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A comparison of the temperature dependence of the modulus, yield stress and ductility of nanocomposites based on high and low MW PA6 and PA66

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Abstract

Nanocomposites with both organically modified and unmodified silicate have been prepared by an extrusion process using low and high molecular weight grades of PA6 and a low MW grade of PA66. Mechanical properties have been tested at temperatures ranging from 20 to 120 °C. The modulus increase in all nanocomposites with organically modified nanocomposites is similar: at room temperature an increase in the modulus of approximately 10% for each wt% of silicate is found. PA66 nanocomposites display an identical normalized modulus increase as PA6 nanocomposites, while unmodified silicate nanocomposites show a smaller increase in the modulus. The yield stress also increases with the addition of layered silicate. Low MW PA6 and PA66 nanocomposites show brittle fracture behaviour at room temperature, while high MW PA6 nanocomposites are ductile. With increasing temperature all nanocomposites become ductile at a certain temperature.

Keywords: Nanocomposite; Polyamide; Mechanical properties

1. Introduction

In the last decade many polymer nanocomposites based on exfoliated layered silicates have been developed to improve properties such as modulus, flammability and barrier properties. Compared to traditional polymer composites containing larger particles such as talc or short fibres (glass, carbon or aramid), nanocomposites have the advantage of achieving their optimal properties at relatively low filler content, resulting in a lower density and better surface smoothness and transparency. These improved properties at low filler content are mainly due to the exfoliated nature of the layered silicate filler, resulting in very thin particles with large aspect ratios [1,2].

Nanocomposites based on a polyamide 6 (PA6) matrix containing exfoliated organically modified layered silicate particles have been produced by in situ polymerisation of ε-caprolactam [3–5] and by high shear mixing in the melt in an extrusion process [6–11]. In both processes an organic modification on the silicate layers is necessary to achieve good exfoliation. The organic modification (or surfactant) increases the layer distance and improves the compatibility between the matrix and the silicate platelets, thereby facilitating mixing on a molecular level.

An alternative type of process has recently been reported, in which unmodified layered silicate has been used to reach an adequate level of exfoliation in PA6 [12,13]. In this process water is used to swell the silicate layers and make the inter-gallery accessible for the polymer and thereby improve exfoliation. The possibility to use unmodified silicate is interesting because of the potential reduction of the raw materials cost, the increased thermal stability due to the absence of the thermally unstable surfactants and the

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lower viscosity of this type of nanocomposite due to the reduced degree of exfoliation [14].

In the last years several authors have reported the successful production of polyamide 66 (PA66) nanocomposites [15–19] with a similar extrusion process as used for PA6 nanocomposites.

The main improvement in mechanical properties of nanocomposites relates to the large increase in modulus. An increase in the modulus of approximately 10% per wt% filler has been shown in both in situ polymerized and melt processed PA6 nanocomposites [8]. However, this modulus increase usually levels off above 10 wt% of filler [7,9]. The amount of modulus increase is strongly dependent on the aspect ratio of the reinforcing particles [20], and therefore on the degree of exfoliation. The degree of exfoliation in PA6 nanocomposites depends both on the production method (in situ polymerised or melt processed) and the type and amount of surfactant.

The interaction between the polymer chain and the silicate for the three types of PA66 nanocomposite are schematically shown in Fig. 1. Fig. 1(A) shows the non-modified silicate nanocomposite, Fig. 1(B) shows the melt-exfoliated modified silicate nanocomposite in which the surfactant chains are mixed with the polymer, and Fig. 1(C) shows the in situ polymerised nanocomposite in which the polymer has reacted with the surfactant resulting in ionic bonds with the silicate particles.

In the present study all three types will be investigated. In extrusion processes the degree of exfoliation does not only depend on favourable thermodynamic interactions between the polymer chains and the surfactant, but also on the amount of shear that can be transmitted to the particles [21]. Therefore, intermeshing twin screw extruders are capable of producing a better exfoliation than single screw extruders, and high shear screw designs provide better results than low shear screws [10]. Apart from the type of mixer, also the type of matrix material plays a role in the amount of stress that can be transferred to the platelets. It has been shown that a higher molecular weight of the polymer can result in an improved exfoliation, and therefore higher moduli [22], although the effects on the modulus are not that large. The yield stress of PA6 nanocomposites usually increases upon addition of layered silicate, but at higher silicate content samples often become brittle, resulting in a lower strength at high silicate content [9,23]. The more brittle fracture behaviour of PA6 nanocomposites is evident from the large reduction in elongation at break reported by several authors [9,10,22,24–26]. It has been shown that the elongation at break in nanocomposites depends on the molecular weight of the matrix polymer; a higher MW leads to much higher elongations [22]. It is often reported that impact strength is not much affected by the addition of layered silicate fillers, but the values reported are usually of brittle fractures in all cases, including the unfilled reference polymer [9,27]. In the case of brittle fractures not much influence of the filler can be measured, only at elevated temperatures the PA6 matrix polymer becomes ductile in notched impact tests [8] and can be compared with the nanocomposites. Increasing the test temperatures will eventually lead to ductile fracture behaviour, as was shown for both in situ polymerized and melt processed nanocomposites [8,27,28]. It has been shown that in nanocomposites the T_{bd} increases more or less linearly with increasing silicate content [8].

