

## Synthesis of polyamide 6/11 copolymers and their use as matrix polymer in wood-plastic composites

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**ABSTRACT:** The goal of this study was to investigate the synthesis and the resulting thermal, rheological, and mechanical properties of polyamide 6/11 copolymers (PA 6/11) as a function of their composition and to further investigate their usability as matrix polymers for wood-plastic composites (WPC). A significant composition dependency of the melting temperature was found due to the hindered crystallization of the PA 6/11 copolymers with increasing content of the minor component. In result, the lowest melting temperature of the copolymers was measured at 120 °C for 40 wt % of  $\epsilon$ -caprolactam (PA 6/11-40/60) by DSC analysis. Due to its low melting point and feasible mechanical properties, a copolyamide with 70 wt % of  $\epsilon$ -caprolactam (PA 6/11-70/30) was chosen as matrix material for the processing of WPC. Incorporation of 30 wt % of wood fibers into PA 6/11-70/30 caused a significant increase in tensile modulus and a decrease in tensile strength and strain at break. However, the processed WPC still showed an exceptional ductility with a strain at break of 15 to 20%. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 44155.

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### INTRODUCTION

The demand of sustainable and eco-friendly materials has constantly increased in recent years due to legislative regulations and customer requirements in many industries. Especially the automotive industry has to implement new and sustainable materials and technologies to fulfill the social demand for ecological mobility concepts in the medium term future.<sup>1</sup> Given this, major efforts are made toward the use of lightweight structures from polymer composites instead of previous metal elements to reduce weight and consequently CO<sub>2</sub> emissions.<sup>2</sup>

For many years also wood-plastic composites (WPC) have been used as construction materials due to their beneficial properties in comparison to synthetic fiber composites, like decreased density and lower cost.<sup>3</sup> For processing of WPC mainly polyolefin thermoplastics, such as polyethylene, polypropylene or polyvinylchloride, and wood flour or fibers from softwood like spruce or pine are used.<sup>4–6</sup>

A strategy to improve the sustainability of already existing composite parts is the usage of polymers and reinforcing fibers from renewable resources instead of conventional petroleum-based materials.<sup>7</sup> However, such a drop-in approach requires sophisticated and technical biopolymers without biodegradability but with comparable properties to polyolefins like polyethylene or polypropylene.<sup>8</sup> A positive trend in this direction is the

increasing adoption of bio-based polyethylene (bio-PE) from sugar cane.<sup>9</sup> Another promising approach is the usage of bio-based polyamides (bio-PA) from castor oil, which are gradually entering the market.<sup>10</sup> These bio-PAs, such as polyamide 11 (PA 11), polyamide 10.10 (PA 10.10), and polyamide 6.10 (PA 6.10), provide superior mechanical and thermomechanical properties as well as chemical resistance in comparison to bio-PE, which make them interesting as matrix polymers for sustainable composites in technical applications.<sup>11</sup>

With the exception of PA 11, a major disadvantage of the most existing bio-PA in comparison to bio-PE is the typically higher melting temperature, which limits their usage as matrix polymers in WPC due to required processing temperatures above the thermal degradation of the wood fibers at around 220 °C.<sup>12</sup> Solutions to solve this problem have been found in the improvement of the thermal stability of the wood fibers by chemical treatment or by technological adjustments of the compounding process.<sup>13,14</sup> Nevertheless, the broad implementation of such complete bio-based wood-plastic composites (bio-WPC) from bio-PA requires the processability on typical process equipment and the applicability of natural wood fibers.

Therefore, another approach is the synthesis of copolyamides as matrix polymers with lower melting temperatures than their corresponding homopolymers. This behavior has already rudimentarily

been demonstrated for some novel polyamide 6/11 copolymers from aminoundecanoic acid and up to 30 wt %  $\epsilon$ -caprolactam.<sup>15,16</sup> As both of the monomers can be derived from renewable resources, aminoundecanoic acid from castor oil and  $\epsilon$ -caprolactam from fermented glucose, polyamide 6/11 can be seen as a novel type of a sustainable copolyamide with an advantageous melting behavior for WPC processing.<sup>17</sup>

These novel types of bio-WPC could be used as sustainable drop-in materials for technical applications in the medium term future. However, systematic studies concerning structure/property relationships for PA6/11 over the whole range of copolymer composition do not exist up to now. For economic reasons, particularly PA6/11 with high ratios of caprolactam are of interest as matrix polymers for WPC. The aim of this study was, therefore, to investigate the synthesis and the resulting thermal and mechanical properties of polyamide 6/11 as a function of the copolymer composition. Additionally, the usability as matrix polymer for WPC and the resulting mechanical properties were investigated.

## EXPERIMENTAL

### Materials

$\epsilon$ -caprolactam was purchased from Alfa Aesar and vacuum-dried at 50 °C in presence of phosphorus pentoxide for 24 h. 11-Aminoundecanoic acid was donated by ARKEMA and dried in the same way. Processing of WPC was done with two different types of fibers from beech wood (*Fagus sylvatica*) provided by the Institut für Holztechnologie Dresden gGmbH. These different wood fibers were produced by thermo-mechanical pulping and mechanical chipping, respectively. The pulped beech fibers (BF) and chipped beech fibers (BC) were dried at 100 °C to a water content of approximately 6.5% as measured by Karl Fischer titration before composite processing.

