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# Curing of epoxy/novolac system modified with reactive liquid rubber and carbon filler

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## Summary

The curing behaviour of epoxy resins modified with reactive liquid rubber, using a novolac resin as a hardner was studied by means of differential scanning calorimetry in isothermal (100, 130 and 150°C) and non-isothermal conditions (2, 5, 10 and 15°C $\text{min}^{-1}$). The influence of carboxyl- (CTBN) and epoxy- (ETBN) terminated butadiene-acrylonitrile copolymers on the kinetic parameters and glass transition temperature ($T_g$) of cured epoxy systems was determined. The effect of grinded bituminous coal as an organic filler into epoxy network was also investigated. The carboxyl-end groups strongly enhanced the curing rate, in contrast to the epoxy-terminated rubber (ETBN) that had only a minor effect on the curing reactions. The presence of coal accelerated curing in its early stage. The $T_g$ of completely cured epoxy was practically unaffected by the presence of carbon filler and reactive rubbers and was equal about 132°C. The apparent curing activation energies were determined. A smaller activation energy was observed only for CTBN/epoxy/novolac system. The effect of reactive rubber and coal on the Charpy impact resistance of cured epoxy systems was also discussed.

## Introduction

Epoxy-phenolic resins are very important thermosetting polymers used as a matrix component for high performance fibre or powder containing composites [1-5]. This material combines the properties of phenolic resin (low cost, high impact resistance and hardness) and properties of epoxy resin (flexibility and low shrinkage) [6]. The epoxy compounds containing new or modified additives and/or fillers offer possibilities as materials with special properties or new combination of properties. The disadventageous decrease in the impact strength of filled epoxies can be minimized by introducing elastomeric materials [7,8]. Numerous works have been carried out on the toughening of epoxy materials by introduction of soft or rigid particles [8-15], but most often the flexible copolymers like liquid rubbers based on the carboxyl-terminated (CTBN) and epoxy-terminated butadiene-acrylonitrile (ETBN) were used for modification of epoxy resins [8-11].

The first works in the field of the epoxy-phenolic resin were conducted by Schechter and Wynstra [16]. They investigated the reactions between the epoxy and polyphenols and proposed to take two reaction into account: one between phenol hydroxyl and epoxy groups, and the other between secondary hydroxyl generated from the opening of the oxirane group and the epoxy group. Gualpa and co-workers [6] studied novolac and epoxy reaction by means of differential scanning calorimetry. They observed only one peak in dynamic thermograms at different heating rates, both reactions ocurred simultaneously.

Extensive discussions on the curing kinetics studied by thermal analysis were published by Prime [17] and other authors [18,19]. The particle size and concentration of rubber also depend on the curing and interactions between the rubber and epoxy resin [8,9]. Wise and co-workers [19] studied the epoxy resin modified with carboxyl functionalized butadiene-acrylonitryle rubber and cured with diaminodiphenylomethane. They suggested that the accelerating effect on the rate of crosslinking reaction appeared to be principally caused by the carboxyl end-groups present in CTBN molecules. To avoid this effect, CTBN rubber is often prereacted with an excess of diepoxide. The resulting ETBN adduct participates in the curing with diamine and rubber-rich domains bonded to the matrix are created. In experiments on a similar system, where the CTBN rubber was pre-reacted with the epoxy, Verchere et al. [20] reported that there was only a relatively small change in the reaction rate of the rubber containing epoxy/amine systems, as compared to the unfilled system. The effect of different fillers such as silica, kaolin, glass beads or $CaCO_3$ fillers on the properties of polymeric materials was presented by many authors [see, e.g. ref. 21-24]. Some reports illustrated the advantages of hybrids structures being the combination of rubber particles and fillers in toughening epoxy matrices [25].

New possibilities for controlling properties of composites based on thermosets are opened up by using non-traditional fillers such as powdered carbon materials [26-28]. In our work, bituminous coal was used as organic filler. It is a naturally occurring mineral of high strength and good thermal stability. Its effect on the morphology, rheology, thermo-mechanical properties and impact strength of rubber-modified epoxy networks was already described [28,29]. If coal were regarded as an aromatic macromolecular material with functional groups attached to its surface, a coal-based material could be obtained using typical methods of polymer modification, such as grafting, blending, and filling [27,30]. This paper reports on the effect of both the carboxy-terminated and epoxy functionalized butadiene-acrylonitrile copolymers on the rate of curing epoxy resins with novolac. The influence of the coal particles was also investigated. The studied epoxy/novolac series with epoxy-terminated rubber and coal particles was applied as a matrix component for short fibres and powder containing composites. Besides the influence of the liquid rubbers and coal on kinetic parameters and $T_g$, the fracture properties of epoxy materials are mentioned.

