Tomas Bata University in Zlín
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English Doctoral Thesis

The study of using of nanofillers in polyolefinic matrix

Studium možností použití nanoplniv v polyolefinické matrici

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OUTLINE

ABSTRACT

PhD thesis was focus on problematic of polyolefine/clay nanocomposites – preparation of (nano) composites and properties of prepared nanocomposites. Two polymer matrixes were used for study. Different types of (nano) fillers were used. (Nano) composites were prepared at different conditions (time of compounding, speed of rotations). Changes of mechanical and barrier properties were study. Influence of conditions to properties was study too.

First part of research is focus on barrier properties of PE and PP nanocomposites. Second part was focus on use of nanofiller in PP matrix, the following research is focused on study of influence of conditions of preparation to mechanical properties of (nano) composites, and application of mathematic model for evaluation of mechanical properties.

It was obtained that polypropylene/clay nanocomposites had better barrier properties than polyethylene/clay nanocomposites. The following study shows that all prepared (nano) composites have higher mechanical properties in comparison with unfilled polymer matrix. The optimal condition of preparation was determined by using of 3D graph. New mathematic model which was used for description of mechanical properties very good describes measured data.

KEY WODRS

nanocomposite, mechanical properties, barrier properties, mathematic model

ABSTRAKT

Doktorská práce byla zaměřena na problematiku polyolefin/jíl nanokompozity – přípravu (nano) kompozitů a vlastnosti připravených nanokompozitů. Dvě polymerní matrice byly použity pro přípravu. Různé typy (nano) plniva byly použity. (Nano) kompozity byly připraveny při rozdílných podmínkách přípravy (doba míchání, rychlost míchání). Změny mechanických a bariérových vlastností byly studovány. Vliv podmínek přípravy na vlastnosti (nano) kompozitů byl studován taktéž.

První část výzkumu se zaměřuje na bariérové vlastnosti PE a PP nanokompozitů. Druhá část se zaměřuje na použití rozdílných druhů nanoplniva v PP matrici, následující výzkum se zaměřuje na studium vlivu podmínek přípravy na mechanické vlastnosti (nano) kompozitů a využití matematického modelu pro hodnocení mechanických vlastností.

Bylo zjištěno, že polypropylen/jíl nanokompozity měli lepší bariérové vlastnosti než polyetylen/jíl nanokompozity. Následující studie ukázala, že všechny připraveny (nano) kompozity měly vyšší mechanické vlastnosti než neplněná polymerní matrice. Optimální podmínky přípravy byly určeny pomocí 3D grafů. Nový matematický model, který byl použitý pro hodnocení mechanických vlastností, velmi dobře popisuje naměřené hodnoty.

KLÍČOVÁ SLOVA

nanokompozity, mechanické vlastnosti, bariérové vlastnosti, matematický model

1. INTRODUCTION

Nanocomposites are materials which study had been started in 90th years of last century. The reasons of study of nanocomposites are their unique properties in comparison with a pure polymer matrix.

Nanocomposites are composed of polymer matrix and nanofiller. Polymer matrix can be based on polypropylene, polyethylene, polyamide, polystyrene [1-8]. Montmorillonite, saponite, bentonnite are clay minerals which are used like nanofillers [7, 9-17].

Studies showed that the use of small concentration of nanofiller improved mechanical properties, flammability or gas permeability [18-24].

The process of preparation is very complicated. The complication of preparation is caused by different properties of polymer matrix and nanofiller. This PhD work was focused to the problematic of preparation of nanocomposites and influence of condition of preparation to the final properties of nanocomposites.

Different types of nanofillers and fillers were used for preparation of (nano)composites. The conditions of preparation were different too. All prepared (nano)composites were study from morphological view and also from mechanical properties too. Mathematic model was used for characterization of prepared nanocomposites.

Gas permeability was study due to of theory that contain of nanofiller causes decrease of gas permeability. Lower gas permeability is very necessary in food packaging.

2. POLYMER MATRIX

Polymer matrix is one of part of nanocomposites. In our study both type of polymer matrixes were used: polyethylene and polypropylene. This chapter describes properties, use and technology of use polymer materials.

Polyolefinic materials (polyethylene and polypropylene) were used in our work. Polyolefinic are materials which contained double bond in polymeric chains. Homopolymers and copolymer of polyethylene are the most important types of polyolefins.

2.1. POLYETHYLENE

Polyethylene (PE) is called homopolymer of ethylene and their copolymers which contain less than 10 wt. % of co-monomer. The properties of polyethylene are based on molecular weight, spatial of monomer in chain of macromolecule and degree of crystallinity. All initiate properties are depended on preparation of PE.

The first polyethylene was prepared in 1935. The polyethylene was prepared under pressure 100-400 MPa at the temperature 150-300°C. A small concentration of oxide was used as initiator.

The preparation of PE was modified. Today, PE is prepared by suspension, emulsion polymerization. The products have an average molecular weight between 15 000 and 40 000, melting temperature from 105°C to 120°C and the chains of macromolecular are branched. Classification of polymer can be from following perspectives: structure, density and preparation. [25-26]

Polyethylene is classified from the structure to:

- linear polyethylene,

- branched polyethylene.

Classification of polyethylene based on density:

- low density polyethylene (LD-PE),
- high density polyethylene (HD-PE),
- ultra high molecular weight (UHMW-PE),
- linear low density polyethylene (LLD-PE),
- medium density polyethylene (MD-PE).

The last classification is from the view of a preparation. These types are high-pressure polyethylene and low-pressure polyethylene.

The chemical resistance is based on degree of crystallinity (higher degree of crystallinity causes higher resistance of PE). Polyethylene is resistant to water, non oxide chemicals at normal temperature. However, the resistance to non polar solvents is depended on temperature. [25-26]

Polyethylene is white and transparent at normal temperature. The transparency increases in degree of branch of macromolecules an theirs molecular weight.

Polyethylene is processed by injection moulding and extrusion. Application of PE is very various: PE materials are used for preparation of packaging, house wares. PE is used in medical science too. [25-26]

2.2. POLYPROPYLENE

Polypropylene (PP) is prepared by radical or cationic polymerization of propylene. This type of polypropylene is low molecular ataxic product. Guilio Natta discovered that the presence

of Ziegler catalyst caused the preparation of high molecular polypropylene which is very crystalline isotactic polypropylene. [27-29]

The structure of polypropylene is non polar. The degree of crystallinity of polypropylene is from 60 % to 75 %. This fact causes that polypropylene is non transparent polymeric material in comparison with polyethylene. Melting temperature of isotactic polypropylene is 176°C; however, the commercial products have the melting temperature from 160°C to 170°C. Today, polypropylene is produce to low-pressure polymerization. [27-29]

The properties of polypropylene are different in comparison with polyethylene. The following properties - density of polypropylene, cold-resistant, oxidation resistant, weather-resistant, are lower than polyethylene. On the other hand, strength, hardness and abrasionproof are higher in comparison with PE. [27-29]

Polyethylene is processed by injection moulding and extrusion. Low gas permeability and moisture vapour transmission are the reason of application of polypropylene as packaging materials. Components of machine, automotive, consumer industry are the other areas of application of polypropylene. The next application of polypropylene is preparation of fibers. The prerequisite is that the index of isotactic is higher than 90 %. [27-29]

3. CLAY MINERALS

Clay minerals are group of minerals which are used for preparation of nanofiller. The definition of clay is following: *clays are mixed nature material which is primary compound from fineness of grain minerals. Generally, clay is plastic at adequate contain of water. Clays indurate by dried or calcination.* This definition was defined by Guggenheima and Martina from 1995. [30]

The definition of clay is connected to clay minerals. Clay minerals are distinguished by two groups:

- ✓ *Clay minerals* – all classes of phylosilicates, minerals of class allophane, some hydroxide, oxy-hydroxide and oxide which contribute the plasticity to clay minerals and clay minerals can be dried or calcinated. In contrast of phylosilicates, the other minerals are minority part of clay minerals.
- ✓ *Accompanying minerals* – are minerals which can contain clay minerals; however, these minerals are not in the previously class of clay minerals. [30]
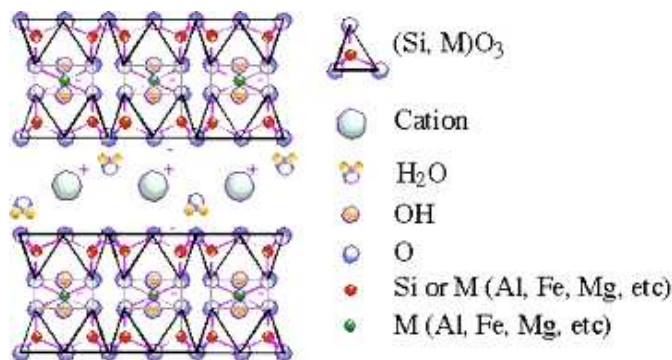

Fig. 1 The basic structure of clay minerals [31]

3.1.   PHYLOSILICATES

Tetrahedrite [TO_4] and octahedrite [MA_6] are classified as basic co-ordinate polyhedron for stablishment of structure of phylosilicate. The central cation of tetrahedrite is usually represented by Si^{+4}. Al^{3+}, Fe^{3+} or Ge^3 are the other types of central cations of tetrahedrite.

The central cations of octahedrite are Al^{3+}, Fe^{3+} Fe^{2+}, Mg^{2+}, Mn^{2+}, Ca^{2+} or Li^+. The sign of anion A is used due to of possibility of presence of anion of octahedrite O, OH, or F in sheet silicates. [30]

a) b)
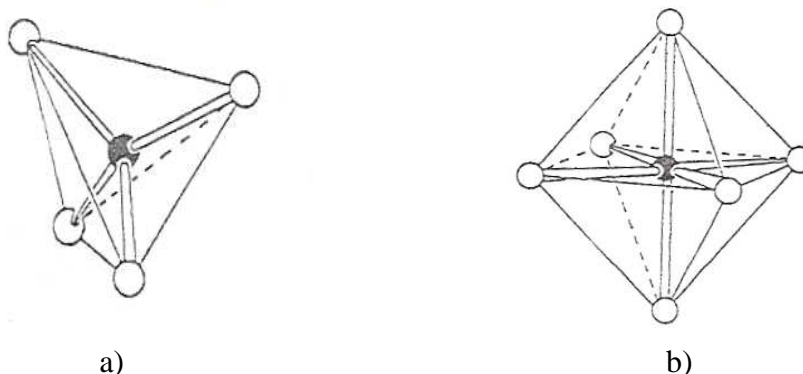
Fig. 2 The chart of a) tetrahedrite and b) octahedrite. The black points represent central cation and white points represent anion. [30]

3.2. MONTMORILLONITE

The name of montmorillonite is derived from the deposit Montmorillon which is in France. Montmorillonite is clay mineral which is classified in class of dioctahedral smectite. Montmorillonite is hydrophilic clay mineral. The structure of montmorillonite is 2:1 – two silicon tetrahedral layers and one aluminum octahedral layer. Fig. X shows the structure of montmorillonite. [30]
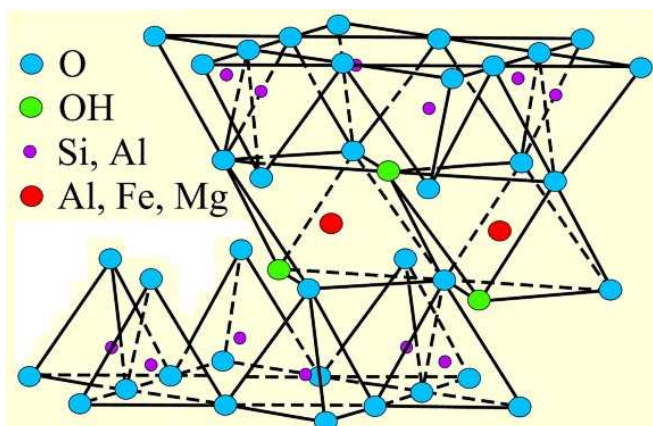
Fig. 3 Structure of montmorillonite [32]

The tetrahedral position of montmorillonite have not got any or very low degree of substitution of Al^{3+} for Si^{4+} due to the charge of 2:1 layer is caused by octahedral substitution. [30]

The chemical formula of montmorillonite is $(Na,Ca)_{0.33}(Al,Mg)_2Si_4O_{10}(OH)_2 \cdot n(H_2O)$. The colour of montmorillonite is usually white or grey but sometimes is pink. The hardness of montmorillonite is 1 or 2 and the density of montmorillonite is 2350 $kg.m^{-3}$. The main property of montmorillonite is possibility of acceptance or elimination of water depending on surrounding condition. [30]

Fig. 4 Montmorillonite [34-35]

4. CALCIUM CARBONATE

Calcium carbonate is the next type of filler which is used for preparation of composite materials. Low price and high number of deposit of calcium carbonate are the main reason why calcium carbonate is used as filler.

The chemical formula of calcium carbonate is $CaCO_3$. Colour of calcium carbonate is very variable: from white to black. The hardness of calcium carbonate is 3 and the density is 2380 $kg.m^{-3}$.

Calcium carbonate is commonly used as filler in polymeric industry. The main reason is very easy – the price of filler is lower in comparison with nanofiller. The next argument is possibility to polypropylene or polyethylene matrixes.

In polymer industry, two types of calcium carbonate can be used. Micronized calcium carbonate is the first type, micro coagulate calcium carbonate is the second type. [36-40]

5. COMPOUNDING

Compounding is a technological process of nanocomposite preparation. The compounding of only pure polymer matrix and clay mineral is not possible due to different polarity of polymer matrix and a nature clay mineral. The finally product will be separated into two different phases because the effect will be the same as a mixing of water and oil.

Fig. 5 shows levels of dispergation of clay mineral in polymer matrix. Fig 5 shows two different phases' clay mineral and polymeric material. Fig. 5 a) shows two different phases – polymer and nanofiller. Polymer is not intercalated between layers of nanofiller. As it can be seen from Fig. 5 b), polymeric material is intercalated between layers of clay minerals in second level. The layers are delayed but the bonds are not cut. Exfoliation is the highest level of dispergation of clay mineral layers in polymer and this situation is represented by Fig 5 c). The attractive forces are cut and layers of clay minerals are dispersed in materials. [41-43]
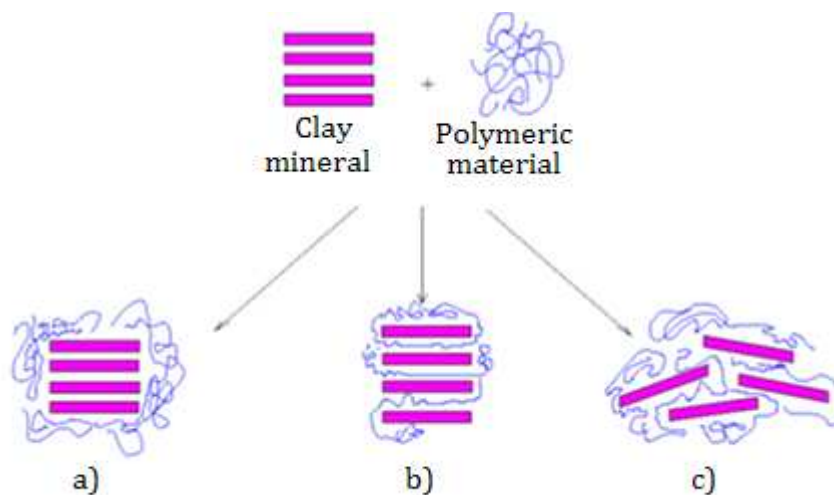
Fig. 5 Levels of dispergation of clay mineral in polymer matrix

Maleic anhydride polymer is used in order to increase the compatibility between polymeric materials and clay mineral. The concentration cannot be higher than 5 wt. % due to a change of mechanical properties. [44-48]

Type of compounding device, conditions of preparation, used materials can influence final level of distribution and dispergation of clay mineral in polymer matrix.

The Japanese scientists prepared nanocomposites in two steps as first. The first step is based on compounding of maleated polypropylene and clay mineral. This step is necessary for better compatibility between polymer matrix and nanofiller. The second step is the compounding of polymer matrix and blend.

The suitable compounding device is very important for preparation. Better distribution and dispergation were reached when the nanocomposites were prepared by two screw extruder or kneader. [49]

The conditions of preparation can influence final properties of nanocomposites too. The temperature of processing must be higher than melting temperature; however, there is the possibility of degradation of polymeric materials or nanofiller modifier. This is the reason why the preparation of blend or nanocomposite is very complicated. Time of compounding and speed of rotation of kneaders can influence final properties of nanocomposites too. [41]

6. AIMS OF WORK

The preparation of nanocomposites is difficult. Polymeric materials, nanofillers, compounding device and condition of preparation can influence the properties of nanocomposites. The type of nanofillers and their concentration can influence final properties of nanocomposites.