### Methods

**Synthesis of PA 6/11 Copolymers.** Synthesis of the polyamide 6/11 copolymers was done in a lab scale autoclave (Kiloclave 1.5 l, Büchi Glas Uster) equipped with a stirrer in batches of 600 g according to Wang *et al.*<sup>15</sup> Atmospheric oxygen was removed from the reactor by repeated rinsing with nitrogen and subsequent evacuation. The autoclave was heated to 190 °C and the reaction mixture of 11 aminoundecanoic acid,  $\epsilon$ -caprolactam and 4 wt % of deionized water was stirred for 2 h in autogenous pressure conditions. Then the reactor was slowly decompressed to ambient pressure with simultaneous increase of the temperature to 230 °C. Afterwards, polycondensation took place in vacuum with continuous pressure reduction up to approximately 20 mbar and was finished by the time no further increase of torque and accordingly viscosity occurred. Time of polycondensation varied between 2.5 and 4 h. After completion of polymerization the melt was drawn through the bottom valve under 3–5 bar pressure, cooled, and granulated. To remove residual monomers, the pellets were treated with hot water for 24 h and dried subsequently. Following this procedure, eight different PA 6/11 copolymers containing 20 to 90 wt % aminohexanoic acid units were synthesized. They were named PA 6/11-*x/y*, in which *x* means wt % of aminohexanoic acid units and *y* means wt % of aminoundecanoic acid units. We mark these copolymers PA 6/11 to distinguish them from the AA-BB-polyamide PA 6.11.

**Processing of WPC and Preparation of Test Specimens.** Preparation of WPC was carried out by discontinuous mixing in a two-roll internal mixer (PolyLab, Thermo Scientific). Composites of PA 6/11-70/30 and the BF as well as the BC were processed with fiber contents of 30 wt %. The processing conditions were kept constant at 196 °C melt temperature and 50 rpm rotation speed. After 3 min of melting of the PA 6/11-70/30, the beech fibers were added and the components were mixed for 5 min. Subsequently, the composites were removed from the mixing chamber and directly injection molded into standard test specimens by a lab scale plunger injection molding machine (MiniJet, Thermo Scientific) according to ISO 527. Processing parameters for the preparation of the test specimens were kept constant at 220 °C melting temperature, 110 °C mold temperature, 3.5 min melting time, 900 bar injection pressure, and 460 bar hold pressure. The processed test specimens were immediately sealed in multilayered aluminum foil to prevent water uptake (fresh as-molded).

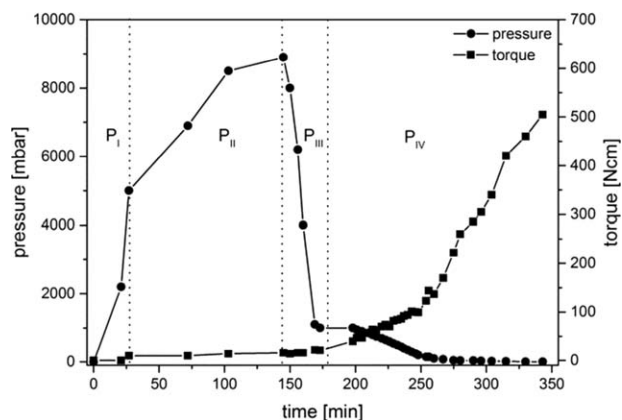
### Instruments

**Size Exclusion Chromatography of PA 6/11 Copolymers.** Measurements were performed with a test device (SEC-3010, WGE Dr. Bures), containing a pump with degasser (flow: 0.8 mL/min HFIP + 0.05 mol/l  $C_2F_3NaO_2$ ), an autosampler with column oven at 35 °C, a Dn-2010 RI-detector and a MALLS-detector from Brookhaven. Used columns were 2 × PL HFIP gel (300 × 7.5 mm) and PL HFIP guard (50 × 7.5 mm) from Agilent. For each measurement a sample of 20 mg was diluted in 5 mL HFIP and 0.05 mol/L  $C_2F_3NaO_2$  overnight and filtrated through a syringe filter with a mesh size of 0.2  $\mu$ m.

**<sup>13</sup>C-NMR Spectroscopy of PA 6/11 Copolymers.** For NMR measurements, the spectrometer (Unity INOVA 500, Varian Inc.) was utilized at a <sup>13</sup>C measuring frequency of 125.7 MHz and a <sup>1</sup>H decoupling frequency of 499.8 MHz with the standard pulse sequence s2pul under quantitative conditions (inverse gated decoupling). The 90° pulse width was 6.8  $\mu$ s, the relaxation delay was 5 s and the spectral width was 35 kHz. For each measurement, 50 to 100 mg of the powdered materials were dissolved in about 1 mL of 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) under intensive stirring. The high-viscosity solutions were transferred into 5 mm NMR sample tubes. The measurements were performed without deuterium lock at room temperature and about 15000 scans were accumulated per spectrum. The chemical shifts were referenced to the  $-CF_3$  signal of the HFIP at 121 ppm relatively to TMS (0 ppm). The processing of the spectra and the quantitative analysis were made with the internal VnmrJ software from Varian Inc.

**Differential Scanning Calorimetry of PA 6/11 Copolymers.** A calorimeter (Q 1000, TA Instruments) was used to determine the melting temperatures and enthalpies of the copolymers at a heating and cooling rate of 5 K/min from 20 to 220 °C. Two cycles were run in a nitrogen atmosphere and the second heating and cooling run was used for analysis, respectively.

**Rheological Characterization of PA 6/11 Copolymers and WPC.** For rheological characterization, relative viscosities and viscosity numbers (IV) of the PA 6/11 copolymers were determined at 25 °C in m-cresol using an Ubbelohde-viscometer. The concentration of the solutions was 5 mg/cm<sup>-3</sup>. Additionally, the



**Figure 1.** Pressure and torque during the synthesis of PA 6/11-50/50.

Melt Flow Index (MFI) of the copolymers and WPC was measured with a MFI tester (Meltflier LT, Haake) at 235 °C and a load of 2.16 kg according to ISO 1133.

**Mechanical Characterization of PA 6/11 Copolymers and WPC.** Testing of the mechanical properties of the synthesized PA 6/11 copolymers and the processed WPC was done by tensile testing with an universal testing machine (Z050 AllroundLine, Zwick) according to ISO 527. For each copolymer and WPC, six specimens were tested and mean values of the mechanical parameters were calculated. The testing was done on fresh as-molded (sealed) specimens to eliminate the impact of water uptake on the mechanical properties. The morphology of the processed WPC was characterized by optical light microscopy on polished test specimens.

