

*Oleh Shevchuk¹, Udo Wagenknecht², Sven Wiessner^{2,3}, Natalya Bukartyk¹,
Maxym Chobit¹ and Viktor Tokarev¹*

FLAME-RETARDANT POLYMER COMPOSITES ON THE BASIS OF MODIFIED MAGNESIUM HYDROXIDE

¹*Lviv Polytechnic National University, 12 S. Bandery str., 12, 79013 Lviv, Ukraine;
oshevch@polynet.lviv.ua*

²*Leibniz Institute of Polymer Research, 6 Hohe str., 01069 Dresden, Germany*

³*Technical University of Dresden, Institute of Materials Science, 01062 Dresden, Germany*

Received: July 07, 2014 / Revised: August 28, 2014 / Accepted: November 20, 2014

© Shevchuk O., Wagenknecht U., Wiessner S., Bukartyk N., Chobit M., Tokarev V., 2015

Abstract. Flame-retardant polymer composites based on homo- or copolymers of propylene as the matrix polymer and dispersed magnesium hydroxide, surface-modified by polyperoxides, as the filler have been obtained and characterized. The influence of the polyperoxide nature and the content of peroxide groups immobilized at the filler surface onto the mechanical and rheological properties as well as flame retardancy of composites have been studied. The peroxide surface modification of magnesium hydroxide results both in more even distribution of inorganic particles in the polymer matrix and strong interaction at the filler-polymer interface that in turn provides an appreciable improvement in the composite physico-mechanical properties.

Keywords: polyperoxide, magnesium hydroxide, surface modification, propylene homo- and copolymers, polymer composites, flame retardancy.

1. Introduction

Nowadays the possible use of dispersed metal hydroxides, especially magnesium hydroxide (MH) as halogen- and acid-free flame-retardants is widely studied to reduce the flammability of polymer composite materials on the basis of polyolefins [1, 2]. However, obtaining composites with desired flame retardancy needs a high loading level of MH that brings about a decrease of physico-mechanical properties because of incompatibility of mineral filler and polymer matrix. There is a considerable difference between the surface energy of the dispersed phase and that of the dispersive medium in such systems. This causes poor wettability of the highly polar surface of filler particles by low polar matrix polymer. Moreover, the developed surface and consequently the high free energy of the dispersed phase cause the spontaneous

aggregation of the filler particles leading to decreasing composite homogeneity. The general approach to solving this problem consists in increasing the component compatibilization in composite materials, that can be achieved by applying a number of different methods and techniques which allow to control an interaction at the phase boundary [3-6]. In the case of mineral-organic materials the phase compatibilization can be achieved by means of the formation on the filler surface of polymer encapsulating shell with definite chemical and physical properties. As a result, the surface energy of mineral filler decreases and becomes close to the surface energy of polymers, which provides an improvement in the filler compatibility with matrix polymer.

In our previous reports we have shown that the modification of the surface of fine mineral fillers with reactive copolymers allows to localize there diverse functional groups, particularly peroxidic ones, that makes it possible to design the compatibilizing polymer layers with determined thickness and functionality at the phase boundary [7, 8].

This work is devoted to the study of the effect of dispersed magnesium hydroxide modification by functionalized polyperoxides (FP) onto the properties of the filled polymer composites based on propylene polymers.

2. Experimental

2.1. Materials

Magnesium hydroxide FR20-100D-S7 with specific surface of 7 m²/g (Dead Sea Bromine Compounds Ltd., Israel) was used as filler for polymer composites. Three different types of propylene polymers (PP), namely MOPLen HP 501 M (propylene homopolymer, HPP),

MOPLEN EP 240 P (propylene-ethylene block copolymer, BPP), and MOPLEN RP 220 M (propylene-ethylene random copolymer, RPP) purchased from LyondellBasell Industries (The Netherlands) were used as polymer matrices. Functional monomer triallyl cyanurate (TAC) supplied by Merck was introduced into composite as a free radical trapping agent for preventing of the radical induced degradation of PP macromolecules.

Monomers: butyl acrylate (BA, Merck), allyl alcohol (AA) were purified by double vacuum distillation, maleic anhydride (MA, Merck) was purified by recrystallization from chloroform. Peroxidic monomer 5-*tert*-butylperoxy-5-methyl-1-hexene-3-yne (PM) was synthesized via technique described elsewhere [9].

