The Influence of the Extrusion Temperature on the Mechanical Properties of MMT Filled PA 6 Composite

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SUMMARY

Effects of varying extrusion temperatures on the mechanical properties of polyamide 6 (PA 6) matrix montmorillonite (MMT) filled composites were investigated in this paper. Five different temperature programs were used for producing composites with 1 wt.% nanoparticles content. The mechanical properties were evaluated by tensile and flexural tests and SEM pictures were taken from the fracture surfaces. X-ray diffraction patterns were also measured to obtain some information about the structures of the materials. The results showed that the lower extrusion temperatures resulted in better mechanical properties of the composite.

1. INTRODUCTION

Nanocomposites, which are made of polymer matrices and nanofillers, are among the most investigated materials nowadays. Nanoparticles are often utilized to modify mechanical-, abrasion-, thermal-, barrier-, etc. properties of polymer matrices. One of the most often applied nanoparticles is montmorillonite (MMT), which is certain clay. In polymer engineering the most applied thermoplastic matrices are from the family of polyamides, not just because of their good mechanical and thermal properties but also their good adhesive properties to other reinforcing materials. These good adhesive properties still exist if we use the nanoparticles as reinforcing material. One of the best combination are the MMT reinforced polyamide 6 (PA 6) matrix nanocomposites. This matching leads to advantageous mechanical and chemical properties[1-5].

The chemical aspects of nanocomposites, and also the treatment of layered silicates have been widely studied in the last decade, and their effects have become known in some instances[2,5,6]. However, the manufacturing of nanocomposites is still difficult due to the high aggregation tendency of nanoparticles. There are several methods to break up these aggregates[2]. One of them is simple melt mixing. Due to its simplicity, it is the most often used polymer processing technique for this purpose. In this case, the nanoparticles are separated apart from each other by the great shear force occurring in the polymer melt. High shear forces can be achieved, for example, by kneaders or twin-screw extruders. If melt viscosity is high, shear forces are high, too. Melt viscosity can be increased by choosing proper matrices (low melt flow index), using additives or decreasing the processing temperature. Processing temperature dependent properties of nanocomposites have been reported[2,3,6-11].

Modesti *et al.*[9] investigated the effect of processing temperatures on mechanical properties of polypropylene based nanocomposites. Two different (low and high temperature) programs were applied. The low temperature program was found to be more efficient in dispersing the nanoparticles in the matrix. The better dispersion resulted in enhanced mechanical properties of composites.

Chavarria *et al.*[10] dealt also with the effect of the processing temperatures in the case of MMT containing PA 6 matrix nanocomposites. They used two different extrusion temperatures (240 and 270 °C). They concluded that there is not significant difference between the mechanical properties of the nanocomposites as a function of extrusion temperature.

Low-density polyethylene was used as matrix material by Shah *et al.*[11]. Beside other measurements, the tensile modulus of the composites was analyzed as a function of processing

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*Corresponding author: László Mészáros, email: meszaros@pt.bme.hu temperature. The aggregation process was less pronounced in the case of lower processing temperatures, and it resulted in favourable changes in the properties of the obtained composites.

As a summary, the influence of extrusion temperature is less investigated than other processing parameters. Although this parameter was found to be relevant to the final properties of nanocomposites, not many comprehensive papers have been published. Only a few of those use more than two different processing temperatures.

Nevertheless the processing temperature can affect the mechanical properties of the composites considerably. We chose a PA 6 matrix and just 1 wt.% MMT content. In this case, the nanoparticles can influence the mechanical properties noticeably but not affect the melt properties of the polymer greatly. So the melt properties of the matrix just influence the dispersion, and the rate of layer separation. Just small differences in the mechanical properties were expected but these differences can still show the way that they are connected to the melt mixing. The aim of this paper was to investigate the role of extrusion temperature to mechanical properties. The only variant was the extrusion temperature, while all the other parameters (screw speed, screw type, filler content, etc.) were constant.

