

Thermal Degradation and Combustion of Polymeric Blends

S. M. Lomakin, E. V. Koverzanova, S. V. Usachev, N. G. Shilkina, G. E. Zaikov

Institute of Biochemical Physics of Russian Academy of Sciences, Kosygin 4, Moscow 119991, Russia

Received 26 February 2001; accepted 15 February 2002

ABSTRACT: The thermal stability of polymer blends was investigated by means of gas chromatography–mass spectroscopy (GC/MS) and thermal analysis. Evaluated changes in thermal stability can be attributed to blending. On the other hand, we were interested in whether blending may provide a method to control thermal stability and combustibility of polymeric materials. A new scheme of thermal degradation for polystyrene-polydimethylsiloxane (PDMS) blend was suggested. In the case of polystyrene (PS) as a part of the blend, the products of degradation of PS diffuse through the phase boundary, which cause interaction with PDMS polymers. Apparently, PDMS acts as an inert component, slowing down the termination reaction by dilution of macroradicals formed in random scission degradation process of the PS component. On the other hand, it stabilizes the PS by means of interpolymer recombination, which leads to cross products of thermal degradation. Two of the degradation products: 2-phenyl-4(1',3',3',5',5'-pentamethylcyclotrisiloxane)-butane and 2-phenyl-4(1',3',3',5',5',7',7'-hep-

tamethylcyclotrisiloxane)-butane were assigned to the products of cross-interpolymer recombination which can accelerate the process of PDMS depolymerization by means of radical initiation of PS* fragments. The connection between a polymer thermal oxidative degradation and its combustion under diffusion flames condition was shown by using composition of polypropylene-polypropylene-co-polyethylene (PP/PP-co-PE). In general, the solid-phase polymer reaction can play a very important role in the reduction of polymer combustibility. It was shown that the composition of PP/PP-co-PE (62 : 38) has the highest induction period of autooxidation, which correlates with its combustibility. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 3300–3311, 2002

Key words: polymer blend; polystyrene; polydimethylsiloxane; thermal degradation; oxidation; pyrolysis; GC-MS analysis; thermogravimetric analysis; depolymerization; combustion

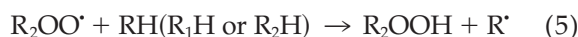
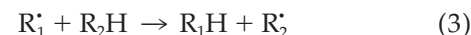
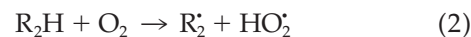
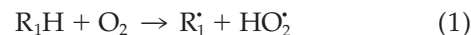
INTRODUCTION

During preparation of this material, it was assumed that the title would start with the word unpredictability. However, we decided to replace this word with the word singularity because it is quite possible to predict the polymer blends' behavior if one could know their mechanisms of oxidation and combustion.

The singularity of oxidation of organic compounds was first discovered by Emanuel et al.¹ They studied the co-oxidation of decane (C₁₀H₂₂) and ethylbenzene (C₆H₅C₂H₅). It was established that, in liquid phase at ~ 150°C, decane can be easily oxidized to decyl hydroperoxide (C₁₀H₂₁OOH). Under these conditions, the ethylbenzene is easily oxidized in appropriate hydroperoxide as well (C₆H₅CH(OOH)CH₃). However, a mixture with decane ethylbenzene is even faster to oxidize, and decane completely ceases to oxidize in a mixture.

Thus, ethylbenzene is thought to be an inhibitor of the decane oxidation process, and decane is the catalyst of the ethylbenzene oxidation in their mixture.

The reason for this phenomena is a special mechanism of co-oxidation of these two organic compounds. Let us designate the decane as R₁H and the ethylbenzene as R₂H. Then, the mechanism of the co-oxidation process up to the first molecular product, hydroperoxide, appears as:



The basic feature of the decane oxidation and acceleration of the process of ethylbenzene oxidation in their mixture is described by reaction (3), when the alkyl radical of decane reacts with ethylbenzene. Under this condition, the molecule of decane is regenerated and the molecule of ethylbenzene converts into the alkyl radical.

The rate of reaction (3) depends on bond energy of the R₂—H bond. The smaller the bond energy, the larger the rate of this process will be. Thus, nonaddi-

Correspondence to: G. E. Zaikov (chembio@glasnet.ru).

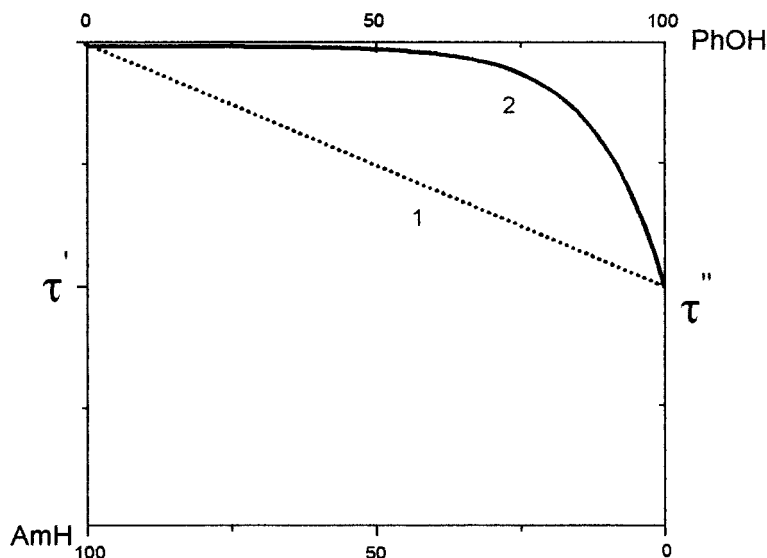
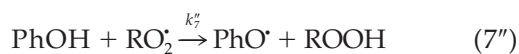
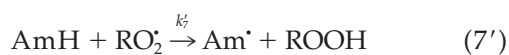


Figure 1 Induction period of ethylbenzene oxidation in the presence of amine (τ') and phenol (τ'') and their mixture. Line 1, theoretical (additive) induction period of oxidation of the composition of amine and phenol; curve 2, experimental dependence of the induction period on a ratio of amine and phenol in a mixture.

tivity during oxidation processes of organic mixtures is determined by the bond energies of oxidizing components in a mixture.

The other example of nonadditivity can be illustrated as a result of cooperative action of two inhibitors during the oxidation process of organic compounds. This phenomena was established by Emanuel et al.² One could imagine two inhibitors of oxidation process: amine (Am—H) and phenol (Ph—OH). It is known that the mechanism of their inhibitive action consists of inhibitor interaction with peroxide radical (ROO \cdot) of the oxidizing organic compound (RH):



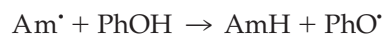
Let us take the case where amine is a much more effective inhibitor than phenol. Kinetically, it means that the rate constant of reaction, k'_7 , is considerably higher than the rate constant, k''_7 , $k'_7 \gg k''_7$, and the induction period of the oxidation process in the presence of amine (τ') is much higher than the period of induction upon the oxidation in the presence of phenol (τ''):

$$\tau' \gg \tau''$$

Figure 1 illustrates the dependence of the induction period during ethylbenzene oxidation on a ratio of amine and phenol in a mixture at various concentrations of inhibitors.