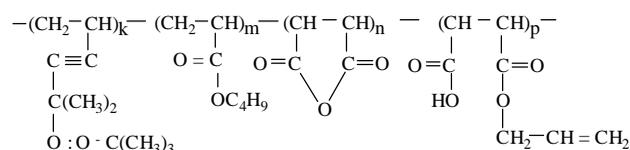
2.2. Procedures

2.2.1. Synthesis of functionalized polyperoxides

Functionalized polyperoxides FP1 and FP2 (see Table 1) were synthesized *via* radical terpolymerization of 5-*tert*-butylperoxy-5-methyl-1-hexene-3-yne, butyl acrylate and maleic anhydride in acetone in the presence of lauroyl peroxide as an initiator as described elsewhere [10].

Functionalized polyperoxide FP3 with pendant double bonds (Scheme 1, Table 1) containing monoallyl maleate (MAA) species was synthesized *via* polymer-modification reaction as follows: 6 g of FP2 was dissolved in 50 ml of acetone at 333 K in a three-necked vessel equipped with blade stirrer and reflux condenser. After FP2 complete dissolving, 10 ml of allyl alcohol and triethyl amine (catalyst) solution in acetone, that

corresponds to the mole ratio of reactive species [MA groups in FP] : [AA] = [MA groups in FP] : [TEA] = 2:1 was added dropwise under continuous stirring. Afterwards the reactive mixture was stirred for 4 h more. The synthesized FP3 was precipitated and reprecipitated twice into hexane and then dried under vacuum at ambient temperature till constant weight.



Scheme 1. Structure of functionalized polyperoxide FP3

The content of peroxide fragments in FP was determined via their thermal decomposition at 483 K under argon for 30 min, followed by gas chromatographic analysis of the final decomposition products – acetone and *tert*-butyl alcohol [11].

2.2.2. MH surface modification

The surface modification of dispersed MH was achieved *via* FP adsorption from solution. The process was performed in a water solution of FP (pH = 8.0–8.5, FP concentration = 1–2 wt %) at $T = 313$ K using a bead mill. MH to solution weight ratio was 1:1. The content of peroxide fragments immobilized at the MH surface was estimated similarly to that for FP as described above (Subsection 2.2.1). Some characteristics of modified MH samples are shown in Table 2.

Table 1

Characteristics of the functionalized polyperoxides used for the surface modification of dispersed MH

No	FP composition, mol %				Content of peroxide groups $[O_{act}] \cdot 10^4$, mol/g _{FP}	Intrinsic viscosity in acetone η , l/g
	PM	BA	MA	MAA		
FP1	9.5	41.0	49.5		8.0	0.013
FP2	19.9	30.8	49.4		16.0	0.010
FP3	19.9	30.8	25.1	24.3	14.4	0.012

Table 2

Characteristics of MH filer modified by FP

FP nature	A_{FP}^* , mg/g _{MH}	Content of peroxide groups $[O_{act}] \cdot 10^5$, mol/g _{MH}
FP 1	11.2	0.9
FP 2	14.2	2.3
FP 3	20.6	3.0

* adsorption value of FP per g of filer

2.2.3. PP composite preparation

The samples (60g) of filled composites with MH content of 60 % were prepared *via* mixing in an electrically heated internal mixer Brabender WHT 50 (Brabender GmbH & Co., Germany) with a net chamber volume of 55 cm³ equipped with two roller type blades and connected to a Plasticorder PL2000 recording unit. Mass temperature and torque were recorded during mixing. The mixing procedure was as follows:

24 g of PP-pellets were charged into the mixer chamber first and melted under continuous mixing until stabilization of both the torque and the mass temperature. Then the FP-modified MH powder was added; and mixing was performed until both torque and mass temperature reached a constant value. In the case when TAC as coagent was used, 1.2 g of TAC were charged into the mixer chamber just before MH adding. Once mixing was completed, the material was taken out and immediately pressed to flat samples on a cooled metal sheet. After 48 h of conditioning the material was ground to pellets with a Wanner mill (Thiele & Kor Plastics Machinery B. V., Netherlands). Before further investigation and processing all the samples were dried at 353 K in vacuum for 3 h.

To produce the tensile test specimens according to ISO 527/S2 and the impact test specimens a BOY 22 A HV injection molding machine (Dr. Boy GmbH & Co., Germany) with 220 kN clamping force and a screw diameter of 18 mm was used. The samples for impact testing were notched centrally through their thickness according to ISO 180.