## RESULTS AND DISCUSSION

### Polycondensation to Polyamide 6/11 Copolymers

The synthesis of PA 6/11 copolymers is subdivided into four phases as can be seen in Figure 1. The first phase ( $P_I$ ) with heating up to 190 °C is followed by a 2-h pressure phase ( $P_{II}$ ). The decompression to ambient pressure with simultaneous increase of the temperature to 230 °C is the third phase ( $P_{III}$ ). In the fourth phase ( $P_{IV}$ ), the condensation polymerization under vacuum takes place. However, during the third and fourth phase of the synthesis the resulting water needs to be distilled from the reaction mixture. The torque and thereby the viscosity of the melt and the molecular weight of the particular PA 6/11 copolymer is only increasing in the fourth phase.

Due to the varying molecular weights of the different PA 6/11 copolymers a variation of the final torque of each experiment was observed. Increasing the  $\epsilon$ -caprolactam content from 20 to 40 wt % led to a very pronounced decrease in molecular weight while with a further increase from 40 to 90 wt % the decrease is less pronounced or, considering the inherent errors of the analytical methods, the molecular weight stays even more or less constant. This can be seen in Figure 2 from the results of the size exclusion chromatography (SEC) and viscosity measurements. Although both data are known to be prone to some systematic error due to the varying average repeating unit length with feed, this general trend is expected to be valid. The average repeating unit length changes continuously over the whole range of the  $\epsilon$ -caprolactam content. Therefore, the observed behavior

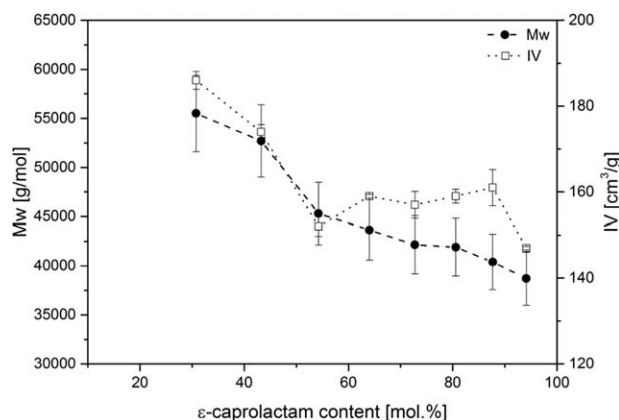
of a pronounced change in apparent molecular weight with  $\epsilon$ -caprolactam contents between 20 and 40 wt % followed by nearly constant values for  $\epsilon$ -caprolactam contents between 40 and 90 wt % is not supposed to be solely caused by deviations in average unit length. End group analysis, which could support SEC and viscosity data, was not carried out in the scope of this study.

In contrast to our findings, Wang *et al.*<sup>15</sup> reported a 17% increase of the intrinsic viscosities for copolymers with increasing  $\epsilon$ -caprolactam content from 5 to 30 wt %. To evaluate this apparent discrepancy, the different reaction conditions between<sup>15</sup> and our work have to be considered. In the fore mentioned work, for molecular weight determination all samples were taken after 3 h of polycondensation and no information on the applied vacuum is given. Nevertheless, it is stated that the polycondensations were not finished after 3 h since a further increase in intrinsic viscosities at longer reaction times is reported. In combination with the missing values for pressure during polycondensation, these results are hardly comparable to our work, in which polycondensation was stopped after reaching a constant torque at 230 °C and 20 mbar, that is, after reaching equilibrium under these conditions. Keeping this in mind, the relation between molecular weight and  $\epsilon$ -caprolactam content could be due to the more hydrophilic nature of  $\epsilon$ -caprolactam in comparison to aminoundecanoic acid. An increasing  $\epsilon$ -caprolactam content is thus believed to impede the distillation of the resulting water of the polycondensation reaction, leading to an increased equilibrium content of water and, therefore, limiting the molecular growth for PA 6/11.

All PA 6/11 copolymers contained different amounts of residual monomers and were, therefore, purified before further investigation by treatment with hot water for 24 h. The thereby occurring weight loss was between 1 and 3.5%. It was observed that the applied method was effective to remove the monomers but also caused a decrease in molecular weight of the copolymers. The resulting molecular weights and polydispersities of the synthesized copolymers are given in Table I.

### Molecular Weight Distribution of Polyamide 6/11 Copolymers

Selected copolymers were additionally characterized by <sup>13</sup>C-NMR spectrometry. The results given in Table II show the conformity of



**Figure 2.** Molecular weight ( $M_w$ ) and viscosity number (IV) of the PA 6/11 copolymers (raw) as a function of the  $\epsilon$ -caprolactam content.

**Table I.** Molecular Weights ( $M_w$ ) and Polydispersities (PD) of the Synthesized PA 6/11 Copolymers before and after Purification

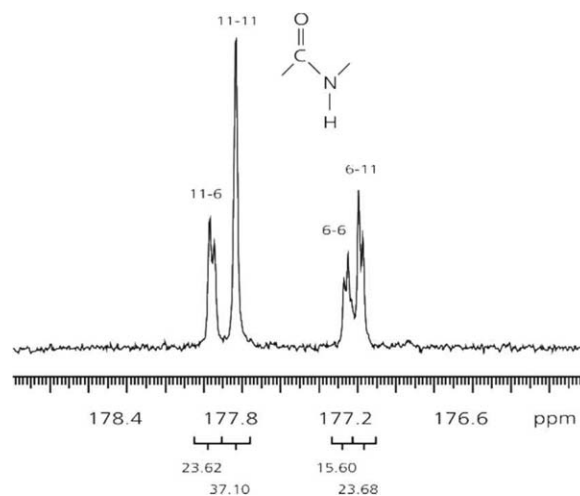
PA 6/11	$\epsilon$ -caprolactam content		Raw		Purified	
	(wt %)	(mol %)	$M_w$ (g/mol)	PD	$M_w$ (g/mol)	PD
90/10	90	94.1	38700	2.11	33600	1.92
80/20	80	87.7	40400	2.18	36200	2.05
70/30	70	80.6	41900	2.06	35150	2.18
60/40	60	72.7	42150	2.12	37500	2.17
50/50	50	64.0	43650	2.08	39950	2.08
40/60	40	54.2	45300	2.31	37700	2.03
30/70	30	43.3	52700	2.15	48700	2.24
20/80	20	30.8	55500	2.04	56900	2.07

