Kinetic Investigation of Thermooxidative Degradation of Poly(vinyl chloride)/Acrylonitrile–Butadiene–Styrene Blends by Isothermal Thermogravimetric Analysis

I. KLARIĆ, U. ROJE, N. STIPANELOV

Department of Organic Chemical Technology, Faculty of Technology, University of Split, Teslina 10/V, 21000 Split, Croatia

ABSTRACT: The thermal degradation of poly(vinyl chloride)/acrylonitrile–butadiene–styrene (PVC/ABS) blends of different compositions was investigated by means of isothermal thermogravimetric analysis at temperatures of 210°–240°C in flowing atmosphere of air. The Flynn equation, the method of stationary point, and kinetic equation using the Prout–Tompkins model proved to be satisfactory in describing the thermooxidative degradation in the range of 5–30% conversions. The apparent activation energy E and preexponential factor Z were calculated for all compositions of PVC/ABS blends. The ratios $E/\ln Z$ are constant for pure and modified PVC and point to the unique mechanism of degradation process. Upon increasing the ratio of ABS in the PVC/ABS blend up to 50%, only the rate of the process is changed; the mechanism remains unchanged. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 833–839, 1999

Key words: isothermal thermogravimetric analysis; kinetic parameters; PVC/ABS blends; thermooxidation degradation

INTRODUCTION

A way to formulate a polymeric material with improved properties is to blend polymers so that the resulting material has properties superior to those of the components. On blending poly(vinyl chloride) (PVC) with acrylonitrile–butadiene–styrene (ABS), polymer modificator, the processibility and impact strength of PVC are improved. Optimal improvement of the blend's processing characteristics is achieved by adding 15 to 20% ABS. However, by modifying the polymer material, the thermal stability of the blend is also changed.[1,2]

During processing of PVC at high temperatures, considerable degradation occurs due to the polymer's rather poor thermal stability. Efforts to solve this problem have led to the performance of much research of the thermal degradation and stabilization of PVC, both fundamental and applied.[3–8] Thermal degradation of PVC starts yet at the glass transition temperature with the evaluation of hydrogen chloride, which is the main volatile degradation product up to 330°C. Simultaneously with dehydrochlorination of the polymer chain, conjugated double bonds (polyenes) develop that alter the physical and chemical properties of the polymer. Generally, the primary process of PVC degradation consists of three elementary events, which are the same irrespective of the type of degradation (thermal, thermooxidative, photo, and mechanical).[6] These events are initiation (random at normal repeat units and at structural defects), fast zip elimination of HCl and polyene formation in the backbone of the polymer, and termination of zip. The primary pro-

cesses in thermal degradation are followed by several secondary processes[9–11] (e.g., cyclization of polyenes, crosslinking, and benzene formation). In the presence of oxygen, thermal degradation is accelerated and becomes more complex.[4,6,11–15] Molecular oxygen reacts with the PVC chains and with conjugated polyenes, with the production of oxygen-containing groups, initially hydroperoxides. These unstable hydroperoxides decompose by producing radicals that may attack the polymer chains, resulting in secondary initiation of HCl loss and additionally accelerate the dehydrochlorination of PVC.

On heating, ABS produces traces of low molecular weight hydrocarbons, NH_3 and HCN at the temperature as low as 100°C, whereas the main degradation products (styrene, acrylonitrile, HCN, and acetylene) occur at 400°C.[16]

It is well established that, under degradation conditions, considerable interactions may occur between the components in the polymer blend and their degradation products. The type of interaction will depend on the degree of miscibility of the components, as well as on their ratio in the blend.[1,2,17] Therefore, the effect of certain polymer modifiers on the thermal stability of PVC can be different.

To investigate the influence of different ratios of ABS on the stability of PVC in oxidizing atmosphere, isothermal thermogravimetric (TG) analysis was applied. From the TG data, kinetic parameters for thermooxidative degradation of PVC/ABS blends were calculated after the Flynn method,[18] stationary point method,[19] and the Prout–Tompkins method.[20,21]

EXPERIMENTAL

Materials and Methods

The materials used in this study were suspension grade PVC (K-value 70; M_v = 85,000; chlorine content = 55.9%; purity = 98.37%) supplied by Inavinil, Croatia, and ABS Ravikral type MA emulsion polymerized with a composition ratio of ABS (22 : 32 : 46) by mass, supplied by Anic (Italy).

