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THERMAL ANALYSIS STUDY OF THE DYNAMIC DECOMPOSITION OF POLYMERS DURING RAPID HEATING; LIMITING TEMPERATURES OF THERMOLYSIS

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A new technique is presented for study of the thermal behaviour of materials. Experimental and theoretical bases are established for the limiting temperatures of thermal decomposition of different polymers.

A gravimetric technique is presented that differs from traditional common methods of thermal analysis in that the weighing procedure is separated from the heating procedure. The experimental equipment is characterized by the small thermal inertia of the heater, which allows rapid heating of the samples up to the given temperature. Thus, it is possible to measure the mass loss of the sample even 1–2 s after the onset of heating, when the sample has attained the temperature.

Experimental

The experiment is carried out in four steps.

(1) Preparation of the samples

The samples are weighed in 0.01 m thick, 15 × 15 mm metal foil enveloped to preserve them from the external medium. Such packaging makes it possible to test powders and films. Envelopes prepared in this way are placed between the pages of the register.

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(2) Switching on the heater

The electrical heater consists of 2 metal rods. The rods can move toward one another when heated and press the envelope. For prolonged experiments, the heater is supplied with an automatic temperature regulator.

(3) Heating run

The enveloped sample is taken out from the register and pressed between the end faces of metal rods preheated to the desired temperature. The temperature is kept constant throughout the test. The sample is kept in position during the predetermined exposure time, then taken out in a gas flow and put back into the register.

(4) Determination of results

The samples are taken out of the register and weighed again. The mass loss is calculated.

Another method of rapid heating is described in Ref. 1.

Figures 1–4 present some results obtained with several polymers.

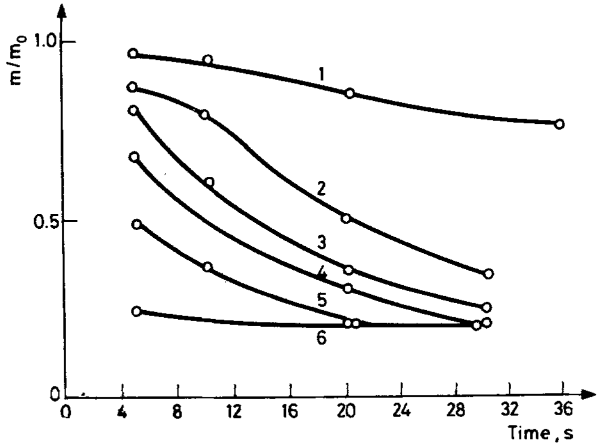

Fig. 1 Isothermal thermogravimetric curves of polyvinyl chloride. T = (1) 310°, (2) 320°, (3) 350°, (4) 370°, (5) 400°, (6) 450°

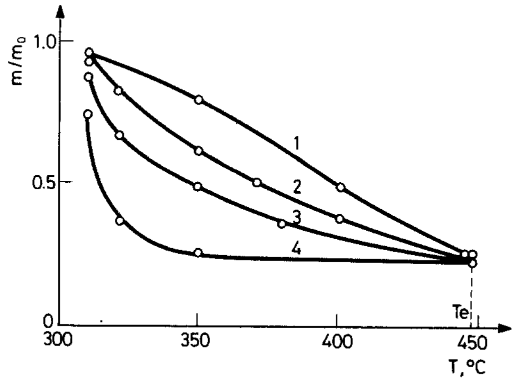

Fig. 2 Isochronous thermogravimevric curves of polyvinyl chloride. t = (1) 5 s, (2) 10 s, (3) 15 s, (4) 30 s

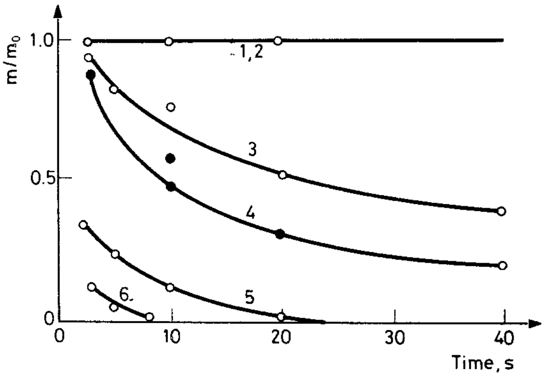

Fig. 3 Isothermal thermogravimetric curves of cellulose nitrate (photo film), T = (1, 2) 355° and 380°, (3) 400°, (4) 430°, (5) 460°, (6) 480°.

