TECHNICAL TRANSACTIONS | **CZASOPISMO TECHNICZNE**
CHEMISTRY | CHEMIA

1-Ch/2013

TOMASZ M. MAJKA, KRZYSZTOF PIELICHOWSKI, AGNIESZKA LESZCZYŃSKA*

COMPARISON OF THE RHEOLOGICAL PROPERTIES OF POLYAMIDE-6 AND ITS NANOCOMPOSITES WITH MONTMORILLONITE OBTAINED BY MELT INTERCALATION

PORÓWNANIE WŁAŚCIWOŚCI REOLOGICZNYCH POLIAMIDU-6 ORAZ JEGO NANOKOMPOZYTÓW Z MONTMORYLONITEM OTRZYMANYCH METODĄ DYSPERGOWANIA W STOPIE POLIMERU

Abstract

Each varying parameter which can contribute to the quality of final products plays an important role in the processing of polymer nanomaterials. Rheological properties are useful in proper formulation of new polyamide-6 (PA-6) based materials and selecting processing parameters. However, the measured rheological properties depend strongly on the sample preparation method, humidity regulation, and time-temperature history during the measurement and not least on the kind of rheometer being used. The results of the preliminary investigation show the changes in visco-elastic properties of two types of PA-6 and their nanocomposites with montmorilonite.

Keywords: *nanocomposite*, *polyamide*, *montmorillonite*, *rheology*

Streszczenie

W przetwórstwie nanomateriałów polimerowych istotną rolę odgrywa każdy zmienny parametr, który może przyczynić się do jakości otrzymanych produktów. Znajomość właściwości reologicznych polimeru może być potrzebna do poprawnego opracowania formuły kompozycji polimerowej oraz ustawienia parametrów przetwórstwa. Należy jednak podkreślić, że mierzone właściwości reologiczne zależą przede wszystkim od historii termicznej próbki, metody przygotowania, rozkładu wilgotności, temperatury oraz czasu, w jakim wykonywany jest pomiar, a także od rodzaju używanego reometru. W niniejszym artykule przedstawiono wyniki wstępnych badań właściwości lepko-sprężystych dwóch typów handlowego poliamidu-6 oraz ich nanokompozytów z montmorylonitem.

Słowa kluczowe: *nanokompozyt*, *poliamid*, *montmorylonit*, *reologia*

---

* MSc. Eng. Tomasz M. Majka, Prof. Krzysztof Pielichowski, PhD. Agnieszka Leszczyńska, Department of Chemistry and Technology of Polymers, Fsculty of Chemical Engineering and Technology, Cracow University of Technology.

1. Introduction

Polymer nanocomposites are nowadays the subject of intensive research efforts owing to their various unique properties [1–5]. In recent years, polymer/clay nanocomposites have attracted great attention both in industry and academia in achieving various excellent properties of nanocomposites compared to conventional ones. Polymer/clay nanocomposites have been obtained using different preparation methods such as melt mixing to get the intercalated or exfoliated structures in homopolymers [6].

Although polyamide-6/montmorillonite nanocomposites gathered industrial interest, only a few scientific papers on its rheological properties have been published [1–4]. In polymer processing, such an injection molding and extrusion, the rheological properties of the nanocomposites are of vital importance. A polymer network is generally visco-elastic with a complex shear modulus having both elastic and viscous components of similar magniture over a large range of frequencies. It is suggested that rheological measurements are performed at a humidity lower than 0.1% using relatively short measurement times. The rheological properties of polymer are changed by introducing the filler compound. Montmorillonite particles due to nanometric dimensions cause noticeable increase in viscosity at very low concentrations (below 5 wt%). Solid like behavior of polymer melt was reported at higher concentrations. Nanocomposite formulations generally requires high shearing and long dwell times. When producing new polymeric nanocomposite by direct melt mixing a thermomechanical degradation of polymer matrix should be considered as a cause of variation of rheological properties. In most of the scientific work on the thermal degradation of polyamide, the polymer was severely damaged at temperatures much above 300°C [5]. The solid end-product can hardly be called polyamide any more. Only a few papers describe investigations on the thermal degradation of polyamide-6 under milder conditions, i.e., at temperatures lower or not much higher than those at which the polymer is processed [4–5]. Other publications report studies at moderate temperatures, but with very long annealing times.