2.3. PP Composite Testing

Prior to testing, all samples of composites were conditioned at 296 K and 50 % relative humidity for at least 88 h.

The melt volume flow rates (MVR) were detected using a melt index tester MeltFlow @on (Karg Industrietechnik, Germany) according to ISO 1133 standard at 503 K and a load of 2.16 kg. The tensile properties were tested according to ISO 527 using a ZWICK 1456 universal test machine (Zwick Inc., Germany). The IZOD notched impact strength was determined using a PSW pendulum (Zwick Testing Machines Ltd., UK).

The study of morphology of the composite materials pressed into a thin film was performed using an OLYMPUS BH2 microscope (Olympus Inc., USA) equipped with an OLYMPUS DP71 digital camera. The morphology of the fracture surface close to the notch after impact testing was studied by SEM after gold sputtering using a Leo 1455 microscope (Leo Electron Microscopy Ltd, UK).

To determine flammability of the composite samples the measurements of the limited oxygen index (LOI) according to EN ISO 4589 were done using an FTA II Instrument (Stanton Redcroft, UK). The lowest oxygen concentration that keeps the sample burning for 3 min was taken as the LOI index in vol %.

3. Results and Discussion

The study of the melt volume flow rates confirms a significant effect of peroxide-containing modifiers immobilized at the surface of dispersed MH on the rheological properties of materials (Fig. 1).

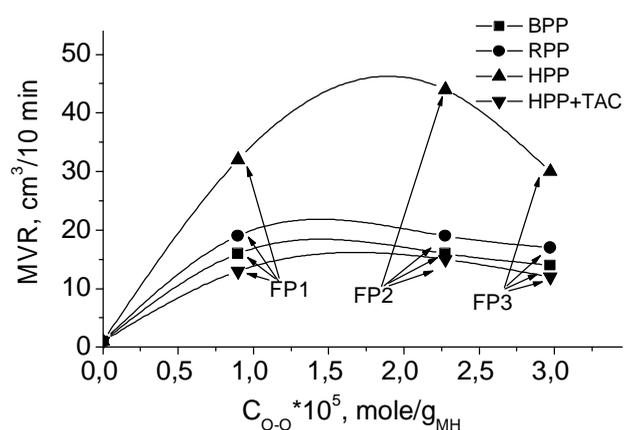


Fig. 1. Effect of the content of peroxide groups immobilized at the MH surface on MVR of composites based on different type of polymer matrix

Whereas the composites based on unmodified MH show nearly no flow, the composite flow rate increases drastically if FP is applied. This effect is the most pronounced for PP homopolymer. The MVR increase can be explained by the destruction of polypropylene matrix caused by free radicals which are generated at the melt temperature by FP immobilized at the filler surface. Very interesting is the result that for all of three polymers the melt index drops again for MH modified by FP with allylic double bonds in spite of the fact that this sample has the highest content of peroxide fragment (Table 2). Evidently, the efficiency of PP chain destruction is reduced in these composites because allylic double bonds participating in the chain transfer reactions form less active radicals than initial ones, that suppresses PP chain visbreaking. Once again, PP homopolymer is the most sensitive to this effect.

An introduction of TAC containing allylic double bonds into the composites also leads to a decrease in their MVR similarly to the presence of allylic groups in FP. A high sensitivity of HPP to the presence of both the peroxide groups and allylic fragments in FP (*i.e.* a sharper

increase and decrease of the melt flow rate, respectively) is explained by higher inclination of propylene homopolymer to the chain destruction reaction caused by free radicals as compared with its copolymers with ethylene.