2. MATERIALS AND METHODS

Schulman, Schulamid AS6MV13F type PA 6 was used as the matrix material. Prior to use, it was dried at 80 ºC for 4 hours. Montmorillonite (MMT) was from Süd-Chemie, Nanofil® 9 type. A Brabender Plasti-Corder PL2100 type twin-screw extruder was used for blending. The screw speed was 10 rpm. The extruder device had four different independent heatable zones. The first zone was the feeding-zone; the second and the third were the melting and compressing zones, and the last was the metering zone. **Table 1** summarizes the applied five different temperature programs.

The composites contained 1 wt.% of MMT related to the polymer weight in all cases. This relatively low MMT content can be explained by the fact that in this case the MMT particles did not affect one another. The degree of the layer separation depends only on the shear forces arising in the polymer melt. After the extrusion, the samples were injection-moulded with the same parameters (pressure, mould temperature, etc.) by an Arburg Allrounder 320C 600-250 injection moulding machine. The MFI of the materials was evaluated using a Ceast modular melt flow 7027-000 type instrument at different temperatures and a load of 2.16 kg. Before the mechanical tests, the specimens were kept in 50% relative humidity for at least 48 hours. Tensile tests were performed on a Zwick Z020 universal testing machine, according to EN ISO 527. The tensile modulus was determined in the strain range of 0.1 to 0.5% by using a crosshead speed of 5 mm/min; above a strain of 0.5%, 50 mm/min was set. The flexural tests were carried out also on this machine with the following parameters: crosshead speed: 1 mm/min; gauge length: 64 mm. The ultimate flexural stresses were measured at a maximum deflection of 7 mm. The XRD measurements were made on a Philips type diffractometer with PW 1730 type generator. The scan range was: $2\Theta = 1 - 28°$, the wavelength $\lambda = 1.54186$ Å. The surface morphology was studied by a 6380LVa Scanning Electron Microscope (JEOL, Japan), after sputtering with Au/Pd alloy. The dispersion of the MMT in the PA6 matrix was assessed by transmission electron microscopy (TEM). TEM images were taken from thin section of the rubber 10 phr MMT-containing PA6 using a Leo 912 Omega microscope (Oberkochen, Germany) with an accelerator voltage of 120 kV. The thin sections (ca. 100 nm) were cryo-cut with a diamond knife at ca. -120 °C and used without staining.

3. RESULTS AND DISCUSSION

3.1 MFI Tests

From the viewpoint of the properties of the polymer melt that could influence the final mechanical properties of the nanocomposites, only the viscosity changed significantly with the conditions. **Figure 1** shows how the MFI of neat PA 6 changed as a function of extrusion temperature. Higher measuring temperatures showed higher MFI, so the viscosity of the polymer melts decreased. At 220 °C and 2.16 kg load the MFI was 0, and from our previous publication, the α crystalline peak of the PA6 is very close to 220 °C [11]. In the face of these phenomena, the polymer was extrudable because the state of the polymer melts depends not just on the temperature but also on the shear forces. This means that at the lowest temperatures, there were the highest shear forces in the melt.

3.2 Tensile Tests

The presence of 1 wt.% MMT in the system resulted in higher tensile strength values compared to those

Table 1. Processing temperatures by extruder zones

Nr. (marked)	1. zone (°C)	2. zone (°C)	3. zone (°C)	4. zone (°C)
1. (220)	215	220	220	225
2. (230)	225	230	230	235
3. (240)	235	240	240	245
4. (250)	245	250	250	255
5. (260)	255	260	260	265

of the pure matrix. In the case of the composites, the extrusion temperatures do not influence significantly the tensile strength (**Figure 2**). It has to be mentioned that the extrusion temperatures affected the properties more in the case of the pure matrix; this can be explained on the basis that higher processing temperatures caused thermal degradation of the PA 6. If we compare the two curves, at lower temperatures, the slope of the increment is equal to that we found in the case of the pure matrix. But the differences are more pronounced at higher extrusion temperatures; so there is a thermal stabilization effect of the MMT, and it seems that it works more at higher extrusion temperatures.

The elastic modulus is plotted as a function of the processing temperature in **Figure 3**. The effect of the presence of MMT was similar to what it was on the tensile strength. The modulus of the neat PA 6 was decreased significantly by increasing the processing temperature, while for the MMT containing ones it was approximately constant. The highest value was at the lowest extrusion temperature.