The purpose of the present investigation was to define the proper conditions of oscillatory measurements of PA-6/MMT nanocomposites and evaluate the effect of nanoparticles dispersed in polyamide-6 on its visco-elastic behavior.. Also it was the task of this study to find out whether processing conditions affect the rheological properties of polyamide-6 and nanocomposites with layered silicate, and whether these initial conditions are chosen appropriately.

2. Experimental

2.1. Materials

Polyamide-6 (PA-6) was purchased from Zaklady Azotowe w Tarnowie – Moscicach S.A. under the trade name Tarnamid® T27 and Tarnamid® T30.

Montmorillonite (DELLITE® 72T – trade name) was supplied by Laviosa Chimica SpA Mineraria. DELLITE® 72T is a nanoclay deriving from a naturally occurring montmorillonite especially purified and modified with a quaternary ammonium salt (dimethyl dihydrogenated tallow ammonium).

2.2. Nanocomposite samples: preparation by melt compounding

Before the preparation of nanocomposites, materials were dried in a laboratory vacuum oven. Polyamide was dried at 80°C for 3 hours. Polyamide-6 and polyamide-6/montmorillonite nanocomposite samples were prepared using a mini process line (twin co-rotating screw extruder Thermo Scientific Rheomex PTW 16/25 XL, cooling tank of ZAMAK and granulator ZAMAK G-16/325). The materials were processed at the processing temperatures shown in Table 1, at 240 rpm rotation of the screws. The sample bars in shape of plates were made using a laboratory injection molding machine ZAMAK WT 12.

Table 1

Processing parameters of polyamide-6 and polyamide-6/montmorillonite nanocomposites obtained by melt intercalation

<table>
<tr><th colspan="9">Twin co-rotating screw extruder</th></tr>
<tr><th>Flow rate [%]</th><th>Rotational speed [1/min]</th><th colspan="7">Heating zones</th></tr>
<tr><td>0,3</td><td>240</td><th>1</th><th>2</th><th>3</th><th>4</th><th>5</th><th>6</th><th>Die</th></tr>
<tr><th colspan="2">Temperature [°C]</th><td>245</td><td>245</td><td>245</td><td>250</td><td>255</td><td>250</td><td>260</td></tr>
<tr><th colspan="2">Atmospheric venting</th><td>-------</td><td>-------</td><td>-------</td><td>-------</td><td>YES</td><td>-------</td><td>-------</td></tr>
<tr><th colspan="2">Length of the zones [mm]</th><td>80</td><td>60</td><td>60</td><td>64</td><td>60</td><td>76</td><td>23</td></tr>
<tr><th colspan="2">L/D</th><td>5,00</td><td>3,75</td><td>3,75</td><td>4,00</td><td>3,75</td><td>4,75</td><td>-------</td></tr>
<tr><th colspan="9">Cooling tank</th></tr>
<tr><th colspan="3">Length of cooling surface [mm]</th><td colspan="6">1500</td></tr>
<tr><th colspan="3">Tank volume [dm³]</th><td colspan="6">27</td></tr>
<tr><th colspan="3">Height of bath [mm]</th><td colspan="6">1081</td></tr>
<tr><th colspan="3">Water temperature [°C]</th><td colspan="6">18</td></tr>
<tr><th colspan="9">Granulator</th></tr>
<tr><th colspan="3">Size of pellets [mm]</th><td colspan="6">1</td></tr>
<tr><th colspan="3">Rotational speed [1/s]</th><td colspan="6">12</td></tr>
</table>

2.3. Characterization techniques

The rheological investigations have been performed using modular advanced rheometer platform – HAAKE MARS III. The research were carried out with plate – plate sensor system. Diameter of plate was 20 mm. The plate-plate system is determined by the plate radius and the variable distance the stationary and the movable plate. This distance should be not be smaller than 0,5 mm and not larger than 3 mm as other measurements error, depending on the materials, could be experienced. In these tests, width of gap was 1,8 mm.