feed and copolymer composition. A triad analysis of the  $^{13}\text{C}$ -NMR data revealed the virtually statistic distribution of amino-hexanoic acid and aminoundecanoic acid units in the copolymers. To illustrate this, a so called run number  $R$  was calculated from the NMR data. The run number  $R$  of a polymer is the number of uninterrupted monomer sequences per 100 monomer units in a copolymer, which means that for a completely alternating copolymer  $R = 100$  and for a diblock copolymer with 100 monomer units  $R = 2$ .<sup>18</sup>

It can be seen in Figure 3 that the  $^{13}\text{C}$ -NMR allows to differentiate between the possible links within a PA 6/11 chain as well. There are four possible links in PA 6/11 copolymers—aminohexanoic acid linked to aminohexanoic acid (6-6), aminohexanoic acid linked to aminoundecanoic acid (6-11), aminoundecanoic acid linked to aminoundecanoic acid (11-11), and aminoundecanoic acid linked to aminohexanoic acid (11-6). As each PA 6 sequence in a PA 6/11 copolymer is terminated by a 6-11 link and each PA 11 sequence by a 11-6 link, the experimental  $R$  number ( $R_{\text{exp}}$ ) can be calculated from the sum of the fractions of 6-11 and 11-6 links from  $^{13}\text{C}$ -NMR as  $R_{\text{exp}} = (6-11) + (11-6)$  (dimensions in mol % of all linkages). The results are shown in Figure 4 in comparison to a statistic  $R$  number ( $R_{\text{stat}}$ ), which is calculated as  $R_{\text{stat}} = [C] \times [A]/50$  with  $[C]$  and  $[A]$  being the molar concentrations in mol % of  $\epsilon$ -caprolactam and aminoundecanoic acid in the feed, respectively. It can be seen that  $R_{\text{exp}}$  and  $R_{\text{stat}}$  are in good agreement which proves a statistical distribution of the monomeric units in the PA 6/11 copolymers.

**Table II.** Composition of Selected PA 6/11 Copolymers in Comparison to Feed Composition as Measured by  $^{13}\text{C}$ -NMR

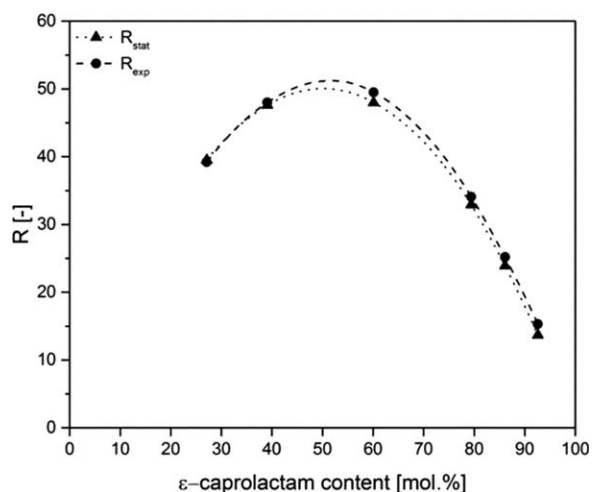
Feeded mass ratio ( $\epsilon$ -caprolactam/11-aminoundecanoic acid)	Measured mass ratio (PA 6/PA 11)
90/10	91/9
80/20	78/22
70/30	68/32
60/40	60/40
50/50	48/52
30/70	29/71

**Figure 3.** Detail of  $^{13}\text{C}$ -NMR spectrum of PA 6/11-30/70.

### Thermal Properties of Polyamide 6/11 Copolymers

The thermal properties of the synthesized copolyamides were investigated by differential scanning calorimetry (DSC) to analyze their processability with the thermal sensitive wood fibers to WPC by melt mixing. As expected, the melting and crystallization behavior of the copolymers was varying in dependence on their composition. This can be seen in Figure 5 by the DSC traces of the 2nd heating and cooling cycle of selected copolymers. The various PA 6/11 copolymers exhibit different melting temperatures and the shape of the melting peaks is also varying.

The composition dependency of the melting temperature and heat of fusion can be seen in Figure 6 for all copolymers and the homopolymers, respectively. It was found that the melting temperatures range from 120 to 210 °C and pass through a minimum for PA 6/11-40/60. Beside the melting temperatures also the crystallization behavior, which correlates to the heat of fusion, is strongly influenced by the composition of the copolymers. This can be attributed to a hindered crystallization of the copolymers with increasing irregularity in molecular structure

**Figure 4.** Run numbers of selected PA 6/11 copolymers as a function of the PA 6 content.  $R_{\text{stat}}$  - theoretical value for statistical copolymers,  $R_{\text{exp}}$  - calculated value from  $^{13}\text{C}$ -NMR.

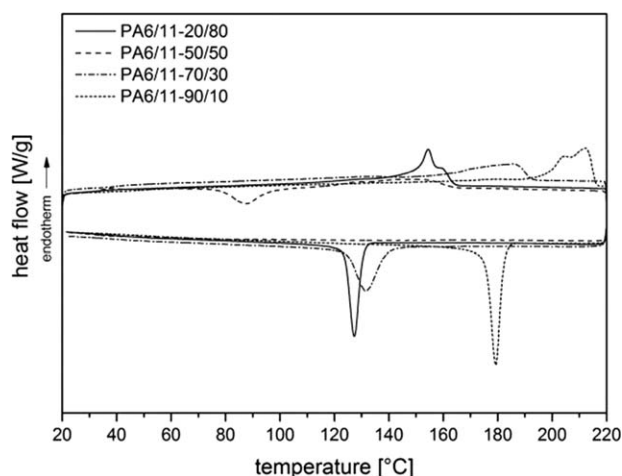


Figure 5. DSC thermograms of selected PA 6/11 copolymers.

when the content of minor component increases. The chain microstructure regarding co-monomer distribution and crystallizable amino hexanoic acid and aminoundecanoic acid segments strongly influences the crystallization of PA 6/11 copolymers. In consequence, with exception of PA 6/11-50/50 the crystallization usually occurs during cooling.