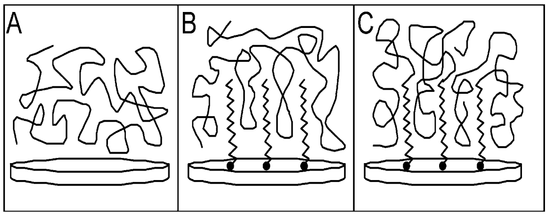

Fig. 1. Schematic representation of the three types of nanocomposite used: (A) non-modified silicate with polymer, (B) modified silicate mixed with polymer (melt-mixed), (C) modified silicate connected with polymer (in situ polymerisation).

The fracture behaviour of polymers depends on many molecular factors such as the chain architecture, the molecular weight and the intermolecular order of the polymer (such as crystallinity), and in addition on test conditions such as test speed, temperature and sample size [29,30]. In composites also stress concentrations, the size and orientation of the particles and the interfacial adhesion play a role. In general the transition from brittle to ductile fracture behaviour is explained by the existence of two different failure mechanisms, one leading to brittle failure and one leading to ductile shear yielding. In this scheme, known as the Ludwig–Davidenkov–Orowan hypothesis [31], the failure mechanism that requires the lowest stress under certain conditions is the one determining the failure mechanism: when the yield stress is lower than the brittle failure stress ductile failure occurs, when the brittle stress is lower brittle failure occurs. Because the brittle failure mechanism is less temperature dependent than the yield stress, which decreases strongly with increasing temperature, a temperature exists above which the failure behaviour becomes ductile. This transition temperature is known as the brittle to ductile transition temperature (T_{bd}). The brittle fracture stress is increased by increasing the molecular weight of the polymer, both for amorphous and for semi-crystalline polymers, which causes a reduction of T_{bd}. The underlying mechanism for this is that higher MW chains can form more intermolecular connections such as entanglements in amorphous polymers and tie-chains in semi-crystalline polymers. These connections between the chains form a network with improved load carrying capabilities, which increases the ductility. The effect of MW is especially strong at MW below 20,000, such as is the case in PA6, at very high MW ($>100{,}000$) the effects are less pronounced [29]. Increasing crystallinity increases the modulus and the yield stress, and, therefore, decreases the ductility and increases T_{bd} [31]. For PA66 it has been shown that reduction of the size of the spherulites increases the modulus and yield stress, while reducing the elongation at break [32]. In (nano)composites the reinforcing particles can influence the fracture behaviour by additional factors such as the introduction of stress concentrations, other deformation mechanisms and by influencing the intermolecular structure.

One important issue with respect to the production of PA66 nanocomposites is the thermal stability of the surfactant molecules. It is known that the most commonly used quaternary ammonium surfactants are not very stable at temperatures above 200 °C [33]. It has been shown that the combination of high processing temperatures in combination with high shear stresses causes even more degradation than at high temperatures without shear. For short processing times the degradation is not much of a problem in the case of PA6 (processed at 240 °C), but at the temperatures required for PA66 melt processing (minimum 270 °C) the problem is much more serious. It has been reported that PA66 nanocomposites cannot be made via the same process and with the same modified silicates [19], while other authors have shown that it is possible, with reasonably good results [15].

In this paper we describe the mechanical properties of various types of polyamide nanocomposite. We compare various concentrations of organically modified silicate in two different MW PA6 matrix materials. In addition, we have prepared nanocomposites with several silicate concentrations in PA66, using the same modified silicate. The two different MW PA6 matrix materials are also used to make a nanocomposite with the same silicate without surfactant, to compare the influence of the surfactant on exfoliation and mechanical properties. All these nanocomposites have been tested over a temperature range varying from 20 to 120 °C, to compare the modulus, yield stress and fracture behaviour. From this data brittle to ductile transitions can be determined and the influence of the matrix polymer and the type of modification can be determined.

2. Experimental

2.1. Material

2.1.1. Polyamide 6, low molecular weight (LMW PA6)

Akulon K222D, injection-moulding grade PA6 from DSM, The Netherlands. $M_n = 16{,}000$, $M_w = 32{,}000$ g/mol, $T_m = 220$ °C.

2.1.2. Polyamide 6, high molecular weight (HMW PA6)

Akulon K136, film/extrusion grade PA6 from DSM, The Netherlands. $M_n = 35{,}600$, $M_w = 71{,}000$ g/mol, $T_m = 220$ °C.

2.1.3. Polyamide 66, low molecular weight (PA66)

Akulon S223D, injection-moulding grade PA66 from DSM, The Netherlands. $M_n = 16{,}000$, $M_w = 32{,}000$ g/mol, $T_m = 260$ °C.

2.1.4. Commercial polyamide 6 nanocomposites

Two commercial PA6 nanocomposites are used (MW unknown). From Ube, Japan, with 2.5% silicate and from Unitika, Japan, with 4.6% silicate. These nanocomposites are made by in situ hydrolytic polymerisation of ε-caprolactam in the presence of swollen organically modified silicates. The organic surfactant is the initiator for polymerisation, so the polymer chains are bound to the surfactant via covalent bonds. Since the surfactants have an ionic bond with the silicate layers, the polymer is ionically bound to the silicate layers, unlike in the melt-processed nanocomposites.