Nanomaterials based on plastics are non-Newtonian substances which only start flowing after being subject to shear stress i.e. after certain yield point. The yield point strongly depends on external parameters like temperature and change rate of the acting force. Practical yield point of plastics is determined taking in account the environmental conditions specific for the application. Therefore, for these materials, the measuring mode for determination of relaxation modulus named as Controlled Deformation (CD) have been chosen.

3. Results and discussion

3.1. Linear Visco-elastic Range (LVR)

In the first step the Oscillation Stress Sweep Mode (OSS) was applied in order to determine Linear Visco–elastic Range (LVR) of tested materials. The OSS is to say that the measurement parameters are set in this manner that stress and strain amplitude have a linear relationship which can be described by the following equation:

$$\tau_0 = G' \cdot \gamma_0 \tag{1}$$

A more practical way to indentify the LVR is to look for the region where the material function as e.g. *G'* is independent of shear stress value.

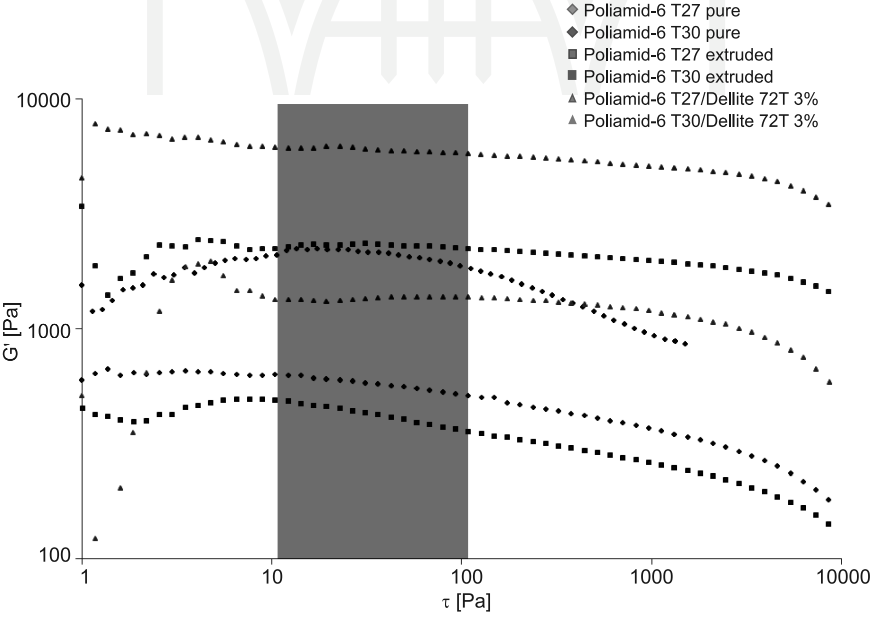

Fig. 1. The determination of material's Linear Visco-elastic Range (LVR)

Rys. 1. Wyznaczanie liniowego zakresu lepko-sprężystego (LVR)

Figure 1 shows the LVR determined for investigated samples. For four of the six samples, linear visco-elastic range was observed from 10 to 100 Pa. For Oscillation Frequency Sweep (OFS) the value of shear stress 50 Pa have been taken.

3.2. Oscilation Frequency Sweep (OFS)

Before the main test, a movable plate was heated in 232°C for 2 minutes. The distance between stationary and movable plate was 0,1 mm. Next, the samples were heated in 232°C for 5 minutes to obtain a melt. When the samples were melted, the structures were pretreated using pre-test in the range of 12–14 Hz. This procedure is necessary to remove stresses remaining in polymer sample after injection moulding and relax polymer chains.

In most cases 0.1 Hz should be a suitable for start frequency, and 14 Hz for end frequency. Lower values require a longer measurement time. Each data point has an estimated test time of the reciprocal of the actual frequency, multiplied by the number of cycles running through. Each data point requires at least 2 cycles – one pre-run and one test run repetition. In this test start frequency and end frequency were 0,01 Hz and 20 Hz respectively.

