

NANOCOMPOSITE MATRIX FOR IMPROVED FIBER REINFORCED COMPOSITES PROPERTIES

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Abstract

Three-phase continuous fiber reinforced composites (CFRP) consisting of traditional woven glass fiber and polyamide-6 matrix dispersed with nanoclay were prepared and investigated in this study. A manufacturing process using film extrusion and hot pressing technique was developed to produce CFRP with different weight percentages of Somasif®MEE nanoclay. The fabrication was successful when the matrix contains less than 5 %wt nanoclay. Tension tests of nanocomposite specimens show enhancement in thermomechanical properties due to the high aspect ratio and high stiffness of the layered silicates. Compression tests show that 5 %wt nanoclay reinforced composites offer the largest improvement in compressive properties by 50% at 120°C, in dry condition. Failure surface study of compression samples was carried out by scanning electron microscopy (SEM) analysis. By utilizing a nanocomposite matrix, improvement of stiffness and strength, as well as thermal and barrier properties is obtained without any change in processing temperature of fiber composites.

1 Introduction

In recent years, polymer/layered silicate nanocomposites have attracted great interest due to the possibility of exceptional mechanical property enhancements, e.g. increased modulus and improved barrier properties, at low filler levels. The key to such performance depends on the ability to exfoliate and disperse individual, high-aspect ratio silicate platelets within the polymer matrix. The technique of melt processing is particularly attractive due to its versatility and compatibility with existing processing infrastructure. Many research studies show that melt processing in a well-designed twin screw extruder

[1-6] can produce well exfoliated nanocomposites for many types of thermoplastic matrix.

Engineering polymers such as polyamide-6 (PA6), which have good mechanical properties and moderate processing requirements, could be cheaper alternative matrix materials for continuous fiber reinforced thermoplastic composites used for structures requiring low weight (e.g. space, aerospace and automotive). However, PA6 possesses poor moisture barrier properties and have relatively low glass transition temperatures (T_g), above which modulus decreases rapidly.

Nanocomposites based on PA6 can retain a relatively high modulus at temperatures above T_g [7] and in the presence of absorbed moisture [8], and have a strongly reduced creep compliance [9]. Nanocomposites can eliminate or reduce the disadvantages associated with PA6 as matrix material for fiber composites. Previously published research [10-11] on the concept of a nanomaterials reinforced matrix for fiber composites show that the flexural and compressive strength is indeed achieved. However, the full potential of layered silicates for improving thermomechanical properties of the fiber composites was not reached, apparently since the nanoclays were not fully exfoliated in the matrix phase in order to compromise with the ease of fiber impregnation.

In this study, the melt mixing approach was used to disperse Somasif®MEE, surface modified layered silicates, in PA6 matrix. The three-phase CFRP laminates were fabricated using compression molding method in a hot press. Due to high viscosity of the exfoliated nanocomposite matrix, which can lead to filtering of the nanoparticles by the fiber bundles, porosity, incompletely wetting, etc., temperature and pressure cycle during processing was experimentally investigated. The optimum processing procedure for nanoclay reinforced fiber composite was then selected for fabrication of

mechanical test specimens. The results of compressive tests at various temperatures and after moisture conditioning on PA6 nanocomposite matrix reinforced with woven glass fibers are presented. The effect of organoclay contents on the compressive strength of the fiber composites is also discussed. Microscopic approach was used to investigate the fracture behavior and mechanism of fracture.

2 Experiment Details

2.1 Materials

A low viscosity polyamide-6 Akulon® K222D (DSM, The Netherlands) was used as a reference matrix material. The nano-reinforcement was the platelet-shaped synthetic mica layered silicates supplied from Coop Chemicals, Japan. The Somasif®ME-100 is the unmodified silicate sheets and Somasif®MEE is the silicate sheets modified with coco-bis(2-hydroxyethyl) methyl ammonium surfactant. The woven E-glass fabrics were supplied from Ten Cate Advanced Composites, the Netherlands. The woven fabric is categorized as the 8 harness satin weave E-glass fibers with density of 300 g/mm² (E = 77 GPa).

