Available online at www.sciencedirect.com

SCIENCE DIRECT®

polymer

Polymer 46 (2005) 12226–12232

www.elsevier.com/locate/polymer

Synthesis, structure, thermal and mechanical properties of nanocomposites based on linear polymers and layered silicates modified by polymeric quaternary ammonium salts (ionenes)

Michail V. Burmistr [a], Kostyantyn M. Sukhyy [a,*], Valery V. Shilov [b], Policarpos Pissis [c], Anna Spanoudaki [c], Irina V. Sukha [a], Vitalij I. Tomilo [a], Yuri P. Gomza [b]

[a] Ukrainian State Chemical Technology University, Pr. Gagarina, 8, Dnepropetrovsk 49005, Ukraine
[b] Institute for Macromolecular Chemistry, Ukraine National Academy of Sciences, Kharkivski shausse, 48, Kyiv 02160, Ukraine
[c] National Technical University of Athens, Department of Physics, Zografou Campus, Athens 15780, Greece

Received 15 February 2005; received in revised form 18 August 2005; accepted 20 October 2005
Available online 10 November 2005

Abstract

Polymer–clay composites has been prepared by melt blending an organo-bentonite with linear polymers (polyamide, polysterene and polypropylene) in a disk-screw extruder. In first time organo-clay was prepared by surface treatment of Na-forms bentonite with polymeric quaternary ammonium salts (PQAS). XRD indicated that organo-bentonite layers were exfoliated and dispersed into polyamide and polystyrene. Addition of 2 wt% organo-bentonites (optimal concentration) to polyamide increased tensile strength by 53% and Sharpy impact by 140%. With the incorporation of 2 wt% organo-bentonites (optimal concentration) into polystyrene the tensile strength increased to 28% and the Sharpy impact increased to 25%. For polypropylyne–organo-bentonites composites we did not observe delamination of layered structure, and as result absence of reinforcements. TGA showed that the polyamide and polystyrene nanocomposites have higher decomposition temperature in comparison with the original polymers.

Keywords: Layered silicates; Polymeric quaternary ammonium salts; Nanocomposites

1. Introduction

Polymer/layered silicate nanocomposites have drawn research attention over the last 20 years [1]. The major reason is that, as it has been demonstrated, introducing clay into polymers at the nanoscale level one can obtain improved mechanical, thermal, flammability and other properties at low clay contents (1–10 wt%). Polymer layered silicates have been prepared in different ways: intercalation in solution [2], in situ polymerization [3] and direct melt intercalation [4].

Layered silicates are classified as dioctahedral or trioctahedral. In clay minerals, the smallest structural unit contains three octahedral sites. If all three octahedral sites are occupied, i.e. have octahedral cations at their centers, the sheet is classified as trioctahedral. If only two octahedral sites are occupied and the third octahedron is vacant, the sheet is classified as dioctahedral. The 2:1 type layered silicates have various cation substitutions in both the tetrahedral and octahedral positions. Substitutions within the layers by ions of less charge, notably Si^{4+} by Al^{3+} in tetrahedral positions and Al^{3+} or Fe^{3+} by Mg^{2+} or Fe^{2+} in octahedral positions, result in negative charges on the layers. These are normally counterbalanced by alkali or alkali earth cations situated in the interlayer space. In pristine layered silicates the interlayer cations are usually hydrated Na^+, K^+, Ca^{2+} and Mg^{2+} ions but a wide range of other cations, including organic ions, can be introduced by exchange reactions [5].

The replacement of inorganic exchange cations in the galleries of the native clay by cationic surfactants such as alkylammonium ions is known to help compatibilize the surface chemistry of the clay and the hydrophobic polymer matrix. The role of alkylammonium cations in the organosilicate is to lower the surface energy of the inorganic host and improve its wetting characteristics with the polymer. Additionally, organic cations may provide various functional groups that can react with the polymer to improve adhesion or initiate

---

* Corresponding author. Tel.: +380 504 801 116; fax: 380 562 473 316.
E-mail address: ksukhyy@rambler.ru (K.M. Sukhyy).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.10.094

polymerization of monomers to improve the strength of the interfacial bond between the silicate and the polymer [6].

Three main types of composites (phase separated, intercalated and exfoliated or delaminated structure) may be obtained when a layered clay is associated with a different polymer matrix: polyamides [7–33], polystyrene [34–46], polypropylene [47–59], polyethylene, poly(methyl methacrylate), polyethylene oxide, epoxy polymer and other [60–94]. These primarily depend on the method of preparation and the nature of components used (layered silicates, organic cation and polymer matrix). As organic surfactant quaternary ammonium salts, aliphatic amines and various silicon-organic reagents are used.

In the present investigation polymeric quaternary ammonium salts (PQAS), were used to achieve organo-clay intercalation. Use of polymeric modifiers is explained by the following factors. In first, the polymeric quaternary ammonium salts have higher thermal stability in comparison with low-molecular quaternary ammonium salts and aliphatic amines. The thermal stability of which low-molecular surfactances, as a rule, does not exceed 200 °C. As against it thermal stability of polymeric quaternary ammonium salts more than 250 °C. It allows to be sure for what absence of any degradation processes at polymers processing.

