STUDY OF PP/CLOISITE MMT NANOCOMPOSITE PROPERTIES

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Abstract *This paper deals with the explanation of the preparation process for polymer nanocomposites. As a reference matrix, Mosten PND 33-301 was used, filled with montmorillonite-based nanofillers (Cloisite 20A, Cloisite 3010). A twin-screw extruder and an injection molding machine were used for the preparation of material and samples, and the relevant parameters are described in the first part of the article. Changes in the basic properties of these PNCs were tested and described in the experimental part of this article. The structures of the materials were observed by SEM microscopy.*

1 INTRODUCTION

It has been more than 50 years since physicist Richard Feynman delivered his lecture titled “There is plenty of room at the bottom” to the American Physical Society. Such a lecture is a landmark in the development of nanotechnology, as Feynman proposed the use of nanotechnology to store information as well as a series of new techniques to support this technology. From then on, the technological and scientific mastery of the nanometric scale has continually become stronger due to new research tools and theoretical and experimental developments. In this scenario, the worldwide nanotechnology market, in the next five years, is expected to be on the order of one trillion dollars. [1]

Nevertheless, only in the late 1980s was the great landmark in the development of polymer clay nanocomposites published by Toyota regarding the preparation and characterization of PA6/organophilic clay nanocomposite to be used in timing belts in cars [2-4]. This new material, with only 4.2 weight percent, showed an increase of 40% in the rupture tension, 68% in Young’s modulus and 126% in the flexural modulus, as well as an increase in the heat distortion temperature from 65°C to 152°C in comparison with the pure polymer [5]. Since then, several companies have introduced thermoplastic nanocomposites, such as polyamide and polypropylene, in automotive applications [6].

2 POLYMER NANOCOMPOSITES

A polymer composite is made by the combination of a polymer and synthetic or natural inorganic filler. Fillers are employed to improve the desired properties of the polymer or simply to reduce costs. Nowadays, the application of polymer composites as engineering materials has become state-of-the-art. Polymer composites with improved mechanical, thermal, barrier and fire retardancy properties are widely used in very large quantities in a variety of applications. Application of conventional fillers such as talc, calcium carbonate, fibers, etc., often requires the use of a large amount of filler in the polymer matrix to produce any significant improvements in

the composite properties, and which may result in some other undesired properties such as brittleness or loss of opacity. [7]

A polymer nanocomposite is defined as a composite material in which at least one dimension of at least one component is on the nanometer size scale (< 100 nm). In recent years the characterization and control of structures on the nanoscale has been studied, investigated and exploited by learning from our natural surroundings. Consequently, nanocomposite technology has emerged as an efficient and powerful strategy for upgrading the structural and functional properties of synthetic polymers. This is the new nanocomposite science, that was started by the Toyota report [8] on the superior improvements in the properties of nylon-6 by preparation of exfoliated nylon-6/clay nanocomposites and has been continued by more recent studies on the use in polymeric composites of carbon nanotubes, carbon nanofillers, exfoliated graphite, nanocrystalline metals and fibers modified with inorganic fillers. [9]

3 EXPERIMENTAL PART

The aim of this paper is to present the possibilities for manufacturing PP/MMT nanocomposites and describe the changes in the properties of polypropylene Mosten PND 33-301. For this experiment, montmorillonite nanofillers were chosen:

- Cloisite 20A - Montmorillonite modified with a quaternary ammonium salt. It improves various physical properties of plastics, such as reinforcement, HDT, CLTE and barrier properties, modified by hydrogenated tallow (2M2HT ~65% C18; ~30% C16; ~5% C14), Anion: Chloride,
- Cloisite 3010 - is bentonite treated with a surfactant (supplied by Sud-Chemie); the surface modifier used is dimethyl benzyl hydrogenated tallow alkyl ammonium.