2.1.5. Organically modified layered silicate

Somasif MEE (Synthetic Mica) from Co-op Chemicals, Japan. This is synthetic fluorine mica, covered with a methyl bis-2-hydroxyethyl coco quaternary ammonium surfactant (28.5 wt%).

The manufacturer has added the organic surfactant on the silicate platelets, and the amount of organic surfactant was determined with thermo-gravimetric analysis (TGA) in a Perkin–Elmer TGA-7 Thermal Gravimetric Analyzer at 800 °C for 1 h in air.

2.1.6. Unmodified layered silicate

Somasif ME-100 (Synthetic Mica) from Co-op Chemicals, Japan. This is water-swellable synthetic fluorine mica, which does not contain any organic surfactant. The inorganic part is identical to Somasif MEE.

2.2. Preparation

2.2.1. Extrusion

The nanocomposites with Somasif MEE were prepared by mixing in PA6 and PA66 in a Werner and Pfleiderer ZDS-K28 co-rotating twin-screw extruder. The screw layout was designed to produce high shear stresses, achieved by incorporating several kneading blocks followed by small backflow elements. The modified layered silicate powder was mixed with the polymer granules and fed into the extruder at a constant rate via a Plasticolor 2500 feeding unit. The extruder was operated at a screw speed of 200 RPM and a feeding rate of approximately 3 kg/h.

The temperature in the feeding zone was 150 °C, for PA6 all the other zones where heated to 230 °C and for PA66 all the other zones where heated to 270 °C. Cooling was applied to keep the temperature constant since the high shear forces in the melt can produce too much heat.

First a master batch with a high concentration (11.9 wt% for PA6, 10.3 wt% for PA66, based on the inorganic content of the filler) was made. Other concentrations were made by diluting the master batch with unfilled polymer in a second extrusion step.

The nanocomposites with Somasif ME-100 were 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. 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. Injection moulding

Dumbbell shaped samples according to ISO 527 standards were injection moulded on an Arburg Allrounder 221-55-250 injection-moulding machine. For PA6 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. For PA66 the melting and mixing zones were heated to 275 °C and the nozzle was heated to 290 °C.

2.2.3. Determination of silicate content

Thermo-gravimetric analysis (TGA) measurements were done to determine the exact silicate content in the tested samples after processing. A Perkin–Elmer TGA-7 Thermal Gravimetric Analyzer was used to determine the weight fraction of silicate by heating a sample in air at 800 °C for 1 h. The silicate levels mentioned in this paper are the weight percentages of the inorganic part of the filler as measured with TGA, the weight of the surfactant is not included in this value. The resulting ash had a black colour, which is caused by graphite layers that get formed between well-exfoliated silicate layers. These graphite layers are single layers [34], and, therefore, they cause only a negligible error in the calculated silicate content.

2.2.4. Conditioning

All samples have been tested dry; the injection-moulded samples were dried further in a vacuum oven at 80 °C for at least 48 h before testing.

2.2.5. Measurement of the crystallinity

The level of crystallinity of the samples and the ratio of the two crystal phases, α and γ, was determined with differential scanning calorimetry on a Perkin–Elmer DSC-7. DSC samples of approximately 5 mg were cut from the centre of the tensile test bar. The DSC measurements were performed at a heating rate of 10 °C/min between 25 and 270 °C. The crystallinity was calculated using a heat of fusion of 213 J/g for the gamma crystals, and 243 J/g for the alpha crystals [11,20].

2.2.6. Measurement of the glass transition temperature

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

2.3. Testing of mechanical properties

The samples were tested on a Zwick 1445 tensile tester with a 10 kN force cell, equipped with a climate chamber. For the modulus measurement Zwick clip-on extensometers were used. The test speed was 5 mm/min and the temperature in the climate chamber was varied between 20 and 120 °C. For each temperature and composition five samples were tested to determine the average values.

3. Results and discussion

3.1. Modulus

The modulus of the nanocomposites is plotted versus temperature in Fig. 2. Fig. 2(a) shows the results for low MW PA6, Fig. 2(b) for high MW PA6, Fig. 2(c) for PA66 and Fig. 2(d) for two commercial PA6 nanocomposites. The modulus increases with increasing silicate content and decreases with increasing temperature, as expected. The largest drop in modulus can be seen between 40 and 80 °C, which is the temperature range at which the glass transition temperature (T_g) is crossed. This causes the amorphous part of the polymer to become soft, but it is clear that the nanoparticles are also very effective for increasing the modulus above T_g.

The three different matrix polymers have slightly different moduli and, therefore, the moduli of the nanocomposites have been divided by the matrix modulus to compare the efficiency of reinforcement between the various nanocomposites. This way the normalized modulus ($E_{\text{nanocomposite}}/E_{\text{matrix}}$) is calculated, and the values for 23 °C are shown in Fig. 3 as a function of silicate content. Fig. 3 shows that the modulus increase for the high MW nanocomposites are comparable to the increase for low MW nanocomposites, although previously a higher modulus for higher MW matrix polymers due to higher shear forces during extrusion has been reported [22]. Probably the exfoliation in the low MW nanocomposites was already very efficient due to the high shear screw design in the extruder; therefore, the extra shear due to the higher MW does not improve the exfoliation much. However, the high melt viscosity of the high MW nanocomposites apparently induced some additional degradation due to extra heat created in the extrusion process, which resulted in a stronger discoloration in the high MW nanocomposites.

