

## **Thermal degradation of epoxy-silica organic-inorganic hybrid materials**

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### **Abstract**

Degradation kinetics of organic-inorganic hybrid materials based on epoxy resin was investigated by thermogravimetric analysis (TGA). The hybrid materials were prepared from diglycidyl ether of bisphenol A (DGEBA) and 3-glycidyloxypropyltrimethoxysilane (GLYMO) polymerised simultaneously by poly(oxypropylene)diamine (Jeffamine D230). Nanometric level of homogeneity in the hybrids was verified by electron microscopy. Energy of activation of degradation processes for the hybrids with varying inorganic content, as well as for the unmodified epoxy-amine system, was determined by isoconversional Kissinger-Akahira-Sunose method, and was found to be significantly higher for the hybrid materials than for the unmodified epoxy-amine system. The degradation process was described by empirical kinetic models. The results indicated that presence of the inorganic network influences the mechanism of degradation of organic phase. Greater thermal stability of hybrid materials was confirmed by other parameters obtained from TGA curves.

*Keywords:* degradation kinetics, hybrid materials, sol-gel process, thermogravimetric analysis

### **1. Introduction**

Improvement of end-use properties of polymer materials, including their thermal stability, is a lasting challenge. Formation of stable char is one of desirable mechanisms of flame retardation in polymers, since the char layer acts both as thermal insulator and as a barrier to oxygen diffusion. A

good way to augment char formation is by addition of inorganic fillers, since the presence of inherently stable inorganic phase makes char more voluminous and mechanically stronger, consequently improving its insulating and barrier properties [1]. In recent times, nanocomposites have emerged as promising class of materials with good fire resistance.

The organic-inorganic hybrid materials could also be called nanocomposites, as the inorganic phase is dispersed in polymer matrix at molecular (nanometric) level. But unlike the nanocomposites prepared by mixing pre-existing nano-sized filler into the matrix, in hybrids the inorganic phase is formed *in situ* by hydrolysis and condensation of metal (usually silicon) alkoxydes [2]. This leads to much more homogeneous material than would be possible with hard to disperse nano-sized filler, and in consequence basically the whole volume acts as interphase [3]. Thus the hybrid materials unite the qualities of both organic and inorganic phase in synergistic manner, and are expected to possess superior properties [4].

Degradation of epoxy systems has been widely studied due to their widespread use as engineering polymers. It was determined that it proceeds *via* three overlapping mechanisms. The first, starting already at 240°C, consists of homolytic scission of chemical bonds in the network, which influences its physical properties but does not cause a large weight loss [5, 6]. The first major weight loss in both oxidative and non-oxidative degradation of amine cured epoxies is caused by dehydration due to elimination of water molecule from oxypropylene group,  $-\text{CH}_2\text{-CH}(\text{OH})-$ , and subsequent formation of double bonds. This dehydration is concurrent with network breakdown [5, 7, 8]. The final degradation proceeds through reactions of isomerisation, intramolecular cyclisation, chain transfer and other reactions that involve the radicals formed in the initial stages of degradation [6].

In this work, thermal degradation kinetics of epoxy-silica organic-inorganic hybrids, with 3-glycidyloxypropyltrimethoxysilane (GLYMO) as the inorganic precursor, is studied. These hybrid materials were previously characterised and their cure kinetics studied [9, 10]. The inorganic phase

is expected to enhance thermal properties epoxy matrix, both acting as flame retardant and by increasing char formation [11, 12].

