

Kinetics of Thermal Decomposition of Unsaturated Polyester Resins with Reduced Flammability

Ewa Kicko-Walczak

Industrial Chemistry Research Institute, Warsaw, Poland

Received 1 May 2002; accepted 26 June 2002

ABSTRACT: In this article, the kinetics of thermal decomposition of unsaturated maleic-phthalic polyester resins, flame-retarded with zinc hydroxystannate, was studied by thermogravimetric analysis at different heating rates. At the first stage, it was found, on the basis of isoconversional analysis by the methods of Friedman and of Ozawa-Flynn-Wall, that the value of the (apparent) activation energy (E) characteristically changes in three steps during the degradation. Further kinetic studies using nonlinear regression methods revealed the best fits for both pristine and stabilized resins. It was observed that the course of E versus the degree of conversion (α) during degradation of zinc hydroxystannate-containing resins ($\alpha > 0.8$) was characterized by higher values of E —this phenomenon can be explained in terms of the flame-retardation action of zinc hydroxystan-

nate, which is believed to operate primarily in the condensed phase. At the next stage, kinetic analysis by the nonregression method was performed to find the kinetic model [$f(\alpha)$ function] of the decomposition process; hence, for pristine resin, the best fit was found for the Avrami-Yerofeeyev model (nuclei growth), and for stabilized samples, the n th-order function with catalysis proved to be the best approximation. The obtained kinetic parameters in the form of E , the preexponential factor A , and the model function $f(\alpha)$ allow a prediction of the polyester resin's thermal behavior in an extrapolated range of degree of conversion, time, and temperature. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2851–2857, 2003

Key words: polyesters; resins; flame retardance

INTRODUCTION

Unsaturated polyester resins (UPRs) are among the most used thermosetting materials for composite applications, structural parts of automobiles, building and coating materials, and electrical parts.^{1,2} Since UPRs are extensively used in enclosed spaces, it is essential for safety reasons to possess detailed knowledge about their thermal behavior, with particular attention paid to the kinetic aspects of decomposition. In that respect, kinetic parameters give an additional insight into the mechanism of degradation and make possible prediction of the system's behavior in an extrapolated range of degree of conversion, time, and temperature.

A literature survey on the kinetics of decomposition of UPRs revealed that, in spite of the large amount of work that has been done in the polymer chemistry of polyesters, there has been less work on their decomposition features—the better knowledge of them is important from both a fundamental and a technological point of view. From the view of fundamental research, the thermal decomposition of a polymeric material is a complex, heterogeneous process, consisting of several partial reactions. The course of decomposition is affected by different factors, connected with the sample, with the degradation process alone

and with the surroundings determined by analytical equipment. A valuable tool toward a better understanding of degradation mechanisms offer methods for the evaluation of kinetic parameters, provided that the basic relationships and assumptions on which they are based are properly taken into account. From the application (technological) point of view, the investigation of decomposition processes has a dual meaning: The first concerns stabilization of a polymer to obtain novel materials with a desired set of thermal properties which will be able to fulfill demands of contemporary materials engineering. The role and action of a stabilizer may be more effective if a better understanding of polymer decomposition schemes is provided during its development. The second meaning of the decomposition studies concentrates on the safe disposal or recycling of plastic wastes, which have become a social problem of growing importance nowadays.³ Both aspects are not contradictory, but, rather, complementary, particularly in the case of widely used polymers, such as UPRs.

The results of studies of the thermal behavior of unsaturated polyesters (UPs) have been published in recent years,^{4–6} but there is little data concerning the kinetics of decomposition. Baudry et al. studied the thermal degradation of UPRs with the cyclopentadiene end cap.⁷ It was found that, at the beginning of the thermal degradation, the energy of activation (E) was about 100 kJ/mol, which corresponds to polysty-