PhD study was focused on the choose of optimal polymeric materials and new types of nanofillers. Polyethylene and polypropylene were used as two materials in the first phase of work. The data from mechanical tests and morphology leads to the polypropylene using in the following study.

PhD study is focused on following aims:

- Preparation of packaging materials based on polyolefin/clay, study of morphology, mechanical and barrier properties

- Usu of kneader Brabender for preparation of nanocomposites at variable condition of preparation and concentration of nanofiller

- Comparison of commercial nanofillers and composites filled with micronized calcium. Composites prepared at the same conditions

- Application of mathematic model for description of mechanical properties of prepared nanocomposites

- Determination of optimal concentration of nanofiller, compounding device and condition of preparation

BIBLIOGRAPHY

1.   ZHONG, Yang, et al. Mechanical and Oxygen Barrier Properties of Organoclay-Polyethylene Nanocomposites Films. *Polymer Engineering and Science* [online]. 2007.

2.   SHAOFENG , Wang, et al. Preparation of Polyethylene-Clay Nanocomposites Directly from Na Montmorillonite by a Melt Intercalation Method. *Journal of Applied Polymer Science* [online]. 2003, vol. 89.

3.   NAM, Pham Hoai, et al. A hierarchal structure and properties of intercalated polypropylene/clay nanocomposites. *Polymer* [online]. 2001, vol. 42.

4.   SVOBODA, Petr, et al. Morphology and Mechanical Properties of Polypropylene/Organoclay Nanocomposites. *Journal of Applied Polymer Science* [online]. 2001, vol. 85.

5.   VLASVELD, D.N.P., et al. Analysis of the modulus of polyamide-6 silicate nanocomposites using moisture controlled variation of the matrix properties. *Polymer* [online]. 2005, vol. 46.

6.   FORNES, T.D., et al. Effect of organoclay structure on nylon 6 nanocomposite morphology and properties. *Polymer* [online]. 2005, vol. 46.

7.   MORGAN, Alexander B., CHU, Lih-Long, HARRIS, Joseph D. A flammability performance comparison between synthetic and natural clays in polystyrene nanocomposites. *Fire and Materials* [online]. 2005, vol. 29.

8.   NAZARENKO, S., et al. Gas barrier of Polystyrene Montmorillonite Clay Nanocomposites: Effect of Mineral Layer Aggregation. *Fire and Materials* [online]. 2005, vol. 29.

9.   KATO, Makato, USUKI, Arimitsu, OKADA, Akane. Synthesis of Polypropylene Oligomer-Clay Intercalation Compounds. *Journal of Applied Polymer Science* [online]. 1997, vol. 66.

10.   TJONG, S. C., MENG, Y. Z. Impact-Modified Polypropylene/Vermiculite Nanocomposites. *Journal of Polymer Science: Part B: Polymer Physics* [online]. 2003, vol. 41.

11.   TJONG, S. C., MENG, Y. Z., XU, Y. Preparation and Properties of Polyamide6/Polypropylene-Vermiculite Nanocomposite/Polyamide 6 Alloys. *Journal of Applied Polymer Science* [online]. 2002, vol. 86.

12.   KU, Bon-Cheol, et al. Cross-linked Multilayer Polymer-Clay Nanocomposites and Permeability Properties. *Journal of Macromolecular Science : Part A: Pure and Applied Chemistry* [online]. 2004.

13.   WU, Tzong-Ming, LIEN, Yi-Hsin, HSU, Sung-Fu. Isothermal Crystallization Kinetics and Melting Behavior of Nylon/Saponite and Nylon/montmorillonite Nanocomposites. *Journal of Applied Polymer Science* [online]. 2004, vol. 94.

14.   VAN OLPHEN, H. (1977). Clay Colloid Chemistry, Wiley, New York.

15.   REICHERT, P., NITZ, H., KLINKE, S., BRANDSCH, R., THOMANN, R. and MULHAUPT, R. Poly(propylene)/Organoclay Nanocomposite Formation: Influence of Compatibilizer Functionality and Organoclay Modification, *Macromol. Mater. Eng.,* 275: 8–17. 2000.

16.   VAIA, R.A., TEUKOLSKY, R.K. and GIANNELIS, E.P. Interlayer Structure and Molecular Enviroment of Alkylammonium Layered Silicates, *Chem. Mater.,* 6: 1017–1022. 1994.

17.   MERINSKA, D. et al., Structure Analysis of Montmorillonite Intercalated With Cetylpyridinium and Cetyltrimethylammonium: Molecular Simulations and XRD Analysis, *J. Colloid Interface Sci.*, 236(1): 127–131. 2001

18.   GILMAN, J.W., KASHIWAGI, T. and LICHTENHAN, J.D. Nanocomposites: A Revolutionary New Flame Retardant Approach, *SAMPE J*., 33(4): 40–46. 1997.

19.   GILMAN, J.W. Flammability and Thermal Stability Studies of Polymer Layered-Silicate (clay) Nanocomposites, Appl. Clay Sci., 15(1–2): 31–49. 1999.

20.   WANG, S.F., HU, Y., ZONG, R.W., TANG, Y., CHEN, Z.Y. and FAN, W.C. Preparation and Characterization of Flame Retardant ABS/Montmorillonite Nanocomposite, *Appl. Clay Sci*., 25(1–2): 49–55. 2004.

21.   QIN, H.L., ZHANG, S.M., ZHAO, C.G., HU, G.J. and YANG, M.S. Flame Retardant Mechanism of Polymer/Clay Nanocomposites Based on Polypropylene, Polymer, 46(19):8386–8395. 2005.

22.   DROZDOV, A.D., CHRISTIANSEN, J.D., GUPTA, R.K. and SHAH A.P. Model for Anomalous Moisture Diffusion Through a Polymer-Clay Nanocomposite, J. Polym. Sci., Part B: Polym. Phys., 41(5): 476–492. 2003.

23.   GORRASI, G., TAMMARO, L., VITTORIA, V., PAUL, M.A., AEXANDRE, M. and DUBOIS, P. Transport Properties of Water Vapor in Polylactide/Montmorillonite Nanocomposites, J. Macromol. Sci. Part B Phys., B43(3): 565–575. 2004.

24.   CHAIKO, D.J. and LEYVA, A.A. Thermal Transitions and Barrier Properties of Olefinic Nanocomposites, Chem. Mater., 17(1): 13–19. 2005.

25.   DOLEŽAL , V. *Plastické hmoty*. [s.l.] : SNTL Praha, 1965.

26.   DUCHÁČEK, V. *Polymery: výroba, vlastnosti, zpracování, použití*. [s.l.] : VŠCHT Praha, 1995.

27.   ŠTĚPEK, J., *Polymery v obalové technice,* SNTL Praha, 1981.

28.   TOMIS, F., *Gumárenské a plastikářské stroje, díl 2.,* SNTL Praha, 1988.

29.   TOMIS, F., *Základy gumárenské a plastikářské technologie*, SNTL Praha, 1975.

30.   WEISS, Z., KUŽVART, M., *Jílové minerály: jejich nanostruktura a využití*, Prague: Carolinum. 2005.

31.   *Marine Geoscience Electron Microscopy Facility at the Naval Research Laboratory* [online]. 2005 [cit. 2009-04-14]. Available from webpage http://www7430.nrlssc.navy.mil/facilities/emf/nanocomp.htm

32.   *Teaching Mineralogy* [online]. 2009 [cit. 2009-04-17]. Available from webpage: http://serc.carleton.edu/NAGTWorkshops/mineralogy/clay_mineralogy.html

33.   *Webmineral* [online]. 1997 [cit. 2009-04-14]. Available form webpage: <http://www.webmineral.com/data/Montmorillonite.shtml>.

34.   *Geonet* [online]. 2007 [cit. 2009-03-14]. Available form webpage: <http://www.geonet.cn/UpLoadFiles/Editor/2007-5/20070531234312304.jpg>.

35.   GUISEWITE, A. *Mineral Collection Images* [online]. 2007 [cit. 2009-03-23]. Available form webpage: <http://www.cs.cmu.edu/%7Eadg/adg-psspimages.html>.

36.   ČAUČÍK, Pavol, et al. *Prísady do plastov*. Vyd. 1. Bratislava : Alfa Bratislava, 1985. 488 s.

37.   *Moravec.net* [online]. 9.4.2008 [cit. 2010-05-26]. Studijní materiály. Dostupné z WWW: <http://vyuka.z-moravec.net/download/3-03prehled-pigmentu-bile.pdf>.

38.   PRITCHARD, Geoffrey; BRIGGS, C.C. *Plastics additives: an A-Z reference* [online]. Geoffrey Pritchard.: Springer, 1998 [cit. 2010-05-26]. 633 s. Available from webpage: http://books.google.cz/books?id=Oa7d1BhGAJMC&lpg=PP1&pg=PP1#v=onepage&q&f=fal s. ISBN 041272720X , 9780412727207.

39.   *Florida Department of Environmental Protection* [online]. 11.5. 2006 [cit. 2010-05-26]. Ocala Limestone. Available from webpage: www.dep.state.fl.us/.../ocala_limestone.jpg.

40.   CHAN, C., et al. Polypropylene/calcium carbonate nanocomposites. Polymer [online]. 43, 2981-2992 [cit. 04-12-09]. 2002.

41.   MĚŘÍNSKÁ, Dagmar. *Polymers based on organofilized clays.* [s.l.]. 78 p. Doctoral thesis. 2002

42.   NGUYEN, Quang T., BAIRD, Donald G. An improved technique for exfoliating and dispersing nanoclay particles into polymer matrices using supercritical carbon dioxide. *Polymer* [online]. Vol. 48. 2007

43.   PEREIRA, D. A., et al. Development of new polyolefin films with nanoclays for application in food packaging. *European Polymer Journal,* [online], 2007.

44.   LEE, J.H., JUNG, D., HONG, C.E., RHEE, K.Y. and ADVANI, S.G. Properties of Polyethylene-Layered Silicate Nanocomposites Prepared by Melt Intercalation with a PP-g-MA Compatibilizer, *Compos. Sci. Technol.*, 65(13): 1996–2002. 2005.

45.   DOLGOVSKIJ, M.K., FASULO, P.D. and LORTIE, F. Effect of Mixer Type on Exfoliation of Polypropylene Nanocomposites, In: ANTEC 2003, Nashville, May 2003, pp. 2256–2258. 2003.

46.   LERTWILMOLNUN, W. and VERGNES, B. Influence of Compatibilizer and Processing Conditions on the Dispersion of Nanoclay in a Polypropylene Matrix, Polymer, 46(10): 3462–3471. 2005.

47.   MISHARA, J.K., KIM, I., HA, C.S., JIN-HO, R. and GUE-HYUN, K. Structure-Property Relationship of a Thermoplastic Vulcanizate (TPV)/Layered Silicate Nanocomposites Prepared Using Maleic Anhydride Modified Polypropylene as a Compatibilizer, *Rubber Chem. Technol*., 78(1): 42–53. 2005.

48.   ZHONG, Y. and DE KEE, D. Morphology and Properties of Layered Silicate-Polyethylene Nanocomposite Blown Films, *Polym. Eng. Sci.,* 45(4): 469–477. 2005

49.   HASEGAWA, N., KAWASUMI, M., KATO, M., USUKI, A. and OKADA, A. Preparation and Mechanical Properties of Polypropylene-Clay Hybrids Using a Maleic Anhydride-Modified Polypropylene Oligomer, *Appl. Polym. Sci.*, 67(1): 87–92. 1998.

SUMMARY OF ARTICLES

First publication, ***Polyolefin/Clay Nanocomposites: Comparing of Mechanical and Barrier Properties***, was concentrated on the matter of use of polymer/clay nanocomposite in food packaging industry. Packaging materials were prepared and following this tested to gas permeability. The additional measurements were study of mechanical properties and morphology structure of prepared nanocomposites. Nanocomposites were prepared in two steps. In the first step, blends (polyethylene and polypropylene nanofillers) were prepared by KO kneader. The following step was the preparation of films which were used for study of gas permeability. Prepared blends of nanocomposites were used for preparation of samples used to testing of morphologic and mechanic properties. Morphologic properties were studied by X-ray diffraction, transmission and scanning electron microscopy. Mechanical properties were focused to study of change of tensile strength, yield strength and E modulus. Permeability of water vapour and gas were the main properties which were studied. X-ray patterns showed that the dispergation and dispersion of nanofiller was better for polypropylene nanocomposites which were filled series of nanofiller Nanofil. Polypropylene matrixes filled by nanofillers Cloisite contained agglomerate of add nanofiller. This theory was supported by results of transmission and scanning electron microscopy. It was obtained that the thickness of nanofillers (Nanofil) was about 250 nm. Results from morphology were worse for PE polymer matrixes. Mechanical tests and gas permeability showed the same situation we can observe for mechanical and barrier properties. Results from mechanical tests of PE/Nanofil were lower than polyethylene matrix and polypropylene/Nanofil nanocomposites. Data from gas permeability were very important and interesting. Results of gas permeability showed marked difference. Gas permeability was lower only for polypropylene matrix and used nanofiller but polyethylene matrix had permeability higher than unfilled polymer matrix. The reason of marked difference of results from morphology, mechanical tests and gas permeability was unsuitability of nanofiller for polyethylene matrix.

The second publication, ***Processing and Properties of Polyethylene/Montmorillonite Nanocomposites***, was focused on study of influence of compounding device to properties of nanocomposites. Compounding device AVP twin-screw extruder and KO kneader BUSS were used. Prepared nanocomposites were based on polyethylene which was filled by two different types of nanofiller – Cloisite and Nanofil. The concentration of nanofiller was 5 wt. %. The concentration of maleic anhydride polyethylene was 5 wt. % too. Prepared nanocomposites were studied and compared from morphological, mechanical points of view.

Barrier properties were studied too. Results from morphology showed that prepared nanocomposites by using of APV twin-screw extruder had higher level of dispersion and distribution than nanocomposites prepared by KO kneader BUSS. The main difference was observed at X-ray diffraction pattern and TEM picture. Nanocomposites prepared by KO kneader BUSS contained agglomerates of nanofillers. The distribution of nanofillers was poor in comparison with samples of AVP device. Only PE/Cloisite 30 B prepared in AVP device had worse distribution and dispergation of nanofiller. The same situation was observed when prepared nanocomposites were taken to mechanical tests. Dynamical mechanical analysis showed that all prepared nanocomposites had higher E modulus but samples E modulus of samples prepared by KO kneader was higher. However, mechanical tests showed the difference situation. AVP samples had higher tensile strength than KO samples. Only both series of samples (AVP and KO) filled by Cloisite 93 A and Nanofil 5 improved tensile strength of prepared nanocomposites. Barrier properties of prepared nanocomposites showed that only samples prepared by AVP twin-screw extruder and filled with Cloisite 25 A and PP with Cloisite 30 B had the worst barrier properties. To sump up, AVP twin-screw extruder is better for preparation of nanocomposites in comparison with KO kneader BUSS. Nanocomposites prepared by AVP had higher level of distribution and dispergation of nanofillers, mechanical properties, and lower barrier permeability than nanocomposites prepared by KO kneader BUSS.

The third publication, ***PP/Clay Nanocomposite: Optimization of Mixing Condition with Respect to Mechanical Properties***, was focused on comparison of different types of nanofillers and possibility to find the optimization of preparation of nanocomposites. Series of nanofiller Dellite (Dellite 72 T and Dellite 67 G) were used as nanofiller. Concentrations of nanofiller were 2, 4, 6, and 10 wt. %. The concentration of maleic-anhydride polypropylene, which were added, was 5 wt. %. The conditions of preparation were variable. Time of compounding (10, 20, 30, 40 min.) and speed of rotation (40, 60 and 80 rpm) were various. Prepared nanocomposites were obtained from morphological point of view (X-ray diffraction and electron microscopy) and changes of mechanical properties (tensile strength). First, the comparison of nanofillers is presented. X-ray diffraction and pictures of electron microscopy showed that better dispersions and distributions were obtained for polypropylene nanocomposites filled by Dellite 72 T than nanocomposites contained Dellite 67 G. The same situation was obtained for tensile strength. The maximum was obtained for PP/2 wt. % of

Dellite 72T prepared which condition of preparation was 80 rpm at 40 min. The dependence of tensile strength on concentration of nanofiller showed that nanocomposites (condition of preparation was 10 min at 80 rpm) contained Dellite 72 T had almost the same level of tensile strength to the contrary to polypropylene filled with Dellite 67 G. However, all measured data of mechanical tests were higher than value of unfilled polymer matrix. The optimal conditions of preparation were determined from 3D graph. 3D graph was constructed from data of tensile strength, time of compounding and speed of rotation. Optimal condition was determined to 30 min. and 60 rpm.

