

Kaolin Modified with New Resin–Iron Chelate as Flame Retardant System for Polypropylene

A. B. Shehata, M. A. Hassan, N. A. Darwish

National Institute of Standards, Tersa Street, El-Haram, P.O. Box 136, Giza no. 12211, Egypt

Received 25 April 2003; accepted 17 October 2003

ABSTRACT: Polypropylene's fire-retardant properties can be improved by using modified kaolin. Modification was done by reaction of kaolin with a prepared resin–iron chelate. Polypropylene samples were loaded with different amounts of kaolin, modified kaolin, and their mixture. Ignition properties of the produced samples were evaluated using cone calorimeter, UL 94, and thermogravimetric analysis techniques. It was found that sample S2 loaded with a mixture of kaolin and modified kaolin had significantly

reduced the smoke generation and had a heat release rate comparable to that with kaolin. It was also found that samples S4 and S5 loaded with modified kaolin burned out earlier than did the other samples. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 3119–3125, 2004

Key words: resin; chelation; kaolin modification; thermal properties; fire retardant

INTRODUCTION

Synthetic polymers are a pervasive part of today's society. They can be found in nearly every commercial building, residential houses, and transportation vehicles, for example. They permeate our surroundings. Today, synthetic polymer materials are rapidly replacing more traditional materials such as steel, nonferrous metals, and natural polymer materials such as wood, cotton, natural rubber, and so on. However, one weak aspect of synthetic polymer materials compared with steel and other metals is that these materials are combustible under certain conditions. Thus the majority of polymers containing end products (e.g., cables, carpets, furniture computer cabinets, etc.) must have a satisfactory degree of resistance to ensure public safety from fire. The fire safety of materials can be enhanced by increased ignition resistance, reduced flame spread rates, smaller heat release rates, and reduced amounts of toxic and smoke products. The use of more thermally stable polymers, of which many are available, would be a valid solution to these requirements but generally the cost of these materials is relatively high and furthermore their physical properties or processability may not be as desirable as those of less-stable polymers. Instead, the most common approach to enhance fire safety performance is the use of flame-retardant additives in inexpensive polymers, for example, polypropylene (PP), polyethylene, acry-

lonitrile–butadiene–styrene, and nylons. Although halogenated flame retardants are highly effective in reducing the heat release rate of polymers, nowadays the environmental impact of processing and combustion of certain halogenated flame retardants has become an important issue. Therefore there is a need for new environmentally friendly flame-retardant materials as alternatives. Beside their flame-retardant properties, mineral fillers for use in reinforced plastics or resins offer several advantages such as aid in producing a smooth surface finish, reductions in cracking and shrinkage, contribution to high dielectric strength, and resistance to chemical action and weathering.¹

China clay (kaolin) is a two-layered hydrous alumina silicate consisting of chemically bonded layers of silica and gibbsite (hydrous alumina) and has the form of hexagonal platelets.² Kaolin filler, in particular, is widely used in polymer compounds because it gives improved flow in the molding process and hence ensures uniform distribution of reinforcement.² Also the addition of kaolin to polymers improves bonding with polymers, ease of dispersion, and nonreactivity in critical applications.³ Le Bras and Bourbigot⁴ found that the addition of natural clay materials in intumescent PP-based formulations leads either to a decrease or to an increase of their fire-retardant performance versus the chemical or the physical characteristics of the clay materials. Zaikov et al.^{5–7} studied the effect of modification intercalation of kaolin on its properties as flame retardants for polymers. In this study an attempt was made to modify kaolin with a prepared polymeric resin–iron chelate and the product was incorporated into PP samples as a flame retardant. The

Correspondence to: A. Shehata.

TABLE I
Specifications of Polypropylene

Property	Value
Melt flow rate, dg/min	12.00
Density, g/cm ³	0.900
Tensile strength at yield, MPa	27.00
Elongation at yield, %	5.000
Flexural modulus, MPa	1450

flammability and gas emission properties of the prepared PP samples were assessed using cone calorimetry, UL 94, and thermogravimetric analysis techniques.

