

# EPOXY-LAYERED SILICATE NANOCOMPOSITES AS MATRIX IN GLASS FIBRE REINFORCED COMPOSITES

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## ABSTRACT

Epoxy nanocomposites based on an organophilic layered silicate and amine-cured epoxy resin have been synthesised and implemented as matrix in glass fibre-reinforced composites. The structure of the nanocomposite, investigated with x-ray diffraction and transmission electron microscopy, reveals the presence of long-range ordered silicate layers with an interlamellar spacing of ca. 9 nm. Environmental scanning electron microscopy shows the presence of silicate layers at the surface of the glass fibres. The nanocomposite matrix seems to present a synergetic effect with the glass fibre reinforcement, improving the modulus and the flexural strength by, respectively, 6 and 27 %. The glass transition temperature of the nanocomposites is reduced by 10-15°C. Water absorption is increased in the nanocomposite despite the presence of silicate layers throughout the epoxy matrix.

## 1. INTRODUCTION

Layered silicate such as clays and talc have long been used as fillers in polymer systems because of their low cost and the improved mechanical properties of the resulting polymer composite. All other parameters being equal, the efficiency of a filler to improve the physico-mechanical properties of a polymer system is sensitive to its degree of dispersion in the polymer matrix [1]. This is related to the extent of interaction between the surface of the filler and the polymer chains.

Understanding this important issue, Toyota researchers [2] discovered in the early 90's that treatment of a montmorillonite clay with amino acids allowed dispersion of individual 1 nm-thick clay layers on a molecular scale in polyamide 6. The resulting material showed at low clay content (1.6 vol%) major improvements in physical and mechanical properties and was used later to manufacture timing belt covers for automotive engines. This new material provided a weight saving of 25 % compared with a conventional glass fibre-reinforced polyamide 6. Following this successful material development, researchers performed numerous investigations in this new research field. Polymer-layered silicate nanocomposites based on polymethylmethacrylate [3], polyimide [4] but also epoxies [5-7], unsaturated polyesters [8] and polyurethanes [9] were synthesised and their properties were characterised in great details.

Interestingly, little has been done to implement these nanoreinforced polymers as matrices in fibre-reinforced composites. Rice et al. [10] attempted to manufacture carbon fibre/nanocomposite unidirectional composites via resin film infusion and wet winding. They did not achieve significant improvement of the mechanical properties of the laminates. If they showed in one of their publication [11] that they were able to obtain a nanocomposite from the epoxy system used in this study, they did not demonstrate that the matrix of their carbon-

fibre reinforced laminates had the same nanocomposite structure. More recently, Haque et al. [12] reported the manufacture of S2-glass/epoxy polymer nanocomposites via vacuum assisted resin infusion method. Even though the nanocomposite matrix of the laminates presented only an intercalated nanostructure with an interlamellar spacing of 35 Å, the interlaminar shear and fracture strength as well as the fracture toughness of the resulting laminates were improved respectively, by 44, 24, and 23 % in comparison with conventional laminates and this at low layered silicate content (1 wt%).

The objectives of the present study were to synthesise a delaminated nanocomposite based on an amine-cured epoxy resin and an organophilic layered silicate and to implement this nanocomposite matrix in glass fibre-reinforced laminates. The structure of the nanocomposite matrix in the bulk and once implemented in the laminate has been investigated using X-ray diffraction, transmission electron microscopy, and environmental scanning electron microscopy. The mechanical properties, as well as the water absorption of the nanocomposite matrix and of the resulting laminates have been investigated.

## **2. EXPERIMENTAL**

### **Materials**

The layered silicate, fluorohectorite ME-100 with a cation-exchange capacity of 100 meq/100g was supplied by CO-OP, Japan. The compatibilising agent, octadecylamine, was provided by Fluka Chemie GmbH, Germany. The epoxy system Araldite CY225/Araldite HY925 (diglycidylether of bisphenol A/anhydride curing agent) was supplied by Vantico AG, Switzerland. The satin mat EC9-204 (280 g/m<sup>2</sup>, thickness 0.3 mm) was provided by Suter-Kunststoffe AG, Switzerland.