It is very important that modification of the MH particle surface by FP has an effect of discoloration of the composite samples (see Fig. 2). This phenomenon reason may be found when considering the reactions that occur at the MH interface and cause the color appearance while they are suppressed when the mineral surface is shielded by thin film of the functionalized polyperoxide. Similar effects are reported by V. Khunova *et al.* [12], who studied the interaction of polymer and inorganic filler at the interface of PP-MH composites by means of model reactions. They observed the same color changes of these composites and correlated this effect with the interaction of the conjugated PP carbanions with Mg^{2+} ions at the MH surface. They also found that the formation of PP-radicals, as a step for the color reactions, occurred just due to thermooxidative destruction during composite mixing. At the same time, the TAC addition leads to further lightening of the samples (Fig. 2). Evidently, TAC due to presence of allylic bonds acts as a trapping agent for free radicals formed in PP matrix thus preventing their interaction with the filler surface. The relevant tensile properties (tensile strength, elongation at break and tensile modulus) of the composites obtained have been studied to reveal the effects of the nature of FP surface-modifier and polymer matrix (Fig. 3). One can see that PP-homopolymer exhibits the highest tensile strength as well as elastic modulus accompanied with the lowest elongation at break. On the contrast, the random copolymer shows the highest elongation values with comparable tensile strength but lower modulus. On the other hand, the obtained data prove the significant effect of peroxidic modification of the MH surface on the composite properties. An increase in the peroxide group content at the MH surface enhances both the elongation at break and the tensile strength up to 30 %, while tensile

modulus remains rather constant. It should be also noted that the FP with allylic double bonds provides the best stress-strain values of composites among all others, that is in a good agreement with the rheological behavior of the composite melts.

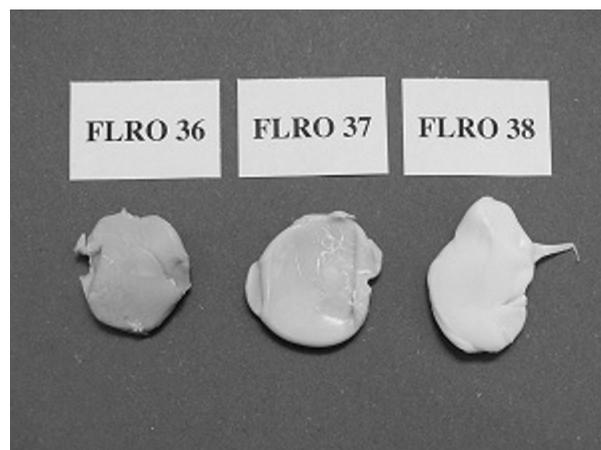


Fig. 2. The color intensity of MH-RPP composite depending on the composition: with unmodified MH (FLRO 36); with MH modified by FP2 (FLRO 37); with MH modified by FP 2 and 2%TAC (FLRO 38)

The dependences of filled composite impact strength on the content of peroxide groups at the MH surface and the nature of polymer matrix are shown in Fig. 4. One can see that composites based on propylene copolymers with ethylene exhibit higher impact strength if FP is present in the composites (especially in the presence of FP containing double bonds), and the impact strength enhances with increasing amount of O–O groups whereas impact strength of PP homopolymer composite decreases slightly in this row. The introduction of additional amount of double bonds with TAC into HPP matrix allows to increase the impact strength of the composite to the values higher than that of composites on BPP and RPP basis.

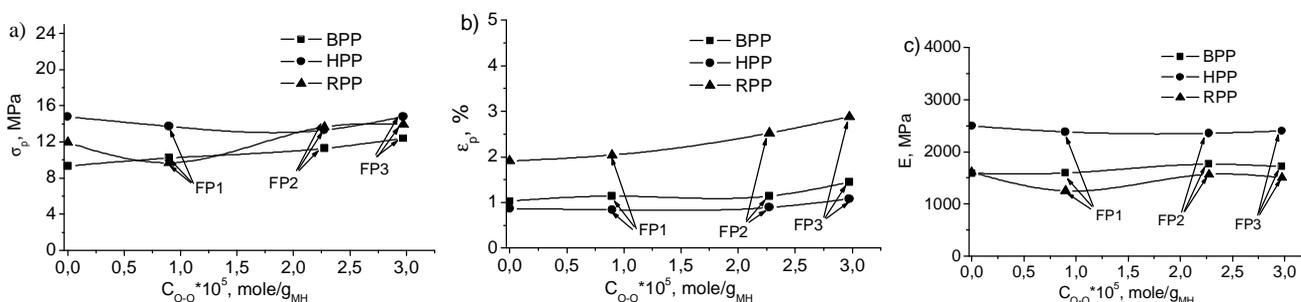


Fig. 3. Effect of the content of peroxide fragments at the MH surface on the physico-mechanical properties of MH-PP composites: tensile strength (a), elongation at break (b) and tensile modulus (c)