EXPERIMENTAL

Materials

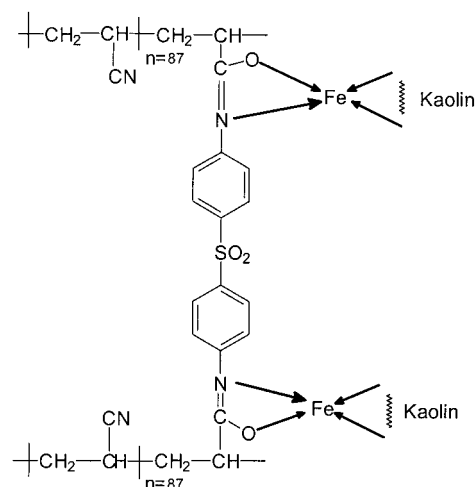
Di-amino-diphenyl sulfone and azobisisobutyronitrile (AIBN) were supplied by Fluka Chemie (Buchs, Switzerland). Acrylonitrile, acryloylchloride, triethylamine, and ferric chloride were supplied by Merck (Darmstadt, Germany). All solvents used and kaolin were provided by EDWIC (Egypt). Polypropylene was supplied by HMC Polymers Co. (Thailand). Its specifications are shown in Table I.

Preparation of the resin-iron chelate and modification of kaolin

Acrylonitrile (135 mL) in DMF was mixed with 5 g of the crosslinking agent⁸ dissolved in DMF, and 0.45 g of AIBN was added as initiator. The mixture was heated at 60°C for 15 min until the target resin was formed. The obtained resin was transferred into a 500-mL beaker. The same experiment was repeated to obtain another amount of the resin, which was also transferred to the same 500-mL beaker. About 300 mL DMF was added to the beaker and the resin was mechanically stirred for 30 min. A number of grams of FeCl₃ were dissolved in acetone and added dropwise to the resin under stirring, which continued overnight at 50°C for chelation. The resin-iron complex was allowed to cool after which it was decanted, filtered, washed with acetone, then dried and milled to a fine powder. After that kaolin was mixed with the milled resin-iron chelate in a ratio of 2 : 1, respectively, in DMF and stirred at 60°C for 72 h to produce the modified kaolin. The solution was left to cool then filtered and the precipitate was dried. The proposed structure of the modified kaolin resin is shown in Scheme 1.

Mixing and molding

Samples containing different amounts of the modified kaolin/resin-iron chelate were added to 100 parts of



Scheme 1 Modified kaolin/resin-iron chelate.

PP and mixed in a Brabender apparatus at 200°C (C. W. Brabender Instruments, South Hackensack, NJ), then pressed at 200°C and 10 bars. The prepared formulations are shown in Table II.

Thermogravimetric analysis (TGA) of the prepared resin-cobalt chelate and the formulated PP samples was performed using a Shimadzu analyzer (Shimadzu, Kyoto, Japan). Flammability characteristics were assessed using a flame chamber UL-94 and cone calorimeter, fire testing technology at a heat flux of 35 kW/m² according to ASTM E 1354-92.

RESULTS AND DISCUSSION

Thermogravimetric analysis

Characteristic DSC thermograms of kaolin, iron chelate, and modified kaolin are shown in Figure 1(a). It is clear that kaolin decomposed endothermically at 550°C, and the prepared iron chelate decomposed exothermically at 300°C. Meanwhile, the modified kaolin sample decomposed exothermically in two stages at 330 and 410°C, but with less heat released, and finally it decomposed endothermically with behavior similar to that of kaolin. This means that the modified kaolin sample possesses a combination of thermal decomposition properties of kaolin and iron chelate, which is a

TABLE II
Polypropylene Samples Loaded with Modified Kaolin

Ingredient	Sample						
	S1	S2	S3	S4	S5	S6	S7
PP	100	100	100	100	100	100	100
Kaolin	40	30	20	—	—	50	—
Modified kaolin	10	20	30	40	30	—	—