### **Preparation of the organophilic layered silicates, the nanocomposites, and the laminates**

The preparation of the organophilic layered silicates was reported in an earlier work [13]. The nanocomposites were prepared by mixing a given amount of Araldite CY225 with a quantity of organosilicate corresponding to 10 wt% of the epoxy system (CY225 + HY925) at 80°C for one hour. A stoichiometric amount of the curing agent Araldite HY925 was added. The mixture was stirred for 10 minutes and then outgassed in a vacuum oven. It was then poured in an aluminium mould preheated at 140°C. The plates were cured 2 hours at 140°C, demoulded, and then postcured 10 hours at 140°C.

The laminates were prepared by hand lay-up. Eight plies (17 x 17 cm) of the glass fibre mat were impregnated with epoxy or epoxy/organosilicate mixture and then superimposed on an aluminium plate preheated at 80°C. The laminate was then outgassed in a vacuum oven and then placed in a vacuum bag under an hydraulic press. After vacuum was applied, a pressure of 2 bars was applied to the laminates which were first cured 2 hours at 140°C. Released from the aluminium plate, they were then postcured 10 hours at 140°C in an oven.

### **X-ray diffraction**

X-ray diffraction analyses were performed using a computer controlled Siemens D500 diffractometer with Cu radiation (40 kV, 40 mA). The scanning speed and the step size were 0.05°/5s and 0.05°.

## **Microscopy**

Transmission electron microscopy (TEM) samples were cut from nanocomposite blocks using an ultramicrotome Reichert & Jung Ultracut E equipped with a diamond knife at ambient temperature. Thin specimens of about 70 nm were cut from a mesa of about 0.5 x 0.5 mm. They were collected in a through filled with water and placed on a 400 mesh copper grid. Transmission electron micrographs were taken with a LEO 912 apparatus at an acceleration voltage of 120 kV.

Environmental scanning electron microscopy (ESEM) samples were prepared by fracturing the laminates parallel to the fibres at cryogenic temperatures. The fracture surface were coated with gold and analysed with an ElectroScan ESEM 2020 equipped with a GSED detector under a 5-bar atmosphere and at an acceleration voltage of 23-26 kV

## **Mechanical properties**

Young's modulus, tensile strength, and elongation at break were measured by means of tensile tests according to ISO 527 using a Zwick Z010 tensile machine equipped with a 10 kN loadcell at a speed of 2 mm/min. Three samples for each composition were tested. Flexural modulus, flexural strength and flexural strain at break were determined following EN ISO 14125 with the same tensile machine equipped with a four point bending rig. The vertical displacement speed of the rig during the test was 5 mm/min. Four specimens of each composition were tested.

Dynamic mechanical properties were measured with a Dynamic Mechanical Analyser EPLEXOR 500N from GABO GmbH, Ahlden, Germany from  $-130^{\circ}\text{C}$  to  $+250^{\circ}\text{C}$  at a heating rate of  $2^{\circ}\text{C}/\text{min}$  and a frequency of 10 Hz. Laminate samples (10 x 2 x 60 mm) were tested under three-point bending with a static strain of 0.07 % and a superposed dynamic amplitude of 0.01 % using a load cell of 150 N.

## **Water absorption experiment**

4 specimens per material were cut from the two polymer plates (dimensions 30 x 20 x 4 mm) and the two laminates (dimensions 30 x 20 x 1.9 mm). The samples were preliminarily dried for 24 hours at  $50^{\circ}\text{C}$  and cooled down to room temperature in a dessicator for 72 hours. For each material, two specimens were placed in demineralised water at room temperature ( $23^{\circ}\text{C} \pm 2^{\circ}\text{C}$ ) and two others were placed in a sealed bottle containing demineralised water placed in an oven at  $50^{\circ}\text{C}$ . For each measurement, the samples were removed from the water, dried with a lint-free tissue, weighed and re-immersed in demineralised water. The water absorption for each material was taken as the average value of the two specimens.