TABLE I
Description of the Samples

| Sample no. | Amount of ZHS (wt. %) |
|------------|-----------------------|
| 1 | 0 |
| 2 | 2 |
| 3 | 5 |
| 4 | 10 |
| 5 | 40 |

rene depolymerization; for a degree of conversion (α) equal to 0.5, which corresponds to UP network degradation, E was 170 kJ/mol. In another study, Agraval et al.⁸ investigated the kinetics of decomposition of three novel unsaturated polyesters, based on diethylene glycol and isophthalic/adipic/maleic or fumaric acid, by isothermal thermogravimetric analysis (TGA). By assuming the first-order kinetic equation, the authors calculated E for the two stages of decomposition; it was observed that E was characterized by higher values at the first decomposition stage and was also higher for a resin with a more ordered and regular structure, as confirmed by X-ray diffraction patterns. The invariant kinetic parameters (IKPs) method was applied by Mortaigne et al. to study the thermal behavior of (low styrene emission) UP resins.⁹ The authors calculated the probability distribution associated with the kinetic function and found that the mechanism of degradation is rather complex; for one resin, decomposition seems to follow an elementary low-diffusion model of cylindrical symmetry. The goal of this study was to determine the kinetic parameters of the thermal decomposition process of UPRs, flame-retarded by ZHS, using an advanced approach containing a model-free evaluation of the (apparent) activation energy and nonlinear regression-based determination of the reaction function.

EXPERIMENTAL

Materials

The UPR (commercial reference P163-53, produced by the Organika-Sarzyna Co., Poland) was of the malate/phthalate/brominated glycol type. The UPR (styrene solution) was cured by mixing it with methyl ethyl ketone peroxide, cobalt naphthenate, and zinc hydroxystannate (ZHS) (Alcan Co., UK). (See Table I.)

TGA

TGA was performed on a Netzsch TG 209 thermal analyzer operating in a dynamic mode at heating rates of 2.5, 5, 10, and 20 K/min. The conditions were the sample weight, ~5 mg; atmosphere, argon or air; and an open α -Al₂O₃ pan. The raw data were converted to ASCII files and kinetic analysis was carried out using

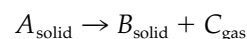
an in-house program and a Netzsch Thermokinetic Program (v. 99/10) on an IBM-compatible computer with a Pentium III processor.

RESULTS AND DISCUSSION

The results of the TGA of samples 1–5 are shown in Figure 1. The thermal decomposition of unmodified polyester resin starts at about 280°C and proceeds in one step to about 420°C. The maximal decomposition rate occurred at 360°C, as evidenced by the DTG profile. Samples containing ZHS undergo a two-step degradation; the first step was found to be operational at the temperature range of 240–340°C, while the second one occurs at 340–420°C. It should be noted that the char residue at 500°C accounts for 9% of the resin and for 20, 25, 29, and 43% of the 2, 5, 10, and 40% additive-containing samples, respectively.

The decomposition pathways of a general-purpose resin made from a glycol, phthalic anhydride, and maleic anhydride were described in the literature as a three-stage process. The first stage was due to the elimination of phthalic anhydride. The second stage, around 350°C, was caused by the release of styrene and a complex mixture of other materials, while the third stage above 500°C was the loss of high-boiling tars and the oxidation of the char formed.⁴ In another study, the mechanism of thermal degradation of polyesters was studied on the basis of model compounds.¹⁰ It was found that a β -CH hydrogen transfer is involved, leading to the formation of oligomers with olefin and carboxylic end groups. Additionally, even when a quite small proportion of ester decomposition occurs, the residual acid or the corresponding anhydride units tend to block the passage of the depolymerization along the polymer chains so that monomer production tends to be retarded.¹¹

To gain additional insight into the mechanism of decomposition, kinetic analysis was performed; hence, our approach is based on the reaction expressed by the stoichiometric equation



The rate of reaction can be described in terms of two functions: $k(T)$ and $f(\alpha)$; thus,

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

where α is the degree of conversion.

