Thermooxidative Degradation of Poly(vinyl chloride)/Acrylonitrile–Butadiene–Styrene Blends

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SYNOPSIS

The thermal degradation process of poly(vinyl chloride)/acrylonitrile–butadiene–styrene (PVC/ABS) blends was investigated by dynamic thermogravimetric analysis in the temperature range 50–650°C in air. The thermooxidative degradation of PVC/ABS blends of different composition takes place in three steps. In this multistep process of degradation the first step, dehydrochlorination, is the most rapid. The maximal rate of dehydrochlorination for the PVC blends containing up to 20% ABS-modifier is achieved at average conversions of 23.5–20.0%, i.e., at 13.5% for the 50/50 blend. The apparent activation energies ($E = 103$–116 kJ mol^{-1}) and preexponential factors ($Z = 2.11 \times 10^9$–3.45×10^{10} min^{-1}) for the first step of the degradation process were calculated after the Kissinger method. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Poly(vinyl chloride) (PVC) is one of the most important thermoplastics and is very often blended with other polymers. Blending one polymer with another is one method of modifying the physical properties of a polymer in desired manner. Blending can, however, have profound and sometimes unexpected effects on thermal stability, which cannot simply be predicted on the basis of the behavior of the components and their relative proportions.[1,2]

Pure PVC is a polymer of rather poor thermal stability that has been thoroughly investigated.[3,4] The thermal degradation of PVC starts at the glass transition temperature by elimination of hydrogen chloride, which is the main volatile product up to about 330°C. The intramolecular dehydrochlorination proceeds in allyl-activated steps producing conjugated double bonds (polyene sequences) in the polymer chain. After a certain induction period the intermolecular dehydrochlorination of PVC chains starts. The polyenes can undergo secondary reactions, e.g., intramolecular cyclization and crosslinking with neighboring PVC or polyene chains. As a result of these reactions and also of the scission reactions of predechlorinated product, a number of aromatic and aliphatic hydrocarbons are formed up to 600°C.

The process of thermal degradation is accelerated in the presence of oxygen and becomes even more complex.[4-7] The molecular oxygen can react with the original PVC chains or directly with conjugated polyenes. The primary process is the polymer oxidation with the formation of the corresponding oxygen-containing groups, initially hydroperoxides. The unstable hydroperoxides decompose and give different radicals. In the direct oxidation of conjugated polyenes the cyclic peroxides (that is, peroxy radicals) are formed. In both cases, the newly formed radicals will initiate new decomposition chains and accelerate dehydrochlorination of PVC.