## **3. RESULTS & DISCUSSION**

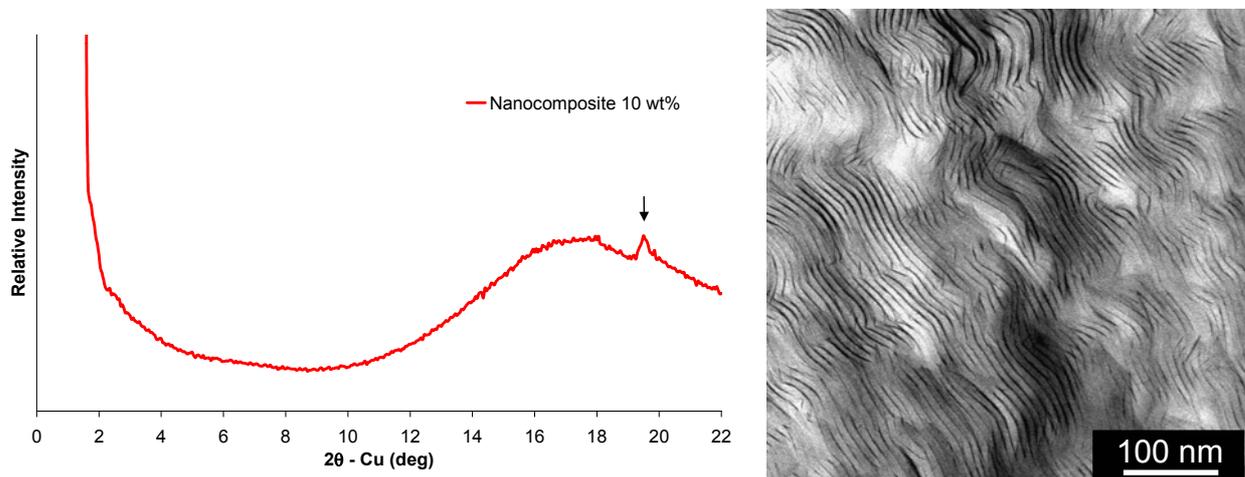
### **Intercalation of the compatibilising agent**

The layered silicate (Somasif ME-100) was analysed by X-ray diffraction before and after the treatment with the compatibilising agents (octadecylammonium ions). The interlamellar spacing of the layered silicate measured from the (001) reflection at low angle increased from

0.95 nm to 1.98 nm after treatment, indicating that octadecylammonium ions had been intercalated between the silicate layers. The presence of long-chain alkylammonium reduces the Van der Waals interactions between the silicate layers so that the interlamellar spacing increases by about 1 nm.

### Structure of the epoxy-layered silicate nanocomposite

The organophilic layered silicate was swollen in the DGEBA resin and the curing agent was added to the resulting mixture. The processing temperature (140°C) was optimised in order to favour the diffusion of the curing agent molecules between the silicate layers so that intragallery polymerisation was favoured and could participate in the separation of the silicate layers on a molecular level. The structure of the resulting epoxy-layered silicate nanocomposite was analysed using X-ray diffraction and transmission electron microscopy (see Fig. 1).



**Fig. 1.** X-ray diffractogram (left) and transmission electron micrograph (right) of an epoxy-layered silicate nanocomposite with 10 wt% organosilicate. The interlamellar spacing is ca. 9 nm. The arrow on the diffractogram indicates a peak corresponding to crystallographic planes (110) and (020) of the layered silicate.