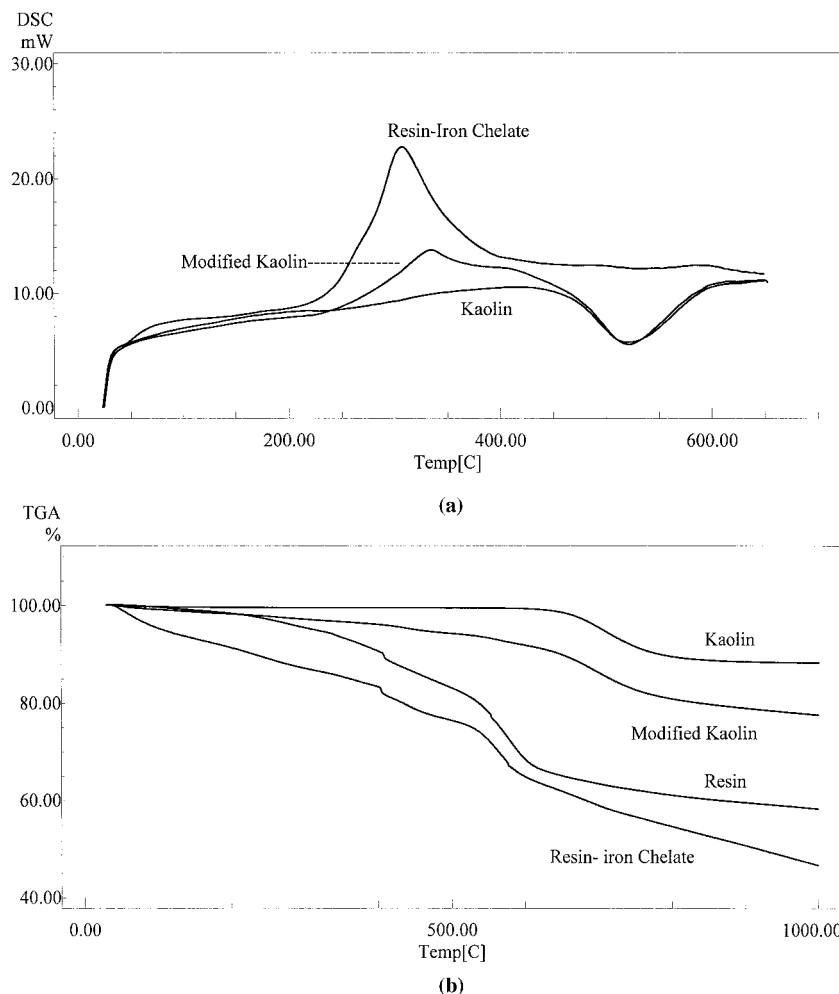


Figure 1 (a) DSC thermograms of kaolin, iron-chelate resin, and modified kaolin samples. (b) Collective TGA thermogram of kaolin, modified kaolin, resin, and resin-iron chelate.

clear indication that modification of kaolin has occurred. Figure 1(b) illustrates the TGA behavior of the prepared acrylonitrile resin, its iron chelate, kaolin, and modified kaolin. It can be noticed generally that the resin and its iron chelate are less stable than kaolin and modified kaolin. They decomposed in three stages and their main decomposition temperatures are 580 and 600°C, respectively. They also showed 40 and 50% weight loss. Meanwhile, kaolin is the most thermally stable followed by its modified product with the prepared resin chelate. They decomposed at 700 and 750°C and showed 10 and 20% weight loss, respectively. TGA of PP samples shown in Table II was also studied and the results are given in Table III. Although samples containing kaolin and modified kaolin in different compositions (S1–S6) started to decompose earlier than pure PP (S7) they are more thermally stable, as can be seen from weight loss percentage. The lowest weight loss percentage, 72.037% among these samples, was observed for sam-

ple S3, loaded with 20 phr kaolin and 30 phr modified kaolin. On the other hand, the sample containing 30 phr of modified kaolin (S5) showed the highest starting decomposition temperature, 359°C, and its end of decomposition temperature was about 5°C higher than that of sample S6 loaded with kaolin. Meanwhile

TABLE III
TGA Properties of Polypropylene Samples

Sample	Decomposition temperature (°C)		Weight loss (%)
	Start	End	
S1	313.00	812.00	75.098
S2	371.00	802.00	73.753
S3	336.00	773.00	72.037
S4	541.00	810.00	83.409
S5	359.70	798.33	80.835
S6	339.00	793.98	73.829
S7	401.00	698.00	98.090

TABLE IV
Ignition Properties of Polypropylene Samples Filled with Pure and Modified Kaolin

Sample	TTI (s)	Peak HRR (kW/m ²) (% versus control)	Average HRR (kW/m ²)	Average SEA (m ² /kg)	Average CO yield (kg/kg)
S1	54	1048 (45.90)	853	1059	0.0002
S2	58	942 (41.25)	790	622	0.0002
S3	40	937 (41.02)	803	1041	0.0001
S4	37	1371 (60.06)	1045	979	0.0002
S5	34	1311 (57.40)	1005	1079	0.0003
S6	113	870 (38.09)	713	891	0.0002
S7	71	2283 (100.0)	1486	888	0.005

the sample containing a mixture of 40 phr kaolin and 10 phr modified kaolin (S1) showed the lowest starting decomposition temperature, 313°C, but its end of decomposition temperature was the highest (812°C); that is, it was more thermally stable. It can generally be concluded that kaolin or modified kaolin imparted considerable thermal stability to PP samples.

