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KINETICS OF ISOTHERMAL THERMOGRAVIMETRICAL DEGRADATION OF PVC/ABS BLENDS

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Abstract

The PVC/ABS blends were degradated by means of isothermal thermogravimetry at temperatures of 210...240°C in nitrogen. Applying the stationary point method to the data obtained from thermogravimetric curves, apparent activation energy, preexponential factor and compensation parameter for each blend were calculated. The constancy of compensation parameters points to an unchanged mechanism of poly(vinyl-chloride) (PVC) thermal degradation in the presence of acrylonitrile butadiene-styrene (ABS). Upon increasing the fraction of ABS in the blend up to 50% only the kinetics of the process is changed.

Keywords: kinetics, PVC/ABS blends, TG

Introduction

In general terms, the solid state degradation of polymers is a heterogeneous reaction on which the increase of temperature causes the loss of mass. The degree of conversion α is determined by ratio [1]

$$\alpha = \frac{m_o - m}{m_o} \tag{1}$$

where m_o is mass measured in the initial and m in instantaneous state. The rate of degradation $(\mathrm{d}\alpha/\mathrm{d}t)$ is equal to the rate of change of measured variable $(-1/m_o)(\mathrm{d}m/\mathrm{d}t)$ if physical factors, that can affect heterogeneous system, are kept constant, that is

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)f(\alpha) \tag{2}$$

In the Eq. (2) $f(\alpha)$ is algebraic function which describes the mechanism of the process (the kinetic model), $k(T)$ is the reaction rate constant given by Arrhenius equation

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$$k(T) = Z\exp(-E/RT) \tag{3}$$

where Z is preexponential factor, E is the activation energy, R is the gas constant, T is the thermodynamic temperature.

The kinetic parameters of the process are calculated from the differential kinetic Eq. (2) or its integral form

$$\int_0^1 \frac{\mathrm{d}\alpha}{f(\alpha)} = \int_0^t k(T)\mathrm{d}t \tag{4}$$

the solution of which is

$$g(\alpha) = k(T)\mathrm{d}t \tag{5}$$

It is not simple to choose the function $f(\alpha)$ for heterogeneous reactions. The satisfactory kinetic model is the one which ensures the linearization of kinetic equations in the appropriate coordinate system. In isothermal kinetics, however, the stationary point method [2], which does not require the previous knowledge of the mechanism of the process, is often used for the calculation of kinetic parameters. The stationary point $S(t_m, V_{max})$ is defined on the differential curve $\mathrm{d}\alpha/\mathrm{d}t$ *vs.* t as the point at which the derivation $(\mathrm{d}^2\alpha/\mathrm{d}t^2)$ is zero. The rate will have the maximum $V_{max}=(\mathrm{d}\alpha/\mathrm{d}t)_{max}$ at the time t_m. Simultaneously the inflection point $P(t_m,\alpha_m)$ is defined on the integral sigmoid curve α *vs.* t or $(1-\alpha)$ *vs.* t. t_m and α_m are the time and degree of degradation at the greatest rate of degradation. These coordinates are read from the experimental TG and DTG curves.

The activation energy is calculated by the linearization of the Eqs (6) or (7) in the appropriate coordinate system

$$\frac{\mathrm{d}\ln V_{max}}{\mathrm{d}(1/T)} = \frac{\mathrm{d}\ln k}{\mathrm{d}(1/T)} = -\frac{E}{R} \tag{6}$$

$$\frac{\mathrm{d}\ln t_m}{\mathrm{d}(1/T)} = \frac{\mathrm{d}\ln t}{\mathrm{d}(1/T)} = \frac{E}{R} \tag{7}$$

Experimental

To prepare the PVC/ABS blend we used: suspension PVC (K-value 70, chlorine ratio 55.9%), INAVINIL - Split, and ABS (acrylonitrile : butadiene : styrene of the composition 22% : 32% : 46%), ANIC, Ravenna.

