

MACROMOLECULAR CHEMISTRY  
AND POLYMERIC MATERIALS

## Specific Features of Thermal Degradation of Polypropylene in the Presence of Magnesium Hydroxide

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Received October 10, 2003

**Abstract**—Specific features of thermal oxidative degradation of polypropylene and its composite with Mg(OH)<sub>2</sub> were studied by pyrolytic gas chromatography–mass spectrometry and thermal gravimetric analysis.

An urgent problem of the modern polymer industry is to reduce the combustibility of polymers and polymeric materials. Of particular interest are fireproofing agents that combine high performance with environmental safety. One of a few fire retardants meeting these criteria is magnesium hydroxide, Mg(OH)<sub>2</sub>. It is commonly believed that its fireproofing effect is due to dilution of gaseous pyrolysis products with water vapor formed by endothermic ( $\Delta H$  1450 J kg<sup>-1</sup>) decomposition of Mg(OH)<sub>2</sub> above 340°C [1]:



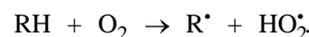
The heat consumed in this reaction considerably decreases the temperature on the surface of the degrading polymer. On the other hand, large amount of the released water vapor dilutes the mixture of volatile degradation products, altering the thermal balance in the combustion zone.

Since the decomposition point of Mg(OH)<sub>2</sub> is higher than the temperatures of industrial processing of such polymers as ethylene–vinyl acetate copolymer, polypropylene, and polyamides and corresponds to the temperatures at which these polymers start to degrade, there are no problems with preparing composites of reduced combustibility from these components.

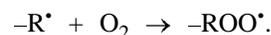
Polymeric composites of polypropylene, Nylon 6, and ethylene–vinyl acetate copolymer, containing 50 wt parts of Mg(OH)<sub>2</sub> and more, showed considerably decreased combustibility, as determined from the oxygen index and con calorimeter method [2].

In this work, the fire-retarding effect of Mg(OH)<sub>2</sub> on polypropylene was evaluated by mass-spectrometric analysis of polypropylene pyrolysis products.

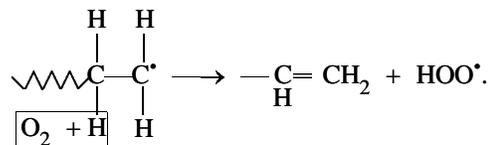
The mechanism of thermal degradation of polypropylene (PP) at temperatures close to the processing temperatures had been comprehensively studied [3–7]. It is known that, in the absence of oxygen, PP decomposes without residue to give large amounts of aliphatic compounds: alkanes, alkenes, and dienes. The primary thermal degradation of the polymeric chain involves scission of the weakest bonds. Oxygen chemisorbed on the polymer surface initiates radical formation at approximately 250°C and causes ignition at 470–540°C:



Furthermore, peroxy radicals are formed at approximately 350°C:

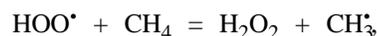
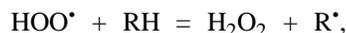


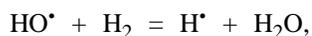
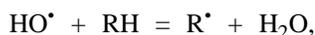
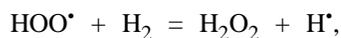
Above this temperature, dehydrogenation of polymeric radicals results in formation of a polyene and HO<sub>2</sub><sup>•</sup>:



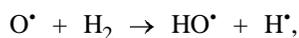
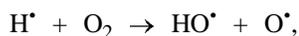
This reaction pathway prevails in the range 350–500°C.

According to the classical scheme of radical initiation [7], the peroxy radicals initiate the following reactions of chain propagation:





and chain branching:



It is generally accepted that fire retardants can actively participate in pyrolytic reactions and inhibit radical generation in the combustion zone or directly before it. Jha *et al.* [8] subdivided fire retardants with respect to the mechanism of their effect into two groups: (1) additives acting in the gas phase (terminating generation of free radicals in the preliminary flash and combustion front zones); (2) additives acting in the solid phase (decelerating common pyrolysis by increasing the amount of coke, thus insulating the polymer melt from the intense high-temperature flame flow or ignition source, or altering the pyrolysis course so as to prevent dropping of the polymer melt).

It is commonly believed that magnesium hydroxide belongs to the first group.

In this work we studied how magnesium hydroxide affects solid-phase coke formation enhancing the fire resistance of polypropylene.

## EXPERIMENTAL

Polypropylene was of BE677MO brand (Borealis), and its composite with magnesium hydroxide (FD905-U brand, Borealis) contained 40% Mg(OH)<sub>2</sub>.

Pyrolysis of pure polypropylene and its composite with Mg(OH)<sub>2</sub> was performed at 300, 500, and 700°C in a tubular flow-through pyrolytic cell in air (flow rate ~40 ml min<sup>-1</sup>). The outflowing gases were passed through a bubbler filled with 4 ml of hexane and cooled on an ice bath, to trap the pyrolysis products.