Last publication, ***Polyolefin/Clay Nanocomposites: Comparison of Different Types of Fillers and Using of Mathematic Model***, studied the possibility of using of another type of filler in polypropylene matrix and application of mathematic model. Polymer matrix was based on polypropylene material. Two types of nanofillers (Dellite 72 T and Dellite 67 G) were completed micronized calcium carbonate Omya 1 SP. Laboratory kneader Brabender PL 2000 was used for preparation. The conditions of preparations were various (speed of rotation was 40 and 60 rpm, time of compounding was 30 min). The concentrations of fillers were 2, 4, 6, 10, 20 and 40 wt. %. Maleic anhydride polypropylene was used as compatibilizer and the concentration was 5 wt. %. Prepared (nano) composites were evaluated from morphological and mechanical points of view. The morphology was represented by X-ray diffraction and electron microscopy. Mechanical tests evaluated changes of tensile and yield strength. Nanocomposites contained 4 wt. % of Dellite 72 T had poor distribution and dispergation which was shown in X-ray pattern. This theory was supported by TEM and SEM pictures. Pictures showed agglomerates of fillers of nanofiller. Composites which were filled by micronized calcium carbonate contained some agglomerates which size was about 1 μm. However, worst dispergation or distribution of fillers did not influence mechanical properties because all prepared (nano) composites had higher value of tensile or yield strength. It is interesting that composite filled by 20 wt. % of micronized calcium carbonate had higher mechanical properties than unfilled polymer material. The maximum of tensile strength was measured for polypropylene filled with 6 wt. % of micronized calcium carbonate and Dellite 72 T. Both samples were compounded 30 min. and speed of rotation was 40 rpm. The second chosen condition of mixing was 60 rpm at 30 min. The results were different than previously condition. The maximum of tensile strength was obtained for samples contained 10 wt. % of

Dellite 67 G and micronized calcium carbonate. To sum up, all prepared (nano) composites had better mechanical properties than unfilled polymer materials in spite of poor distribution of (nano) filler in polypropylene matrix. Mathematic model was used for the evaluation of mechanical properties. Resulting stress was derived from total stress attached to matrix, stress equal to initial particles and stress equal to bonded particles. Prepared mathematic model was applied to measured data and the graph of dependence of stiffness on content of filler described very good measured data.

ARTICLE I.

POLYOLEFIN/CLAY NANOCOMPOSITES: COMPARING MECHANICAL AND BARRIER PROPERTIES

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ABSTRACT

Polyolefin/clay nanocomposites were filled by the series of commercial filler Nanofil. Maleated polyolefins were used for better compatibility between polymer matrix and filler. The morphology and properties were evaluated. The properties of nanocomposites were tested by using mechanical tests and barrier properties. The results of PE/clay nanocomposites showed that the mechanical and barrier properties were not higher than the virgin polymer. However, polyethylene contained filler Nanofil 9 had better mechanical properties in compare with the virgin polymer. PP/clay nanocomposites had higher mechanical properties for both used concentration and PP/Nanofil 9 and 3000 had better barrier properties than the virgin PP.

1 INTRODUCTION

Nanotechnology is a science which studies preparation, properties and applications of nanocomposites. The nanotechnology has been started at 90 years of last century. Screw extruder, twin screw extruder can be used for the preparation of nanocomposites. The mechanical properties, barrier properties were measured and compared with the pure polymer matrix. The comparison of nanocomposites and the virgin polymer matrix (polyethylene, polypropylene and so one) showed better properties of prepared nanocomposites [1-4]. The application of nanocomposites is very variable: automotive, food packaging, aerospace and so one.

2 MATERIALS

Two different polymer matrixes were used. The first type of polymer matrix was polyethylene DOWLEX 2035 E. Maleated polyethylene AMPLIFY GR 216 was used for a better compatibility between polymer matrix and filler. Both types of polyethylene were produced by Dow Chemical Company, Belgium. The second type of polymer matrix was polypropylene MOSTEN 52.412 from company Chemopetrol Litvinov, Czech Republic. Maleated polypropylene EXXELOR PO 1015 was used as a compatibilizer for the polypropylene matrix. The characteristic of both polymer matrixes shows Tab. 1. The series of nanofillers Nanofil (Nanofil 5, Nanofil 8, Nanofil 9 and Nanofil 3000) were produced by company Südchemie, Germany.

	Melt Flow Index [g/10 min]	Density [g/cm^3]
Polyethylene DOWLEX 2035 E	6.0	0.919
Maleated polyethylene AMPLIFY GR 216	1.25	0.916
Polypropylene MOSTEN 52.412	3.2	0.907
Maleated polypropylene EXXELOR 1015	22.0	0.900

Table 1.Characteristic of used polymeric materials

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3 PREPARATION OF POLYOLEFIN/CLAY NANOCOMPOSITES

All blends of nanocomposites were prepared by using a screw extruder KO BUSS. The link of extrusion was comprised by screw extruder, which had as the first part the calender; water bath and granulating device. The calender was heated by heating zones. The homogenization and the transport of materials were caused by screw. The conditions of preparation of PE/clay nanocomposites were following: temperatures of heating zones were 110, 150, 160, 170, 190 and 190 °C; the speed of screw was 67 rpm and speed of kneader was 280 rpm. The conditions of PP/clay nanocomposites were following: 155, 1165, 170 and 180 °C; speed of screw was 65 rpm and speed of kneader was 270 rpm.

The desks for study of morphology and mechanical properties were prepared by compression moulding. The temperature of moulding of PE and PP samples were 180°C for 8 min.

The films for barrier properties were prepared on extrusion link. The link comprised from a screw extruder Brabender, extrusion wide slotted head, cooling calender and retracing device. The conditions of extrusion for PE/clay film were following: the temperatures were 110, 150, 160, 170, 190 and 190°C; speed of screw was 40 rpm and speed of retract was 2.8 rpm. The conditions of extrusion for PP/clay film were following: the temperatures were 150, 210, 230, 230, 230 and 230°C; speed of screw was 35 rpm and speed of retract was 3.2 rpm. The thickness of both films was 0.05 mm.

4 CHARACTERIZATION OF POLYOLEFIN/CLAY NANOCOMPOSITES

The morphology was evaluated by X-ray diffraction and transmission electron microscopy (TEM). The X-ray diffraction was measured by using diffractometer URD at Tomas Bata University in Zlin, Czech Republic. The reflection mode was 3-30 2θ with steep 0.5 s and the stamina was 5 s. TEM pictures were obtained Macromolecular Chemistry AS CR, v.v.i., Prague, Czech Republic. Samples were prepared on ultracryomicrotome LEICA ULTRACUT UTC. Samples were measured by JEM (JOEL) at 100 kV. The mechanical properties were measured on device T 200 Alpha Technologies. The moving clamp was 60 mm and speed of displacement was 25 mm/min. Barrier properties were measured for O_2 and CO_2 according to the norm CSN 64 0115-B at 25°C. The measurement was provided by Institute of Testing and Certification, a.s. Zlin, Czech Republic. The conditions of measurement were following: the temperature/ the relative humidity/ the time were 23°C/45 %/ 48 hours.

5 RESULTS AND DISCUSION

The X-ray diffraction and TEM pictures showed that the level of intercalation of filler was not perfect because the agglomerates of filler are visible from X-ray pattern as a peak. Fig. 1 presented X-ray pattern of a) PE and b) PP nanocomposites.
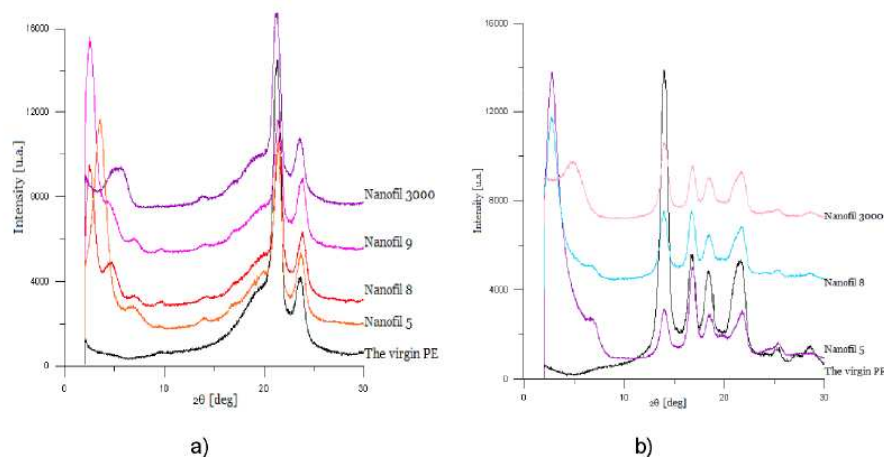

Fig. 1 X-ray pattern of prepared nanocomposites a) PE/3 wt.% of filler, b) PP/3 wt. % of filler

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As can be seen from TEM pictures both types of prepared nanocomposites contained agglomerates of fillers (Fig. 2). The situation is the same for both types of polymer matrixes.
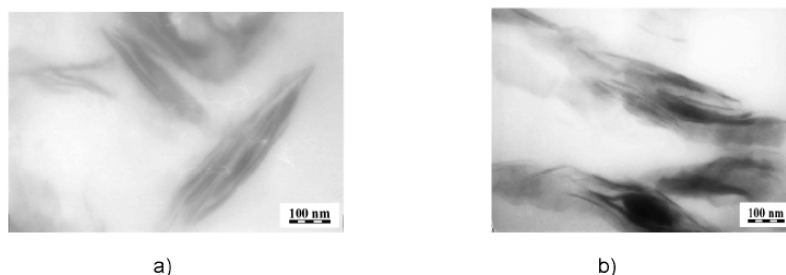

a)

b)

Fig. 2 a) PE matrix contained 5 wt. % of Nanofil 5, b) PP matrix filled by 5 wt. % of Nanofil 5

The Tab. 2 presents results of mechanical and barrier properties of PE/ clay nanocomposites containing 3 wt. % filler. As can be seen, the maximum of tensile strength was measured for PE/ 3 wt. % of Nanofil 9. However, all prepared nanocomposites had lower tensile strength than the virgin PE. The barrier properties of prepared films were better than the virgin polyethylene. The results of barrier properties showed that the dispergation and the intercalation of filler were not perfect.

PE/clay nanocomposites			
	Tensile strength (MPa)	Q_{O2} $(m^2.Pa^{-1}.s^{-1})$	Q_{CO2} $(m^2.Pa^{-1}.s^{-1})$
The virgin PE	14.725	$2.97\ 10^{-17}$	$9.39\ 10^{-17}$
Nanofil 5	14.196	$5.12\ 10^{-17}$	$1.48\ 10^{-17}$
Nanofil 8	3.393	$5.11\ 10^{-17}$	$1.10\ 10^{-16}$
Nanofil 9	14.828	$8.81\ 10^{-17}$	$1.71\ 10^{-16}$
Nanofil 3000	12.459	$7.72\ 10^{-17}$	$1.68\ 10^{-16}$

Table 2 Properties of PE nanocomposites contained 3 wt. % of filler

6 CONCLUSIONS

This work studies and compares two prepared nanocomposites: PE/clay and PP/clay nanocomposites. The results from morphology supported the results of mechanical and barrier properties. PE/clay nanocomposites had lower mechanical and barrier properties in compare with the virgin PE matrix, however, only PE/Nanofil 9 had better mechanical properties than the virgin PE. The different situation was obtained for polypropylene matrix. The mechanical properties of PP/clay nanocomposites are better for both used concentration of filler, only PP filled by Nanofil 8 had very lower mechanical properties in compare with the pure PP. The barrier properties were different too, because some nanocomposites with Nanofil 9 and Nanofil 3000 had lower permeability than the virgin PP.

References

1. D. Měřínská, Polymer nanocomposites based on organofilized clays: Doctoral thesis, 2002

2. Jacquelot, E., Espuche, E., Gérard, J.-F., Duchet, J. and Mazabraud, P., Journal of Polymer Science:Part B:Polymer Physics, Vol. 44, 431-440(2006)

3. Pereira de Abreu DA et al., Development of new polyolefin films with nanoclays for appliacation in food packaging, Eur Polym J (2007), doi: 10.1016/j.eurpolymj.2007.01.021

4. Zhong, Y. and all, Polymer Engineering and Science, doi 10.1002/pen.20792, 2007

ARTICLE II.

Processing and Properties of Polyethylene/Montmorillonite Nanocomposites

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ABSTRACT: Polyethylene (PE) nanocomposite samples were prepared with Cloisite 25 A, 30B, and 93 A and Nanofil 5 and 3000 nanofillers. The amount of modified Na^+ montmorillonite (MMT Na^+) was fixed to 5 wt%. For the compounding of PE matrix and nanofillers, two different compounding equipments were used, KO Kneader Buss and APV twin-screw extruder. In all samples, maleic anhydride-modified PE (PEMa) was added as a compatibilizer. The content of PEMa in mixtures was always 5 wt%. The level of MMT exfoliation in the nanocomposite systems was studied by X-ray diffraction and by transmission electron microscopy observations. The properties of samples were evaluated by dynamical mechanical analysis (E^* modulus at 30°C) and by the measurement of tensile properties (stress and strain at break). Because of the possibility of usage of prepared materials in packaging industry, barrier properties were measured with focus on oxygen, carbon dioxide, and water vapor permeability. The influence of two different used compounding equipments on the prepared nanocomposite samples of PE nanocomposites was discussed.

KEY WORDS: polymer nanocompositemontmorillonitePEcompoundingCloisite-Nanofil.

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INTRODUCTION

NOWADAYS, IT IS very well known that nanocomposite material represents a material in a polymer area, where filler particles in nano-sizes are homogenously dispersed in a polymer matrix. This type of fillers has taken a considerable position in preparing filled materials in the last decade either in polar polymer or in nonpolar, such as polyethylene (PE) or polypropylene. A study of polymer nanocomposites involves either the own preparation process or an observation of phenomena, which take place in nanocomposite properties. What is very important for filled materials generally is in the same way important for nanocomposites. Interactions between polymer matrix and filler particles have a significant importance in polymer/clay nanocomposites. Clay nanoparticles can have a function, for example, as a novel flame retardant [1–4] or they can cause increased dimensional stability. Later, also barrier properties are being studied [5–7]. Although some of these improvements can be achieved with conventional fillers (mineral or glass), the content has to be quite high (20–40 wt%) compared to typical 3–5% charge in case of nanoclay.

Layered nanoparticles come especially from minerals of the group of layered clays. Currently, one of the widely studied and used one is montmorillonite (MMT). Montmorillonite belongs to the group of the structure 2:1 minerals. Its structure is being described as one aluminium oxide octahedral layer sandwiched by two layers of silicon oxide [8,9].

The natural montmorillonite disintegration into individual platelets in nanoscale demands two main steps. The first one is a modification of MMT by an intercalation (organofilization) of certain organic compounds. Intercalation is an organic compound (i.e., octadecylamine [10,11] or quaternary ammonium salts [12]) insertion between MMT layers. When the distance of layers becomes higher, the molecular bonds become weaker and another step – compounding with polymer – than the energy for a layer separation is lower [13].

Two main modes of organofilization were published. The first one is based on the ion-exchange reaction where the inter-layer cations (usually sodium) are replaced with onium organocations. The most common onium ions are quartenary ammonium salts or acid salts of amines [14,15]. Another mode is based on the ion–dipole treatment, where organic molecules containing a sufficiently strong dipole (or more dipoles) coordinate to the sodium in the gallery space [16,17].

The mixing of modified montmorillonite with the polymer (compounding) is usually performed in melt in a screw compounder. To evaluate the nanocomposite morphology, two main expressions are used – intercalation and delamination, exfoliation, respectively. The intercalated level is the state

wherein the nanocomposite well-ordered multi-layered structures are noticeable. The extended polymer chains are inserted into an interlayer. The delaminated or exfoliated state represents the structure with the individual silicate layers. They are homogenously dispersed in a polymer. Actually, in a polymer matrix, both structures can co-exist together [18].

Generally, the compounding equipment has a big influence on the montmorillonite particles exfoliation in either polar polymer matrix (PA) or nonpolar one (polyolefins). Unfortunately, the MMT exfoliation is not that simple, as it was expected. And the connection of highly polar nanofiller layers with nonpolar PE matrix brings extra problems. It is the reason, why studies concerning this topic have been published during several past year [7,19,20]. The better level of MMT exfoliation can be achieved by higher amount of energy brought in a system. This can be achieved by the starting of compounding in a single screw when one can study the effect of increasing screw speed. The next step could be twin-screw extruder or even special types of very high efficient extruders (with conic screws, etc.) [21].

