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Non-isothermal degradation kinetics of glass-reinforced epoxy resin

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Abstract

The results obtained from the thermal analysis (TG, DTG, DTA) of glass-reinforced epoxy resin are presented. It has been shown that on heating in air up to 320°C, an exothermic process with formation of volatile products takes place. The non-isothermal kinetic parameters of this process have been determined by various methods.

INTRODUCTION

Thermal analysis methods have been used to predict the thermal lifetime of polymeric materials [1–6]. These predictions are based on the hypothesis that the first degradation process observed in the thermogram is responsible for the deterioration of the property of interest (electrical or mechanical) in the polymeric material. It is assumed that the activation energy of degradation, estimated from non-isothermal data, is equal to the activation energy of the process which accounts for the deterioration of the electrical or mechanical properties. It has been shown [7] that this hypothesis is not valid for the thermal degradation of all polymeric materials.

The purpose of this paper is to check that application of this hypothesis to the thermal degradation of glass-reinforced epoxy resin. The results of the isothermal accelerated ageing of this material in air and in oxygen have been presented in a previous paper [8] in which the variation of flexural strength with thermal ageing was reported. A kinetic equation for the dependence of degradation on temperature, oxygen pressure and duration of the accelerated thermal ageing has been derived and shown to be applicable. The activation energy of the process accounting for the deterioration in mechanical property was found to be 69.4 kJ mol^{-1}; and the degradation rate increases with oxygen pressure. The chemical process which is responsible for the change in mechanical property is thermo-oxidative.

This paper presents the results obtained from the thermal analysis (TG, DTG, DTA) of glass-reinforced epoxy resin. From the results, the non-isothermal degradation kinetic parameters were determined by various means and the activation energy, estimated from non-isothermal data, is compared with that measured previously from the isothermal change in mechanical property [8].

EXPERIMENTAL

Thermal analyses were carried out on a combined Paulik–Paulik–Erdey-type TG/DTA unit, Q-1500D (MOM, Budapest), in a static air atmosphere in the temperature range 20–500°C, at 0.72, 1.45, 2.97, 6.08 and 12.5 K min^{-1} heating rates. Derivatograms were also recorded in argon atmosphere, at a heating rate of 2.5 K min^{-1}. The glass-reinforced epoxy resin used was a complex material produced by IUC-Fagaras, Romania, and formed from thermo-rigid epoxy resin (40%) reinforced with fibre-glass (40%), polyamide hardener (4%), plasticizer and ftoroplast (16%).

METHODS OF PROCESSING THE EXPERIMENTAL DATA

In order to estimate the non-isothermal kinetic parameters, the Coats–Redfern [9], the Coats–Redfern modified by Urbanovici and Segal [10], the Flynn–Wall isoconversion [11, 12] and the Kissinger [13] methods were used. A BASIC program [14, 15] run on a TIM-S computer was used to analyse the experimental data. A program to regenerate the thermogravimetric curves from the kinetic parameters determined by the Coats–Redfern method, was also used [15]. With this program, the degree of fit of the experimental points to the regenerated TG curve could be assessed.

RESULTS AND DISCUSSION

Figure 1 shows the weight change and the rate of weight loss from the glass-reinforced epoxy resin plotted as a function of temperature on heating in static air at 6.08 K min^{-1}, together with the corresponding DTA curve. Similar dependences were obtained for other heating rates. An exothermic process, with formation of volatile products, is present up to about 320°C. Similar measurements in an inert atmosphere (argon) showed two slightly endothermic processes accompanied by the formation of volatile products. The degradation process which occurs in the air heating is thermo-oxidative, and non-isothermal kinetic parameters were estimated using different kinetic relationships.

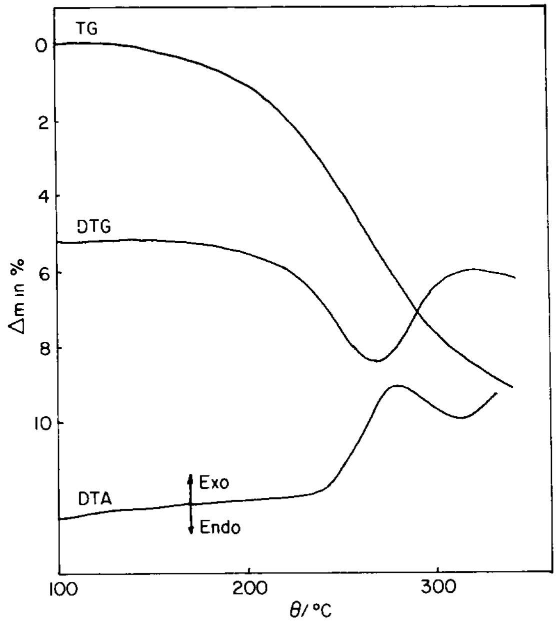

Fig. 1. TG, DTG and DTA analyses of glass-reinforced epoxy resin. Heating rate 6.08 K min^{-1}.