Besides the fastening of polymeric quaternary ammonium salts on exchange positions layered silicates is statistical. And thus a part of ammonium groups are in a free condition (for low-molecular analogues it is impossible).

This fact allows in the greater degree to realize their useful qualities and to carry out the directed influence on processes of structure formation and improvement of the operational characteristics of polymeric composites.

In particular the polymeric quaternary ammonium salts are effective inhibitors of oxidizing degradation [95]. And, was shown, that they are more effective in comparison with low-molecular quaternary ammonium salts.

It is explained to that the quaternary ammonium salts particles brake electronic process basically at the expense by creation of adsorption potential by the positively charged atom of nitrogen, and the polymer, alongside with it, brakes process and at the expense of blocking a surface of polymeric structure.

Thus it is possible to combine of nanoscale layered silicates barrier properties and property of the polymeric quaternary ammonium salts to slow down the oxidizing degradation.

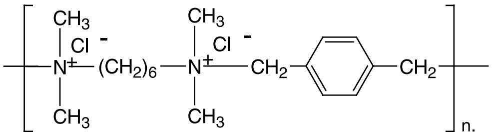
We investigated the effect of PQAS on the intercalation behaviour of linear polymer/organo-bentonite composites. The degree of intercalation is estimated using wide-angle X-ray diffraction, while mechanical and dynamic thermal analysis (DTA) are conducted to examine the effect of the PQAS-bentonite inclusions on the relevant material properties.

2. Experimental

2.1. Materials

The Bentonite powders were provided by Dash-Bent Trading Company and contained exchangeable cations of primarily Na^+, K^+ and Ca^{2+}. Bentonite is a fine powder with average particle size of 50 µm and a cation exchange capacity of 75 mequiv/100 g.

The polymeric quaternary ammonium salts were prepared by reaction between p-xylylenedichlorides (Aldrich) and diamines (Aldrich) [96].



Equimolar amounts of dichlorides and *N*,*N*,*N*′,*N*′-tetramethyl-1,6-hexanediamine were dissolved in acetone to obtain a 0.1 M solution of each reactant, stirred for 6 h at 40 °C. The product was dried at 60 °C/20 mm Hg and stored in a desiccator.

Polyamide-6 was provided by Caprolit (Russia), polystyrene—by Kaucuk (Czechia) and polypropylene—by Linos (Ukraine).

2.2. Preparation of organo-bentonite

Organo-bentonite was prepared by cationic exchange between the inorganic cations in the bentonite galleries and PQAS N^+-cations in an aqueous solution. Before this step we have increased concentration of montmorillonites fraction in bentonites.

One hundred and ten grams of bentonite were suspended in 10 l of distilled water. The dispersion was stood for 1 h, after which the finely disperse fraction was separated. This operation was repeated 3–4 times. After that, an aqueous solution of 5 g Na_2CO_3 was added gradually in order to exchange all inorganic cations in the bentonite galleries to Na^+ cations. The mixture was agitated vigorously for 15 min at boiling temperature. Then, 20 g of PQAS in 200 ml distilled water was added to the dispersion. The mixture was stirred for 24 h at 40 °C and then filtered, washed with hot water and dried at 60 °C in vacuum. The organo-bentonite thus obtained is highly hydrophobic. Particles potential of water suspension is for pure bentonite $\xi = -32$ mV whereas for organo-bentonite $\xi = +34$ mV.

2.3. Compounding

The preparation of polymer–clay composites has been conducted in two steps. Melt blended composites were prepared using an ED-2.2 disk-screw extruder at a constant rotating speed of 30 rpm and at temperature 200 ± 5 °C. Prior to each melt processing step, the samples based on polyamide were dried in a vacuum oven for 10 h at 80 °C.

Extruded composites were injection molded into standard speciments using a Kuasy 25–32 injection molding machine at optimal temperature ranges. The same procedure was used to prepare the pure polymers.

2.4. Characterisation

2.4.1. Wide-angle X-ray scattering

Wide-angle X-ray scattering (WAXS) profiles of the samples were collected in the transmission mode using a DRON-2,0 diffractometer. Nickel-filtered Cu K_α radiation (radiation wavelength $\lambda = 0.154$ nm) was produced by an IRIS-M7 generator at an operating voltage of 30 kV and a current of 30 mA. The scattering intensities were measured using a scintillation detector scanning in 0.2° steps over the range of angles of 2–40°. The diffraction curves obtained were normalized for the intensity of the primary beam and the scattering volume by the usual technique [97].

2.4.2. DTA-analysis

The DTA analysis was conducted on a Paylic-Paylic-Erday derivatograph, using a heating rate of 10 °C/min, from room temperature to 900 °C.

2.4.3. Mechanical testing

Tensile strength tests were conducted using a FP10/1 tension-testing machine. Yield strength and elongation at break were determined at a crosshead speed of 5.1 cm/min. Sharpy impact tests were performed using an impact testing machine KM-5T. Property values reported here represent an average of the results of five test runs on different samples.