Preparation of PE nanocomposites because of their high hydrophobicity also should be performed with a compatibilizer in order to improve the affinity of the modified MMT and a polymer matrix. Currently, maleic anhydride-modified polypropylene is being studied and widely used [20–23].

The aim of this study was to investigate the process of MMT exfoliation by transmission electron microscopy (TEM) and X-ray diffraction (XRD) in PE matrix when the two different types of compounding equipments were being used. Then, the mechanical properties were evaluated with focus on modulus by DMA, tensile strength, and barrier properties.

EXPERIMENTAL

Commercial modified MMT nanofiller, Cloisite 25A, 30B, and 93A, from *Southern Clay Products, Inc.,* and Nanofil 5 from *Südchemie Germany* were used as nanofillers. Differences among individual nanofillers lie in the different types of intercalant agents (details can be found on the websites of above-mentioned companies). All samples were prepared with 5 wt% of MMT. The polymer/clay composites were compounded with KO Buss kneader $D = 30$ mm, $L/D = 18$, at the temperature of 180°C and in twin-screw laboratory extruder APV MP19-25TC from APV Baker, $D = 19$ mm, $L/D = 25$ at the same conditions. After pelletization of the strands, the pellets of mixtures were pressed into the sheets. The achieved level of exfoliation of the prepared sheets after a compounding process was

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Table 1. The data of DMA measurement.

Sample	E^* modulus (MPa) KO	E modulus (MPa) APV	Loss angle KO	Loss angle APV
Unfilled PE		286.4		0.1613
25A	459.9	471.2	0.1224	0.1115
30B	469	478.2	0.1284	0.1156
93A	514.9	526.1	0.1324	0.1292
Nanofil 5	466.27	470.1	0.1187	0.1056

measured by XRD. Compounded samples were analyzed by XRD powder diffractometer (INEL) equipped with the curved position sensitive detector CPS 120 (120° 2θ), reflection mode with a germanium mono-chromator ($Cu_{\alpha 1}$ radiation). Samples were placed in a holder and exposed for 2000 s.

From mechanical properties, E^* modulus, loss angle, and tensile strength were evaluated. The measurement of E^* modulus was carried out by DMA DX 04T (R.M.I., Czech Republic) at 30°C. The specimens were cut out from the pressed sheets. The DMA values are summarized in Table 1.

Transmission Electron Microscopy

For the transmission electron microscopy (TEM; JEM 200CX), the specimens were cut using Leica cryo-ultramicrotome at sample temperature −100°C and knife temperature −50°C to obtain ultra-thin sections with the thickness approximately 50 nm and an acceleration voltage of 100 kV was used.

Barrier Properties

PE/Cloisite nanocomposite-molded films with the thickness about 50 μm were used for the measurement carried using the device for gas permeability with a pressure pickup LMP 150 (made in Tesla Rožnov, Czech republic), at the temperature 25°C and the hypertension 0.4–0.6 MPa. On this device, oxygen and carbon dioxide permeability coefficient measurements were carried out.

The water vapor permeability was measured in the agreement with the ASTM E 95-96 – Standard Test Methods for Water Vapor Transmission of Materials. Out measurement was carried out at 30°C and 50% relative humidity.

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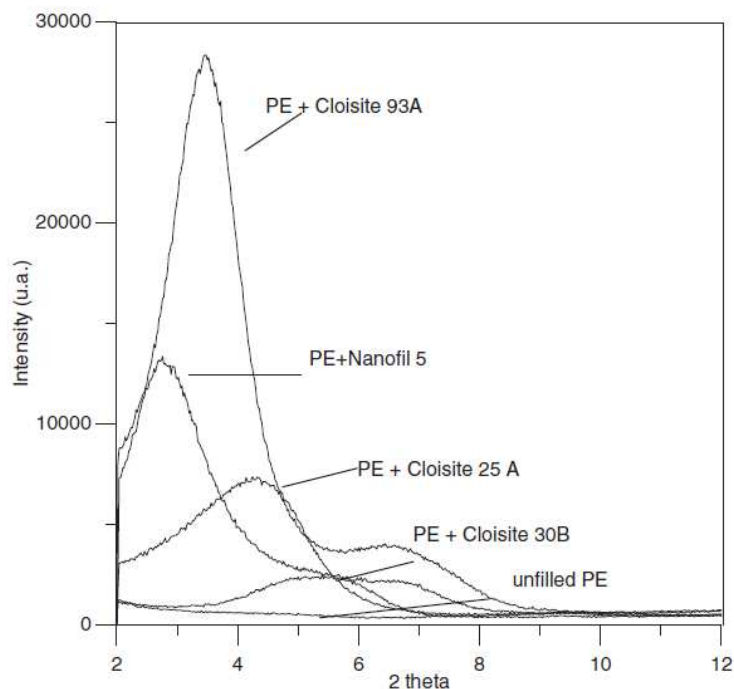
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Figure 1. XRD patterns of PE/clay samples (5% of MMT loading) prepared in KO kneader Buss.

DISCUSSION

In order to compare the influence of different compounding devices on the level of exfoliation, the XRD technique was used. Figure 1 shows XRD patterns of samples prepared by KO Buss kneader. In all cases, it is possible to notice that the exfoliation of MMT particles did not happen completely. In the comparison with the pattern of unfilled PE, all other curves exhibit peaks with various heights and peak positions, which belong to the nonexfoliated montmorillonite agglomerates. The patterns of samples filled by Cloisite 93A and Nanofil 5 even exhibit the next broadening peak. Thus, as it was said, already from this first observation, it can be concluded that MMT here is not well exfoliated. Figure 2 shows the patterns of nanocomposite samples prepared on APV twin-screw extruder. The shape of patterns here is completely different from those in Figure 1. The noticeable maxima are present only in two shown patterns. However, they
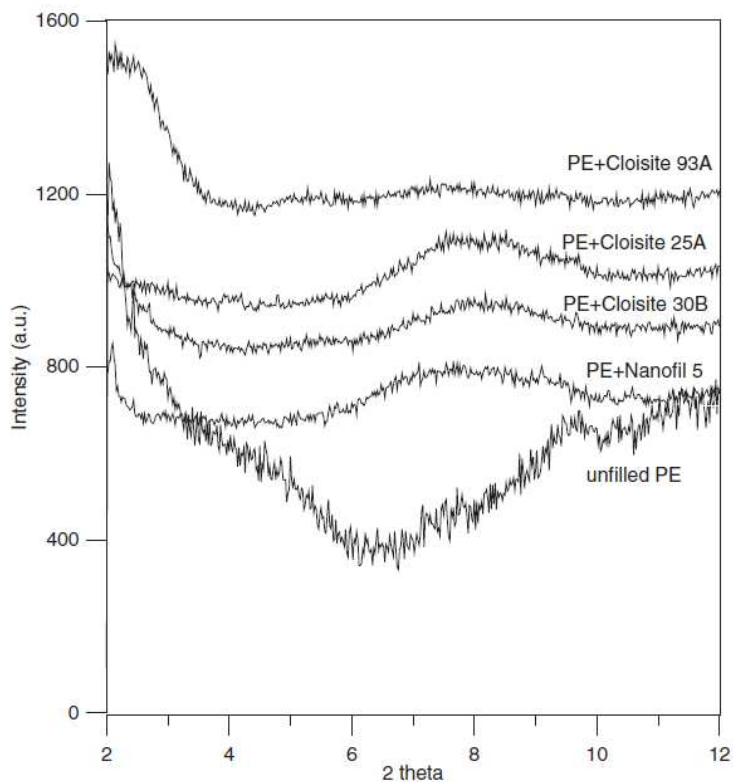
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Figure 2. *XRD patterns of PE/clay samples (5% of MMT loading) prepared in APV twin-screw extruder.*

are not high and sharp. Moreover, in the area between 2.5° and 7°, the curve is flat without any significant peaks. It indicates that the level of exfoliation after the compounding in APV achieved much higher level. To show the difference more clearly, two selected fillers are plotted in one graph (Figure 3). The curves belonging to samples prepared in APV device are almost without any peak – there are no measurable multilayer regularly arranged structures. XRD analysis has indicated better mixing in twin-screw extruder. To confirm these results, we had carried out also TEM observations of the structures.

TEM allowed us to obtain the images of the sample morphology in two different magnifications. These images are shown in Figures 4(a),
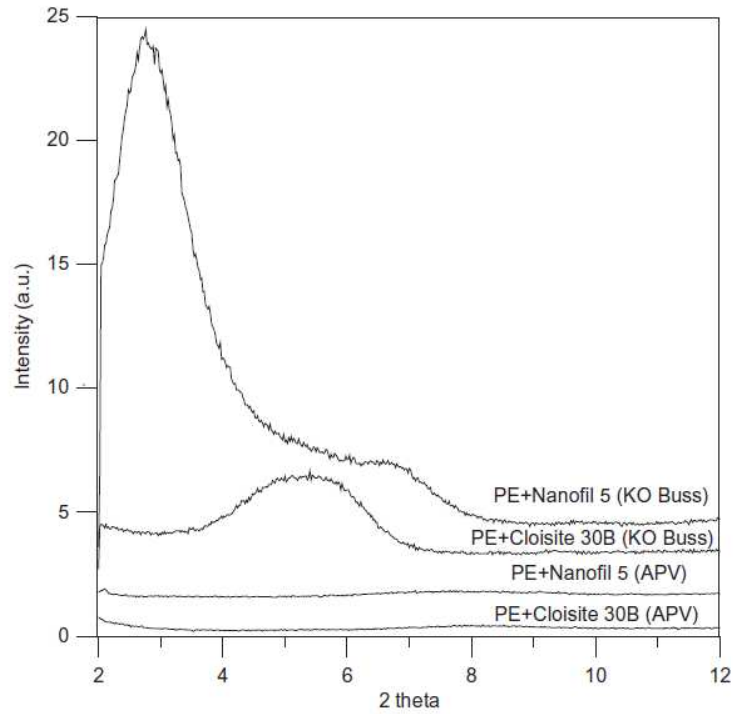
Figure 3. XRD patterns of PE/clay samples (5% of MMT loading) prepared in KO kneader Buss and APV twin-screw extruder – the comparison.
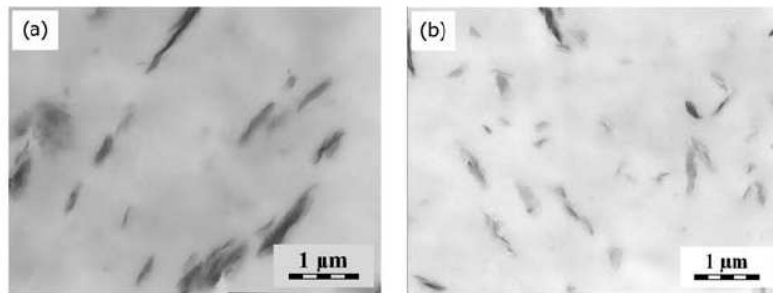

Figure 4. TEM images of the sample PE/Cloisite 25A prepared in: (a) KO Buss and (b) APV twin-screw extruder.
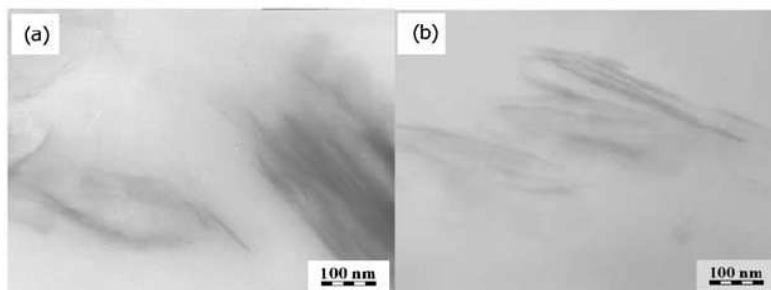
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Figure 5. *TEM images of the sample PE/Cloisite 25A prepared in: (a) KO Buss and (b) APV twin-screw extruder (higher magnification).*
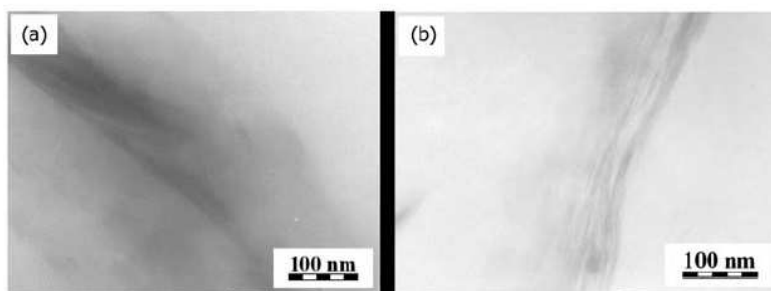

Figure 6. *TEM images of the sample PE/Cloisite 93A prepared in: (a) KO Buss and (b) APV twin-screw extruder (higher magnification).*

(b) and 5(a), and (b) for PE/Cloisite 25A composite. The first pair of TEM images (Figures 4 and 5) belongs to the samples of nanocomposite PE/Cloisite 25A, (a) shows the sample prepared by compounding in KO Buss, (b) shows the images of sample prepared by APV extruder. It is possible to see clearly the bigger MMT agglomerates in case of KO Buss kneader preparation. The size of montmorillonite particles in figure b is noticeably lower. The same trend confirms the second pair of TEM images with higher magnification (Figure 5(a) and (b)). The thickness of MMT particle in figure b (APV extruder) is significantly smaller; it is close to tens of nanometer. The similar situation is possible to describe in the case of the next used nanofillers, Cloisite 93 A and Nanofil 5 (Figures 6 and 7(a) and (b)). In both cases, it is possible to recognize in the images the presence of
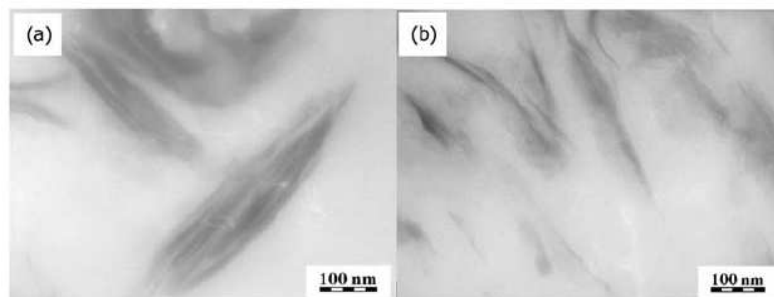
Figure 7. *TEM images of the sample PE/Nanofil 5 prepared in: (a) KO Buss and (b) APV twin-screw extruder (higher magnification).*

bigger and thicker (with more MMT layers together, only intercalated, not exfoliated) particles of clay nanofiller for the samples prepared in KO kneader Buss. In contrast, the particles in the samples compounded in APV device, the particles are smaller with the thickness going to the particular MMT layers dispersed in the PE matrix.

To sum up, the results of TEM observation support the results from XRD measurement. The level of exfoliation was higher for the samples prepared by APV twin-screw extruder.

For the practical applications of prepared nanocomposite materials, mechanical properties are very important. Dynamical mechanical analysis (DMA) is a powerful method for obtaining values of modulus and loss angle tan δ. The data from DMA are listed in the Table 1 and in two graphs (Figures 8 and 9). Figure 6 represents the data of E^* modulus. It is clear that all prepared samples, prepared either by KO Buss or by APV extruder, show about 50% increase in E^* (the improvement of stiffness). Moreover, this graph brings the information that there is no significant difference between values obtained for both observed devices.