If the moduli of the PA66 nanocomposites in Fig. 2(c) are compared with the nanocomposites based on the low MW PA6 in Fig. 2(a) (both have comparable MW), it is clear that the PA66 nanocomposites have a slightly higher modulus at all concentrations. The unfilled PA66 has a higher modulus than PA6, and from Fig. 3 it becomes clear that the increase

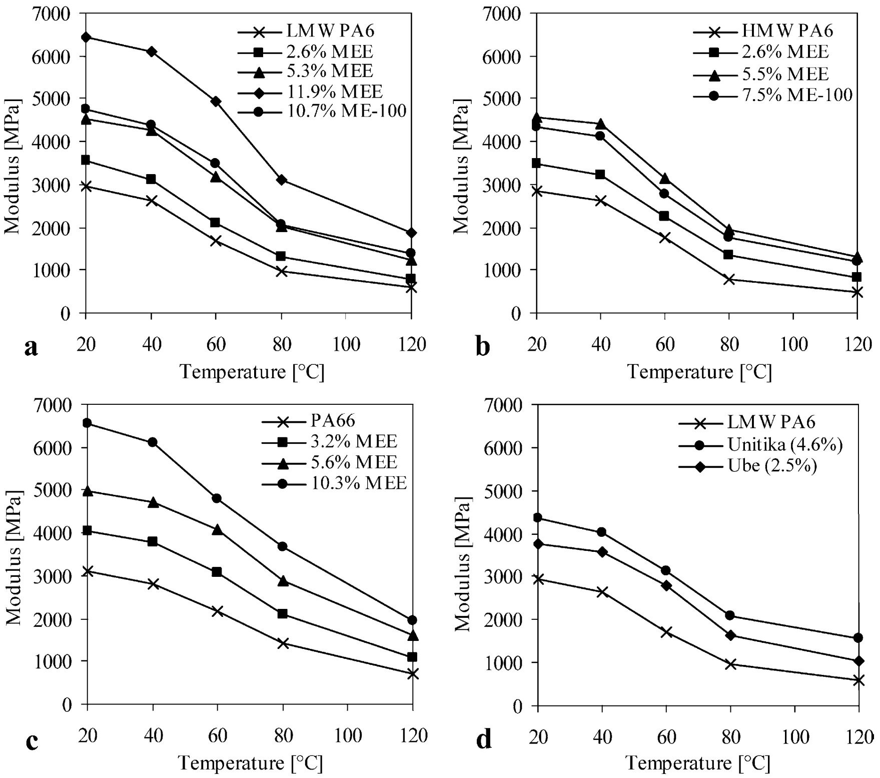

Fig. 2. Young's modulus as a function of temperature, (a) low MW PA6 nanocomposites, (b) high MW PA6 nanocomposites, (c) low MW PA66 nanocomposites, (d) commercial nanocomposites.

in modulus with increasing silicate content is equal to the increase in PA6. The increase in modulus is higher than reported before for PA66 [15,18], while no difference in compatibilizer or mixing procedure compared to PA6 nanocomposites was necessary. Apparently, despite the higher processing temperatures the degradation of the surfactant was not so severe that the degree of exfoliation was reduced. It has been shown previously that increasing the extrusion temperature for PA6 nanocomposites from 240 to 280 °C does not have any significant influence on the mechanical properties [8]. In addition, no more discoloration was seen in our PA66 samples than in the low MW PA6 nanocomposites. These results for PA66 show that this type of organically modified silicate and the same extrusion process can be used just as effectively in nanocomposites based on PA66 as those based on PA6, contrary to previous observations [19].

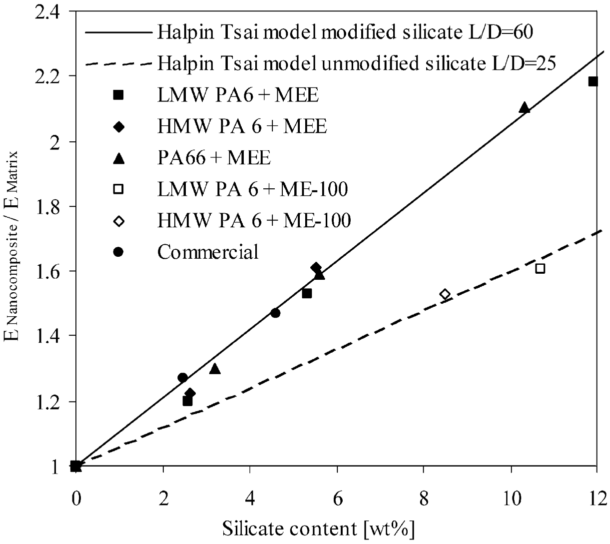

Fig. 3. Normalized modulus as a function of silicate content (20 °C).