3. Results and discussion

3.1. Characterization of organo-bentonites

As layered silicates are highly organized materials, wide-angle X-ray scattering gives valuable information on changes of their structure, especially concerning intercalation, exfoliation and delamination. The diffraction patterns of the pure bentonite and organo-bentonite are shown in Fig. 1. The X-ray patterns of pure bentonite revealed the diffraction peak at $2\theta = 5.3°$, that corresponds to a layer spacing $d = 1.03$ nm. The layer spacing d was calculated from the peak position using Bragg's low ($d = \lambda/2\sin(\theta)$). This value for pure bentonite is the same as documented for Na-forms montmorillonite [98].

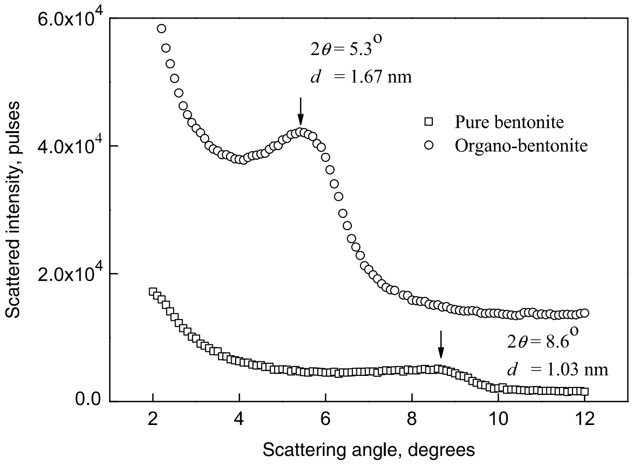


Fig. 1. X-ray diffraction patterns of bentonite and organo-bentonite.

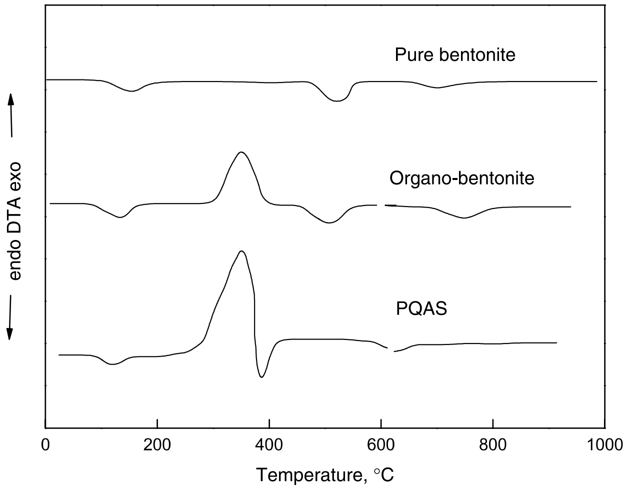


Fig. 2. DTA curves of bentonite, organo-bentonite and PQAS.

The primary silicate reflection at $2\theta = 8.6°$ in the organo-bentonites corresponds to a layer spacing $d = 1.67$ nm which represent an increase approximately to 0.6 nm. Thus varies not only position of the maximum containing the information on periodicity in an arrangement of basaltic planes, but also the form of this maximum (intensity and width), directly connected with the degree of perfection of the macrolattice. For organo-bentonite we observed more precise peak. It testifies to formation of more perfect structure at modification.

The thermal decomposition behavior of pure and organo-bentonites and PQAS is shown in Figs. 2 and 3. The DTA-peak observed in organo-bentonite at 280 °C corresponds to the degradation of PQAS. From TG-curves (Fig. 3) the concentration of PQAS in organo-bentonites was calculated to be 12 wt%.

3.2. Morphology of polymer–organo-bentonite composites

X-ray diffraction analysis is a powerful tool for examining the structure of polymer–organoclay nanocomposites. X-ray

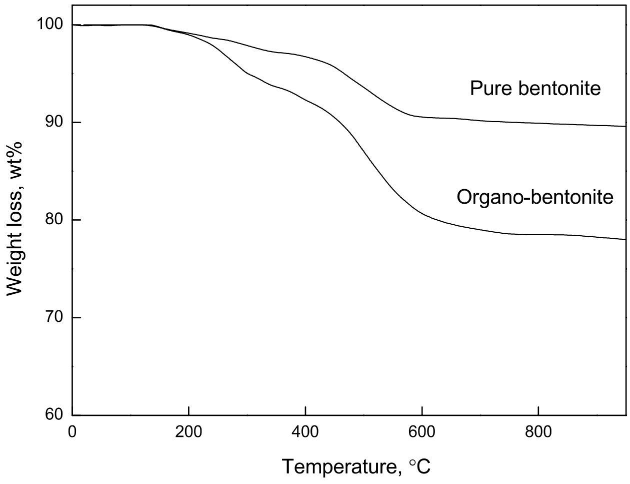


Fig. 3. TGA of bentonite and organo-bentonite.

