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Nanocomposite matrix for increased fibre composite strength

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Abstract

A new type of three-phase thermoplastic composite has been made, consisting of a main reinforcing phase of woven glass or carbon fibres and a PA6 nanocomposite matrix. Nanocomposites have the potential to improve the matrix dominated flexural and compressive strength by increasing the matrix modulus. Good quality fibre composites have been made with several types of PA6 nanocomposite and unfilled PA6 in combination with glass and carbon fibre reinforcement. Flexural tests on commercial PA6 fibre composites have shown the decrease of the flexural strength upon increasing temperature and this has been compared with the decrease of the matrix modulus. The nanocomposites used in this research have moduli that are much higher than unfilled PA6, also above T_g and in moisture conditioned samples. The strength of glass fibre composites can be increased by more than 40% at elevated temperatures and the temperature range at which a certain minimum strength is present can be increased by 40–50 °C. Carbon fibre composites also show significant improvements at elevated temperatures, although not at room temperature. The advantage of the use of nanocomposites instead of other polymers to improve the fibre composite properties is that the properties can be improved without any change in the processing conditions.

Keywords: Nanocomposite; Fibre composite; Hybrid compound

1. Introduction

Continuous fibre reinforced thermoplastic composites have been developed as an alternative to thermoset fibre composites with a wide variety of matrix polymers, ranging from cheap commodity plastics to very expensive high performance polymers. Polymer nanocomposites based on exfoliated layered silicate are a different type of composite material, containing extremely small particles with a thickness in the range of 1 nm. The length scales of the reinforcement in fibre composites and nanocomposites are very different; for example, the thickness of an exfoliated silicate sheet is 10,000 times smaller that the diameter of a typical glass fibre. Therefore, the two composites can be combined in a new type of three-phase hybrid composite. In this new three-phase composite the main reinforcing phase are continuous fibres, which are used at a high volume fraction (for example $V_f = 0.5$ in woven fibre composites). The matrix itself is a composite too in the new three-phase composite, containing particles on the nanometer length scale. In Fig. 1 a schematic drawing shows this concept: The fibres are long and continue through the entire length of the sample and the particles in the matrix material fit between the fibres, without reducing the fibre volume fraction. No fibres are replaced by nanoparticles, but the matrix-dominated properties of the fibre composite can benefit from the improved properties of the nanocomposite.

Thermoplastic fibre composites were first developed with high performance polymers such as polyetheretherketone (PEEK) as matrix material, to improve on the mechanical properties of thermoset matrix resins for aerospace applications. Because of the high cost and high processing temperatures of this and other aromatic high performance polymers the applications are limited to fields in which the price is of little importance, such as in military aircrafts and space vehicles. The advantages of thermoplastic composites

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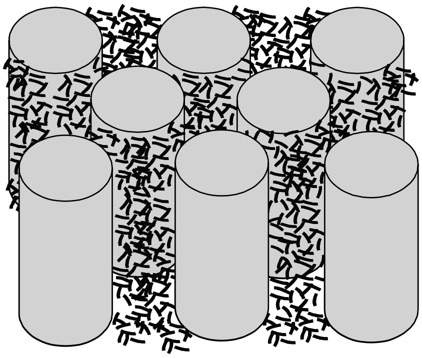

Fig. 1. Nano-particle reinforcement of the matrix in a continuous fibre composite.

in processing, such as the long shelf life of prepregs and zero emissions during processing, have led to the development of thermoplastic fibre composites in many different price- and performance classes. Polyamide 6 (PA6) is an engineering plastic that is positioned between the cheapest commodity plastics and the high performance polymers, both in price, performance and processing temperature. It is an interesting polymer for use as fibre composite matrix material because it has good mechanical properties while being relatively cheap, and it has a low melt viscosity and a relatively low melting point of 220 °C [1]. However, PA6 has a relatively low T_g and its tendency to absorb moisture from the environment lowers the T_g further. The modulus decreases strongly above T_g, and, therefore, the performance at high temperatures and in moist environments could be improved.

Nanocomposites based on PA6 have a much higher modulus [2], they retain a relatively high modulus at temperatures above T_g and in the presence of absorbed moisture [3], and have a strongly reduced creep compliance [4]. Therefore, nanocomposites can eliminate or reduce the disadvantages associated with PA6 as matrix material for fibre composites.

The nanoparticles in the matrix nanocomposites are only intended to improve the matrix-dominated properties of the fibre composite. The fibres dominate the modulus and the tensile strength of the fibre composites, and, therefore, the increased matrix modulus does not provide a significant increase in the composite modulus or tensile strength. The most important improvement that the nanocomposite matrix can provide is an increase in the compressive and flexural strength of the fibre composite. The compressive strength of continuous fibre composites is usually lower than the tensile strength, because the fibres can easily buckle under a compressive load. The compressive strength depends on the modulus of the matrix [5–9], because a higher modulus increases the lateral support of the fibres and, therefore, reduces the tendency for fibre micro buckling or kinking. The flexural strength of a continuous fibre composite is dominated by the compressive strength because failure usually starts at the compressive side due to micro buckling or kinking, as can be seen in the PA6 glass fibre composite sample in Fig. 2.

For this reason, flexural measurements are a good way to measure the effect of nanocomposite matrix materials on the matrix dominated properties of the fibre composites. Bending loads are often encountered in the applications of composite materials, therefore, the flexural strength is also of great practical importance.

