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LIMITING TEMPERATURES OF THE THERMAL DECOMPOSITION OF POLYMERS AND THEIR DETERMINATION BY RAPID THERMAL ANALYSIS

O. F. Shlensky, A. A. Matyukhin and *E. F. Vaynshteyn**

MENDELEEV INSTITUTE OF CHEMICAL TECHNOLOGY, MOSCOW, AND
*INSTITUTE OF CHEMICAL PHYSICS OF THE ACADEMY OF SCIENCES
OF THE U.S.S.R., MOSCOW, U.S.S.R.

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Experimental and theoretical foundations are established for the limiting temperatures of thermal decomposition of thermoplastic polymers. The correlation between the limiting temperatures and the intermolecular interactions of the polymers investigated is reported.

Experimental study of the kinetics of thermal decomposition.

It was found earlier by TG and DTA methods that when the heating rate is increased up to some degrees per second, the thermoanalytical curves of polymers, shifted into the high-temperature region, assume extreme positions [1]. The limiting temperatures T_f above which the initial materials no longer exist independently of the heating rate were determined. In this paper it will be demonstrated that above finding is valid for even higher heating rates too exceeding 10^3 deg/s.

Experimental

To raise the heating rate, contact heaters made of high thermal conductivity metal were applied. The experiments were carried out in the following manner. The metal plate was heated to a constant temperature controlled by a steady-state potentiometer with an accuracy of ±6°. The substance to be studied was applied onto the surface of the plate as a thin layer of its melt. At film thicknesses of around 5 μm, the sample is clearly observable in reflected light. The heating time t_n for a melt film of this thickness to attain the temperature T_2 of the plate did not exceed 0.01 s, corresponding at $T_2 = 500°$ (793 K) to an average heating rate of $b = T/t_n = 5 \cdot 10^4$ deg/s.

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At high heating rates, significant temperature gradients and drops will arise in the sample, and therefore the accuracy is of decisive importance in these experiments. The error calculations of temperature measurements in the sample and in the heater will be discussed in a separate section at the end of this paper. The method is described in more detail in [2].

After application of the film onto the heater plate, thermal decomposition and evaporation of the polymer proceed at constant temperature during the interval t. Its value was determined both via the disappearance of the polymer film from the surface of the plate and via the record of the electromotive force of the differential thermocouple, one junction of which was attached to the surface of the plate in the zone where the melt film was applied. The experiments were carried out in inert gas or in the gaseous decomposition products of the polymer. Since the life time of the film was very short at high temperatures, a movie camera was used to determine the time interval t.

Results

Figure 1 presents the results obtained with several polymers, in the form $\log W = \log 1/t$ *versus* the reciprocal temperature $1/T$. It may be seen from the Figure that the slope of the tangents to the curves $\tan \alpha = \dfrac{\mathrm{d}\log(1/t)}{\mathrm{d}(1/T)}$ is not constant:

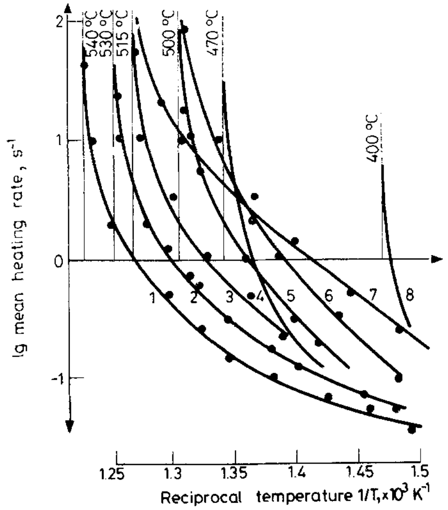

Fig. 1 Effect of temperature on the time of thermal decomposition of various polymers
1 – polystyrene (impact-resistant), 2 – polystyrene (block polymer), 3 – high-density polyethylene, 4 – poly(vinyl chloride), 5 – poly(ethylene terephthalate), 6 – low-density polyethylene, 7 – poly(methyl methacrylate), 8 – colemanite (mineral with a polymeric structure)

it increases with temperature, indicating that the rate of the process increases more rapidly with temperature than should follow the Arrhenius equation with parameters determined at lower temperatures. The asymptotic trend of the curves to definite limiting temperatures T_l is also observable in the Figure; at $T = T_l$, $\tan \alpha \to \infty$. The limiting temperatures T of the polymers studied correspond to the limiting values T_f obtained with the TG and DTA methods [2].