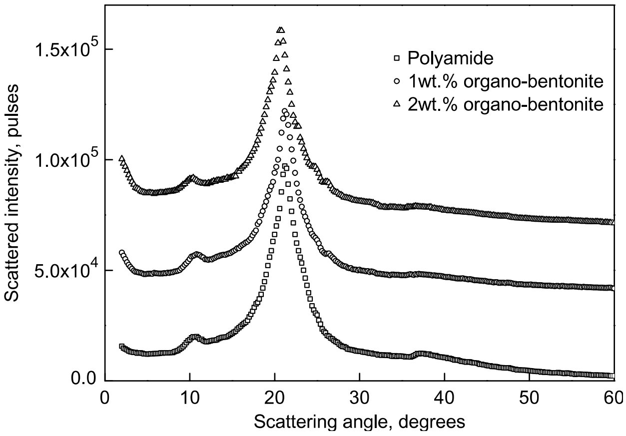


Fig. 4. X-ray diffraction patterns of PA and PA–organo-bentonite composites.

diffraction patterns of investigated polyamide, polystyrene and polypropylene composites with 1 and 2 wt% organo-bentonite contents are presented in Figs. 4–6 respectively. We studied only these concentrations as at the big concentration decrease in properties is observed that speaks about excess percolation barriers. For all investigated polymeric composites the degree of crystallinity has not changed.

The peak observed in organo-bentonites at $2\theta = 8.6°$ ($d = 1.67$ nm) has disappeared in the polyamides and polystyrenes composites containing 1 and 2 wt% of organo-bentonites. This result indicates the exfoliation of organo-bentonites of the elementary layers in the polymer matrix.

In polypropylene composites we see a different situation. For polypropylene composites containing 1% of organo-bentonites practically there is no peak in the small angles, characteristic for organo-bentonites. It can be connected with partial exfoliation of polypropylene composites.

The practically identical curves for polypropylene–organo-bentonite composites with 2 wt% of organo-bentonites and organo-bentonites (Fig. 6) show that there is no intercalation of the polymer matrix between the layers. This situation corresponds to that of a conventional filled polymer were each primary particle is dispersed in the polymer matrix.

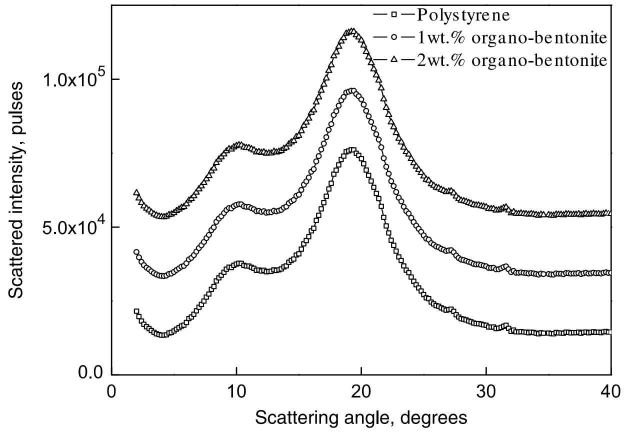


Fig. 5. X-ray diffraction patterns of PS and PS–organo-bentonite composites.

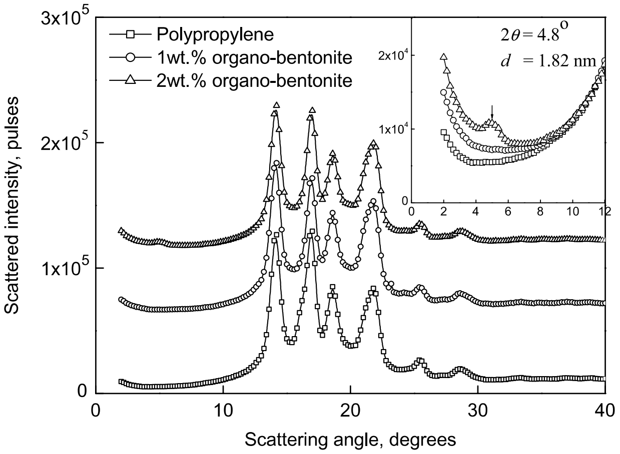


Fig. 6. X-ray diffraction patterns of PP and PP–organo-bentonite composites.

3.3. Mechanical properties of polymer–organo-bentonites composites

The mechanical properties of all the composites were examined. For pure PA the tensile strength is 31 MPa and Sharpy impact 32 kJ/m^2. With the incorporation of 1 wt% organo-bentonite, the tensile strength increased to 46 MPa (which is 50% higher than that of the pure PA) and, surprisingly, the Sharpy impact also increased to 68 kJ/m^2 (which is 115% higher than that of the pure PA). Addition of 2 wt% organo-bentonites (optimal concentration) increased tensile strength by 53% and Sharpy impact by 140%.

For the polystyrene composites a similar situation is observed, but more modest. With the incorporation of 2 wt% organo-bentonites (optimal concentration) the tensile strength increased to 22 MPa (which is 28% higher than that of the pure PS) and the Sharpy impact increased to 20 kJ/m^2 (which is 25% higher than that of the pure PS).

As summarized in Table 1, there was a clear tendency that both mechanical properties (tensile strength and Sharpy impact) improve with increasing organo-bentonite content up to 2 wt% in PA and PS composites. The decrease for 5 wt% seems consistent with the reduced exfoliation beyond 2 wt%. This deterioration of the mechanical properties can be attributed to the aggregation of the organo-bentonite nanolayers.