As expected, the heat of fusion  $\Delta H_m$  and the melting temperature  $T_m$  increase in the direction of both homopolymers. This behavior is already described for other copolyamides. The difference in the melting temperature between PA 6 and the lowest melting copolyamide PA 6/11-40/60 is about 85 K and hence in the same range as described by Garner and Fasulo<sup>19</sup> for PA 6/12 copolymers and by Zilberman *et al.*<sup>20</sup> for PA 6/6.9 copolymers. In contrast to this, lower differences of about 60 K in melting temperature are reported by Kehayoglou and Arvanitoyannis<sup>21</sup> for PA 8/12 copolymers. The homopolymers of the PA 8/12 series show the same crystallographic  $\gamma$ -form, which facilitates co-crystallization.<sup>22</sup> Hence, no or minor co-crystallization seems to occur for PA 6/11 just like for PA 6/12 and PA 6/6.9.

These findings show the significant influence of the copolymer composition on the thermal properties and confirm the feasibility of the approach of low temperature processing of WPC

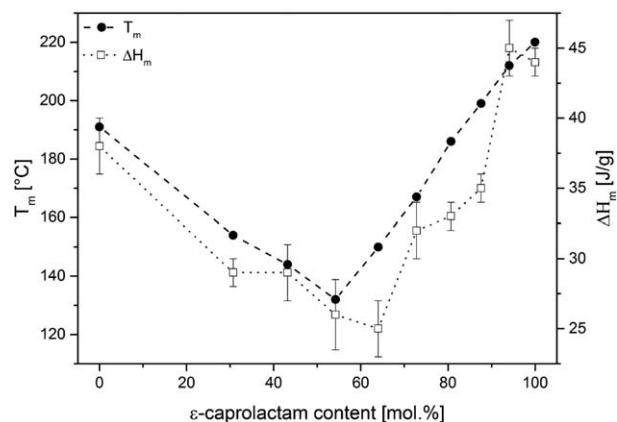


Figure 6. Melting temperatures ( $T_m$ ) and heat of fusion ( $\Delta H_m$ ) of PA 6/11 copolymers as a function of the  $\epsilon$ -caprolactam content.

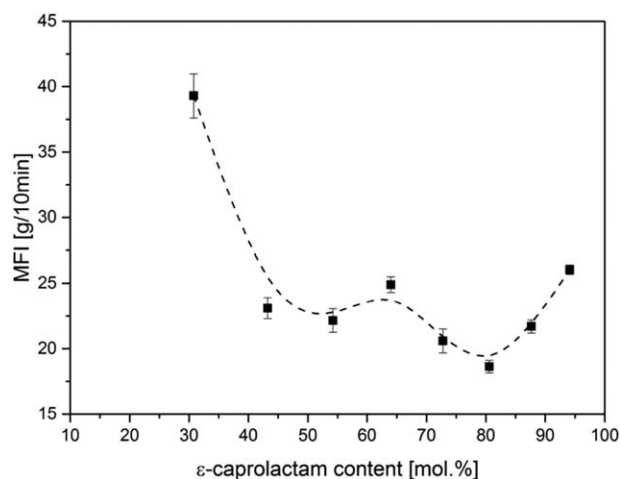


Figure 7. MFI of the PA 6/11 copolymers as a function of the  $\epsilon$ -caprolactam content.

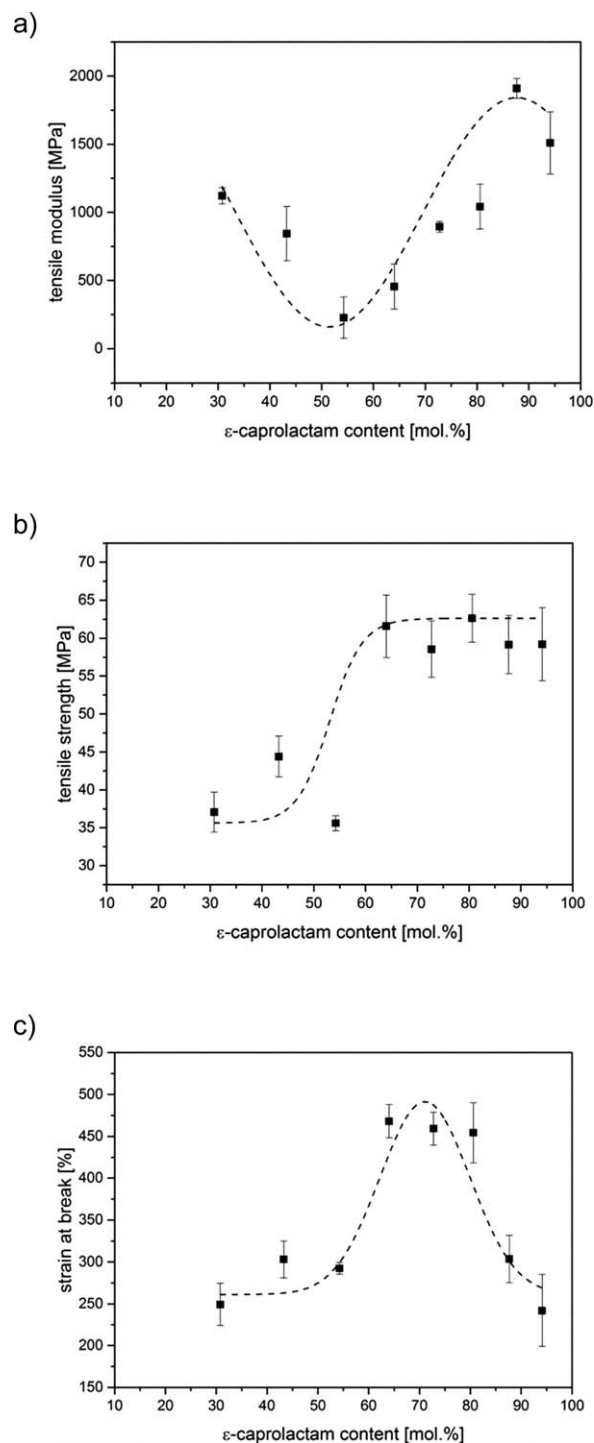
processing with low melting copolyamides. However, beside the thermal properties the rheological and mechanical properties of the copolyamides have to be considered to assure a good processability and mechanical performance.