By substitution of the Arrhenius equation [$k(T) = A \exp(-E/RT)$], the following equation results:

$$d\alpha/dt = A \exp(-E/RT)f(\alpha) \quad (2)$$

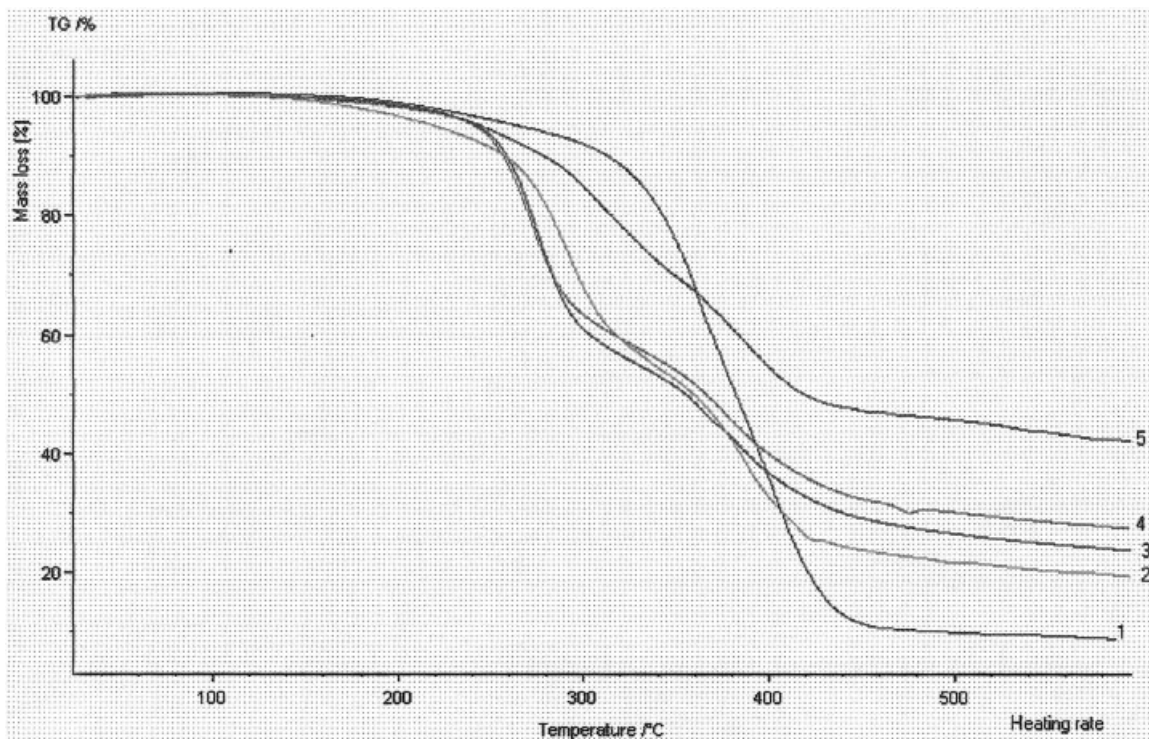


Figure 1 Thermogravimetric curves of samples 1-5 at 10 deg/min.

After introduction of the constant heating rate $\beta = dT/dt$ and rearrangement, one obtains

$$\frac{d\alpha}{f(\alpha)} = \left(\frac{A}{\beta}\right) \exp\left(-\frac{E}{RT}\right) dT \quad (3)$$

where T is the temperature in Kelvin; $f(\alpha)$, the type of reaction; $k(T)$, the rate constant; E , the activation energy; A , the preexponential factor; and R , the gas constant.

A subsequent integration of eq. (3) leads to the equation

$$G(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T \exp\left(\frac{-E}{RT}\right) dT \quad (4)$$

which cannot be expressed by a simple analytical form since its right-hand side corresponds to a series of infinite γ functions. In mathematical practice, logarithms are taken:

$$\ln G(\alpha) = \ln\left(\frac{AE}{R}\right) - \ln \beta + \ln p(x) \quad (5)$$

and the exponential integral $p(x)$ is introduced:

$$p(x) = \frac{e^{-x}}{x} - \int_\infty^x \frac{e^{-x}}{x} dx \quad (6)$$

where $x = E/RT$.