Unlike an assumption of separate inhibitor action which is involved in a pure additive mechanism of two inhibitor actions (theoretical line 1, Fig. 1), the other experimental dependence is observed (curve 2, Fig. 1). Apparently the active amine is replaced by the low-active phenol. At first our system does not notice this fact and keeps working as the system with only pure amine. Then, under circumstances of amine replacement by the phenol, the system suddenly realizes that amine is consumed and the induction period, τ , begins to decrease drastically.

Such type of behavior is determined by the reaction of regeneration of amine in account of phenol:



Thus, the amine is working as the phenol is consuming. The rate of this reaction depends on the bond energy of PhO—H. These two abovementioned examples give us an idea of the realization of a similar model for organic polymer blends' thermal oxidation and combustion processes.

In general, many polymers are blended together to enhance physical and mechanical properties. In the present article, we evaluate changes in the thermal stability that can be attributed to blending. On the other hand, we were interested in whether blending may provide a method to control thermal stability.

There are some publications that describe different polymer mixtures of thermal degradation behavior. Richard and Salter studied the thermal degradation of polystyrene blended with poly(α -methylstyrene).⁴ They found an increased yield of styrene monomer which they explained by the ability of poly(α -methyl-

styrene) radicals to initiate the depropagation step for polystyrene thermal decomposition.

Mizutani et al.⁵ suggested that polypropylene degradation is accelerated by the presence of vinyl polymers, such as polystyrene or poly(methylmethacrylate) (PMMA). During the degradation process, the polymers were incorporated into the polypropylene chain, forming graft or block copolymers by a mechanism involving attack by a vinyl polymer radical on the polypropylene chain.

Gardner et al.⁶ studied the rates of degradation of polystyrene and poly(α -methylstyrene) with acrylate polymers and reported that the rates of degradation of blends were significantly different from those measured for the polymers.

Grassie et al.⁷ compared the degradation behavior of polymethylmethacrylate–polystyrene blends and methylmethacrylate–styrene copolymers. The copolymers differed significantly from the blends.

McNeill^{8–10} studied a variety of blends and considered the degradation of many polymer blends to fall into one of two categories:

- (1) Small molecule migration: Poly(vinyl chloride) (PVC), poly(chloroprene), and chlorinated natural rubber blended with PMMA result in the migration of HCl into the PMMA phase, which stabilizes the polymer by converting some ester side groups into anhydride rings, which interfere with depolymerization.
- (2) Small radical migration: Chlorine radicals are believed to be involved in chain mechanism in the decomposition of PVC and chlorinated rubber. There is evidence that in blends of PVC with PMMA, polystyrene, polycarbonate, poly(α -methylstyrene), and polydimethylsiloxane (PDMS), low-temperature degradation of the second polymer is promoted by Cl^{*} radicals.

In the work of Bate and Lehrle,¹¹ an attempt was made to determine to what extent the following factors are important to evaluate the rates and mechanism of the degradation of blends (PMMA/PS, PMMA/HDPE, PMMA/PVC):

1. Miscibility/compatibility of the polymers;
2. Physical effects (diffusion control, viscosity);
3. Cross reaction.

The results show that heterogeneous blends degrade predominantly within their phase-separation regions, but may also give rise to some cross products, which may form by small radical or molecule migration across these phase boundaries. For the systems studied, this cross-product formation is a secondary effect, because the observed rate of formation of methyl methacrylate (MMA) monomer from the heterogeneous blends was not found to be significantly

different from that shown by the homopolymer. Pyrolysis of homogeneous blends was shown to involve interacting mechanisms, which may or may not lead to cross-product formation. However, rates of formation of major pyrolysis products are found to change significantly, in some cases by one order of magnitude, and these results were interpreted in terms of degradation mechanism. In particular, it was suggested that the following effects are involved in the degradation mechanism of homogeneous blends.

1. Cross-termination of depropagation chains. This effect is to stabilize both components of the blend.
2. Intermolecular transfer of a hydrogen atom from the first component to the depropagation chain of the second component. This effect activates the degradation of the first component and stabilizes the second component.
3. Diffusion restriction of intramolecular transfer. If the first component is present as an inert diluent in the vicinity of an end-bite (intramolecular transfer), the facility with which the latter can occur is reduced. This reduces the possibility of oligomer formation.
4. Diffusion restriction of termination. If the two components in a homogeneous blend depropagate independently and cross termination is not favored, then each component dilutes the bimolecular termination process of the other, causing enhancement of the overall rate.

EXPERIMENTAL

Polymer blends were prepared as described previously.³ The polystyrene (PS) was the commercial sample used in the earlier investigation. The PDMS was also a commercial product, with ultrahigh molecular weight (10^6), methyl end groups, and gummy texture.

The pyrolysis of PS, PDMS, and their blend (80 phr of PS : 20 phr of PDMS) was done in tube-pyrolytical cells at temperatures of 300, 400, 500, and 600°C in air (flow rate, 30 ml/min). The products of pyrolysis were dissolved in hexane at 0°C. Extensive pyrolysis of samples over a 1-min period of time was carried out in a laboratory model pyrolyzer in air atmosphere under 400°C. The oven temperature was monitored with a thermocouple and a stability of $\pm 5^\circ\text{C}$ was attainable.

Thermal analysis

Vertical TG balance Derivatograf 950Q (nitrogen or air flow of 100 ml/min) was used for kinetic study of polymer samples thermal degradation.

Gas chromatography (GC) analysis

Samples of degradation products were analyzed by gas chromatography analysis Zvet 500M by using an

electron capture detector. A glass column (3 mm \times 4 m) filled by OV-17 (phenylmethyl silicon) was used in the GC analysis. Temperature of column was 230°C.

Gas chromatography/mass spectrometry (GC/MS) analysis

GC/MS analysis of samples was performed by using a Varian 3300 gas chromatograph connected with mass spectrometer detector (ion trap) Finnigan MAT ITD 800. A DB-5 fused capillary column (0.32 mm \times 30 m) temperature programmed from 50 to 270°C at 10°C per min was used in GC/MS analysis. Mass spectra detection was accomplished in the electron impact mode scanned from 40 to 650 Da with the energy of 70 eV. All mass spectra were searched against the NB mass spectral library.

