

Use of Nanoclay in Various Modified Polyolefins

Michael Tupý, Alice Tesaříková-Svobodová, Dagmar Měřínská, Vít Petránek

Abstract—Polyethylene (PE), Polypropylene (PP), Polyethylene (vinyl acetate) (EVA) and PE-ionomer nanocomposite samples were prepared by mixing of the polymer with organophilized montmorillonite fillers Cloisite 93A and Dellite 67G. The amount of each modified montmorillonite (MMT) was fixed to 5% (w/w). The twin-screw kneader was used for the compounding of polymer matrix and chosen nanofillers. The level of MMT exfoliation was studied by the transmission electron microscopy (TEM) observations. The mechanical properties of prepared materials were evaluated by dynamical mechanical analysis at 30°C and by the measurement of tensile properties (stress and strain at break).

Keywords—Polyethylene, Polypropylene, Polyethylene (vinyl acetate), Clay, Nanocomposite, Montmorillonite.

I. INTRODUCTION

THE nanocomposite is a material composed from polymer matrix and a clay filler in nano dimension particles. In this application, various polymeric present materials were used as polymer matrix [1]–[6]. Montmorillonite, vermiculite or saponite were clay minerals used as nanofiller [7]–[10]. The reason of preparation of nanocomposites was the expectation to achieve unique properties which cannot be obtained by micro-size fillers in the same chemical composition. The presence of nanoclay particles improve mechanical and barrier properties and a flame resistance [11].

However, the proper preparation of these unique materials is very difficult. This problem is by the reason of hydrophobic character of polyolefins and the hydrophilic character of montmorillonite filler [11]. Thus, the preparation of nanocomposites starts by modification of natural clay mineral, e.g. montmorillonite. The modification of clay mineral is called organophilization. This process can be performed by two different methods. The first method is named ion dipole method. It can be performed in melt polymer phase and therefore it is called “dry” method. The second method is ion exchange reaction and it is running in wet phase due to the necessity of the washing out of the Na⁺ by-product [12]. The

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wet method is more effective because Na⁺ ions are completely substituted by the quarter ammonium salts.

The MMT exfoliation in each layer can be influenced by the intercalation or of clay minerals. The degree of intercalation has three levels which are shown in Fig. 1 [13]. The first level is called phase separation level because the polymer does not enter between clay layers and the clay particles are mixed in polymer matrix as a whole. Thus, the observation can find two phases, the polymer and the clay. The second level is called intercalation level. The polymer enters between clay layers in low extent which causes slight increasing in plates distance. However, this lever is still no effective as necessary. On the other hand, the highest level is exfoliation of clay layers. As Fig.1 shows, clay particles have random orientation in polymeric matrix. This exfoliated structure is called nanostructure. When the polymer is mixed with the clay, the processing (kneading) temperature must be above the melting point of used polymers. A used compounding device can be single screw extruder or twin screw extruder, however, the second one is more effective [12]. Conditions of compounding can influence consequent degree of intercalation level which results in improvement of polymer mechanical properties. Conditions which can improve the compounding efficiency are process time and the temperature, rotation speed of kneaders [13]. Hence, the same processing time and the rotation speed were used. The process temperature depended on used polymer matrix (between 160-210°C). On the other hand, various polyolefins and different modified MMT and different polyolefins were used in our study. Degree of exfoliation of filler was observed by transmission electron microscopy (TEM), tensile properties and dynamical mechanical analyses at 30°C were evaluated.

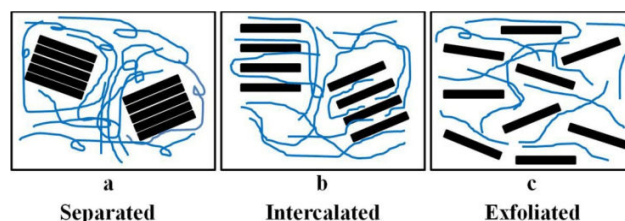


Fig. 1 Various composites of montmorillonite with polymer matrix

II. EXPERIMENTAL

A. Materials

Four kinds of polymers were used in this research: polypropylene (PP) Borealis RB 707 CF, (*Borealis AG*), polyethylene (PE) Bralen RB 03-23 (*Slovnaft Petrochemicals Bratislava*), polyethylene (vinyl acetate) (EVA) Ultra FL 00218 (*Invos*) and Surlyn A 8940 (*PE ionomer manufactured by DuPont*).