On the X-ray diffractogram, no (001) reflection can be seen at low angle indicating that the silicate layers were separated by more than 8.8 nm which corresponds to the detection limit of the XRD analysis. At high angle, a small reflection (see arrow) around  $2\theta = 20^\circ$  can be seen corresponding to crystallographic planes ((110) and (020)) of the silicate layers.

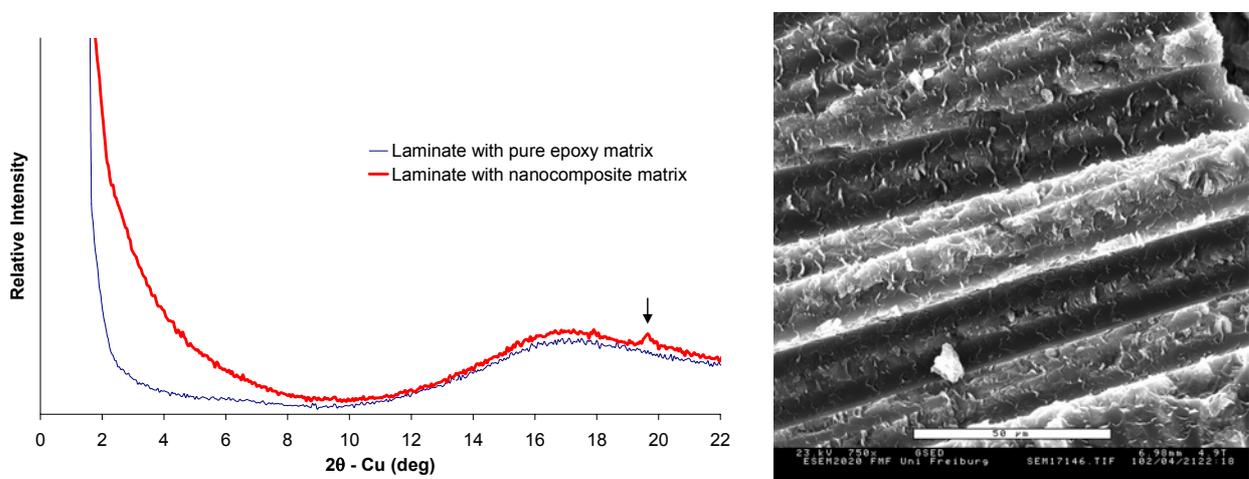
The transmission electron micrograph of the nanocomposite shows the presence of single layers presenting a long-range order with an interlamellar distance of ca. 9 nm. This observation correlates well with the XRD analysis and confirms that the material studied is a true nanocomposite.

### Structure of the laminates

The structure of the laminates was analysed by X-ray diffraction and environmental scanning electron microscopy (see Fig. 2). Unfortunately, it was not possible to assess the nanostructure of the matrix in the epoxy-layered silicate nanocomposite fibre-reinforced

composite with an other method, since TEM samples could not be prepared due to the presence of the glass fibres.

The X-ray diffractograms of the two laminates (with epoxy and nanocomposite matrices) present both similar patterns than what was observed earlier in the case of the nanocomposite. No (00l) reflection can be seen at low angle indicating the formation of a nanocomposite structure. Interestingly, the diffractograms of the two laminates differ only by the presence at high angle of the reflection corresponding to the crystallographic planes of the silicate layers in the case of the laminate with nanocomposite matrix (see arrow).