The effect of organo-bentonite loading on the mechanical properties of polypropylene composites are also shown in Table 1. Compared to the other samples, PP composites show a different behaviour. This means that the increase of mechanical properties is not based on the reinforcement effect of the dispersed organo-bentonite nanolayers. As mentioned above, this situation is similar to what is observed for conventional filled polymer. The fact that the PP–organo-bentonite composites have higher mechanical properties than the PP with pure bentonite can be explained as follows: The organo-bentonite surface is much more hydrophobic than the surface of pure bentonite, therefore organo-bentonite has good thermodynamical compatibility with the polymer matrix, which results to improved mechanical properties.

Table 1
Physical-mechanical properties of nanocomposites

Polymer	Properties	Content of pure bentonite (wt%)				Content of organo-bentonite (wt%)		
		0	1	2	5	1	2	5
Polyamid 6	Tensile strength (MPa)	30.86	39.84	36.76	32.71	46.17	47.12	34.61
	Sharpy impact (kJ/m^2)	31.78	28.15	24.12	21.71	68.13	76.12	51.20
	Elongation at break (%)	28.75	22.15	18.31	10.81	35.00	34.61	17.22
Polysterene	Tensile strength (MPa)	17.50	18.80	18.41	16.50	21.15	22.34	17.72
	Sharpy impact (kJ/m^2)	15.50	10.42	12.50	9.12	17.31	19.62	11.98
	Elongation at break (%)	13.53	25.00	19.75	8.17	39.51	42.15	12.34
Poly-propylene	Tensile strength (MPa)	14.78	12.77	15.50	6.73	19.36	21.08	20.27
	Sharpy impact (kJ/m^2)	53.35	25.40	21.55	21.82	43.37	47.73	36.65
	Elongation at break (%)	61.33	80.00	90.67	40.00	133.00	157.21	26.67

Summarising, we observed a strong relationship between morphology and mechanical behaviour of the investigated polymer–organo-bentonite composites. At full exfoliation of organo-bentonites layered structure more essential reinforcement of composites (polyamides and polystyrenes composites) is observed, and at partial exfoliation of layered structure the mechanical characteristics of composites essentially do not vary in comparison with pure polymer (polypropylene composites).

3.4. Thermal behaviour of polymer–organo-bentonite composites

Figs. 7–9 show the TGA results for pure polymer matrix (PA, PS, PP corresponding) and for the composites containing 2 wt% of the organo-bentonites.

The changing of thermal behaviour of investigated polymers composites are corresponding with described above structures and mechanical properties. For PA and PS composites we can see an essential changing of thermal properties, whereas this is not observed for PP composites. The PA and PS composites have higher thermal stability compared to pure polymer matrices. The similar results of higher thermal decomposition temperature of nanocomposites based on different organo-clay were reported before [16,20, 21,26,32].

For PA composites the initial thermal decomposition was increased from 350 °C for pure PA to 410 °C for nanocomposites containing 2 wt% organo-bentonites. Organo-bentonites possesses not only high thermal stability but also a different character of thermodegradation. Its layer structure exhibits great barrier effect, hindering the evaporation of the low molecular weight compounds during thermal degradation and slows down the diffusion of molecular oxygen into the polymeric matrix.

For PS composites the temperature of thermodegradation increased from 280 °C for virgin PS to 310 °C for nanocomposites containing 2 wt% organo-bentonites. Nevertheless, we did not observe a change of the thermodegradation process - the thermal degradation of PS composites is the same as that of the pure polymer.

For PP composites we did not observe essential change of properties.

The effects are more evident in PA composites, where the silicate is exfoliated and well dispersed. This may be partly due to kinetic effects, with the platelets retarding diffusion of oxygen into the polymer matrix.

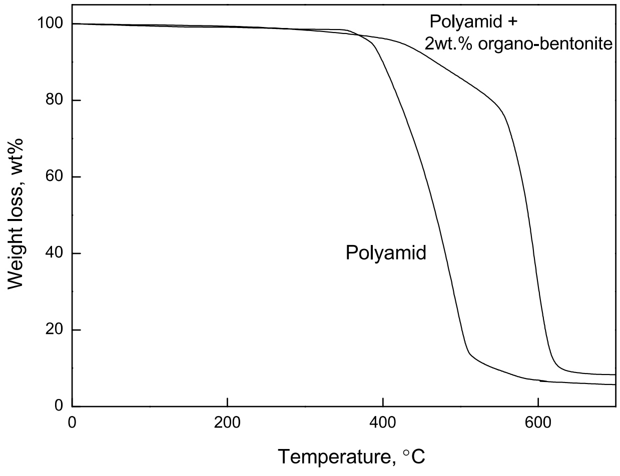


Fig. 7. TGA of PA and PA–organo-bentonite composites.