#### Rheological Properties of Polyamide 6/11 Copolymers

Interestingly, the decreasing molecular weight of the PA 6/11 copolymers with increasing  $\epsilon$ -caprolactam content did not lead to a better flowability as measured by the MFI. It can be seen in Figure 7 that the MFI of the copolymers is initially decreasing with increasing  $\epsilon$ -caprolactam content, reflecting a reduction in flowability at low shear rates. Furthermore, a raised  $\epsilon$ -caprolactam content above 70 wt % leads to an increase in MFI and an improved flowability of the copolymer. This is in contrast to the findings of Hu *et al.*,<sup>16</sup> who investigated the rheological properties of PA 6/11 copolymers with  $\epsilon$ -caprolactam contents between 5 and 25 wt % with capillary rheometry experiments at high shear rates and found a shear thinning behavior of the copolyamides with higher viscosities than the neat PA 11. This was attributed to an increase in molecular weight of the copolyamides.

In general, the viscosity of a polymer at given temperature and load is governed by the free volume of the melt, the entanglement density, and the intermolecular interactions.<sup>23</sup> As a reduced molecular weight results in a higher free volume and a decreased entanglement density, both promoting a lower viscosity, the reduced flowability of the copolyamides in this study with increasing  $\epsilon$ -caprolactam content up to 70 wt % has to be attributed to increased intermolecular interactions. With increasing  $\epsilon$ -caprolactam content, the number of amide groups is increasing and, therefore, stronger intermolecular interactions and a greater resistance to the sliding motion of the molecules due to hydrogen bonds are generated. Corresponding findings have also been reported for polyether-ester-amide copolymers from Gosh *et al.*<sup>24</sup>

At  $\epsilon$ -caprolactam contents above 70 wt % the reduced entanglement density due to the decreasing molecular weight is the prominent factor and the flowability of the copolyamides is increasing. In result, the copolyamides in fact showed a reduced



**Figure 8.** Mechanical properties of PA 6/11 copolymers as a function of the PA 6 content; (a) tensile modulus, (b) tensile strength, and (c) strain at break.

MFI in comparison to the corresponding homopolymers but still have a sufficient flowability for the processing of WPC.

#### Mechanical Properties of Polyamide 6/11 Copolymers

The mechanical properties of the synthesized PA 6/11 copolymers as measured by the uniaxial tensile test are shown in Figure 8. It can be seen in Figure 8(a) that the tensile modulus is

initially decreasing with increasing  $\epsilon$ -caprolactam content, reaching a minimum of 227 MPa for PA 6/11-40/60. Further increase in the  $\epsilon$ -caprolactam content led to an enhanced stiffness of the copolymers. This can be attributed to the composition dependent crystallization behavior of the copolyamides as already shown in the DSC results. According to Starkweather Jr. *et al.*,<sup>25</sup> a higher crystallinity affects a higher stiffness in polyamides. However, the highest tensile modulus of the investigated copolymers was found for PA 6/11-80/20 with 1910 MPa.

A different trend can be seen in Figure 8(b) for the tensile strength that shows two plateaus. The first plateau of approximately 35 MPa retains to an  $\epsilon$ -caprolactam content of 40 wt % while further increase in the  $\epsilon$ -caprolactam content led to a significant increase of the tensile strength to a new plateau value of approximately 60 MPa. This increased strength has to be attributed to increased intermolecular interactions of the copolyamide molecules by hydrogen bonds as the number of amide groups is increasing with increasing  $\epsilon$ -caprolactam content.<sup>26</sup> Partial deviations from this general trend have to be addressed to the complex crystallization behavior of the copolymers as already discussed for the DSC results.