Next data obtained from DMA measurement focus on loss angle tan δ. Values of tan δ are calculated as the ratio of loss modulus E' and storage modulus E'' (tan $\delta = E'/E''$). This tan δ value describes the level of material elasticity. Many times higher elasticity is considered as a positive change with exception to shock absorbing application when high tan δ is required. And the elasticity is influenced by the level of MMT exfoliation in a polymer matrix, better exfoliation causes higher elasticity. So, it can be considered to be one of the possible evaluations of MMT exfoliation. Figure 9 shows values of tan δ of observed samples. We can say, that the results are in good agreement with the results of E^*. All values of filled samples are lower
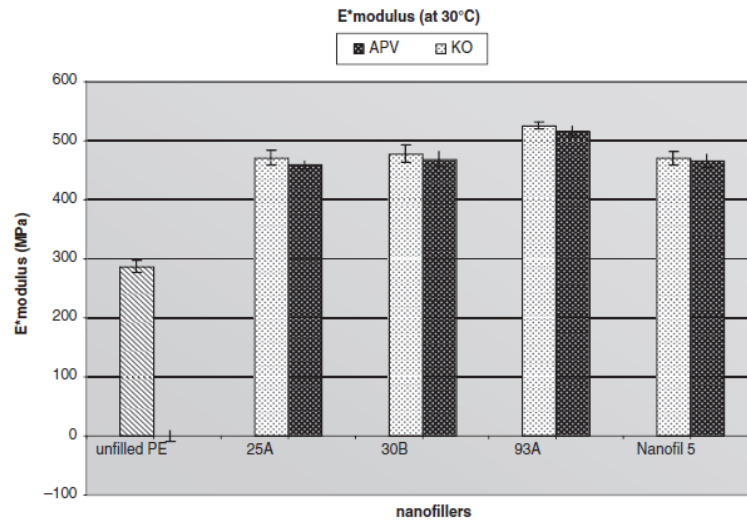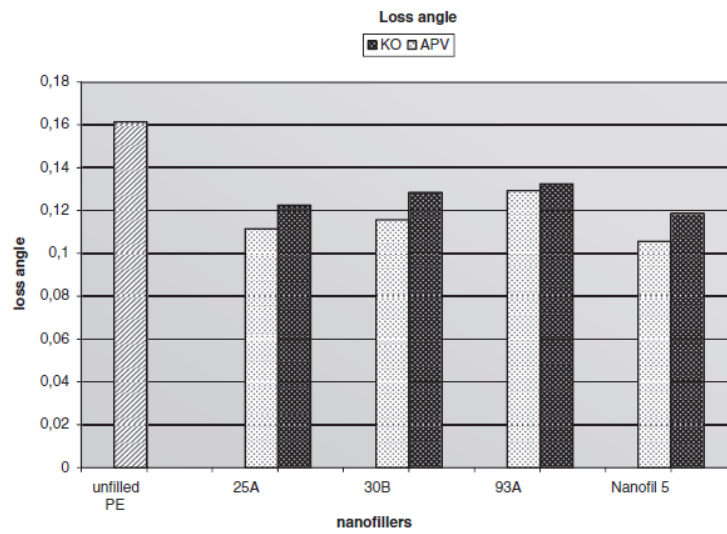
Figure 8. Graph of DMA – E* modulus.

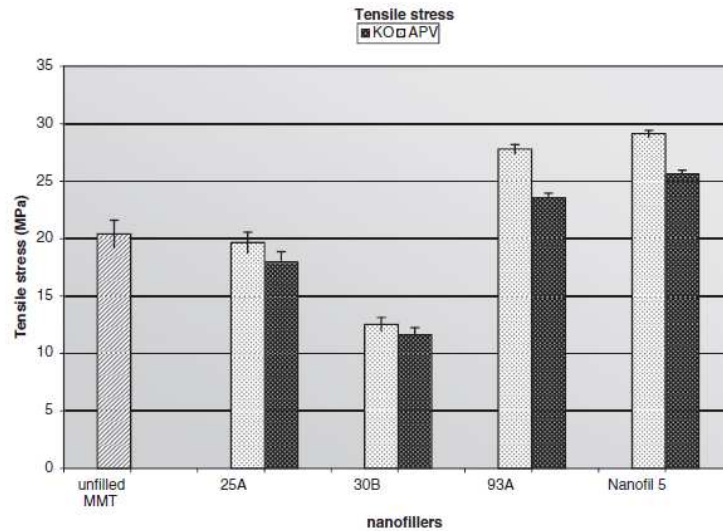**Figure 9.** Graph of DMA – loss angle (tan δ).

Figure 10. Graph of mechanical properties measurement – tensile strength.

(we have achieved better elasticity), than for unfilled PE and there is also the same tendency, APV samples are better than KO Buss ones. To sum up, the use of twin-screw extruder brings the better level of MMT particles exfoliation.

The data from tensile stress measurement are plotted in graph in Figure 10. The tendency here is quite different from the DMA results. Values of tensile stress vary in higher scale and not all of them are better then unfilled PE. The best results were achieved for the sample PE/Nanofil 5 and not significantly lower the value of sample PE filled with Cloisite 93A. In addition, here the differences between values related to both used compounding devices have better visibility. Samples prepared by APV extruder show much higher improvement compared to the case of KO Buss. The tensile test represents a mechanical behavior of samples during a destruction process. The explanation of lower values of destruction properties can be that bigger MMT agglomerates (compare Figures 4 and 5 – TEM images) cause stress concentration during the tensile measurement. Better dispersion of the nanolayer causes increase in tensile strength such as it was shown for example for PE/Nanofil 5 (compare Figures 7 and 10). These results are in very good agreement with the TEM observation.

PE nanocomposites have been studied for longer period of time as materials that would be possible used in a packaging industry [24]. That is

Oxygen permeability coeficient

◻ KO ▨ APV
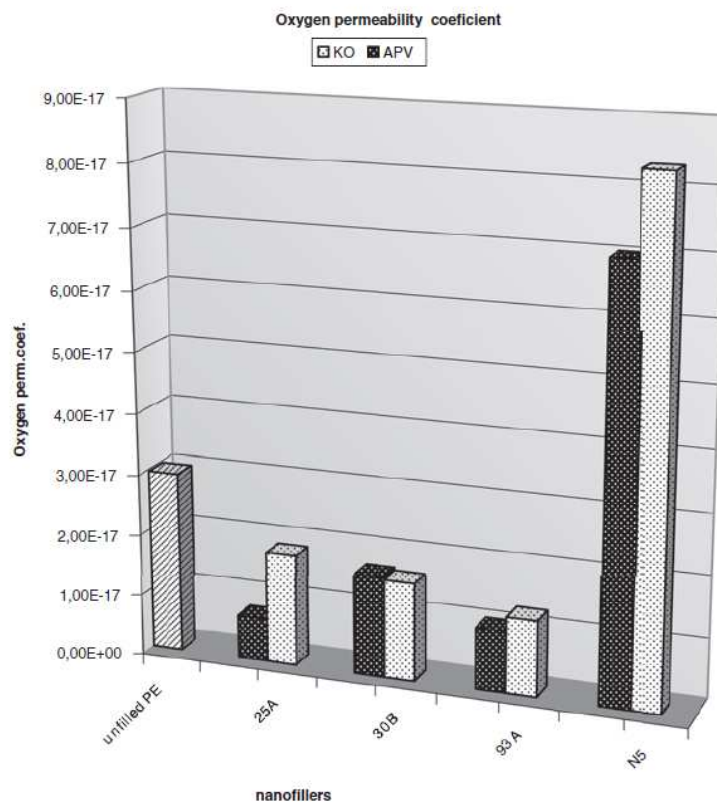
Figure 11. *Graph of permeability – oxygen permeability coefficient.*

why also in our work, we were interested in the measurement of permeability properties. Figures 11–13 represent three graphs showing permeability coefficients for oxygen, carbon dioxide, and water vapor. Figure 11 exhibits the observation of oxygen permeability. The values plotted here show that the sample PE/Nanofil 5 is the worse one, which is exactly the opposite result to the tensile strength measurement. All composites containing Cloisites exhibit lower permeability coefficient in comparison with the unfilled PE matrix. When we focus on the differences between samples prepared by different compounding devices, the tendency is not the same, but almost in all cases, the values are lower for samples prepared by APV extruder.
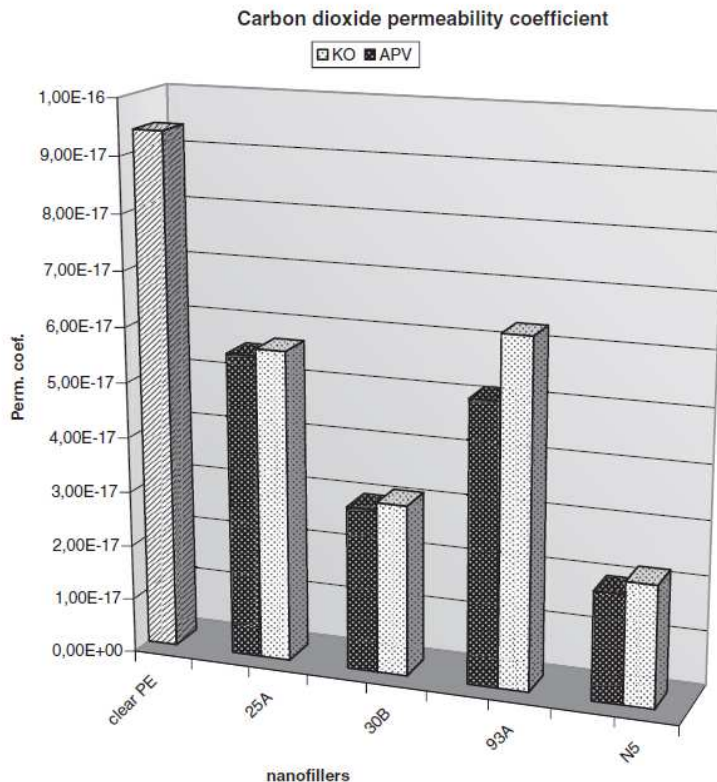
Figure 12. *Graph of permeability – carbon dioxide permeability coefficient.*

Similarly to the first-described graph (Figure 11), the next one deals with CO_2 coefficient (Figure 12). However, here the values for Nanofil 5 are better in comparison with unfilled PE; surprisingly, it is the lowest from all observed samples. This result can be explained by different sizes and polarities of O_2 and CO_2 molecules, which also influence the transmission of these gases through the PE film. Nevertheless, the results of APV samples exhibited here also have the lowest values of CO_2 permeability coefficient.

The water vapor permeability was the last-studied property. The measurement is not the same as in cases mentioned above (it was described in 'Experimental' section). The data are presented in Figure 13. The results

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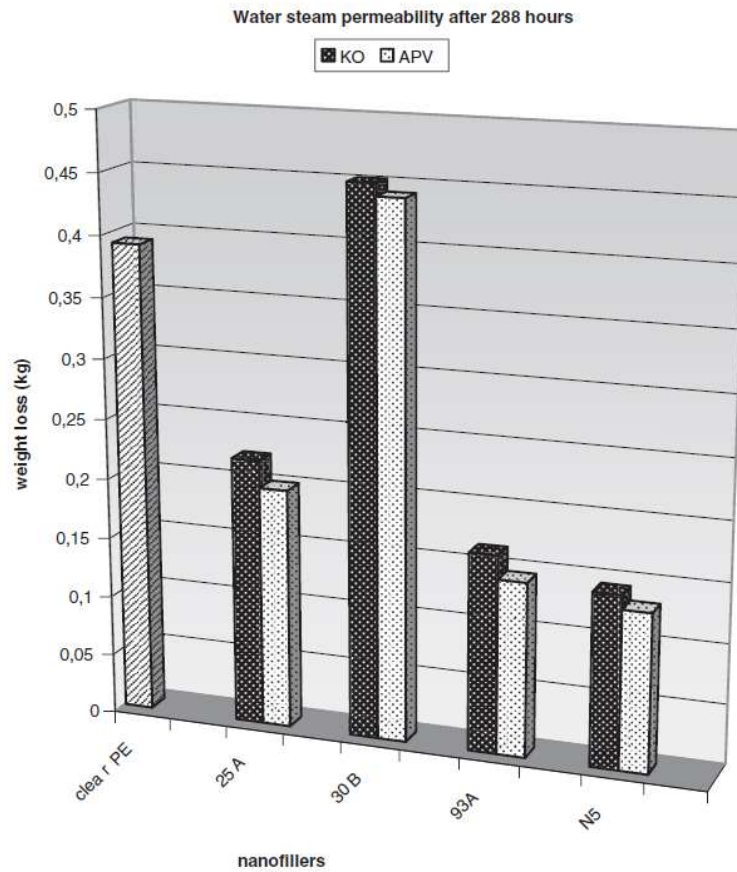
Figure 13. Graph of permeability – water vapor permeability.

show that the permeability after 288 h of observation was lower for almost all studied samples in comparison with a clean PE, except of PE/Cloisite 30B. It indicates that all other samples can be used for the decreasing of water vapor permeability. The big influence of different preparation methods was obtained in case of nanofiller Cloisite 25A and Nanofil 5.

Any product (in our case nanocomposite) has to be evaluated many angles and not just from one point of view. This overall summary is shown in Table 2. The best composite in our case was PE/Cloisite 93A, second

Table 2. The summary evaluation of measured properties.

Nanofiller	Cloisite 25 A		Cloisite 30 B		Cloisite 93 A		Nanofil 5	
Modification (www.pages)								
	APV	KO	APV	KO	APV	KO	APV	KO
E^* modulus	+	+	+	+	+	+	+	+
tan δ	+	+	+	+	+	+	+	+
Tensile strength	0	−	−	−	+	+	+	+
Oxygen permeability	+	+	+	+	+	+	−	−
Carbon dioxide permeability	+	+	+	+	+	+	+	+
Water steam permeability	+	+	−	−	+	+	+	+
Total	0	1	2	2	0	0	1	1

+, positive effect; 0, almost no effect; and −, negative effect.

being PE/Cloisite 25 A prepared by twin-screw extruder. The worst in our study was PE/Cloisite 30 B. This shows the importance of modification at the clay manufacture and the selection for the particular polymer matrix.

CONCLUSIONS

In this study, the influence of different compounding devices on the PE/nanofiller properties was observed. The samples with choice type of commercial nanofiller were prepared either by the use of KO Buss kneader or APV twin-screw extruder. The morphology, mechanical properties, and permeability of three gases were studied.

Generally, almost in all cases, the results obtained for samples prepared by twin-screw extruder were better than those obtained for KO Buss samples. This phenomenon was different only in the case of E^* modulus measurement, where all values increased in the same level disregarding the way of preparation or the type of nanofiller. A little bit different is the situation in case of values tan δ, where the improvement was observed also for all samples, but it is possible to notice the influence of compounding devices. By contrast, the tensile stress did not exhibit the improvement for all samples; here PE with nanofillers Cloisite 93A and Nanofil 5 can be used for the increasing tensile stress. To lower the permeability for observed substances, oxygen, carbon dioxide, and water vapor samples with Cloisite 25A and 93 A seem to be the most suitable.

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To sum up, the best results were obtained for the sample of PE/Cloisite 93A prepared by APV extruder.

The future work will follow presented work and it will be focused mainly to the elaboration of influence of other modified conditions used for PE nanocomposite preparation on its properties.

REFERENCES

1. Gilman, J.W., Kashiwagi, T. and Lichtenhan, J.D. (1997). Nanocomposites: A Revolutionary New Flame Retardant Approach, *SAMPE J.*, 33(4): 40–46.
2. Gilman, J.W. (1999). Flammability and Thermal Stability Studies of Polymer Layered-Silicate (clay) Nanocomposites, *Appl. Clay Sci.*, 15(1–2): 31–49.
3. Wang, S.F., Hu, Y., Zong, R.W., Tang, Y., Chen, Z.Y. and Fan, W.C. (2004). Preparation and Characterization of Flame Retardant ABS/Montmorillonite Nanocomposite, *Appl. Clay Sci.*, 25(1–2): 49–55.
4. Qin, H.L., Zhang, S.M., Zhao, C.G., Hu, G.J. and Yang, M.S. (2005). Flame Retardant Mechanism of Polymer/Clay Nanocomposites Based on Polypropylene, *Polymer*, 46(19): 8386–8395.
5. Drozdov, A.D., Christiansen, J.D., Gupta, R.K. and Shah A.P. (2003). Model for Anomalous Moisture Diffusion Through a Polymer-Clay Nanocomposite, *J. Polym. Sci., Part B: Polym. Phys.*, 41(5): 476–492.
6. Gorrasi, G., Tammaro, L., Vittoria, V., Paul, M.A., Alexandre, M. and Dubois, P. (2004). Transport Properties of Water Vapor in Polylactide/Montmorillonite Nanocomposites, *J. Macromol. Sci. Part B Phys.*, B43(3): 565–575.
7. Chaiko, D.J. and Leyva, A.A. (2005). Thermal Transitions and Barrier Properties of Olefinic Nanocomposites, *Chem. Mater.*, 17(1): 13–19.
8. Schmidt, D.F., Qian, G. and Giannelis, E.P. (2000). Nanocomposites from novel synthetic organo-layer silicates, *Abstr Pap. Am. Chem. Soc.*, 219: U477–U477.
9. Bujdak, J., Hackett, E. and Giannelis, E.P. (2000). Effect of Layer Charge on the Intercalation of Poly(ethylene oxide) in Layered Silicates: Implications on Nanocomposite Polymer Electrolytes, *Chem. Mater.*, 12: 2168–2174.
10. van Olphen, H. (1977). *Clay Colloid Chemistry*, Wiley, New York.
11. Reichert, P., Nitz, H., Klinke, S., Brandsch, R., Thomann, R. and Mülhaupt, R. (2000). Poly(propylene)/Organoclay Nanocomposite Formation: Influence of Compatibilizer Functionality and Organoclay Modification, *Macromol. Mater. Eng.*, 275: 8–17.
12. Vaia, R.A., Teukolsky, R.K. and Giannelis, E.P. (1994). Interlayer Structure and Molecular Enviroment of Alkylammonium Layered Silicates, *Chem. Mater.*, 6: 1017–1022.

