Note

ON THE THERMAL STABILITY OF SOME MACROMOLECULAR COMPOUNDS

SANDA CIUTACU

Institute for Electrotechnic Research and Design (ICPE), Soseaua Vitan, Bucharest (Romania)

D FĂTU and E SEGAL

Department of Physical Chemistry and Electrochemical Technology, Faculty of Chemical Technology, Polytechnic Institute of Bucharest, Bulevardul Republicii 13 (Romania)

(Received 9 November 1987)

ABSTRACT

The thermal behaviour of bakelite, polyethylene, polyamide, polycarbonate, ABS (acrylonitrile–butadiene–styrene copolymer) and insulation rubber, was investigated using the derivatographic technique The kinetic analysis of the thermal destruction curves suggested to the authors that the thermal stability of macromolecular compounds should be characterized by means of the reciprocal value of the rate constant

INTRODUCTION

In general, the properties of polymeric materials remain unchanged over a given temperature interval Consequently, the knowledge of the thermal behaviour of such materials allows the maximal temperature under which they can be stoked, worked and used to be determined.

EXPERIMENTAL

The thermal curves were recorded using a derivatograph (MOM Budapest type, Paulik–Paulik–Erdey). The powdered samples were prepared by ICPE, diluted with alumina as the inert material, and heated in a static air atmosphere with various heating rates in the range 2.5–10 K min^{-1}

RESULTS AND DISCUSSION

The thermal decomposition of the macromolecular compounds investigated is a multi step, complex process [1] As an example, Fig 1 shows the derivatograms corresponding to the thermal destruction of polycarbonate samples

The thermal stability of a macromolecular compound can be determined by the temperature T_i at which the TG curve begins to exhibit deviations from its base line The value of T_i determined in such a way depends on instrumental (the sensitivity of the balance) and operational factors (heating rate, furnace, gas atmosphere) Another way of defining thermal stability is to indicate the temperature T_i' at which the tangents of the TG curve baseline and in the inflexion point of the TG curve intersect [Fig 1(a)] This allows the initial temperature to be located more exactly, but the value obtained is higher than the true one corresponding to the beginning of the thermal degradation

At a heating rate of 10 K min^{-1} the decomposition curve exhibits two steps The first step (step 1) occurs over the temperature interval 330–510°C, and the second (step 2) over the temperature interval 510–620°C At a heating rate of 5 K min^{-1} the initial temperature at which the weight begins to decrease is $T_i = 325$°C and the first step (1) splits into 1' (325–420°C) and 1'' (420–465°C) as seen in Fig 1(b)

The light products of the degradation (H_2O, CO, CO_2) come from the degradation of heavier fragments which result from the breaking of the polar bond At higher temperatures, those C–C bonds which are characterized by higher bond energies are broken
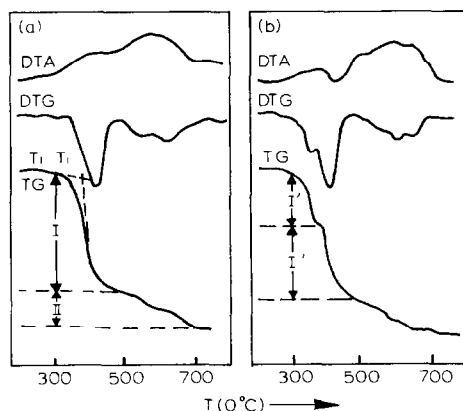

Fig 1 The derivatograms corresponding to the thermal degradation of polycarbonate in static air atmosphere ($m = 65$ mg) (a) $\beta = 10$ K min^{-1}, (b) $\beta = 5$ K min^{-1}

According to the literature [2–4] the decomposition mechanism of poly-carbonates is radical including depolymerizations, random scissions, hydro-lyses and alcoholyses

When using low heating rates the sample is kept at a low temperature for long enough to enable the occurrence of processes characterized by low activation energies At higher temperatures, processes with higher activation energies occur, thus changing the slope of the TG curve

When using higher heating rates, the sample is brought to higher tempera-tures more quickly, thereby determining the occurrence of processes char-acterized by low or high activation energies In such cases, only one process is recorded on the TG curve