## Experimental

### *Materials*

The epoxy resin used was a commercial grade prepolymer of diglycidyl ether of bisphenol A (EP) kindly supplied by Shell Co., as Epikote 827, with an epoxide equivalent weight (EEW) of 181.8. Phenol-formaldehyde novolac (NZ) obtained from Chemical Plants in Nowa Sarzyna (Poland) was used as the curing agent ($T_m$ = 66°C,

$M_n$ = 570 g mol$^{-1}$). 2-Ethyl-4-methylimidazole (0.3 wt.% EMI, Merck) was a catalyst. Two kinds of end-functionalized rubbers were used. The first was carboxyl terminated butadiene-acrylonitrile copolymer Hycar CTBN 1300X8 (BF-Goodrich) with 18% acrylonitrile content and molecular weight of 3550 g/mol. The other one was an epoxy terminated copolymer (ETBN), which was prepared by reacting the carboxyl groups of the CTBN with an excess of epoxy resin, in the presence of triphenylphosphine (TPP, Fluka) as catalyst at 80°C [11,18,31]. The content of CTBN and ETBN rubber (the latter expressed in relation to that of CTBN) in epoxy matrix was 6 wt.%. This amount of rubber was established in preliminary experiments carried out for rubber content varied from 0 to 16 wt.% [27,28]. Polish coal of a medium rank from Bielszowice mine was used as a filler. The basic characteristics of the coal as obtained by the ultimate analysis are: 83.6% C; 4.5% H; 11.9% O+N+S; 3.6% ash, moisture 0.5% wt., density 1.38 g/cm$^3$, BET surface area 5.5 cm$^2$/g, the particles size 20-90 μm.

### *Sample preparation*

The curing agent was not soluble in epoxy prepolymer at room temperature and therefore, the stoichiometric amounts of novolac and epoxy resin calculated according to their functionality were heated up to 80°C and mixed together until clear mixture was obtained. After degassing, the catalyst was added. Then the epoxy/novolac mixture was quickly frozen and stored in refrigerator.

Rubber-filled samples were prepared by first dissolving CTBN or ETBN rubber in epoxy resin at approximately 80°C. Than, the procedure was similar to that applied for unfilled epoxy samples. The coal-filled samples were prepared by mixing epoxy resin with grinded filler. The weight fraction of coal was 16%. The starting sample of coal was fine powdered to 0.1 mesh pass, degassed and vacuum dried. Dispersion of coal in epoxy prepolymer was achieved with a high-speed stirrer at 100°C for 6h. The rubber-modified epoxy samples filled with coal were prepared by first mixing the epoxy resin with coal at 100°C and then adding rubber. Epoxy resin filled with coal and containing rubber was then mixed with novolac and catalyst as described above.

### *Measurements*

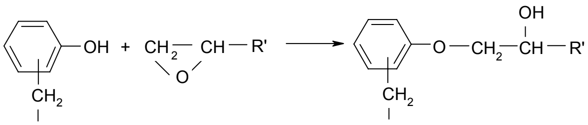
Calorimetric measurements were carried out using a differential scanning calorimeter (TA Instruments DSC 2920) in a dry nitrogen atmosphere (50 ml/min). Calibration was carried out with a high purity indium. Small quantities of the sample of about 7 mg were placed in nonhermetical aluminum pans. Samples were cured isothermally in the DSC instrument. Isothermal experiments were conducted in 100, 130, 150°C. After completing the isothermal curing runs, the partially cured epoxy samples were quenched using liquid nitrogen to about –50°C and then reheated to 250°C at 10°C/min in order to determine the residual heat and glass transition temperature ($T_g$). The integrated area under the exothermic peak was used to calculate the heat of reaction. The $T_g$ was measured as the inflection point of heat flow, when the polymer passed from glass to rubbery state. A fractional conversion $\alpha$ was calculated as the ratio of the residual heat $\Delta H_{res}$ and the total heat $\Delta H_{tot}$, according to the equation:

$$\alpha = \frac{\Delta H_t}{\Delta H_{tot}} = \frac{\Delta H_{tot} - \Delta H_{res}}{\Delta H_{tot}} \qquad \textbf{(1)}$$

