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ON THE THERMAL DECOMPOSITION OF THE COPOLYMER ABS AND OF NYLON POLYAMIDE

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ABSTRACT

The authors present some results concerning the thermal stability of the acrylonitrile butadiene styrenic (ABS) copolymer and of the nylon polyamide using thermogravimetric and thermal differential analysis techniques. The non-isothermal kinetic parameters values are sensitive to the previous thermal treatment as well as to the irradiation time of the samples. Two criteria of thermal stability have been proposed. Using X-ray diffraction, the graphitization of the carbon decomposition residue has been demonstrated. The diffractometric data enabled the evaluation of the mean crystallite sizes as well as the degree of crystallinity of the original samples.

INTRODUCTION

In a previous note [1], the thermal stabilities of some macromolecular compounds used in the electrotechnical industry were investigated. A kinetic index of thermal stability defined through the reciprocal value of the kinetic constant of decomposition was introduced in addition to the initial decomposition temperature. In order to assess the influence of the thermal treatments as well as of the irradiation dose on the thermal decomposition of ABS and nylon polyamide, the authors use the kinetic index as well as a corrected form of the temperature index.

EXPERIMENTAL

Powdered samples of 0.05 g were used. The thermal decomposition curves (TG, T, DTG and DTA) were recorded using a Paulik–Paulik–Erdey Q

1500 derivatograph in static air atmosphere with heating rates from 2.5 K min^{-1} to 10 K min^{-1}. A Philips PW-1140 diffractometer with chromium $K\alpha$ radiation was used to obtain the X-ray diffractograms of the investigated samples.

RESULTS AND DISCUSSIONS

Firstly, the influence of the heating rate on T_i (the initial temperature corresponding to the change in sample weight), T_m (the temperature corresponding to the maximum decomposition rate) and T_f (the final temperature of decomposition) was investigated. All these temperatures changed linearly with the heating rate for 2.5 K $\text{min}^{-1} < \beta < 10$ K min^{-1}. The values of the slope are respectively: $\Delta T_i/\Delta\beta = 1.6$ min, $\Delta T_m/\Delta\beta = 2.4$ min and $\Delta T_f/\Delta\beta = 4$ min, thus for an increase in the heating rate of 10 K min^{-1}, T_i, T_m and T_f change by 16, 24 and 40 K respectively. The temperature T_i is less sensitive to change in the heating rate. This is why T_i is used to characterize the thermal stability of materials. As the thermal stability depends on the temperature interval $T_f - T_i$ in which the thermal decomposition also occurs, the following corrected temperature index, T_c, is suggested

$$T_c = T_i + (T_f - T_i)\frac{A_i}{A_t} \qquad (1)$$

where A_i and A_t are the areas delineated by the ABCDA and ABCEA contours in Fig. 1.

The increase in the interval $T_f - T_i$ with the heating rate is partially attenuated by the decrease of the ratio A_i/A_t with the same conditions. This is seen in the change of the T_c values corresponding to the decomposition of ABS with various heating rates.

T_c (°C)	324	328	329
β (K min^{-1})	2.5	5	10

The T_c parameters can be used even when the sample contains non-volatile ingredients because by definition the area ECFGE, which is proportional to the weight of the solid residue, was not considered. As $A_i/A_t < 1$,

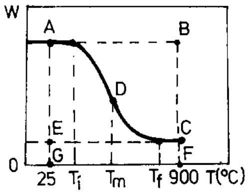

Fig. 1. The characteristic temperatures of TG curves and the areas necessary to evaluate the temperature index: *W*, the weight of the sample; *T*, temperature.

TABLE 1

Thermal stability criteria and non-isothermal kinetic parameters for ABS

β (K min^{-1})	T_i (°C)	T_m (°C)	T_f (°C)	Method	n	E (kcal mol^{-1})	$A \times 10^{-3}$ [a] (s^{-1})	r [b]	$\frac{1}{k} \times 10^{-4}$ (s)
Step I									
2,5	250	340	400	C–R	0	20.1	2.5	0.991	7.9
				C–R$_m$	0.1	20.2	2.8	0.989	
				F–W	0	20.1	2.6	0.991	
5	260	350	428	C–R	0	23.3	0.98×10^2	0.997	2.2
				C–R$_m$	0	23.4	1.2×10^2	0.998	
				F–W	0	24.5	4.0×10^2	0.998	
10	262	358	445	C–R	0	24.3	2.0×10^2	0.988	3.0
				C–R$_m$	0	25.1	4.2×10^2	0.989	
				F–W	0	25.6	8.7×10^2	0.990	
Step II									
10	500	590	683	C–R	2	43.0	4.9×10^5	0.996	1.6
				C–R$_m$	2	43.3	9.8×10^5	0.995	
				F–W	2	43.0	9.2×10^5	0.997	

[a] As in the kinetic equations the variable used was the degree of conversion; the pre-exponential coefficient and the kinetic constant are both expressed in s^{-1}.