The moduli of commercially available in situ polymerized nanocomposites, shown in Fig. 2(d), are comparable with the moduli of the melt-exfoliated nanocomposites with equivalent silicate content. Fig. 3 shows that the normalized modulus of all melt exfoliated nanocomposites with organically modified nanoparticles, whether they are based on low MW PA6, high MW PA6 or PA66, is equal to the modulus increase obtained in the commercially produced in situ polymerized nanocomposites. The increase in modulus in all these materials is approximately 10% per wt% silicate, which is in line with previous results [8].

However, the nanocomposites containing unmodified silicate particles (ME-100) are exceptions to this rule. The 10.7% ME-100 in low MW PA6 has a modulus that is similar to the modulus of 5.3% MEE nanocomposite. The fact that nanocomposites based on unmodified silicate need a higher filler content to reach a similar modulus than with organically modified silicate can be explained by a reduced degree of exfoliation. This can be explained by the reduced thermodynamic driving force for exfoliation due to the absence of the surfactant. On the other hand, the fact that the 10.7% ME-100 nanocomposite has a modulus comparable with a nanocomposite with 5.3% well exfoliated modified particles (MEE), shows that the exfoliation process with water works rather well. In Fig. 3 it can also be seen that the modulus increase with unmodified silicate is at a lower level compared to the increase with modified silicates, the slope is approximately half, i.e. about 5% modulus increase per wt% silicate. In a comparable process to exfoliate unmodified silicate with the help of water in an extrusion process, a modulus increase equal to that of organically modified silicate was reported [13], although the reported value was at a much lower silicate content of 1.6 wt% and it is, therefore, difficult to compare with our results at 10 wt% silicate. The superior modulus increase at low silicate content reported previously [13] could be a result of the longer time available to the silicate to swell in water when clay slurry is used, compared to the process we used, in which the silicate only comes into contact with water in the extruder.

Using the Halpin Tsai composite model [35,36], the effective aspect ratio (*L*/*D*) of the platelets can be estimated [20]. In Fig. 3 two lines are added which are calculated with the Halpin Tsai model, showing a best fit through the collective data of the modified silicate series and the unmodified series. The modulus increase depends on the aspect ratio of the reinforcing particles, and therefore on the degree of exfoliation. The fit for the modified silicate corresponds to an effective aspect ratio of 60, while the fit for unmodified silicate corresponds to an effective aspect ratio of 25. This means that the average stack size of the silicate layers is approximately 2.4 times larger for the unmodified silicate nanocomposites. The reduced exfoliation is in line with expectation due to the lower compatibility between the unmodified nanoparticles and the matrix polymer.

3.2. Yield- or fracture stress

The yield stress of the nanocomposites has been determined, but some nanocomposite samples broke in a brittle way before reaching the yield point; in that case the fracture stress was determined. Fig. 4(a) shows the yield- or fracture stress for low MW PA6, Fig. 4(b) for high MW PA6, Fig. 4(c) for PA66 and Fig. 4(d) for commercial nanocomposites. When the yield stress was not reached, the maximum stress shown in Fig. 4 is the brittle fracture stress. The maximum stresses when samples fractured in a brittle manner are indicated by open symbols and yield stresses are shown by solid symbols.

All unfilled polyamide samples, low and high MW PA6 and PA66, are ductile and show yielding and neck formation. However, the nanocomposites based on low MW PA6 and PA66 are brittle at room temperature, even at the lowest silicate concentrations. With increasing temperature ductile yield behaviour is reached, and for higher silicate concentrations the temperature has to be raised further to reach ductile behaviour.

The use of unmodified silicate (ME-100) results in a yield stress, yield/fracture behaviour and modulus, which is similar to nanocomposites containing approximately half the amount of modified silicate (MEE). The use of higher MW PA6 for the melt processing has a very positive effect on the fracture behaviour, while it does not have much effect on the modulus as was shown in Fig. 3. Nanocomposites based on high MW PA6 are ductile at all temperatures, even at room temperature. However, concentrations above 5.5% silicate were not investigated because of the extremely high melt viscosity at higher loadings. The nanocomposite based on ME-100 was not ductile at room temperature, but only at 60 °C, which is higher than expected based on the results for low MW PA6. A reason for this more brittle behaviour could be a decrease in MW due to the extrusion process in the presence of water.

The PA66 nanocomposites showed a similar trend as the low MW PA6 nanocomposites, the yield point was not reached at room temperature, but at elevated temperatures the samples became ductile.

In the high MW PA6 series and at higher temperatures for the other matrix polymers the influence of the silicate content on the yield stress can be seen clearly. The nanocomposites show an increase in yield stress, approximately 10% at 2.6% silicate and 20% at 5.5% silicate, which is a much smaller increase than the increase in modulus.

