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A STUDY OF NANOCLAY COMPOSITES FABRICATED BY LIQUID COMPOSITE MOLDING

N. Kchit, F. Bensadoun, T. Carrozani, C. Billotte, E. Ruiz, F. Trochu

*Chair on Composites of High Performance (CCHP), École Polytechnique de Montréal,
Department of Mechanical Engineering, P.O. Box 6079, Station "Centre-Ville",
Montreal, Canada, H3C 3A7, Research Center on Plastics and Composites (CREPEC)
Corresponding author's E-mail: edu.ruiz@polymtl.ca*

ABSTRACT: This study seeks to improve the mechanical and flammability properties of glass fiber reinforced unsaturated polyester composites by introducing nanoclays particles in the resin. The dispersion of nanoparticles is the most important parameter to take into account in nanocomposite fabrication. In this work several mixing techniques were evaluated, and the blends and final parts were analyzed by rheology and mechanical testing. The best approach was found to be the sonication of the nanoparticles dissolved in the styrene, followed by the addition of the unsaturated polyester (UP) resin while stirring mechanically the mixture and finally, letting the added styrene evaporate. Fiber glass/UP/Cloisite30B nanocomposites were manufactured by vacuum assisted resin infusion VARI. Mechanical properties such as interlaminar shear strength, flexural properties and fracture toughness were determined and compared to conventional fiber glass/UP composites. The flammability properties were also measured for the 60 s vertical burn test and compared to conventional fiber glass/UP composites. The addition of 3wt% of nanoclays improved the impact resistance by 10% and the flammability by 30% compared to the conventional composite. Hence using nanoclays brings a definite improvement as long as the viscosity of the mixture remains reasonable for processing by resin infusion.

KEYWORDS: nanocomposite, resin infusion, unsaturated polyester, nanoclays, dispersion, rheology, Ammonium Polyphosphate, flammability, mechanical properties.

INTRODUCTION

Thanks to their high specific properties fiber-reinforced polymer composites (FRP-C) have found use in applications ranging from construction to aerospace materials, and sport materials [1]. FRP-C have excellent mechanical properties in the planar directions due to the high stiffness of the fibers, while in the transverse direction their properties are governed by the polymer matrix and often need to be improved. Enhancement of the electrical, mechanical and thermal properties of a matrix could in fact improve the global behavior of the composite part. It is well known that adding inorganic, organic or metallic fillers increases the properties of the polymer. Polymers reinforced with organoclay were among the first nanocomposites and have been widely studied this last decade since Toyota researchers successfully enhanced the mechanical properties of nylon6 [2]. The incorporation of a few percents of nanoclays improves mechanical properties [3,4], thermal stability [5], gas barrier [6] and flame retardant properties [7] of matrix polymers. A good dispersion of nanoparticles in the polymer matrix is required in order to ensure enhanced properties. Recently much scientific work has focused on the synthesis of new advanced FRP nanocomposites (FRP-NC). Dean et al [8] using a vacuum assisted resin infusion molding (VARI) process showed an improvement of 31% in flexural modulus and 24% in flexural ultimate strength for 2% layered silicate fiber-reinforced nanocomposites. However, no enhancement was observed for interlaminar shear and fracture toughness. Haque et al. [9] using resin infusion showed a large improvement in the mechanical properties of their S2-glass fiber laminates and this for very low nanoclay content. With only 1 wt% of layered silicate dispersed homogeneously in the matrix, the shear strength, the flexural strength, and the fracture toughness of the resulting fiber-reinforced composites were increased by 44%, 24%, and 23% respectively. Li-Yu et al [10] using a vacuum-assisted resin transfer molding (VARTM) process related that introducing a small amount of organoclay to the glass fiber/epoxy composites enhanced their mechanical and thermal properties, confirming the synergetic effect of combining glass fibers and clays in the composite.

In this study reports the fabrication of FRP-NC by vacuum assisted resin infusion (VARI) technique using glass fibre, nanoclays particles and unsaturated polyester. Before infusing the nanocomposites into dry glass fibres, the dispersion quality was evaluated by analyzing the rheological and mechanical properties of the matrix. Mechanical properties such as interlaminar shear strength, flexural properties and fracture toughness were determined and compared to conventional FRP composites. The flammability properties were also investigated in this study for the 60 s vertical burn test and compared to conventional FRP composites.