## **2. Experimental**

An epoxy resin, diglycidyl ether of bisphenol A (DGEBA, Epikote 828 EL, Shell Chemicals) with the epoxy equivalent weight of 190 g/mol, and 3-glycidyloxypropyltrimethoxysilane (98%, Aldrich Chemicals) were used to synthesize organic-inorganic hybrid materials, with poly(oxypropylene) diamine (Jeffamine D230, Huntsman Corporation) acting both as curing agent for epoxy and as basic catalyst for GLYMO hydrolysis. The materials were used as received. Stoichiometric amount of Jeffamine D230 was added to DGEBA or GLYMO (30 phr and 23.8 phr, respectively). Mixtures were stirred at room temperature in a closed vessel for 90 min. To prepare hybrid materials, DGEBA and GLYMO were blended in weight ratios of 1:2; 1:1; and 2:1 at room temperature in a closed vessel for 90 min. After addition of stoichiometric amount of Jeffamine D230, the mixtures were stirred for another 60 min. Samples were designated according to the mass ratio of GLYMO to DGEBA: G1E2, G1E1 and G2E1 for ratios 1:2, 1:1 and 2:1 respectively, and G1E0 for hybrid material prepared solely from GLYMO. Curing was effected at room temperature for 30 days, making use of air humidity for GLYMO hydrolysis. To determine whether the preparation of hybrids with nanometric level of homogeneity was successful, the materials were inspected by transmission electron microscopy (TEM), in JEOL 200 CX microscope with 120 kV acceleration voltage. The materials were then postcured for 24 h at 120°C in an oven. Weight loss of fully cured samples was measured by thermogravimetric analysis (TGA), using a Perkin Elmer thermobalance TGS-2. Samples weighted at ~10 mg were heated from room temperature to 1000°C at heating rates of 5-25 K min<sup>-1</sup> in a nitrogen gas flow of 150 cm<sup>3</sup>/min.

### 3. Results and discussion

The TEM images of prepared organic-inorganic materials show complete absence of discernible structure even at the highest magnifications (Fig. 1), which indicates nanometric level of dispersion of inorganic phase in organic epoxy-amine matrix and confirms the hybrid nature of material.

#### 3.1. Isoconversional kinetic analysis

To test the possibility of describing the whole degradation process with a single kinetic model, isoconversional kinetic analysis of TGA curves was performed first. Unlike classical model-fitting ones, isoconversional methods do not presume a kinetic model,  $f(\alpha)$ , in order to calculate the activation energy of a reaction, but instead calculate an apparent activation energy directly from the TGA curves. As a result a functional dependence of apparent activation energy on conversion is obtained, which can indicate the complexity of reaction mechanism. Integral isoconversional methods, such as Kissinger-Akahira-Sunose (KAS) [13, 14] or Flynn-Wall-Ozawa (FWO) [15, 16], are suited to analysis of TGA curves since they do not require the experimental data to be differentiated beforehand [17]. As the two integral methods are mathematically equivalent [18], KAS was chosen since it was shown to be correct for a wider interval of activation energies [19].

The conversion,  $\alpha$ , was calculated according to the equation (1), where  $m_0$  is the initial and  $m_\infty$  the final sample mass. The initial loss of mass at temperatures under 300°C, which is ascribed to evaporation of adsorbed moisture, was disregarded.

$$\alpha(T) = \frac{m_0 - m(T)}{m_0 - m_\infty} \quad (1)$$

Activation energy,  $E_a$ , was then calculated for values of  $\alpha$  in 0.05-0.95 range according to KAS equation (2), where  $\beta$  is the heating rate,  $T$  the temperature,  $k_0$  the preexponential factor,  $R$  general

gas constant and  $G(\alpha)$  the integrated form of kinetic model  $f(\alpha)$ . An example of isoconversional plots for the case of unmodified epoxy-amine resin is given in Figure 2.

$$\ln\left(\frac{\beta}{T^2}\right) = \left[ \ln\left(\frac{k_0 R}{E_a}\right) - \ln G(\alpha) \right] - \frac{E_a}{RT} \quad (2)$$

The resulting dependence of  $E_a$  on  $\alpha$  for all investigated systems is displayed in Figure 3. It can be seen that  $E_a$  of unmodified epoxy-amine system is almost constant, and that the dependence grows more complex as GLYMO content in the hybrid materials increases. The values of activation energies fall between those for homolytic scission and dehydration of epoxy-amine resins [6]. The increase of activation energy with GLYMO content is obvious but not linear, which is probably caused by incomplete reaction of epoxy groups in GLYMO with amine as determined in our previous work [9]. The unreacted functional groups act as centres of chain scission and thus lower the activation energy for this reaction [6].