3.1 Preparation of polymer nanocomposite

A concentrate containing 10% nanofiller in the PP polymer matrix was prepared at the Institute of Engineering Polymeric Materials and Colors in Toruń, Poland (Instytut Inżynierii Materiałów Polimerowych i Barwników, Toruń). The processing of materials was performed in a Buhler twin-screw extruder BTSK 20/40D, shown in Figure 1. The technical parameters of the extruder are given in Table 1. The final processing characteristics are shown in Table 2.

Figure 1: Buhler BTSK 20/40D twin-screw extruder, 1- drive, 2- longitudinal valve, 3- segmental screws, 4- vent points

Table 1: Buhler BTSK 20/40D twin-screw extruder parameters

Screw diameter	20mm	Max. power	4kW
Channel depth	3,75mm	Max. speed	600rpm
Length of cylinder	800mm	Maximum column temperature	350°C
Length L	40D	Type of cylinder wall cooling	water

Table 2: Final processing parameters of PP/MMT preparation process

Screw configuration	K3
Torque	32Nn
Input power	0,47kW
Melt temperature in the extruder head	275°C
Melt pressure in the extruder head	4bar
Screw speed	250 rpm
Granulate cooling method	air
Temperature ranges	270-280-280-270-260°C
Performance of feeder	10kg/hour

Samples for tensile tests were molded by an ARBURG Allrounder 370S injection molding machine in an experimental mold manufactured at KTaM, TUKE under ISO standards. Each material was blended at the three-volume concentrations of 2%, 4% and 6% of nanofiller and then pre-dried in a vacuum oven according to the technological conditions.

3.2 Methodology of experiments

The mechanical properties of the prepared samples were tested on a TiraTest 2300 tensile test machine under the STN ISO 527-1 standard. Before all tests, samples were before conditioned according to the EN ISO 291 standard. The impact strength of the material was tested using a Charpy impact hammer under the EN ISO 179-1 standard. TGA and DSC analyses were performed on a TA Instruments Q600 SDT under EN ISO 11358.

Table 3: Labeling of used materials for tests

Material	Label	Material	Label
Mosten PND 33-301	PP	PP + 2% CLOISITE SE 3010	B2
PP + 2% CLOISITE 20A	A2	PP + 4% CLOISITE SE 3010	B4
PP + 4% CLOISITE 20A	A4	PP + 6% CLOISITE SE 3010	B6
PP + 6% CLOISITE 20A	A6		

3.3 Assessment of the properties of polypropylene / clay nanocomposites

Based on the measured values, we can conclude that the addition of nanofiller Cloisite 20A or Cloisite SE 3010 into the polymer matrix had no positive effect on tensile strength and elongation of the material. The addition of 6% of Cloisite 20A caused a decrease in tensile strength of 17.1%. Also, adding a small amount of filler Cloisite 20A at a rate of 2% caused a

reduction in the yield strength of the material by 4.7%. Material with 6% of organically modified Cloisite SE 3010 showed a decrease in tensile strength of 23.7%, as seen in Figure 2.

Figure 2: Tensile strength of materials PP/A and PP/B

Figure 3: Impact strength of materials PP/A and PP/B

Study of the influence of the addition of the Cloisite fillers on the resulting impact strength obtained positive results. Addition of nanofiller Cloisite 20A at rate of 6% achieved an increase in the impact strength of the material by 14.6% from the original 77.4 kJ.m⁻² to 88.7 kJ.m⁻². The material containing 6% filler Cloisite SE 3010 showed an increase in impact strength of 16.9%. Then the hardness of the samples was measured using a Mitutoyo HARDMATIC Type D according to ISO standard 868 and values are illustrated on Figure 4. From the measurements it is clear that the addition of nanofillers in the base material did not have a significant effect on the hardness of the material.