The PVC/ABS blends of different mass fraction of polymers (100/0, 90/10, 80/20, 50/50, and 0/100) were homogenized with a laboratory roller mill at 140°C for 60 s. The thickness of the drawn-out foils were ~ 0.5 mm.

Isothermal TG analysis was conducted with a Perkin-Elmer TGS-2 system coupled to a microprocessor programmer System 4 as the temperature control unit. The sample of blend (2.0 ± 0.1 mg) was degradated isothermally in the thermobalance at temperatures of 210°, 220°, 230°, and 240°C under an air flow (30 mL min^{-1}). The sample was initially heated at the heating rate of 80°C min^{-1} from the start (50°C) to the selected degradation temperature and then held at this temperature for 180 min. The result of measuring is an integral TG curve, mass against time.

Kinetic Analysis

During the thermal degradation of the polymer, the mass loss defines the degree of conversion[18] (the fractional extent of reaction) as

$$\alpha = \frac{m_0 - m}{m_0} \tag{1}$$

where m_0 is the initial and m instaneous mass of the sample during the degradation process.

By differentiating eq. (1) with respect to time, the rate of overall global degradation is $d\alpha/dt = -1/m_0(dm/dt)$, and this rate will be equal to the rate of fractional mass loss $d\alpha/dt = dm/dt$. According to the fundamental differential kinetic relation, the rate is

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

where $f(\alpha)$ is an algebraic function that describes the mechanism of the process (kinetic model) and $k(T)$ is the reaction rate constant. Considering an Arrhenius type variation of the kinetic constants with temperature than

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

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

By integrating eq. (2), an integral type of kinetic equation is obtained

$$g(\alpha) = k\ t \tag{4}$$

where $g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)}$.

Figure 1   TG curves for PVC/ABS blends of different compositions at 210°C: (1) 100/0, (2) 90/10, (3) 80/20, (4) 50/50, and (5) 0/100.

By taking eq. (3) into account and by logarithming eq. (4), the Flynn equation is obtained.

$$\ln t = \ln[g(\alpha)] - \ln Z + E/RT \qquad (5)$$

It is possible from eq. (5) to calculate the apparent activation energy at a given degree of conversion, if $g(\alpha)$ is constant, without previously knowing the form of the $f(\alpha)$ function.

Otherwise, the various kinetic models $f(\alpha)$ can be applied for studying heterogeneous reactions due to the change in mechanism, geometry, or chemistry.[21] The satisfactory model will be the one that leads to good fitting with experimental data.

RESULTS AND DISCUSSION

The mass against time curves obtained by isothermal heating of PVC/ABS blends of different

Figure 3   TG curves for PVC/ABS blends of different compositions at 230°C: (1) 100/0, (2) 90/10, (3) 80/20, (4) 50/50, and (5) 0/100.

composition in air are shown in Figures 1–4. These curves (except 5) are sigmoid, and their shape depends on degradation temperature, as well as the composition of the blend. The mass loss at the end of the isothermal heating of the sample is the greatest for PVC and the lowest for ABS. At a certain temperature, the final mass loss reduces with the increased ratio of ABS in the blend. The mass loss corresponded with the first degradation step (dehydrochlorination of PVC and the formation of polyenes) on the TG curve recorded in the dynamic condition.[22,23] The times during which the mass loss reaches 5–30% are shown in Table I. These times increase successively as follows: 90/10, 80/20, PVC, 50/50, and ABS. In the early stages of degradation, when the mass loss is under 2%, the appropriate times are the shortest for ABS.

Figure 2   TG curves for PVC/ABS blends of different compositions at 220°C: (1) 100/0, (2) 90/10, (3) 80/20, (4) 50/50, and (5) 0/100.

Figure 4   TG curves for PVC/ABS blends of different compositions at 240°C: (1) 100/0, (2) 90/10, (3) 80/20, (4) 50/50, and (5) 0/100.