Using an approximation of the exponential integral in a form proposed by Doyle,¹²

$$\ln p(x) = -5.3305 + 1.052x \quad (7)$$

it is possible to determine the activation energy of the thermal process by following the specific heat flow of a process at several different heating rates:

$$\ln \beta = \ln\left(\frac{AE}{R}\right) - \ln G(\alpha) - 5.3305 + 1.052x \quad (8)$$

Equation (8) generates a straight line when $\ln(\beta)$ is plotted against $1/T$ for isoconversional fractions, the slope of the line being equal to $-1.052E/R$ during a series of measurements with a heating rate of $\beta_1 \dots \beta_j$ at a fixed degree of conversion of $\alpha = \alpha_k$. The temperatures T_{jk} are those at which the conversion α_k is reached at a heating rate of β_j . This method was developed independently by Ozawa¹³ and Flynn and Wall.¹⁴ Another isoconversional procedure, introduced by Friedman,¹⁵ used as its basis the following relationship:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln f(\alpha) + \ln A - \frac{E}{RT} \quad (9)$$

which makes it possible to find the activation energy value from the slope of the line ($m = -E/R$) when

TABLE II
Kinetic Model Functions

| Model | Symbol | $f(\alpha)$ |
|---|-------------|---|
| Phase boundary-controlled reaction (contracting area) | R2 | $(1 - \alpha)^{1/2}$ |
| Phase boundary-controlled reaction (contracting volume) | R3 | $(1 - \alpha)^{2/3}$ |
| Random nucleation. Unimolecular decay law | F1 | $(1 - \alpha)$ |
| Reaction n th order | F n | $(1 - \alpha)^n$ |
| Johnson–Mehl–Avrami | JMA | $n(1 - \alpha)[- \ln(1 - \alpha)]^{1 - 1/n}$ |
| Two-dimensional growth of nuclei (Avrami equation) | A2 | $2[- \ln(1 - \alpha)^{1/2}](1 - \alpha)$ |
| Three-dimensional growth of nuclei (Avrami equation) | A3 | $3[- \ln(1 - \alpha)^{2/3}](1 - \alpha)$ |
| One-dimensional diffusion | D1 | $1/2\alpha$ |
| Two-dimensional diffusion | D2 | $1/[- \ln(1 - \alpha)]$ |
| Three-dimensional diffusion (Jander equation) | D3 | $3(1 - \alpha)^{2/3}/2[1 - (1 - \alpha)^{1/3}]$ |
| Three-dimensional diffusion (Ginstling–Brounshtein) | D4 | $3/2[(1 - \alpha)^{-1/3} - 1]$ |
| n -Dimensional nucleation (Avrami–Erofeev equation) | An | $n[- \ln(1 - \alpha)^n](1 - \alpha)$ |
| Reaction of first order with autocatalysis | C1 | $(1 - \alpha)(1 + K_{\text{kat}} \alpha)$ |
| Reaction of n th order with autocatalysis | C n | $(1 - \alpha)^n(1 + K_{\text{kat}} \alpha)$ |
| Prout–Tompkins equation | B $n\alpha$ | $(1 - \alpha)^n \alpha^a$ |

$\ln(d\alpha/dt)$ is plotted against $1/T$ for isoconversional fractions.

In eq. (1), the term $f(\alpha)$ represents the mathematical expression of the kinetic model. The most frequently cited basic kinetic models are summarized in Table II. The results of the kinetic analysis by the Ozawa–Flynn–Wall method for sample 1 are shown in Figure 2.

Nonisothermal curves of a thermal reaction can satisfy the kinetic equations developed for the kinetic analysis of “ n th-order reactions,” even if they follow a quite different mechanism. The results of the comparative studies lead to the conclusion that the actual mechanism of a thermal process cannot be discriminated from the kinetic analysis of a single TG trace.¹⁵ Besides, both the activation energy and the preexponential factor, given in eq. (2), may be mutually correlated. As a consequence of this correlation, any TG curve can be described by an apparent kinetic model instead of the appropriate one for a certain value of the apparent activation energy.

Therefore, the kinetic analysis of the TG data cannot be successful unless the true value of the activation energy is known.^{16,17}

On the basis of isoconversional analysis, it is possible to show the dependence of the (apparent) activation energy (E) from the degree of conversion (α) (Fig. 3). As can be seen, the activation energy barrier is higher for flame-retarded samples for $\alpha > 0.8$, which corresponds to the temperature levels of about 400°C. Basically, three stages of decomposition can be observed for sample 1: The beginning of the thermal degradation has an activation energy of about 130 kJ/mol. This value of E may correspond to the depolymerization of styrene micronodules formed in the gelation phase.¹⁸ The second step, with an activation energy of about 150–170 kJ/mol, may be attributed to the decomposition of the polyester network, whereby the third step (E equal or higher than 200 kJ/mol) can be associated with random scission reactions that lead to the formation of low molecular weight products, as evidenced in ref. 4.