When PVC is mixed with acrylonitrile–butadiene–styrene (ABS), blends with exceptionally good mechanical properties are obtained; but their thermal stability can be significantly changed due to the possible interactions of the polymer blend components and their degradation products. The types of interaction which can occur in heterogeneous systems are limited to those which involve diffusion of a small mobile product species (molecule or radical)
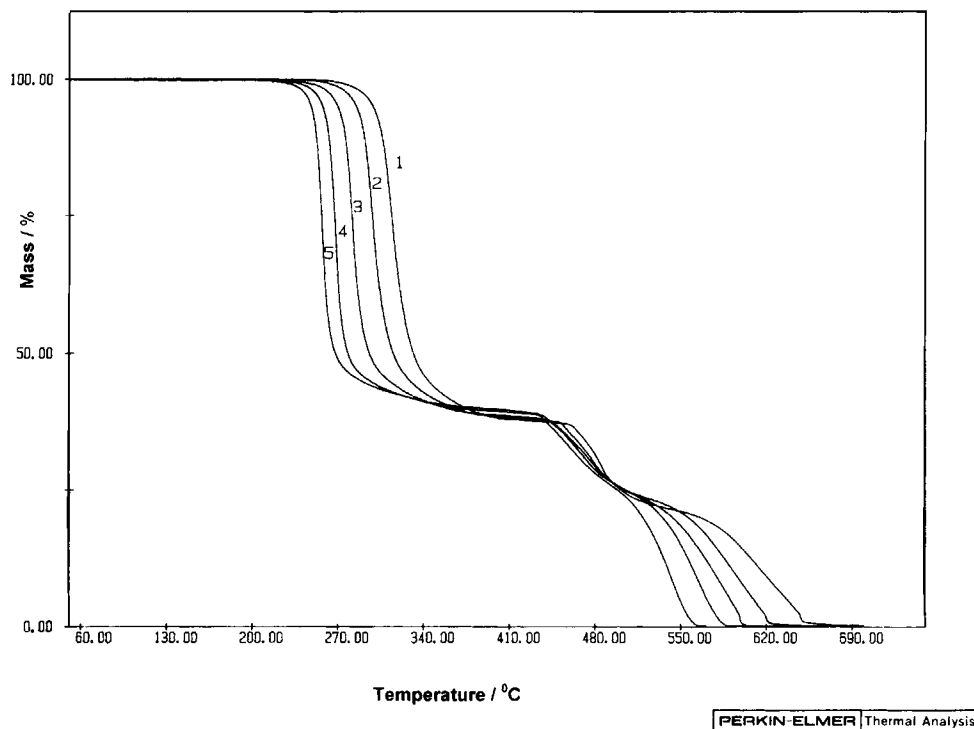
Figure 1 TG curves for PVC at different heating rates: (1) 40°C min^{-1}, (2) 20°C min^{-1}, (3) 10°C min^{-1}, (4) 5°C min^{-1}, (5) 2.5°C min^{-1}.

from one polymer phase into the other, where it reacts. When chemical interaction depends on diffusion of species between phases, it would be expected that the behavior could be dependent on the degree of dispersion of the phases.[8,9]

In order to investigate the influence of different ratios of ABS on the stability of PVC, dynamic thermogravimetric analysis was applied. From the thermogravimetric data, conclusions were made on the kinetics of thermooxidative degradation of the PVC/ABS blends. The kinetic parameters for the first degradation step were also calculated, by means of the Kissinger integral method.[10]

EXPERIMENTAL

Materials and Methods

The materials used in this study were commercially available polymers. The suspension PVC (K-value 70; $\bar{M}_v$ = 85,000; chlorine ratio 55.9%; purity 98.37%) was supplied by INAVINIL, Croatia. ABS was Ravikral type MA emulsion prepared with a composition ratio of acrylonitrile/butadiene/styrene 22 : 32 : 46 by mass, supplied by ANIC, Italy.

The PVC/ABS blends of different mass fractions of polymers (100/0, 95/5, 90/10, 85/15, 80/20, and

50/50) were prepared by homogenization of premixed polymer powders using the laboratory roller mill at 140°C temperature for 60 s. The thickness of the drawn-out foils was about 0.5 mm.

The thermal degradation was carried out thermogravimetrically (Perkin-Elmer TGS-2 instrument with TADS microprocessor) under dynamic conditions in the temperature range of 50–650°C under an air flow of 30 mL min^{-1} at heating rates 2.5, 5, 10, 20, and 40°C min^{-1} and sample mass 2.0 ± 0.1 mg.