Table I Results of Isothermal Thermooxidative Degradation of PVC/ABS Blends

PVC/ABS:	100/0				90/10				80/20				Conversion (α)	50/50			
Temperature (°C)	210	220	230	240	210	220	230	240	210	220	230	240		210	220	230	240
Conversion (α):	Time (t/min)				Time (t/min)				Time (t/min)					Time (t/min)			
0.05	61.45	34.36	19.12	11.20	45.55	27.93	16.92	10.72	49.78	30.07	17.07	11.05	0.050	60.32	33.63	22.32	13.62
0.10	79.26	44.37	24.13	19.83	59.42	36.28	21.17	13.03	65.39	39.24	21.48	13.87	0.075	72.69	44.31	24.70	15.87
0.15	89.87	50.23	27.27	15.43	68.21	41.56	23.92	14.47	76.34	45.34	24.28	15.58	0.100	83.12	50.73	28.60	17.61
0.20	97.33	54.62	29.76	16.72	75.30	45.92	25.98	15.62	84.79	50.22	26.53	16.97	0.125	91.94	55.10	31.00	19.05
0.25	104.00	58.77	32.11	17.86	81.67	49.92	27.96	16.68	94.24	54.97	28.70	18.24					
0.30	110.40	63.59	34.68	19.09	88.45	54.32	30.12	17.82	104.70	60.06	31.08	19.93					

Figure 5 Thermooxidative degradation of the 80/20 PVC/ABS blend. (a) Application of the Flynn method. (b) The kinetic compensation effect.

The fitting of experimental data for PVC/ABS blends degradation to Flynn eq. (5) is shown in Figure 5(a) for the 80/20 blend. The time t needed to achieve a certain degree of conversion α at different temperatures was read off from Table I. The parameters of straight lines ln t vs. $1/T$ (ordinate intercept a, slope b) were determined by the linear regression analysis, and the activation energy for conversions 5–30% was estimated (Table II). It can be seen that the apparent activation energy of degradation for the same PVC/ABS blend slightly increases with the increase of conversion. The variation of activation energy with conversion of degradation can be interpreted in terms of the kinetic compensation effect.[18,24] If parameters a and b were correlated by the equation

$$a = A + B\,b \qquad (6)$$

where A and B are constants; it implies that any increase of the activation energy is accompanied

Table II Activation Energies of Thermooxidative Degradation of PVC/ABS Blends for Different Conversions Determined by the Flynn Method

PVC/ABS	Activation Energy (E/kJ mol^{-1})							
Conversion (α/%)	5	7.5	10	12.5	15	20	25	30
100/0	117.3	—	120.4	—	121.5	121.3	121.3	121.3
90/10	99.7	—	104.8	—	107.2	108.9	110.1	110.1
80/20	104.7	—	108.3	—	111.1	112.6	114.9	114.9
50/50	100.5	107.7	110.9	114.9	—	—	—	—

by an increase of the preexponential factor. The two parameters vary in parallel to keep the rate constant k nearly unchanged. The relationship [eq. (6)] is valid for all compositions of the PVC/ABS blend; in Figure 5(b), the example for the 80/20 blend is shown.

By an electronic differentiation of mass loss curves, the derivative thermogravimetric (DTG) curves, the mass loss rate *vs.* time, were obtained. In Figure 6, an example of DTG curves for the degradation of the 80/20 PVC/ABS blend at temperatures of 210°–240°C are given. The mass loss rate changes from 0 over the maximum down to 0 again. The maximal rate is achieved in the stationary point of DTG curve, which corresponds with the inflection point of TG curve with coordinates (t_m, α_m). For isothermal thermooxidative degradation of PVC/ABS blends of composition 100/0–80/20, this rate is achieved at the average conversion of $\alpha_m = 20$–23% and at 13% for the 50/50 blend, respectively (Table III). The time t_m to achieve the maximal rate decreases 1.6–1.9 times simultaneously with the

increase of degradation temperature for every 10°C in the interval of 210°–240°C.