### 3.2. Modelling of degradation kinetics

Degradation of polymer materials often follows a complex mechanism, and elucidating the kinetics for every step is a very demanding procedure. In case the degradation is studied in order to ascertain the processing parameters and appropriate working conditions for the material, the use of simple empirical models in kinetic analysis is justified [20]. Since the degradation of epoxy-amine system itself is complex as previously described, the same complexity was supposed in degradation mechanism of hybrid materials, and flexible empirical  $n^{\text{th}}$  order reaction model (eq. 3) and autocatalytic model (eq. 4) were chosen:

$$\frac{d\alpha}{dt} = k_0 \exp(-E_a / RT)(1-\alpha)^n \quad (3)$$

$$\frac{d\alpha}{dt} = k_0 \exp(-E_a / RT)\alpha^m (1-\alpha)^n \quad (4)$$

where  $d\alpha/dt$  is the rate of reaction, and  $m$  and  $n$  are empirical coefficients.

If  $E_a$  does not vary extremely with conversion, it is possible to describe the whole reaction interval by a single kinetic model even if the real reaction mechanism is complex. Taking into account the conversion interval between 0.2 and 0.8 where  $E_a$  does not vary extremely, an average value of  $E_{a,KAS}$  was calculated for each system to be used in modelling of degradation kinetics (Table 1). The chosen models were fitted simultaneously to experimental datasets obtained at different heating rates (program Wolfram Mathematica 5.0). The average values of  $E_{a,KAS}$  were used as initial values, and if necessary modified to obtain the most satisfying fit. The results of kinetic modelling are displayed in Table 1 and Figure 4.

It can be seen that all hybrid systems follow a degradation mechanism that significantly differs from that of unmodified epoxy-amine system. Obviously the presence of nano-sized inorganic network not only shifts the degradation of hybrid materials to higher temperatures and facilitates char formation [9], but also changes the degradation mechanism. Only unmodified epoxy-amine and G1E0 hybrid system show satisfying fit with  $E_{a,KAS}$ , and those are the systems that displayed the least scatter of  $E_a$  with  $\alpha$  (Fig. 3). In the remaining hybrid systems, the fitted value of  $E_{a,fit}$  is noticeably higher than  $E_{a,KAS}$ , which lead us to suppose that the true reaction mechanism for these systems is even more complex. As kinetic parameters for these three systems vary very little, we suggest that the mechanism of degradation does not differ significantly in spite of major changes in inorganic content. As thermal analysis by itself is insufficient to separate various degradation steps, more powerful experimental methods are to be used to elucidate the degradation mechanism for these systems. G1E0 has lower  $E_{a,fit}$  than the three other hybrids, which implies that the degradation starts more easily, presumably because of the presence of unreacted epoxy groups, but the lower values of  $k_0$  and  $n$  indicate slower course of reaction due to significant interference of the dense inorganic network.

### 3.3. Thermal stability

It is difficult to compare the thermal stability of investigated hybrids solely from the results of kinetic modelling, so other available data were taken from the curves at an arbitrary heating rate (15 K min<sup>-1</sup>) and displayed in Table 2. While the first two parameters, residual weight at 1000°C,  $w$ , and temperature of maximal degradation rate,  $T_{\max}$ , describe just one point of the experimental curve, the integral procedural decomposition temperature [11], IPDT, takes into account the whole degradation process. Both  $w$  and  $T_{\max}$  exhibit the behaviour corresponding to the previously published results [9], with lesser variations that are due to differences in instrument and experimental conditions (heating rate and sample mass). The value of IPDT was found to increase linearly with GLYMO content in hybrid materials (Figure 5), which was to be expected from previously published results [9] and which confirms improved thermal stability of hybrid materials.

## 4. Conclusions

Degradation kinetics of organic-inorganic hybrid materials based on epoxy resin and GLYMO was investigated by TGA. Degradation  $E_a$  was determined by isoconversional KAS method, and kinetics described with empirical models. Hybrid materials have significantly higher  $E_a$  of degradation and follow a different mechanism of degradation than epoxy-amine system, probably due to presence of inorganic network. It was supposed that the true reaction mechanism for these systems is a complex one, with sole exception of G1E0 system. Additional parameters,  $w$ ,  $T_{\max}$  and IPDT were determined, and confirmed increased thermal stability of hybrid materials, which is in accordance with previous investigations.