The PVC/ABS blends of different mass fraction of polymers (100/0, 95/5, 90/10, 85/15, 80/20 and 50/50) were prepared by means of homogenization of premixed polymer powders (100 g of the blend) using the laboratory roller mill at 140°C temperature in 60 s time. The thickness of the foils drown out were 0.5 mm. The samples of blend, size (2.0±0.2) mg, were degraded for 180 min in thermobalance at the temperatures of 210, 220, 230 and 240°C under the nitrogen flow of 30 mL·min^{-1}. The Perkin-Elmer TGS-2, System 4 instrument with TADS microprocessor was used [3]. The sample was heated from the starting (50°C) to the assigned degradation temperature at the rate of 80 deg·min^{-1}.

Results and discussion

The PVC degradation starts above the glass transition temperature. The basic degradation reaction at moderate temperatures (<350°C) is dehydrochlorination where hydrogen chloride is released and polyene sequences are formed simultaneously. The physical and chemical properties of polymer are weakened.

During the degradation process of PVC/ABS blends the main degradation product in the investigated temperature range, between 210 and 240°C, is also hydrogen chloride, while degradation of ABS practically starts after the dehydrochlorination of PVC has been finished [4].

The results of isothermal degradation of PVC/ABS blends with different polymer ratioes are shown in Figs 1 to 6.

The integral thermogravimetric curves (TG curves), the residual mass versus time, for all degradation temperatures and for all blend compositions are of sig-

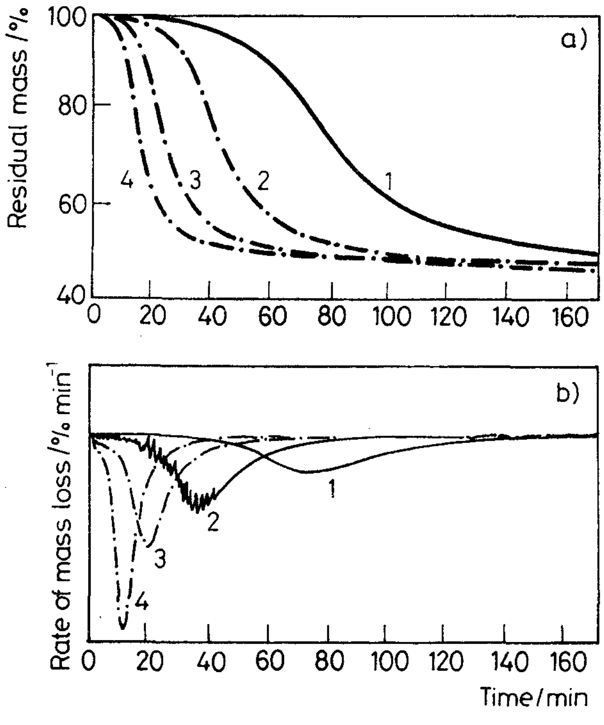

Fig. 1 TG (a) and DTG curves (b) for PVC/ABS (100/0) blend at different temperatures: 1) 210°C; 2) 220°C; 3) 230°C; 4) 240°C

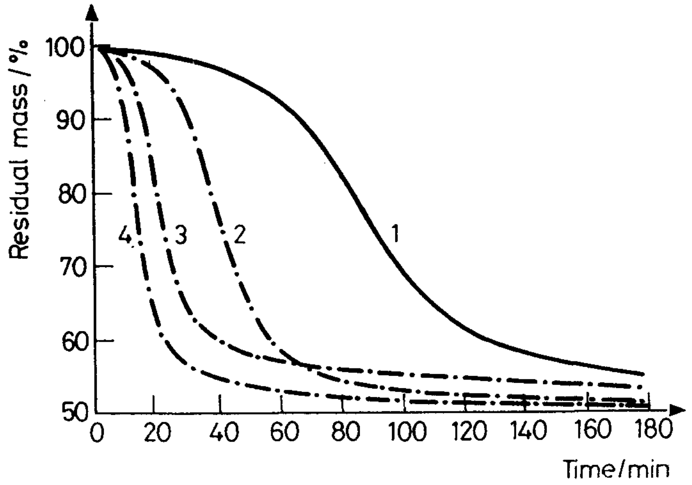

Fig. 2 TG curves for PVC/ABS (95/5) blend at different temperatures: 1) 210°C; 2) 220°C; 3) 230°C; 4) 240°C

moid form which is characteristics for the reaction with the zero starting rate, i.e. an autocatalytic reaction.