3.3. Elongation at break

The elongation at break of the nanocomposites is shown in Fig. 5(a) shows the elongation for low MW PA6, Fig. 5(b) for high MW PA6, Fig. 5(c) for PA66 and Fig. 5(d) for commercial nanocomposites. The displacement of the clamps that could be reached in the tests was limited by the size of the climate chamber. Therefore, in the case of fully ductile samples, the tests were stopped at 50% strain, which in that case is shown in Fig. 5 as the maximum strain. The samples would probably reach a much higher strain than 50% if not limited by the test equipment. In each graph in Fig. 5 a line is drawn at 7.5% strain, which is approximately the borderline between brittle and ductile behaviour. Samples that break below this value are brittle, samples that break around this value are breaking just at or around the yield point, and samples that break at much higher values show yielding and neck formation.

It can be seen in Fig. 5 that all unfilled samples are ductile, although the PA66 samples show a much smaller elongation; at room temperature PA66 samples break just after reaching the yield point, before a neck could be formed. The nanocomposites show a sharp transition from a low elongation at break to a high elongation, which is known as the brittle to ductile transition. When the brittle to ductile transition has been passed, all samples, including the

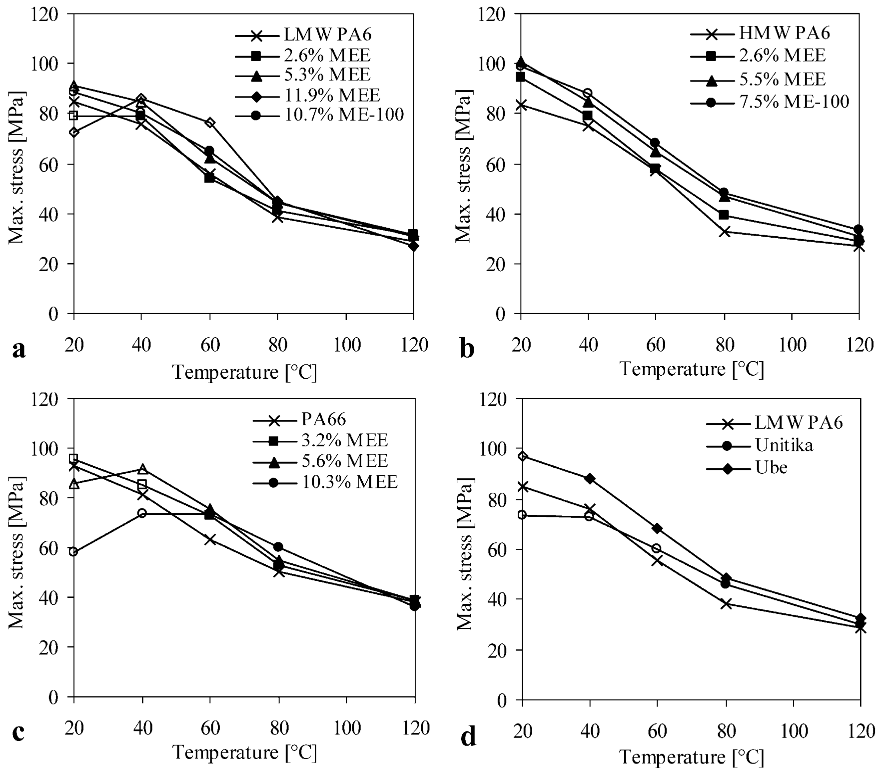

Fig. 4. Maximum stress as a function of temperature, (a) low MW PA6 nanocomposites, (b) high MW PA6 nanocomposites, (c) low MW PA66 nanocomposites, (d) commercial nanocomposites. Open symbols: brittle failure stress, solid symbols: yield stress.

nanocomposites with the highest silicate concentrations, can form a neck that can propagate trough the entire sample to reach high elongations. The two commercially available nanocomposites (Fig. 5(d)) show the same transition behaviour, although the highest concentration from Unitika is brittle up to quite high temperatures; only at 80 °C it shows neck-formation and high elongations.

3.4. Glass transition temperature and crystallinity

The dynamic loss modulus was measured for the low MW PA6 MEE nanocomposites to see if the silicate layers influence the glass transition temperature. In Fig. 6 the loss modulus curves are shown, and from the position of the peak maximum it is clear that T_g is not significantly changed by the presence of the silicate layers. However, the loss peaks show a broadening with increasing silicate content at temperatures above T_g.

In Fig. 7 the crystallinity of the PA6 matrix in the nanocomposites is plotted as a function of the silicate content. It is clear that the crystallinity is hardly changed by the addition of the silicate in these samples, and it can therefore be concluded that the influence of the crystallinity on the mechanical properties of the nanocomposites is probably of minor importance.

3.5. Brittle to ductile transition temperatures

The low MW nanocomposite PA6 and PA66 samples for each silicate content show a transition from brittle to ductile fracture behaviour upon increasing temperature as is clear from Fig. 5. The high MW samples are ductile at all test temperatures, so for this series no transition was determined. Fig. 8 shows the temperatures at which the transition from brittle to ductile fracture behaviour takes place, known as the brittle to ductile transition temperature (T_{bd}), as a function of silicate content. The T_{bd} for PA66 nanocomposites is approximately 10 °C higher than T_{bd} of PA6, and both series show approximately the same increase in the T_{bd} with increasing silicate content. The T_{bd} increases roughly with 3 °C with a 1 wt% increase in the silicate content, which confirms the trend that was found for melt compounded PA6 nanocomposites in Izod impact tests [8].