## **Acknowledgment**

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## Figures

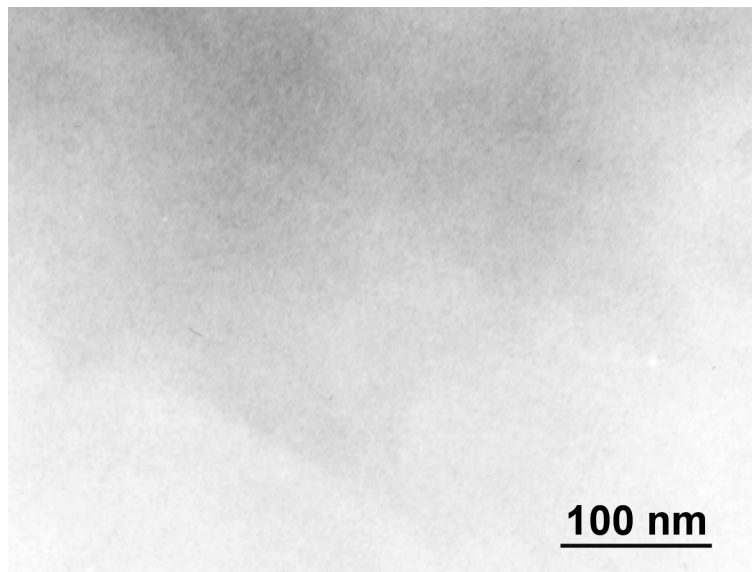


Figure 1. TEM image of G1E1 hybrid material, showing no discernible structure

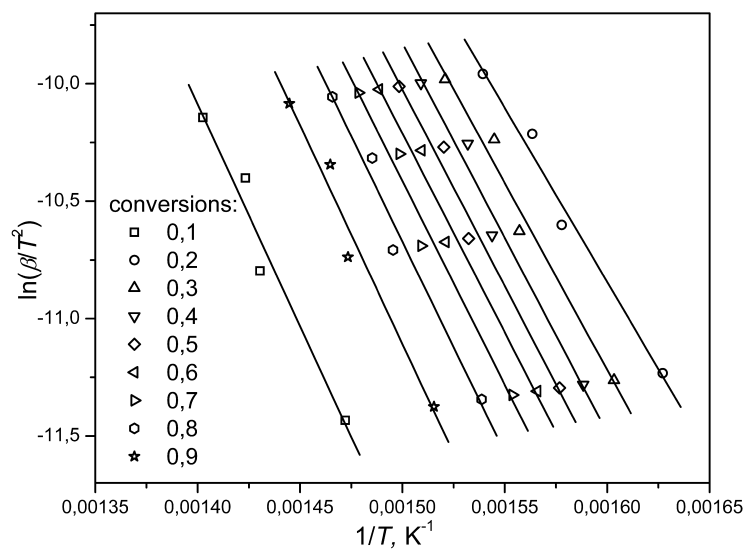


Figure 2. Isoconversional plots used to calculate activation energy at listed conversions by Kissinger-Akahira-Sunose method, for unmodified epoxy-amine system