Table 1 lists the non-isothermal kinetic parameters for the thermo-oxidation of glass-reinforced epoxy resin, evaluated by the Coats–Redfern [9], the Coats–Redfern modified by Urbanovici and Segal [10], and the Flynn–Wall for constant heating rate [11] methods. The non-isothermal kinetic parameters at different heating rates, are all in reasonable agreement, but the values of these parameters, especially the apparent reaction order, are dependent on the heating rate.

Figures 2 and 3 show two TG curves regenerated using the Coats–Redfern values for the kinetic parameters. The experimental points lie practically on the regenerated curve, thus indicating the validity of the non-isothermal kinetic parameter values.

However, as regards the application of the Coats–Redfern, the modified Coats–Redfern and the Fynn–Wall for constant heating rate methods, some remarks are necessary. According to these methods, one considers the rate expression

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = kf(\alpha)$$

where $f(\alpha) = (1-\alpha)^n$ is the conversion function which corresponds to the reaction order model.

It is well known that one can also assume more complex expressions for $f(\alpha)$ [16]. It has been shown [17] that different kinetic equations can

TABLE 1

Values of the non-isothermal kinetic parameters of the thermo-oxidation of glass-reinforced epoxy resin

Heating rate /(K min^{-1})	Methods											
	Coats–Redfern				Modified Coats–Redfern				Flynn–Wall, a = const.			
	E/ (kJ mol^{-1})	n	A/(s^{-1})	r	E/ (kJ mol^{-1})	n	A/(s^{-1})	r	E/ (kJ mol^{-1})	n	A/(s^{-1})	r
0.72	58.1	1.2	8.596×10^2	0.9928	59.8	1.2	1.434×10^3	0.9933	62.7	1.2	5.062×10^3	0.9945
1.45	55.6	1.5	3.559×10^2	0.9987	56.8	1.5	5.805×10^2	0.9987	58.9	1.4	1.769×10^3	0.9990
2.97	58.5	1.0	8.860×10^2	0.9977	58.7	0.9	9.955×10^2	0.9975	61.4	0.9	3.763×10^3	0.9984
6.08	52.7	0.8	2.504×10^2	0.9998	54.3	0.6	4.326×10^2	0.9998	58.1	0.8	2.117×10^3	0.9998
12.5	46.8	0.6	6.687×10^2	0.9993	48.1	0.6	1.092×10	0.9996	52.2	0.6	7.305×10^2	0.9994

Key: E is the activation energy, n is the apparent reaction order, A is the pre-exponential factor and r is the correlation coefficient of linear regression.

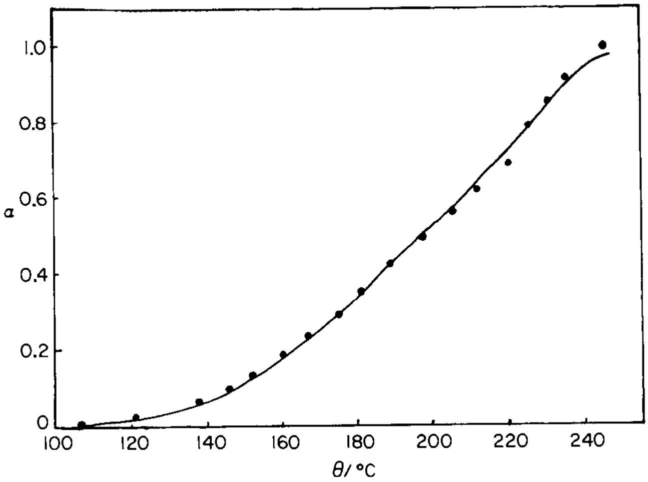

Fig. 2. Regenerated TG curve (α, θ/°C) of the degradation of glass-reinforced epoxy resin. Heating rate 0.72 K $\min^{-1}$: —— calculated; ● experimental.

satisfactorily describe the same experimental data. Therefore, the application of integral methods involving a single thermogram is recommended only when the mechanism of the studied process and, implicitly, the isothermal process kinetic equation are known.

In these methods, it is also assumed that the activation energy is constant over the whole range of conversion degree. However, this assumption is not valid for all polymer degradation. Therefore, in the study of the isothermal and non-isothermal degradation of polychloroprene rubber [18], the activation energy is strongly dependent on the extent of degradation (E has

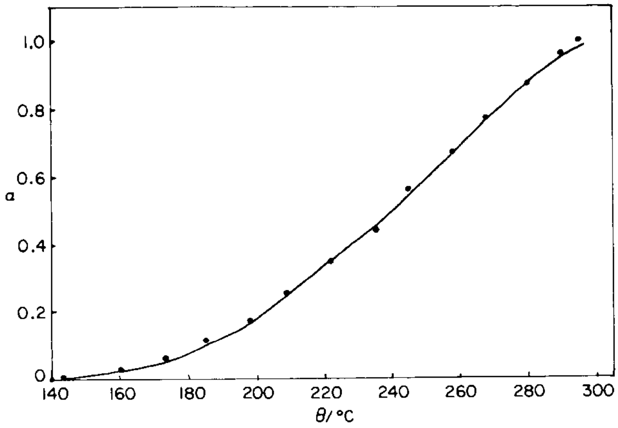

Fig. 3. Regenerated TG curve (α, θ/°C) of the degradation of glass-reinforced epoxy resin. Heating rate 2.97 K $\min^{-1}$: —— calculated; ● experimental.