Flammability properties

The potential hazard of any material depends on many factors including ignitability, heat release rate, mass loss rate, smoke evolution, and evolution of toxic gases (e.g., CO). Cone calorimeter data address most of these factors. The following parameters were calculated and used as criteria to compare the effectiveness of kaolin and modified kaolin on the flammability properties of polypropylene: time to sustained igni-

tion, peak heat release rate (HRR), time to peak, and average HRR at 60 and 180 s.

Ignition and heat release

The time to sustained ignition of PP samples containing kaolin and modified kaolin is shown in Table IV. It is clear that sample S6, containing 50 phr of kaolin, showed the highest ignition time, 113 s. Moreover, addition of modified kaolin to PP compositions reduces the ignition time in general and sample S5 was the lowest at 34 s. On the other hand, all PP compositions containing either kaolin or modified kaolin showed a lower HRR peak than that of the pure PP sample, which showed HRR peak at 2383 kW/m². Sample S6, containing pure kaolin, showed the lowest HRR peak, 870 kW/m², which is 38.1% of the value shown by S7 (pure PP). It can also be noticed that there

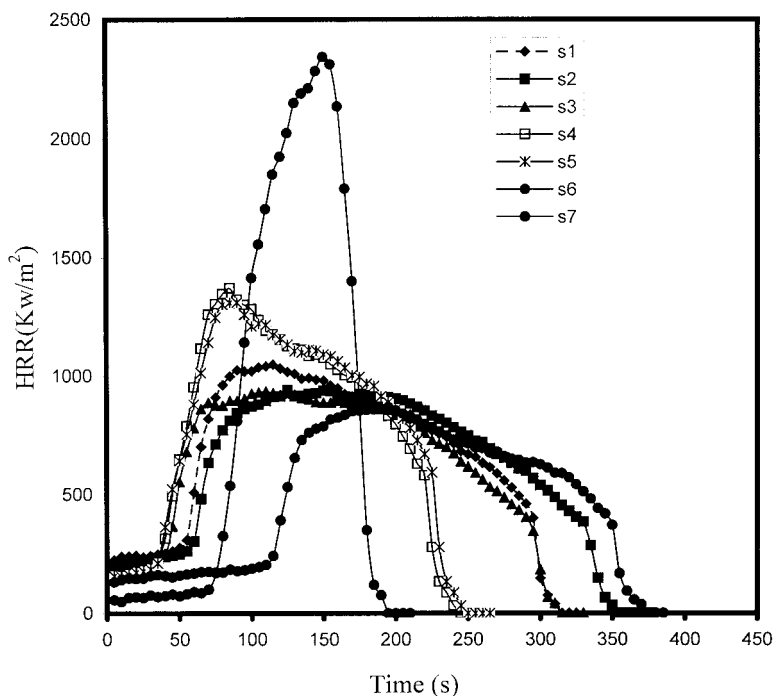


Figure 2 Comparison of heat release rate (HRR) at a heat flux of 35 kW/m².

TABLE V
Ignition Properties of Polypropylene Samples Filled with Pure and Modified Kaolin After 60 and 180 s

Sample	Average HRR (kW/m ²)	
	At 60 s	At 180 s
S1	863.58	595.557
S2	748.589	849.414
S3	792.865	851.613
S4	1018.849	0.000
S5	892.201	0.000
S6	683.957	734.607
S7	1300.791	0.000

is only a slight difference in the HRR peaks between samples S2 and S3, which contain mixtures of different compositions of kaolin and modified kaolin, where they reduced the HRR about 59%. Furthermore, S4 and S5, which are loaded with modified kaolin, only

showed HRR peaks at 1371 and 1311 kW/m², respectively, which are higher than those of samples containing a mixture of kaolin and modified kaolin. Figure 2 gives an overview on HRR behavior of all samples. It can be further seen that samples S4 and S5 loaded with modified kaolin burned out earlier than did the other samples. For greater understanding of the ignition behavior, the average HRR results at 60 and 180 s of PP compositions are shown in Table V and as bar charts in Figures 3 and 4.