Previously published research on the concept of a nanocomposite matrix for fibre composites concerned nanocomposites based on epoxy resins. These nanocomposite matrices did not lead to an improvement of the fibre composite strength [10–12], apparently due to problems with fibre impregnation or because the fibre were damaged in the process.

In this article the results are described for a three-phase thermoplastic composite based on PA6 nanocomposites reinforced with woven glass and carbon fibres. In order to understand the influence of the temperature and absorbed moisture on the flexural strength of the fibre composite, the strength of PA6 composites is first studied over a wide temperature range and after moisture conditioning. Subsequently, the properties of the nanocomposite matrix materials that are important for the impregnation step and for the mechanical properties of the fibre composite are discussed. The improvement of the flexural strength the nanocomposites can provide at various temperatures in both dry and moisture-conditioned samples compared with the composites with an unfilled PA6 matrix shows the potential importance of this new class of composites.

2. Experimental

2.1. Materials

2.1.1. Fibre composite

A commercially available glass (TEPEX® Dynalite 102) and carbon fibre composite (TEPEX® Dynalite 202) based on PA6 as matrix from Bond Laminates, was used to

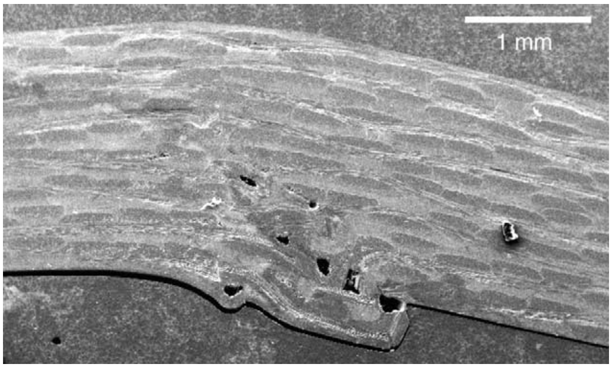

Fig. 2. Compressive failure of a PA6 glass fibre composite sample in a flexural test.

investigate the strength as a function of temperature of this type of thermoplastic composite.

2.1.2. Matrix

2.1.2.1. PA6 matrix material. As reference matrix material an injection moulding grade PA6, Akulon® K222D from DSM, The Netherlands, was used ($M_n \approx 16{,}000$, $M_w \approx 32{,}000$ g/mol, $T_m \approx 220$ °C).

2.1.3. Melt exfoliated PA6 nanocomposite

Melt-exfoliated PA6 nanocomposites have been made based on Akulon® K123D, an injection moulding grade PA6 from DSM, The Netherlands. This PA6 grade is very similar in all properties to the K222D reference material ($M_n \approx 16{,}000$, $M_w \approx 32{,}000$ g/mol, $T_m \approx 220$ °C).

2.1.4. Nanoparticles

The nanocomposite contains 10 wt% Somasif® ME-100 synthetic mica layered silicate nanoparticles from Coop Chemicals, Japan. Somasif® ME-100 is a water-swellable synthetic fluorine mica, which, according to the supplier, has been synthesized by heating talc with Na_2SiF_6 for several hours. The crystal structure is similar to mica and montmorillonite, with two tetrahedral silicate sheets surrounding an octahedral $Mg(OH)_2$ sheet. In the octahedral sheet the OH groups are partially substituted by F, and the negative charge in the layers is compensated by exchangeable Na^+ counter ions between the silicate sheets.

2.1.5. In situ polymerized PA6 nanocomposite

In addition, a commercially available PA6 nanocomposite, Unitika M1030D from Unitika, Japan, has been used.

This nanocomposite contains 4.6% exfoliated layered silicate and is made by in situ hydrolytic polymerisation of ε-caprolactam in the presence of swollen organically modified silicate. The organic surfactant is the initiator for polymerisation, so the polymer chains are bound to the surfactant via covalent bonds.

2.1.6. Fibre reinforcement

2.1.6.1. Glass fibres. Ten Cate Advanced Composites SS0303, 8 Harness satin weave E-glass fibres, 300 g/mm^2, (Style 7781) ($E = 77$ GPa).

2.1.6.2. Carbon fibres. Ten Cate Advanced Composites CD0286, 5 Harness satin weave T300JB high strength carbon fibres, 300 g/mm^2 ($E = 230$ GPa).

2.2. Preparation

2.2.1. Somasif® ME-100/Akulon® K123D nanocomposite

The nanocomposite with Somasif® ME-100 was made by feeding a mixture of cryogenically milled PA6 and ME-100 powder in a Werner and Pfleiderer ZSK 30/44 D co-rotating twin-screw extruder. To enhance the exfoliation of the water-swellable ME-100 silicate, water was injected into the extruder at a rate of 25 ml/min, and removed by venting at the end of the extruder [13]. The addition of water in the extruder strongly improves the exfoliation of the unmodified layered silicate in the mixture of water and molten PA6. It is used as an alternative to the use of an organic modification on the layered silicate to improve the exfoliation.

The extruder was operated at a temperature of 240 °C at a rotation speed of 200 rpm and a feeding rate of approximately 10 kg/h.