RESULTS AND DISCUSSION

In the present study, an attempt was made to analyze the different behavior of the blend (PS and PDMS) in comparison with the thermal degradation of pure polymers. Previously a kinetic approach was used for the evaluation of this phenomena.³

Kinetic study of blends thermal degradation

Direct integrational/computational method as well as the Kissinger method were used to determine the experimental (apparent) values of the activation energy and the preexponential factor for the blends of thermal degradation.³ The Kissinger method assumes that the sample temperature is uniform, and the thermal degradation of the solid is a single first-order reaction with Arrhenius kinetics:

$$A/r = E/RT_{\max}^2 \exp(E/RT_{\max})$$

where A is the preexponential factor; $r = dT/dt$ is the heating rate; and T_{\max} is the temperature at which the mass flux from solid to gas is a maximum. Namely, when the rate of change of mass flux with time is zero;

$$d^2(1 - c)/dt^2 = 0$$

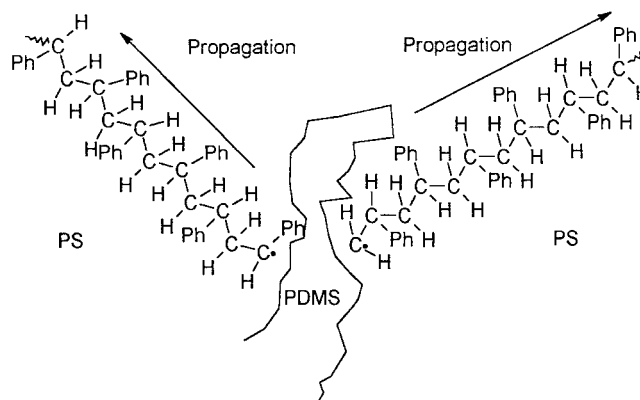
E is the activation energy and R is the universal gas constant.

By using the equation $A/r = E/RT_{\max}^2 \exp(E/RT_{\max})$, the activation energies and preexponential factors were determined.³

It was found that the values of activation energy and preexponential factors of PS, as a part of blend, and thermal degradation in nitrogen are about 30% more than for pure PS. On the other hand, the values of activation energy and preexponential factors of

PDMS, as a part of thermal degradation in nitrogen, are \sim 25% lower than for pure PDMS.^{3,12}

In the case of PS as a part of blend, the products of degradation of PS diffuse through phase boundary, which causes interaction with PDMS polymers. Preliminary GC/MS analysis of products of degradation from the were made at temperatures of 500 and 700°C (Flash pyrolysis). The detailed analysis of the mechanism of thermal degradation of blends was discussed in ref. [3]. Apparently, PDMS acts as an inert component, slowing down the termination reaction by dilution of macroradicals formed in a random scission degradation process of PS component. On the other hand, it stabilizes the PS by means of interpolymer recombination, which leads to cross products of thermal degradation.³



This dilution leads to a reduction in the rate of termination and increases the overall rate of the PS-part thermal degradation. As a result of this phenomena, the energy of activation of the PS part can be lowered. However, the visual effect of stabilization of the PS part in the blend can be explained by way of interpolymer recombination which caused the stabilization of the first degraded component, PS.

For the second component of the blend, PDMS, the values of activation energy and preexponential factor are about 25% lower than for pure PDMS.³ This means that the second component is becoming less thermally stable in the blend than when heated alone. Because we have found cross-degradation products (see below, GMS analysis section) for these components, we explained the behavior of the blend by kinetic factors. During the decomposition of the second-component PDMS, the interpolymer recombination caused the termination of radical depolymerization (propagation step) of PS. On the other hand, the process of PDMS-component thermal degradation is accelerated by means of radical initiation of PS* fragments, which is why it becomes less thermally stable.

The analysis and identification of chromatograms and mass spectra showed that the major pyrolysis product of pure PS at 300, 400, 500, and 600°C in air is the styrene (54.9, 76.2, 67.0, and 57.9%, respectively)

TABLE I
Products of PS Pyrolysis at Different Temperatures

Temperature (°C)	Products	Retention time	Intensity (r.u.)	Concentration (wt %)
300	Styrene	4 : 40	165,916	54.9
	Benzaldehyde	5 : 41	88,830	29.4
	β -Methylstyrene	6 : 01	7754	2.6
	Acetophenone	7 : 21	7324	2.4
	Nonidentified products	—	—	10.6
400	Methylbenzene	3 : 13	149,903	8.3
	Ethylbenzene	4 : 17	40,508	2.3
	Styrene	4 : 46	1,369,616	76.2
	Allylbenzene	5 : 29	11,069	0.6
	Benzaldehyde	5 : 41	64,023	3.6
	α -Methylstyrene	6 : 02	97,858	5.4
	Acetophenone	7 : 22	1876	0.1
	1,3-Diphenylpropane	15 : 54	11,502	0.6
	Ethylbenzene dimer	16 : 44	26,807	1.5
	Nonidentified products	—	—	1.3
	500	Methylbenzene	3 : 13	41,683
Ethylbenzene	4 : 17	11,457	0.9	
Styrene	4 : 42	866,148	67.0	
Benzaldehyde	5 : 41	92,948	7.2	
Phenol	5 : 54	6464	0.5	
α -Methylstyrene	6 : 01	53,926	4.2	
β -Methylstyrene	6 : 43	12,054	0.9	
Benzacetaldehyde	6 : 58	59,896	4.6	
Acetophenone	7 : 21	17,531	1.4	
Diphenylethane	14 : 13	12,968	1.0	
1,3-diphenylpropane	15 : 53	12,967	1.0	
Ethylbenzene dimer	16 : 43	39,715	3.1	
Styrene pentamer	20 : 01	12,503	1.0	
Nonidentified products	—	—	4.0	
600	Methylbenzene	3 : 13	726,061	15.3
	Ethylbenzene	4 : 17	354,604	7.5
	Styrene	4 : 45	2,746,957	57.9
	Cumene	5 : 15	35,209	0.7
	Allylbenzene	5 : 28	26,936	0.6
	Propylbenzene	5 : 35	19,777	0.4
	Benzaldehyde	5 : 40	123,162	2.6
	Phenol	5 : 52	37,886	0.8
	α -Methylstyrene	6 : 01	305,752	6.4
	Cyclopropylbenzene	6 : 10	11,213	0.2
	Benzofuran	6 : 15	13,180	0.3
	β -Methylstyrene	6 : 42	21,539	0.5
	Benzacetaldehyde	6 : 58	44,364	0.9
	Indene	7 : 12	15,704	0.3
	Acetophenone	7 : 20	33,811	0.7
	Naphtalene	9 : 18	27,837	0.6
	Biphenyl	12 : 14	6032	0.1
	Diphenylethane	14 : 12	45,492	1.0
	1,3-Diphenylpropane	15 : 53	13,545	0.3
	Ethylbenzene dimer	16 : 43	28,292	0.6
	Nonidentified products	—	—	2.2

(Table I). Obviously, the process of radical depolymerization (initiated by oxygen) remains the dominant reaction upon the PS degradation in the temperature range of 300–600°C.

PS

The analysis and identification of chromatograms and mass spectra showed that the major pyrolysis product of pure PS at 300, 400, 500, and 600°C in air is the styrene (54.9, 76.2, 67.0, and 57.9%, respectively) (Ta-

ble I). Obviously, the process of radical depolymerization (initiated by oxygen) remains the dominant reaction upon the PS degradation in the temperature range of 300–600°C.¹³

At 300°C, the most abundant products of PS thermal oxidative degradation are styrene (54.9%) and benzaldehyde (29.4%) (Table I). At 400°C, among the identified products are methylbenzene (8.4%), ethylbenzene (2.3%), allylbenzene (0.6%), and α -methylstyrene (5.4%) (Table I). Under pyrolysis conditions at 500°C, a rise of the degradation product concentrations was noticed.