Figure 4 shows the strain at break of the materials. It is typical for these types of nanocomposites that the presence of MMT causes some decrease in the strain at break; this effect is also observable for our samples. However for the composites, the measured values did not differ significantly from one another, the highest value was measured in the case of the composite which was extruded at the lowest temperature.

3.3 Flexural Properties

Since the properties of the layered silicate-containing composites depend on the direction of the load, flexural tests were also performed on the materials. As expected the relatively low MMT content caused a more intensive increase in the ultimate flexural stress,

Figure 1. The MFI of the pure matrix at different temperatures

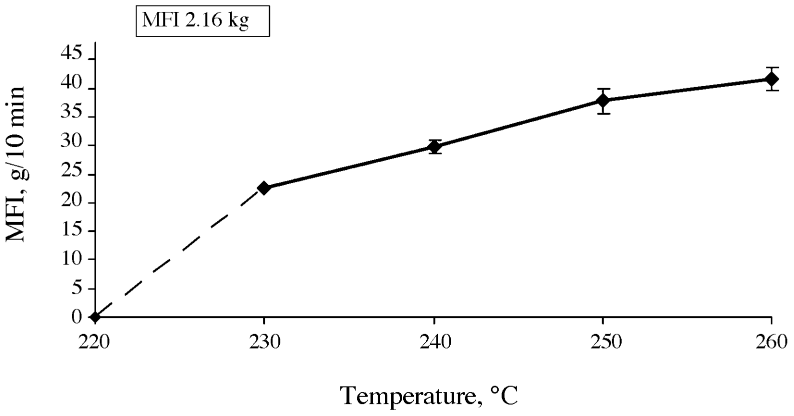


Figure 2. Tensile strength as a function of extrusion temperature

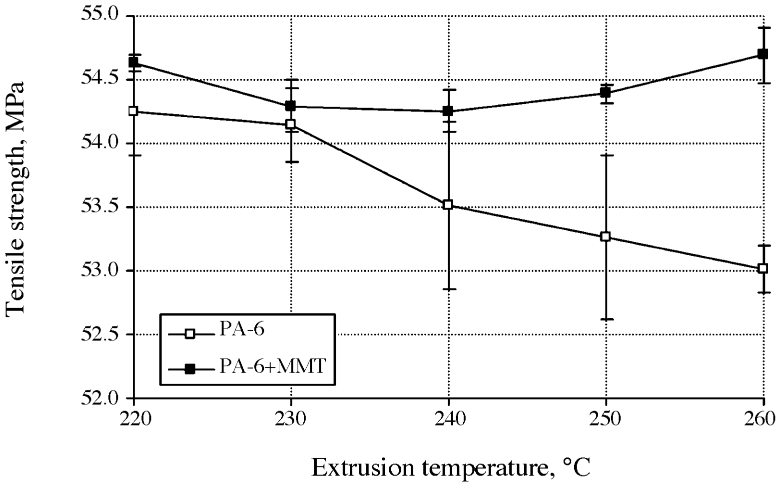


Figure 3. Tensile modulus as a function of extrusion temperature

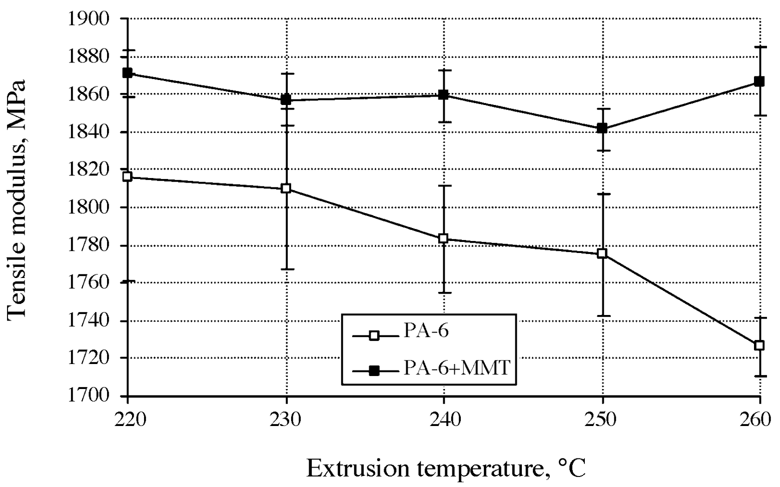


Figure 4. Strain at break as a function of extrusion temperature

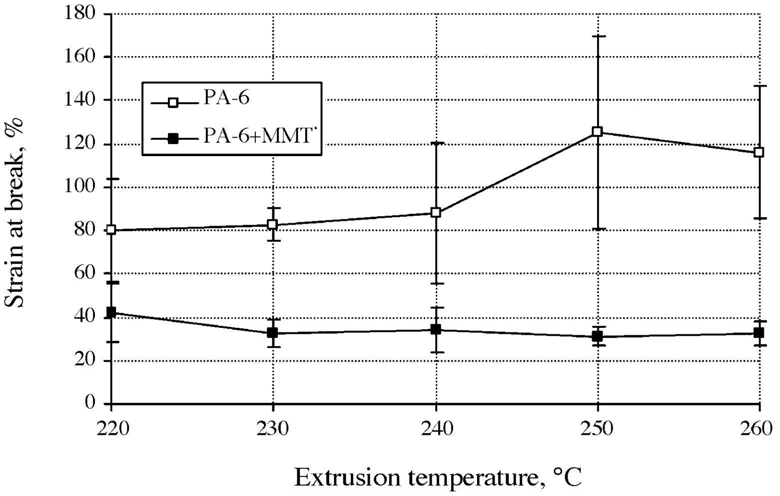


Figure 5. Ultimate flexural stress as a function of extrusion temperature

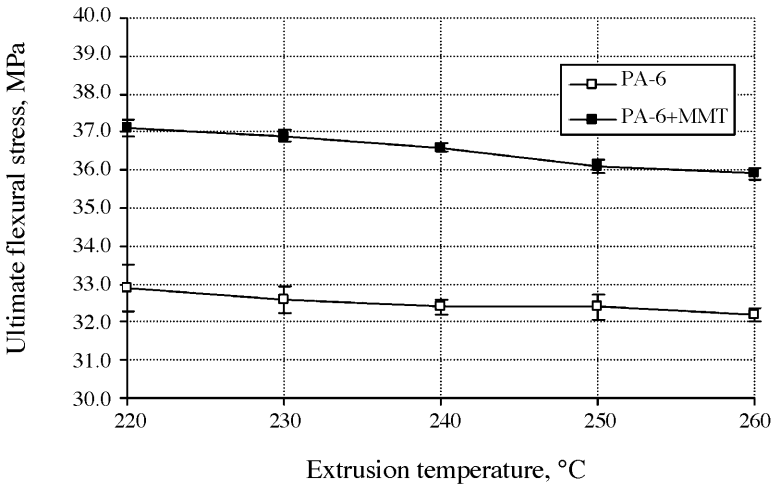
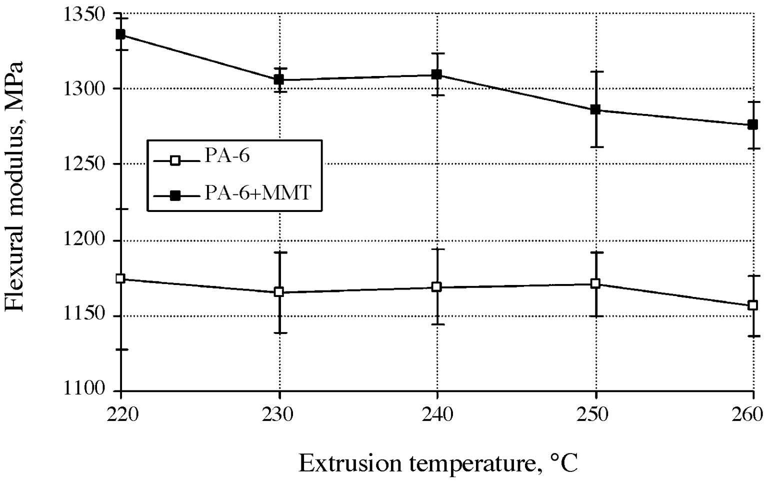