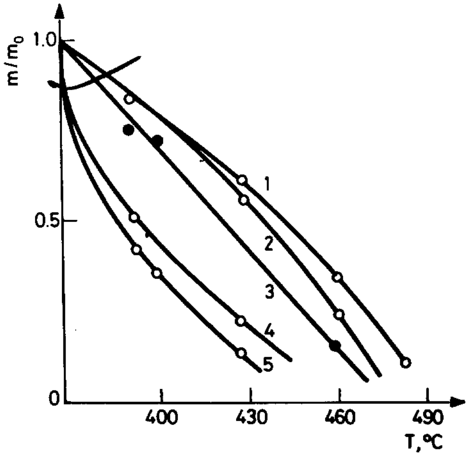

Fig. 4 Isochronous thermogravimetric curves of cellulose nitrate (photo film). t = (1) 2 s, (2) 5 s, (3) 10 s, (4) 20 s, (5) 40 s

Theoretical analysis of the results

In the construction of the mathematical model of the thermal decomposition of polymers, it is necessary to take into account that the rate constants of decomposition of associated and non-associated monomeric units are different. The intermolecular association of polymeric molecules is achieved through the formation of bonds between monomeric units. The rate of establishment of thermodynamic equilibrium in the formation of intermolecular bonds is higher than the rate of chemical decomposition. The concrete mechanisms of chemical decomposition for associated and non-associated monomeric units are the same, although the rate constant of the latter, k_n, is the higher: $k_n > k_a$.

Slow and rapid heating up to a given temperature involves the decomposition of different polymeric structures, but mainly the decomposition of non-associated units occurs ($k_n > k_a$). The block size from which decomposition of the middle of the block begins is determined by the equation $\Delta G = 0$, where ΔG is defined as the difference between the free energies of formation of the two parts of the decomposed block and the initial non-associated block.

With increasing temperature, the character of the process can change from an end-group reaction to a middle-group reaction. With increase of the non-associated block size, its decomposition rate constant will increase. For a definite block length two or more types of decomposition are possible. At a certain temperature, the non-associated blocks ("gaseous polymer") will collapse. This is the reason for the existence of a limiting (or ultimate) temperature, T_1. The intermolecular interaction energy estimated for polymethylmethacrylate and polystyrene is $D = RT_1 \sim 1620$ cal/mole, which coincides with the literature value [2]. Hence, $T_1 = D/R \sim 800$ K.

Kinetic equations

The thermal decomposition processes of different linear polymers (middle-group reaction) are described by the following kinetic equations.

The rate of change in the initial molecule number, n_N, is

$$-\frac{\mathrm{d}n_N}{\mathrm{d}t} = k_a N n_N p_a + k_n N n_N p_n \qquad (1)$$

Where N is the number of monomeric units of macromolecules, and p_a and p_n are the relative proportions of associated and non-associated units, respectively.

The equilibrium equation of association (van't Hoff equation) is

$$p_a/p_n = A \exp(-\Delta H/RT) \qquad (2)$$

Where ΔH is the equilibrium enthalpy for the formation of intermolecular bonds.

The rate of change in the current number, n_i, of fragments with length is

$$-\frac{\mathrm{d}n_i}{\mathrm{d}t} = -2k_a p_a \sum_{i+1}^{N} n_j - 2k_n p_n \sum_{i+1}^{N} n_j + k_a i n_i p_a + \\ + k_n i n_i p_n + k_{ev} n_i \tag{3}$$

where the rate of evaporation is

$$k_{ev} = \frac{a(p_i^s - p_i)}{\sqrt{2\pi RT/M_i}} \tag{4}$$

Here, a is the accommodation coefficient.

The equilibrium partial pressure of component i is

$$p_i^s = A_1 \exp\left(-\Delta H_{ev} M_i/RT\right) \tag{5}$$

Here, $\Delta H_{ev} = \Delta H^\circ(1 - T/T_i)^{0.38}$ (Watson–Gambill equation).

The solution of the equation at $T = \text{const.}$ for a fragment n_i is

$$n_i = n_0 \sum_{j=1}^{1+2} \alpha_{ji} C_j \exp(\lambda_j t) \tag{6}$$

Where

$$C_j = c_j/n_0,\ \alpha_{ij} = \frac{2}{\lambda_i - \lambda_j} \sum_{s=j+1}^{i} \alpha_{is},\ n_0 = n_N(0),$$

$$C_j = N - \sum_{s=j+1}^{N} c_s \alpha_{sj},\ \lambda_i$$

are the roots of the characteristic equation, and C_j, α_{ij} and c_s are coefficients.

The given equations permit a description of the processes of polymer thermal decomposition up to the limiting (ultimate) temperature.

Conclusion

The rapid heating technique in thermal analysis allows increase of the temperature of the samples and entry into a previously insufficiently studied sphere of the thermal decomposition of polymers. The existence of the limiting (ultimate) temperatures of polymers is associated with the cessation of intermolecular interactions and the subsequent explosion-like decomposition of the labile macromolecules of the thermodynamically instable "polymeric gas".

References

1 O. F. Shlensky, A. A. Matyukhin and E. F. Vaynshteyn, J. Thermal Anal., 31 (1986) 107.

2 O. F. Shlensky, A. G. Shashkov and L. N. Aksenov, Thermophysics of decomposing materials (in Russian), Energiya, Moscow, 1985.

Zusammenfassung — Es wird ein neues Verfahren zur Untersuchung des thermischen Verhaltens von Stoffen vorgestellt. Es wurden experimentelle und theoretische Grundlagen zur Bestimmung von thermischen Zersetzungstemperaturen verschiedener Polymere erstellt.

Резюме — Для изучения термического разложения полимеров предложена методика контактного нагрева образцов. Представлены экспериментальные и теоретические доказательства ускорения термолиза линейных полимеров вблизи предельной температуры.