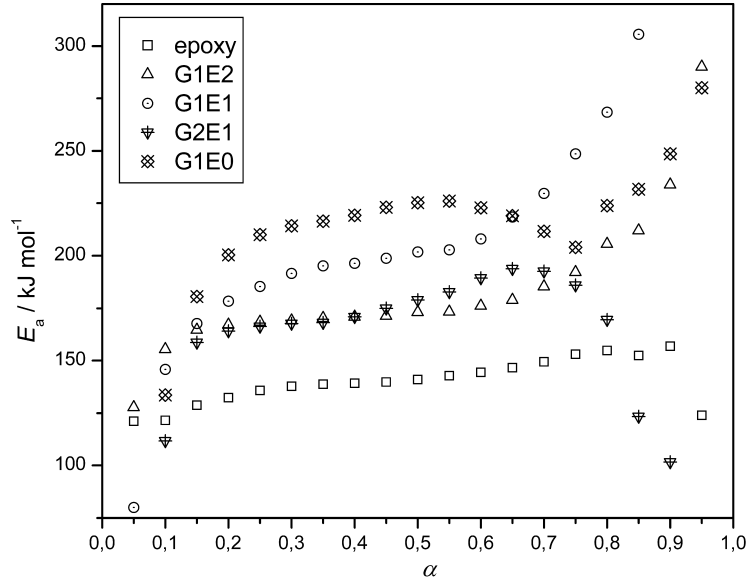


Figure 3. Dependence of apparent activation energy on conversion as obtained by Kissinger-Akahira-Sunose method, for all investigated systems

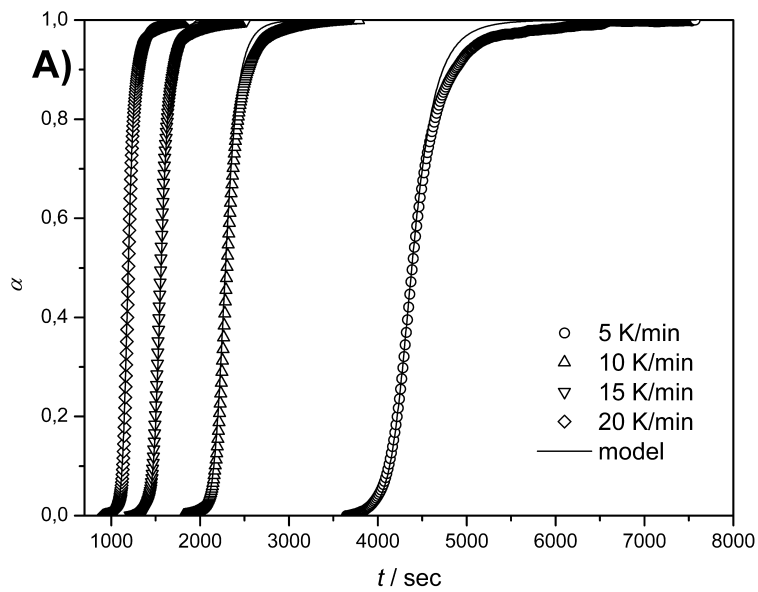


Figure 4. Comparison of experimental data with kinetic models obtained for investigated systems for all heating rates: A) unmodified epoxy-amine system; B) hybrid G1E2 system; C) hybrid G1E1 system; D) hybrid G2E1 system; E) hybrid G1E0 system