2.2.2. Fibre composites

The fibre composites were made by film stacking and fibre impregnation in a hot plate press. The composite is build up by alternating layers of matrix material films and woven fibre reinforcement. In the glass fibre composites eight fibre layers were used and in the carbon fibre composites six fibre layers were used, both for a 2 mm thick composite plate. The matrix layer thickness was calculated to result in a fibre volume fraction of 50%. The matrix films were pressed from granules of the extruded PA6 or nanocomposite. The number of layers of matrix material was one more than the layers of fibres (nine for glass, seven for carbon), and the outside layers were half the thickness of the layers between the fibres because they only need to impregnate the fibres on one side. To reach a composite thickness of approximately 2 mm and a volume fraction of 50% the total thickness of the combined films for each composite plate needed to be 1 mm. Using the density of the matrix material, the weight of each film was calculated and the exact weight of granules was measured to press each film. The films were pressed between 5 mm thick aluminium plates of 50×45 cm^2 covered with a PTFE/glass fibre release film. The granules were spread evenly and heated at 240 °C for 6 min without pressure and subsequently pressed for 6 min at a pressure of 10 bar (PA6) or 25 bar (nanocomposites) at the same temperature. A higher pressure was used for the nanocomposite films because of the higher viscosity (pressing for a longer time at a lower pressure would also work).

The films and fibre layers were stacked and heated for 6 min at 240 °C between the same plates. Subsequently, the composite plate was impregnated under a pressure of 20 bar for 7 min and cooled under the same pressure. The press was cooled with water at a rate of approximately 20 °C/min.

The composite samples of 12.5 mm wide and 120 mm long were cut with a water-cooled diamond saw.

2.2.3. Injection moulding

Dumb-bell shaped samples according to the ISO 527 standard were injection moulded on an Arburg Allrounder 221-55-250 injection-moulding 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 to prevent solidification when the nozzle is in contact with the cold mould.

2.2.4. Determination of silicate content

Thermo-gravimetric analysis (TGA) was used to determine the exact silicate content in the materials. The samples were heated in air at 800 °C for 1 h in a Perkin–Elmer TGA-7 Thermal Gravimetric Analyzer to determine the inorganic content. The silicate levels mentioned in this article are the weight percentages of the silicate filler as measured with TGA.

2.2.5. Conditioning

The dry samples were dried further after processing in a vacuum oven at 80 °C for at least 48 h 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 2.7 wt% in the PA6 phase. This moisture content is similar to the moisture content the material would reach at 23 °C and 50% RH, but the equilibrium concentration is reached much faster.

2.2.6. Measurement of the glass transition temperature

The glass transition temperatures (T_g) of the samples were determined with dynamic mechanical analysis (DMA). Samples with a thickness of 0.2 mm were pressed at 240 °C and tested in a Perkin–Elmer DMA 7e at a temperature range from −100 to 200 °C. The temperature at the maximum of the loss modulus represents T_g.

2.3. Testing

2.3.1. Density and fibre volume fraction

The densities of the matrix materials and the fibre composite samples were measured by weighing the samples in air and water. Two samples for each composite plate were measured and the fibre volume fraction V_f was calculated from the density of the components. For the small variation in V_f around 0.50 a fibre volume correction factor of ($0.5/V_{f,measured}$) was calculated. This factor was used to correct the measured stresses for small deviations from the intended V_f.

2.3.2. Mechanical properties

All samples were tested on a Zwick 1445 universal test machine with a 10 kN force cell. The machine was equipped with a temperature chamber to test the samples at elevated temperatures.

The modulus of the injection moulded matrix samples was measured in tension at a speed of 5 mm/min at 20 °C intervals according to the ISO 527 standard.

The fibre composites were tested in 3 point bending according to the ASTM D790M test standard. The samples were 12.5 mm wide (Bond Laminates composites 25 mm), 2 mm thick and the span in the bending test was 80 mm, and the loading point for the test was in the centre. The test speed was 5 mm/min. For each temperature and composition five samples were tested to determine the average values. The commercially available glass and carbon fibre composites were tested at 20, 40, 60, 80, 100, 120, 140, 160 and 180 °C. The composites with a nanocomposite matrix and the PA6 matrix reference materials were tested at 20, 80 and 120 °C, and some also at 160 °C.

The measured average failure stress was corrected for small deviations from the intended V_f of 0.50 by multiplying them with a fibre volume correction factor ($0.5/V_{f,measured}$). This way the influence of small deviations from the intended V_f on the results was minimized. The deviations from the intended fibre volume fraction and the corrections of the strength are below 5%. The small variations in the thickness of the samples are accounted for in the calculation of the strength.

For all tests on moisture conditioned matrix and fibre composite samples at 80 °C the specimen were transported shortly before the test from the climate chamber, which was at 70 °C, to the test machine. The samples were allowed to heat up to 80 °C for 5 min, after which the test was started immediately to prevent as much as possible the loss of water in the relatively dry test chamber.

2.3.3. Electron microscopy

Scanning electron microscopy (SEM) on the fibre composite has been performed on a Philips XL 20 SEM. Samples were embedded in epoxy resin and polished with water using sandpaper and a very fine polishing paste.

Transmission electron microscopy (TEM) has been performed on a Philips CM 200 TEM at an acceleration voltage of 120 kV. Films with a thickness of 70 nm were cut from extruded pellets with a diamond knife at −100 °C.

3. Results and discussion

3.1. The influence of the temperature on the flexural strength of PA6 glass and carbon fibre composites

Commercially available PA6 based fibre composites containing 46 vol% woven glass and carbon fibres were tested at temperatures from 20 to 180 °C with 20 °C intervals. In Fig. 3 the results for the flexural strength of glass and carbon fibre composites are plotted as a function of the temperature.