Figure 6. Flexural modulus as a function of extrusion temperature

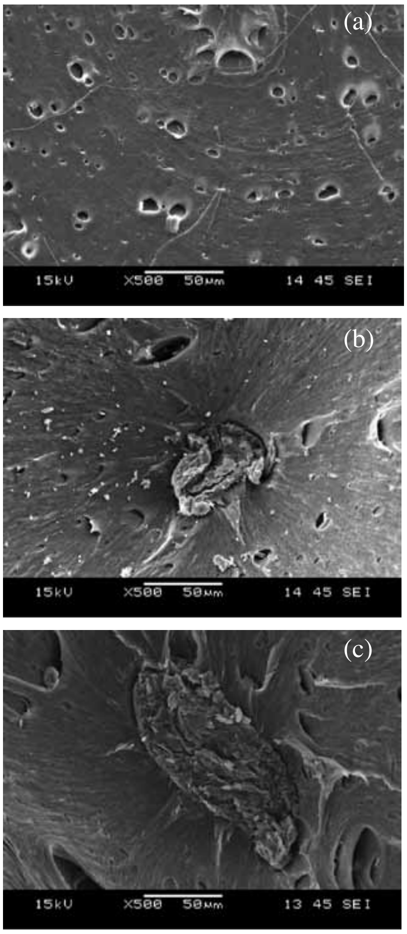


then at the tensile strength (**Figure 5**). The highest values are at the lowest processing temperature in both cases. The same phenomenon was at the flexural modulus (**Figure 6**). At the lowest temperature only 1 wt.%, MMT caused a 14% increment in the flexural modulus. It has to be mentioned that the standard deviation of the ultimate flexural stress and of the flexural modulus were less for the MMT containing samples than for the pure matrix.

3.4 SEM Pictures

The SEM pictures show that there remained some aggregates in the system in every case (**Figure 7**). These

Figure 7. SEM from the fracture surfaces after tensile tests. a) extruded at 240 °C PA6; b) 1 wt.% MMT containing sample extruded at 240 °C; 1 wt.% MMT containing sample extruded at 250 °C



aggregates were the centres of the fractures. One can also see that the connection between the matrix and the MMT was relatively good and still existed after the fracture. This good adhesion behaviour can explain why the mechanical properties were increasing.

3.5 XRD

Although the SEM pictures showed remaining aggregates, better dispersion was confirmed by the XRD measurements. In the low-angle part of the measurements, intercalated MMT was observable. According to the Bragg equation[13], the distance between the MMT layers increased from 1.99 nm to 2.27 nm.

At higher angles, it turned out that the MMT acted as a nucleating agent in the case of the γ-crystalline form of PA 6. The presence of the α phase could also be detected, although in a low amount.

3.6 TEM

For further investigation of the morphology of the composites, transmission electron microscopy (TEM) was performed in the case of the composite which was extruded at 230 °C (**Figure 10**). It can be seen that aggregates remained in the matrix, but exfoliated MMT is also observable.

4. CONCLUSIONS

In this paper, the effect of the processing temperature was investigated on the mechanical properties of MMT filled PA 6 composites. MMT filled PA 6 nanocomposites have better mechanical properties, and the clays were dispersed more at low processing temperatures.

Referring to tensile properties, the lower extrusion temperatures were found to be beneficial, which resulted in the highest elastic moduli of the composites. The SEM pictures showed

Figure 8. XRD pattern of the materials in 2Θ = 1-9° angle interval (MMT: pure montmorillonite; PA 6 (240): neat PA 6 extruded at 240 °C; PA 6+MMT (220): PA 6+1 wt.% MMT extruded at 220 °C; PA 6+MMT (260): PA 6+1 wt.% MMT extruded at 260 °C