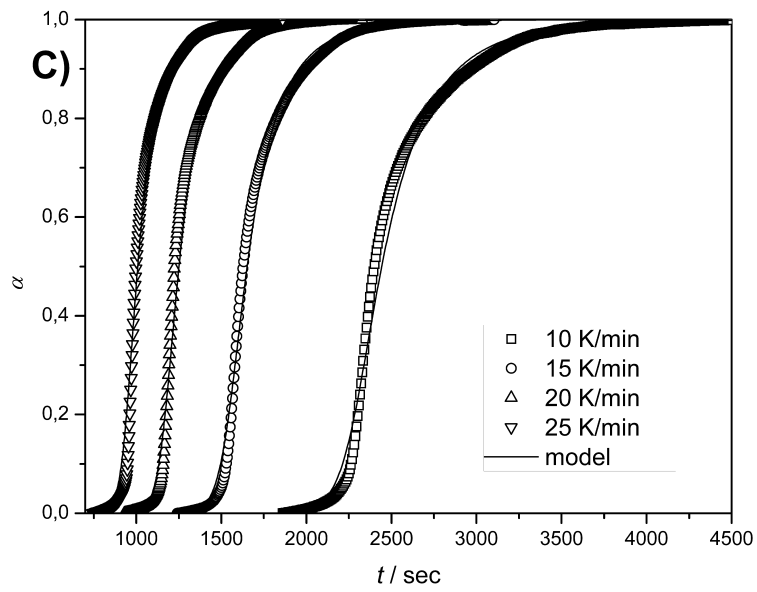
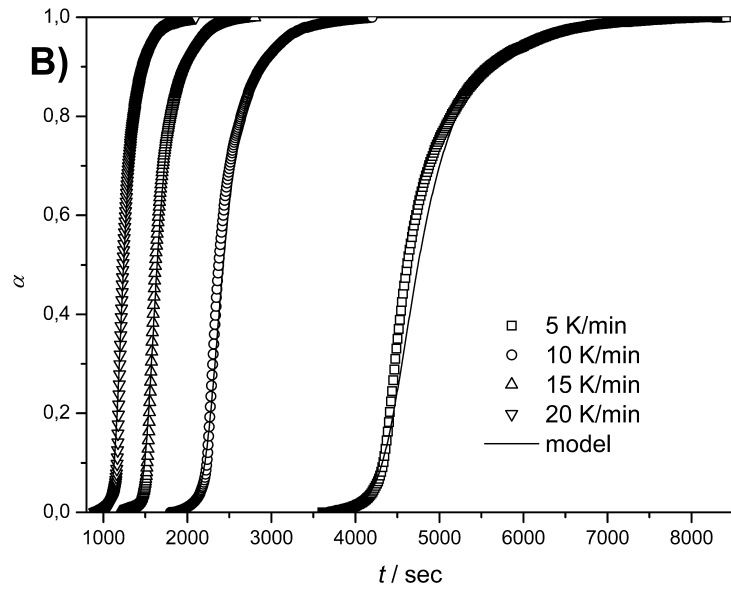


Figure 4. continued

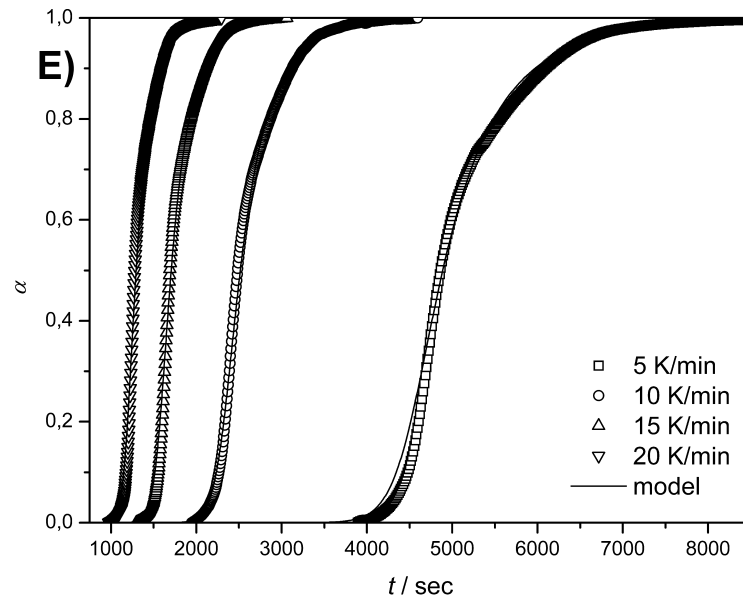
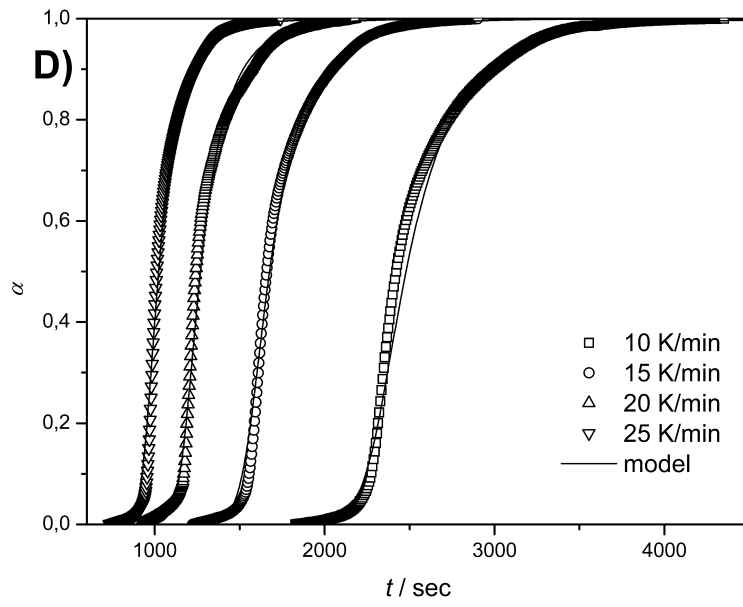
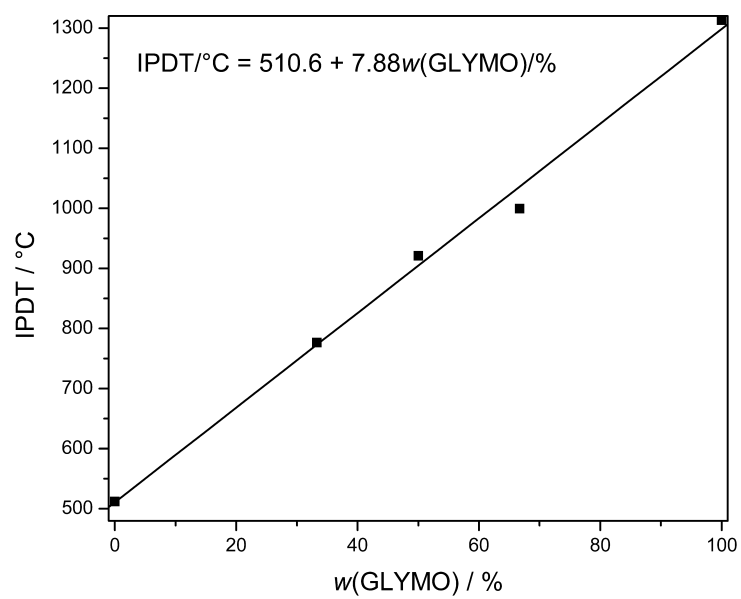