[b] r is the correlation coefficient of the linear plot characteristic of the method applied.

$T_i < T_c < T_f$. In Fig. 1, the temperature interval 25–900 °C proposed by Doyle [2] was considered because all organic polymers undergo thermal decomposition within it.

The thermal degradation of the copolymer ABS is preceded by melting. Its endothermic effect is located on the DTA curve in the temperature interval 70–100 °C. At $\beta = 2.5$ K min^{-1}, two decomposition steps of the copolymer ABS can be seen. The first, which occurs between 260 and 450 °C, corresponds to the loss of the light (volatile) compounds. A 27.5% weight change is recorded in this first step. The second step (5–6% weight change) corresponds to the breaking of the stronger bonds from the reticulated product of the first step.

The non-isothermal kinetic parameters were evaluated by the Coats–Redfern [3], the modified Coats–Redfern [47] and the Flynn–Wall [5] methods. The data were handled using a versatile program written in BASIC [6].

In Table 1, the characteristic temperatures, the non-isothermal kinetic parameters (n is the reaction order, A is the pre-exponential factor and E is the activation energy) and the kinetic stability index, defined as the reciprocal value of the kinetic constant at $T = T_i$, are listed for ABS.

A zero value for the reaction order for step I can be assigned to the diffusion of the volatile product through the decomposed solid product.

As can be seen from Table 1, the second step seems to be chemically controlled, the decomposition rate being directly proportional to the $(1-\alpha)^2$ where α is the degree of conversion. A slightly increasing trend in activation energy with an increase in heating rate can be noticed for step I. The thermal degradation of polymers is a complex process with many steps having different activation energies. At lower heating rates, the sample is kept for a long time at the lower temperatures at which the reactions with lower activation energy occur. At higher heating rates, the samples rapidly reach the higher temperatures at which the reactions characterized by higher activation energy occur, those characterized by lower activation energy not yet being completed. Thus at higher heating rates, partial overlapping and an increase in the apparent activation energy can be noticed.

For the same heating rate (10 K min^{-1}), the activation energy of step II is higher than the activation energy of step I because step II corresponds to the decomposition of a product with a high degree of reticulation. Nevertheless the kinetic stability $1/k$ for step II is lower than for step I. Although step II needs a higher activation energy, it occurs with a higher rate than the first step.

The decomposition of nylon polyamide is also preceded by melting. This occurs in the temperature interval 70–80 °C. In the interval 270–470 °C, a first decomposition step is recorded corresponding to the breaking of the C–H, C–N and C–C bonds. Thus, double bonds are formed and the macromolecular chain undergoes changes of the form

$$\mathrm{R{-}NH{-}CO{-}(CH_2)_4{-}CO{-}NH{-}(CH_2)_6{-}NH{-}CO{-}R'}$$

$$\rightarrow \mathrm{R{-}NH{-}CO{-}(CH_2)_4{-}CO{-}NH_2} + \mathrm{CH_2{=}CH{-}(CH_2)_4{-}NH{-}CO{-}R'}$$

This first step, occurs with a 66.8% weight change.

The second step, which occurs in the interval 450–580 °C, consists of cyclization, homolytic detachment of the resultant products and oxidative degradation with generation of carbon monoxide, carbon dioxide, nitriles, ammonia and hydrocarbons.

The results concerning the thermal stability for two samples are listed in Table 2.

The values of T_m are not included as the TG curves did not exhibit a clear inflexion point.

For $\beta = 10$ K min^{-1}, the kinetic stability in the first step for both ABS and nylon polyamide is practicaly the same (3×10^4 s and $2{,}8 \times 10^4$ s for sample 2). In step II, a clear difference between the kinetic stabilities can be noticed, the kinetic stability of the copolymer ABS being two orders of magnitude higher than that of nylon polyamide.

Nylon polyamide sample 1 was submitted to a thermal treatment at 140 °C. Figure 2 shows the changes in activation energy for step I (curve a) and step II (curve b) with the time of thermal treatment.

