Masterbatch Production of Polyamide 6-Clay Compounds via Continuous *In Situ* Polymerization from Caprolactam and Layered Silicates

Bernd Rothe, Eike Kluenker, Walter Michaeli

Institute of Plastics Processing (IKV), RWTH Aachen University, Seffenter Weg 201, 52074 Aachen, Germany

ABSTRACT: Mechanical properties of thermoplastic polymers can be improved by incorporation of nanoscaled layered silicates. To achieve a significant improvement, the silicates have to be well exfoliated within the polymer matrix. However, it is not always possible to produce exfoliated nanocompounds with the standard procedure of melt compounding. As an alternative to melt compounding, an *in situ* process for the production of polyamide 6-nanocompounds is investigated. During the *in situ* production, the layered silicates are dispersed in the monomer caprolactam prior to the step of polymerization in a twin-screw extruder, leading to an intercalation of the silicate filler. The production of a polyamide compound containing 0, 2, and 4 wt % nanoscaled silicates was successful. Young's modulus was increased by ~ 30–60%. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 571–579, 2012

Key words: anionic polymerization; nanocomposites; clay; polyamides; reactive extrusion; caprolactam; masterbatch; dispersions; mechanical properties

INTRODUCTION

Polymers filled with nanoparticles are of major interest in research due to the potential of nanoparticles to enhance mechanical, thermal, and barrier properties compared to standard fillers.[1–7] Commonly used nanoparticles are modified natural products like clay or produced by synthesis, that is, carbon nanotubes.[8–11] Due to the high availability of clay, especially montmorillonite is often used as a nanofiller for polymers. Montmorillonite is a member of the smectite category with a 2 : 1 structure consisting of two tetrahedral layers which enclose one octahedral layer. The primary montmorillonite sheets feature a thickness of 1 nm, a width of 50–500 nm, and a length of 200–800 nm. Due to its sheet like geometry, the montmorillonite has a specific surface area of ~ 800–1400 m^2/g. The high specific surface area provides a good interaction between polymer and montmorillonite and therefore enables the optimization of the polymer properties. The optimization thereby bases upon montmorillonite sheets completely separated and well dispersed in the polymer matrix, which is called "exfoliation." Several studies focus on optimal nanocomposite properties based on exfoliation of the montmorillonite in the polymer.

Multiple strategies were investigated to improve the dispersion of the montmorillonite and to achieve exfoliation. A chemical modification of the montmorillonite is important to improve the fillers' compatibility to the polymer in the first place. Therefore, sodium ions and neutral organic molecules, which are positioned in the interlayer space between the unmodified montmorillonite sheets, are replaced with larger ions to also expand the interlayer spacing. Ternary or quaternary ammonium ions are used as spacing agents. Investigations on the modification of the interlayer space in the clay and special compatibilizing agents were performed by Modesti et al. and Garcia-Lopez et al.[12,13] Several studies also discussed different ways of nanocomposite production including melt intercalation, exfoliation adsorption, or *in situ* polymerization.[14–17] Melt intercalation as well as exfoliation adsorption can be performed on existing equipment with a process adapted to nanocomposite production. The definition of a solvent, which has no significant influence on the polymer and which can be easily removed from the polymer in the step of extrusion, thereby is a major challenge of exfoliation adsorption. *In situ* polymerization on the other hand needs special equipment and can only be performed with certain polymers. As a major advantage, *in situ* polymerization provides a good exfoliation of the

TABLE I
Production Processes for Polyamide 6

Hydrolytic polymerization	Anionic polymerization
Step-growth reaction	Chain reaction
Water and CA as educts	Activator, initiator and CA as educts
8–10 h	1–5 min
Discontinuous process (batch wise)	Continuous process
T = 240–300°C	T < 200°C
High amount of residual monomer	Low amount of residual monomer
	Precise feeding necessary
Approx. 98% of the market	Cast polyamide and other specialities

montmorillonite sheets due to an intercalation of the monomer in the nanoclay interlayers.[18] A process scale-up to large production scale as well as to assure a high reproducibility furthermore is a challenge to all mentioned ways of nanocomposite production.

Present studies in the field of *in situ* polymerization of polyamide 6 (PA 6) nanocompounds focus on the synthesis route of hydrolytic polymerization. Hydrolytic polymerization is performed discontinuously in a stirred tank with a reaction time of between 20 and 48 h.[19] The process has reached industrial scale and different companies produce PA 6 nanoclay compounds via this synthesis route.

An alternative to the hydrolytic polymerization is the activated anionic polymerization.[19–22] This synthesis is commonly used in a discontinuous casting process to produce large parts, that is, wind turbine blades for wind power parks. Table I shows a comparison of the hydrolytic and anionic polymerization reaction. A continuous activated anionic polymerization of polyamide 6 can be achieved by the use of a twin-screw extruder as a chemical reactor. Performing a chemical reaction in a twin-screw extruder is then called reactive extrusion.[23–26]

Reactive extrusion enables to directly produce PA 6 profiles from the monomer.[23,24] The existing knowledge at the Institute of Plastics Processing at RWTH Aachen University, Germany, gives a good opportunity to analyze the production of PA 6 nanocompounds via *in situ* polymerization.