2.2 Preparation

The nanocomposite was made via melt mixing in a Werner and Pfleiderer ZSK 30/44D co-rotating twin-screw extruder operated at a temperature of 240 °C, at a rotation speed of 200 rpm and a feeding rate of approximately 25 ml/min followed by palletizing or film extrusion. The nanocomposites with 2.5 %wt, 5 %wt, and 10 %wt of organically modified layered silicates (MEE) and 10 %wt of unmodified layered silicates (ME-100) were produced for this study.

Dumbbell shaped samples according to ISO 527 standards were produced by injection molding of the nanocomposite pellets on an Arburg Allrounder 221-55-250 machine. The feeding zone was heated to 150°C, the melting and mixing zones heated to 240°C and the nozzle was heated to 270°C.

The 12-ply fiber composites of 25 cm x 25 cm were made by film stacking and fiber impregnation in a hot press. The composite is build up by alternating layers of matrix material films and woven fiber reinforcement. In order to ensure full fiber impregnation and less than 5% voids in the final products, several temperature and pressure cycles (summarized in Fig. 1) applied during

processing were under investigated. The composite samples were cut with a water-cooled diamond saw.

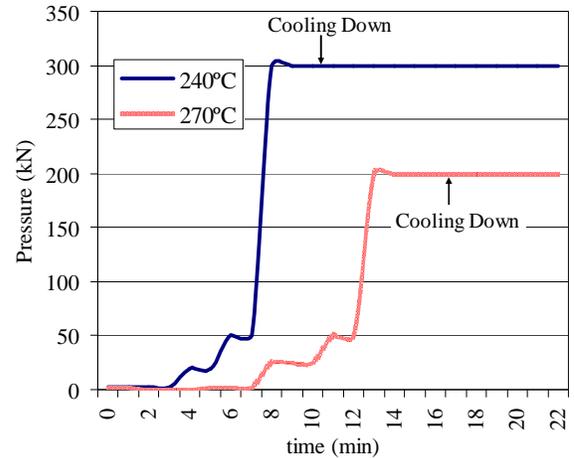


Fig. 1. Pressure cycles applied during the fabrication of fiber composites. At time $t = 0$, the mold temperature has reached the final setting temperature indicates in the legend.

The dry samples were dried further after processing in a vacuum oven at 80°C for at least 48 hours before testing. The moisture-conditioned samples were stored in a climate chamber at 62% RH and 70°C (ISO 1110). These conditions result in a moisture content of 3 %wt in the PA6 phase.

2.3 Testing

2.3.1. Tensile tests on the pure matrix materials

The modulus of the nanocomposite samples was measured in tension at a crosshead speed of 5 mm/min at 20°C intervals according to the ISO 527 standard on a Zwick 1445 universal test machine with a 10 kN load cell. The machine was equipped with a temperature chamber to test the samples at elevated temperatures.

2.3.2. Compression tests on the 12-layer glass fiber composites

The compression test of the composite laminates was performed according to the ASTM D6641M test standard on a Zwick/Roell Z250 universal test machine with a 25 kN load cell equipped with an environmental chamber. The compressive force is introduced into the specimen by combined end- and shear-loading using a

combined loading compression (CLC) test fixture (see Fig. 2). The test specimen is an un-tabbed rectangular strip of the composite laminate with dimension of 140 mm long and 12 mm wide, and has an unsupported gage length of 12 mm. The crosshead speed was 5 mm/min. The composites with a PA6 and nanocomposite matrix were tested dry at 20, 80 and 120°C. For each test condition, five samples were tested to determine the average values.



Fig. 2. Compression Test Set-up and the combined loading compression (CLC) test fixture.

2.3.3. Electron microscopy

Scanning electron microscopy (SEM) on the fiber composite has been performed on a Philips XL 20 SEM. The sample was embedded in epoxy resin and the surface was prepared using polishing wheel, followed by cleaning in an ultrasonic bath. The fracture specimens from the compression tests were not polished.