At 60 s, it can be noticed that samples are arranged in the order: S7 > S4 > S5 > S1 > S3 > S2 > S6, which means that the lowest average, 684 kW/m², was reached by the addition of 50 phr pure kaolin. On the other hand, sample S4 showed an average HRR of 1019 kW/m², which comes after sample S7 (the highest) that showed 1301 kW/m². If these results are compared with those obtained at 180 s, it can be observed that samples S4 and S5 burned out earlier,

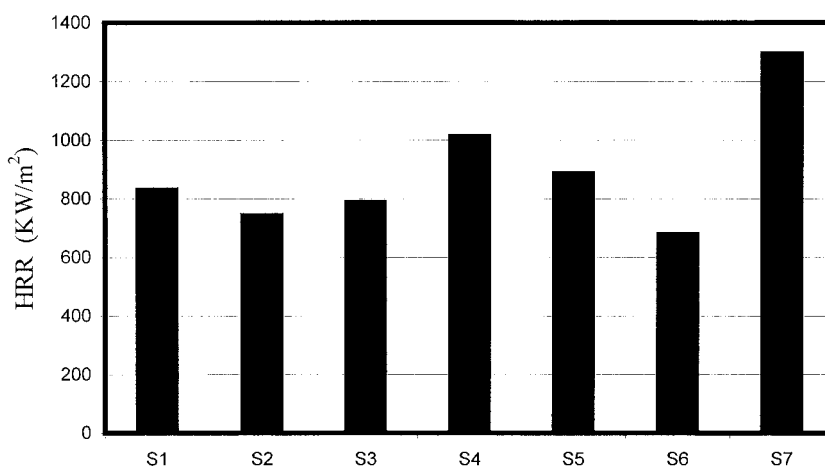


Figure 3 Comparison of average HRR at 60 s.

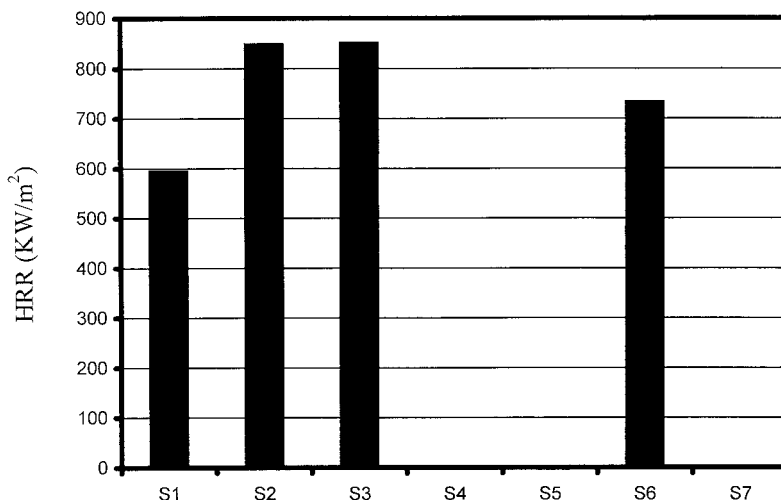


Figure 4 Comparison of average HRR at 180 s.

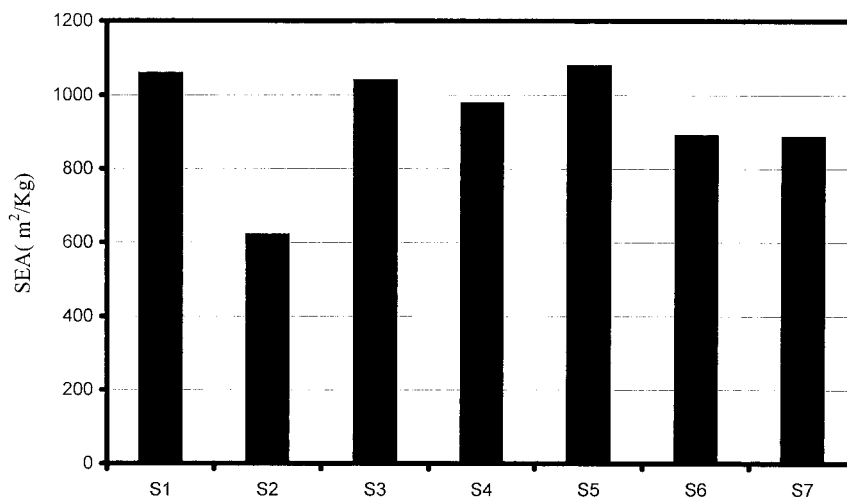


Figure 5 Comparison of average smoke-specific extinction area (SEA).