By an electronic differentiation of integral TG curves, the derivative thermogravimetric curves (DTG curves), the mass loss rate versus time, were obtained. The shape of DTG curves (examples are in the Figs 1 and 6) shows the complex mechanism of process. The rate of the process, increases from zero to the maximum value whereupon it decreases and gravitates to zero, represents the overall rate.

From TG and DTG curves the values for t_m and α_m are read while the values V_{max} are determined after Delmon method [5]. All the values are given in Table 1.

Increasing the degradation temperatures 10°C in the range of 210...240°C, the maximum degradation rate is increased 1.6–1.8 times for PVC and 1.5–2.5 times for PVC/ABS blends respectively. At a certain temperature PVC is degradated most rapidly, and 50/50 blend most slowly. The fraction of 50% of ABS in the blend decreases the maximum degradation rate of PVC for 4 times on the average at the temperature 220...240°C, and 6 times at 210°C. The degree of conversion α_m depends on the degradation temperature as well as on the composition of the blend. Increasing the temperature and the fraction of ABS in the blend moves it to the lower values.

The values t_m, α_m and V_{max} from the Table 1 are used for the graphic determination of activation energies and preexponential factors. According to the Eq. (6) $E=-R$ slope, $Z=\exp$ (segment); the parameters of the most probable straight lines (slope and segment) are calculated by the method of the least squares. The activation energies in Table 1 are apparent and represent a combi-

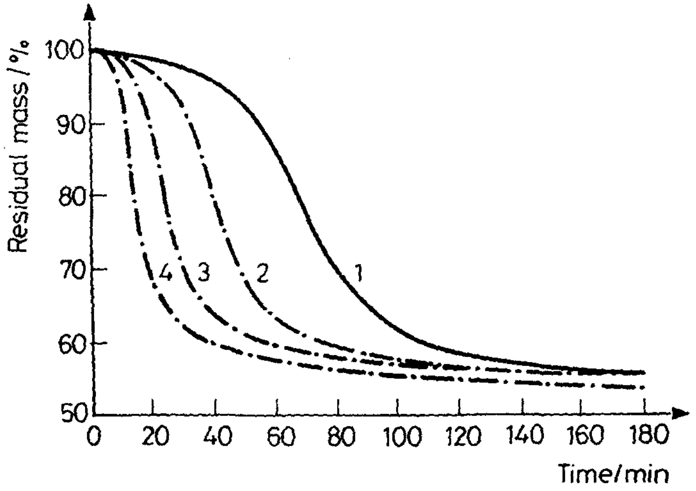

Fig. 3 TG curves for PVC/ABS (90/10) blend at different temperatures: 1) 210°C; 2) 220°C; 3) 230°C; 4) 240°C

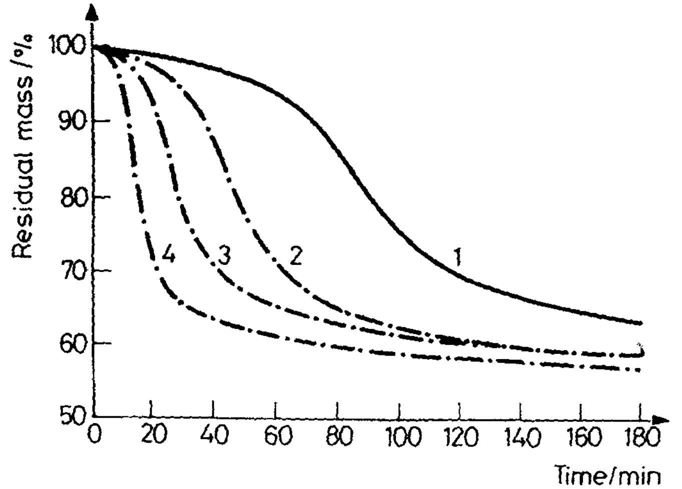

Fig. 4 TG curves for PVC/ABS (85/15) blend at different temperatures: 1) 210°C; 2) 220°C; 3) 230°C; 4) 240°C