The thermal gravimetric analysis of PP and its composite with Mg(OH)<sub>2</sub> was performed on a 950Q derivatograph in air at a heating rate of 10 deg min<sup>-1</sup>.

The screening analysis of the pyrolysis products was performed on a Tsvet 500 M gas chromatograph (electron capture detector, ECD; 4000 × 3-mm packed

glass column; stationary phase OV-17 phenylmethylsilicone; column and injector temperatures 230°C; detector temperature 290°C; carrier gas nitrogen, flow rate 16 ml min<sup>-1</sup>; sample volume 2 μl).

Analysis of the most representative samples by gas chromatography–mass spectrometry was performed on a laboratory complex consisting of a Varian 3300 gas chromatograph, a Finnigan MAT ITD 800 mass spectrometric detector of the ion trap type, and a computer system for data processing. Separation was performed on a quartz capillary column (30 m long, 0.32 mm i.d.) coated with a 0.25-μm film of DB-5 phenylmethylsilicone. The column was heated at a 10 deg min<sup>-1</sup> rate from 50 to 270°C; the injector temperature was 200°C. The carrier gas was helium (inlet pressure 0.1 MPa). Samples (1 μl) were injected without flow division; the time before the start of purging of the sample inlet unit was 30 s. The mass spectra were taken with the electron impact (70 eV) ionization mode at a scanned rate of 1 mass spectrum per minute; the scanning range was 40–650 amu.

At 300 and 500°C, the major reaction products are alkenes, alkanes, dienes, and also alcohols and ketones. The composition and percent content of components in pyrolysis products of PP and its composite with Mg(OH)<sub>2</sub> are given in the table. The strongest peaks in the chromatograms correspond to 2,4-dimethyl-1-heptene, 4-methyl-2-heptanone, 2,6-dimethyl-4-heptanone, isomers of dimethyloctanol, and some other hydrocarbon derivatives. At low pyrolysis temperatures, Mg(OH)<sub>2</sub> exerts no noticeable effect on the composition of pyrolysis products, whereas at higher temperatures this effect becomes significant. Benzene derivatives appear at 500°C. At this temperature, we identified allylbenzene. Its content in the pyrolysis products of the composite (1.5%) was lower compared to pure PP (2.8%). At 700°C, the number and content of aromatic compounds grow. We identified toluene, ethylbenzene, xylenes, and isomeric ethyltoluenes and methylstyrenes. As seen from the table, their content in pyrolysis of the composite is considerably higher compared to pure PP. As for compounds with fused benzene rings, the pyrolysis products of pure PP contain no methyl-naphthalene and dihydronaphthalene isomers detected in pyrolysis of the composite. The content of naphthalene in the pyrolysis products of the composite was two times higher compared to pure PP. In pyrolysis products of the composite, we also identified biphenyl. Thus, in the presence of Mg(OH)<sub>2</sub> formation of aromatic compounds (mononuclear compounds, naphthalenes, biphenyls) is more intense.

The TG analysis of the composite revealed forma-

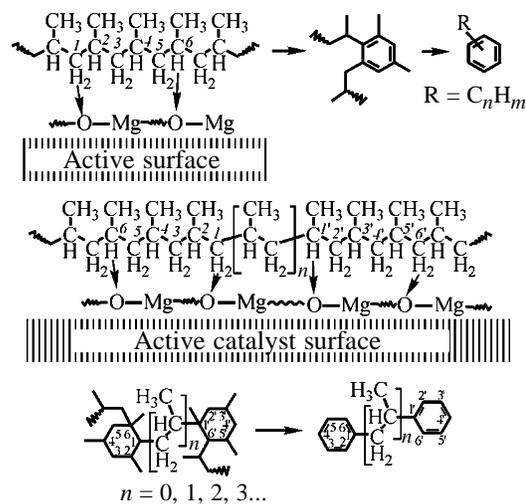
Composition and content of components in pyrolysis products of PP and its composite with Mg(OH)<sub>2</sub>