In this article, a continuous laboratory scale production of a polyamide 6 nanocomposite is presented. To enable an easy further processing a masterbatch (MB) with 15 wt % of montmorillonite, which can easily be diluted to the desired final montmorillonite concentration was produced. *In situ* polymerization with different montmorillonite addition strategies was analyzed and results compared to a standard melt intercalation process.

MATERIALS

The ε-caprolactam type AP-caprolactam (CA) is supplied by L. Brüggemann KG (Heilbronn, Germany). AP-CA provides a maximum moisture of 0.01 wt % and is specially designed for the anionic polymerization (AP).

The reaction system, activator "Aktivator B" and initiator "Katalysator M," is also supplied by L. Brüggemann KG (Heilbronn, Germany). As the activator-content determines the length of the polymer chains and the molecular weight, its amount is kept constant to 2 wt % on the total mass. The initiator concentration depends on the processing and the amount of montmorillonite. Due to the moisture in the montmorillonite and the moisture sensitivity of the initiator, an initiator excess needs to be added to prevent a deactivation of the whole reaction system. The concentrations for the initiator regarding the clay concentrations are listed in Table II.

The clay used in this study, Nanofil SE 3010, is supplied by Rockwood Clay Additives GmbH (Moosburg, Germany). It consists of organomodified montmorillonite specially designed for an incorporation into a polyamide matrix. The interlayer ions are replaced by quaternary alkylammonium salts. Interlayer spacing therefore is increased to 2 nm.

The nanoclay product consists of ∼ 55 wt % of raw clay as measured by thermogravimetric analysis. The coating represents the remaining 45 wt % in the nanoclay product from Rockwood. The bulk density is 450 kg/m³, which is very low compared to the density of 1700–2700 kg/m³ for standard uncoated montmorillonite. The median particle size of the modified clay is less than 10 μm. This shows that the clay is not delivered as a nanoproduct and the clay agglomerates need to be broken down to nanoparticles. The clay has yet no special surface modification to enhance the chemical bond between clay and CA, and it stays inert during the chemical reaction of the polyamide.

EXPERIMENTAL

The process set-up used for reactive extrusion is shown in Figure 1. The monomer (ε-CA) is molten and mixed with activator or initiator in heated

TABLE II
Nanoclay and Initiator Concentration

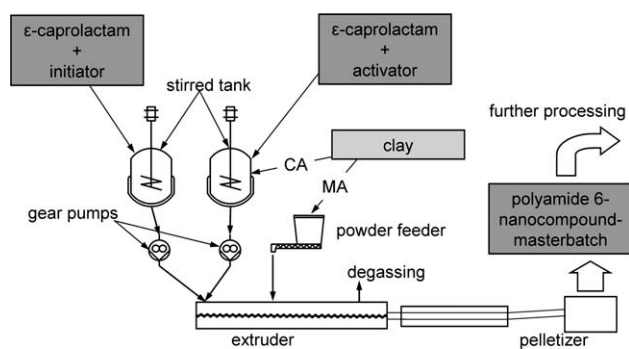| Processing	Unfilled PA	Clay addition to the CA	Clay addition to the polymer melt
Nanoclay concentration [wt %]	0	15	15
Initiator concentration [wt %]	3	11	3

Figure 1 Process set-up for the reactive extrusion of PA 6 nanocomposites.

stirred tanks. The activator and initiator need to be separately molten to prevent a start of the polymerization reaction. The nanoclay is added to the activator tank to prevent a reaction of initiator and clay due to moisture, which may occur and deactivate the reaction system. Two different strategies for adding clay to the polymer system were analyzed. The first possibility is the addition of clay to the CA and activator, CA addition, directly into the stirred tank. The other possibility is to add the clay into the polymer melt, melt addition, (MA) during extrusion after the occurrence of the polymerization reaction. As a comparison to the latter strategy, a standard melt intercalation process is performed.

For the CA, the montmorillonite is predried in a vacuum oven for a minimum of 12 h at 80°C and 200 mbar to prevent the deactivation of the initiator caused by residual moisture in the clay. For the MA, the predried clay and an unconditioned montmorillonite are used.

For the CA, the clay is fed in the oil-tempered stirred tank, which temperature is set at 90°C to assure a liquid CA. The mixture is stirred for a minimum of 45 min to allow the swelling and intercalation of the clay in the CA. After the swelling time, the reaction system is added (activator and initiator) and mixed for 5 min.

At the end of the mixing step in the stirred tanks, the reaction system is introduced into the twin screw extruder by heated gear pumps. The gear pumps are heated to 110°C and feed the educts into the extruder volumetrically. All components of the reaction system are then mixed in the extruder and the polymerization reaction starts. The barrel temperature of the polymerization zone is set to 180°C, whereas the temperature of the subsequent functional zones is set to 220°C. Finally, the polymer strand is formed via a single strand die, cooled in a water bath, and pelletized.