nation of energies of the elementary reactions of heterogeneous process. The apparent activation energy can be used as a thermal stability measure only if, other kinetic parameters (Z and $f(\alpha)$) are constant [6]. Different activation energy values do not confirm different stability. Therefore, it has been suggested to characterize the thermal degradation process by means of compensation parameters [7, 8] ($S_p = E/\log Z$) in order to exclude the effect of experimental factors on the shape and position of TG curve and consequently on E and Z values.

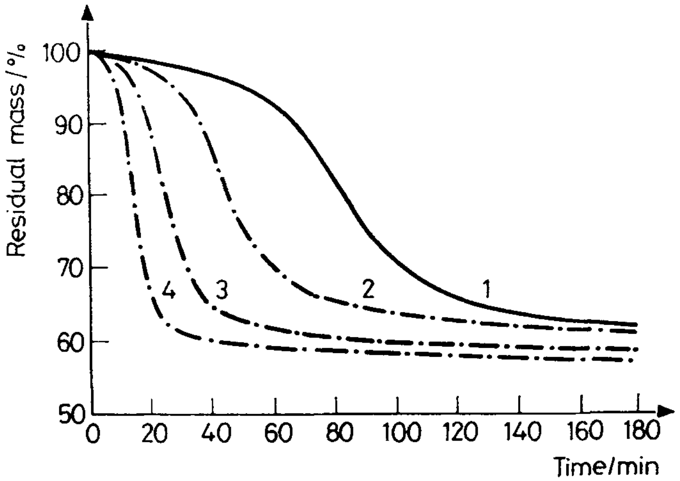

Fig. 5 TG curves for PVC/ABS (80/20) blend at different temperatures: 1) 210°C; 2) 220°C; 3) 230°C; 4) 240°C

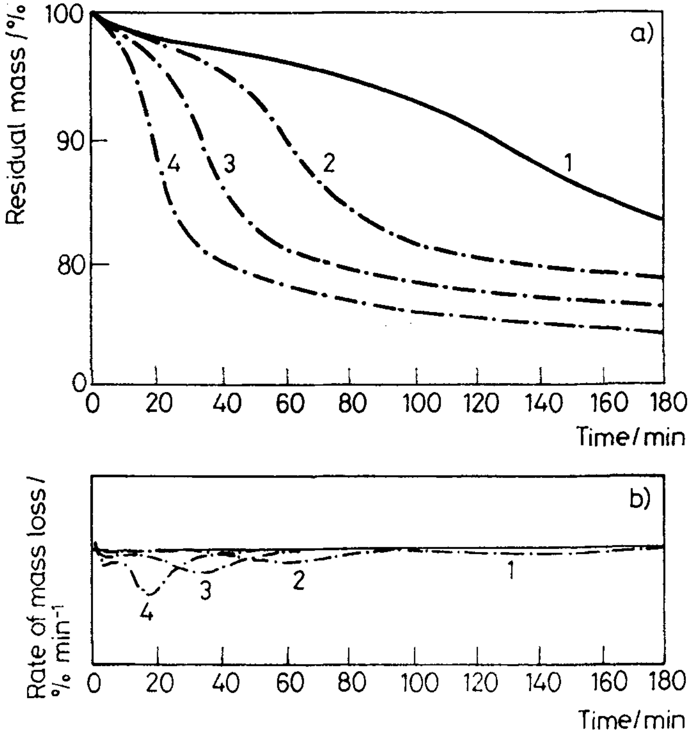

Fig. 6 TG (a) and DTG curves (b) for PVC/ABS (50/50) blend at different temperatures: 1) 210°C; 2) 220°C; 3) 230°C; 4) 240°C