RESULTS AND DISCUSSION

The thermogravimetric (TG) curves obtained by thermooxidative degradation are shown in the Figures 1 to 3 for PVC, 50/50 PVC/ABS blend, and ABS. The thermooxidative degradation of PVC occurs through three degradation steps (Fig. 1). The first degradation step presents the process of dehydrochlorination and the formation of polyenes; the second step presents the degradation of polyene residue and the formation of compounds with lower molecular masses, and the third step is a total degradation without residue.[11] ABS shows the two-step (Fig. 3) while the PVC/ABS blends show the three-
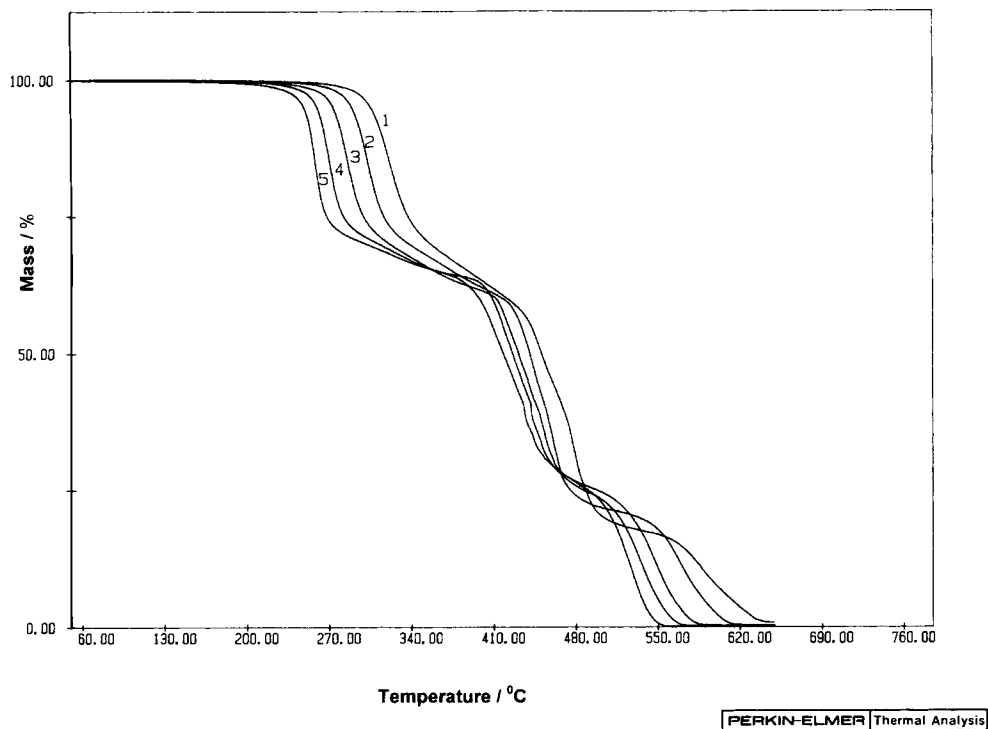
Figure 2   TG curves for 50/50 PVC/ABS blend at different heating rates: (1) 40°C min^{-1}, (2) 20°C min^{-1}, (3) 10°C min^{-1}, (4) 5°C min^{-1}, (5) 2.5°C min^{-1}.
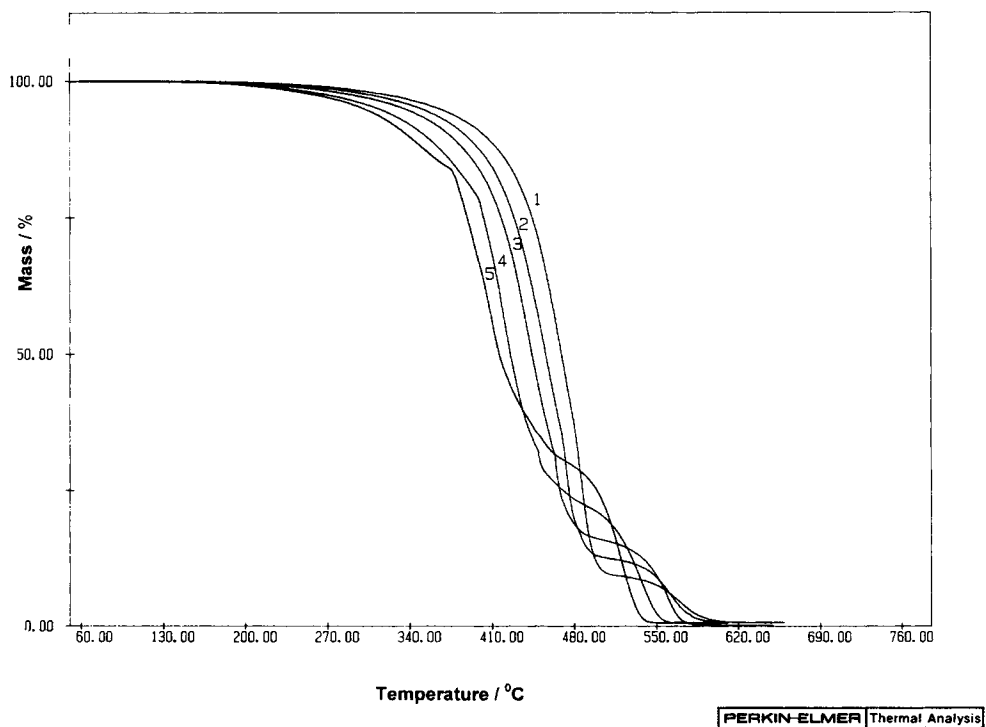
Figure 3   TG curves for ABS at different heating rates: (1) 40°C min^{-1}, (2) 20°C min^{-1}, (3) 10°C min^{-1}, (4) 5°C min^{-1}, (5) 2.5°C min^{-1}.