The barrel and screw configuration (Fig. 2) needs to fulfill different tasks, which can be summarized to feeding, mixing, reacting, degassing, and pressure

build-up to overflow the die. Feeding, mixing, and reacting take place in the polymerization zone of the extruder. It mostly consists of conveying screw elements. Conveying screw elements allow a fair mixing and a sufficient residence time for the polymerization reaction. Mixing screw elements directly positioned after the educt inlet in the extruder provide a mixing of activator and initiator to start the reaction. To increase the residence time in the polymerization zone, the pitch of the conveying screw elements needs to be as small as possible. Two counter conveying screw elements are used to separate the polymerization zone from the functional zones. The counter conveying screw elements are completely filled with high-viscous polymer and separate the liquid reacting phase from the higher viscous polymer phase. After the polymerization zone, neutral kneading blocks or left-handed elements separate all subsequent processing zones from each other. The first mixing zone is designed for the incorporation of the clay in the MA process. The degassing zone is used for atmospherical degassing in both processes, MA and CA, followed by an output zone.

As extruder a corotating, intermeshing twin-screw extruders, type ZSK 26 Mc of Coperion GmbH (Stuttgart, Germany) is used. The L/D ratio is 54 D. Throughput for the reactive trials is set at 10 kg/h with a screw speed of 350 revolutions per minute.

For the production of the reference material, the screw and barrel configuration (Fig. 3) is adapted from the information of the clay supplier.[27] For the MB production via melt intercalation, a polyamide from BASF SE (Ludwigshafen, Germany) type Ultramid B40 is used.

The throughput is set at 15 kg/h with a screw speed of 500 rpm to meet to the specifications of the clay supplier. After pelletizing, the material is washed six times in boiling water at 95°C to extract the residual monomer. The materials are then dried for a minimum of 12 h at 80°C before being injection molded to test specimens for tensile testing. For the dilution of the MB in injection, molding the same
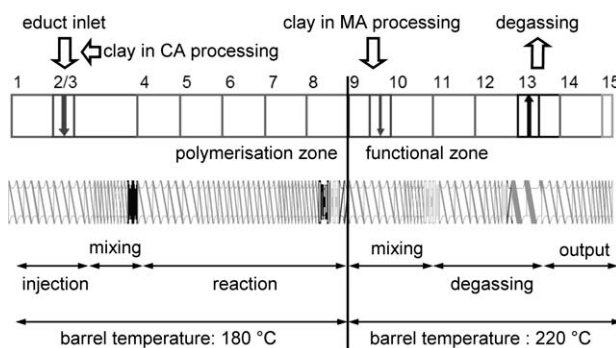

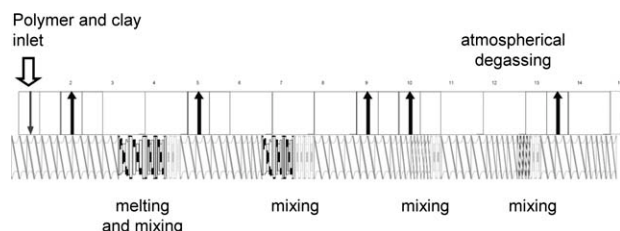**Figure 2** Barrel and screw set-up.

Figure 3 Barrel and screw set-up for the production of the reference MB.

polyamide type Ultramid B40 from BASF (SE, Ludwigshafen, Germany) is used. Injection molding trials are carried out on an Arburg Allrounder 320 S 500–150 made by Arburg GmbH + Co. KG (Loßburg, Germany). During the injection molding, all parameters are kept constant.

Tensile tests according to DIN EN ISO 527-1 similar to ASTM D 638 are performed on a Z100 made by Zwick GmbH and Co. KG (Ulm, Germany). A minimum of 6 tensile bars was tested for each processing point. The ultra microtome sections were done with an Ultracut E from the company Reichert-Jung (Nußloch, Germany). The transmission electron microscopy pictures were taken with an EM 900 from Carl-Zeiss AG (Oberkochen, Germany) with a acceleration speed of 80 kV.

RESULTS AND DISCUSSION

Table III shows a comparison of the standard MB processing and the reactive process in means of energy input.

$$\text{SEI} = \frac{U_{act}}{U_{max}} \times \frac{\text{torque}_{act}}{100} \times \frac{P_{max}}{\dot{m}}$$

U = screw speed
P = power of the extruder
m = through-put

The specific energy input (SEI) can be calculated from the power of the extruder, the screw speed and the torque that is generated during the process. As in a standard process, the polymer has to be molten in the first place and the SEI is more than two times compared to the reactive extrusion process used in

TABLE III
Comparison of the Specific Energy Input (SEI)

Parameters and process	Standard master batch production with hydrolytic PA6	Reactive extrusion for the master batch production (CA and MA)
Screw speed (min^{-1})	500	350
Through-put (kg/h)	15	10
Torque (%)	72	32
SEI (kWh/kg)	0.373	0.174

this article. Therefore, the reactive process is more energy-efficient then the standard process. The energy needed to melt the CA in the stirred tanks is insignificantly small compared to the power needed for the extruder. The total energy necessary for a clay MB production a clay MB using the reactive processing is considerably lower as the standard two-step process. In addition, due to its modularity it is also more flexible.