Theoretical analysis of the results

The significantly lower "life time" of the polymer film at temperatures close to the limiting temperature as compared to the value calculated from the Arrhenius equation cannot be explained solely in terms of the increased evaporation rate of the fragments of the macromolecules, whose size increases with temperature increase. In fact, the phenomenon also exists with end-group reactions (depolymerization of polystyrene). In such reactions, monomers and small fragments will evaporate above all, while their share in the overall mass of the decomposition products is insignificant. However, the phenomenon can be explained from the aspect of the thermodynamics and kinetics of the process, if the important stage of the reaction common with all polymers studied, namely the change of intermolecular interaction with temperature and the decrease of the "cage" effect, is examined [1]. Let us consider thermodynamic relationships taking into account the structure of polymer macromolecules.

Since the rate of establishment of thermodynamic equilibrium in the formation of intermolecular bonds is higher than the rate of chemical decomposition reactions, in the analysis of the overall process at T_l it is necessary to take into account equilibrium amounts and proportions of associated and non-associated monomeric units. Let us assume that the free energy components contributed are all additive.

The free energy of formation of a film consisting of isolated units, i.e. without intermolecular bonds, G_{is}, is equal to

$$G_{is} = G_{ch} + G_b \tag{1}$$

where G_{ch} is the free energy of straight chain formation ("chemical" component), and G_b is the free energy of chain bending.

Strictly speaking, one should also consider the existence of chain conformation, the free energy of the conformers and the number of their permutations in the chain. However, since the transition energy between the conformers is low at high temperatures, i.e. the chains are capable of free rotation, for simplicity's sake these components of free energy are left out of consideration. The free energy of formation of associated chains bound by intermolecular interactions is

$$G_{ass} = G_{ch} + \bar{n}G_{int} - \bar{R}T \ln W + \sum_j G_{bj} \tag{2}$$

where $\bar{n}$ is the mean number of induced intermolecular bonds, G_{int} is the free energy of formation of intermolecular bonds, and W is the number of ways to establish n bonds in a molecule containing N monomeric units, assuming that all these bonds are equivalent. The term G_{bj} in Eq. (2) is the free energy of bending in a chain portion between two neighbouring intermolecular bonds with j non-associated monomeric units between them; the value of j varies between one and the highest value possible for the polymer in question.

The number of intermolecular bonds n varies between the minimum value defined by the condition $\Delta G = G_{ass} - G_{is} = 0$ and the maximum possible value n_{max} determined by the structure of the chain. The value $\bar{n}$ is the arithmetical mean of the number of bonds: $\sum nN_n = \bar{n}N$, where N_n is the concentration of molecules containing $\bar{n}$ bonds. The minimum number of intermolecular bonds according to the condition $\Delta G = 0$ is then

$$n_{min} = (G_b + \bar{R}T \ln W - \sum_j G_{bj})/G_{int} \tag{3}$$

It is known that both for association and for adsorption on a surface, a minimum number of linkages is required to keep the chain in the associate or on the surface [3, 4]. With increasing temperature, G_{int} decreases, tending towards zero, while G_b increases, tending towards the limit defined by chain length and structure. As a result of the decreasing G_{int} and increasing G_b with increasing temperature, n_{min} will increase and will attain, at a definite temperature, the maximum value possible for the polymer in question $(n_{min})_{max}$. Consequently, the mean number of induced intermolecular bonds relative to the concentration of associated molecules will increase with increasing temperature, though the ratio of associated and non-associated monomeric units will decrease ($\bar{n}$ decreases with increasing temperature). If the maximum number of bonds between the given monomeric units and neighbouring molecules is q $(q \geqslant 1)$, the maximum number of bonds between the chain and other molecules cannot exceed Nq, where q is an integer.