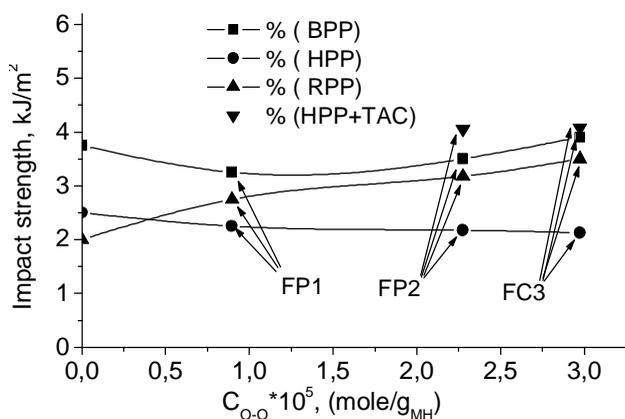


Fig. 4. Effect of the content of peroxide fragments at the MH surface and the polymer matrix nature on impact strength of MH-PP composites

The reason why the random copolymer based composite with non-modified MH has lower impact strength than the corresponding homopolymer based one is not clear. The probable explanation can be connected with the fact that for highly filled systems the minor differences in particle dispersion or particle concentration can cause a sharp decrease of mechanical properties, especially the impact values of notched samples, and these differences are usually hardly controllable. At the same time, modification of the filler surface by functionalized polyperoxides serving as compatibilizers provides an even distribution of MH particles in the polymer matrix (Fig. 5).

On the other hand, the increase in impact strength of two PP-copolymers with modified MH might be explained by a modification of the ethylene phase in the polymer matrix, that causes its branching or cross-linking induced by free radicals formed. This could also lead to the formation of a gradually cross-linked shell around the filler particles because FP is immobilized on the MH

surface, so the action of radicals may be limited by interphase area.

This results also in different relaxation times that becomes obvious under high speed deformation as in impact testing. Furthermore, branched ethylene sequences can act as the nucleation centers inducing a self-nucleation effect that can influence the degree of polymer crystallinity; the rate of crystallization and spherulite size could also be responsible for changing the impact properties. In turn, polyfunctional monomer TAC can serve as a free radical trapping agent as well as form additional nucleation and crystallization centers causing partial polymer cross-linking.

In Fig. 6 SEM-images of the fracture surfaces close to the notch after impact testing are shown for composites based on RPP. One can see that the sample based on unmodified MH fractures in a brittle manner showing the clear fracture at the particles-polymer boundary without any indication of yielding or fibrillation of the matrix (Fig. 6a). When peroxidized MH is loaded into the composite the picture changes drastically (Figs. 6b and 6c): cohesive fracture is observed and the composites demonstrate a tendency to matrix fibrillation, that is especially well visible in Fig. 6b. This correlates with the data of impact strength studies for these composites – rather low values for unmodified MH and sharp increase of impact strength if MH modified by FP is used.

Hence, the value of impact strength depends significantly on the energy required to delaminate the matrix from the particle surface. If this energy is too high a cohesive fracture in the matrix can occur. If the energy is low an adhesive fracture occurs. If there is a proper balance, the stress for local matrix yielding is reached upon impact, hence the matrix can undergo yielding. This is a typical picture of plastic deformation at a strain driven process, which absorbs the impact energy and leads to increased impact strength.