These considerations explain the observed increase in the apparent activa-tion energy of the initial decomposition step with increase in heating rate For the degradation, using the methods of Piloyan et al [5], Coats and Redfern [6], and Freeman and Carroll [7] activation energies of 28, 34 and 36 kcal mol^{-1} are obtained for heating rates of 2 5, 5, and 10 K min^{-1}, respectively

As these data show, the comparison of macromolecular compounds in terms of thermal behaviour obviously needs thermal curves to be recorded under identical conditions Besides the temperature T_i, we need to evaluate the thermal degradation rate at this temperature The determination of the slope of the TG curve at T_i is rather difficult, which is why we have recommended the use of the initial portion of the TG curve for evaluating the pre-exponential factor, A, the activation energy, E, and the rate con-stant, k In this work the reciprocal values $1/k(T_i)$ of the rate constant at temperature T_i was used as an index, I_k, of kinetic thermal stability The index I_k is defined as

$$I_k = \frac{1}{k(T_i)} = \frac{1}{A\, e^{-E/RT_i}} \tag{1}$$

From the rate equation

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \tag{2}$$

where α is the conversion (decomposition) degree and n is the reaction order and relationship (1) it turns out that

$$I_k = \frac{dt}{d\alpha}(1-\alpha)^n \tag{3}$$

Under the chosen working conditions, for $T \to T_i$, $\alpha \ll 1$ and so eqn (3) takes the approximate simple form

$$I_k \approx \frac{\Delta t}{\Delta \alpha} \tag{4}$$

TABLE 1

The kinetic parameters of the decomposition steps

Material	Step	E (kcal mol^{-1})	n	A (s^{-1})	Temperature interval (°C)	$k(T_i)$ (s^{-1})	I_k	$\log I_k$	r	Thermal effect
1 Bakelite	1	24 6	1	$4\,5\times10^{6}$	160–380	$2\,1\times10^{-6}$	$5\,5\times10^{5}$	5 7	0 999	exo
	2	15 6	1	38	380–610	$2\,4\times10^{-4}$	$4\,1\times10^{3}$	3 6	0 990	exo
2 Polyethylene	1	15 9	1	$1\,8\times10^{3}$	230–380	$2\,5\times10^{-4}$	$4\,0\times10^{3}$	3 6	0 992	exo
	2	29 1	1	$2\,6\times10^{6}$	380–550	$5\,5\times10^{-4}$	$1\,8\times10^{3}$	3 2	0 994	exo
3 Insulation rubber	1	22 4	1	$6\,8\times10^{5}$	230–380	$1\,5\times10^{-4}$	$6\,9\times10^{3}$	3 8	0 990	exo
	2	36 6	1	$5\,7\times10^{8}$	380–470	$3\,8\times10^{-4}$	$2\,6\times10^{3}$	3 4	0 994	exo
4 ABS	1	20 0	1	$2\,5\times10^{3}$	250–470	$1\,3\times10^{-5}$	$7\,9\times10^{4}$	4 9	0 988	exo
	2	40 6	0	$1\,0\times10^{8}$	470–630	$1\,4\times10^{-4}$	$7\,2\times10^{3}$	3 9	0 950	exo
5 Polyamide (Relon)	1	26 4	1	$1\,9\times10^{5}$	290–520	$1\,2\times10^{-5}$	$8\,2\times10^{4}$	4 1	0 985	endo
	2	–	–	–	520–610	–	–	–	–	exo
6 Polycarbonate	1	36 2	1	$2\,8\times10^{8}$	330–510	$4\,6\times10^{-5}$	$3\,8\times10^{4}$	4 6	0 992	exo
	2	21 6	1	$3\,8\times10^{8}$	510–620	$3\,9\times10^{-3}$	$2\,5\times10^{2}$	2 5	0 969	exo

As for $\Delta\alpha = 1$, $I_k = \Delta t$, the index of kinetic thermostability represents the virtual time taken for total degradation if the reaction occurs at temperature T_i with the rate constant $k(T_i)$

In order to characterize the thermal behaviour of macromolecular compounds it is convenient to use a heating rate of 10 K min^{-1} as, under such conditions, the analysis is not too lengthy and the TG curves exhibit, in most cases, two main decomposition steps Obviously, for more refined kinetic studies lower heating rates must be used [8]