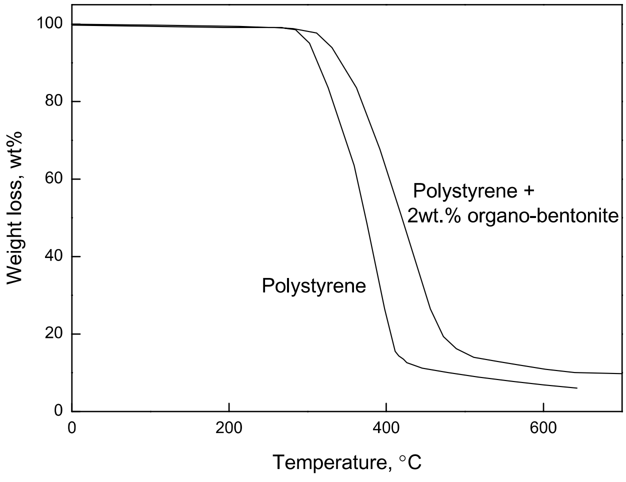


Fig. 8. TGA of PS and PS–organo-bentonite composites.

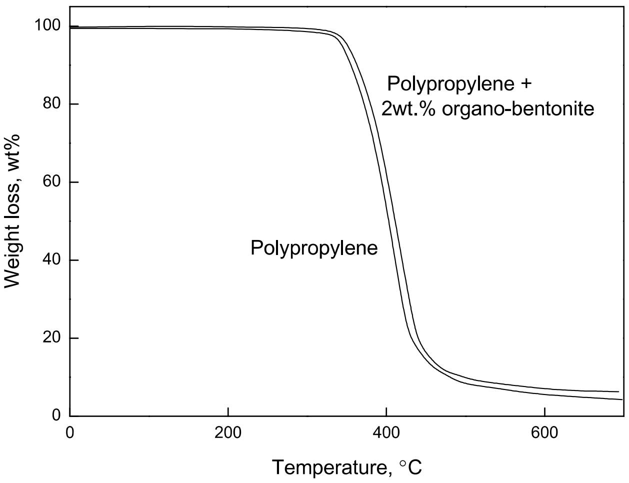


Fig. 9. TGA of PP and PP–organo-bentonite composites.

4. Conclusions

For the first time, polymeric quaternary ammonium salts, a cationic polymer was used for preparation of exfoliated linear polymer–organo-bentonite composites.

The preparation of nanocomposites by extrusion of linear polymers with organo-bentonites depends on the level of polymer's polarity. For non-polar polypropylene we did not observe the full exfoliation of organo-bentonites at this order preparation of composites. As a result, the mechanical and thermal properties were not improved. However, other authors have achieved delamination for PP–organo-clay under other conditions [47–59].

The PA and PS–organo-bentonites nanocomposites show improved mechanical properties: both tensile strength and, surprisingly, Sharpy impact were higher than the ones of the pure polymer. The PA and PS–organo-bentonite nanocomposites have also higher thermal stability compared to the pure polymer matrix. The PA and PS–organo-bentonite nanocomposites showed the best balance in properties at 2 wt% of clay loading.