The OFS test tells about the structural conditions of the sample. Rheological behaviour at high frequencies is normally used to estimate the effect of the filler on processing properties. Low-frequency behaviour is sensitive to the structure of the percolation state of nanofillers within the composite. Fig. 2 and Fig. 3 show an increase in the storage modulus (*G′*) and loss modulus (*G″*), by the incorporation of 3wt% clay into neat Tarnamid T27 and Tarnamid T30 matrices (Fig. 2 and Fig. 3 respectively).

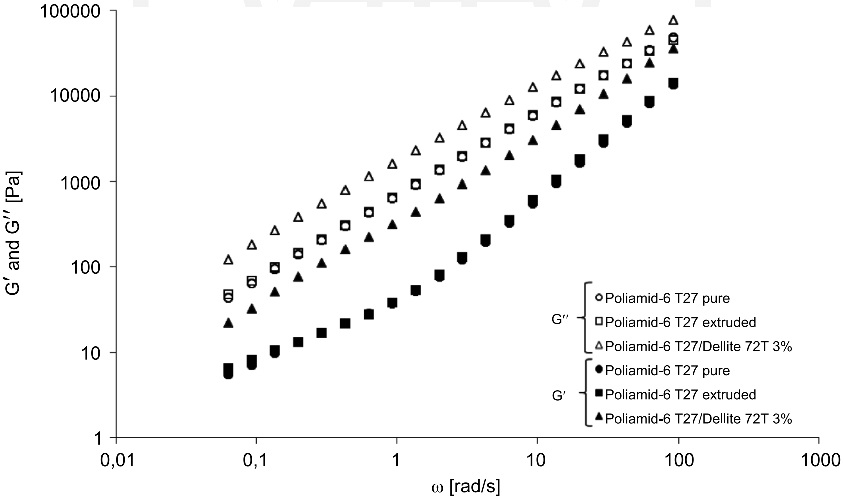

Fig. 2. Frequency dependence of *G′* and *G″* for samples based on PA-6 (T27)

Rys. 2. Zależność ω od *G′* i *G″* dla próbek wytworzonych w oparciu o PA-6 (T27)

This enhancement in the oscilation modulus is significant, in particular, at low frequencies regime. At low frequencies, the degree of dependence of G’ on the frequency was sensitive to the effect of clay on visco-elastic properties of the nanocomposites. It was reported elsewhere that when the clay loading exceeded 3wt% due to degradation process of matrix, the dependency of *G’* of PA-6 nanocomposites on the frequency increased linearly [7]. The results indicates that, when the matrix is degraded, the clay loading exceeded 3wt%, the liquid-like behavior of PA-6/MMT nanocomposites gradually changed to a pseudo-solid like behavior. As shown in Fig. 2 *G′* does not become independent on the frequency at low frequencies because plateau does not appear in the low frequencies regime starting from 0.1 rad/s. This indicates a formation of the intercalative or partial intercalative structure of nanocomposites rather than full exfoliation. The values of loss modulus and storage modulus for polyamide-6/montmorillonite nanocomposite with modified clay increase by many order of magnitude. For example at ω 0,063 rad/s, *G″* of Tarnamid T30/montmorillonite nanocomposite with 3wt% of modified clay is higher by factor about 3,3 times than extruded polymer, and about 3,9 times than pure not extruded Tarnamid T30. For Tarnamid T27/montmorillonite nanocomposite with 3wt% of modified clay, *G″* at ω 0,063 rad/s is higher by factor about 2,5 times than extruded polymer, and about 2,8 times than pure not extruded Tarnamid T27. At the same value of ω, the storage modulus of Tarnamid T30/montmorillonite nanocomposite with 3wt% of modified clay is greater by factor about 5,8 times than extruded polyamide-6, and about 7,3 times than neat polymer. Meanwhile the storage modulus of Tarnamid T27/montmorillonite nanocomposite with 3wt% of modified clay is higher around 3,4 times than extruded polyamide-6, and about 3,9 times than neat polyamide. As shown in Fig. 2 and Fig. 3, the loss modulus was dominant at all range of measurement, so at all range of ω, the viscous properties was dominant over elastic, indeed.