EXPERIMENTAL SETUP

Materials

The resin used in this work was an unsaturated polyester *Altek R937-DPE24* provided by *AOC* with an average viscosity of 0.18 Pa.s at room temperature. The promoter used was a cobalt ethylexanate (12%), the catalyst was methyl ethyl ketone peroxide (MEKP925), an organic peroxide from *Norox*®**.** The reinforcing nanoclays, *Cloisite 30B*, were provided by Southern Clay Products®, which is a montmorillonite particle (MMT).

Nanocomposites preparation: nanoclay dispersion and mixing

The technique of dispersion used in this study was the ultrasonication followed by high speed mechanical stirring. The parameters of the sonication were optimized and fixed at a frequency of 35 kHz and power of 100 Watts for two 30 minutes separated by a 15 minutes break to prevent the formation of microgels. A proportion of 3% in weight of C30B nanoclay particles was incorporated and dispersed under four approaches A1 to A4 as summarized the diagram of Fig.1. In order to compare with the nanophased system, the resin without nanoparticles has undergone the same treatment for sample A0, namely sonication followed by stirring.

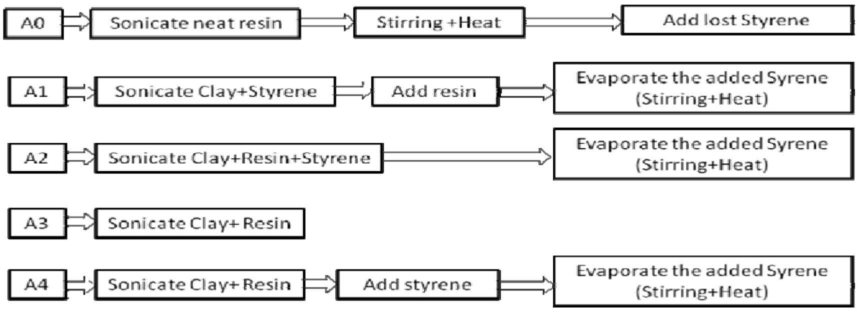


Fig. 1 - Processing techniques used to disperse nanoclay particles on polyester resin.

Fabrication of FRP nanocomposites

The manufacturing procedure chosen was the VARI infusion process. The addition of nanoclay to the matrix makes it more difficult to impregnate the laminate, which is composed of 8 layers of a high performance $0^o/90^o$ woven fabric for the composite reinforcement. Two layers of glass fiber mat were added in the middle of the laminate to improve resin distribution and avoid filtration of the nanoparticles. This method renamed “VARI Modified” is schematically represented in Figure 2.

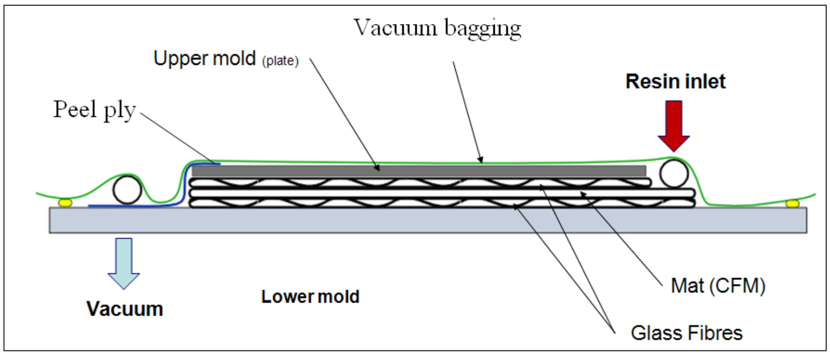


Fig. 2 - Schematics of fabrication by resin liquid infusion VARI.

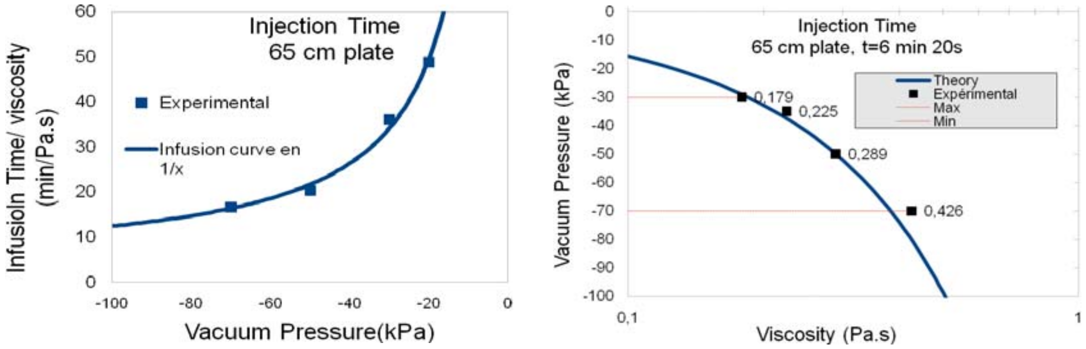
Process parameters: Pressure

The infusion pressure was chosen by taking into account the viscosity of the nanoreinforced resin and the maximum allowable pressure to prevent the vaporization of the styrene in the resin and, the formation of air-styrene bubbles. The viscosity of the mix is important because it limits the impregnation of the fibers and influences the filling time of the part.