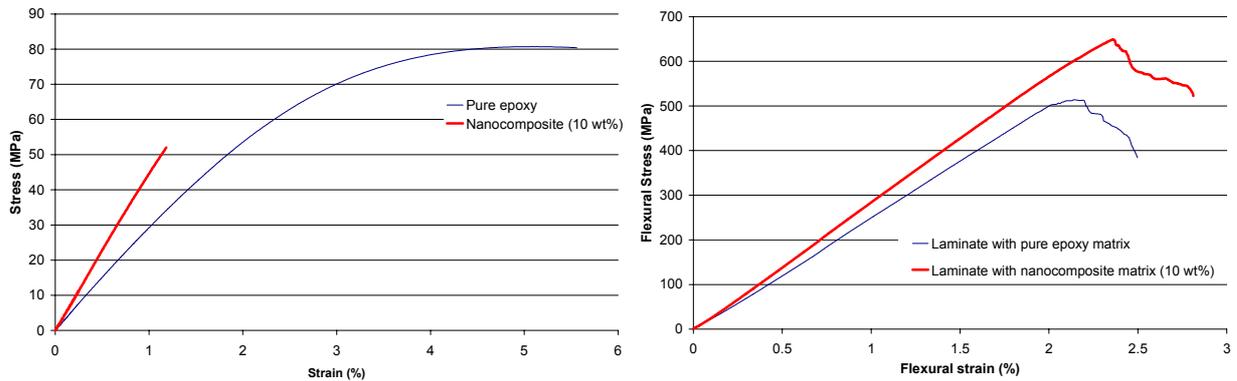
**Fig. 2.** X-ray diffractograms of the laminates with and without nanocomposite matrix (10wt%) (left). The arrow indicates a peak corresponding to crystallographic planes (110) and (020) of the layered silicate. Environmental scanning micrograph of the fracture surface of a glass fibre-reinforced laminate prepared with a nanocomposite matrix (right). The white bar represents 50  $\mu\text{m}$ .

The environmental scanning micrographs of the fracture surface of a glass fibre laminate prepared with a nanocomposite matrix revealed a scaled structure due to the presence of the silicate layers dispersed in the epoxy matrix. In contrast, micrographs of the laminate prepared with pure epoxy matrix showed only smooth and somewhat brittle fracture surface with bad adhesion between the fibres and the matrix. In the case where the nanocomposite matrix was used, it seems that the silicate layers are sticking onto the surface of the fibres, possibly increasing their interfacial properties.

### Mechanical properties

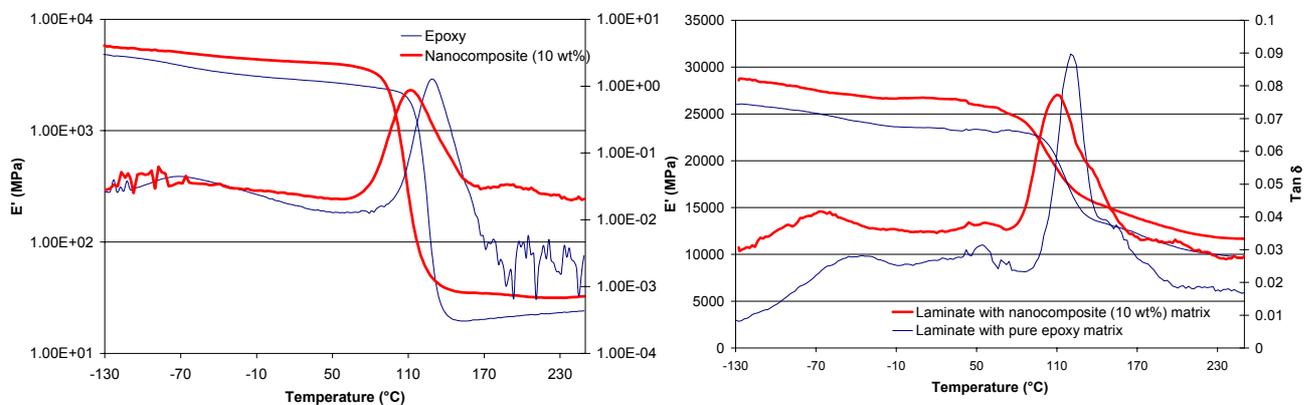
Fig. 3 presents the typical curves for the tensile tests of epoxy and nanocomposite samples and for the flexural tests of laminates manufactured with the corresponding matrices.