TABLE II
Products of PDMS Pyrolysis at Different Temperatures

Temperature (°C)	Products	Retention time	Intensity (r.u.)	Concentration (wt %)
300	Cyclotrisiloxane, hexamethyl	3 : 42	20,587	6.1
	Cyclotetrasiloxane, octamethyl	6 : 08	235,336	69.4
	Cyclopentasiloxane, decamethyl	8 : 38	59,708	17.6
	Nonidentified products	—	236,447	6.9
400	Cyclotrisiloxane, hexamethyl	3 : 42	94,977	7.1
	1,3,3,5,5-pentamethyl cyclotrisiloxane-1-heptamethyl pentosiloxane	3 : 44	147,810	11.1
	Cyclotetrasiloxane, octamethyl	6 : 08	623,542	46.7
	Cyclopentasiloxane, decamethyl	8 : 39	318,358	23.8
	Cyclohexasiloxane, dodecamethyl	11 : 17	20,430	1.5
	Cycloheptasiloxane, tetradecamethyl	13 : 42	10,584	0.8
	Nonidentified products	—	120,275	9
500	Cyclotrisiloxane, hexamethyl	3 : 42	132,672	5.5
	1,3,3,5,5-pentamethyl cyclotrisiloxane-1-heptamethyl pentosiloxane	3 : 44	760,469	31.4
	Cyclotetrasiloxane, octamethyl	6 : 11	904,768	37.3
	Cyclopentasiloxane, decamethyl	8 : 39	409,250	16.9
	Cyclohexasiloxane, dodecamethyl	11 : 16	33,299	1.4
	Cycloheptasiloxane, tetradecamethyl	13 : 41	13,621	0.6
	Cyclododecasiloxane, tetracosamethyl	15 : 52	8122	0.3
600	Nonidentified products	—	162,145	6.8
	Cyclotrisiloxane, hexamethyl	3 : 42	100,988	12.5
	1,3,3,5,5-pentamethyl cyclotrisiloxane-1-heptamethyl pentosiloxane	3 : 44	111,361	13.8
	Cyclotetrasiloxane, octamethyl	6 : 09	459,471	57.0
	Cyclopentasiloxane, decamethyl	8 : 39	6851	0.8
	Cyclohexasiloxane, dodecamethyl	11 : 16	18,125	2.2
	Cycloheptasiloxane, tetradecamethyl	13 : 41	13,865	1.7
600	Cyclododecasiloxane, tetracosamethyl	15 : 51	5141	0.6
	Nonidentified products	—	6851	0.8

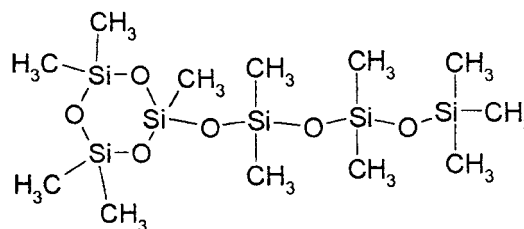
The major amounts of the products (except for styrene) belong to methylbenzene (3.2%), benzaldehyde (7.2), benzacetaldehyde (4.6%), and ethylbenzene dimer (3.1%) (Table I).

At 600°C, a further increase of the degradation products is clearly seen. The condensed aromatics occur except for, listed above, products of pyrolysis (naphtalene, 0.6%; benzofuran, 0.3%; biphenyl, 0.1%) (Table I).

PDMS

The most abundant products of PDMS thermal and thermal oxidative degradation are ciclotrisiloxane hexamethyl (D3) and cyclotetrasiloxane octamethyl (D4) followed by ciclopentasiloxane decamethyl (D6) (Table II). As the temperature rose, the occurrence (increase) of the contribution of cyclic siloxane oligomers was observed, such as cyclohexasiloxane dodecamethyl, cycloheptasiloxane tetradecamethyl (D7), and cyclododecasiloxane tetracosamethyl (D12), which was previously described in terms of molecular depolymerization.¹²

At temperatures > 400°C, a new product was found which was supposedly identified as 1,3,3,5,5-pentamethyl cyclotrisiloxane-1-heptamethyl pentasiloxane. Characteristic peaks for this compound are at $m/e = 73, 102, 193, 341, 429$.



The products PDMS thermal oxidative degradation are given in Table II.

PS/PDMS blend

At 300°C, the most abundant products of the blend are the products of PS thermal oxidative degradation: styrene (14%) and benzaldehyde (31%) (Table III). The composition of products of blend pyrolysis at 400 and 500°C does not differ from the basic product distribution of the initial PS and PDMS pyrolysis (Tables I–III).

PS component

Methylbenzene (2.1 and 6.6%, accordingly), ethylbenzene (0.8 and 1.5%), styrene (64.2 and 62.9%), benzaldehyde (7.7 and 4.2%), methylstyrene (4.6 and 3.2%), and PDMS component: D3 (3.8 and 6.4%,

TABLE III
Products of PDMS and PS Blend Pyrolysis at Different Temperatures

Temperature (°C)	Products	Retention time	Intensity (r.u.)	Concentration (wt %)
300	Styrene	4 : 40	15,158	14.4
	Benzaldehyde	5 : 41	32,864	31.3
	Nonidentified products	—	57,125	54.3
400	Methylbenzene	3 : 13	22,615	2.1
	Cyclotrisiloxane, hexamethyl	3 : 42	40,689	3.8
	Ethylbenzene	4 : 17	8822	0.8
	Styrene	4 : 42	683,228	64.2
	Benzaldehyde	5 : 41	82,140	7.7
	α -Methylstyrene	6 : 01	48,567	4.6
	Cyclotetrasiloxane, octamethyl	6 : 08	34,958	3.3
	Cyclopentasiloxane, decamethyl	8 : 38	67,072	6.3
	Cyclohexasiloxane, dodecamethyl	11 : 16	9229	0.9
	1,3-Diphenylpropane	15 : 53	9475	0.9
	Ethylbenzene dimer	16 : 43	28,678	2.7
	500	Nonidentified products	—	29,233
Methylbenzene		3 : 13	69,112	6.6
Cyclotrisiloxane, hexamethyl		3 : 42	67,698	6.4
Ethylbenzene		4 : 14	15,284	1.5
Styrene		4 : 43	661,811	62.9
Benzaldehyde		5 : 41	43,698	4.2
α -Methylstyrene		6 : 01	33,712	3.2
Cyclotetrasiloxane, octamethyl		6 : 08	55,620	5.3
Cyclopentasiloxane, decamethyl		8 : 38	85,889	8.2
Cyclohexasiloxane, dodecamethyl		11 : 16	9598	0.9
Nonidentified products		—	13,332	0.8
600		Methylbenzene	3 : 13	463,443
	Cyclotrisiloxane, hexamethyl	3 : 42	161,336	2.6
	Ethylbenzene	4 : 17	247,026	4.0
	Styrene	4 : 45	3,016,246	49.0
	Cumene	5 : 09	32,893	0.5
	Allylbenzene	5 : 28	34,133	0.6
	Propylbenzene	5 : 35	13,268	0.2
	Benzaldehyde	5 : 41	233,407	3.8
	Phenol	5 : 53	34,530	0.6
	α -Methylstyrene	6 : 01	358,626	5.8
	Cyclotetrasiloxane, octamethyl	6 : 08	192,533	3.1
	Benzofuran	6 : 16	42,878	0.7
	β -Methylstyrene	6 : 42	33,684	0.5
	Benzacetaldehyde	6 : 58	62,372	1.0
	Indene	7 : 20	42,060	0.7
	Acetophenone	7 : 21	28,590	0.5
	2-phenyl-4(1',3',3',5',5'-pentamethylcyclotrisiloxane)-butane	8 : 11	18,645	0.3
	Cyclopentasiloxane, decamethyl	8 : 38	451,506	7.3
	Naphthalene	9 : 19	29,188	0.5
	2-phenyl-4(1',3',3',5',5',7',7'-heptamethylcyclotrisiloxane)-butane	10 : 18	14,707	0.2
	Cyclohexasiloxane, dodecamethyl	11 : 16	173,587	2.8
	Biphenyl	12 : 14	13,733	0.2
	Cycloheptasiloxane, tetradecamethyl	13 : 41	31,841	0.5
	Diphenylethane	14 : 12	70,077	1.1
	1,3-Diphenylpropane	15 : 53	25,178	0.4
	1,2-Diphenylethylene	16 : 36	25,902	0.4
	Ethylbenzene dimer	16 : 43	75,180	1.2
Anthracene	17 : 35	11,797	0.2	
Styrene pentamer	18 : 50	12,927	0.2	
Nonidentified products	—	201,878	3.6	