TABLE 2

Thermal stability criteria and non-isothermal kinetic parameters for two samples of nylon polyamide ($\beta = 10$ K min^{-1})

Sample	T_i	T_f	Method	n	E (Kcal mol^{-1})	A (s^{-1})	r	$1/k$ (s)
Step I								
1	290	458	C–R	1.5	29.5	1.4×10^7	0.992	1.5×10^4
			C–R_m	1.7	30.3	3.1×10^7	0.996	
			F–W	1.5	30.0	2.2×10^7	0.993	
2	275	450	C–R	1.6	33.1	4.1×10^8	0.991	2.8×10^4
			C–R_m	1.4	31.1	8.7×10^7	0.992	
			F–W	1.4	32.4	2.6×10^8	0.992	
Step II								
1	458	542	C–R	0.7	58.5	2.7×10^{14}	0.998	8.7×10^2
			C–R_m	0.7	60.0	7.7×10^{14}	0.998	
			F–W	0.7	58.5	2.7×10^{14}	0.998	
2	450	560	C–R	1.2	62.4	8.1×10^{15}	0.991	6.6×10^2
			C–R_m	1.1	61.6	4.4×10^{15}	0.994	
			F–W	1.2	62.2	7.2×10^{15}	0.995	

The decrease in activation energy following 125 hours of thermal treatment in air can been explained by the production of perioxides which initiate the oxidative degradation of the chain. This long treatment stabilizes the polymer through partial reticulation. Correspondingly, there is an increase in the apparent activation energy.

The irradiation of nylon polyamide sample 2 with γ radiation at a dose rate of 0.12 Mrad h^{-1} also induces changes in the activation energy of both steps, as shown in Fig. 3. A decrease in the activation energy of step I with irradiation time (curve a) can be seen. Thus, the irradiation kinetically favours the first decomposition step by generation of the initial reaction

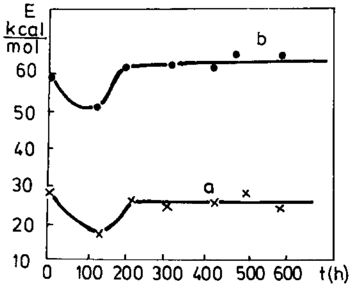

Fig. 2. Activation energy–time curves: a, step I; b, step II.

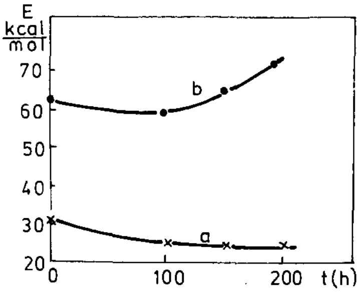

Fig. 3. The change in activation energy with irradiation time at a dose rate of 0.12 Mrad h^{-1} for nylon polyamide: a, step I; b, step II.

centres. As far as step II is concerned, a slight decrease in the activation energy is followed by an increase with time (curve b). This is probably due to the reticulation induced by the long irradiation time.

The parameter T_c is also sensitive to irradiation: for 500 h of treatment at 140 ° C, it decreases from 434 ° C (for the untreated sample) to 421° C.

Samples irradiated with a dose rate of 0.12 M rad h^{-1} for 200 h are characterized by a T_c of 455 ° C, while for the unirradiated samples, T_c = 438 ° C. This increase in the temperature index could also be a result of the reticulation process.

The decrease in activation energy due to thermal treatment is not always accompanied by an increase in the decomposition rate as there is a simultaneous decrease in the pre-exponential factor (compensation effect).

The diffractogram of the ABS sample suggests a 10% degree of crystallinity. From the same diffractogram, using Scherrer's formula, the mean size of the crystallites can be estimated as 350 Å.

For the nylon polyamide, there was a 25% degree of crystallinity and a mean crystallite size of 250 Å.

The carbonized residue obtained by heating the samples in air exhibits a crystalline structure similar to graphite. A slight difference was observed in the d_{002} values which are higher (3.42 Å) than those of graphite (3.38 Å). The diffraction lines corresponding to the other planes exhibit low intensities, showing that the graphitization is not complete. Similar behaviour has been observed in the case of carbon fibre crystallites [7].

The degree of graphitization is higher in the residue of nylon polyamide than in the ABS residue as the structure of the copolymer contains the more stable benzene ring. Thus, nylon polyamide is more easily changed to carbon fibres.

The mean crystallite size of the graphite crystallites obtained by ABS degradation is 2,600 Å. For the graphite crystallites from nylon polyamide, the mean crystallite size is 2,700 Å.

CONCLUSIONS

It has been demonstrated that the heating rate influences the characteristic temperatures corresponding to the thermal degradation of ABS and a corrected thermal stability index T_c, less sensitive to the heating rate, has been proposed.

The values of the kinetic parameters characteristic for thermal degradation are sensitive to the heating rate, thermal treatment and irradiation time.

The carbon residue from the thermal degradation process undergoes graphitization, more readily for nylon polyamide than ABS, which can therefore be used to generate carbon fibres.

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