3 Results and Discussion

3.1 Modulus of PA6 and nanocomposite matrix materials

The influence of the organically modified layered silicates (Somasif®MEE or MEE) and unmodified layered silicates (Somasif®ME-100 or ME-100) contents on the stiffness of the nanocomposites can be seen in Fig. 3 (Concentration is in %wt of silicates). A large increase in the

modulus and gradual loss of stiffness above the glass transition temperature (T_g) compared to the unfilled polymer is illustrated. The increased modulus of the nanocomposites can be attributed to the large aspect ratio and high stiffness of the silicate platelets [12]. The higher modulus above T_g is responsible for the much higher heat distortion temperature (HDT) as reported in literature [13]. At a specific weight percentage, tensile modulus of the nanocomposite specimen with the modified Somasif®MEE particles are higher than those with the unmodified Somasif®ME-100 particles (Fig. 3) because the surface modification improves the exfoliation, leading to more individual particles with higher aspect ratios.

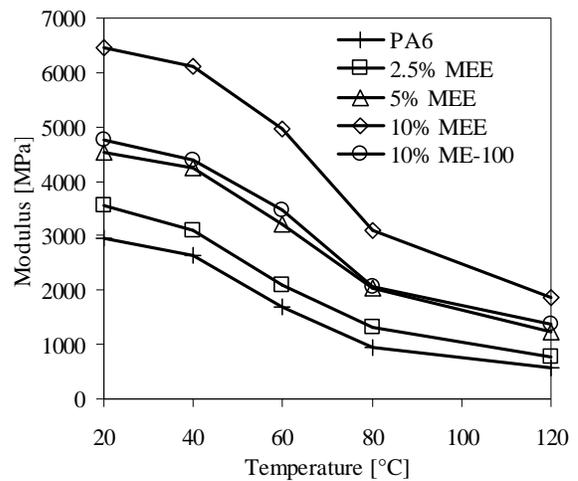


Fig. 3. The tensile modulus of nanocomposites with two types of layered silicates and as a function of volume fraction and temperature.

A similar result can be expected for moisture-conditioned samples. In Fig. 4, all the specimens were conditioned to the control value of 3 %wt moisture content. The nanocomposite specimens have a modulus after moisture-conditioning equal to dry PA6 when tested at room temperature (20°C), and in a hot-wet condition (a combination of 3 %wt water and 80°C) the modulus of the nanocomposite is almost 3 times higher than that of unfilled PA6, and still higher than moisture-conditioned PA6 at room temperature. Therefore, it can be expected that the negative effects of moisture absorption on the fiber composite strength can be reduced to a large extent by utilizing nanocomposite materials.

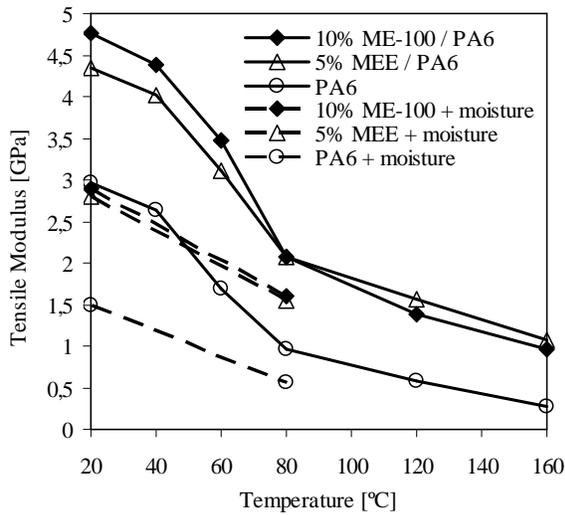


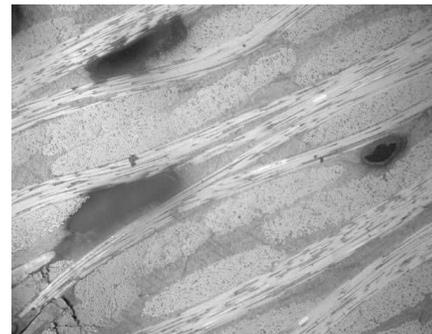
Fig. 4. The tensile modulus of PA6 nanocomposites and unfilled PA6 as a function of the temperature in dry (solid lines) and wet conditions (dotted lines)

The increased modulus of the nanocomposites can offer extra support to the fibers at increased temperatures and in moisture conditioned, reducing the tendency for buckling and kinking of the fibers in the composite under compression. Therefore, it can be expected that the strength of the fiber composites remains high up to much higher temperatures, extending the application window for PA6 as matrix material.