Two similar organofillization of MMT nanofillers were tested: Dellite 67G and Cloisite 93A; with their concentration was 5 wt% in used polymer matrix. DELLITE® 67G was supplied by Laviosa Chemical Mineraria S.p.A., Italy. It is nanoclay deriving from a naturally occurring montmorillonite especially purified and modified with high content of quaternary ammonium salt (dimethyl dihydrogenated tallow ammonium). Cloisite 93A was supplied by Southern Clay Products, Inc., The formula of the methyl dehydrogenated tallow in Cloisite 93A nanoclay is shown in Fig. 2, where HT is Hydrogenated Tallow.

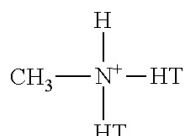


Fig. 2 Modification structure of nanoclay Cloisite 93A

B. Sample Preparation

The polymer/clay composites were homogenized and compounded with twin screw kneader in company SYNTHOS Kralupy (Czech Republic). The automatic mixer KLAD was used in order to disperse fillers and each polymer matrices. Mixing was carried out for 5 minutes with rotation speed 10 rpm. The homogenizing process was achieved with twin screw kneader Berstorff ZE 25 with both screws diameter 28 mm, DE = 38. The process temperature 210°C for PP and PE, for EVA it was 160°C and 200°C for Surlyn A were used. The rotation speed was 15 rpm. Extruded string was cut and pelleted as well.

Specimens for tensile strength measurement were prepared by sintering of pellets. Tested material was placed between two PET sheets in order to avoid direct contact of steel and polymer. Then, the material was sintered at 1.5 MPa at the same temperatures as these were processed before. The sintering time was for 7 minutes of each of them; samples with EVA were sintered less than 15 minutes. After that, plates of the material were placed into cool pressure and cooled to room temperature.

C. Tests

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

Mechanical properties were determined by using a T 2000 Tensile tester (Alpha Technologies) with the displacement rate in 2 stages. 1st stage had speed configuration of 1 mm/min up to strain 2.00 % and 2nd stage had speed configuration of 100 mm/min till the sample was broken. The measurement was carried out at room temperature. Tensile strengths and strain were determined according the norm EN ISO 527-3.

Dynamical mechanical analysis (DMA) was carried out by DMA DX 04T (R.M.I., Czech Republic) at 30°C. The specimens were cut out from the pressed sheets. These were evaluated by mechanical properties of samples in size 50x10x2 mm. The measurement resulted from values of E^* modulus, loss angle, and tensile strength. The complex dynamic modulus E^* was obtained from a dynamic mechanical test consists of “real” and “imaginary” parts. The real part describes the ability of the material to store potential energy and release it upon deformation. The imaginary (loss) portion is associated with energy dissipation in the form of heat upon deformation. The equation is rewritten for shear modulus as (1):

$$E^* = E' + iE'' \quad (1)$$

The loss modulus was calculated as a ratio of real modulus and loss modulus. The phase angle δ was determined according to (2):

$$\tan \delta = \frac{E''}{E'} \quad (2)$$

where E' is the storage modulus and E'' is the loss modulus. The phase angle δ describes the viscoelasticity of tested material, high $\tan \delta$ equals to be more viscoelastic (toughness) material.

III. RESULTS AND DISCUSSION

A. Transmission Electron Microscopy

In order to confirm the exfoliation level, the Transition electron microscopy (TEM) technique was used. The first result is explained by Fig. 3 which presents images of PE matrix with MMT Cloisite 93A. This picture was chosen as the reference because it is possible to notice that the exfoliation of MMT particles in PE was almost complete. Similar result was observed in case of Surlyn and both used nanoclays in this matrix. However, the exfoliation of MMT particles did not happen well in case of PP and EVA. Figs. 4, 5 show remaining un-homogenized particles of MMT; there are still in huge un-exfoliated aggregates in the matrix. Its size is estimated in approx. some hundred nanometers.