In both composites the strength decreases at increasing temperature. The carbon fibre composites have a higher strength at room temperature than the glass fibre composites, as can be expected, but at increasing temperature the difference is rapidly decreasing. At 80 °C the strength of both types of composite is almost identical, and above 100 °C the glass fibre composites have a slightly higher strength than the carbon fibre composites. In bending of a composite a complex combination exists of tensile stresses on the fibres on the outside, compressive stresses on the

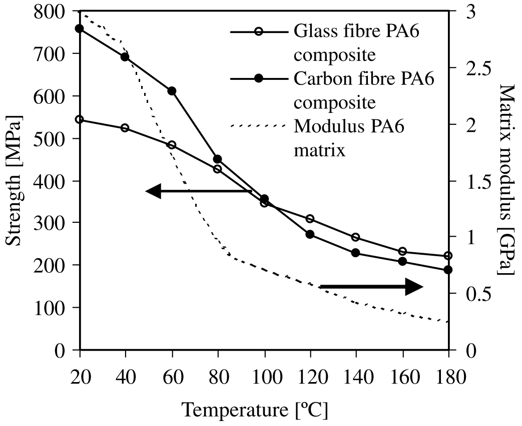

Fig. 3. Flexural strength of commercially available glass and carbon fibre composites with PA6 matrix (dry) as a function of the temperature. The dotted line represents the matrix modulus as a function of the temperature.

fibres on the inside, and shear stress between the layers of the composite. With the ratio of the test length (l) to the composite thickness (t) used in this ASTM 790D test ($l/t=40$) the shear stresses between the layers are low enough to prevent shear failure. The flexural strength is in this case limited by the compressive strength, as can be seen in the SEM picture of the cross-section of a failed glass fibre specimen (Fig. 2). The compressive strength of the composite depends on the amount of buckling of the fibres, which depends on the lateral support provided by the matrix. The temperature dependence of the strength in Fig. 3 can be explained by the decrease of the matrix modulus, which occurs at increasing temperatures. To illustrate this, the modulus of the matrix (PA6) is plotted versus the same temperature scale in Fig. 3, with the modulus values on the right axis. The fast decrease of the matrix modulus around the T_g of PA6 shows a correlation with the composite strength. It is likely that the decrease in matrix modulus decreases the lateral support of the fibres, which leads to premature failure due to fibre buckling. Carbon fibre composites seem to be more sensitive to this effect, probably because of the lower failure strain of carbon fibres. Buckling of fibres with a lower failure strain will lead more quickly to fibre failure and subsequent composite failure. In Fig. 4 the composite strength of both fibre composites is plotted as a function of the matrix modulus. Fig. 4 shows for both composites a decrease of the strength with decreasing matrix modulus, which is stronger for carbon fibre composites. The decrease of the strength is much stronger when the matrix modulus drops below approximately 1 GPa (note that this is close to the modulus at the heat distortion temperature (HDT)). In unfilled PA6 this modulus is reached at approximately 80 °C in dry conditions (Fig. 3).

3.2. Nanocomposite matrix materials

The new three-phase composite is made with two different nanocomposites as matrix material, and an unfilled PA6 matrix as reference. One is a commercially available PA6 nanocomposite (Unitika M1030D) and the other a nanocomposite (10% ME-100 in low MW PA6) that has been developed and selected after various previous tests on fibre bundle impregnation, mechanical properties, melt flow behaviour and adhesion with the fibres [14,15]. In Fig. 5 a TEM picture of a Somasif ME-100 nanocomposite is shown. It can be seen that a combination of individually dispersed exfoliated silicate platelets and stacks of multiple platelets is present. In the Unitika nanocomposite, the particles are mainly present as single platelets. Therefore, the effective (average) aspect ratio of the particles in the ME-100 nanocomposite is lower than in the Unitika nanocomposite.

Initial attempts to make melt-impregnated fibre composites with nanocomposites often resulted in fibre composites with more voids and lower strength than the reference material. It proved to be difficult to achieve good fibre

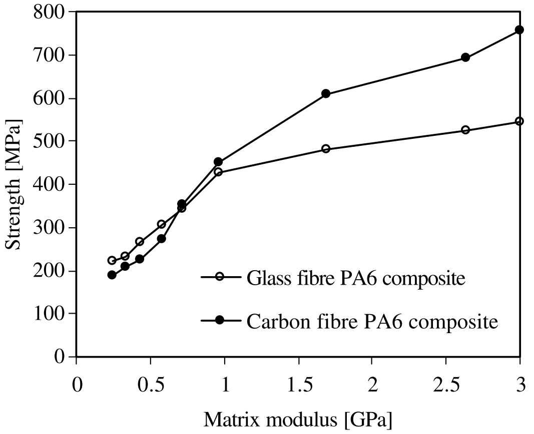

Fig. 4. Flexural strength of commercially available PA6 glass and carbon fibre composites (dry) as a function of the matrix modulus.