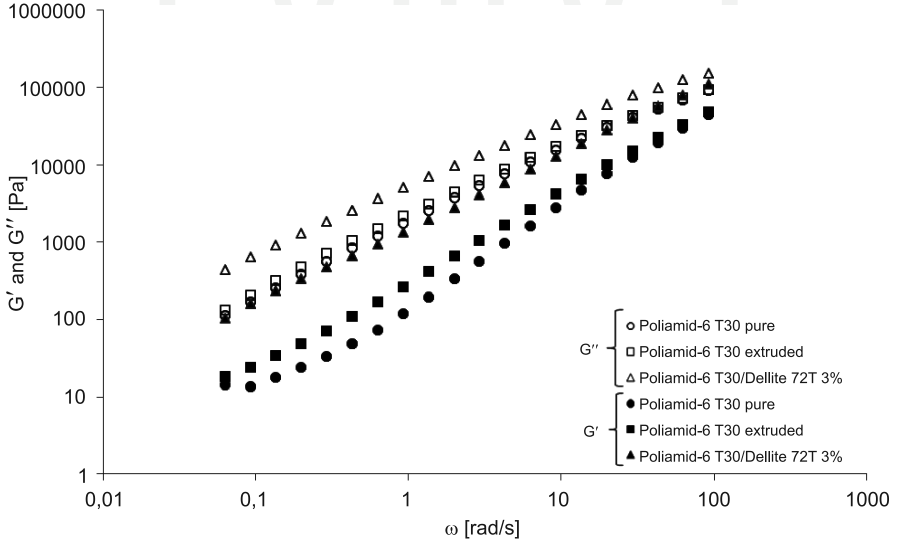

Fig. 3. Frequency dependence of *G′* and *G″* for samples based on PA-6 (T30)
Rys. 3. Zależność ω od *G′* i *G″* dla próbek wytworzonych w oparciu o PA-6 (T30)

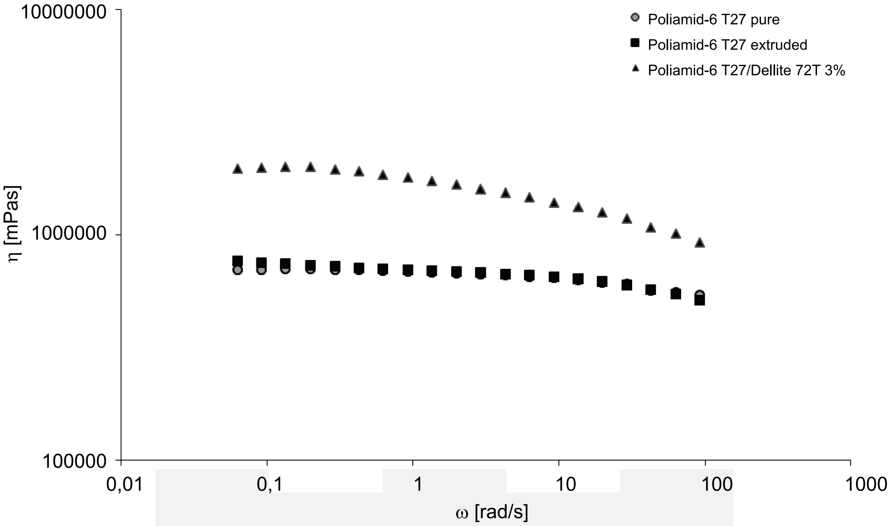

Fig. 4. Frequency dependence of viscosity for samples based on PA-6 (T27)

Rys. 4. Zależność η od ω dla próbek wytworzonych w oparciu o PA-6 (T27)