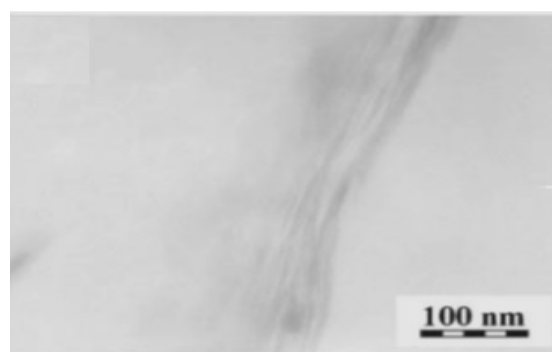


Fig. 3 TEM analysis of composition: Cloisite 93A in PE matrix



Fig. 4 TEM analysis of composition: Dellite 67G in PP matrix

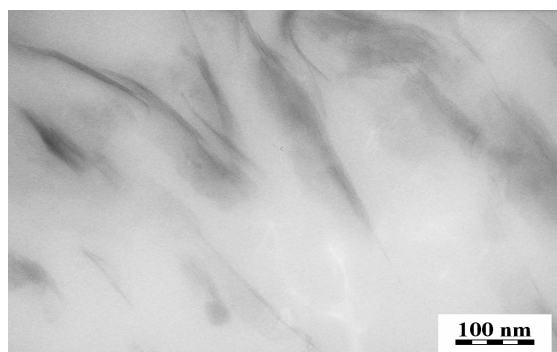


Fig. 5 TEM analysis of composition: Cloisite 93A in EVA matrix

B. Tensile Strain

Tensile tests were performed in order to obtain the initial knowledge about the effect of the filler and used matrix. Fig. 6 shows values of pure and filled tested polymers. These PE and EVA materials became to have higher tensile strength when they contained fillers. On the other hand, the reduction of tensile strength was mostly observable in the case of filled PP matrix with nanoclays. Its tensile strength was reduced about 71% in case of both applied nanofillers. As it was mentioned in the TEM analysis, this decline was surprising. Both mixtures with nanofiller (PP/Dellite 67 and PP/Cloisite 93A) were out of our expectation, at least at low filler content of 5% (w/w). On the other hand, totally different results were obtained in case of DMA measurements, see Figs. 7, 8.

Marginally improved results were obtained in case of PE. This material was no comparable with similar PP; even these polymer materials have the same polarity. The only one explanation exists; it is imperfect exfoliation of clay in PP matrix which has increased melt flow index than PE has. The hypothesis of clay mixability in PE and PP was confirmed by TEM observations, see Figs. 3, 4. The solution of better exfoliation can be usage of harder kneading conditions such as process temperature, rotation speed and the mixing time. As mentioned before, the application of nanofiller in PE matrix resulted in greatly encouraging result. The use of 5% (w/w) Cloisite 93A yielded in tensile strength increased about 35%, compared with pure PE. Unfortunately, results with PE/Dellite 67 were not obtained. This composition was not mixed well; its result is not published.