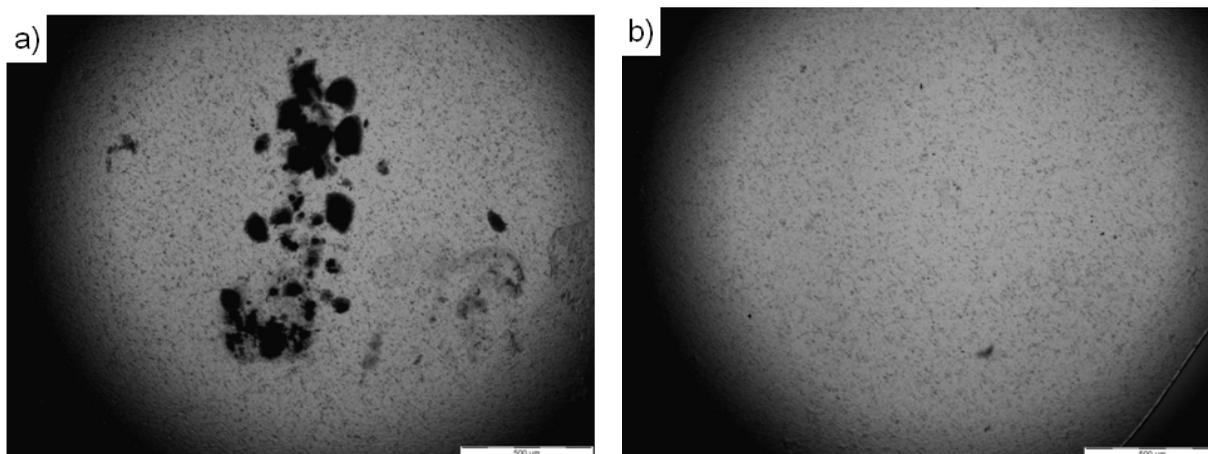


Fig. 5. Optical micrographs of MH-HPP composites: unmodified MH (a) and MH modified with FP 2 (b). Bar –500 µm

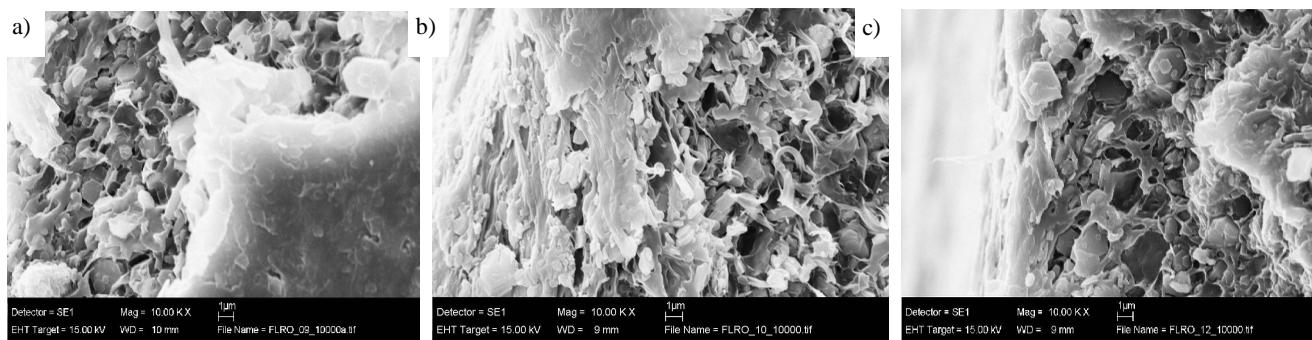


Fig. 6. SEM micrographs of fracture surfaces of RPP/MH – composites based on unmodified MH (a); MH modified with FP 1 (b) and FP 3 (c)

Since the main goal of this work is to create flame-retardant composites we have studied the influence of the filler peroxidic modification on flammability of the filled materials. One can see (Fig. 7) that the use of peroxidized MH causes flame retardancy improvement of the composites based on all three studied types of polymer matrix.

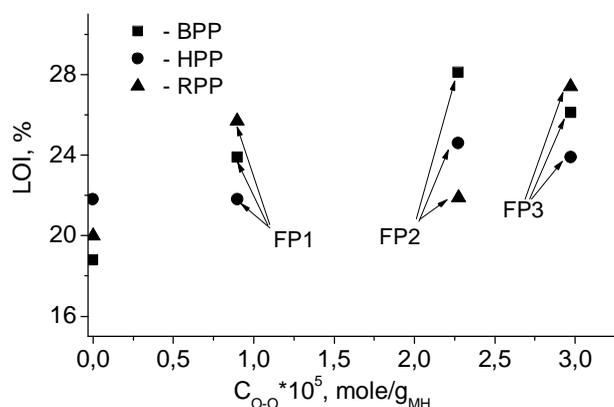


Fig. 7. Effect of the content of peroxide fragments at the MH surface and the polymer matrix nature on the composite oxygen index LOI

The worst flame retardancy is observed for HPP composites, for which the influence of MH modification on the flammability is expressed weakly. The composites based on BPP, that have the lowest flame retardancy in the case of unmodified MH, demonstrate very high LOI values for peroxidized MH as well as the trend toward this index enhancement when O-O content increases with the maximum for FP2. For RPP such trend is observed not so clearly though this composite exhibit rather high flame retardancy. It should be noted, however, that the burning process is very complicated and the differences in the matrix behavior (*e.g.* viscosity, easiness to form a char, capability to intumescence), which are evidently affected by the FP introduction into the system, can influence composite flammability and should be taken into consideration.