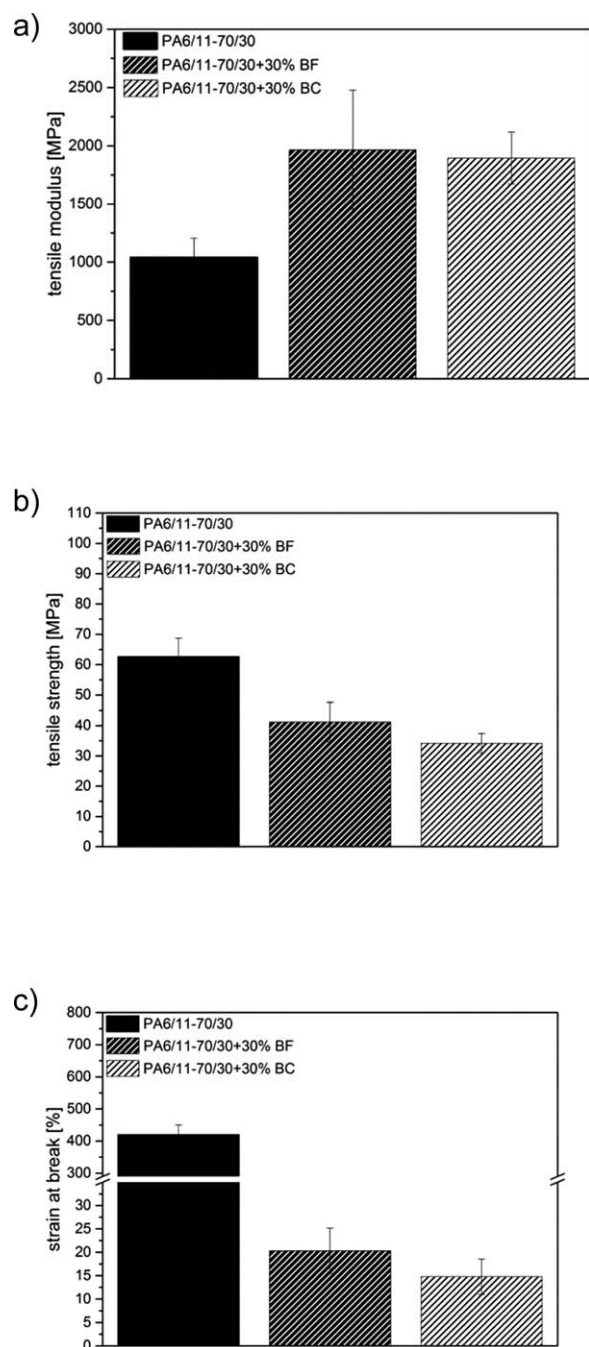
However, the maximum value is already reached at an  $\epsilon$ -caprolactam content of 50 wt % and a further increase in the  $\epsilon$ -caprolactam content affects no further increase in tensile strength. The strain at break of the copolymers was found to be complementary to their stiffness and the dependency on the  $\epsilon$ -caprolactam content can, therefore, be attributed to the composition dependent crystallization behavior of the copolyamides as well. This can be seen in Figure 8(c) since the elongation at break is initially increasing with increasing  $\epsilon$ -caprolactam content to a maximum of 468% at 50 wt % of  $\epsilon$ -caprolactam due to the decreased crystallinity and improved mobility of the copolyamide molecules. Increasing the  $\epsilon$ -caprolactam content above 70 wt % led to a significant drop in strain at break due to the increased crystallinity and reduced mobility of the copolyamide molecules. Nevertheless, the copolymer PA 6/11-90/10 still had a high strain at break of 242%.

#### WPC from Polyamide 6/11 Copolymers

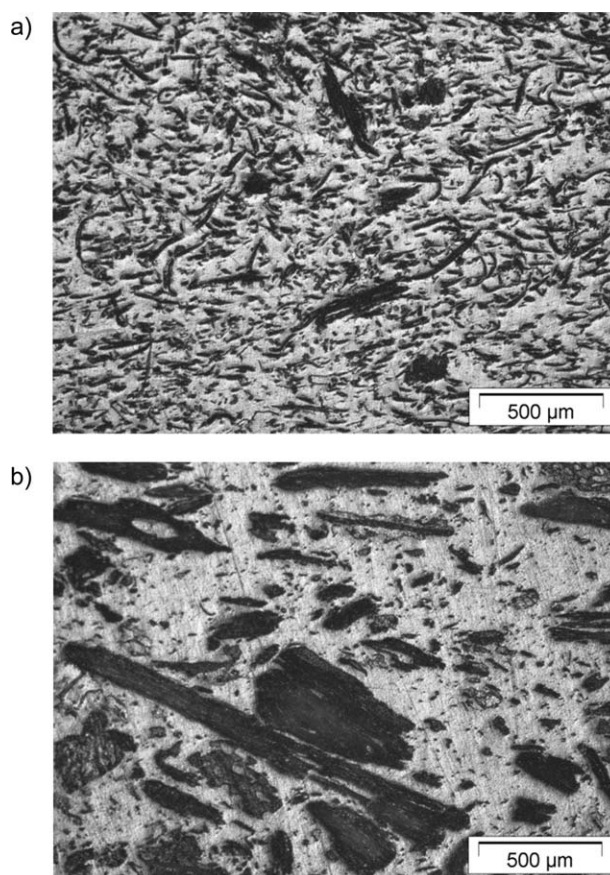
Processing of WPC was done by discontinuous melt mixing of the PA 6/11-70/30 copolymer with pulped (BF) and BC. The fiber content of all processed WPC was 30 wt %. Based on the results of the investigations on the thermal, rheological and mechanical properties of the copolyamides, the PA 6/11-70/30 copolymer was chosen as matrix polymer because of its favorable balance of these properties.

The resulting mechanical properties of the WPC are shown in Figure 9. It can be seen that the incorporation of beech fibers had a significant effect on stiffness, strength, and strain at break. The tensile modulus shown in Figure 9(a) was found to be 1966 MPa for the BF-WPC and 1894 MPa for the BC-WPC, which is almost doubled in comparison to the neat PA 6/11-70/30 with 1041 MPa. This behavior is in good agreement with the general reinforcing effect of wood fibers in thermoplastic polymers due to the significant higher stiffness of the wood fibers in comparison to the polymer matrix.<sup>27</sup> A significant influence of the wood fiber geometry on the stiffness of the WPC was not

noticed. As can be seen in Figure 9(b), an opposite trend was found for the tensile strength. By addition of both fiber types a drop was observed leading to a value of 41 MPa for the BF-WPC and 34 MPa for the BC-WPC while the neat PA 6/11-70/30 had a tensile strength of 62 MPa. The higher strength of the BF-WPC in comparison to the BC-WPC can be attributed to the higher aspect ratio of the BF, which promotes a better fiber/matrix-adhesion due to a higher number of hydrogen bonds with the PA 6/11-70/30 matrix. Analogue trends have been



**Figure 9.** Mechanical properties of the wood-plastic composites based on PA 6/11-70/30; (a) tensile modulus, (b) tensile strength, and (c) strain at break.