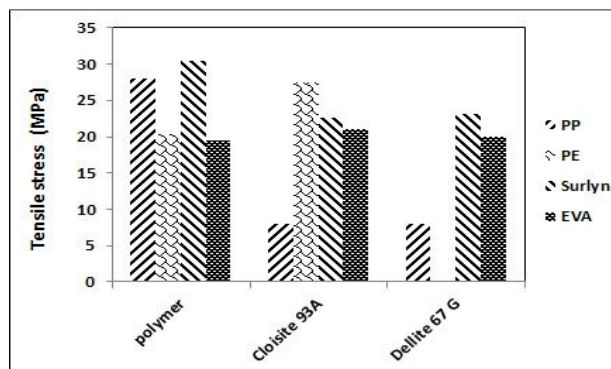


Fig. 6 Tensile strength of various polyolefins with used nanoclays

By the reason of the similar polarity of polymers EVA and Surlyn, similar degree of filler exfoliation was expected. Anyway, this expectation was not confirmed by obtained values of the mechanical properties. Surlyn with MMTs showed slight reduction degree of tensile strength than EVA matrix was. This trend was observable despite of the higher degree of exfoliation in Surlyn matrix determined by TEM. The nanocomposites Surlyn/Cloisite 93A and Surlyn/Dellite 67G lost about 25%, respectively 24% of tensile strength compared with pure Surlyn. The loss of tensile strength was probably achieved by the reduction of cohesive strength of used matrix when mentioned fillers were used. Much better result was provided by mixing of MMTs with EVA matrix. The application of nanoclay yielded a tensile strength slightly higher than the pure polymer matrix was. However, the presence of fillers in EVA matrix did not bring any special improvement, probably by the inappropriately chosen organofillization of used fillers.

C. Dynamical Analysis

The DMA measurements were carried out on samples of the molded plates. The results were obtained in temperature of 30°C. Recorded values of dynamic modulus (E^*) and loss angle ($\tan \delta$) are placed in Figs. 7, 8. The highest values of the dynamic elastic modulus brought compositions of PP with both used montmorillonites Dellite 67 and Cloisite 93A. This phenomenon pointed out to totally different behavior when it was obtained by the measurement of mechanical properties. Conversely lowest dynamic modulus was recorded in all samples of polymer EVA. Generally, the comparison of values dynamic modulus of pure polymers and samples contained nanofiller figured out in increased values dynamic modulus in every case.

Although the dynamic modulus was increased in every case of the tested polymer, the opposite dependence was observed in case of the loss angle ($\tan \delta$). The highest values were recorded for samples with PE and EVA and the lowest values were found in PP. Values of ($\tan \delta$) were lower than PE by the reason of low toughness of PP. Thus, the hardness of PP is higher than EVA or PE. It was achieved by lower viscoelastic properties of mentioned polymer. This is described by lower loss angle ($\tan \delta$). Nevertheless, the effect of the nanoclay addition was not significant in all cases of tested polyolefins.

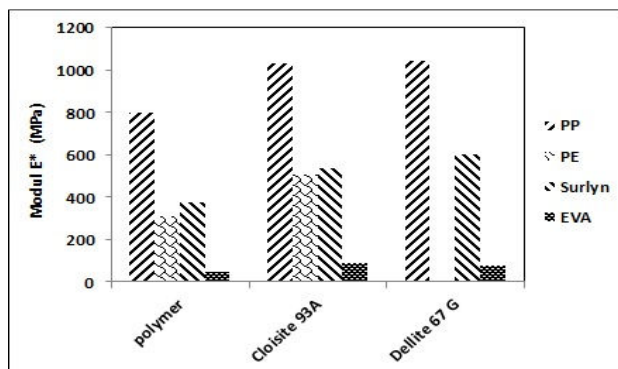


Fig. 7 Dynamic modulus of various polyolefins with used nanoclays; measured at 30°C

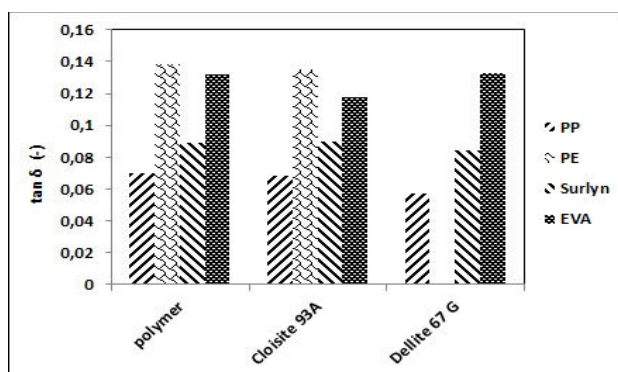


Fig. 8 Loss modulus ($\tan \delta$) of various polyolefins with used nanoclays; measured at 30°C

IV. CONCLUSIONS

Two types of nanofillers and various polyolefin matrixes were used. The morphology and exfoliation degree of applied nanoclays was studied by transmission electron microscopy; mechanical properties were focused on measurement of the tensile strength and the dynamical mechanical analysis. Both methods were carried out at 30°C. Obtained pictures of TEM analysis showed that the exfoliation level was no perfect, especially in case of PP matrix. The problem was caused by present no exfoliated agglomerates of MMT in PP matrix. Even it was used recommended processing conditions, the polypropylene needs higher kneading temperature, rotation speed or the process time.