In analyzing the process, one must take into account the number of intermolecular bonds, calculated as the mean value, the number of associated units and the number of bonds between monomeric units $(q \neq 1)$. At $T = T_l$, the number of bonds in the associated molecules is equal to the maximum possible number, i.e. $\sum G_{bj} = 0$; since the molecules are stretched, and $\bar{R}T \ln W = 0$, then $nG_{int} = \bar{R}T$.

When the formation of intermolecular bonds differing in energy can take place, the limiting temperatures are determined by the maximum possible energy. It should be noted that at $T < T_l$ the number of intermolecular bonds in the bulk is higher than on the surface, and therefore the decomposition rate of the chains on the surface is higher than in the bulk of the polymer.

At $T = T_l$, the free energies of formation are equal for associated and non-associated molecules; the free rotation of chain units in non-associated macromolecules is attained, leading to decomposition by reason of, for example, inertia at $RT = G_{int}$. If the simplifying approximation utilized in the deduction of this formula are taken into account, T_l acquires a simple physical meaning: at this temperature the energy of formation of intermolecular bonds becomes equal to the thermal energy. In other words: any bond, including chemical bonds, begins to dissociate when the thermal (kinetic) energy begins to exceed the potential energy of the bond [5]. For a large number of intermolecular bonds and only this case exists at the limit the entropy losses on bond formation tend towards zero, and for polymers

$$\bar{R}T_l = D_{int} \tag{4}$$

where D_{int} is the energy of dissociation of the intermolecular bond.

Above this temperature, the thermodynamic functions of the chains or the processes taking place in them may be considered to be those for isolated molecules. Such calculations of standard enthalpy, entropy and free energy changes for different decomposition paths of polyethylene and polytetrafluoroethylene demonstrated [6] that the process must take place even at ambient temperature with a high change in negative free energy, i.e. explosion-like. This must be all the more so at higher temperatures. The characteristic temperatures of thermal decomposition of polymers are shown in Fig. 2. These temperatures were obtained, using data from [7], as the intersection points of the plots $G(T)$ of the monomer, the liquid polymer and the hypothetical gaseous polymer. The dashed line indicates the decrease in Gibbs energy due to intermolecular interaction and viscosity in the bulk of the reacting polymer. The section FK corresponds to the Gibbs energy gain when the temperature T_s is reached. The intermolecular interaction whose energy reduces the overall free energy, and the cage effect resulting from it, do not allow explosion-like decomposition of the macromolecules to take place at temperatures below T_l. The temperature T_l can only be reached at high heating rates during a period of time insufficient for completion of the reaction proceeding by the normal path. When the temperature T_l is exceeded, the reaction mechanism will change: if the splitting of the bonds takes place preferably as depolymerization below T_l, then this temperature decomposition will proceed as described in [8]: $T_{sv} \leqslant T_l \leqslant T_{sp}$.

The above concept is confirmed by the good agreement of the energy of

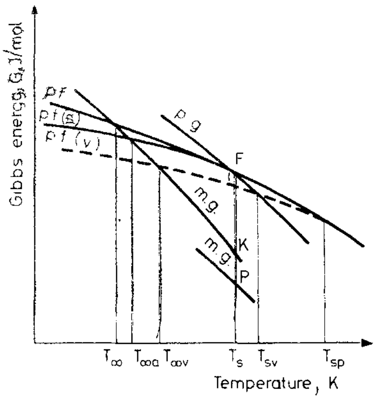

Fig. 2 Characteristic temperatures of polymer decomposition.
p.f. – polymer – liquid (ideal solution); p.f(a) – polymer – liquid (surface); p.f(v) – polymer – liquid (bulk of melt); p.g. – polymer – gas; m.g. – monomer – gas; T_∞ – equilibrium limiting decomposition temperature; $T_\infty = \Delta H/\Delta S$; $T_{\infty v}$ – same in bulk; $T_{\infty a}$ – same on surface; T_s temperature of phase transition; T_{sp} temperature of the spinoidalic point; KP – change in G at pressure change