Figure 4. continued



*Figure 5.* Linear dependence of integral procedural decomposition temperature, IPDT, on GLYMO content in material

Table 1. Activation energy ( $E_a$ ), preexponential factor ( $k_0$ ) and empirical exponents  $m$  and  $n$  for given systems and models

| <b>System</b> | $E_{a,KAS} / \text{kJ mol}^{-1}$ | $E_{a,fit} / \text{kJ mol}^{-1}$ | $k_0 / \text{s}^{-1}$ | $m$  | $n$  | <b>Model</b> |
|---------------|----------------------------------|----------------------------------|-----------------------|------|------|--------------|
| epoxy         | 143                              | 143                              | exp(22.3)             | 0.60 | 1.84 | (eq. 4)      |
| G1E2          | 177                              | 276                              | exp(45.4)             | --   | 3.90 | (eq. 3)      |
| G1E1          | 209                              | 263                              | exp(42.8)             | --   | 3.90 | (eq. 3)      |
| G2E1          | 177                              | 271                              | exp(44.1)             | --   | 4.20 | (eq. 3)      |
| G1E0          | 217                              | 217                              | exp(33.8)             | --   | 3.84 | (eq. 3)      |



Table 2. Residual weight at 1000°C ( $w$ ), temperature of maximal degradation rate ( $T_{\max}$ ) and the integral procedural decomposition temperature (IPDT) for given systems, at heating rate of 15 K min<sup>-1</sup>

| <b>System</b> | <b><math>w</math> / %</b> | <b><math>T_{\max}</math> / °C</b> | <b>IPDT / °C</b> |
|---------------|---------------------------|-----------------------------------|------------------|
| epoxy         | 7.62                      | 389                               | 512              |
| G1E2          | 19.85                     | 391                               | 777              |
| G1E1          | 25.47                     | 395                               | 921              |
| G2E1          | 28.06                     | 402                               | 999              |
| G1E0          | 35.38                     | 410                               | 1313             |