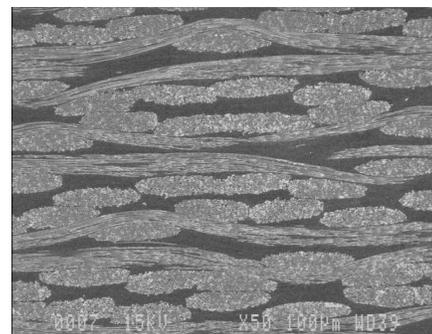
3.2 Fiber impregnation with nanocomposite matrices

It is also observed in Fig. 4 that in this material the largest improvement in modulus is obtain at the 10 %wt of organically modified layered silicates (10% MEE/PA6). However, the addition of nanoparticles, particularly in a perfectly exfoliated nanocomposite, can result in a very large increase of viscosity [14], especially at low shear rates, due to the formation of a network structure [15]. At high shear rates the network can be broken down, resulting in a strong shear thinning behavior. Melt-impregnation of fiber bundles with nanocomposites often proved to be difficult due to the higher melt viscosity and the occurrence of a yield stress in the melt. This melt flow behavior can cause large voids in the fiber composites, which can lead to a decreased in strength. In addition, the adhesion of many nanocomposites with the fibers was shown to

be weaker [16]. Fig. 5 shows micrographs of fiber reinforced composite laminates with the 5 %wt Somasif®MEE/ PA6 matrix processed at 240°C and 270°C. The pressure profiles during consolidation were described in section 2.2. It is noticed that the lower processing temperature and higher pressure does not facilitate the impregnation in the fiber composites as large voids are often obtained. In contrary, at the higher temperature but lower pressure, the viscosity of the nanocomposite resin reduced and the time allowed for melt impregnation was sufficient. However in the case of 10 %wt Somasif®MEE/ PA6 matrix, it was impossible to fabricate good quality fiber composites even at high processing temperature of 270°C. Application of higher pressure does not help as it pushes the reinforced fiber out of the mold. Increasing the temperature is not recommended since PA6 can oxidize faster. Large voids and incomplete wet out in the fiber reinforced composite laminates with the 10 %wt Somasif®MEE/ PA6 matrix is illustrated in Fig. 6.



(a) Processing temperature of 240°C



(b) Processing temperature of 270°C

Fig. 5. SEM micrographs of fiber reinforced composite laminates with the 5 %wt Somasif®MEE/ PA6 matrix processed at (a) 240°C and (b) 270°C

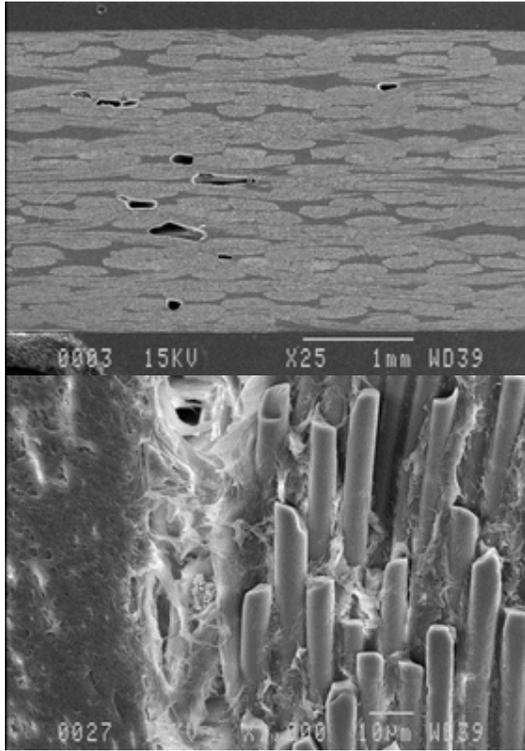


Fig. 6. Incomplete wet out in 10 wt.% Somasif@MEE/PA6 composite

In our previous study [11,16], the 10 %wt ME-100/PA6 nanocomposite was chosen as the best compromise between the increase in modulus, good melt flow behavior and good adhesion. Therefore, it does not give problems with fiber bundle impregnation and adhesion, and can show the expected improvement of the composite properties.