The best result was observable with PE matrix (PE/Cloisite 93A). The tensile strength measurement pointed out to improving of mechanical properties of 35%, compared with pure PE. The evaluation of dynamical mechanical analysis found that values of dynamic modulus of samples contained nanofiller increased in every case. Nevertheless, the loss angle values ($\tan \delta$) were no changed when each polymer was mixed with some of used nanofillers. The change of obtained values was very low.

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REFERENCES

- [1] P.H. Nam, P. Maiti, M. Akamoto, T. Kotaka, N. Hasegawa, A. Usuki, "A hierarchical structure and properties of intercalated polypropylene/clay nanocomposites". *Polymer*, vol. 42, pp.9633–9640, 2001
- [2] P. Svoboda, C. Zeng, C. Wang, J. Lee, D.L. Tomasonko, "Morphology and mechanical properties of polypropylene/organoclay nanocomposites", *J. Appl. Polym. Sci.*, vol. 85, pp. 1562–1570, 2002
- [3] Y. Zhong, D. Janes, Y. Zheng, M. Hetzer, D.D. Kee, "Mechanical and oxygen barrier properties of organoclay-polyethylene nanocomposites films", *Polym. Eng. Sci.*, vol. 47, pp. 1101–1107, 2007
- [4] W. Shaofeng, Y. Hu, Y. Tang, Z. Wang, Z. Chen, W. Fan, "Preparation of polyethylene-clay nanocomposites directly from Na montmorillonite by a melt intercalation method", *J. Appl. Poly. Sci.*, vol. 89, pp. 2583–2585, 2003
- [5] A.B. Morgan, L.-L. Chu, J.D. Harris, "A flammability performance comparison between synthetic and natural clays in polystyrene nanocomposites", *Fire Mater.*, vol. 29, pp. 213–229, 2005
- [6] S. Nazarenko, P. Maneghetti, P. Julmon, B.G. Olson, Quttubuddin, "Gas barrier of polystyrene montmorillonite clay nanocomposites: effect of mineral layer aggregation", *Fire Mater*, vol. 29, pp. 213–229, 2005
- [7] M. Kato, A. Usuki, A. Okada, "Synthesis of polypropylene oligomer-clay intercalation compounds", *J. Appl. Polym. Sci.*, vol. 66, pp. 1781–1785, 1997
- [8] S.C. Tjong, Y.Z. Meng, Y. Xu, "Preparation and properties of polyamide6/polypropylene-vermiculitenanocomposite/polyamide 6 alloys", *J. Appl. Polym. Sci.*, vol. 86, pp. 2330–2337, 2002
- [9] B.C. Ku, D. Froio, D. Steeves, D., et al, "Cross-linked multilayer polymer/clay nanocomposites and permeability properties", *J. Macromol. Sci. A*, vol. 41, pp. 2441–2446, 2002
- [10] T.M. Wu, Y.H. Li, S.F. Hsu, "Isothermal crystallization kinetics and melting behavior of nylon/saponite and nylon/montmorillonite nanocomposites", *J. Appl. Polym. Sci.*, vol. 94, pp. 2196–2204, 2004
- [11] Q.T. Nguyen, D.G. Baird, "An improved technique for exfoliating and dispersing nanoclay particles into polymer matrices using supercritical carbon dioxide", *Polymer*, vol. 48, pp. 6923–6933, 2007
- [12] N. Hasegawa, A. Usuki, "Silicate layer exfoliation in polyolefin/clay nanocomposites based on maleic anhydride modified polyolefins and organophilic clay", *J. Appl. Polym. Sci.* vol. 93, pp. 464–470, 2004
- [13] D. Martin, et al, "Polyethylene/layered silicate nanocomposites for rotational molding", *Polymer Int.*, vol. 52, pp. 1774–1779, 2003