If the epoxy samples showed a large plastic deformation with more than 5 % strain, the nanocomposite samples appeared more brittle but their Young's modulus was more than 50 % higher than that of the epoxy matrix and this with only 10 wt% of layered silicate. The tensile strength was reduced by 36 % due to the presence of the silicate layers.



**Fig. 3.** Typical curves for the tensile tests of epoxy and nanocomposite samples (left) and for the flexural tests of laminates manufactured with the corresponding matrices (right).

The corresponding laminates present a different behaviour. The flexural modulus of the laminates based on the nanocomposite matrix is ca. 6 % higher than that of the laminates with pure epoxy. However, the flexural strength is significantly increased by 27 %. This effect may be link to the possible interfacial improvement of the glass fibre observed with environmental scanning electron microscopy. Interestingly, this synergetic effect of the nanocomposite matrix with glass fibre reinforcement was also observed by other researchers [12] and requires further investigations.



**Fig. 4.** Dynamic mechanical properties of epoxy and nanocomposite samples (left) and of laminates manufactured with the corresponding matrices (right).

Dynamic mechanical analyses were also performed on the epoxy and nanocomposite samples and their corresponding laminates (see Fig. 4). A systematic decrease of the glass transition temperature of 10-15°C was observed both in the polymeric samples and in the laminates when nanocomposites were used. This decrease is possibly due to a cation exchange between the alkylammonium ions situated between the silicate layers and the diamine curing agent molecules. Indeed, free alkylamine molecules may react with the epoxy network and decrease the overall crosslink density of the thermoset, which then would induce a glass transition temperature decrease. The differences observed in the storage modulus  $E'$  at room temperature are somewhat similar those seen with the static tests.

## Water absorption

The water absorption of the epoxy and the corresponding nanocomposite were very similar at 23°C, reaching approximately 1 wt% after 2000 hours. At 50°C, the water absorption of the two materials was similar at early stages but the nanocomposite water absorption was much larger as time passed. After 2000 hours, the water absorption of the nanocomposite was twice that of the epoxy reaching 2 wt%. Interestingly, Okada et al.<sup>2</sup> observed in polyamide-clay nanocomposites, in contrast, a decrease of rate of water absorption of 40% as compared with the pristine polymer. This effect was attributed to the large aspect ratio of the silicate layers, which increases the tortuosity of the path of the water molecules as they diffuse into the nanocomposite. In the present case, we observed the inverse phenomenon at 50°C. According to the dynamic mechanical analyses of the two materials, the presence of the layered silicate in the epoxy has affected the crosslink density of the epoxy. The network is looser in the case of the nanocomposite so that water diffuses faster in the material even though the silicate layers are acting as barriers throughout the material. This difference was not seen at 23°C because diffusion increases exponentially with temperature and is therefore greater at 50°C. Similar variations have been observed in the two laminates.

## 4. CONCLUSIONS

Epoxy nanocomposites based on octadecylamine-modified fluorohectorite and amine-cure epoxy resin have been successfully synthesised. They have been implemented as matrix in glass fibre-reinforced composites via a combination of the hand lay-up, vacuum bagging and hot pressing techniques. X-ray diffraction and transmission electron microscopy have revealed the presence in the nanocomposite of long range-ordered silicate layers with an interlamellar spacing of ca. 9 nm dispersed in the matrix. Environmental scanning electron micrographs have shown that silicate layers are present onto the surface of the glass fibres, improving apparently the interfacial properties. Mechanical tests indicate a possible synergetic effect between the nanoreinforcement of the matrix and the glass-fibre reinforcement with an increase of flexural strength of 27 % as compared with the conventional laminate. Epoxy nanocomposites present a higher water absorption at 50°C than pure epoxy despite the presence of silicate layers in the matrix. This effect is apparently linked to a reduction of network density in the epoxy matrix due possibly to a cation exchange between the compatibilising agent and the curing agent molecules.

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