Table 1 lists the nonisothermal kinetic parameters of the decomposition steps, the temperature interval of which they occur, the rate constants, the correlation coefficient (r) of the experimental data with the linear form of the kinetic equation, and the sign of the thermal effects (exo. endo) Owing to the high values of I_k it is necessary to use logarithmic values log I_k

Inspection of Table 1 shows that the thermal degradation of the macromolecular compounds investigated occurs in two steps The low-temperature step (step 1) is characterized by lower activation energies which correspond to the breaking of the weaker bonds with release of light gas molecules The second step (step 2) recorded at higher temperatures, corresponds to the breaking of the stronger bonds from the reticulated product of step 1, being characterized by higher values of the activation energy There are two notable exceptions to this, for which $E_2 < E_1$, these are the cases of bakelite and the copolymer ABS This inversion is probably due to some peroxidic compounds generated in the first step which act as initiators for the oxidation process in step 2

The values $n = 1$ in Table 1 show that the degradation rate depends linearly on the unreacted polymer fraction The value $n = 0$ for the last decomposition step of the copolymer ABS probably indicates a mass transfer control of the process

From the temperatures T_i in Table 1, it can be seen that bakelite exhibits the lowest thermal stability ($T_i = 160\,^\circ$C) and polycarbonate the highest ($T_i = 330\,^\circ$C) On the other hand, for polycarbonate log $I_k = 4\,6$ and for bakelite log $I_k = 5\,7$ Thus the decomposition of polycarbonate begins at a higher temperature but, once initiated, the reaction occurs at a higher rate than in the case of bakelite

Obviously, of two materials with the same T_i, the better one in terms of its thermal behaviour is the one with the highest I_k An example of such a pair of materials is polyethylene and insulation rubber The latter material is characterized by a higher value of I_k for the first step (log $I_k = 3\,8$) compared with polyethylene (log $I_k = 3\,6$)

The lower thermal stability of bakelite and polyamide is due to the presence of polar bonds in these materials and to water traces from the sample The release of water at low temperatures (up to $160\,^\circ$C) produces a relatively disordered structure which exhibits a lower thermal stability

The TG curves corresponding to step 2 of the thermal degradation of

polyamide are not kinetically workable due to their irregularities

The thermal degradation of insulation rubber is preceded by an ex-othermic phase change (crystallization) at 227°C, the thermal effect as calculated from the peak area is $Q = 125$ cal g^{-1} The energy evolved during crystallization is used to initiate the thermal degradation

The break up of macromoleculees in air is accompanied by oxidation processes and, therefore, the overall thermal effect is exothermic in most cases

CONCLUSIONS

In this work the thermal degradation of some macromolecular compounds used in electronics was studied, and the following conclusions were drawn

(1) In addition to the temperature, T_i, at which the thermal degradation begins, the authors suggest that a material should be characterized by the index of kinetic thermal stability, defined as the reciprocal value of the rate constant for the initial step

(2) The stability of macromolecular compounds depends on various factors, such as the polarity of the bonds, the degree of polymerization or polycondensation, the degree of crystallinity, the presence of water, and phase changes which can initiate thermal degradation

REFERENCES

1 C Vasile, E M Călugăru, A Stoleriu, M Sabliovski and E Mihai, The Thermal Behaviour of Polymérs (in Rumanian), Publishing House of the Academy of R S Romania, Bucharest, 1982
2 S H Marrill and S E Petrie, J Polym Sci, A-1-3 (1965) 2189
3 R L Bartoseiwicz and C Both, Eur Polym J, 10 (1974) 791
4 B M Kovarskaia, Vîsocomol Soedn, 5 (1963) 649
5 F O Piloyan, I O Ryabchikov and O S Novikova, Nature, 212 (1966) 1299
6 A W Coats and J P Redfern, Nature, 201 (1964) 68
7 E S Freeman and B Carroll, J Phys Chem, 62 (1958) 394
8 E Segal and D Fătu, Introduction to Nonisothermal Kinetics (in Romanian), Publishing House of the Academy of R S Romania, Bucharest, 1983