The mechanical properties of the different MBs are compared concerning Young's modulus and maximum tensile strength. The results of Young's modulus are shown in Figure 4.

Three different MBs with different processing conditions are compared. The first MB is produced with the standard processing based on a hydrolytic polyamide and processing guidelines of the clay supplier. The two other MBs are produced by reactive extrusion and therefore consist of an anionic polyamide (REX PA) as basic material. The difference for both anionic MBs (REX MB) is the addition of the clay either in the CA or in the polymer melts after the reaction (MA). For comparison purpose, Young's modulus of the unfilled polyamides is also listed in the table. The hydrolytic Ultramid B40 has a modulus of 2650 MPa and the anionic polyamide (REX PA) gains a modulus of 2950 MPa. The dilution of the standard MB achieves the lowest modulus with less then 3000 MPa for 2 wt % and 3150 MPa for 4 wt % clay loading. The highest moduli are reached with the dilution of the REX MB with clay addition into the polymer melt (MA). The composite with 2 wt % clay has a Young's modulus above 3200 MPa. A loading of 4 wt % clay shows values of above 3400 MPa. The *in situ* polymerized MB with clay addition into the CA achieves similar values for 2 wt % clay compared to the dilutions of the standard MB with a value of ∼ 3000 MPa.

For the dilution to 4 wt % clay a value of 3300 MPa is reached. The comparison of the moduli of the pure MBs at 15 wt % clay loading without any dilution shows the highest value of 3800 MPa for the MB based on Ultramid B40 with the standard processing. The MB processed by reactive extrusion and melt addition
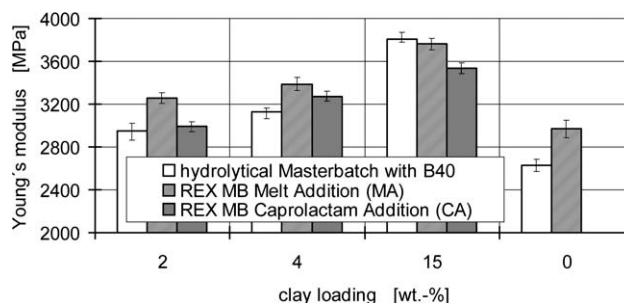

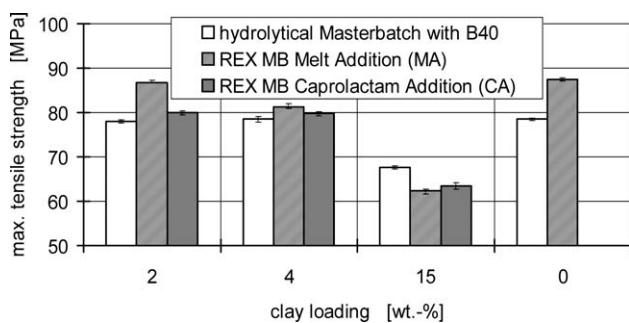**Figure 4** Dependence of the processing of the MB on Young's modulus.

Figure 5 Dependence of the processing of the MB on the maximum tensile strength.

has a comparable value of $\sim$ 3750 MPa. The MB processed by reactive extrusion and CA addition has a Young's modulus of 3550 MPa due to the high amount of initiator, which has a softening effect on the material.

In general, the dilution of all MBs into Ultramid B40 enables an increase of Young's modulus compared to unfilled Ultramid B40. For a clay loading of 2 wt %, Young's modulus can be improved to 13–25%, whereas a loading of 4 wt % leads to an increase of 20–32%. The MBs produced by reactive extrusion reach higher moduli then the MBs produced with Ultramid B40 in melt intercalation process. This is due to the set-up and processing of reactive extrusion and due to a low viscosity in the extruder. The difference between those MBs produced by reactive extrusion is due to the high amount of initiator necessary for the polymerization reaction. The maximum tensile strength of the different dilutions, MBs, and pure materials is shown in Figure 5.