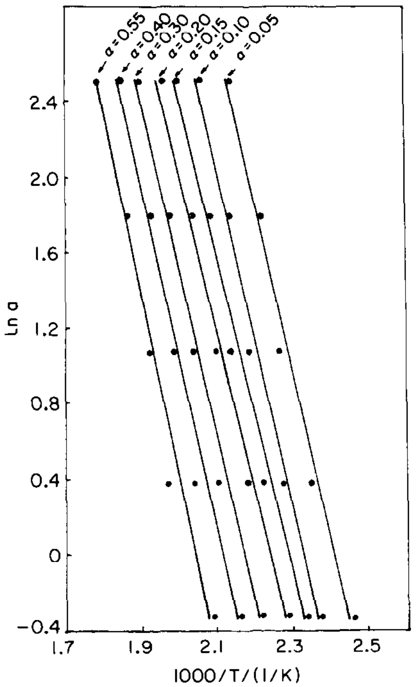

Fig. 4. Flynn–Wall diagram for the thermal degradation of glass-reinforced epoxy resin.

values ranging from 46 to 112.9 kJ mol^{-1}). These drawbacks do not occur in the case of the Flynn–Wall isoconversion method [12] which does not require any knowledge of the conversion function and allows the activation energy to be determined from the degree of conversion. The degradation of the glass-reinforced epoxy resin in static air atmosphere has been analysed for conversion degrees ranging between 0.05 and 0.85 using the Flynn–Wall procedure. A linear variation of $\ln a$ versus $1/T$ was obtained (see Fig. 4). The correlation coefficients of the linear regression are greater than 0.98. The activation energy value of the thermo-oxidative process does not depend on the heating rate.

The activation energy was calculated from the slopes of the Flynn–Wall lines; Fig. 5 shows the variation of activation energy with the conversion degree. It is apparent that for $0.05 \leq \alpha \leq 0.45$, E is practically constant, ranging from 68 to 73 kJ mol^{-1}; for $\alpha > 0.45$, E increases with the conversion degree, reaching a value of 80.7 kJ mol^{-1}.

Finally, the activation energy of the thermo-oxidation process of glass-reinforced epoxy resin has previously been evaluated by the Kissinger method [13], from analysis of the exotherm on the DTA curve: E was found to be 60.6 kJ mol^{-1} ($r = 0.9820$).

In a previous paper [8], the accelerated thermal degradation of glass-reinforced epoxy resin was studied in air and under oxygen. It was

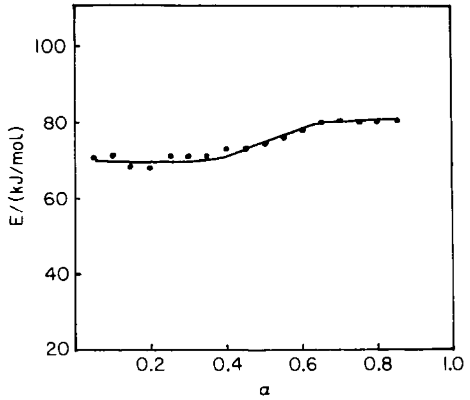

Fig. 5. The variation of the activation energy of the non-isothermal degradation process of glass-reinforced epoxy resin with extent of conversion.

established that the change in flexural strength is a result of the accelerated thermo-oxidative degradation. A value of 69.4 kJ mol^{-1} was obtained for the activation energy, very close to the values obtained from analysis of the non-isothermal data. Mechanical degradation is a result of the thermo-oxidation process studied in the thermograms.

The results presented in this paper show that the activation energy obtained by means of the Flynn–Wall isoconversion method, for $\alpha \leq 0.45$, is closest to the value of E evaluated from the isothermal data. It should be noted that not all polymeric materials will give the same activation energy value from isothermal and non-isothermal methods [7]. The main reason for this is the complexity of the polymer degradation processes. However, in the deterioration of the mechanical and electrical properties of some materials, the limiting step is the diffusion of oxygen into the polymer, as in the case of the thermal degradation of ethylene–propylene rubbers [7].

CONCLUSIONS

An investigation of the thermal degradation in air of glass-reinforced epoxy resin was made using thermal analysis (TG, DTG, DTA). It was shown that with heating in air up to 320°C, the material undergoes an exothermic oxidation process which is accompanied by the formation of volatile compounds. The non-isothermal kinetic parameters of this process have been evaluated by means of the Coats–Redfern, the Coats–Redfern modified by Urbanovici and Segal, the Flynn–Wall for constant heating rate, the Flynn–Wall isoconversion and the Kissinger methods. The values of the activation energy evaluated by these methods were compared with the value of the activation energy obtained in the study of the thermo-mechanical degradation of this material. It was shown that the best agreement is obtained by using the Flynn–Wall isoconversion method.

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