intermolecular interaction D_{int} calculated via Eq. (4) with data in the literature [9]. For polystyrene and polymethyl methacrylate, D_{int} = 1.62 kcal/mol; in [9] the value is 1.623 kcal/mol. For the other polymers, the following values were found for D_{int}: impact-resistant polystyrene 1.626 kcal/mol, poly(ethylene terephthalate) and low-density polyethylene 1.546 kcal/mol. In the literature, data are reported on explosion-like decomposition of polymers accompanied by dispersal and atomization in a great volume for high heating rates [8] and for the sharp decrease of high pressures [10], and also when certain perlites are heated, e.g. colemanite [11], a mineral with polymeric structure (cf. Fig. 1).

As to the kinetics of thermal decomposition, we wish to note that at $T < T_l$ the decomposition of both associated and non-associated groups takes place. The rate constant of decomposition is higher for non-associated groups than for associated groups, explaining why the observed lifetime of the film decreases more rapidly with temperature increase than corresponding to the Arrhenius equation (linear portions of the curves), although this equation is satisfied for each individual elementary step of the process. From a comparison of the thermodynamic functions of isolated molecules and molecules on the surface not associated with other molecules, it can be observed that a geeat number of states cannot be achieved with the molecule on the surface as compared to the isolated molecule; this is in an (as it were) excited state, resulting in a large gain of free energy. Consenquently, the sharp increase of the process rate at $T \approx T_l$ is explained mainly by entropy reasons, this being generally characteristic for polymeric substances.

Error computation for temperature measurements

Thermal conduction processes in the polymer film in contact on one side with the metal heater and on the other side with the gas phase are described by the following equations:

$$\frac{\partial T_1}{\partial t} = a_1 \frac{\partial^2 T_1}{\partial x^2} - F; \ \frac{\partial T_2}{\partial t} = a_2 \frac{\partial^2 T_2}{\partial x^2}; \ \frac{\partial T_3}{\partial t} = a_3 \frac{\partial^2 T_3}{\partial x^3} \tag{5}$$

where $T_1(x, t)$, $T_2(x, t)$ and $T_3(x, t)$ are the temperatures of the polymer film, of the heater and of the decomposition products, respectively, a_1, a_2 and a_3 are temperature conductivities, and F is a function of the neat absorption due to the decomposition of the polymer.

The initial and boundary conditions are:

$$\begin{aligned} & T_1(x, 0) = T_0; \ T_2(x, 0) = T_3(x, 0) = T_c; \\ & T_1(R, T) = T_2(R, t); \ T_1(-R, t) = T_3(-R, t); \\ & \lambda_1 \frac{\partial T_2}{\partial x}(\infty, t) = 0; \ \frac{\partial T_3}{\partial x}(-\infty, t) = 0; \\ & \lambda_1 \frac{\partial T_1}{\partial x}(R, t) = \lambda_2 \frac{\partial T_2}{\partial x}(R, t); \\ & \lambda_2 \frac{\partial T_1}{\partial x}(-R, t) = \lambda_3 \frac{\partial T_3}{\partial x}(-R, t), \end{aligned} \tag{6}$$

where λ_1, λ_2 and λ_3 are the thermal conductivities and $2R$ is the thickness of the film.

The function F depends in a complicated manner (decreasing with time) on the kinetic parameters of the decomposition process, and for exact computations of the temperature fields the system of equations (5) must be completed by the kinetic equation. In this paper, only the question of the experimental error will be dealt with, defined by the maximum temperature gradients. It is therefore expedient to simplify the problem by accepting as a first approximation that the function F is equivalent to the maximum value of heat absorption: $F = Q = \text{const}$ and $R = \text{const}$. In the second approximation it is interest to take into account the thickness decrease of the specimen and the intensity of heat absorption, which may be considered with satisfactory accuracy as decreasing exponentially in the form $F = Q \exp(-\alpha t)$. Here, Q and α are determined by the value of the thermal effect of depolymerization and by the characteristic time $t_0 = 1/\alpha$. At $\alpha = 0$, one obtains the first approximation $F = Q$.