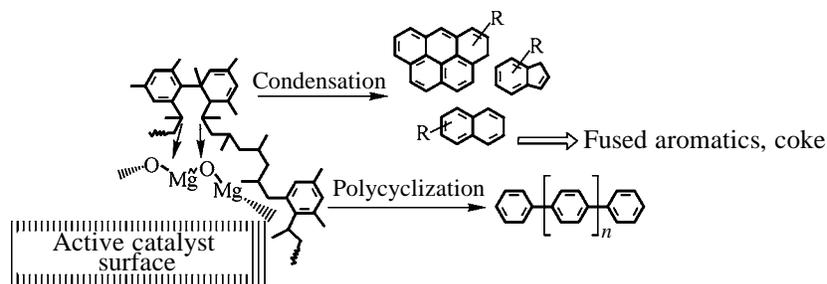
Pyrolysis products	Time, min/s	Content, wt %, at indicated pyrolysis temperature, °C					
		300		500		700	
		PP	composite	PP	composite	PP	composite
Toluene	3/16	–	–	–	–	16.2	19.3
2,4-Dimethyl-1-heptene	4/01	7.0	4.6	33.2	18.2	7.9	–
Ethylbenzene	4/23	–	–	–	–	6.9	9.9
Trimethylcyclohexene	4/26	–	1.0	0.6	1.4	–	–
Xylenes	4/42	–	–	–	–	5.3	7.6
4-Methyl-2-heptanone	5/17	7.5	6.8	1.2	0.9	–	–
	5/42	–	–	–	–	1.4	2.0
Ethyltoluene isomers	6/01	–	–	–	–	1.2	1.3
Dimethyloctene	6/05	5.6	3.8	–	–	–	–
Allylbenzene	6/12	–	–	2.8	1.5	3.8	–
2,6-Dimethyl-4-heptanone	6/15	10.2	8.5	4.4	3.6	–	–
α-Methylstyrene	6/15	–	–	–	–	4.1	5.0
β-Methylstyrene	7/01	–	–	0.2	–	1.9	4.7
	7/26	4.7	2.0	–	0.3	1.0	–
	7/30	5.1	3.5	9.8	7.4	2.8	–
Dimethyloctanol isomers	7/34	4.5	3.4	5.9	3.9	1.5	–
2-Methyl-4-phenyl-1-butene	8/42	–	–	–	–	1.6	4.6
Dihydronaphthalenes	8/48	–	–	–	–	–	2.8
	8/58	–	–	–	–	–	1.1
Naphthalene	9/17	–	–	–	–	6.8	14.6
Methylnaphthalenes	10/59	–	–	–	–	–	5.5
	11/15	–	–	–	–	–	3.3
2,4,6,8-Tetramethylundecene	11/00	5.1	4.3	6.7	11.5	18.0	–
Biphenyl	12/12	–	–	–	–	–	3.2
Hydrocarbons:							
≤C <sub>10</sub>	–	17.4	15.1	17.5	16.3	6.1	2.3
C <sub>10</sub> –C <sub>16</sub>	–	30.5	26.2	13.9	25.7	24.6	5.3
≥C <sub>16</sub>	–	2.5	20.5	5.0	6.5	2.6	3.1
Unidentified aromatic compounds	–	–	–	1.0	2.8	2.4	1.9
	–	100.0	100.0	100.0	100.0	100.0	100.0

tion of a coke residue under conditions of thermal oxidative degradation, whereas with pure PP virtually no residue was obtained (see figure). The amount of the coke residue was about 15%. To account for formation of the coke residue and aromatic compounds, we suggested a scheme of solid-phase catalysis. Magnesium hydroxide starts to decompose at 340°C. The nonvolatile magnesium oxide formed on the polymer surface protects deeper layers of the material. Thus, at elevated temperatures magnesium oxide starts to behave as active fire retardant. Due to the weak basic properties and large active surface area, magnesium oxide is used as additive to oxide catalysts for dehydrogenation of aliphatic compounds [9]. In pyrolysis of polypropylene, apparently, MgO behaves similarly.

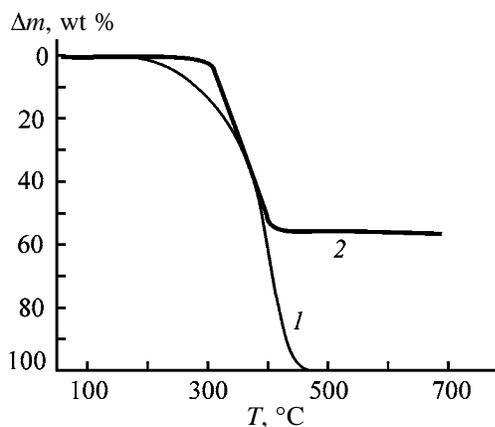
The possible mechanism of formation of aromatic compounds and coke with nonfused and fused ben-

zene rings is shown in the scheme:





The products of PP thermal degradation undergo dehydrogenation on the active MgO surface, yielding aromatic compounds. A similar mechanism involving catalysis with MgO explains formation of structures with benzene rings linked by an alkyl bridge. Then two pathways are possible. The first pathway is formation of diphenylalkanes. The second pathway involves catalytic solid-phase condensation followed by polycyclization, yielding coke on the MgO surface via intermediates with fused benzene rings, such as naphthalene and its derivatives. The detection of naphthalene, methylnaphthalenes, azulene, and biphenyl, and also of benzene derivatives shows that this process is primary.



TG curves of (1) PP and (2) PP-40 wt % Mg(OH)<sub>2</sub> composite, recorded in air. Heating rate 10 deg min<sup>-1</sup>. (Δm) Weight loss and (T) temperature.

## CONCLUSION

Compounding polypropylene with Mg(OH)<sub>2</sub> enhances its resistance to combustion in both the gas and solid phases; one of the factors responsible for this effect is MgO-catalyzed coke formation on the polymer surface.

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