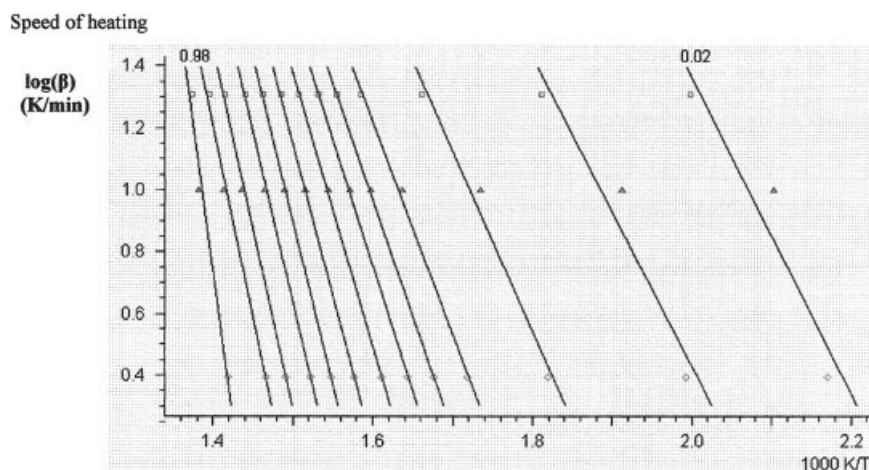


Figure 2 Ozawa–Flynn–Wall analysis of the decomposition process of sample 1.

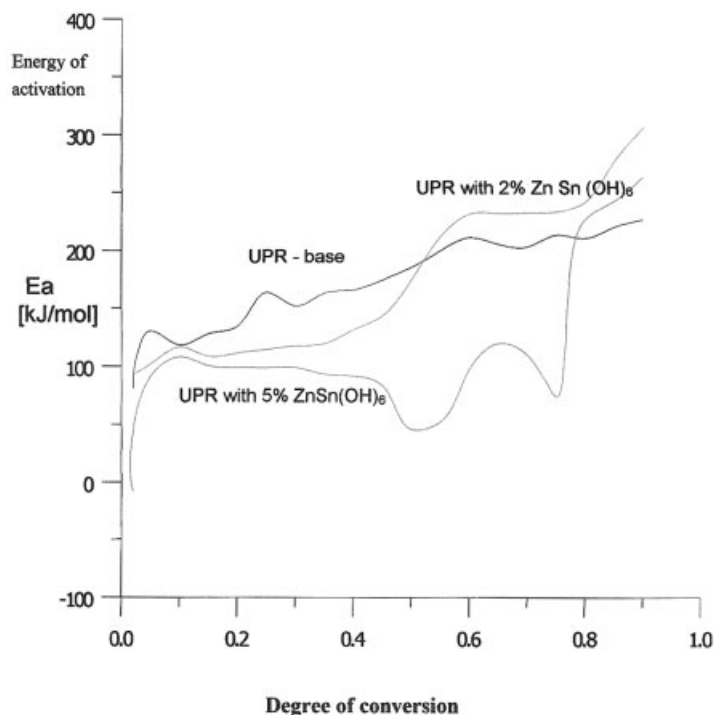


Figure 3 Activation energy (E) as a function of degree of conversion for the decomposition process of samples 1–3 calculated by Ozawa–Flynn–Wall method.

At the next stage, kinetic analysis by the nonregression method was performed to find the kinetic model [$f(\alpha)$ function] of the decomposition process of samples 1, 2, and 3, which displayed the best limiting oxygen index (LOI) values in previous flammability tests.¹⁹ Best fits on the basis of statistical comparison (F -test) are collected in Table III. (See also Fig. 4.) For the pristine resin, the best fit was found for the Avrami–Yerofeyev model (nuclei growth), and for stabilized samples, the n th-order function with catalysis proved to be the best approximation.