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13. Pospisil, M., Capkova, P., Merinska, D., Malác, Z. and Simoník, J. (2001). Structure Analysis of Montmorillonite Intercalated With Cetylpyridinium and Cetyltrimethylammonium: Molecular Simulations and XRD Analysis, *J. Colloid Interface Sci.*, **236**(1): 127–131.

14. Zhang, Y.H. and Gong, K.C. (1998). Effect of Quaternary Ammonium-Modified Montmorillonites on Mechanical Properties of Polypropylene, *Mater. Res. Soc. Symp. Proc.*, **520** (Nanostructured Powders and Their Industrial Applications): 191–195.

15. Bala, P., Samantaraya, B.K. and Srivastava, S.K. (2000). Dehydration Transformation in Ca-Montmorillonite, *Bull. Mater. Sci.*, **23**(1): 61–67.

16. Beall, G.W. (1999). Molecular Modeling of Nanocomposite Systems, In: *57th Annual Technical Conference of the SPE on Plastics Bridging the Millennia (ANTEC 99)*, pp. 2398–2401.

17. Beall, G.W. and Kamena, K. (1999). A New Family of Intercalated Clays for Clay Polymer Nanocomposites, In: *57th Annual Technical Conference of the SPE on Plastics Bridging the Millennia (ANTEC 99)*, pp. 3973–3974.

18. Hasegawa, N., Kawasumi, M., Kato, M., Usuki, A. and Okada, A. (1998). Preparation and Mechanical Properties of Polypropylene-Clay Hybrids Using a Maleic Anhydride-Modified Polypropylene Oligomer, *Appl. Polym. Sci.*, **67**(1): 87–92.

19. Liang, G.D., Xu, J.T., Bao, S.P. and Xu, W.B. (2004). Polyethylene Maleic Anhydride Grafted Polyethylene Organic-Montmorillonite Nanocomposites. I. Preparation, Microstructure, and Mechanical Properties, *J. Appl. Polym. Sci.*, **91**(6): 3974–3980.

20. Lee, J.H., Jung, D., Hong, C.E., Rhee, K.Y. and Advani, S.G. (2005). Properties of Polyethylene-Layered Silicate Nanocomposites Prepared by Melt Intercalation with a PP-g-MA Compatibilizer, *Compos. Sci. Technol.*, **65**(13): 1996–2002.

21. Dolgovskij, M.K., Fasulo, P.D. and Lortie, F. (2003). Effect of Mixer Type on Exfoliation of Polypropylene Nanocomposites, In: *ANTEC 2003*, Nashville, May 2003, pp. 2256–2258.

22. Lertwilmolnun, W. and Vergnes, B. (2005). Influence of Compatibilizer and Processing Conditions on the Dispersion of Nanoclay in a Polypropylene Matrix, *Polymer*, **46**(10): 3462–3471.

23. Mishra, J.K., Kim, I., Ha, C.S., Jin-Ho, R. and Gue-Hyun, K. (2005). Structure-Property Relationship of a Thermoplastic Vulcanizate (TPV)/Layered Silicate Nanocomposites Prepared Using Maleic Anhydride Modified Polypropylene as a Compatibilizer, *Rubber Chem. Technol.*, **78**(1): 42–53.

24. Zhong, Y. and De Kee, D. (2005). Morphology and Properties of Layered Silicate-Polyethylene Nanocomposite Blown Films, *Polym. Eng. Sci.*, **45**(4): 469–477.

ARTICLE III.

ORIGINAL PAPER

PP/clay nanocomposite: optimization of mixing conditions with respect to mechanical properties

H. Kubišová · D. Měřínská · P. Svoboda

Abstract Polypropylene/clay nanocomposites were studied with focus on optimization of mixing conditions. Two different types of commercial nanofillers Dellite® were used (Dellite® 72T and Dellite® 67G). Effect of various concentrations of fillers on morphology and mechanical properties was investigated. Conditions of preparation were varied with respect to mixing time and speed of rotation of kneaders. Results of morphology study showed that nanocomposites contained agglomerates of nanofillers. The comparison of the filler types revealed that better dispersion and distribution was found for nanocomposites containing Dellite 72T which had also better tensile strength. Optimum mixing time was 30 min. 3D graphical analysis showed that the optimum speed of rotation was 60 rpm and with increasing clay content (2–10 wt%) the tensile strength increased.

Keywords Polyolefine · Clay · Nanocomposites · Morphology · Mechanical properties

Introduction

The nanotechnology is a science field which started during the 1990s. The nanocomposite is a material composed from polymer matrix and a filler called nanofiller because of its nano dimensions. Group of polymeric materials, e.g. polypropylene, polyethylene, polyamide and polystyrene, represent materials used as polymer matrix [1–8]. Montmorillonite, vermiculite or saponite are clay minerals used as nanofiller [9–13]. The reason of preparation of nanocomposites was expectation of achieving of unique properties that cannot be obtained by micro-size

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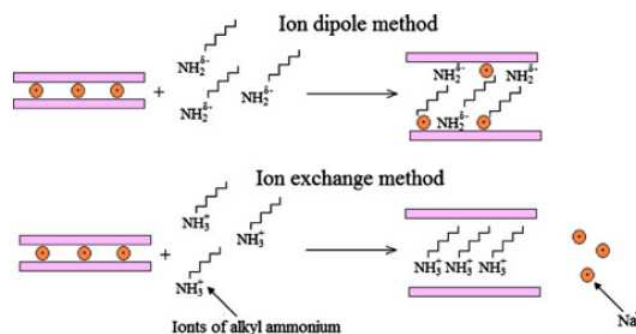e-mail: kubisova@ft.utb.cz

Fig. 1 Principles of modification of clay minerals

fillers. The presence of nanofiller improves mechanical and barrier properties and flame resistance [14].

However, the proper preparation of these unique materials is very difficult. This is because polyolefins are hydrophobic and montmorillonite is hydrophilic [14]. The preparation of nanocomposites starts by modification of natural clay mineral, e.g. montmorillonite. The name of modification is organofilization. Organofilization of clay mineral, respective montmorillonite, can be performed by two different methods. The first method is called ion dipole method that can be performed in melt, and therefore it is called "dry" method.

The second method is ion exchange reaction. Ion exchange method is called wet method due to washing of by-product Na^+ [15]. Both principles of modification of clay minerals are shown in Fig. 1.

The modification can influence the intercalation or exfoliation of clay minerals. The degree of intercalation has three levels which are shown in Fig. 2 [16]. The first level is called phase separated because one can find two phases, polymer and clay (polymer does not enter between clay plates). The second level is intercalated. Polymer enters between clay plates to a lower extent which causes increase in plates distance. The highest level is exfoliated—plates of fillers have random orientation in polymeric matrix. This structure is called nanostructure.

The preparation technique can influence the level of intercalation of filler. The Toyota Corporation prepares nanocomposites in two steps. The mineral clay is modified by organic compound in the first step; the compounding of polymer matrix, maleic anhydride modified polymer with modified nanofiller is mixed in the second step. The processing temperature is above the melting point of the polymers; a compounding device can be single screw extruder or twin screw extruder [15].

Conditions of compounding can influence consequent degree of intercalation or exfoliation that results in a change of mechanical properties. The first quantity is time of compounding; the second is the speed of rotation of screw or kneaders [16]. Theoretically, higher speed of rotation should cause better dispersion and distribution of plates of the filler.

This research describes preparation of polypropylene–montmorillonite nanocomposite. Dellite® (Dellite 72T and Dellite 67G) was used as filler. Various speeds
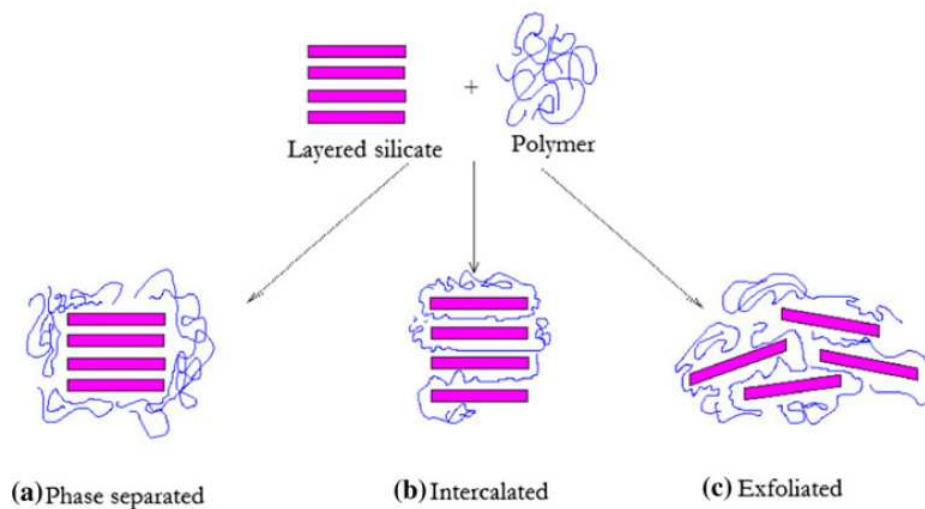
Fig. 2 The level of intercalation/exfoliation of nanofiller in polymeric matrix

of rotation and times of compounding were used in our study; the concentration of nanofiller varied too. Degree of intercalation or exfoliation of filler was obtained by X-ray diffraction and supported by transmission electron microscopy (TEM). Also tensile properties were evaluated.

Experimental

Materials

Three types of materials were used in this research: polypropylene (PP), maleic anhydride modified polypropylene (Table 1) and filler. Polypropylene Mosten GB 003 produced by Chemopetrol Litvinov, Czech Republic was used as the polymer matrix. Maleated polypropylene was supplied by ExxonMobil Chemical Europe, Belgium. Two types of nanofiller Dellite were used (D 72T, D 67G); their concentration was selected 2, 4, 6 and 10 wt%. The nanofillers were supplied by Laviosa Chemical Mineraria S.p.A., Italy.

Table 1 Specifics of polymeric materials

Polymeric materials	Density (g/cm^{-3})	Melt flow index (g/10 min)
Polypropylene Mosten GB 003	907.0	3.2[a]
Maleated polypropylene Exxelor PO 1015	900.0	22.0[b]

[a] At 230 °C

[b] At 190 °C

Table 2 Composition of nanocomposites

	Filler (g)	Polypropylene (g)	PP–MA (g)
2 wt%	1.0	46.5	2.5
4 wt%	2.0	45.5	2.5
6 wt%	3.0	44.5	2.5
10 wt%	5.0	42.5	2.5

Preparation of the polymer–clay nanocomposites and samples

All nanocomposites in this work were prepared by melt mixing in a Brabender Plasticorder compounder. There were two variables: speed of rotation and time of compounding.

Conditions of preparation were the following: the speeds of rotations were 40, 60 and 80 rpm; the times were 10, 20, 30 and 40 min. The temperature of compounding was the same for all samples, 220 °C. The charge was 50 g and it contained the pure polymer, maleic anhydride modified polypropylene and filler (Table 2).

Sample preparation and evaluation techniques

X-ray diffraction measurement (XRD) was performed on diffractometer URD 6, the reflex mode, angle range was 3–30° with a step of 0.05° and the time interval was 5 s. Specimens were prepared by compression moulding. Conditions of preparation were following: the temperature of moulding was 220 °C and time of moulding was 7 min, followed by 8 min cooling. Conditions were the same for all samples.

Transmission electronic microscopy (TEM) was obtained by JEM 200CX (JOEL). The ultra thin specimens were cut with an ultracryomicrotome LEICA ULTRACUT UCT at −110 °C. TEM pictures were take on device JEM 200CX (JOEL) at 100 kV. Pictures were digitalized by using digital camera DXM1200 Nikon. The digital camera was controlled by a computer.

Mechanical properties were tested on tensile test machine Instron 8871. All specimens were tested at following conditions: moving clamp distance was 50 mm and the rate was 50 mm/min for all specimens. The temperature was 23 °C. The test was performed according to the standard CSN EN ISO 527-3.

Results and discussion

XRD measurement of pure montmorillonite and PP/clay nanocomposites

Figure 3 shows X-ray pattern of PP filled with 4 wt% of both nanofillers. The conditions of preparation were: 80 rpm, 10 min. As can be seen, both curves contain peaks which show presence of agglomerate of nanofiller. However, the X-ray pattern shows that PP/Dellite 72T has better level of dispergation of filler in comparison with PP/D 67G which comes from the fact that peak has moved to lower
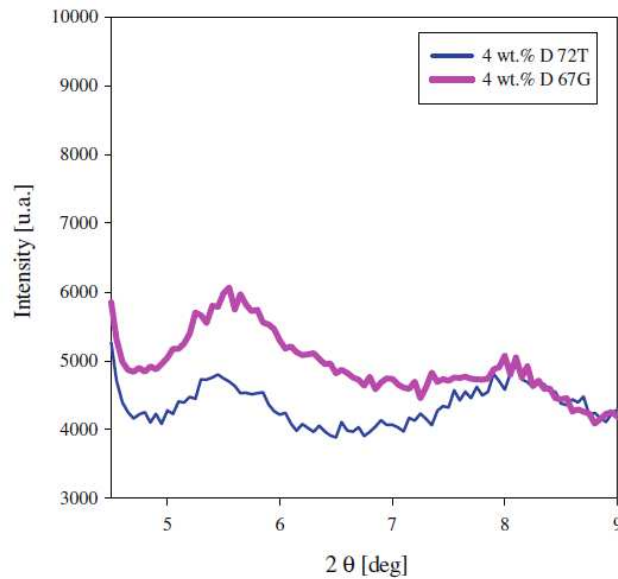
Fig. 3 X-ray pattern of PP/clay nanocomposites mixed at 80 rpm for 10 min

angle (compare 5.55° with 5.4°). TEM pictures confirmed the results of intercalation and/or exfoliation from XRD as follows.

TEM images of PP nanocomposites

TEM images were obtained for PP filled with 4 wt% of D 72T and D 67G mixed for 10 min at 80 rpm, see Fig. 4. Better dispersion and distribution of nanofiller were obtained for samples containing Dellite 72T. The thicknesses of particles were 150 nm, as can be seen at Fig. 4a. Figure 4b shows agglomerate of nanofiller. The dispersion and distribution of nanofiller were better in case of PP/Dellite72T.
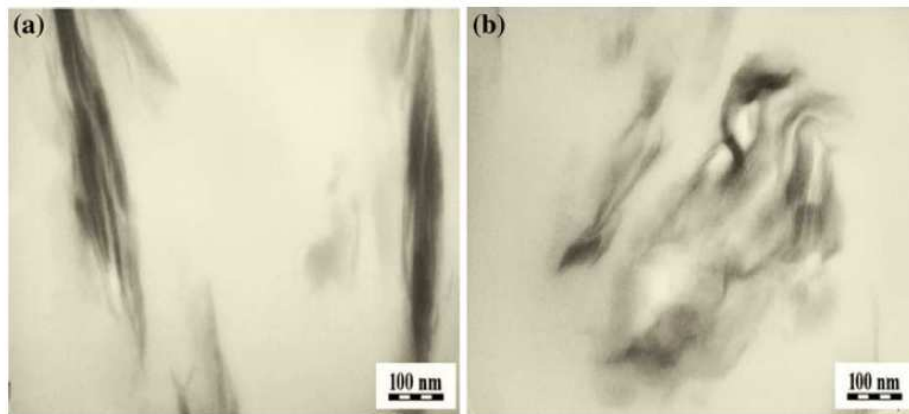
Fig. 4 TEM pictures of PP/4 wt%: **a** Dellite 72T and **b** Dellite 67G (80 rpm/10 min)

Table 3 Data of tensile strength of PP/clay nanocomposites

	2 wt%		4 wt%		6 wt%		10 wt%	
	D 72T	D 67G	D 72T	D 67G	D 72T	D 67G	D 72T	D 67G
Pure PP	12.7	12.7	12.7	12.7	12.7	12.7	12.7	12.7
40 rpm/10 min	26.2	25.2	31.9	21.6	32.9	25.8	32.0	30.6
40 rpm/20 min	32.1	27.8	31.9	27.6	33.0	26.9	32.0	31.7
40 rpm/30 min	30.7	24.8	32.4	27.0	33.0	24.5	28.9	32.8
40 rpm/40 min	28.4	30.7	33.5	28.2	30.9	23.1	33.0	31.3
60 rpm/10 min	27.2	27.9	29.9	27.2	29.7	24.3	28.7	25.6
60 rpm/20 min	33.7	30.5	29.4	27.4	32.4	26.8	30.2	32.3
60 rpm/30 min	34.3	28.2	33.3	29.1	32.5	25.8	30.5	33.1
60 rpm/40 min	33.0	25.9	31.8	26.3	32.1	25.0	34.0	31.0
80 rpm/10 min	32.4	29.4	32.4	25.0	33.1	24.2	31.5	30.8
80 rpm/20 min	28.1	27.1	33.4	28.6	28.4	29.0	32.8	31.8
80 rpm/30 min	28.6	26.6	32.5	26.5	30.7	30.3	32.1	32.4
80 rpm/40 min	34.5	28.7	32.8	24.9	28.0	27.5	22.4	31.5

Mechanical properties of PP/montmorillonite nanocomposites

Mechanical properties (tensile strength) were measured for all prepared nanocomposites and compared with the pure polymer matrix. Measured data are shown in Table 3.