The effect of the different production strategies on the maximum tensile strength is similar to the effect on the Young's modulus. The highest maximum tensile strength of 87 MPa is found for pure anionic polyamide (REX PA), whereas pure Ultramid B40 features strength of 78 MPa. All other materials except the dilution of REX MB by melt addition at low clay loading show smaller values compared to
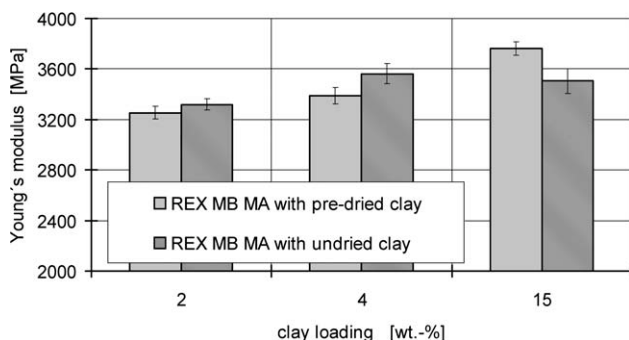
pure REX PA. An improvement of tensile strength compared to the tensile strength of the dilution matrix used (Ultramid B40) to the clay is only reached by the addition of REX MB to total clay loadings of 2 and 4 wt %. The composites with dilutions of the standard MB and all the pure MBs become more brittle due to the clay addition.

The effect of predrying the clay on mechanical properties is investigated by comparing to undried clay added to the system. Both trials were performed using the reactive MB processing and the clay addition to the polymer melts (REX MB MA). The Young's modulus depending on the predrying is shown in Figure 6.

The composites produced with MB using undried clay have moduli of 3300 MPa for 2 wt % clay loading and about 3600 MPa for 4 wt % clay. In comparison, the dilution of MB with predried clay enables a slightly smaller modulus at 2 wt % clay loading, whereas Young's modulus shows a significantly smaller value at 4 wt % clay loading of 3400 MPa. In contrary to the dilutions, the pure MB with predried clay reaches a higher value of 3800 MPa compared to 3500 MPa for the MB with undried clay. The higher humidity in the undried clay causes a loss in the modulus due to a degradation of the polyamide chains. In contrast, better clay dispersion in the diluted MB caused by undried clay leads to an increase of modulus.

An analysis of the morphology of both MBs is necessary to exactly identify the effect causing the increase of modulus. For the MB dilutions, a predrying of the clay does not have a positive effect on the Young's modulus. The comparison of the effect of predrying on the maximum tensile strength is illustrated in Figure 7.

At 2 wt % clay loading drying conditions of clay do not show a significant effect on maximum tensile strength, as both samples reach values of about 87 MPa. At a clay-loading of 4 wt % an effect of the drying conditions is visible. The dilution of MB with undried clay reaches a maximum tensile strength of 84 MPa compared to 81 MPa for the dilution of MB
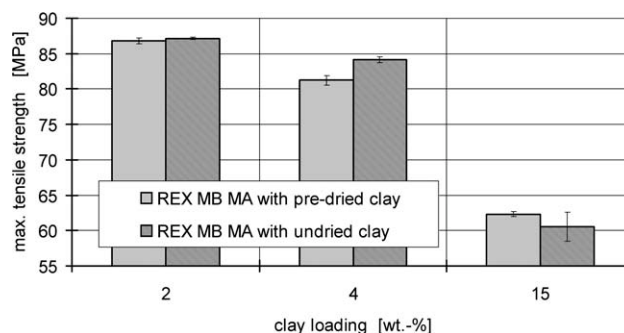

Figure 6 Dependence of the predrying of the clay on Young's modulus.

Figure 7 Dependence of the predrying of the clay on maximum tensile strength.
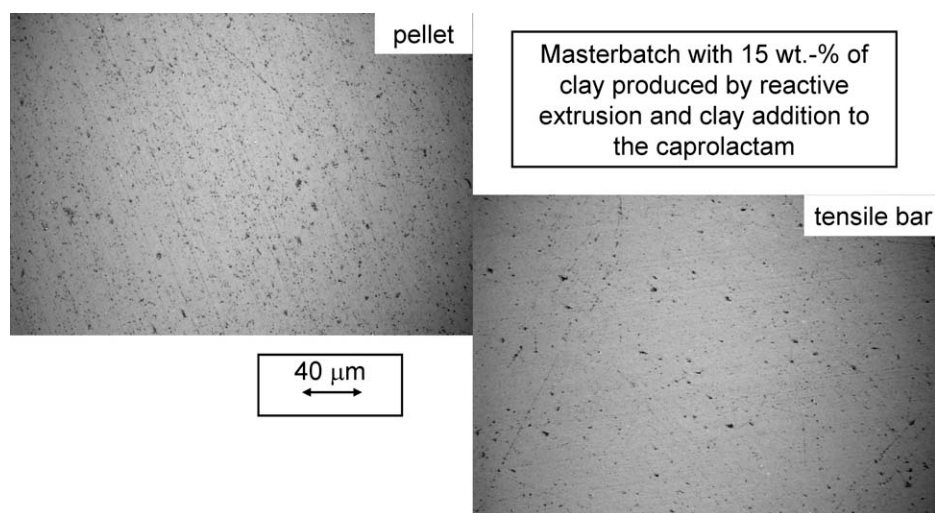
Figure 8 Light microscopy picture of the MB before and after injection molding.

with predried clay. The pure MBs with 15 wt % clay reach a maximum tensile strength of 63 MPa for the MB with predried clay and 61 MPa for the MB with undried clay. The standard deviation of the tensile strength for the MB with undried clay is high compared to the other measurements. This can be due to inhomogeneities in the material caused by moisture in the undried clay. Overall, the compounds made of dilutions from the MB with the undried clay show higher tensile strength than the compounds made with the MB with predried clays. To achieve high moduli and tensile strength, a predrying of the clay for the MB production is not necessary.