Injection time

During infusion, the thickness distribution is not uniform all around the plate; it is higher at the inlet position than at the outlet. This means that the resin infusion has to be fast enough to properly impregnate the reinforcement and allow the post-pressure and thickness equilibrium before polymerization occurs. This step is called post-filling and is much longer than the infusion time. Also, if the resin infusion is too fast, micro and macroscopic voids can appear within the laminate. This will consequently affect mechanical performance and flammability characteristics. To ensure the reproducibility of results, the filling time has to be consistent between all manufactured plates. In order to do this, vacuum pressure has to be compensated according to the viscosity of the nanoclay reinforced resin. Pressure limits were set between -30 kPa to avoid capillary effects and -70 kPa to keep the styrene dissolved in the matrix. Experimental determination of the infusion time/viscosity curve (see Fig. 3a) was made from several experiments at different vacuum pressures. The trend curve relating infusion time and vacuum pressure is presented by equation (1). It is then possible to estimate, for a given viscosity, the vacuum pressure required to infuse the composite in 6min 20s as presented in Figure 3(b).

$$t = \frac{-928.7}{P} + 3.18 \tag{1}$$



a) b)

Fig. 3 - Optimization of the nanoclay composites manufacturing, a) infusion time and b) vacuum pressure required to obtain the same filling time.

Characterization

Rheology

Shear sweep tests were performed on the nanodispersed prepolymers with rheometer from Anton Paar using concentric cylinders geometry.

Mechanical measurements

Thermo-mechanical tests were carried out on a Q800 *DMA* from TA Instruments with a three-point bending clamp. Test samples were 60 × 10 × 3 mm^3 in size. The storage and loss modulus were measured as a function of temperature over a range from 30 °C to 180 °C and at a heating rate of 3 °C/min. The strain region in which the material behaves as linear viscoelastic was determined by amplitude sweep experiments. Tests were carried out at frequency of 1 Hz. Testing of flexural and tensile properties was done with an Instron machine. A crosshead speed of 1.15 mm/min and span length of 60 mm was used according to the ASTM D790. Short beam shear tests were conducted following ASTM D2344 test method. A crosshead speed of 1 mm/min was used. Izod impact tests were performed using a RAY-RAN impact tester following ASTM D256, for a sample size of 3.2×12.7×63.5 mm^3. For all mechanical properties, four tests were carried out to ensure reproducibility.

Flammability test

The flammability of the samples was studied by performing a vertical burning test. Based on the Federal Administration Aviation (FAA), this test method is intended for use in determining the resistance of materials to flame when tested according to the 60-second vertical flame procedure. One important result from this test is the burn length of the sample. Three samples of the same size (5×75×305 mm^3) were tested and evaluated.

RESULTS AND DISCUSSION

Rheology

Figure 4 shows viscosity versus shear rate of different techniques of mixting and depicts the effect of the nanoparticles on the viscosity of the pure resin. The addition of 3%.wt of nanoclays increases the viscosity of resin. The neat resin A0 and the mixtures A2, A3 and A4 follow a Newtonian behavior. Unlike the A1 show a shear thinning behavior with high initial viscosity. This difference in behavior between the mixtures can be related to the quality of the dispersion. A good dispersion will result in higher surface interaction and intercalation due to the polymer diffusion into the galleries of the nanoclays [11]. Increasing nanoclay dispersion/exfoliation will then increase the viscosity of the mixture. Preparation procedure A1 has been then selected for the fabrication of FRP-NC.