As can be seen from Table 3, all prepared nanocomposites had higher tensile strength in contrast with pure polypropylene matrix. The maximum of tensile strength was obtained for PP filled with 2 wt% of Dellite 72T (80 rpm/40 min) and the minimum was found for PP/4 wt% of Dellite 67G (40 rpm/10 min).

Figure 5 shows dependence of tensile strength on the concentration of both types of nanofillers.

Figure 5 shows dependence of tensile strength (TS) on concentration of nanofiller. Specimens were prepared at 80 rpm for 10 min. As can be seen from Fig. 5, the dependences had different shape of curves. The curve of TS of PP/Dellite 72T shows a dramatic increase in range 0–2 wt% and then the value is almost constant. PP/Dellite 67G has the same rapid increase in range 0–2 wt%, but then it decreases with the minimum at 6 wt% and then it increases again with the maximum being at 10 wt%. The difference could cause by different types of fillers. The following Fig. 6 represents dependence of TS on the mixing time.

As can be seen from Fig. 6, the maximum of TS was found to be at 30 min of mixing for all three speeds of rotation of kneaders. The shape of curves had the same tendency; however, the rapid increase of value of TS can be observed only for 60 rpm. The other speeds showed only gradual increase up to 30 min and then a gradual decrease.

In order to observe the influence of speed of rotation and clay concentration on TS in one figure we have created a 3D graph, see Fig. 7. TS is almost linearly
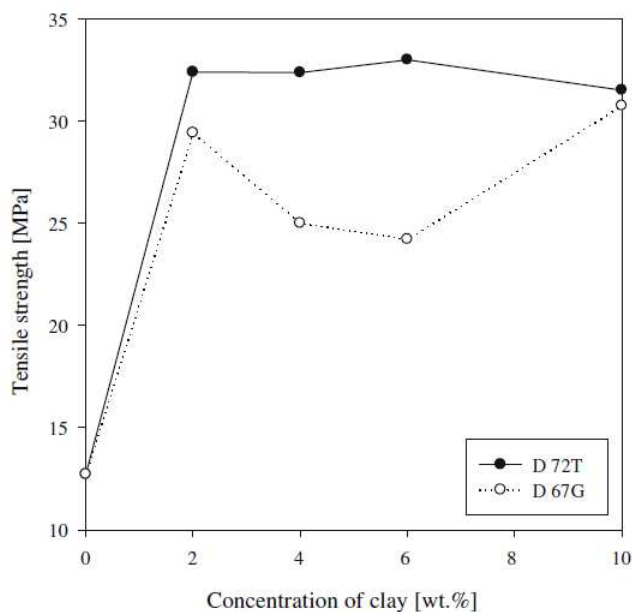
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Fig. 5 Dependence of tensile strength on concentration of clay of nanocomposites (80 rpm/10 min)
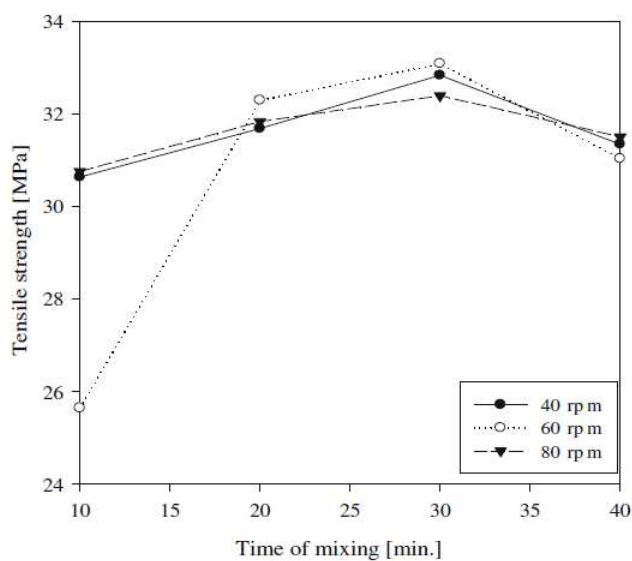

Fig. 6 The dependence of TS on time of mixing (PP/10 wt% of Dellite 67G)

increasing with clay content and the maximum values of TS were found at 60 rpm. At low speed of rotation, the shear stress is not sufficient for good intercalation. At high speed of rotation, there is a possibility of decrease of molecular weight of PP and the temperature increases which causes decrease in viscosity. Decrease in viscosity means less efficient mixing and eventually lower TS. There is an optimum

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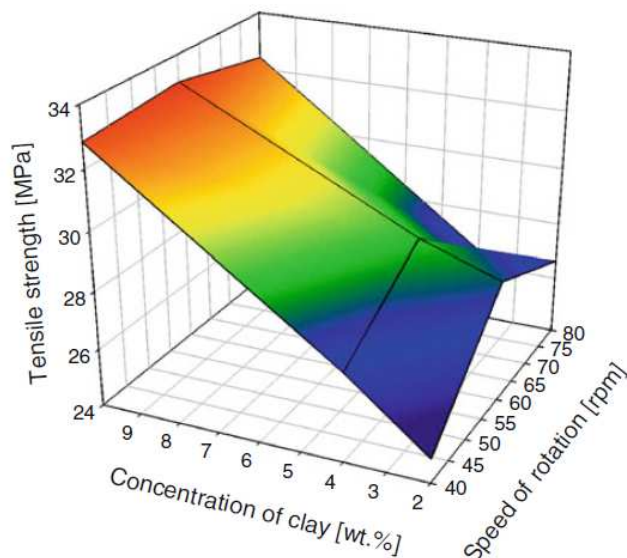
Fig. 7 Tensile strength as a function of clay concentration and speed of rotation of kneaders for PP/Dellite 67 after 30 min of mixing

in speed of rotation (60 rpm) when the mixing is the most efficient and the TS reaches maximum values.

Conclusion

Two types of nanofillers, various concentrations and conditions of preparation were used in this study. The morphology was studied by X-ray diffraction and transmission electron microscopy; mechanical properties were tested with focus on tensile strength.

X-ray diffraction and TEM pictures showed that the level of intercalation or exfoliation was not perfect because the nanocomposites contained agglomerates of filler. However, PP/4 wt% Dellite 72T (80 rpm/10 min) had the distribution, dispersion and intercalation better than the rest of prepared nanocomposites.

Testing of mechanical properties revealed that all nanocomposites had higher tensile strength in comparison with the pure polypropylene. The maximum of tensile strength was obtained for PP filled by 10 wt% of Dellite 72T (34.0 MPa). The minimum of tensile strength was obtained for PP filled by 4 wt% of Dellite 67G (21.6 MPa).

Optimum mixing time was found to be 30 min. The 3D graphical evaluation illustrated that the tensile strength increases with clay content, and there is an optimum for speed of rotation (60 rpm) when the composites had the highest tensile strength.

In future, we would like to study other types of fillers and compare mechanical properties with Dellite 72T and 67G.

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References

1. Nam PH et al (2001) A hierarchal structure and properties of intercalated polypropylene/clay nanocomposites. Polymer 42:9633–9640
2. Svoboda P et al (2002) Morphology and mechanical properties of polypropylene/organoclay nanocomposites. J Appl Polym Sci 85:1562–1570
3. Zhong Y et al (2007) Mechanical and oxygen barrier properties of organoclay-polyethylene nanocomposites films. Polym Eng Sci 47:1101–1107
4. Shaofeng W et al (2003) Preparation of polyethylene-clay nanocomposites directly from Na montmorillonite by a melt intercalation method. J Appl Poly Sci 89:2583–2585
5. Vlasveld DNP et al (2005) Analysis of the modulus of polyamide-6 silicate nanocomposites using moisture controlled variation of the matrix properties. Polymer 46:6102–6113
6. Fornes TD et al (2005) Effect of organoclay structure on nylon 6 nanocomposite morphology and properties. Polymer 46:8641–8660
7. Morgan AB, Chu L-L, Harris JD (2005) A flammability performance comparison between synthetic and natural clays in polystyrene nanocomposites. Fire Mater 29:213–229
8. Nazarenko S et al (2005) Gas barrier of polystyrene montmorillonite clay nanocomposites: effect of mineral layer aggregation. Fire Mater 29:213–229
9. Kato M, Usuki A, Okada A (1997) Synthesis of polypropylene oligomer-clay intercalation compounds. J Appl Polym Sci 66:1781–1785
10. Tjong SC, Meng YZ (2003) Impact-modified polypropylene/vermiculite nanocomposites. J Polym Sci B 41:2332–2341
11. Tjong SC, Meng YZ, Xu Y (2002) Preparation and properties of polyamide6/polypropylene-vermiculite nanocomposite/polyamide 6 alloys. J Appl Polym Sci 86:2330–2337
12. Ku BC, Froio D, Steeves D, Kim DW, Ahn H, Ratto JA et al (2004) Cross-linked multilayer polymer-clay nanocomposites and permeability properties. J Macromol Sci A 41:2441–2446
13. Wu T-M, L Yi-H, Hsu S-F (2004) Isothermal crystallization kinetics and melting behavior of nylon/saponite and nylon/montmorillonite nanocomposites. J Appl Polym Sci 94:2196–2204
14. Nguyen QT, Baird DG (2007) An improved technique for exfoliating and dispersing nanoclay particles into polymer matrices using supercritical carbon dioxide. Polymer 48:6923–6933
15. Hasegava N, Usuki A (2004) Silicate laver exfoliation in polvolefin/clay nanocomposites based on maleic anhydride modified polyolefins and organophilic clay. J Appl Polym Sci 93:464–470
16. Martin D et al (2003) Polyethylene/layered silicate nanocomposites for rotational moulding. Polymer Int 52:1774–1779

ARTICLE IV.

POLYOLEFIN/CLAY NANOCOMPOSITES: COMPARISON OF DIFFERENT TYPES OF FILLERS AND USING OF MATHEMATIC MODEL

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Abstract

This work reported the comparative study on polypropylene/clay nanocomposites. Commercial filler Dellite and modified micronized calcium were used as a nanocomposite filler for the PP-based composite. All nanocomposites were prepared by using Brabender kneader at different speeds of rotation; however, the compounding time was the same. X-ray diffraction and scanning electron microscopy (SEM) were used for evaluation of morphology. The mechanical properties were evaluated by results of tensile strength and the results were presented in graph. The model was used to predict of tensile strength.

Introduction

Nanocomposites are materials which studies and preparation began during 90th of the last century. The nanocomposites such as polypropylene/clay and so on have better mechanical and barrier properties [1-5], and lower flammability [6, 7] compared to the matrix material. The nanocomposites are widely used in food packaging and automotive industry.

Nanocomposites based on the layered nanofiller particles are composed of polymer matrix and clay mineral. Polyethylene, polypropylene, polyamide, polystyrene and so on are used as polymer matrixes [8-12]. The next component, which nanocomposites contain, is maleated polymer.

Clay minerals, like montmorillonite, vermiculite are used as fillers [13-15]. The most used clay mineral is montmorillonite (MMT). MMT is mineral from smectite class of aluminum silicate clays. The MMT is hydrophilic but a lot of polymer materials are hydrophobic [16]. Due to this fact, the preparation of nanocomposites is composed of two steps. The first step of preparation of nanocomposites is a modification of a nature clay mineral. For this modification two methods are used: ion dipole and ion exchange methods. Figure 1 shows the process of modification. Ion dipole method proceeds in melt or liquid state. This method is also called dry method. Ion exchange method proceeds in liquid state. The Na^+ is secondary product which is washout after modification. This method is named wet way and this method is more difficult than the ion dipole method.
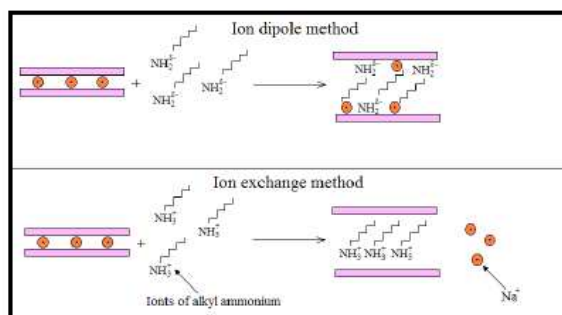

Figure 1. Method of modification of clay minerals

The second step of preparation of nanocomposites is compounding. Toyota Company prepares nanocomposites in two steps: in the first step maleated polymer containing filler melted and in the second, the blending materials mixed (compounded) with the virgin polymer. Used compounding tool and/or the condition of preparation can influence the intercalation and/or exfoliation of filler and consequently influence the properties of final nanocomposites [17].

The modeling of physically-mechanical properties of composite had been started during $50.^{th}$ of the 20th century. However, it was found that these models have not been suitable for nanocomposites. The reason is a higher phase-to-phase area and very small distance between the reinforcing particles. Models, which can be used for nanocomposites, were developed from our previously work [18].

In this study, we prepared nanocomposites containing different concentration of commercial filler and modified micronized calcium. The nanocomposites were prepared at the same speed of rotation but different compounding times. The model was used to predict the results.

Experimental

Materials

Three main components were used in this study. Polymer matrix was formed polypropylene (PP) Mosten GB 003 which was supply by Chemopetrol Litvinov, Czech Republic. Maleated polypropylene (PP-Ma) Exxelor 1015 was supply by ExxonMobile Chemical Europe, Belgium. The concentration of PP-Ma was 5 wt.

%. Table 1 shows the characterization of polymeric materials.

Table 1. Characterization of polymeric materials

	Density, g/cm^3	Melt flow index, g/10 min
PP	0.907	3.2
PP-Ma	0.900	22.0

Commercial fillers Dellite (72T, 67G) and modified micronized calcium (MMC) OMYA EXH 1 SP. Fillers Dellite were supplied from company Laviosa Chemica, Italy. OMYA EXH 1SP was supplied by Fatra Napajedla, s.r.o. as sponsoring present. The concentrations of both groups fillers were 2, 4, 6, 10, 20 and 40 wt. %.

Preparation of nanocomposites

All samples were mixed by using kneader Brabender PL 2000. The temperature was 220ºC; speeds of rotation were 40 and 60 rpm. Time of compounding was 30 min for all samples.

Technique of measuring

The morphology of prepared nanocomposites was obtained by X-ray diffraction supported by scanning electron microscopy (SEM).

X-ray diffraction was measured. The measurement device was diffractometer URD. The angle of measuring was from 3 to 30 2θ and the steep was 0.05.

Specimens for X-ray diffraction were prepared by compression moulding. The temperature of heating was 220ºC, time of moulding was 7 min and time of cooling was 5 min.

Scanning electron microscopy (SEM) was used for evaluation of distribution and dispersion of filler Dellite and modified micronized calcium in matrix.

The mechanical tester was shredder Zwick Roell. The conditions of measuring were following: the speed of clamp displacement was 50 mm per min^{-1}; distance between clamps was 25 mm. The temperature was 25ºC.

The specimens were prepared by compression moulding. The conditions of preparation were consequent: the temperature of heating was 220ºC; time of moulding was 7 min; time of cooling was 5 min.

Results and Discussion

Morphology of nanocomposites

The morphology of nanocomposites was evaluated by using X-ray diffraction and SEM.

As can be seen, Fig. 2 shows X-ray of PP filled with 4 wt. %Dellite 72T and Dellite 67G. The nanocomposites were prepared at 60 rpm for 30 min. The curves of X-ray diffraction show peak which represent presence of filler.

Fig. 2 X-ray pattern of PP/4 wt. % of both types Dellite prepared at 60 rpm for 30 min.
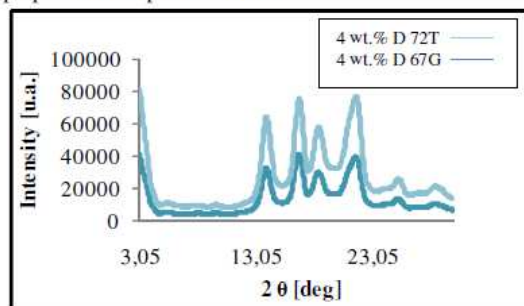
The assumption of presence of agglomerates of fillers in matrix was studied by scanning electron microscopy.