To better understand the dispersion process of the montmorillonite in the polyamide matrix the different morphologies were analyzed using light and transmission electron microscopy. A comparison of

the MB before and after the injection molding is shown in Figure 8.

The picture clearly shows an improvement of clay dispersion after the step of injection molding, as there are more clay agglomerates visible in the picture made directly from the pellet. The amount of bigger agglomerates with a diameter of about 5 microns stays constant. The amount of smaller agglomerates decreases after the step of injection molding.

Figure 9 shows pictures of the same samples made by TEM, which allow a sample comparison on a higher level of magnification. Both upper pictures show a similar dispersion before and after injection molding. The size of the bigger agglomerates is about one micron and the length of the agglomerates reaches up to 4 μm. A further increase of
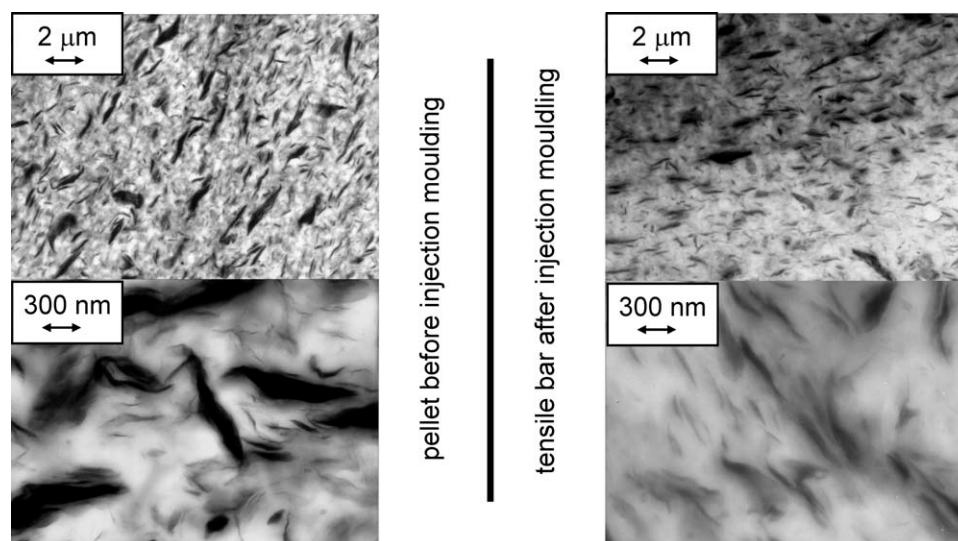

Figure 9 TEM pictures of the reactive MB before and after injection molding.

clay addition into the caprolactam (CA)   clay addition into the polymer melt (MA)
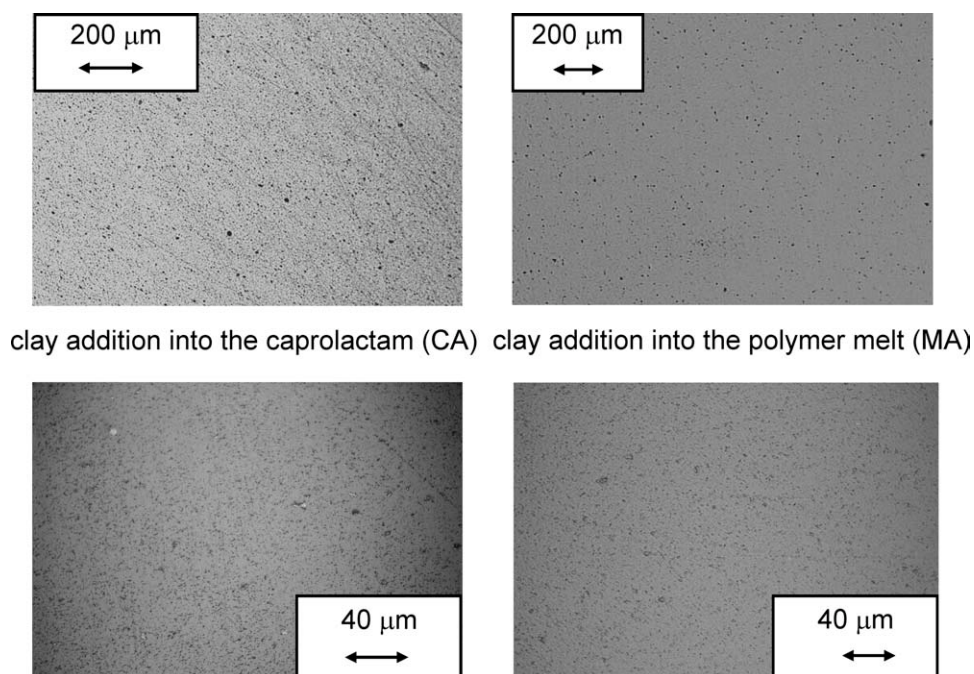
Figure 10   Microscope pictures of MBs with 15 wt % clay loading and different clay addition strategies.

magnification shows a different state of dispersion as seen in the lower pictures. Before injection molding, the agglomerates tend to be more compact and bigger compared to agglomerates after injection molding. It seems like the layers are pealed apart from the agglomerates after injection molding. This would also explain the difference in the light microscope pictures. The better dispersion is due to the additional energy input caused by shear energy, which is necessary to melt the MB in the plasticizing unit of the injection-molding device.