4. Conclusions

The obtained data witness about the significant effect of the surface modification of dispersed MH by functionalized polyperoxides on the rheological and physico-mechanical properties as well as flame retardancy of the filled composites. Such modification results in more even distribution of the MH particles in polymer matrix, that provides the improvement of composite physico-mechanical properties, especially impact resistance. The presence of radical-forming centers in the composition brings about increasing of the melt flow rates, that in turn improves the composite ability to be processed via jet molding. Besides, the presence of peroxide fragments immobilized at the surface of dispersed MH causes the enhancement of impact resistance of the composites based on ethylene-propylene copolymers as a result of chain transfer reactions of generated free radicals onto the ethylene links of polymer matrix, that leads to polymer branching or formation of a gradually cross-linked shell around the filler particles. With the increase of peroxide group content at the MH surface both the tensile strength value and the elongation at break increase up to 30 % while tensile modulus changes weakly. The best mechanical properties are exhibited by composites based on filler modified by the functionalized polyperoxide with allylic double bonds. The positive effect of additional allylic double bonds coming with FP3 on physico-mechanical properties of the filled material is proved by the results obtained at the study of the systems containing additional functional monomer TAC. In all cases, the peroxide surface modification influences positively the composite flame retardancy while this effect magnitude depends on the nature of polymeric matrix.

In our opinion, application of dispersed magnesium hydroxide modified by the functionalized polyperoxides as the filler for diverse propylene polymers is a very promising approach to obtaining the flame-retardant polymer composites with high physico-mechanical characteristics.

Acknowledgements

Part of the presented research has been co-funded by the European Commission within the FP6-project "FLARETPOL" (FP6-NMP 516998). This financial support is greatly acknowledged.

References

- [1] Cabrera-Alvarez E., Ramos-deValle L., Sanchez-Valdes S. *et al.*: Polym. Compos., 2014, **35**, 1060.
- [2] Zhu S., Zhang Y. and Zhang Yi.: J. Appl. Pol. Sci., 2003, **89**, 3248.
- [3] Liu M., Wang Q. and Liu Y.: Polym. Plast. Techn. Eng., 2010, **49**, 367.
- [4] Lipatov Yu.: Physico-Khimicheskie Osnovy Napolnenia Polymerov. Khimia, Moskva 1991.
- [5] Lederer K. and Aust N.: Chemical and Physical Aspects of Polymer Science and Engineering. Wiley-VCH, Weinheim 2002.
- [6] Aneli J., Mukbaniani O, Markarashvili E. *et al.*: Chem. & Chem. Techn., 2013, **7**, 141.
- [7] Shafranska O., Tokarev V., Voronov A. *et al.*: Langmuir, 2005, **8**, 3459.
- [8] Oduola M., Tokarev V., Voronov S. and Lastukhin Yu.: Adv. Mat. Res., 2007, **18-19**, 219.
- [9] Vilenskaya M., Karamov D. and Sorokin E.: Khim. Prom., 1970, **7**, 399.
- [10] Kurganskii V., Puchin V., Voronov S. and Tokarev V.: Polym. Sci. USSR., 1983, **25**, 1152.
- [11] Vasilyev V., Glus L. and Gubar S.: Visnyk Lviv. Polytech. Ins., 1985, **191**, 24.
- [12] Khunova V. and Liauw C.: Proceed. EUROFILLERS 97, UK, Manchester 1997, 199.

ВОГНЕТРИВКІ ПОЛІМЕРНІ КОМПОЗИТИ НА ОСНОВІ МОДИФІКОВАНОГО ГІДРОКСИДУ МАГНІЮ

Анотація. Одержано та охарактеризовано полімерні композити на основі гомо- та кополімерів пропілену як полімерної матриці і дисперсного гідроксиду магнію, модифікованого функціональними поліпероксидами, як наповнювача. Досліджено вплив природи поліпероксида та вмісту іммобілізованих на поверхні наповнювача пероксидних груп на механічні, реологічні властивості та вогнетривкість наповнених композитів. Результатом модифікації поверхні гідроксиду магнію пероксидами є більш рівномірний розподіл частинок гідроксиду магнію в полімерній матриці та посилення взаємодії на межі розділу фаз, що забезпечує покращення фізико-механічних властивостей композиту.

Ключові слова: поліпероксид, гідроксид магнію, модифікація поверхні, гомо- та кополімери поліпропілену, полімерні композити, вогнетривкість.