The compensation parameters calculated for the thermal degradation of PVC/ABS and showed in Table 1 are practically constant for all the compositions of blends ($S_p = 11.38 \pm 0.24$). The degradation mechanism of PVC does not change if ABS-modifier is added up to the fraction of 50%; only the kinetics of the process is changed. The degrees of conversion, reached through the same time of degradation, for PVC/ABS blends are reduced with the increase of the

Table 1 Kinetic parameters of thermal degradation process of PVC/ABS blends calculated by stationary point method

PVC/ABS	T/°C	t_m/min	α_m	$10^2 \cdot V_{max}$/min^{-1}	E/kJ·mol^{-1} Z/min^{-1} S_p
100/0	210	73.36	0.2036	0.9306	111.10
	220	39.07	0.2095	1.5972	
	230	20.24	0.1756	2.6225	$10^{9.97}$
	240	12.93	0.1770	4.7569	11.14
95/5	210	86.57	0.2181	0.7465	112.24
	220	37.95	0.1932	1.5538	
	230	19.96	0.1771	2.4271	$10^{10.04}$
	240	12.65	0.1779	3.9375	11.18
90/10	210	67.74	0.2036	0.9028	93.28
	220	38.23	0.1774	1.3888	
	230	22.77	0.1644	2.0833	$10^{8.03}$
	240	13.21	0.1566	3.5694	11.62
85/15	210	84.32	0.1648	0.5955	110.76
	220	43.05	0.1569	1.0243	
	230	23.89	0.1312	1.6666	$10^{9.74}$
	240	13.49	0.1364	3.0381	11.37
80/20	210	79.83	0.1769	0.6858	116.35
	220	42.44	0.1615	1.1892	
	230	22.77	0.1554	2.1701	$10^{10.41}$
	240	14.05	0.1750	4.3438	11.18
50/50	210	134.57	0.1136	0.1528	136.37
	220	61.68	0.1032	0.3771	
	230	34.35	0.0911	0.6250	$10^{11.96}$
	240	17.96	0.0874	1.1667	11.40

ratio of modifier in the blend in relation to the pure PVC. That is probably the consequence of 'the effect of dilution', but not of interaction of polymers [4].

Conclusion

The sigmoid shape of TG curves points to the autocatalytic nature of the degradation process of PVC/ABS blends in the investigated conditions.

The maximum rate of degradation is achieved at the conversion degrees of $\alpha_m \approx 0.10-0.20$. By the increase of degradation temperature, for a certain blend, the time to achieve the maximum rate is shifted to the side of smaller conversion degrees. The maximum overall rate of degradated process at a certain temperature is the greatest for the pure PVC, while by increasing the ratio of ABS modifier in the blend it has tendency of decreasing.

The constancy of the compensation parameters in the investigated area indicates to the unchanged mechanism of degradation process for all the compositions of PVC/ABS blends.

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Zusammenfassung — Mittels isothermischer Thermogravimetrie in Stickstoff bei Temperaturen von 210 bis 240°C wurden PVC/ABS-Gemische zersetzt. Unter Anwendung der Methode kritischer Punkte an den anhand der thermogravimetrischen Kurven gewonnenen Angaben wurden die scheinbare Aktivierungsenergie, der präexponentielle Faktor und der Kompensationsparameter für jedes Gemisch berechnet. Die Konstantheit der Kompensationsparameter deutet auf einen unveränderten Mechanismus des thermischen Abbaues von Polyvinylchlorid (PVC) in Gegenwart von Acrylonitrilbutadien-Styrol (ABS) hin. Durch Anheben der ABS-Fraktion im Gemisch bis zu 50% wird lediglich die Kinetik des Prozesses verändert.