The commercial nanocomposites show a somewhat unexpected behaviour: the nanocomposite with the highest silicate content (Unitika) has an unusually high T_{bd} for the amount of silicate it contains, while the nanocomposite with the lowest amount of silicate (Ube) has a lower T_{bd} than the melt processed low MW samples. Because the commercial nanocomposites are from different manufacturers and their MW and particle size might vary, it is difficult to determine the precise reason for these differences.

At first sight it seems interesting that the brittle to ductile

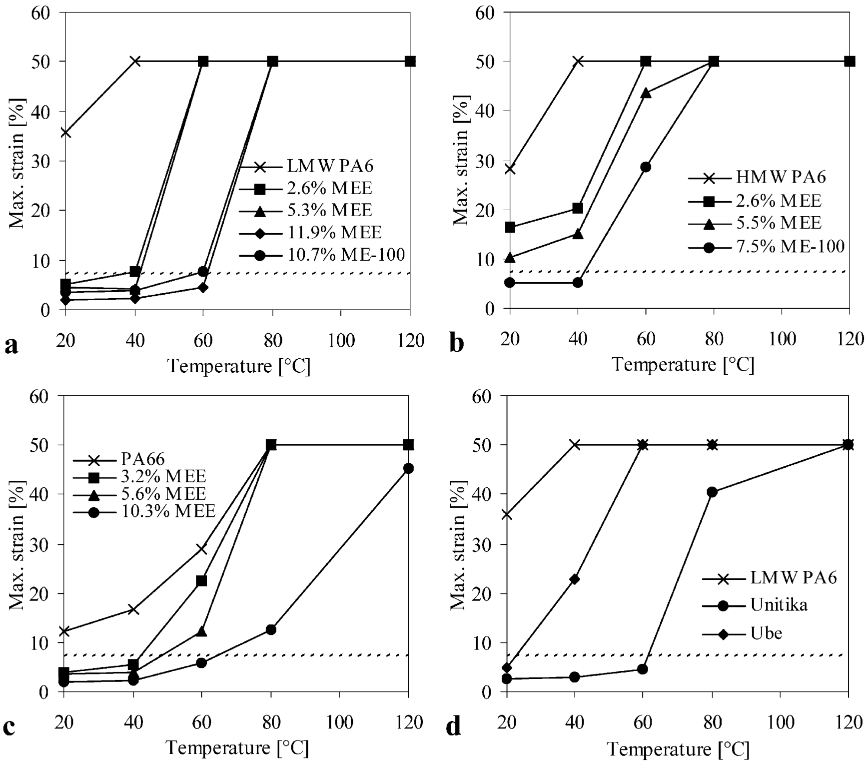

Fig. 5. Maximum strain as a function of temperature, (a) low MW PA6 nanocomposites, (b) high MW PA6 nanocomposites, (c) low MW PA66 nanocomposites, (d) commercial nanocomposites (tests were stopped at a maximum of 50% strain).

transition occurs around the glass transition temperature of the matrix polymer, which is around 55 °C for PA6 and around 60 °C for PA66. However, the change in fracture behaviour around the T_{bd} cannot be simply attributed to the extra mobility associated with the glass transition phenomenon. Evidence for this can be found in the fact the nanocomposite with 11.9% silicate in low MW PA6 is still completely brittle above T_g of PA6, while nanocomposites based on high MW PA6 are already ductile at room temperature up to 5.5% silicate. However, the loss moduli curves in Fig. 6 suggest that, although the main T_g peak is not changed in nanocomposites, a part of the polymer might have a higher T_g due to the interaction with the particle.

The MW of the matrix polymer is very important for the yield or fracture behaviour, as is clear from the differences in maximum elongation in Fig. 5(a) and (b). It was shown previously that a higher MW of the matrix polymer increases the elongation at break and our results confirm this [22].

Fracture behaviour is dependent on many sample and test parameters, and it is, therefore, difficult to determine the exact reason why the fracture behaviour of nanocomposites differs from unfilled polymers on the basis of these results. However, a few possible causes for the decreased ductility and increased T_{bd} in nanocomposites can be suggested:

- As has been shown in Section 3.2 (Fig. 4), the yield stress increases with the addition of silicate and decreases with increasing temperature. This means that higher temperatures are necessary to reduce the yield stress of a

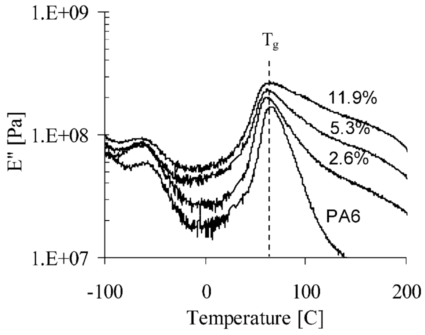

Fig. 6. Loss modulus as function of T for low MW PA6/MEE nanocomposites.

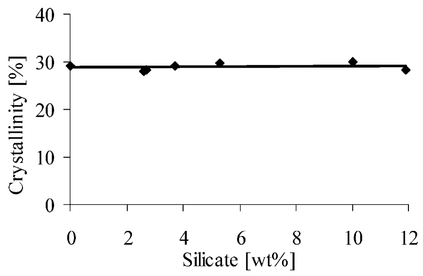

Fig. 7. Crystallinity as a function of silicate content for low MW PA6/MEE nanocomposites.