As can be seen, the best approximation was found for a two-stage consecutive reaction, where the first step was the Avrami–Erofeev nucleation-dependent model and the second step was the chemical reaction (first- or n th-order) model. In analysis of the kinetic data of heterogeneous processes, one assumes a geometrical system consisting of large spherical particles of one phase surrounded by substantially finer particles of the other phase. If it is ensured that the surface of the larger particles is sufficiently covered (e.g., by an excess of the smaller particles) and that they are in

close contact, an ideal case is approached, which can be described by a discontinuous (stationary) model of the shrinking core of the particles. This model has become a basis for the description of most reactions of solids, using a geometrical representation of the reacting system as a set of geometric bodies. The reacting components diffuse through the thin surface layer to the reaction boundary in which they react—the slower of the two principal processes (diffusion or chemical reaction) then becomes the rate-controlling process.¹⁶

In analyzing the origin of the first step, one should bear in mind that in deriving nucleation-dependent kinetic models, for example, the Avrami–Erofeev model, it is assumed that the rate of nucleus formation depends on the number of energetically favorable sites (mostly depending on defects that are introduced during a thermal event). Nucleation of the product N is followed by its growth G , which can have the character either of a surface chemical reaction or of diffusion. To calculate the volume of nuclei capable of further growth, usually a three-dimensional isotropic growth controlled by the surface reaction is considered. An additional feature of an Avrami–Erofeev model is that it involves the description of possible intergrowth of nuclei, that is, a process in which the number of nuclei cannot increase unrestrictedly as the nuclei necessarily meet during their spatial growth and their growth is thus stopped. The overall activation energy of a nucleation-growth process is the sum of the partial energies of nucleation, growth, and diffusion and that

TABLE III
Results of the Kinetic Analysis (Model Functions)

| Sample | Model | $\log A1/s^{-1}$ | $E1$ (kJ/mol) |
|--------|-------|------------------|---------------|
| 1 | An | 10.72 | 162.9 |
| 2 | Cn | 9.33 | 146.2 |
| 3 | Cn | 6.25 | 95.3 |

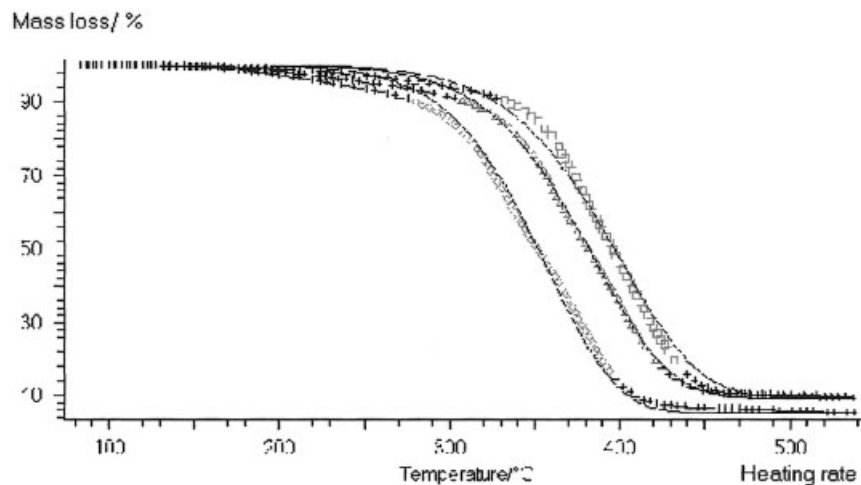


Figure 4 Comparison of the theoretical fits and experimental data for the decomposition process of sample 1. Symbols denote experimental curves, and lines, theoretical ones.

the exponent depends on the shape of the nuclei and the dimensionality of their growth, as well as on the rate of their formation. On the other hand, the preexponential factor depends on the geometry and number of sites capable of nucleation.²⁰ One should, however, bear in mind that kinetic model functions are based on physical-geometrical assumptions of regularly shaped bodies which are required to account for polydispersity, shielding and overlapping, unequal mixing, and/or nonregular shapes and anisotropy. The prolonged reaction tails due to the actual behavior of real particles and the particle nonsphericity in view of the morphology description in terms of characteristic dimensions (usually the longest particle length), interface (average boundary line), and volume (mean section area) contribute to the complex behavior of a macromolecular system.