References

[1] Theng BKG. Formation and properties of clay–polymer complexes. Developments in soil science. Amsterdam: Elsevier; 1979.
[2] Ogata N, Jimenez G, Kawai H, Ogihara T. J Polym Sci, Polym Phys 1997; 35:389–96.
[3] Usuki A, Kojima Y, Kawasumi M, Okada A, Fukushima Y, Kurauchi T, et al. J Mater Res 1993;8:1179–84.
[4] Kawasumi M, Hasegawa N, Kato M, Usuki A, Okada A. Macromolecules 1997;30:6333–8.
[5] Newman ACD. Chemistry of clays and clay minerals. New York: Wiley; 1987.
[6] Krishnamoorti R. Chem Mater 1996;8:1728–34.
[7] Liu X, Wu Q, Berglund LA, Lindberg H, Fan J, Qi Z. J Appl Polym Sci 2003;88(4):953–8.
[8] Liu X, Wu Q. Macromol Mater Eng 2002;287(3):180–6.
[9] Zhang G, Li Y, Yan D. Polym Int 2003;52(5):795–8.
[10] Varlot K, Reynaud E, Kloppfer MH, Vigier G, Varlet J. J Polym Sci, Polym Phys 2001;39(12):1360–70.
[11] Masenelli-Varlot K, Reynaud E, Vigier G, Varlet J. J Polym Sci, Polym Phys 2002;40(3):272–83.
[12] Kojima Y, Usuki A, Kawasumi M, Okada A, Kurauchi T, Kamigaito O, et al. J Polym Sci, Polym Phys 1995;33(7):1039–45.
[13] Kojima Y, Usuki A, Kawasumi M, Okada A, Kurauchi T, Kamigaito O, et al. J Polym Sci, Polym Chem 1993;31(7):1755–8.
[14] Liu L, Qi Z, Zhu X. J Appl Polym Sci 1999;71(7):1133–8.
[15] Kojima Y, Usuki A, Kawasumi M, Okada A, Kurauchi T, Kamigaito O. J Polym Sci, Polym Chem 1993;31(4):983–6.
[16] Hu Y, Wang S, Ling Z, Zhuang Y, Chen Z, Fan W. Macromol Mater Eng 2003;288(3):272–6.
[17] Wu Z, Zhou C, Qi R, Zhang H. J Appl Polym Sci 2002;83(11):2403–10.
[18] Kojima Y, Matsuoka T, Takahashi H, Kurauchi T. J Appl Polym Sci 1994;51(4):683–7.
[19] Maiti P, Okamoto M. Macromol Mater Eng 2003;288(5):440–5.
[20] Lincoln D, Vaia R, Wang ZG, Hsiao BS, Krishnamoorti R. Polymer 2001; 42:9975–85.
[21] Shelley JS, Mather PT, DeVries KL. Polymer 2001;42:5849–58.
[22] Lincoln DM, Vaia RA, Wang ZG, Hsiao BS, Krishnamoorti R. Polymer 2001;42:1621–31.
[23] Ramesh C, Bhoje E. Macromolecules 2001;34:3308–13.
[24] Fornes TD, Yoon PJ, Keskkula H, Paul DR. Polymer 2001;42:9929–40.
[25] Kim GM, Lee DH, Hoffmann B, Kressler J, Stoppelman G. Polymer 2001;42:1095–100.
[26] VanderHart DL, Asano A. Macromolecules 2001;34:3819–22.
[27] Cho JW, Paul DR. Polymer 2001;42:1083–94.
[28] Dennis HR, Hunter DL, Chang D, Kim S, White JL, Cho JW, et al. Polymer 2001;42:9513–22.
[29] Liu T, Lim KP, Pramoda KP, Chen ZK. Polymer 2003;44:3529–35.
[30] Loo LS, Gleason KK. Macromolecules 2003;36:2587–90.
[31] Utracki LA, Simha R, Gsrcia-Rejon A. Macromolecules 2003;36: 2114–21.
[32] Fornes TD, Yoon PJ, Paul DR. Polymer 2003;44:7545–56.
[33] Qin H, Su Q, Zhang S, Zhao B, Yang M. Polymer 2003;44:7533–8.
[34] Wu TM, Hsu SF, Wu JY. J Polym Sci, Polym Phys 2002;40(8):736–46.
[35] Chen GH, Wu DJ, Weng WG, He B, Yan W. Polym Int 2001;50(9): 980–5.
[36] Kim TH, Lim ST, Lee CH, Choi HJ, Jhon MS. J Appl Polym Sci 2003; 87(13):2106–12.
[37] Tseng CR, Wu SC, Wu JJ, Chang FC. J Appl Polym Sci 2002;86(10): 2492–501.
[38] Kim TH, Jang LW, Lee DC, Choi HJ, Jhon MS. Macromol Rapid Commun 2002;23(3):191–5.
[39] Tseng CR, Lee HY, Chang FC. J Polym Sci, Polym Phys 2002;39(17): 2097–107.
[40] Morgan AB, Harris RH, Kashiwagi T, Leonard J. Fire Mater 2002;26: 247–53.
[41] Wu TM, Hsu SF, Wu JY. J Polym Sci, Polym Phys 2003;41(14):1730–8.
[42] Zhu J, Wilkie CA. Polym Int 2000;49(10):1158–63.
[43] Wu TM, Hsu SF, Wu JY. J Polym Sci, Polym Phys 2003;41(6):560–70.
[44] Chen G, Liu S, Chen S, Qi Z. Macromol Chem Phys 2001;202(7): 1189–93.
[45] Meincke O, Hoffmann B. Macromol Chem Phys 2003;204(5–6):823–30.
[46] Chen G, Liu S, Zhang S, Qi Z. Macromol Rapid Commun 2000;21(11): 746–9.
[47] Tang Y, Hu Y, Wang S, Gui Z, Chen Z, Fan Z. Polym Int 2003;52(8): 1396–400.
[48] Zhang Q, Fu Q, Jiang L, Lei Y. Polym Int 2000;49(12):1561–4.
[49] Koo CM, Kim MJ, Choi MH, Kim SO, Chung IJ. J Appl Polym Sci 2003; 88(6):1526–35.
[50] Xu W, Ge M, He P. J Polym Sci, Polym Phys 2002;8(5):408–14.
[51] Ma J, Qi Z, Hu Y. J Appl Polym Sci 2001;82(14):3611–7.
[52] Tang Y, Hu Y, Wang S, Gui Z, Chen Z, Fan W. J Appl Polym Sci 2003; 89(9):2586–8.
[53] Chen L, Wong SC, Pisharath S. J Appl Polym Sci 2003;88(14):3298–305.
[54] Ma J, Zhang S, Qi Z, Li G, Hu Y. J Appl Polym Sci 2002;83(9):1978–85.
[55] Svoboda P, Zeng C, Wang H, Lee LJ. J Polym Sci, Polym Phys 2002; 85(7):1562–70.

[56] Gorrasi G, Tammaro L, Tortora M, Vittoria V, Kaempfer D, Reichert P. J Polym Sci, Polym Phys 2003;41(15):1798–805.

[57] Kato M, Usuki A, Okada A. J Polym Sci, Polym Phys 1997;66(9):1781–5.

[58] Wagenknecht U, Kretzschmar B. Macromol Symp 2003;194(1):207–12.