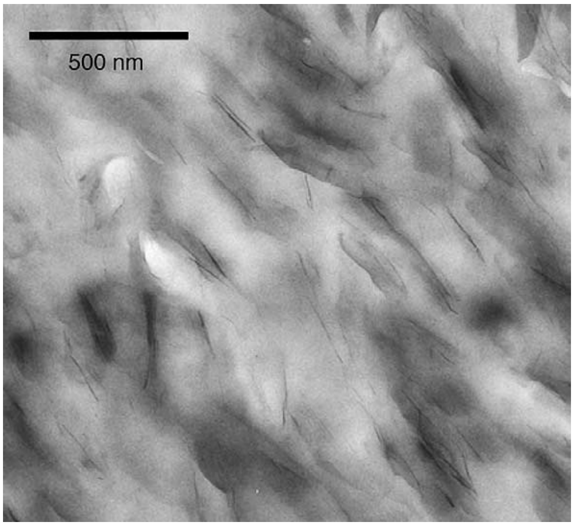

Fig. 5. ME-100 nanocomposite, showing a combination of exfoliated individual particles and stacks of silicate sheets.

bundle impregnation and wetting with many PA6 nanocomposites, probably due to the melt flow behaviour, which is characterized by a higher viscosity and often a yield stress. The adhesion of many nanocomposites with the fibres also proved to be often lower [14]. The two types of nanocomposite described here do not show severe problems with respect to impregnation and adhesion, and they can, therefore, indeed show the expected advantages of nanocomposite matrix materials. In Fig. 6 two SEM pictures are shown of polished cross sections of carbon fibre composites with different matrix materials. In Fig. 6(A) the matrix consists of unfilled PA6, in Fig. 6(B) of Unitika M1030D nanocomposite. It can be seen that in both types of composite no voids are visible, and it is assumed that the void content is very low in the tested samples and that there is no significant difference in quality between the three matrix types.

In Fig. 7 the tensile modulus of the nanocomposites and the PA6 reference material is shown as a function of the temperature. The dotted lines show the results for moisture-conditioned samples at 20 and 80 °C. Fig. 8 shows the loss moduli from DMA measurements on thin films; the peaks indicate the glass transition temperature. T_g is the same in unfilled PA6 and the nanocomposites, but it decreases from around 65 °C (dry) to around room temperature as a result of moisture conditioning. The decrease of $\approx$45 °C in T_g due to moisture conditioning translates to a decrease in the modulus that is similar to an increase of 45 °C in temperature (starting at room temperature).

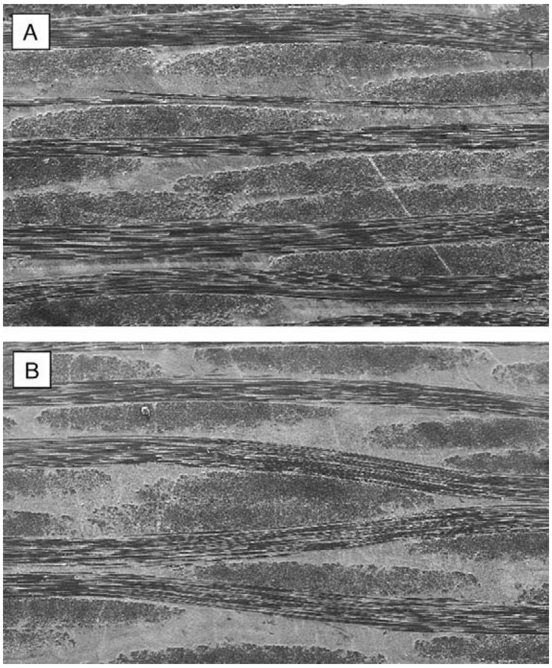

Fig. 6. Cross-section of carbon fibre composites: (A) unfilled PA6 matrix (K222D), (B) Unitika nanocomposite matrix.

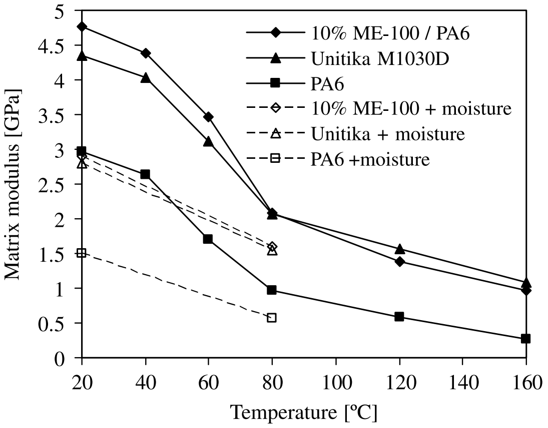

Fig. 7. Modulus of unfilled PA6 and two nanocomposite matrix materials as a function of the temperature, dry (solid lines) and moisture conditioned (dotted lines).

Both unfilled PA6 and nanocomposites show a strong decrease in modulus above T_g (Fig. 7), but even above T_g the nanocomposites have moduli that are more than 1 GPa higher than unfilled PA6 (at 80 °C). However, T_g and the temperature around which the modulus decreases does not change in nanocomposites compared to unfilled PA6 (Fig. 8).

The potential benefits of nanocomposites for the use in fibre composites can be visualized when the results of Figs. 4 and 7 are combined: The nanocomposites have moduli above 1 GPa up to 160 °C, while the unfilled PA6 already has a lower modulus above 80 °C. In Fig. 4 it can be seen that at matrix moduli below 1 GPa the flexural strength decreases rapidly. The 1 GPa barrier (although just an arbitrary value) is shifted up by more than 80 °C in these nanocomposites. Therefore, it can be expected that the strength of the fibre composites remains high up to much higher temperatures, significantly expanding the application window for PA6 as matrix material. A similar result can be expected for moisture-conditioned samples. It can be seen in Fig. 7 that the modulus of the moisture-conditioned nanocomposites is almost the same as the modulus of dry PA6. With the combination of moisture-conditioning and elevated