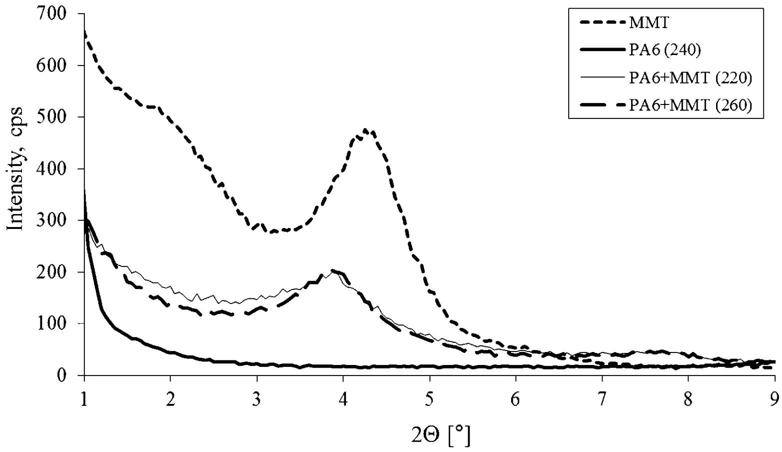


Figure 9. XRD pattern of the materials in 2Θ = 12-28° angle interval (MMT: pure montmorillonite; PA 6 (240): neat PA 6 extruded at 240 °C; PA 6+MMT (220): PA 6+1 wt.% MMT extruded at 220 °C; PA 6+MMT (260): PA 6+1 wt.% MMT extruded at 260 °C

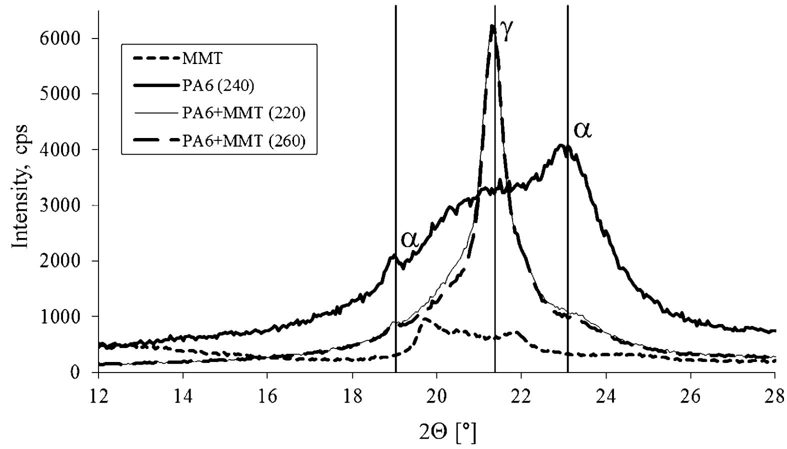
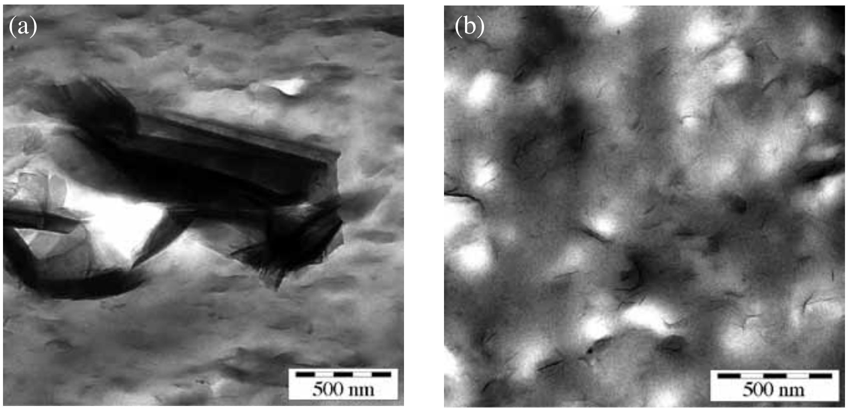


Figure 10. TEM pictures of the composites (PA 6+1 wt.% MMT extruded at 230 °C)



that there remained some aggregates in the system, but the XRD measurements and the TEM pictures proved that the layer separation was partly achieved. It turned out that just changing the extrusion temperature was not enough to achieve a well-dispersed system, but it did influence it. Based on the results, the role of the manufacturing temperatures in the final properties of nanocomposites was not negligible, which is why the choice of a proper processing temperatures is a relevant task of the process engineer.

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