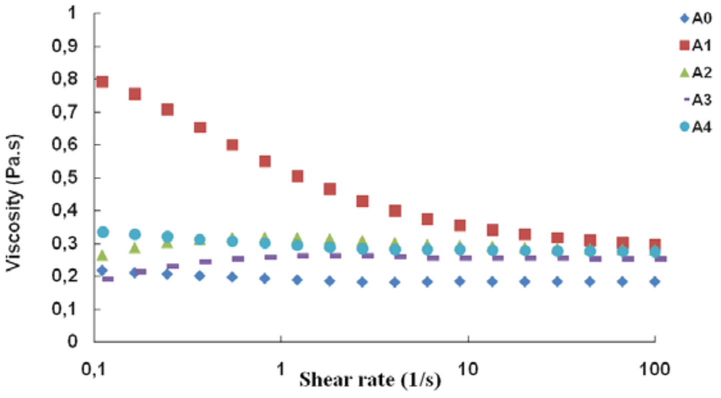


Fig. 4 - Viscosity of pure UP resin and for the different nanoclay preparations at 3wt%.

Thermo-mechanical analyses

Dynamic mechanical analysis (DMA) is a powerful technique for studying the viscoelastic behavior of polymer based materials. It is also the preferred method to measure the glass transition temperature (T_g), which is obtained at the maximum of the loss modulus E”. Fig.5 shows the storage and loss modulus for different nano-charged mixtures compared to the neat resin. The highest storage modulus is given for preparation A1. Table 1 summarizes the values of the storage modulus and T_g. The high modulus value of the preparation A1 could be related to the good dispersion of nanoparticles. This results correlate with the rheological measurement. However, no significant enhancement has observed for T_g.

Table 1 – Thermo-mechanical properties of nanoclay reinforced UP resin.

Sample	A0	A1	A2	A3
E'(MPa)	3600	4118	3900	3850
T_g (C)	112	111.8	113	114

Figure 6 shows the temperature dependence of the storage and loss moduli for the conventional FRP-C and the FRP-NC. The addition of 3%.wt of nanoclays shows a small increase in the storage modulus of conventional composites from (17.8 ± 0.8) GPa to (19.2 ± 1.3) GPa. However, taking into account the standard deviation, the enhancement of storage modulus is negligible. This result is confirmed by the flexural measurements and short beam shear tests as presented in Figures 7 and 8.

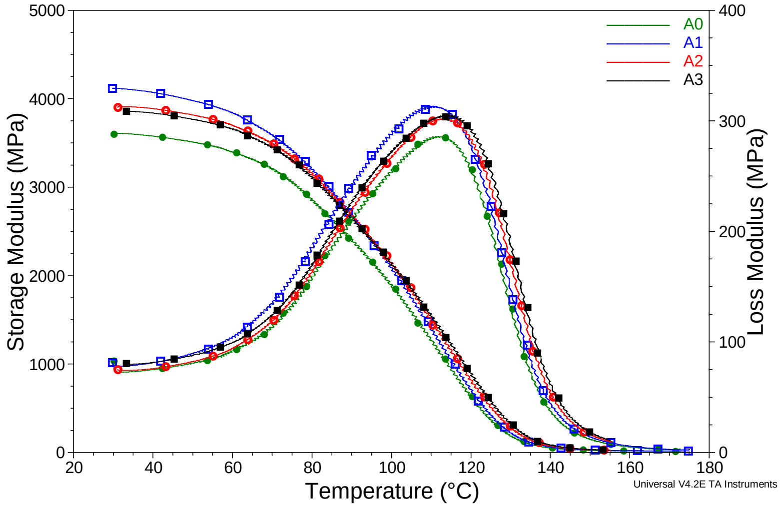


Fig. 5 Storage and loss modulus curves overlay of UP resin/clay nanocomposite.

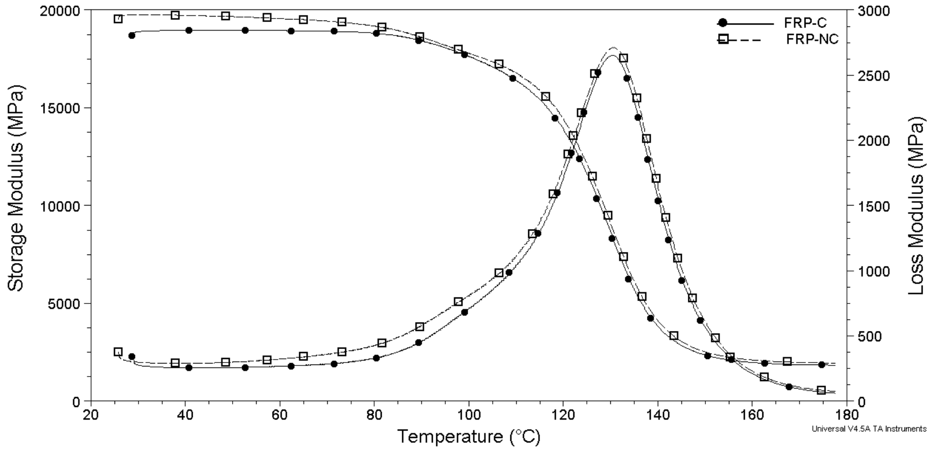


Fig. 6 Storage and loss modulus curves overlay of FRP-C and FRP-NC.