whereas the remaining samples are still burning. This burn out of samples S4 and S5 loaded with modified kaolin can be regarded as a considerable achievement of using modified kaolin as a flame-retardant material for PP.

Smoke generation

Figure 5 shows a comparative chart of the average smoke specific extinction area (SEA) of the seven PP compositions. From the figure one can see that the sample containing a mixture of 30 phr kaolin and 20 phr modified kaolin (S2) showed the lowest SEA value, 622 m²/kg, which is lower than that of pure PP, sample S7. This means that this mixture is the optimum ratio that can be effective in reducing the formation of smoke as a result of PP burning. Sample S5, in contrast, showed the highest SEA value, 1079 m²/kg. The SEA of the other samples are arranged in the following order: S1 > S3 > S4 > S6 > S7.

Generation of CO

The average CO yield for each of PP compositions is shown in Table IV. It can be noticed that the addition

of kaolin and modified kaolin in different compositions reduced the generated average CO to nearly 0.0002 kg/kg, whereas sample S7, representing PP, showed 0.005 kg/kg average CO yield. It may be argued that iron atoms involved in the structure of modified kaolin would have captured the emitted CO molecules by further complexation.

Flame chamber ISO 1210 test

This test was carried out horizontally because all samples did not comply with any of the vertical categories. The results obtained are given in Table VI. It was found that all the samples achieved the category FH3, in which the combustion front passes the 100-mm mark and the linear burning rate does not exceed 40 mm/min. From Table VI it is seen that the lowest rate of burning, 23.43 mm/min, is recorded for sample S1, followed by the rates of samples S2 and S3, which are equal at 25 mm/min, whereas samples S4, S5, and S6 showed higher rates of burning, 30.40, 29.41, and 30.82 mm/min, respectively. It can be concluded that the use of a mixture of modified kaolin and kaolin in different compositions improved the rate of burning better than PP samples containing only kaolin or modified kaolin.

TABLE VI
Rate of Burning of Different Polypropylene Compositions

Sample	Time of burning (s)	Rate of burning (mm/min)
S1	192	23.4
S2	180	25.0
S3	180	25.0
S4	148	30.4
S5	153	29.4
S6	146	30.8
S7	229	18.8

CONCLUSIONS

1. A mixture of 30 phr kaolin and 20 phr modified kaolin included in sample S2 substantially reduced the smoke generated much more than did pure kaolin. The sample also showed ignition properties comparable to those of kaolin.
2. Samples S4 and S5 loaded with modified kaolin burned out earlier than did the other PP samples.

3. All samples loaded with either kaolin, modified kaolin, or their mixture substantially reduced the amount of CO emitted.

References

1. Grim, R. E. International Series in the Earth Sciences: Applied Clay Mineralogy; McGraw-Hill: New York, 1962.
2. Hancox, N. L.; Mayer, R. M. Design Data for Reinforced Plastics; Chapman & Hall: London, 1994.
3. Ferringo, T. H.; Taranto, M. In: Kaolin; Handbook of Fillers and Reinforcements for Plastics; Van Nostrand-Reinhold: New York, 1978; pp. 119–125.
4. Le Bras, M.; Bourbigot, S. Fire Mater 1996, 20, 39.
5. Zaikon, G. E.; Lomakin, S. M. Oxidat Commun 1999, 22, 556.
6. Zaikon, G. E.; Lomakin, S. M.; Uschev, S. V.; Rouban, L. V.; Artsis, M. I. Oxidat Commun 1999, 22, 559.
7. Lomakin, S. M.; Usachev, S. V.; Koverzanova, E. V.; Rouban, L. V.; Kalining, I. G.; Zaikov, G. E. Russ Polym News 2001, 6.
8. Shehata, A. B. Polym Degrad Stab, to appear.