Figure 4: Measured hardness of tested materials

Figure 5: DSC analysis of PP/Cloisite 20A material

The DSC analysis in Figure 5 shows that heating the tested materials to the melting temperature, T_m , shows deviations from the results for the non-composite material. Temperature T_m for virgin polypropylene was achieved in a heating time of 7.93 min, while for the PP/6% Cloisite 20A this temperature was achieved after 8.35 min, which implies an increase in resistance to elevated temperatures and also the possibility of exposure of the material to higher temperatures for longer times without melting.

Table 4: DSC/TGA analysis of material PP/Cloisite 20A

Material	Weight reduction	Temperature T _m	Heat flow
PP	+0,1539%	176,87°C	75,52J/g
A2	-0,1582%	177,51°C	75,52J/g
A4	-0,08317%	176,48°C	75,06J/g
A6	-0,09538%	180,05°C	76,99J/g

To better study the structures of the prepared materials, SEM microscope was used. SEM images of material A6 (Figure 6 and Figure 8) show that the exfoliation of the filler was not performed sufficiently. There are visible clumps of filler, undigested filler and also visible air bubbles in the material, on average 1-2µm diameter. These bubbles may result from the treatment of the material, or as residual traces of moisture in the material. In the case of clusters of already fragmented filler, the probable cause is the inappropriateness of the compatibilizer, quaternary ammonium salt. For further investigation, the matrix/filler will be supplied with a compatibilizer to increase the hydrophilicity of polypropylene. The images in Figure 7 and Figure 9 show the structure of PP / Cloisite SE 3010, where clumps of filler are clearly visible in the matrix. The clumps of filler are uniformly dispersed within the base matrix. Pictured are clearly visible clumps of filler and also turgidity after clumping.

Figure 6: Material PP/A6

Figure 7: Material PP/B6

Figure 8: Material PP/A6

Figure 9: Material PP/B6

4 CONCLUSION

This contribution deals with the study of the influence of montmorillonite in a polypropylene matrix. As it was pointed out in the experimental part of this article, the preparation of polymer nanocomposites is difficult and can lead to the preparation of microcomposites when adhesion forces between the matrix and the filler are not strong enough. In our case, some of the properties were positively influenced, but properties like tensile strength decreased. This decrease was then explained using SEM images, where visible clumps of filler and undigested filler were found. Our next goal is to supply the matrix/filler with compatibilizer to increase the hydrophilicity of polypropylene.

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REFERENCES

- [1] Anadão, P.: Nanocomposites - New Trends and Developments, Intech, 2012, ISBN 978-953-51-0762-0
- [2] Okada, A., et al.: Composite material and process for manufacturing same. Kabushiki Kaisha Toyota Chou Kenkyusho., 1988, US Patent 4739007.
- [3] Kawasumi, M., et al.: Process for producing composite material. .Kabushiki Kaisha Toyota Chuo Kenkyusho, 1989, US Patent 4810734
- [4] Pavlidou, S., & Papaspyrides, C. D.: A review on polymer-layered silicate nanocomposite. Progress in Polymer Science ., 33-1119, 2008
- [5] Nguyen, Q. T., & Baird, D. G.: Preparation of polymer-clay nanocomposites and their properties. Advances in Polymer Technology, 25-270, 2006
- [6] Patterson, T.: Nanocomposites- our revolutionary breakthrough. . In: 4th World Congress in Nanocomposites San Francisco, USA, 2004
- [7] Zhang, Z., Friedrich, K.: Artificial neural networks applied to polymer composites: a review. Composites Science and Technology, Vol. 63, 2029-2044, 2003
- [8] Usuki, A.; Kawasumi, M.; Kojima, Y.; Okada, A.; Kurauchi, T. & Kamigaito, O. J.: Swelling behavior of montmorillonite cation exchanged for V-amino acids by Ecaprolactam. Mater. Res., Vol. 8, No.5, 1174, 1993
- [9] Paul, D.R. & Robeson L.M.: Polymer nanotechnology: Nanocomposites. Polymer, Vol. 49, 3187-3204, 2008