step mechanism of degradation. An example is shown in Figure 2 for the 50/50 blend. Applying the Perkin-Elmer Standard Program, the characteristics of TG curves were obtained: the mass loss at the end of the first and second degradation step (Δm_1, Δm_2), the onset temperature of the first degradation step (T_1^0) determined as the intersection of the extrapolated base line with tangent drawn in the inflection point of the TG curve, the temperature at the maximal rate of degradation in the first step of degradation (T_1^m), and the degree of conversion at the maximal rate (α_1^m). The results obtained are given in Table I.

In the first step of degradation of pure PVC an average loss of mass is 61.7%, whereas in the second step it is 14.5%. Increasing the ratio of ABS in the

PVC/ABS blend linearly lowers the loss of mass in the first degradation step; in the second step it is linearly increased (Fig. 4). The change of mass (2.6–2.7% per 5% of ABS added) could be explained by the effect of the dilution of the mixture.

The onset degradation temperature of the blend depends on the composition of blend as well as on the applied heating rate. The degradation of pure PVC and PVC/ABS blends starts at about 250°C, and the degradation of pure ABS at about 360°C when the heating rate is 2.5°C min^{-1}. The degradation of ABS starts after the dehydrochlorination of PVC has finished; consequently the interaction of its degradation products with PVC is excluded. The degradation products of ABS (HCN and NH$_3$), which might catalyze dehydrochlorination, are