The fits of experimental data are quite good when two consecutive reactions are considered. With regard to $f(\alpha)$, it is possible to distinguish between the results obtained with the An function and F1/Fn function. The granular structure of additives facilitates nucleation growth of a polymer-additive system; then, at temperatures higher than 400°C, the chemical decomposition reaction becomes a kinetically dominating process. The stabilizing action of ZHS additives may be explained by the formation of surface-localized spherical barriers which are grow according to the nucleation growth mechanism and which attenuate the transfer of heat from the decomposition zone to the substrate—this effect was found as dominating in the flame-retardancy mode of action. An additional role may be ascertained to the metal ion-polymer functional groups interaction, which should lead to the formation of long-range structural regularities, which, in turn, thermally stabilize the whole system (“strong interactions model”).

CONCLUSIONS

The kinetic analysis of the thermal decomposition process of unsaturated maleic-phthalic polyester resins, flame-retarded with ZHS, was studied by TGA at different heating rates. It was observed on the basis of isoconversional analysis that the course of E versus the degree of conversion (α) during degradation of the ZHS-containing resins ($\alpha > 0.8$) was characterized by higher values of E —this phenomenon can be explained in terms of the flame-retardation action of ZHS, which is believed to operate primarily in the condensed phase. At the next stage, kinetic analysis by the nonregression method was performed to find the kinetic model [$f(\alpha)$ function] of the decomposition process; hence, for the pristine resin, the best fit was found for the Avrami-Yerofeeyev model (nuclei growth), and for stabilized samples, the n th-order function with catalysis proved to be the best approximation. The stabilizing action of the ZHS additives may be explained by the formation of surface-localized spherical barriers, which grow according to the nucleation growth mechanism and which attenuate the transfer of heat from the decomposition zone to the substrate—this effect was found as dominating in the flame-retardancy mode of action.

References

1. Kicko-Walczak, E. *J Appl Polym Sci* 1999, 74, 379.
2. Kicko-Walczak, E. *Polimery* 2000, 45, 808.
3. Pielichowski, J.; Pielichowski, K. *J Therm Anal* 1995, 43, 505.
4. Atkinson, P. A.; Haines, P. J.; Skinner, G. A. *Thermochim Acta* 2000, 29, 360.
5. Cusack, P. A.; Heer, M. S.; Monk, A. W. *Polym Degrad Stab* 1997, 58, 229.
6. Weil, E. D.; Hirschler, M. M.; Patel, N. G.; Said, M. M.; Shakir, S. *Fire Mater* 1992, 16, 159.
7. Baudry, A.; Dufay, J.; Regnier, N.; Mortaigne, B. *Polym Degrad Stab* 1998, 61, 441.

8. Agraval, J. P.; Sarvade, D. B.; Makashir, P. S.; Mahajan, R. R.; Dendage, P. S. *Polym Degrad Stab* 1998, 62, 9.
9. Mortaigne, B.; Bourbigot, S.; Le Bras, M.; Cordellier, G.; Baudry, A.; Dufay, J. *Polym Degrad Stab* 1999, 64, 443.
10. Buxbaum, L. H. *Angew Chem Int Ed* 1968, 7, 182.
11. Grassie, N.; Johnston, A.; Scotney, A. *Eur Polym J* 1981, 17, 589.
12. Doyle, C. D. *J Appl Polym Sci* 1962, 6, 39.
13. Ozawa, T. *Bull Chem Soc Jpn* 1965, 38, 1881.
14. Flynn, J. H.; Wall, L. A. *Polym Lett* 1966, 4, 232.
15. Friedman, H. L. *J Polym Sci* 1965, C6, 175.
16. Sestak, J. *Thermophysical Properties of Solids, Their Measurements and Theoretical Thermal Analysis*; Elsevier: Amsterdam, 1984.
17. Pielichowski, K. *Solid State Ion* 1997, 104, 123.
18. Yang, Y. S., Lee, L. J. *Polymer* 1988, 29, 1793.
19. Kicko-Walczak, E. *Thermochim Acta*, in preparation.
20. Allnat, A.; Jacobs, P. W. M. *Can J Chem* 1968, 46, 111.