As can be seen from Figure 3, distribution and dispersion of filler D 72T was not good because polymer matrix contained some agglomerates of filler. The guess from X-ray diffraction was confirmed.

Figure 3. SEM picture of PP/ 4 wt. %D 72T mixed at 60 rpm for 30 min
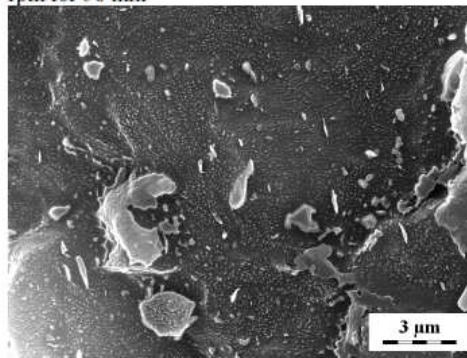
Mechanical properties

Tensile strength (TS) and yield strength (YS) were measured and compared with the virgin polymer matrix. The value of TS of the virgin PP was 12.72 MPa and YS was 30.77 MPa.

As the first, samples mixed at 40 rpm per 30 min were assessed. Data are showed in Table 2. and Graph 1.

Table 2. Mechanical properties of nanocomposites prepared at 40 rpm for 30 min

TS, MPa			
	PP/D 72T	PP/D 67G	PP/MMC
2 wt.%	30.66	24.82	30.60
4 wt.%	32.38	27.05	31.64
6 wt.%	**33.05**	24.50	**33.19**
10 wt.%	28.90	**32.84**	22.57
20 wt.%	25,79	20.70	21.35
40 wt.%	19.65	18.89	-
YS, MPa			
	PP/D 72T	PP/D 67G	PP/MMC
2 wt.%	**34.49**	30.57	30.90
4 wt.%	33.17	29.78	33.37
6 wt.%	34.34	30.49	**35.01**
10 wt.%	**34.49**	33.85	22.86
20 wt.%	26.12	20.91	21.38
40 wt.%	19.85	18.03	-

Table 3. Mechanical properties of nanocomposites prepared at 60 rpm per 30 min

TS, MPa			
	PP/D 72T	PP/D 67G	PP/MMC
2 wt.%	**34.27**	28.18	31.41
4 wt.%	33.31	29.12	31.91
6 wt.%	32.46	25.76	27.77
10 wt.%	30.52	**33.09**	**36.36**
20 wt.%	25.97	23.97	25.35
40 wt.%	18.51	17.08	-
YS, MPa			
	PP/D 72T	PP/D 67G	PP/MMC
2 wt.%	**37.07**	32.37	32.44
4 wt.%	34.72	30.86	32.25
6 wt.%	34.81	30.85	27.93
10 wt.%	32.92	**34.77**	**36.45**
20 wt.%	26.84	24.49	25.38
40 wt.%	18.66	17.23	-

Data showed that the maximum TS for conditions of preparation was obtained for PP 6 wt. % MMC. The same situation was for PP filled with D 72T. The last filler D 67G had the top of TS for 10 wt. %. The shapes of curves of TS of nanocomposites are represented in Graph. 1.

Graph 1. TS of nanocomposites prepared at 40 rpm for 30 min.
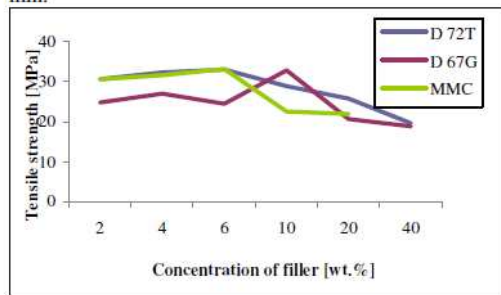
The maximum of YS was measured for PP filled with 6 wt. %. In contrast, different situation was obtained for the remaining filler D 72T and D 67G. PP contained 2 and 10 wt. % of D 72T had the maximum of YS. Finally, polypropylene filled with 10 wt. % D 67G had the maximum as for TS.

As the second, nanocomposites compounded at 60 rpm per 30 min were evaluated. Table 3. shows data from mechanical tests.

The maximum of TS was measured for PP filled with 10 wt. % MMC. PP filled with filler Dellite 72T (D 72T) had the maximum for samples contained only 2 wt. % . The last filler Dellite 67G (D 67G) had the maximum of TS for polypropylene filled with 10 wt. %. The shapes of curves of TS of nanocomposites are showed in Graph 2.

As can be seen, the line of PP/D 72T was decreased with higher concentration of filler. PP filled with D 67G and MMC had the same shape of the curve but data of PP/MMC were higher than PP/D 67G.

Graph 2. TS of nanocomposites prepared at 60 rpm for 30 min.
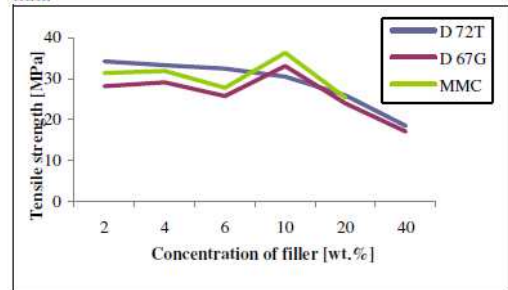
The same situation was for yield strength (YS). The maximums measured for the same samples contained 10 wt. % of D 67G and MMC, resp. 2 wt. % D 72T.

In any case, all prepared samples of nanocomposites had higher tensile strength in comparison with the virgin polypropylene. Yield strength was higher for samples contained max. 10 wt. % of D 72T and 67G. The maximum of PP/6 wt. %, rasp. 10 wt. % MMC had higher YS than the virgin PP.

The model was derived from following equation.

The initial stress σ_0 caused applied deformation at zero delamination:

$$\sigma_0 = \sigma_M / (1 - V_C(1 + h_a/(1 + kV_C))) \qquad (1)$$

Ratio non delaminated particles:

$$V_{Cv} = V_C * \sigma_0/\sigma_d \qquad (2)$$

Stress equal to free particles:

$$\sigma_V = \sigma_M * (1 - V_{Cv}) \qquad (3)$$

The rest of fixedly bonded particles:

$$V_{Cp} = V_C - V_{Cv} \qquad (4)$$

Stress equal to bonded particles:

$$\sigma_P = \sigma_M / (1 - V_{Cp}(1 + h_a/(1 + kV_C))) \qquad (5)$$

The resulting stress:

$$\sigma_K = \sigma_P + \sigma_V - \sigma_M \qquad (6)$$

where σ_M total stress attached to matrix, h_a is relative thickness of non-deformed layers matrix in the vicinity of particles of fillers. The speed of increase degree aggregation of particles considering V_C is presented as k.

Deformation at measured unit and small enough (in order to be responding to Hook´s principle):

$$\sigma_M = E_M \text{ and } E_K = \sigma_K \qquad (7)$$

Equation (6) was applied for measured date of three fillers. The results are showed in Table 3 and Graph 1.

Table 3. E/E_m of nanocomposites prepared at 60 rpm for 30 min

V_c	PP/D 72T	PP/D 67G	PP/MMC
0.000	1.000	1.000	1.000
0.008	1.610	1.499	1.838
0.016	1.614	1.439	2.012
0.024	1.630	1.377	2.053
0.040	1.754	1.666	2.026
0.080	2.112	1.748	2.278
0.160	2.198	1.643	
V_c	M_D 72T	M_D 67G	M_MMC
0.000	1.000	1.000	1.000
0.008	1.446	1.395	1.581
0.016	1.646	1.546	1.846
0.024	1.763	1.624	1.999
0.040	1.903	1.702	2.178
0.080	2.087	1.765	2.395
0.160	2.242	1.685	2.452
h_a	120.000	95.000	95.000
k	180.000	160.000	160.000
σ_δ	20.000	16.000	9.000

As can be seen from Graph 3, used model describes very good measured date.

Graph 3. The dependent of stiffness on content of filler
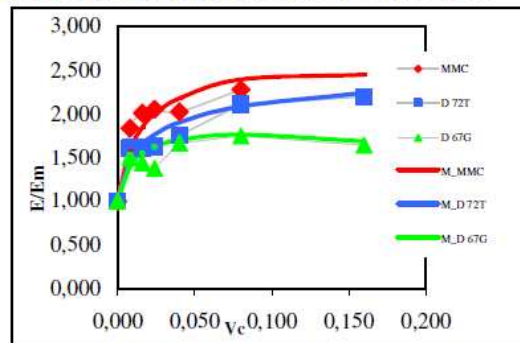
Conclusions

This study describes properties (morphology, tensile strength and yield strength) of nanocomposites prepared at different speed of rotation of kneader. The morphology of PP/clay nanocomposites showed presence of agglomerates all types fillers: Dellite 72T and 67G and MMC. SEM pictures showed that polymer matrix contained some agglomerates of fillers. Mechanical testing pointed that the nanocomposites had higher tensile strength all nanocomposites; however, samples filled with max. 10 wt. % had higher yield strength in comparison of the non filler polypropylene. The mathematic model used E/E_m showed very good depicting of obtained data.

References

1. P. Giannelis, *Appl Organomet Chem*, 12:675, (1998).
2. A. Okada, M. Kawasumi, A. Usuki, Y. Kojima, T. Kurauchi, O. Kamigato, In: W. Shaefer, E. Mark, editors. Polymers based molecular composites. *MRS symposium proceeding*, Vol. **171**, 45-50, (1990).
3. P.C. LeBaron, Z. Wang, T.J. Piannavaia, *Appl. Clay Sci*, 15:65, (1999).
4. K. Sall, *Eur Plast News March*, 14, (2002).
5. P.B. Messersmith, E.P. Giannelis, *Journal Polym Sci, Part A, Polym Chem*, 33:1047, (1995).
6. J.W. Gilman, T. Kashiwagi, J.D Lichtenhan, *SAMPLE J.*, 34:40, (1997).

7. S. Bourigot, M. LeBras, F. Dabrowski, J.W. Gilman, T. Kashiwagi, *Fire Mater*, 24:201, (2000).
8. E. Jacquelot et al, *Journal of Polymer Science: Part B: Polymer Physics*, Vol. **44**, 431-440, (2006).
9. K.H. Wang et al, *Journal of Polymer Science: Part B: Polymer Physics*, Vol. **40**, 1454-1463, (2002).
10. M. Kato, A. Usuki, A. Okada, *Journal of Applied Polymer Science*, Vol. **66**, 1781-1785, (1997).
11. J. Ma et al, *European Polymer Journal*, Vol. **43**, 4931-4939, (2007).
12. J. Li et al, *Journal of Applied Polymer Science*, Vol. **100**, 671-676, (2006).
13. Y. Dong et al, *Journal of Applied Polymer Science*, Vol. **94**, 1194-1197, (2004).
14. S.C. Tjong, S.P. Bao, *Journal of Polymer Science :Part B: Polymer Physics*, Vol. **43**, 253-263, (2005).
15. S.C, Tjong, Z.Y. Meng, *Journal of Polymer Science :Part B: Polymer Physics*, Vol. **41**, 1476-1484, (2003).
16. .Q.T. Nguyen, D.G. Baird, *Polymer*, Vol. **48**, 6923-6933, (2007).
17. D. Merinska: Polymers based on organofilized clays: Doctoral thesis, Tomas Bata University in Zlin, (2002).
18. J. Mikula, D. Merinska, H. Kubisova: Mathematic modeling of PP/MMT nanocomposite, in preparation.

CONCLUSIONS

- ✓ All nanocomposites were prepared at the different condition of preparation.

- ✓ X-ray diffraction showed that the dispersion and distribution of nanofillers and filler was good.

- ✓ TEM and SEM picture confirmed that the level of distribution and dispergation of filler was corresponded to the X-ray diffraction.

- ✓ Mechanical properties of nanocomposites were better for nanocomposites contained 2 and 4 wt%. nanofillers in polymer matrix.

- ✓ Mechanical properties of nanocomposites were higher than pure polymer materials.

- ✓ Barrier properties were higher for nanocomposites in comparison with the pure polymer matrix.

- ✓ Mathematic model used for description of mechanical properties showed that the data almost identify to model.

7. PUBLICATIONS

MERINSKA D., KUBISOVA H., KALENDOVA A., SVOBODA P. and HROMADKOVA J., Processing and Properties of Polyethylene/Montmorillonite Nanocomposites, accepted 9. 4. 2011, *Journal of Thermoplastic Composite Materials.*

KUBISOVA H., MERISNKA D., SVOBODA P., PP/clay nanocomposite: optimization of mixing conditions with respect to mechanical properties, *Polymer Bulletin*, 533–541, 2010.

KUBIŠOVÁ H., MĚŘÍNSKÁ D., SVOBODA P., Polyethylene and polypropylene/clay nanocomposites, accepted 4. 3. 2009, *Macromol. Symposia: Times of Polymers and Composites – TOP*

KUBIŠOVÁ H., MĚŘÍNSKÁ D., Polyolefin/clay nanocomposites: Comparing mechanical and barrier properties, *AIP Conference Proceedings*, Vol. 1042, 178-180, 2008

INTERNATIONAL CONFERENCES – PRESENTATIONS

KUBIŠOVÁ H., MĚŘÍNSKÁ D., Polyolefin/clay nanocomposites: comparison of different types of fillers and using of mathematic model, *22.- 24.6. 2009, Chicago, USA, ANTEC 2009*

DUJKOVÁ Z., MĚŘÍNSKÁ D., KUBIŠOVÁ H. Shape and size of fillers vs. flammability and mechanical properties in PS (nano)composite, *22.-24.6. 2009, Chicago, USA, ANTEC 2009*

KUBIŠOVÁ H., MĚŘÍNSKÁ D., Komerční nanoplniva v PE matrici,
28.9 - 1.10. 2008, Stará Lesná, Slovakia, POLYMÉRY 2008, 2008

KUBIŠOVÁ H., MĚŘÍNSKÁ D., Polyolefin/clay nanocomposites: Comparing mechanical and barrier properties, *21.9. – 24.9. 2008, Ischia, Italy, 4th International Conference on Times of Polymers (TOP) and Composites, 2008*

KUBIŠOVÁ H., MĚŘÍNSKÁ D., Mechanical properties of PP/clay nanocomposites on according to time of compounding and rotation speed, *19.9. - 20.9.2007, Brno, Czech Republic, 5th International Conference "Juniormat 07", 2007*

INTERNATIONAL CONFERENCES - POSTERS

KUBIŠOVÁ H., MĚŘÍNSKÁ D., Polypropylene/clay nanocomposites: preparation condition vs properties, *15.6. -19.6.2008, Salerno, Italy, PPS -24,The Polymer Processing Society 24th Annual Meeting, 2008*

KUBIŠOVÁ H. MĚŘÍNSKÁ D., PP/clay nanocomposites: influence of filling, condition of preparation on properties, *16.4.-18.4.2008, Řím, Italy, 4th International Symposium on Nanostructured and fuction polymer – based materials and nanocomposites, 2008*

KUBIŠOVÁ H., MĚŘÍNSKÁ D., Mechanical properties of PP/clay nanocomposites on according to time of compounding and rotation speed, *8.10.-10.10.2007, Brno, Česká republika, 6th International Conference on Nanosciences and Nanotechnologies NANO 07, 2007*

KUBIŠOVÁ H., MĚŘÍNSKÁ D., VÍTKOVÍ E., PP/clay nanocomposite – preparation, conditions and filling, *8.7.-12.7.2007, Praha, Česká republika, 46[th]Microsymposium of PMM - NANOSTRUCTURED POLYMERS AND POLYMER NANOCOMPOSITES,2007*

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EDUCATION

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PEDAGOGICAL ACTIVITIES

Tomas Bata University in Zlín

Zpracovatelské inženýrství I.	2006-2008
Procesy zpracování polymerů	2008-2008

Supervisor of bachelors work:

Aplikace UHMW-PE v lékařství	2008-2009

Chemická legislativa – nařízení č. 1907/2006 (ES) o chemických látkách (REACH) a jeho dopad na uvádění plastových výrobků na trh

Jílové nanokompozity na bázi styrenových plastů

PLA v obalovém průmyslu

Metody hodnocení interkalace/exfoliace u nanokompozitů na bázi polymer/jíl	2007-2008

Nanokompozity na bázi termoplastických elastomerů

2006-2007

Supervisor of master work:

PP/mikromletý vápenec nanokompozity: optimalizace přípravy

2009-2010

SCIENTIFIC – RESEARCH ACTIVITIES

Project KAN100400701, Hybrid   2007-2009

nanocomposite materials

(2007-2011, AV0/KA), member of solver's team

Project FI-IM3/085 – Nanocomposites   2006-2009

based on polyolefinic materials with polyolefin exceptional

use properties. (2006-2009, MPO/FI), member of solver's team

6. RP Nanofun-Poly, member of solver's team   2006