In this work, with optimized processing condition and appropriate tooling, the full potential of nanoclay for the improvement of fiber composite properties can be investigated without having to compromise for high melt viscosity. Despite the high viscosity, the fiber composites with 2.5 %wt Somasif@MEE nanocomposite matrix and with 5 %wt Somasif@MEE nanocomposite matrix were successfully manufactured via compression molding with less than 5% void content.

3.3 The compressive behavior of fiber composites with nanocomposite matrices

The compressive strength of the fiber composites with 2.5 %wt Somasif@MEE nanocomposite matrix, 5 %wt Somasif@MEE nanocomposite matrix and neat PA6 matrix is

plotted as a function of the temperature in Fig. 7. The fiber composites based on nanocomposite matrices have higher strength at elevated temperatures than the unfilled PA6 fiber composite.

In dry condition, the compressive strength at 120°C of fiber composite with 5%wt MEE nano-reinforcement is the same as the strength of unfilled PA6 composite at 80°C. Therefore, with the nanocomposite matrix it is possible to extend the temperature window for PA6-based composites by 40°C, without changing the processing temperature.

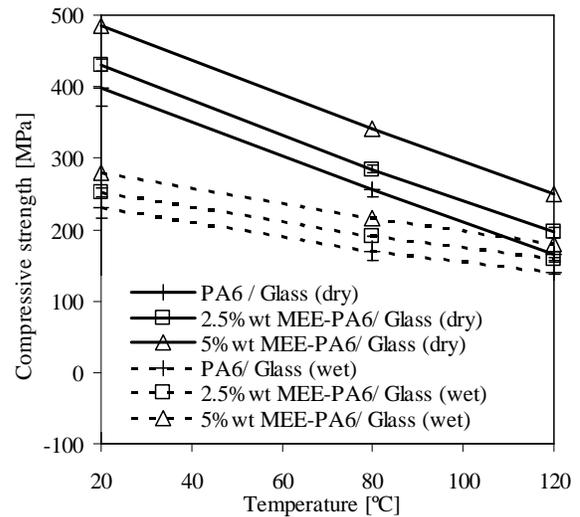
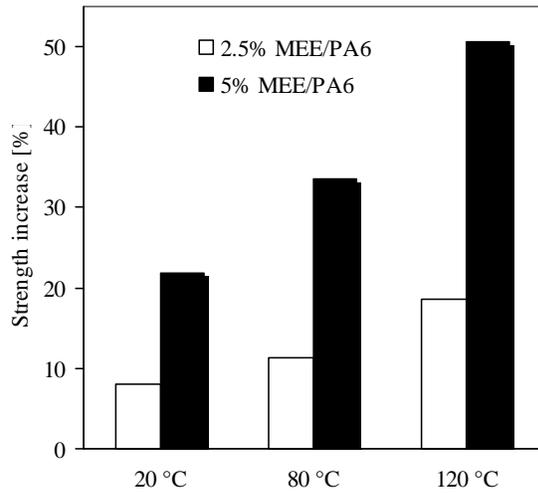


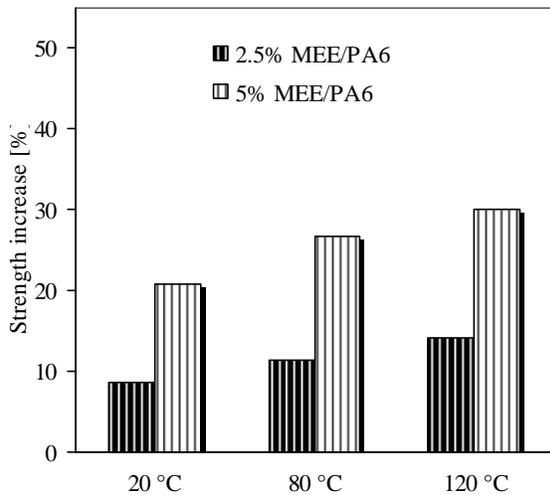
Fig. 7. Compressive strength of glass fiber reinforced composites with nanocomposite matrices compared with neat PA6 matrix as a function of the temperature in dry and wet (3 %wt water) conditions

A similar positive influence of the nanocomposite matrix was found for the moisture-conditioned samples. It is found that the nanocomposite matrix can compensate for the loss of strength due to moisture absorption in the PA6 matrix. At combined hot and wet conditions (moisture-conditioned samples tested at 80°C and 120°C) the fiber composites with nanocomposite matrices show 10 - 30 % higher strength than the one with an unfilled PA6 matrix.