**Figure 10.** Morphology of the wood-plastic composites based on PA 6/11-70/30 (flow direction from left to right); (a) PA 6/11 + 30% BF and (b) PA 6/11 + 30% BC.

found by Zierdt *et al.*<sup>28</sup> for the tensile strength of WPC from PA 11 and BF and BC, respectively.

In result of the increased stiffness of the WPC, a significant reduction of the strain at break was observed in comparison to the neat PA 6/11-70/30 copolymer. However, with a strain at break of 20% of the BF-WPC and 15% of the BC-WPC, as shown in Figure 9(c), the processed composites still showed a distinctive ductility. This is an exceptional behavior for WPC and will be the focus of further studies.

The mechanical behavior of the two different WPC revealed a clear trend toward better properties when the BF are used as reinforcing wood fibers due to their higher aspect ratio. The BF additionally tend to be more easily oriented in the flow direction of the WPC melt, which also improves the mechanical properties of the WPC in the uniaxial tensile test. This can be seen in Figure 10.

## CONCLUSIONS

The synthesis of polyamide 6/11 copolymers and their usability as matrix polymers for WPC were investigated in this study. It was found that the molecular growth of the PA 6/11 copolymers at high contents of  $\epsilon$ -caprolactam is limited. This effect could be due to the impeded distillation of the resulting water of the polycondensation reaction. With increasing content of the

minor component the crystallization of the copolymers is hindered because of the increasing irregularity in molecular structure. In result, the melting temperature of the copolymers has a strong composition dependency with the lowest melting temperature at 120 °C for PA 6/11-40/60. This behavior enables the processing of WPC with PA 6/11 copolymers at temperatures well below the decomposition temperature of wood fibers. The exceptional ductility at high stiffness of the processed WPC from PA 6/11-70/30 and 30 wt % of beech fibers with a strain at break of 15 to 20% will be the object of further studies.

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#### REFERENCES

1. Mayyas, A.; Qattawi, A.; Omar, M.; Shan, D. *Renewable Sustain. Energy Rev.* **2012**, *16*, 1845.
2. Poulidikou, S.; Schneider, C.; Björklund, A.; Kazemahvazi, S.; Wennhage, P.; Zenkert, D. *Mater. Des.* **2015**, *83*, 704.
3. Bledzki, A. K.; Reihmane, S.; Gassan, J. *Polym. Plast. Technol. Eng.* **1998**, *37/4*, 451.
4. Selke, S.; Wichman, I. *Compos. Part A* **2004**, *35*, 321.
5. Kumar, V.; Tyagi, L.; Sinha, S. *Rev. Chem. Eng.* **2011**, *27*, 253.
6. Jiang, H.; Kamdem, D. P. *J. Vinyl Addit. Technol.* **2004**, *10/2*, 59.
7. Koronis, G.; Silva, A.; Fontul, M. *Compos. Part B-Eng.* **2013**, *44*, 120.
8. Endres, H.-J.; Siebert-Raths, A. *Engineering Biopolymers*; Hanser Publications: Cincinnati, **2011**.
9. Babu, R. P.; O'Connor, K.; Seeram, R. *Prog. Biomater.* **2013**, *2/8*, 1.
10. Shen, L.; Haufe, J.; Patel, M. K. *Product Overview and Market Projection of Emerging Bio-Based Plastics PRO-BIP 2009*; University of Utrecht: Utrecht, **2009**.
11. Bledzki, A. K.; Feldmann, M.; Jaszkievicz, A. *Bioplast. Mag.* **2010**, *3/5*, 26.
12. Feldmann, M. *Dissertation*, University of Kassel, Kassel, **2012**.
13. Zierdt, P.; Theumer, T.; Kulkarni, G.; Däumlich, V.; Klehm, J.; Hirsch, U.; Weber, A. *Sustain. Mater. Technol.* **2015**, *6*, 6.
14. Feldmann, M.; Bledzki, A. K. *Compos. Sci. Technol.* **2014**, *100*, 113.
15. Wang, B. B.; Hu, G. S.; Zhao, X.; Gao, F. Z. *Mater. Lett.* **2006**, *60*, 2715.
16. Hu, G. S.; Wang, B. B.; Gao, F. Z. *Mater. Sci. Eng. A* **2006**, *426*, 263.
17. Hermann, B. G.; Blok, K.; Patel, M. K. *Environ. Sci. Technol.* **2007**, *41*, 7915.
18. Hardwood, H. J.; Ritchey, W. M. *J. Polym. Sci. Polym. Lett.* **1964**, *6*, 601.
19. Garner, D. P.; Fasulo, P. D. *J. Appl. Polym. Sci.* **1988**, *36*, 495.
20. Zilberman, A.; Siegmann, A.; Narkis, M. *J. Macromol. Sci. B* **1996**, *35*, 1.
21. Kehayoglou, A. H.; Arvanitoyannis, I. *Eur. Polym. J.* **1990**, *26*, 261.
22. Kehayoglou, A. H.; Arvanitoyannis, I. *Polymer* **1992**, *33*, 4095.
23. Shenoy, A. V.; Saini, D. R.; Nadkarni, V. M. *Rheol. Acta* **1983**, *22*, 209.
24. Gosh, S.; Bhattacharyya, A. K.; Khastgir, D.; Bhowmick, A. K. *J. Appl. Polym. Sci.* **1999**, *71*, 1739.
25. Starkweather, H. W.; Jr.; Moore, G. E.; Hansen, J. E.; Roder, T. M.; Brooks, R. E. *J. Polym. Sci.* **1956**, *21*, 189.
26. Ehrenstein, G. W. *Polymeric Materials: Structure – Properties – Applications*; Carl Hanser Verlag: Munich, **2001**.
27. Ku, H.; Wang, H.; Pattarachaiyakoop, N.; Trada, M. *Compos. Part B-Eng.* **2011**, *42*, 856.
28. Zierdt, P.; Theumer, T.; Weber, A. *Holztechnologie* **2015**, *56/3*, 10.