accordingly), D4 (3.3 and 5.3%), D5 (6.3 and 8.2%), D6 (0.9% and 0.9%), At 600°C, condensed aromatic structures were found, benzofuran (3.8%), naphthalene (0.5%), anthracene (0.2%), and biphenyl (0.2%).

At the same temperature, the new products were identified which were absent at pure PS and PDMS pyrolytic spectra. They were attributed to 2-phenyl-4(1',3',3',5',5'-pentamethylcyclotrisiloxane)-butane

Intensity

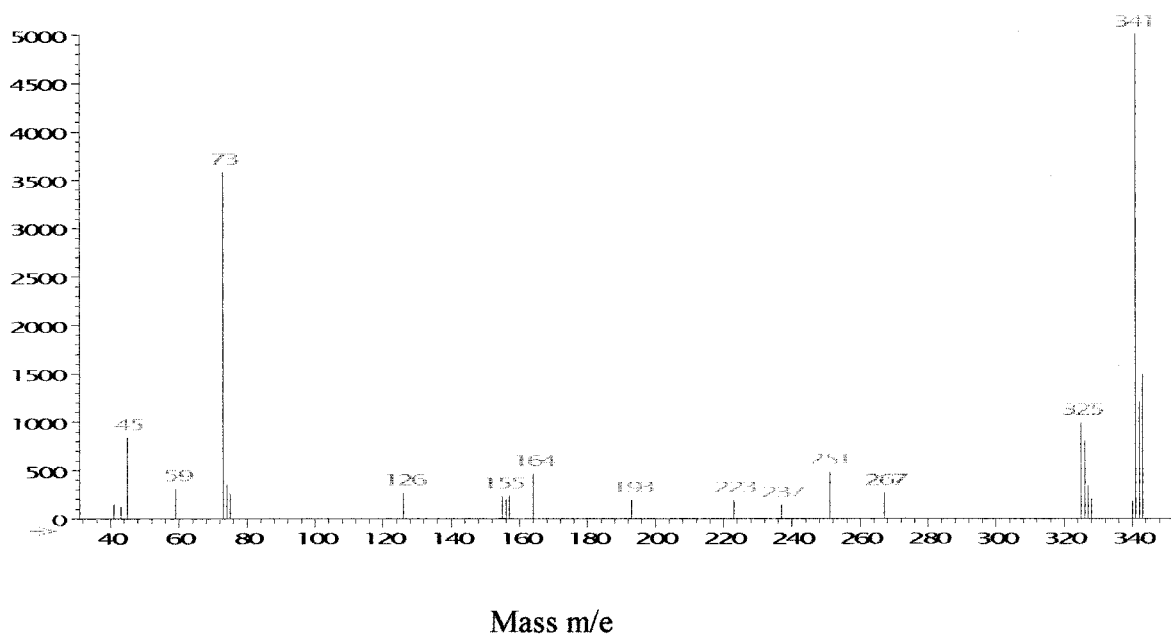
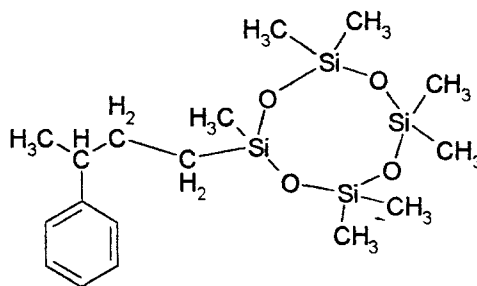
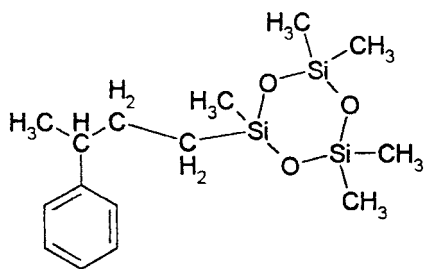


Figure 2 Mass spectrum of 2-phenyl-4(1',3',3',5',5'-pentamethylcyclotrisiloxane)-butane.



and 2-phenyl-4(1',3',3',5',5',7',7'-heptamethylcyclotetrasiloxane)-butane.

The mass spectra of these compounds are shown in Figures 2 and 3. Apparently, these two compounds are

Intensity

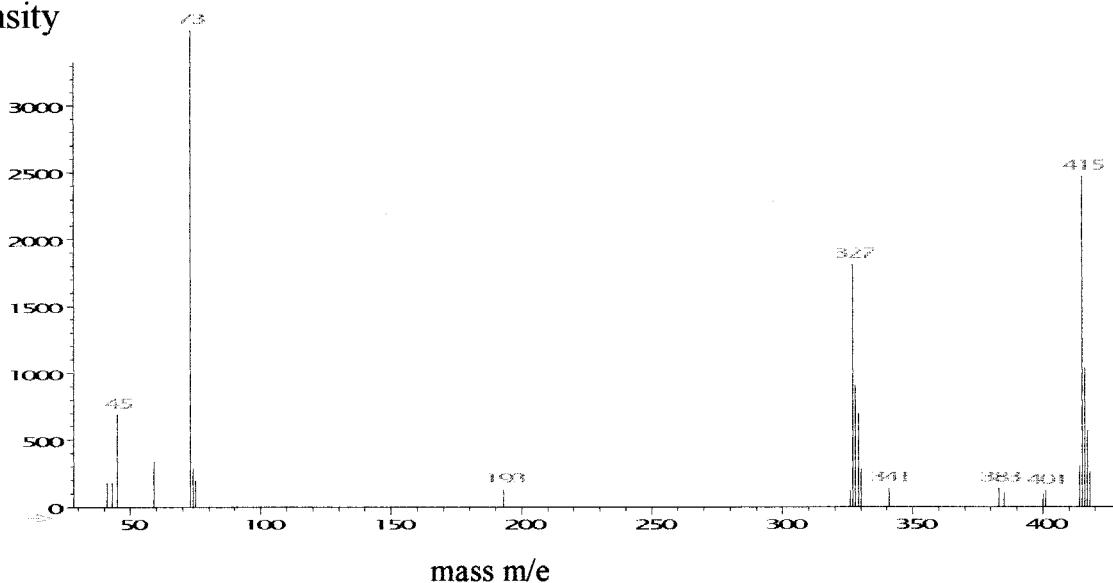
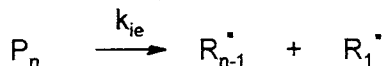


Figure 3 Mass spectrum of 2-phenyl-4(1',3',3',5',5',7',7'-heptamethylcyclotetrasiloxane)-butane.