In Fig. 8 the percentage increase in strength compared to the neat PA6 matrix composite when subject to the same testing conditions is shown for the fiber composites with 2.5%wt Somasif@MEE/PA6 matrix and 5%wt Somasif@MEE/PA6 matrix in both dry and wet condition.



(a) Dry testing condition

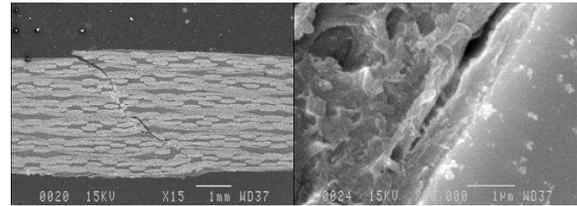


(b) Moisture testing condition

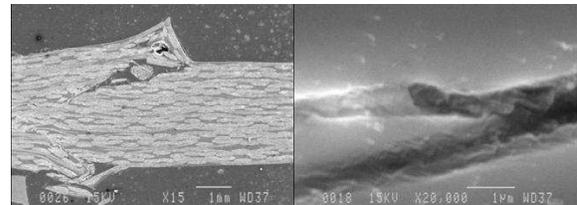
Fig. 8. The percentage increase in strength of fiber composites with 10% wt Somasif®ME-100/PA6 matrix compared to the neat PA6 matrix composite

The compressive failure modes of the test specimens are defined on the basis of the macroscopic failure sites. Fig. 9 shows the SEM micrographs of the failure modes in the fiber composites with (a) unfilled PA6 matrix, (b) 2.5 % wt Somasif®MEE/PA6 matrix and (c) 5 % wt Somasif®MEE/PA6 matrix. The main feature, which was observed in all test specimens, is the 45° through-thickness failure at the gage. For the test

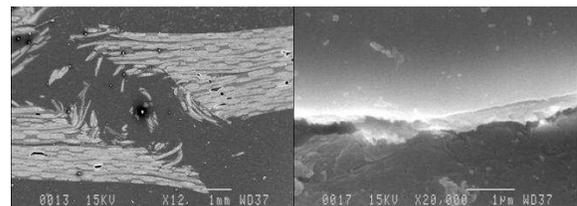
specimens (both with nanocomposite and neat PA6 matrices) tested at 20°C in dry condition, there was an additional brooming failure mode at fracture sites. Brooming failure mode was seen also in the compression test of the fiber composites with nanocomposite matrix at 80°C in dry condition, but it was less apparent. When testing at the same condition, fiber breakage in fiber composites with nanocomposite matrix is more catastrophic than that of fiber composites with neat PA6 matrix because the matrix modulus increases upon the addition of the high aspect ratio silicate platelets. The failure modes of the test specimens confirm that the nanocomposite matrix offers more support in compression both at elevated temperatures and in moisture condition.



(a) Fiber composites with unfilled PA6 matrix



(b) Fiber composites with 2.5 % wt MEE/PA6 matrix



(c) fiber composites with 5 % wt MEE/PA6 matrix

Fig. 9. Fracture surfaces of fiber composites with various matrices. The test condition is at 20°C in dry condition

4 Conclusions

In this study the successful application of a semi-crystalline thermoplastic polyamide-6 nanocomposite as a matrix in a new three-phase thermoplastic composite is described.

The compressive strength of the fiber composites using nanocomposite matrix have been increased up to 50% at elevated temperatures and the temperature window for PA6-based composites is extended by 40°C, without changing the processing temperature.

The possibility to use the composites at these much higher temperatures relies on the possibility to use the semi-crystalline polymer above T_g . Therefore, semi-crystalline thermoplastic polymers are expected to benefit most from this approach. The improved properties of the nanocomposite matrix material can upgrade the properties of relatively low cost thermoplastic composites up to the level of high performance composites and further increase the temperature resistance of existing high-performance composites

5 References

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