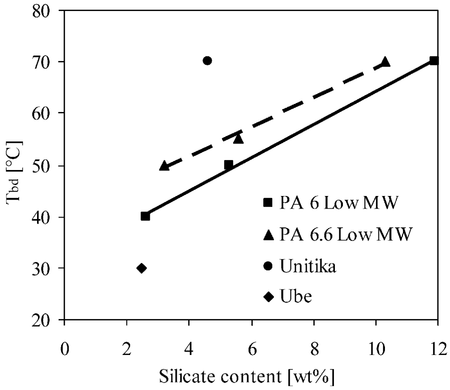

Fig. 8. Brittle to ductile transition temperature (T_{bd}) in the tensile tests as function of silicate content.

nanocomposite sample below the brittle failure stress, which can explain the higher T_{bd} in line with the Ludwig–Davidenkov–Orowan hypothesis [31].

- In general higher MW increases the ductility, and from our results it is clear that this is valid for nanocomposite too. A reduction of the MW causes a large reduction in ductility, and it has been reported that exfoliated silicate catalyses the reduction of the MW in extrusion processes [37]. Therefore, a reduction in MW caused by the silicate layers during processing could have an effect on the ductility and T_{bd}.
- A strong interaction of the polar PA6 chains with the charged silicate layers can exist; therefore the silicate layers could be considered crosslinking points where many polymer chains are connected. These physical crosslinks could significantly reduce the flow possibilities of the polymer in the nanocomposites.
- The loss modulus peak from the dynamic mechanical measurements, see Fig. 6, shows a broadening at higher silicate content. This could indicate that a fraction of the polymer chains only becomes mobile at temperatures above the bulk T_g, which could reduce the deformation possibilities.
- The large amount of impenetrable silicate layers in the material could reduce the amount of tie-chains between crystalline areas, which reduces the possibilities for stress transfer through the sample and leads to more brittle fracture behaviour. In addition, the silicate sheets could reduce the spherulite size, which has been shown to lead to a reduction in elongation at break in PA66 [32].

4. Conclusions

Nanocomposites with different concentrations of organically modified silicate based on two different molecular weight grades of PA6 were prepared by mixing in the melt in a twin-screw extruder. The high MW nanocomposites could not be successfully prepared at concentrations above 5.5 wt% because of the extremely high melt viscosity at the processing temperature. With the same process and the same organically modified silicate a series of nanocomposites based on PA66 was successfully prepared; the only necessary difference was the higher processing temperature. In addition, nanocomposites were prepared from unmodified silicate with a water-assisted extrusion process, both with high and low MW PA6. The samples were tested at temperatures ranging from 20 to 120 °C. The modulus increase is in all nanocomposites with organically modified nanocomposites similar: at room temperature an increase in the modulus of approximately 10% for each wt% of silicate is found. This is equal to the increase in modulus achieved in commercially available nanocomposites (based on an in situ polymerization process leading to nearly perfect exfoliation) and to previously reported results [8].

It is a remarkable result that the PA66 nanocomposites produced in this way have an identical (normalized) modulus increase as PA6 nanocomposites, since results reported so far have shown a much lower increase [15,19] or even required a different organic modification [19]. The unmodified silicate nanocomposites show a smaller increase in the modulus, approximately equal to half the amount of modified silicate.

The yield stress increases also with the addition of layered silicate, but to a smaller extent than the modulus. Low MW PA6 and PA66 nanocomposites show very brittle fracture behaviour at room temperature, while high MW PA6 nanocomposites are ductile. Commercial nanocomposites are brittle too, so the ionic bond between the polymer and the silicate in these in situ polymerized nanocomposites does not seem to influence the ductility. With increasing temperature all the nanocomposites become ductile at a certain temperature. The temperature at which this transition occurs defines the T_{bd}, which increases with increasing silicate content by approximately 3 °C per 1 wt% silicate, both for low MW PA6 and PA66.

The improved fracture behaviour of high MW nanocomposites seems to be an interesting property, but the downside is a big reduction in processability due to the very high viscosity caused by the high polymer viscosity in combination with the large surface area of the exfoliated silicate platelets. The use of unmodified silicate can be interesting due to the lower price of the reinforcing material, but the reinforcing effect is not as effective as the modified silicate.

In all tested properties the melt-mixed nanocomposites are approximately equal to in situ polymerised nanocomposites.

Our results show that PA66 nanocomposites can be processed in the same way as PA6 nanocomposites; the high processing temperatures do not seem to be a problem for the modified silicate. The higher melting point could be an advantage in some cases, and the modulus has been shown to be even higher that that of PA6 based nanocomposites due to the slightly higher matrix modulus. The reduction of the modulus at temperatures above T_g is almost equal to that in PA6 nanocomposites, because T_g of PA66 is not much higher and the ductility is slightly lower than that of PA6 nanocomposites. For the molecular weight of the matrix polymer a compromise has to be made between processability and mechanical properties, as is the case for unfilled polymers.

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