According to the method of stationary point, the apparent activation energy can be calculated applying the equation

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

The dependence of $\ln t_m$ against $1/T$ represents the straight line of slope E/R. The least-squares linear regression of experimental data for the investigated PVC/ABS blends showed a correlation

Table III Activation Energies of Thermooxidative Degradation of PVC/ABS Blends Determined by the Stationary Point Method

PVC/ABS	T (°C)	t_m (min)	α_m (%)	E (kJ mol^{-1})
100/0	210	103.72	24.87	123.0
	220	55.37	21.01	
	230	31.20	22.99	
	240	17.15	21.86	
90/10	210	78.98	22.90	110.7
	220	47.50	22.01	
	230	26.42	21.27	
	240	16.08	21.80	
80/20	210	85.17	19.81	113.6
	220	51.44	21.32	
	230	26.70	20.38	
	240	16.86	19.65	
50/50	210	93.04	12.78	108.8
	220	57.06	13.36	
	230	32.04	13.64	
	240	19.39	13.27	

Figure 6 DTG curves for the 80/20 PVC/ABS blend at different temperatures: (1) 210°C, (2) 220°C, (3) 230°C, and (4) 240°C.

coefficient r higher than 0.99. The calculated activation energies are given in Table III.

The mechanism of thermooxidative degradation of PVC and also PVC/ABS blends is very complex. The sigmoid shape of kinetic curves (Figs. 1–4) indicates acceleration during the degradation process and therefore the experimental data are fitted to the kinetic equation with the Prout–Tompkins model as $f(\alpha)$ function.

$$\ln\frac{\alpha}{1-\alpha} + C = kt \qquad (8)$$

This presumed model will be valid if eq. (8) is linearized in the coordinate system $\ln(\alpha/1 - \alpha)$ $vs.$ t. The reaction rate constant is calculated from the slope of the straight line. The example of fitting experimental data to the kinetic equation is shown in Figure 7(a) for the 80/20 blend. The calculated values of reaction rate constants are given in Table IV. At a constant degradation temperature, the reaction rate constant increases with the addition of 10% ABS and then decreases with the increasing amount of ABS in blends from 10 to 50%. At a constant blend composition, the rate constant values increase with rising temperature. Furthermore, applying Arrhenius eq. (3), the apparent activation energies and preexponential factors for thermooxidative degradation of PVC/ABS blends in the conversion range of 5–30% were calculated, and values are also given in Table IV. These kinetic parameters also indicate linear dependence (kinetic compensation effect), with correlation factors higher than 0.99 [Fig. 7(b)]. The constant ratio $E/\ln Z$ for all blends without regard to the composition points to the unique mechanism of the degradation process in that range of conversions. When changing the composition of blend, only the rate of degradation changes. The value of rate constant (4.32×10^{-2} min^{-1}) for thermooxidative degradation of PVC at 210°C is comparable, in order of magnitude, with the rate constant (1.06×10^{-2} min^{-1}) for degradation of PVC containing allylic chlorines at 200°C in solution.[6] At the same time, activation energy and preexponential factors are comparable with the Arrhenius parameters calculated for dehydrochlorination of some model compounds that contain labile defect structures.[25]

CONCLUSIONS

The thermooxidative degradation of PVC/ABS blends was thermogravimetrically investigated

Figure 7 Thermooxidative degradation of the 80/20 PVC/ABS blend. (a) Application of the Prout–Tompkins model: (1) 210°C, (2) 220°C, (3) 230°C, and (4) 240°C. (b) Plot generally accepted to establish the existence of the kinetic compensation effect.

by isothermal heating experiments at temperatures of 210° to 240°C.

The sigmoid shape of TG curves depends on the composition of PVC/ABS blends and on degradation temperature. The mass loss at the end of isothermal heating is the highest for PVC, and it decreases with the rise of ABS ratio in the blend. In the range of 5–30% conversions, the appropriate degradation times increase from 90/10, 80/20, PVC, 50/50 to ABS, respectively. In the early stages of degradation, the appropriate times are shortest for ABS.

The maximal mass loss rate is achieved in the stationary point at average conversions of $\sim 20–23\%$ for PVC, 90/10 and 80/20 PVC/ABS blends, and at 13% for the 50/50 blend. The time to achieve the maximal rate decreases 1.6–1.9 times with the increase degradation temperature for every 10°C in 210°–240°C temperature interval.

Table IV   Kinetic Parameters of Thermooxidative Degradation of PVC/ABS Blends Calculated According to the Prout–Tompkins Model

PVC/ABS:	100/0	90/10	80/20	50/50
Temperature (°C):	Reaction Rate Constant (k 10^2/min^{-1})			
210	4.32	4.94	3.86	3.16
220	7.33	8.05	7.07	4.60
230	13.67	16.11	15.18	10.93
240	26.94	29.93	24.18	18.40
E (kJ mol^{-1})	125.8	125.5	129.2	126.6
ln Z (min^{-1})	28.1	28.2	28.9	28.0
E (ln Z)	4.5	4.5	4.5	4.5

The apparent activation energies calculated by applying the stationary point method are approximately equal to the energies calculated after the Flynn equation for the same conversions. These values of energies are 109–123 kJ mol^{-1}.