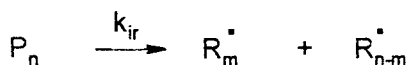
formed by interaction of the radical PS fragment and the PDMS matrix.

A brief summary (scheme) of the assumed radical chain kinetic model for the thermal degradation of PS with the presence of PDMS fragments is presented below.^{3,14} In particular, the reaction steps of the main process are chain initiation to form primary radicals: end chain initiation (1), random scission (1a), β -scission (1b); propagation (unzipping) by intramolecular chain transfer (2); propagation by intermolecular transfer (3); intermolecular transformation (back-biting) (4); primary, secondary radical abstracting and β -scission (5); termination by the first- and the second- (disproportionation, recombination) order reaction (7); interpolymer chain interaction of PS*; and PDMS, which leads to cross products of PS and PDMS thermal degradation (6).

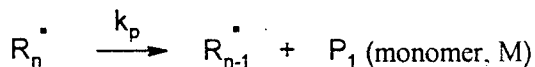
End chain (e) initiation



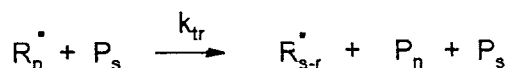
Random chain (r) scission initiation



Propagation by intramolecular chain transfer

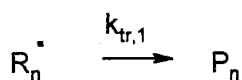


Propagation by intermolecular chain transfer

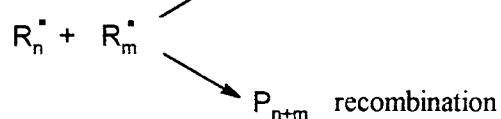


Termination

First order



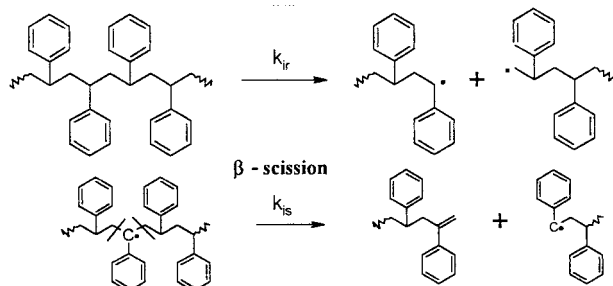
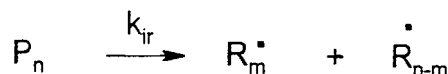
Second order



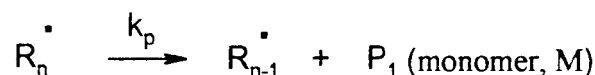
End chain (e) initiation



Random chain (r) scission initiation



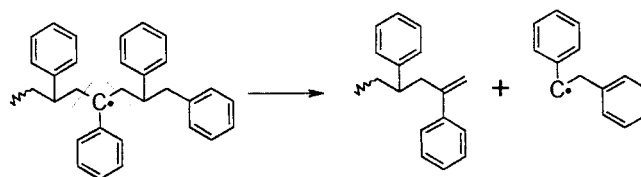
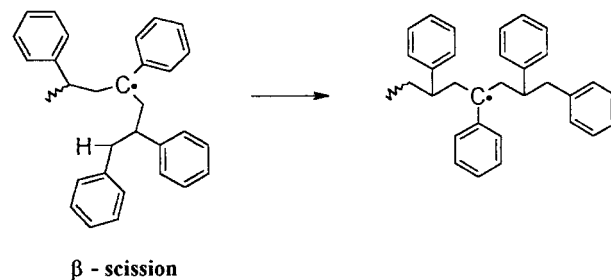
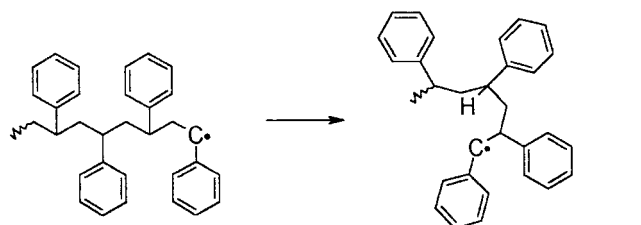
Propagation by intramolecular chain transfer



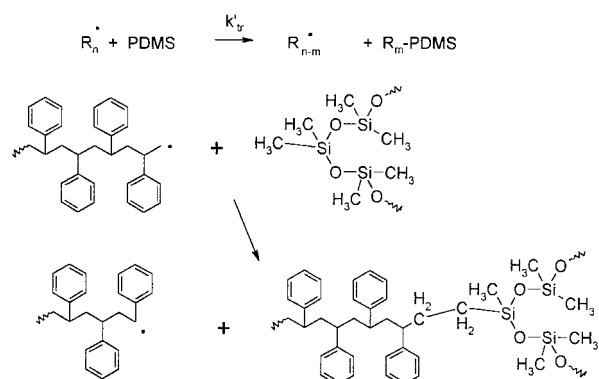
Propagation by intermolecular chain transfer



Intermolecular transformation (back-biting)