Figure 10 shows light microscope pictures of MBs with addition of clay to the CA and to the polymer melt after polymerization reaction (MA).

The picture of the clay dispersion in the MB produced by addition of the clay to the CA shows more agglomerates and visible particle compared to the MB prepared by adding clay to the polymer melt. A large number of montmorillonite particles are too small to be visible with the light microscope. At a higher magnification, the pictures do not show a clearly visible difference between the different addition strategies of the clay. On both pictures, small agglomerates with a size of less then 5 μm are visible. The dispersion of the clay particles seems to be very homogeneous for the whole compound. Figure 11 shows TEM pictures of the same samples at higher magnification.

A comparison of the two samples does not show a significant difference in state of clay dispersion and thus no effect of the clay adding strategy. In both pictures, agglomerates with a thickness of less then
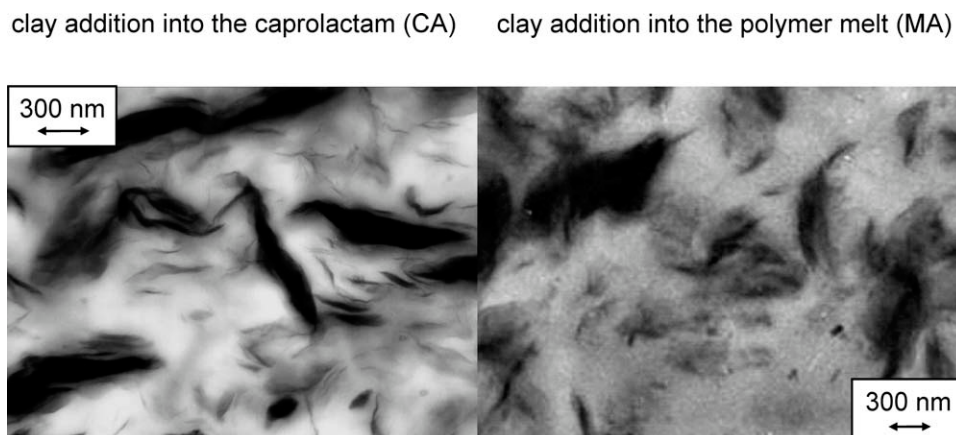
clay addition into the caprolactam (CA)   clay addition into the polymer melt (MA)

Figure 11   TEM pictures of MBs with 15 wt % clay loading and different clay addition strategies.
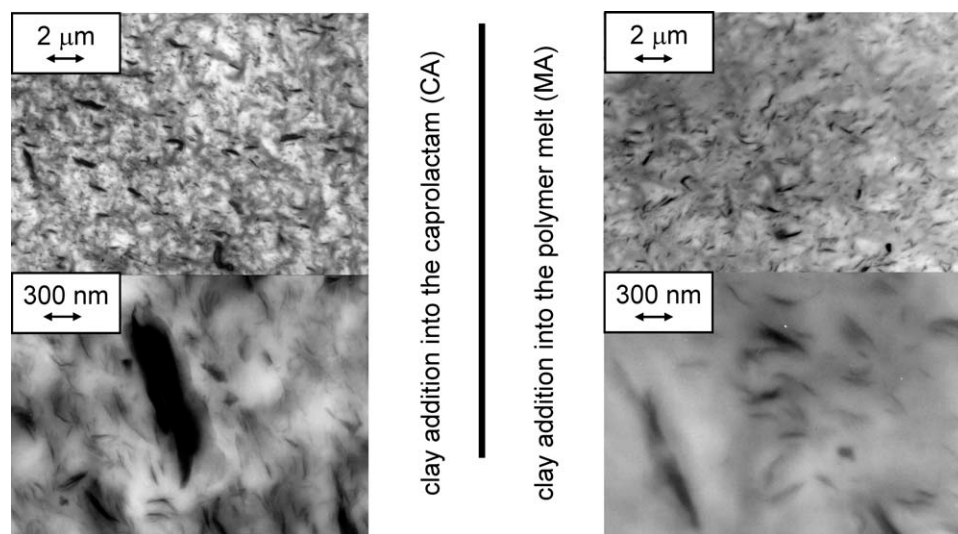
Figure 12 TEM pictures of compounds with 4 wt % clay loading from MB dilution.