The sigmoid form of TG curves indicates the autocatalytic nature of the isothermal thermooxidative degradation of PVC/ABS blends. The fitting of experimental data to the Prout–Tompkins equation is satisfactory in the range of conversions of 5–30%. The calculated apparent activation energies of thermooxidative degradation of PVC/ABS blends are 126–129 kJ mol^{-1} and preexponential factors are 1.60×10^{12}–3.56×10^{12} min^{-1}.

The change of activation energy due to the addition of ABS in PVC is not connected with the change of mechanism, because all the blends show the kinetic compensation effect. When changing the composition of the blend, at a certain degradation temperature, only the rate of degradation changes. Increasing temperature from 210°–240°C, the reaction rate constant of degradation is multiplied about six times for PVC, as well as for modified PVC.

REFERENCES

1. McNeil, I. C. in Developments in Polymer Degradation, Vol. 1, Grassie, N., Ed.; Elsevier Applied Science; London: 1977, 171.
2. McNeil, I. C.; Gorman, J. G. Polym Degrad Stabil 1991, 33, 205.
3. Nass, L. I. in Encyclopedia of PVC, Vol. 1, Dekker, M. New York: 1986, 271.
4. Minsker, K. S.; Kolesov, S. V.; Zaikov, G. E. Degradation and Stabilization of Vinyl-Chloride-Based Polymers, Pergamon Press; Oxford: 1988, 72.
5. Starnes, W. H., Jr. Dev Polym Degrad 1981, 3, 135.
6. Ivan, B.; Kelen, T.; Tüdos, F. Macromol Symp 1989, 29, 59.
7. Bacaloglu R.; Fisch, M. Polym Degrad Stabil 1994, 45, 301.
8. McNeill, I. C.; Memetea, L.; Cole, W. J. Polym Degrad Stabil 1995, 49, 181.
9. Kelen, T.; Ivan, B.; Nagy, T.; Turcsanyi, B.; Tüdos, F.; Kennedy, J. P. Polym Bull (Berlin) 1978, 1, 79.
10. Starnes, W. H., Jr.; Edelson, D. Macromolecules 1979, 12, 797.
11. Nagy, T. T.; Turcsanyi, B.; Kelen, T.; Tüdös, F. React Kinet Catal Lett 1978, 8, 7.
12. Starnes, W. H., Jr. Adv Chem Ser 1978, 169, 309.
13. Rabek, J. F.; Ränby, B.; Böstensson; Flodin, P.; J Appl Polym Sci 1979, 24, 2407.
14. Van Hoang T.; Guyot, A. Polym Degrad Stabil 1991, 32, 93.
15. Bacaloglu R.; Fisch, M. Polym Degrad Stabil 1995, 47, 33.
16. Mitchell, J. Applied Polymer Analysis and Characterization, Hanser Publications; Munich: 1987; p. 189.
17. Braun D.; Kommerling, S. Angew Makromol Chem 1992, 195, 205.
18. Hill, D. J.; Dong, L.; Donnel, J. H. O.; G. Georg, G.; P Pomery Polym Degrad Stabil 1993, 40, 143.
19. Antić M.; Colović, N. Kinetika heterogenih kemijskih reakcija Prosveta, Niš 1983, p. 134.
20. Kurian, E. M. J Thermal Anal 1989, 35, 1111.
21. Haines, P. J. Thermal Methods of Analysis, Principles, Application and Problems; Chapman and Hall; London: 1995, 31.
22. Marcilla A.; Beltran, M. Polym Degrad Stabil 1995, 48, 219.
23. Klarić, I.; Roje, U.; Bravar, M. J Appl Polym Sci 1996, 61, 1123.
24. Budrugaec, R Polym Degrad Stabil 1992, 38, 229.
25. Haynie, S. L.; Villacorte, G. M.; Plitz, J. M.; Starnes, W. H., Jr., Polym Prepr 1983, 24, 3.