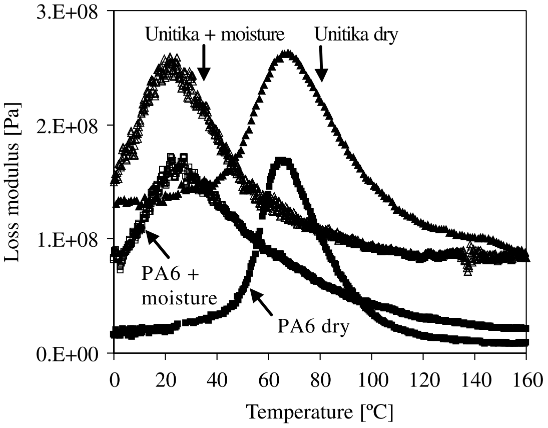

Fig. 8. Loss moduli as a function of the temperature for dry and moisture-conditioned PA6 and a PA6 nanocomposite. The peak represents the glass transition temperature (T_g).

temperature (80 °C), the modulus of the nanocomposites is almost three times higher than in unfilled PA6, and still higher than moisture-conditioned PA6 at room temperature. Therefore, it can be expected that the negative effect of moisture absorption in PA6 on the fibre composite strength can be reduced to a large extent by using nanocomposites. The modulus of the two types of nanocomposite is similar, both in dry and moisture conditioned samples, despite the different amounts of nanoparticles. This can be explained by the fact that the exfoliation of the platelets is not perfect in the ME-100 nanocomposites, as a result of the lack of surfactant on the platelets. This leads to more stacks of un-exfoliated platelets (Fig. 5) and, therefore, to a lower effective aspect ratio in the ME-100 nanocomposites [2]. In this material a higher volume fraction of nanoparticles is necessary to achieve the same modulus as with perfectly exfoliated particles, but the influence of reduced exfoliation on the melt flow properties is beneficial [15].

In Fig. 9 the viscosity of the three matrix materials at the processing temperature of 240 °C is shown. The nanocomposite from Unitika has the highest melt viscosity and the unfilled PA6 the lowest. However, the viscosities are not very high in these matrix materials compared to many nanocomposites [15] and no significant yield stress in the melt was found. It was possible to achieve good fibre bundle impregnation with these three matrix materials.

3.3. The flexural strength of fibre composites with a nanocomposite matrix

In Fig. 10 the flexural strength of the glass fibre composites with nanocomposite and PA6 matrix is shown as a function of the temperature (due to the different materials and production process, these values should not be compared with the values in Fig. 3). Both fibre composites based on a nanocomposite matrix have a higher strength at all temperatures than the PA6-based fibre composite. At elevated temperatures the difference becomes relatively larger, with an increase in flexural strength of 42% at 120 °C for the 10% ME-100 nanocomposite. The strength with a nanocomposite matrix at 120 °C is similar to the strength with a PA6 matrix at 80 °C, and at 160 °C the strength is even higher than at 120 °C with the unfilled PA6 matrix. Therefore, with this nanocomposite matrix it is possible to increase the useful temperature range for PA6 with 40–50 °C, without changing the processing temperature. A similar positive influence of the nanocomposite matrix was found for the moisture-conditioned samples. At 20 °C the moisture conditioned nanocomposite-fibre composite samples have a flexural strength close to the dry fibre composite with a PA6 matrix, so the nanocomposite matrix can compensate for the loss of strength due to moisture absorption in the PA6 matrix. At combined hot and moist conditions (80 °C, moisture-conditioned) the fibre composite with a 10% ME-100 matrix shows a 27% higher flexural strength than the one with an unfilled PA6 matrix.

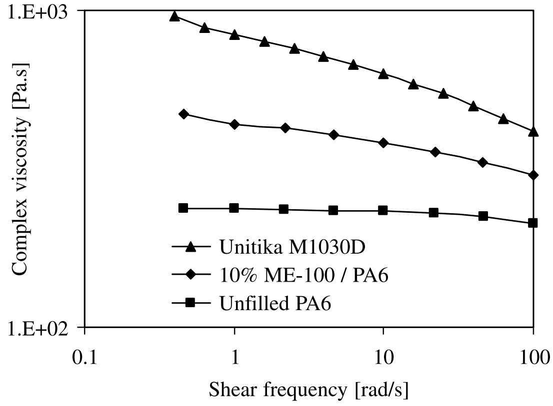

Fig. 9. Viscosity at 240 °C as a function of the shear frequency for the three matrix materials.

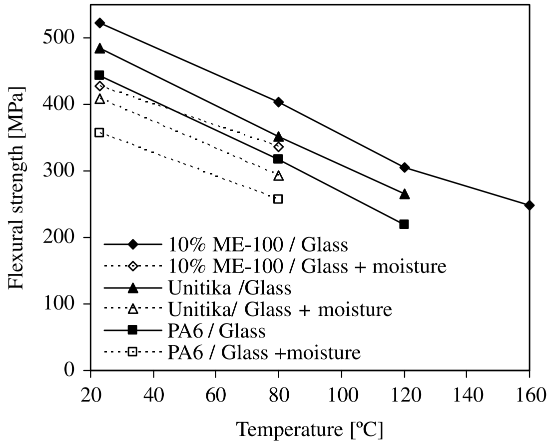

Fig. 10. Flexural strength of glass fibre composites with PA6 and nanocomposite matrix as a function of the temperature (dry and moisture conditioned).