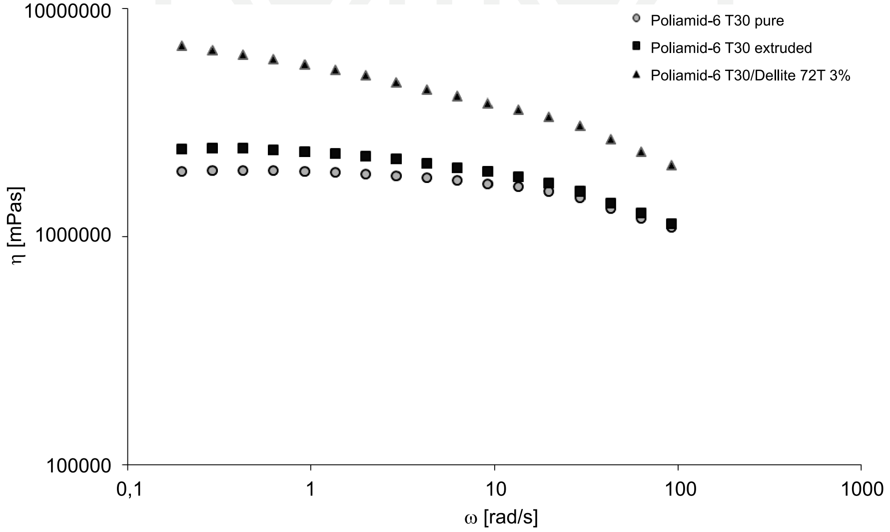

Fig. 5. Frequency dependence of viscosity for samples based on PA-6 (T30)

Rys. 5. Zależność ω od η dla próbek wytworzonych w oparciu o PA-6 (T30)

The viscosity changes with the angular frequency (ω), as can be seen from Fig. 4 and Fig. 5. As shown , the measured viscosity increases by the incorporation of montmorillonite into neat polyamide, particularly, at low frequencies regime. In rheological measurements of polymer melt the viscosity may be influenced by changes in the molecular weight of polymer, presence of gas bubbles, and the plasticizer effect. Molecular mass of tested polymer may be varied by previous processing operation as well as due to thermal decomposition of polymer during the time of rheological measurement. If the bubbles are present in melt the oscillating deformation changes the surface area of the bubbles, thereby changing the surface Gibbs energy and surface tension.

4. Conclusions

In this work, extruded polyamide, polyamide/clay nanocomposites were prepared by using a co-rotating twin screw extruder. The materials were rheologically characterized.

One can conclude that the visco-elastic properties of PA-6 and PA-6/MMT nanocomposites can be determined using the given procedure to obtain comparable and reproducible results. Measurements of rheological properties under the molten state reveal that nanofiller loading leads to an increase in the shear viscosity, the storage modulus (G') and loss modulus (G'') of nanocomposites. The viscosity increases with the incorporation of montmorillonite into neat polyamide, particularly, at low frequencies regime and may be indicative of the dispersion state of nanofiller.

This work was partially financed by the National Science Centre under decision No. DEC-2011/01/M/ST8/06834.

References

[1] Nevalainen K., Hintze C., Suihkonen R, Eteläaho P., Vuorinen J, Järvelä P., Isomäki N., *Rheological properties of melt-compounded and diluted nanocomposites of atomic-layer-deposition-coated polyamide particles*, Annual Transactions of The Nordic Rheology Society, 2008, 16, 1-9.

[2] Chow W.S., Ishak Z.A.M., Karger-Kocsis J., *Morphological and Rheological Properties of Polyamide 6/Poly(propylene)/Organoclay Nanocomposites*, Macromolecules Material Eng., 2005, 290, 122-127.

[3] Chow W.S., Ishak Z.A.M., Ishiaku U.S., Karger-Kocsis J., Apostolov A.A., *The effect of organoclay on the mechanical properties and morphology of injection-molded polyamide 6/polypropylene nanocomposites*, Journal of Applied Polymer Science, 2004, 91, 175-189.

[4] Kim J.H., Creasy T.S., *Measurement of Sintering Characteristics of Clay-Reinforced Polyamide 6 Nanocomposite*, Polymer Testing, 2004, 23, 629-636.

[5] Majka T.M., Pielichowski K, *Degradacja termiczna nanokompozytów poliamid/krzemian warstwowy*, Czasopismo Techniczne, 2011, 20, 133-142.

[6] Gonza´lez I., Eguiaza´bal J.I., Naza´bal J., *Rubber-toughened polyamide 6/clay nanocomposites*, Composites Science and Technology, 2006, 66, 1833-1843.

[7] Wu D., Zhou C., Hong Z., Mao D., Bian Z., *Study on rheological behaviour of poly(butylene terephthalate)/montmorillonite nanocomposites*, European Polymer Journal, 2005, 41, 2199-2207.