Table I Characteristics of Thermooxidative Degradation of PVC/ABS Blends

PVC/ABS	β (°C min^{-1})	T_1^0 (°C)	T_1^m (°C)	α_1^m (%)	Δm_1 (%)	Δm_2 (%)
100/0	40	302.74	313.11	23.10	62.88	16.11
	20	288.35	297.32	23.42	62.23	14.36
	10	273.69	280.94	23.51	61.66	14.65
	5	261.10	267.82	23.78	60.59	14.04
	2.5	250.96	256.55	24.28	59.79	13.45
95/5	40	301.52	313.82	22.37	61.31	17.94
	20	288.03	298.38	22.78	60.36	16.13
	10	272.79	280.84	21.91	60.00	15.19
	5	259.64	267.88	22.46	59.27	15.90
	2.5	250.01	257.14	23.50	58.44	13.04
90/10	40	299.67	311.63	21.22	57.82	19.46
	20	287.65	297.16	21.21	58.06	18.65
	10	272.01	280.85	23.33	56.59	18.49
	5	256.93	263.50	20.86	59.11	18.84
	2.5	246.76	253.86	23.58	55.43	18.42
85/15	40	302.18	316.00	21.49	57.30	23.22
	20	288.08	300.46	23.39	59.15	20.21
	10	274.10	283.03	20.43	55.43	19.76
	5	258.90	266.77	22.62	54.94	20.37
	2.5	249.97	257.15	21.38	53.95	18.66
80/20	40	299.48	314.88	21.39	52.63	25.83
	20	286.83	299.35	19.44	52.24	23.67
	10	271.86	283.02	21.81	51.31	23.08
	5	256.88	265.67	19.34	50.69	22.18
	2.5	245.98	252.77	18.25	49.88	20.75
50/50	40	304.71	320.37	13.72	35.64	44.97
	20	287.78	301.58	13.33	37.97	40.27
	10	275.52	284.10	12.83	37.86	36.64
	5	259.28	270.04	13.92	35.65	39.36
	2.5	249.54	258.24	14.10	33.94	40.48
0/100	40	428.44	470.03	50.75	90.70	—
	20	414.61	455.86	49.86	87.52	—
	10	404.73	440.30	45.61	83.80	—
	5	388.60	418.57	41.02	77.47	—
	2.5	363.23	393.75	28.55	69.42	—
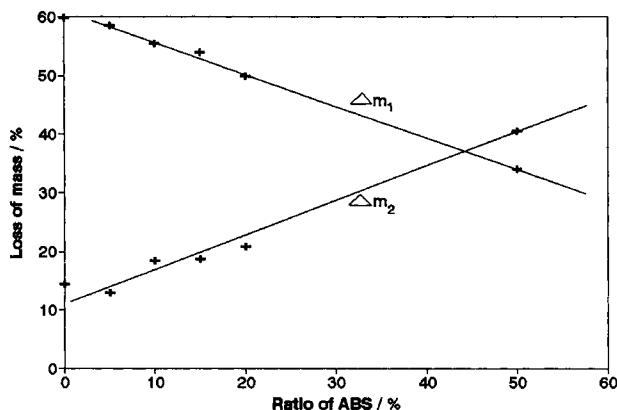
Figure 4   Effect of PVC/ABS blend composition on the mass loss; heating rate 2.5°C min^{-1}.

evolved at a temperature of 100°C in traces whereas the main degradation products (styrene, acrylonitrile, HCN, and acetylene) are isolated at 400°C after dehydrochlorination has been completed.[12]

The temperature interval of every degradation step (the difference in temperatures at the beginning and the end) is evident from the derivative TG curves (DTG curves) (Figs. 5 and 6). At higher heating rates the intervals were shifted toward higher temperatures (Table II).

In the complex process of thermooxidative degradation of PVC/ABS blends, the first step is the most rapid (Figs. 5 and 6). The maximal rate of mass loss is achieved at temperature T_1^m and conversion α_1^m. For the blends 100/0 to 80/20, conversion is about 23.5–20.0%; for the 50/50 blend, about 13.5% (Table I). When compared to the degradation in nitrogen,[13] the dehydrochlorination rates are considerably higher in air. That can be explained by the catalytic influence of oxygen with which polyenes form peroxide radicals as new initiating centers of dehydrochlorination.[8,11] In the second degradation step more peaks are shown on the DTG curves, which is the result of a series of oxidation reactions; that is why the temperatures T_2^0 and T_2^m cannot be determined.

The kinetic parameters were calculated only for the first step of the degradation process. The Kissinger equation[10,14] was applied assuming the first-order reaction. For the stationary point the equation is as follows:

$$\ln \frac{\beta}{T_m^2} = \ln \frac{Z R}{E} - \frac{E}{R T_m} \qquad (1)$$

where β is the heating rate, T_m is the thermodynamic temperature at the maximal rate of degradation, Z
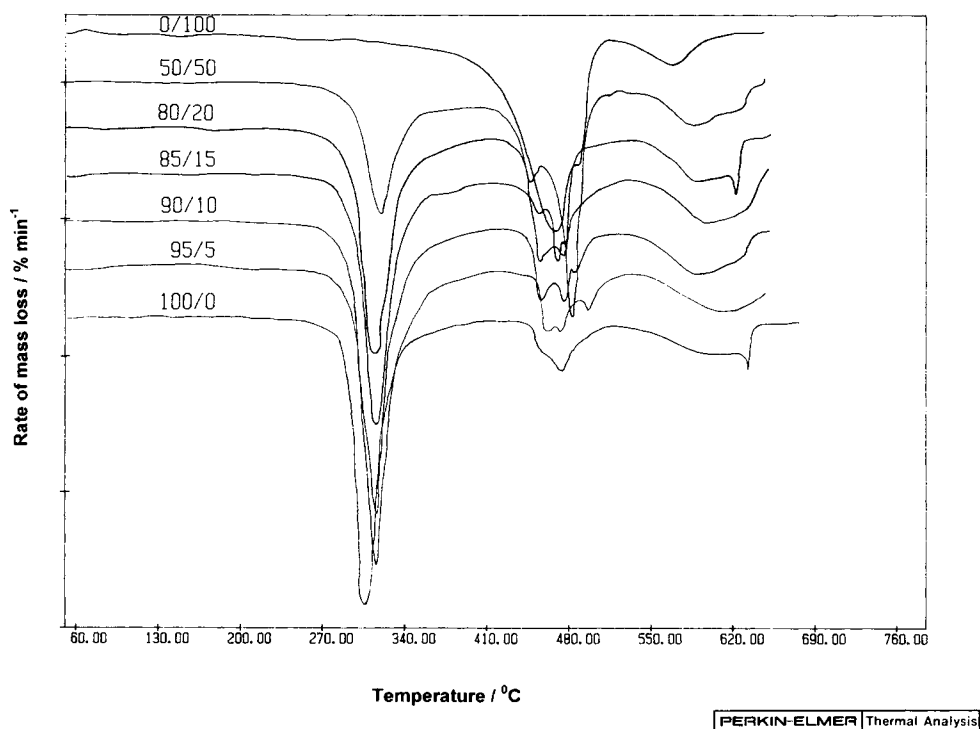
Figure 5   DTG curves for PVC/ABS blends of different compositions; heating rate 40°C min^{-1}.
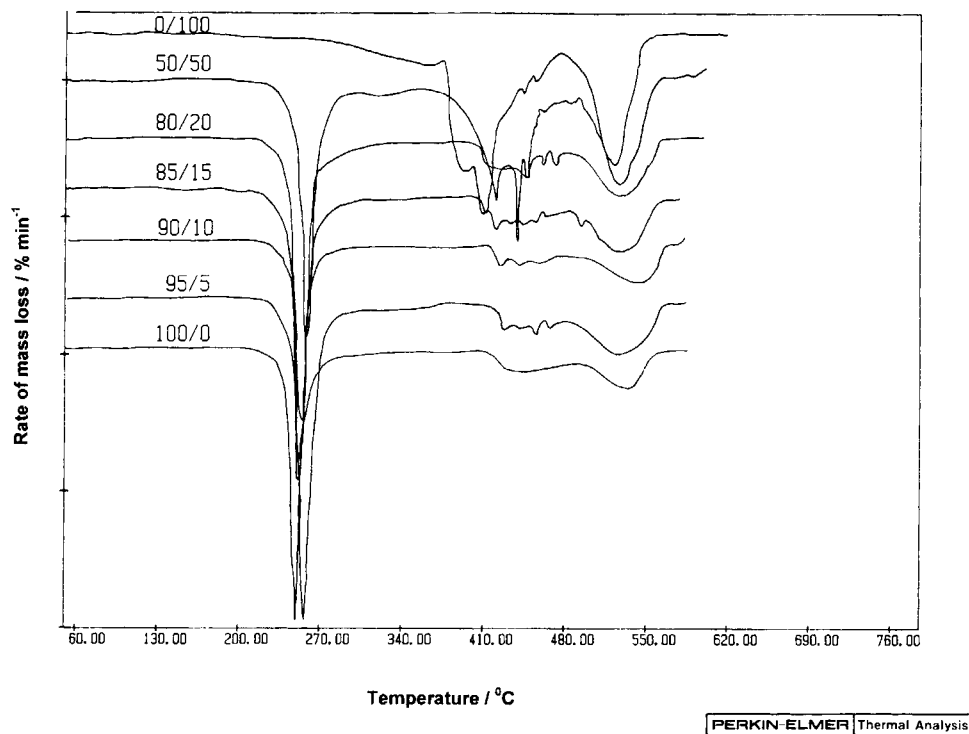
Figure 6 DTG curves for PVC/ABS blends of different compositions; heating rate 2.5°C min⁻¹.