250 nm are visible. Also smaller agglomerates and delaminated clay particles can be detected. In addition, there is no clear orientation of the clay particles seen in the pictures. The clay particles are randomly well dispersed in the polyamide matrix.

As there is no difference detectable in the clay dispersion of the two MBs produced by addition of the clay to the CA or to the polymer melt, the difference in mechanical properties is due to the composition of those MBs. The excess initiator amount needed to produce the MB with the clay addition to the CA has a plasticizing effect on the compound. The addition of clay to the CA or to the melt does not have a clear effect on the dispersion in the MB. A comparison of both addition strategies for the MB production is shown in Figure 12 for a compound with 4 wt % clay produced by dilution of the MBs in Ultramid B40.

At a lower magnification, both compounds show a homogeneous dispersion of clay in the polyamide. Only small agglomerates of less than a micron in size are visible. The clay platelets are randomly zoriented. Both compounds have a comparable amount of agglomerates, intercalated, and exfoliated clay particles. At a higher magnification, an agglomerate with a thickness of 300 nm can be detected in the compound with the MB of the CA production. This picture also shows many intercalated and completely exfoliated clay platelets. In comparison, the lower right picture does not show big agglomerates but some intercalated and exfoliated clay particles. Considering that the pictures only show a very small part of the granule, the dispersion for both production strategies (CA and MA) seems to be similar.

For the MB produced by melt addition (MA), two different ways of predrying the clay were
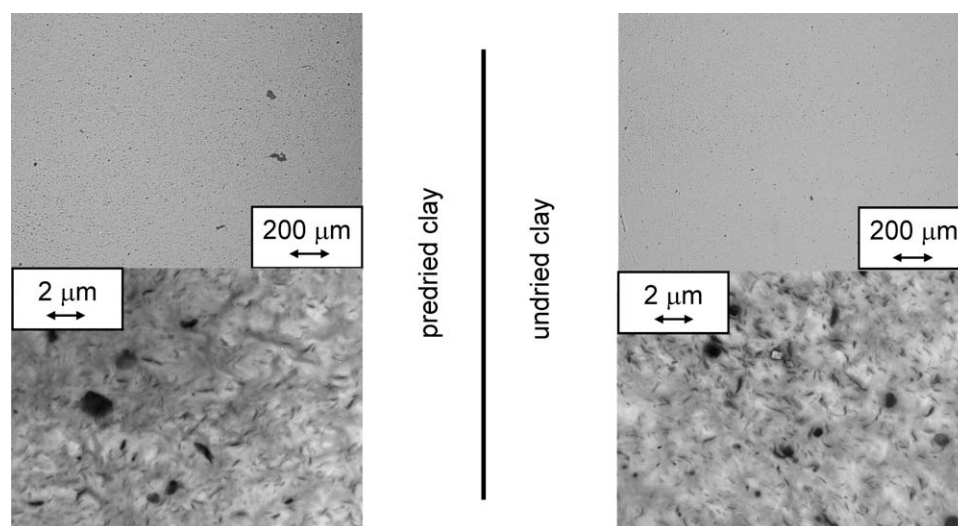

Figure 13 Microscope pictures of parts with 4 wt % clay loading and different predrying conditions.

analyzed. The clay particles were either predried or added without any drying beforehand. The dispersion of the clay particles analyzed by light and transmission electron microscopy is shown in Figure 13.

At a lower magnification, the compound with predried clay particles shows two big agglomerates with a size of nearly 50 μm. In contrast, the compound with undried clay only features small agglomerates with a size of a few microns. At a higher magnification, the pictures show a similar dispersion of the clay particles on the micron scale. In both figures, agglomerates with a size of less then 2 μm and many intercalated and exfoliated clay particles can be found. To minimize the amount of bigger agglomerates, a predrying of the clay is not necessary and even leads to more agglomerates. A change in the state of dispersion on the small micron scale due to the different drying conditions is not visible. Therefore, a predrying of the clay is not necessary to achieve improved clay dispersion. In addition, undried clay leads to an increase of mechanical properties.

CONCLUSIONS AND PROSPECTS

The results of this work demonstrate that it is possible to continuously produce PA 6 nanocompounds in a twin screw extruder. Due to the low viscosity of the educts and due to the omission of the melting the specific energy needed for the reactive process is lower compared to the standard process. A detailed analysis of the energy balance and energy saving potential due to a process implementation of further processing steps, that is, film production, will be investigated in future work.

The maximum improvement of mechanical properties can be achieved with a dilution of a MB where undried clay is added to the polymer melt (MA). A clay loading of 2 wt % leads to an increase of Young's modulus of 20%, whereas a clay loading of 4 wt % leads to an improvement of 30%. The maximum tensile stress also increases with the addition of nanoclay.

The microscopy pictures show that a good dispersion of the clay particles in the polyamide was reached. The clay particles are intercalated and even exfoliated. Some agglomerates are still visible and need to be further dispersed.

A special coating of the clay particles to improve the fillers compatibility to the anionic polyamide might lead to a further improved clay dispersion and a possible increase of mechanical properties.

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