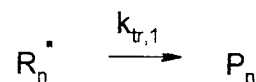


Interpolymers recombination

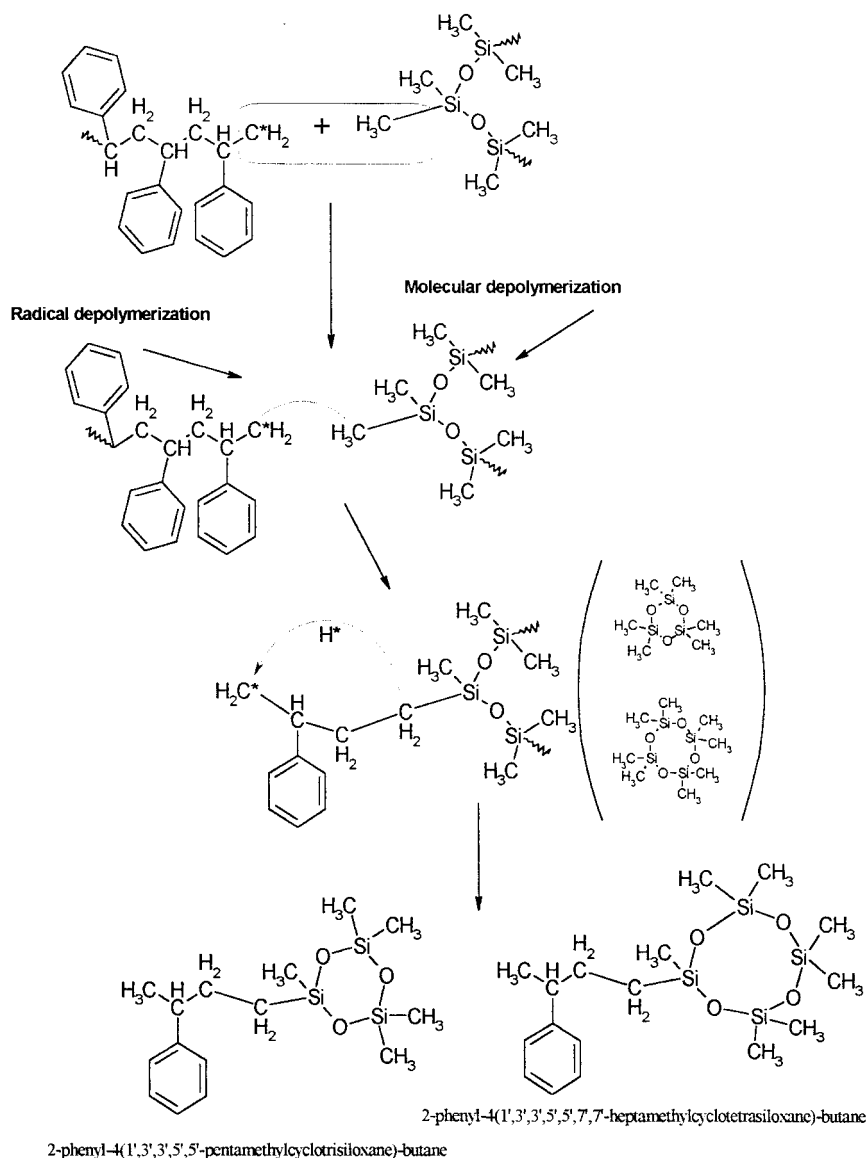
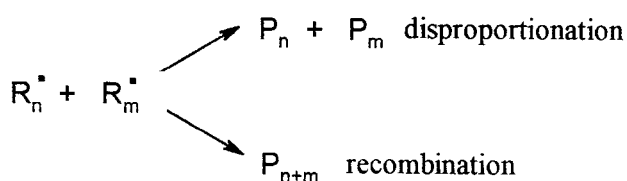


Termination

First order



Second order



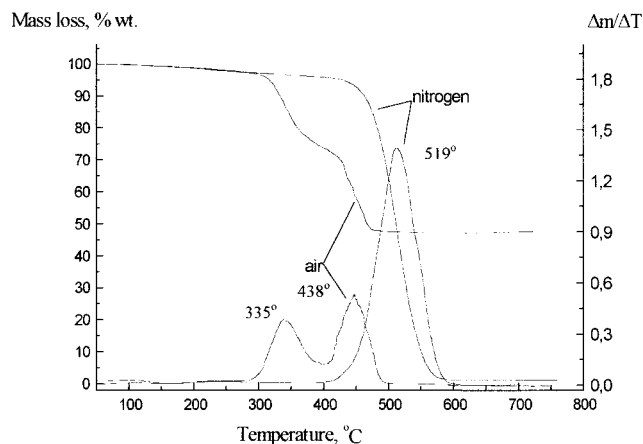


Figure 4 TG and DTG curves of PDMS in nitrogen and in air at a heating rate of $10^\circ/\text{min}$.

Figures 4–8 illustrate the difference in the thermal degradation of PS, PDMS, and their blends at a heating rate of $10^\circ/\text{min}$ in nitrogen and air. From these figures, the influence of oxygen on the degradation process is seen. The thermal degradation of PDMS was studied by Camino et al.¹² The presence of two stages in PDMS (Fig. 4) in air was explained by chain-end oxygen-catalyzed depolymerization followed by random-scission and crosslinking oxidative process.¹² The limiting stage of this process is ultimately the diffusion and evaporation of monomer fragments.

The comparison of experimental TG and DTG curves suggests that the most of PS component in the blend with PDMS decomposes at higher temperatures (Figs. 5–8). On the other hand, the PDMS part of the blend tends to degrade at lower temperatures. The pronounced effect is observed in thermal degradation in air (Figs. 4, 6, and 8).

In a polymer blend of PS/PDMS, the dilution of basic component (PS) by the PDMS leads to its stabilization and destabilization of the second one, PDMS.

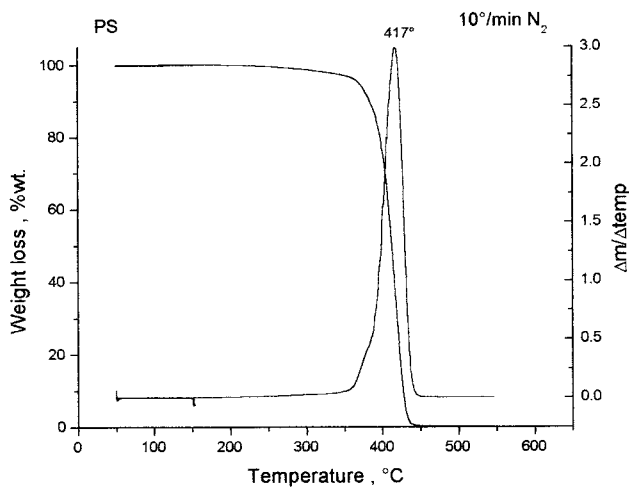


Figure 5 TG and DTG curves of PS in nitrogen at the heating rate of $10^\circ/\text{min}$.

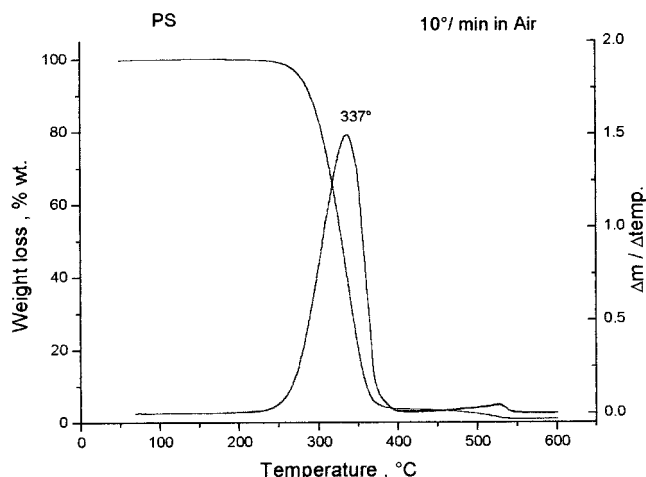


Figure 6 TG and DTG curves of PS in air at the heating rate of $10^\circ/\text{min}$.

