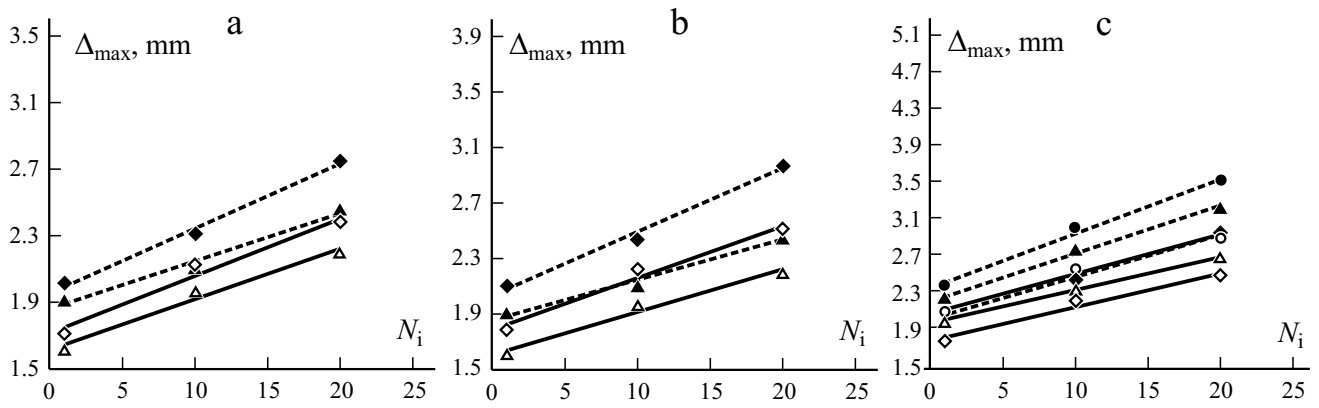


Fig. 4. The same for the maximum displacement Δ_{\max} vs. number of impacts N_i . Designations as in Fig 3.

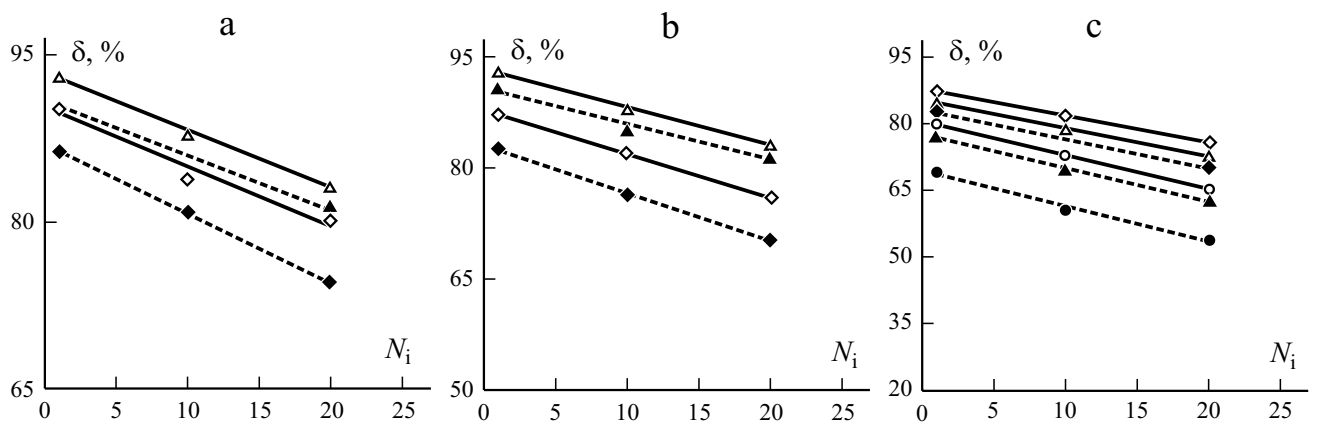


Fig. 5. The same for the elastic recovery δ vs. the number of impacts N_i . Designations as in Fig 3.

A similar picture is seen in Fig. 4 for the maximum displacement Δ_{\max} . As is evident, the displacement increased with the numbers of impacts; however, the displacement was smaller in the laminates with nanoclays. Figure 4a demonstrates the effect of temperature, and it can be observed that, after 20 impacts, the laminates with nanoclays had displacements by 8.2% greater than those at room temperature. For control laminates, this value was by about 12% higher. Figure 4b shows the effect of combined action of water and temperature. In this case, after 20 impacts, the laminates with nanoclays had displacements by 14% greater, while for control laminates, this value was about 21.2%. Finally, Fig. 4c presents the effect of exposure time. As seen, after 30 days of immersion in water, the displacement of laminates, relatively to that at room temperature, increased by 43.8 and 32.2% for control laminates and the nanoenhanced ones, respectively.

In terms of elastic recovery, Fig. 5 shows its variation with the number of impacts for laminates with a neat resin and with a nanoclay-filled ones. Figure 5a depicts the effect of temperature in terms of the elastic recovery. As seen, the elastic energy decreased with the number of impacts. For example, after 20 impacts, the elastic energy decreased by 8.5% for control laminates, while for laminates with nanoclays, this value was about 3.7%. Figure 5b presents the effect of simultaneous action of water and temperature, and the same tendency is observed; however, the drop in the elastic energy was more significant (13.7% for control laminates and 8.7% for laminates with a nanoenhanced resin). Finally, Fig. 5c compares the elastic energy for different exposure times. It is evident that the exposure time decreased the elastic energy significantly. After 30 days, comparing the results of the samples immersed in water at 60°C with those treated at room temperature, the elastic recovery decreased by about 33.8% for control laminates and by 21.4% for laminates with a nanoclay-filled resin.

4. Conclusions

In this work, the low-velocity impact response of carbon/epoxy composites was investigated. The hygrothermal effect and the benefits gained when the resin was doped with nanoclays were analyzed in single- and multi-impact tests. The nanoclay reinforcement of matrix improved the impact response. The maximum load and the elastic recovery by about 2 and 2.5%, respectively. The thermal degradation caused by exposure to 60°C for 10 days was negligible, while the immersion in water at 60°C caused a continuous reduction in the maximum load and the elastic recovery by about 8 and 22%, respectively, for the resin without a nanoreinforcement (by 8 and 13% for the nanoenhanced resin composites) after 30 days of immersion. Multiple impacts led to a continuous and nearly linear degradation in the impact response both for dry and environmentally assisted specimens.

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