[59] Hambir S, Bulakh N, Kodgire P, Kalgaonkar R, Jog JP. J Polym Sci, Polym Phys 2001;39(4):446–50.

[60] Kim J, Oh T, Lee D. Polym Int 2003;52(7):1058–63.

[61] Kim J, Oh T, Lee D. Polym Int 2003;52(7):1203–8.

[62] Kim J, Lee D, Oh TS, Lee DH. J Polym Sci, Polym Phys 2003;89(10): 2633–40.

[63] Salahuddin N, Rehab A. Polym Int 2003;52(2):241–8.

[64] Nah C, Ryu HJ, Han SH, Rhee JM, Lee MH. Polym Int 2001;50(11): 1265–8.

[65] Nah C, Ryu HJ, Kim WD, Chang YW. Polym Int 2003;52(8):1359–64.

[66] Nah C, Ryu HJ, Kim WD, Choi SS. Polym Adv Technol 2002;13(9): 649–52.

[67] Wu YP, Jia QX, Yu DS, Zhang LQ. J Polym Sci, Polym Phys 2003; 89(14):3855–8.

[68] Zhang X, Xu R, Wu Z, Zhou C. Polym Int 2003;52(5):790–4.

[69] Li Y, Zhao B, Xie S, Zhang S. Polym Int 2003;52(6):892–8.

[70] Wang S, Hu Y, Lin Z, Gui Z, Wang Z, Chen Z, et al. Polym Int 2003; 52(6):1045–9.

[71] Drozdov D, Christiansen JC, Gupta RK, Shah AP. J Polym Sci, Polym Phys 2003;41(5):476–92.

[72] Chang JH, An YU, Sur GS. J Polym Sci, Polym Phys 2003;41(1):94–103.

[73] Chang JH, Park DK, Ihn KJ. J Polym Sci, Polym Phys 2001;39(5):471–6.

[74] Paul MA, Alexandre M, Degue P, Calberg C. Macromol Rap Commun 2003;24(9):561–6.

[75] Hsiao SH, Liou GS, Chang LM. J Polym Sci, Polym Phys 2001;80(11): 2067–72.

[76] Chen KH, Yang SM. J Polym Sci, Polym Phys 2002;86(2):414–21.

[77] Alexandre M, Beyer G, Henrist C, Cloots R, Rulmont A, Dubois P. Macromol Rap Commun 2001;22(8):643–6.

[78] El-Nahhal Y, Nir S, Polubesova T, Margulies L, Rubin B. Pesticide Sci 1999;55(8):345–51.

[79] Wang Y, Zhang L, Tang C, Yu D. J Polym Sci 2000;78(11):1879–83.

[80] Pluta M, Galeski A, Alexandre M, Paul MA, Dubois P. J Polym Sci 2002; 86(6):1497–506.

[81] Krikorian V, Kurian M, Galvin ME, Nowak AP, Deming TJ, Pochan DJ. J Polym Sci, Polym Phys 2002;40(22):2579–86.

[82] Huimin W, Minghua M, Yongcai J, Qingshan L, Xiaohong Z, Shikang W. Polym Int 2002;51(1):7–11.

[83] Wang S, Hu Y, Tang Y, Wang Z, Chen Z, Fan W. J Polym Sci 2003;89(9): 2583–5.

[84] Ke YC, Yang ZB, Zhu CF. J Polym Sci 2002;85(13):2677–91.

[85] Liu HJ, Hwang JJ, Chen-Yang YW. J Polym Sci, Polym Chem 2002; 40(22):3873–82.

[86] Lee A, Lichtenhan JD. J Polym Sci 1999;73(10):1993–2001.

[87] Yeh JM, Chin CP, Chang S. J Polym Sci 2003;88(14):3264–72.

[88] Kim JY, Jung WC, Park KY, Suh KD. J Polym Sci 2003;89(11):3130–6.

[89] Wan C, Qiao X, Zhang Y, Zhang Y. J Polym Sci 2003;89(8):2184–91.

[90] Vora RH, Pallathadka PK, Goh SH, Chung TS, Lim YX, Bang TK. Mater Eng 2003;288(4):337–56.

[91] Suh DJ, Park OO. J Polym Sci 2002;83(10):2143–7.

[92] Khayankarn O, Magaraphan R, Schwank JW. J Polym Sci 2003;89(11): 2875–81.

[93] Ma J, Shi L, Yang M, Li B, Liu H, Xu J. J Polym Sci 2002;86(14): 3708–11.

[94] Chang JH, Park DK. J Polym Sci, Polym Phys 2001;39(21):2581–8.

[95] Burmistr MV. Dissertation D. Sci: Institute for Macromolecular Chemistry, Ukraine National Academy of Sciences, Ukraine; 1994.

[96] Burmistr MV, Shilov VV, Sukhyy KM, Pissis P, Polizos G. Polym Sci 2003;45:785.

[97] Lipatov YS, Shilov VV, Gomza YP, Kruglyak NE. X-ray method of analysis of polymer systems. Kiev: Naukova Dumka; 1982 [in Russian].

[98] Emerson WW. Nature 1957;180:48–52.