This phenomenon was explained in terms of interpolymer recombination. Two of the degradation products; 2-phenyl-4(1',3',3',5',5'-pentamethylcyclotrisiloxane)-butane and 2-phenyl-4(1',3',3',5',5',7',7'-heptamethylcyclotrisiloxane)-butane, were assigned to the products of cross-interpolymer recombination which can accelerate the process of PDMS depolymerization by means of radical initiation of PS* fragments.³

Polypropylene/polypropylene-co-polyethylene (PP/PP-co-PE) compositions

To conclude consideration of the connection between behavior (morphology) of polymers in blends and combustion, we included in this article our recent work which describes the new trend in flame retardation—modification of polymer physical structure (morphology) by means of polymer-polymer blends.¹⁵

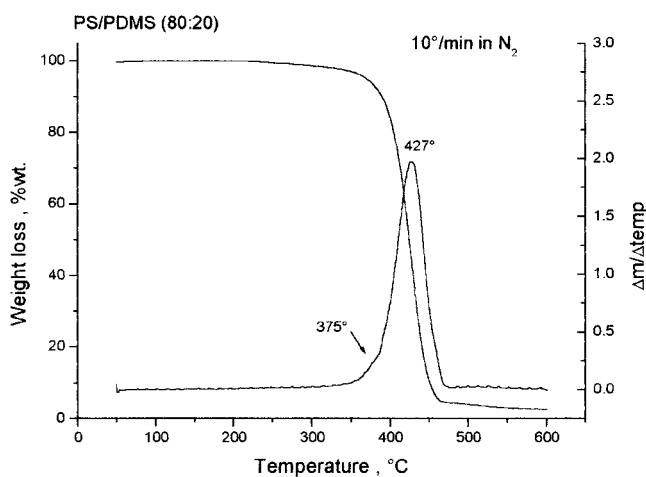


Figure 7 TG and DTG curves of PS/PDMS blend (80 : 20) in nitrogen at the heating rate of $10^\circ/\text{min}$.

An extreme combustion behavior for a system PP/PP-*co*-PE was found,¹⁵ which can be explained in terms of oxidative degradation of polymer materials. We studied the features of autooxidation and combustibility of blends of isotactic polypropylene (PP) and ethylene-propylene copolymers (PP-*co*-PE) as the thin films (50–80 μm). ASTM D2863 (ISO 4589, Part 2) was used to determine the oxygen index (LOI) for polymer films 140 by 52 mm.

The correlation between a polymer thermal oxidative degradation and its combustion under diffusion flames condition may represent an interesting specific application. In general, the solid-phase polymer reaction can play a very important role in the reduction of polymer combustibility. If we can decrease the reaction ability of a polymer relative to an oxygen, the critical conditions of the diffusion flame stability would change. These polymers would have a different combustibility. It was shown that the composition of PP/PP-*co*-PE (62 : 38) has the highest induction period of autooxidation.^{15,16}

Under these circumstances, a theoretical model of a preliminary oxidation localization in interphaseous zone of a polymer sample was proposed.¹⁶ Apparently, the reaction ability of the compositions depends on the chemical structure of the interphaseous zone. It was shown that the increase of PP concentration in the PP/PP-*co*-PE composition from 38 to 62% leads to the lowering of reaction ability of samples. The process of autooxidation begins from the most active ingredient

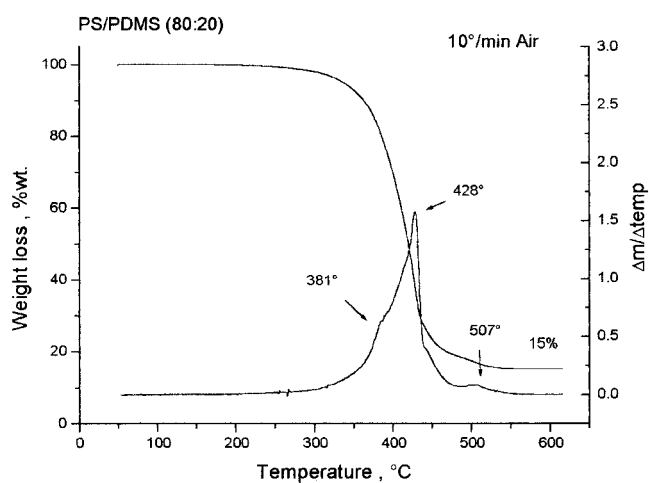


Figure 8 TG and DTG curves of PS/PDMS blend (80 : 20) in air at the heating rate of 10°/min.

TABLE IV
LOI and Char Yield for PP/PP-*co*-PE Compositions¹⁵

Composition	LOI	Char yield (wt %)
PP	17	0
PP/PP- <i>co</i> -PE (37.5/62.5)	19.5	1.5
PP/PP- <i>co</i> -PE (61.5/38.5)	21	3.4
PP- <i>co</i> -PE	18.5	0.5

of a polymer composition, PP or PP-*co*-PE. Interphaseous zone decelerates the polymer oxidation. Otherwise, we simply have a different polymeric system with the different kinetic parameters of oxidation and a different mechanism of the solid-phase reactions.

The combustibility tests confirm this hypothesis (Table IV).¹⁵ The sample with the minimal reaction activity, PP/PP-*co*-PE (62 : 38), has the highest values of LOI (21) and the highest char yield (3.4%).

References

- Emanuel, N. M.; Zaikov, G. E.; Maisus, Z. K. *Oxidation of Organic Compounds. Effect of Media*; Pergamon Press: Oxford, 1984.
- Kritsman, V. A.; Zaikov, G. E.; Emanuel, N. M. *Chemical Kinetics and Chain Reactions. Historical Aspects*; NOVA Science Publ.: New York, 1998.
- Lomakin, S. M.; Koverzanova, E. V.; Shilkina, N. E.; Zaikov, G. E. *Himicheskaya Fizika* to appear.
- Richard, D. K.; Salter, D. A. *Polymer* 1967, 8, 127.
- Mizutani, Y.; Matsuka, S.; Yamamoto, K. *Bull Chem Soc Jpn* 1965, 38, 2045.
- Gardner, P.; Lehrle, R. S.; Turner, D. *J Anal Appl Pyrolysis* 1993, 25, 11.
- Grassie, N.; McNeill, I. C.; Cooke, I. *J Appl Polym Sci* 1968, 12, 831.
- McNeill, I. C.; Neil, D. *Eur Polym J* 1970, 6, 143.
- McNeill, I. C.; Mohammed, M. A. *Eur Polym J* 1972, 8, 975.
- McNeill, I. C.; Mohammed, M. A. *Polym Degrad Stab* 1995, 50, 285.
- Bate, D. M.; Lehrle, R. S. *Polym Degrad Stab* 1998, 62, 57.
- Camino, G.; Lomakin, S. M.; Lazzari, M. *Polymer* 2001, 42(6), 2395.
- Guyot, A. *Polym Degrad Stab* 1986, 15, 219.
- Bockhorn, H.; Hornung, A.; Hornung, U. 27th (International) Symposium on Combustion/The Combustion Institute; 1998; 1343.
- Lomakin, S. M.; Shibryaeva, L. S.; Zaikov, G. E. *Chem Phys Rep* 1999, 17 (12), 2337.
- Shibryaeva, L. S.; Veretennikova, A. A.; Popov, A. A.; Gueveva, T. A.; Kanauzova, A. A. *Polym Sci (Part A): Polym Chem* 1999, 41 (4), 472.