The system of equations (5) was solved by the Laplace transformation method. The greatest difference between the temperature of the polymer on the interface of the film with the decomposition products (at $x = -R$) and the temperature of the heater place T_c is expressed in the Laplace transformation as follows:

$$T_{s1}(-R, s) = \frac{T_0}{s} - \frac{Q}{s(s+\alpha)} + \left(T_c - T_0 + \right.$$
$$\left. + \frac{Q}{s+\alpha}\right) \frac{2K_{13} + (1+K_{12})\exp y - (1-K_{12})\exp y}{s[(1+K_{12})(1+K_{13})\exp y - (1-K_{12})(1-K_{13})\exp y]} \tag{7}$$

where $y = 2\sqrt{\frac{s}{a}}R$; $K_{mn} = \sqrt{\frac{\lambda_m C_m \varrho_m}{\lambda_n C_n \varrho_n}}$; C_m is the heat capacity, ϱ is the density of the respective substance, $m = 1, 2, 3$ and $n = 1, 2, 3$.

By way of example, let us calculate the error of temperature measurement in a polystyrene film. For this polymer, $a_1 = 8 \cdot 10^{-8}$ m^2/s; at a film thickness of some μm, the characteristic heating time is of the order of $t_n = R^2/a_1 \approx 10^{-4}$ s, much less than the time at which temperature is recorded. At $t \gg t_n$, y is a small value, and expansion according to Eq. (7) can be performed for this small parameter. By means of reverse Laplace transformation, we calculated the temperature on the surface of the film. The results are presented in the form of the relative error of temperature measurement. At $t \gg t_n$, we have

$$Q_1 = \frac{T_c - T_1(-R, t)}{T_c - T_0} =$$
$$= \frac{2K_{12}R}{(1+K_{12}K_{31})\sqrt{\pi a_1 t}} \left[1 + \frac{2Qt}{T_c - T_0} \cdot \left(1 - \frac{2}{3}\alpha t\right)\right] \tag{8}$$

After computing the values of the coefficients K_{12} and K_{31} for the steel heater plate and the polystyrene film, we obtain the following expression for the error Q_1 in the second approximation: $Q_1 = 1.5 \cdot 10^{-4}(1 + 8.4t - 5.6t^2)/\sqrt{t}$. For the first approximation at $\alpha = 0$, $Q_1 = 1.5 \cdot 10^{-4}(1 + 8.4t)/\sqrt{t}$.

In the above formulae the coefficients are calculated after introducing t in seconds. It is easy to calculate that even at $t = 10^{-2}$ s the error of temperature measurements is only 0.1%. It may be seen from Eq. (8) that the error is proportional to the thickness of the film, and hence only very thin films, with thicknesses of the order of some μm will ensure the required accuracy of temperature measurement. The accuracy of film thickness measurement is defined by the accuracy of measuring the mass loss of the initial polymer specimen on an analytical balance; it does not exceed 1–3%.

Conclusion

The experiments described in this paper confirmed the earlier conclusion that limiting heating temperatures exist in the thermal decomposition of polymers. The existence of limiting heating temperatures of polymers in the metastable state is associated with the cessation of intermolecular interaction and the subsequent explosion-like decomposition of the labile macromolecules of the thermodynamically unstable polymeric gas.

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Zusammenfassung — Experimentelle und theoretische Grundlagen der Grenztemperaturen der thermischen Zersetzung von thermoplastischen Polymeren werden behandelt. Es besteht eine Korrelation zwischen den Grenztemperaturen und den intermolekularen Wechselwirkungen der untersuchten Polymere.

Резюме — Дано экспериментальное и теоретическое обоснование предельных температур терморазложения термопластичных полимерных материалов. Установлена корреляция между предельными температурами и межмолекулярным взаимодействием изученных полимеров.