Unlike to the mechanicals tests using the DMA and the flexural test, the importance of the nanoparticles in the composite is highlighted by Izod impact test and the flammability test. As shown in Fig.9, the addition of 3%.wt of nanoclay improves the impact resistance by 10% compared to conventional FRP composites. It is well known also that the presence of nanoclays in a polymer can enhance the char formation providing a transient protective barrier and hence slowing down the degradation of the matrix [12, 13]. This effect explains the high improvement of burn length of FRP-C in the presence of nanoclay (see Fig.10).

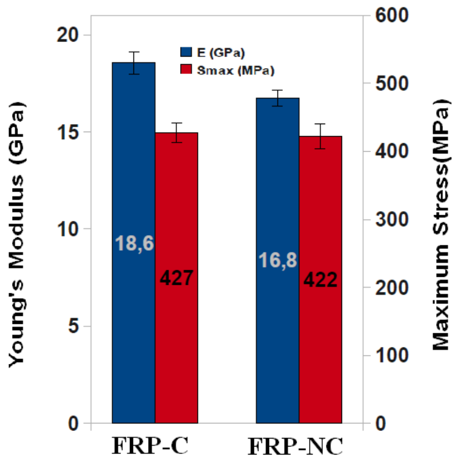


Fig. 7 Young's modulus and ultimate stress

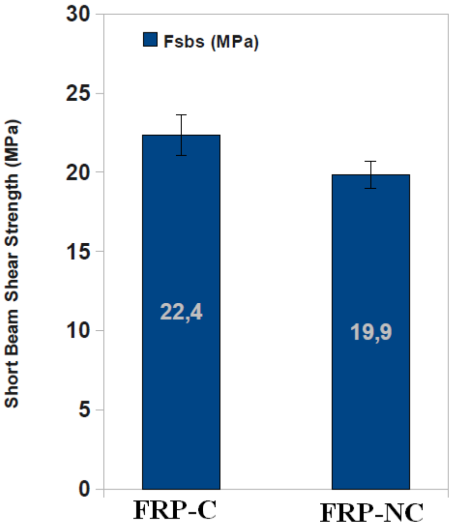


Fig. 8 Short beam shear strengths

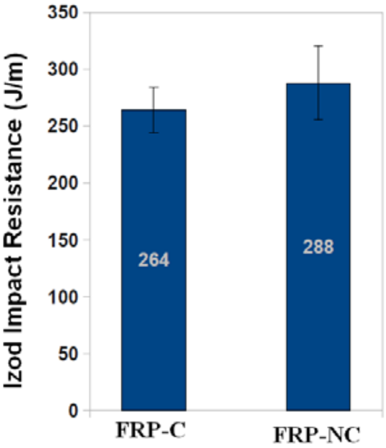


Fig. 9 Impact strengths

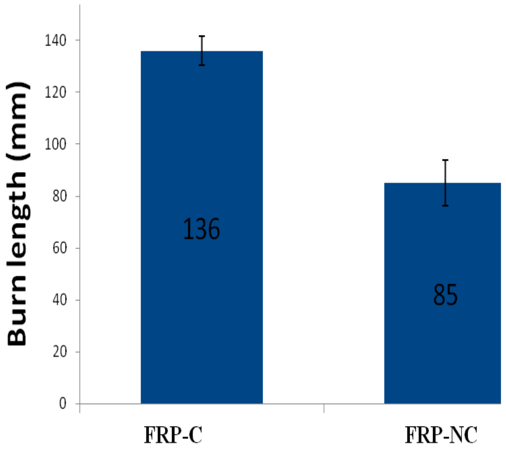


Fig. 10 Flammability test

CONCLUSIONS

In this study, an unsaturated polyester resin was mixed with nanoclay particles. The best approach for good dispersion was found to be the sonication of the nanoparticles dissolved in the styrene followed by the addition of the unsaturated polyester resin while stirring mechanically the mixture and evaporating at the same time the added styrene. Fiber glass/UP/Cloisite30B nanocomposites were manufactured by resin infusion (VARI). The addition of 3% in weight of nanoclays does not seem to enhance the mechanical properties. However the effect of nanoclays has been highlighted on the impact resistance of the nanocomposite and on its flammability resistance.

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