is the preexponential factor, R is the gas constant, and E is the activation energy.

The dependence of $\ln(\beta/T_m^2)$ versus $(1/T_m)$ represents a straight line with slope $(-E/R)$ and segment $\ln(Z R/E)$ on the ordinate. The parameters of the most probable straight lines, out of which the activation energy and preexponential factor were calculated, were obtained by the method of regression analysis. The fitting of experimental data with kinetic eq. (1) is satisfactory, since the coefficient of correlation r^2 is higher than 0.99 for all the PVC/ABS blends.

The results of the kinetic analysis of TG curves according to the Kissinger method are shown in Ta-

ble III. The activation energies are 103–116 kJ mol⁻¹ while the preexponential factors are 2.11×10^9–3.4 $\times 10^{10}$ min⁻¹. In order to estimate the thermal stability of the blends and the reaction capacity of the system, respectively, the compensation parameters[15] $(E/\log Z)$ were calculated. In this manner the effect of procedural factors on E and Z values is eliminated, whereas the investigated PVC/ABS blends, regardless of their composition, show a practically constant ratio $E/\log Z$ of about 11 (Table III). Increasing the ABS ratio in the blend in the first degradation step of the thermooxidative degradation process, only the rate of dehydrochlorination changes; the mechanism of degradation does not change.

Table II Temperature Intervals of Degradation of PVC and ABS

Heating Rate (°C min⁻¹)	2.5	40
Degradation intervals for PVC/°C		
first step	200···340	200···410
second step	340···490	410···520
Degradation intervals for ABS/°C		
first step	270···480	310···510
second step	480···570	510···630

Table III Activation energies E, Preexponential Factors Z, and Ratios $E/\log Z$ for Various Compositions of PVC/ABS Blends

PVC/ABS	E (kJ mol⁻¹)	Z (min⁻¹)	E (log Z)
100/0	115.7	$3.42 \cdot 10^{10}$	10.98
95/5	114.6	$2.63 \cdot 10^{10}$	10.99
90/10	108.9	$8.04 \cdot 10^9$	10.99
85/15	109.1	$7.16 \cdot 10^9$	11.07
80/20	103.3	$2.11 \cdot 10^9$	11.08
50/50	106.6	$3.73 \cdot 10^9$	11.14

CONCLUSION

The thermooxidative degradation of PVC/ABS blends was thermogravimetrically investigated in the temperature range 50–650°C and is a multistep process. The loss of mass in the first and second degradation steps depends on the composition of the blend and is linearly changed with the increase of ABS ratio in the blend, up to 50%. The most rapid part of the degradation process is the first step, characterized by the dehydrochlorination reaction. The maximal rate of mass loss is achieved at average conversions of about 23.5–20.0% (PVC/ABS 100/ 0–80/20), i.e., at 13.5% for the 50/50 blend.

The apparent activation energies for the first step of degradation are 103–116 kJ mol^{-1} and preexponential factors are 2.11×10^9–3.45×10^{10} min^{-1}. Although these kinetic parameters change depending on the composition of the blend, the ratio $E/\log Z$ (compensation parameter) is constant for all compositions. Changing the composition of the blend changes only the rate of the degradation; the mechanism remains unchanged.

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