In Fig. 11 the flexural strength of carbon fibre composites as a function of temperature is shown (due to the different materials and production process, these values should not be compared with the values in Fig. 3). In this type of fibre

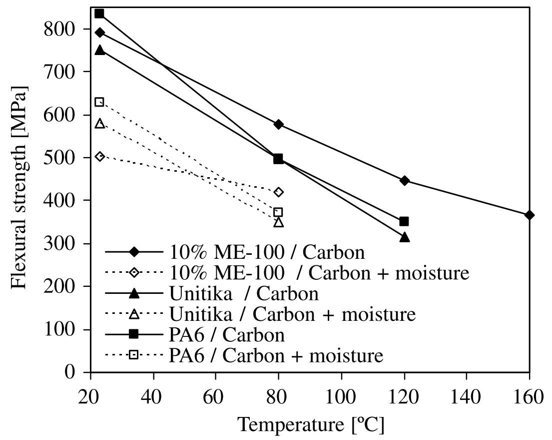

Fig. 11. Flexural strength of carbon fibre composites with PA6 and nanocomposite matrix as a function of the temperature (dry and moisture conditioned).

composite the positive influence of the nanocomposite matrix is not evident at room temperature; at 20 °C the PA6 fibre composite is stronger than with both nanocomposite matrices. However, at elevated temperatures the composite with 10% ME-100 nanocomposite as matrix material has a much higher strength than the one with the unfilled PA6 matrix. For example, at 160 °C the strength of the fibre composite with 10% ME-100 matrix is higher than of the reference material at 120 °C. Remarkably, the fibre composite with the Unitika nanocomposite matrix does not show any improvement in the strength. In moisture-conditioned samples none of the nanocomposites leads to an increased strength at room temperature, and only for the ME-100 composite a small increase is found at 80 °C. It is not clear why the nanocomposite matrix has a better effect on the flexural strength in glass fibre composites than in carbon fibre composites. Based on Figs. 3 and 4, it could be expected that nanocomposites might have an even better effect on the flexural strength of carbon fibre composites, because the influence of a decrease in matrix modulus (due to an increase in temperature) is stronger for carbon fibre composites. However, the sizing on the carbon fibre used in this research has not been specifically developed for use with PA6. Probably the adhesion can still be improved by optimizing the fibre surface treatment. The ME-100 matrix results in a larger increase in strength than Unitika M1030D in the glass fibre composites. In the carbon fibre composites it is the only nanocomposite that has a positive influence on the strength at elevated temperatures. The reason for the better performance of the ME-100 based nanocompsite is probably not a difference in modulus; this is almost identical over the investigated temperature range, as can be seen in Fig. 7. However, what could be the reason behind the better performance of the ME-100 nanocomposite is the difference in the melt viscosity, as shown in Fig. 9. Maybe the higher viscosity of Unitika M1030D leads to a slightly worse fibre wetting at the processing conditions that were used, although no differences could be seen using SEM (Fig. 6).

To investigate how the flexural strength depends on the matrix modulus in these samples, the strength (Figs. 10 and 11) is plotted as a function of the matrix modulus (Fig. 7). In Fig. 12 the results for the dry and moisture conditioned glass fibre composites are shown and in Fig. 13 the same is shown for the carbon fibre composites.

In these figures the points at lower matrix modulus correspond to higher temperatures. All lines through the data series are connected to the point where the modulus = 0 and the strength = 0, because obviously the bending strength approaches zero with a liquid (or no) matrix. In Fig. 12 it can be seen that the data for the glass fibre composites with PA6 matrix all fit reasonably well on one curve, both the dry and the moisture-conditioned samples. The composites with a 10% ME-100 matrix are on the same curve as the PA6 samples for the higher matrix moduli, but at the lower moduli (higher temperatures) the strength is below this curve and, therefore, somewhat lower than could be expected. The glass fibre composites with a Unitika nanocomposite matrix are all on a different curve, and have a lower strength than could be expected based on the matrix modulus. This means that in this case another mechanism is responsible for a decrease in flexural strength, besides the increase caused by the increased matrix modulus. This mechanism is probably the adhesion of the fibres with the matrix. Previous attempts to combine other nanocomposites with fibres often resulted in a strong decrease of the strength, clearly caused by a bad adhesion. In some cases the laminate would even delaminate instead of fail on the compressive side due to the bad adhesion. In the glass fibre composites with the Unitika matrix the adhesion is reasonably good; the increased matrix modulus does indeed increase the strength, but probably the strength could be even higher if the adhesion would be further improved.

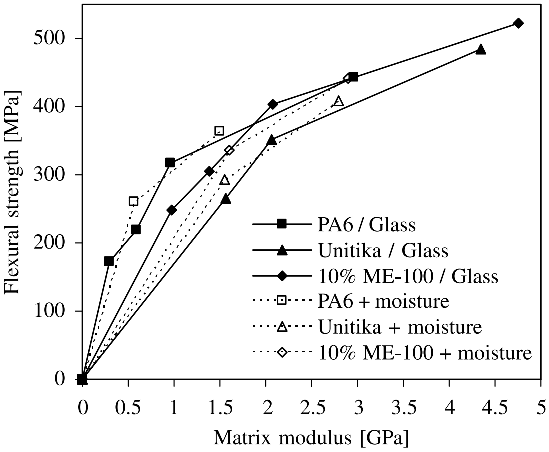

Fig. 12. Flexural strength of glass fibre composites with PA6 and nanocomposite matrix as a function of the matrix modulus (dry and moisture conditioned).

The results for the carbon fibre composites in Fig. 13 are different than for the glass fibre composites: The

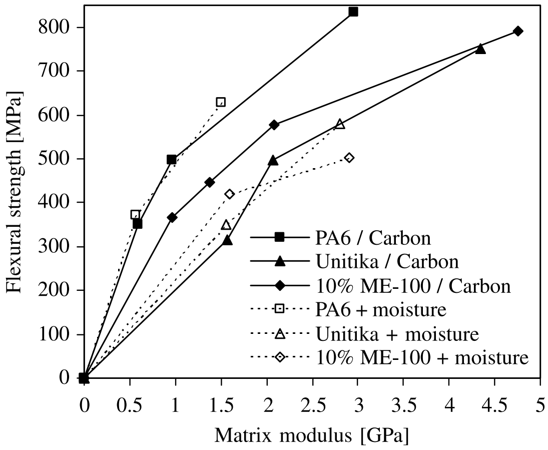

Fig. 13. Flexural strength of carbon fibre composites with PA6 and nanocomposite matrix as a function of the matrix modulus (dry and moisture conditioned).

nanocomposites all are below the points of the unfilled PA6 matrix. In these composites the adhesion between the nanocomposites and the carbon fibres is probably worse than between the unfilled PA6 and the matrix, reducing the potentially positive influence of the increased matrix modulus. The strength versus matrix modulus of the composites with the unfilled PA6 matrix overlaps for dry and moisture conditioned samples, just as for glass fibre composites. For the composite with the Unitika nanocomposite matrix this is also true, although the curve is on a lower level. However, for the composite with the ME-100 matrix this is not the case: The moisture-conditioned samples have a much lower strength than expected, which cannot be explained by the modulus reduction alone. Maybe an additional reduction of the adhesion in the presence of moisture is responsible here. Clearly, more research is necessary on the adhesion between the nanocomposites and the carbon fibres to reach the full potential of the improved matrix properties. However, for the glass fibre composites large increases in flexural strength have been achieved using an optimized matrix material.

4. Conclusions

The concept of combining nanocomposites as matrix material with continuous fibre reinforcement in a new three-phase thermoplastic composite has been shown to be very successful. The main goal of increasing the matrix dominated flexural (and compressive) strength by increasing the matrix modulus has been achieved, with several types of PA6 nanocomposite in combination with glass and carbon fibres.

Based on flexural tests on PA6 based glass and carbon fibre composites over a large temperature range up to near the melting point, it has become clear that for these fibre composites it is important to have a reasonably high matrix modulus: Both glass and carbon composites are very sensitive to a decrease of the matrix modulus below values around 1 GPa. At higher moduli, carbon fibre composites are more sensitive to the matrix modulus than glass fibre composites. While the modulus of unfilled PA6 decreases below the (arbitrary) 1 GPa level just above T_g, the nanocomposites used in this research have moduli that are much higher and stay above the 1 GPa level up to 160 °C, which is more than 80 °C higher than for unfilled PA6. The nanocomposites also show much higher moduli in moisture conditioned samples, and even in moisture conditioned samples tested at 80 °C the modulus is much higher than of the dry unfilled samples, again well above 1 GPa. DMA measurements have shown that the nanocomposites do not show a change of T_g, and that the reduction of the modulus upon absorption of moisture is due to the T_g decrease. T_g decreases with the same amount in the nanocomposites as in the unfilled PA6 upon moisture conditioning.

The nanocomposites used in these continuous fibre composites had to be carefully selected: The flow properties of the nanocomposites often led to difficult fibre bundle impregnation, void formation and reduced adhesion. All these factors led to a reduction of the strength instead of the expected increase. Previous research on the influence of various types of nano-particles on the viscosity, the yield stress and the fibre–matrix adhesion has led to the selection of the two nanocomposites used here [14,15].

The increased modulus of the nanocomposites offers much more support to the fibres at increased temperatures and in moisture conditioned samples, reducing the tendency for buckling and kinking of the fibres in the composite under compression. The flexural strength of the glass fibre composites has been increased by more than 40% at elevated temperatures and the temperature at which the composites strength drops below a certain (arbitrary) value has been increased by 40–50 °C. The results for carbon fibre composites at low temperatures are less impressive, although they also show significant improvements at elevated temperatures, such as a strength at 160 °C that is higher than at 120 °C in the reference material with an unfilled PA6 matrix. However, to reach the full potential of the higher matrix moduli more needs to be understood about the adhesion in this new type of composite, especially in combination with carbon fibres. With additional optimisation of the fibre surface treatment and the composite production process it should be possible to improve the properties further, because the plots of strength versus matrix modulus suggest that higher flexural strengths than measured can be expected.

The advantage of the use of polymer nanocomposites compared to the use of different polymers to improve the high temperature behaviour of fibre composites is that the properties can be improved without any change in the melting temperature and processing conditions. Polymers such as PA6 can be used as matrix material at temperatures up to 50 °C higher at the same composite strength without changes in the impregnation and forming temperature.

The added cost of the nano-filled matrix can be small due to the low amounts of filler necessary for a significant improvement. Another interesting property is that film extrusion (and probably also film blowing) with low MW polymers is much easier with nanocomposites due to the altered melt flow behaviour: A low MW nanocomposite can replace a high MW unfilled PA6 (results are not shown).

The results of the three-phase composite shown in this paper are for PA6 as the matrix material, but the concept can be applied to many different matrix polymers. 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.

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