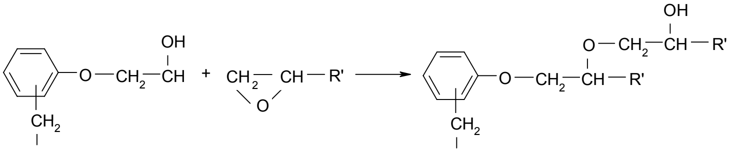
The total heat of cure $\Delta H_{tot}$ was established from dynamic scan carried out for uncured epoxy/novolac conducted at 10°C min$^{-1}$. The glass transition of uncured epoxy system was determined from the first scanning run and the inflection point at this transition was denoted as $T_{g0}$. The glass transition temperature of the completely cured epoxy system was designated as $T_{g\infty}$ and determined during the second heating mode. The temperature was also scanned at different heating rates. Dynamic runs at 2, 5, 10, and 15°C min$^{-1}$ were conducted and the results were used to evaluate the apparent activation energy for curing, according to the Kissinger and Flynn-Wall-Ozawa models [32-34].

## Results and discussion

DSC is extensively used for investigating the curing of thermosets. In isothermal and non-isothermal mode it measures the heat generated during curing as a function of time and temperature. The following reactions were taken into account for epoxy resin cured with novolac:



(1)



(2)

After characterizing the unfilled epoxy/novolac system, which served as a reference, the analysis of rubber and coal-filled epoxy mixtures were carried out. Table 1 summarizes the total heat of curing at 10°C min$^{-1}$, the glass transition temperature of uncured and completely cured epoxy systems and the corresponding changes of heat capacity. Since the dynamically cured samples have not shown any noticeable residual heat in the second heating run, we assumed that the cure reaction reached completion under non-isothermal conditions.

Table 1. Summary of results obtained from dynamic-heating experiments for epoxy/novolac systems

| Epoxy system | $\Delta H_{tot}$ (J·g$^{-1}$) | $T_{g0}$ (°C) | $\Delta c_{p0}$ (J·g$^{-1}$· K$^{-1}$) | $T_g^{\infty}$ (°C) | $\Delta c_{p\infty}$ (J·g$^{-1}$· K$^{-1}$) |
|---|---|---|---|---|---|
| EP/NZ | 275.7 | 0.6 | 0.86 | 131.9 | 0.238 |
| EP/NZ /CTBN | 271.9 | 1.5 | 0.67 | 133.1 | 0.296 |
| EP/NZ /ETBN | 252.5 | 0.3 | 0.73 | 131.9 | 0.391 |
| EP/NZ /coal | 263.6 | 2.7 | 0.60 | 132.0 | 0.343 |
| EP/NZ /ETBN/coal | 267.1 | -0.5 | 0.59 | 129.4 | 0.355 |

As can be seen from Table 1, the overall heat evolved in the curing process does not vary too much. The values are practically not influenced by the presence of rubber and coal. This means that the main reaction mechanism does not seem to be changed by the presence of reactive rubbers and coal in the epoxy/novolac system. The rubber initially dissolves in epoxy resins, but separates during cure in the form of discrete particular phase. The glass transition temperature of fully cured epoxies and the final reaction state appear not to be affected by rubber and filler, as well. The $T_{g\infty}$ of the unfilled epoxy/novolac is 132°C and that for the resin modified with CTBN is equal to 133°C. The $T_{g\infty}$ of the ETBN-modified system is the same as for unfilled epoxy/novolac. Our earlier investigations showed no apparent change of $T_g$ in completely cured epoxy/novolac systems containing up to 29 wt.% of coal [27,28].

Contrary to the lack of effect of coal on $T_g$ of epoxy materials, an influence of powdered coal on the curing reactions of epoxy resin with novolac resin was noticable. The presence of coal and CTBN rubber slightly increased the glass transition temperature of uncured epoxy ($T_{g0}$). A step change in $c_p$ ($\Delta c_p$) reflects the difference in mobility of polymeric chains between the glassy and rubbery states. The magnitude of the change in $c_p$ is sometimes used as an indication of the glass transition intensity. Naturally, due to the increase of crosslink density, the jump in $c_p$ is lower for cured epoxy systems compared with that for uncured samples. The intensity of glass transition for the completely cured epoxy mixtures modified with rubber and coal increase as compared to the plain epoxy/novolac system.

Figure 1 show the dynamic DSC runs for unfilled epoxy/novolac mixtures (curve 1), in the presence of CTBN and ETBN (curves 2 and 3) for the coal-filled system (curve 4) and for ETBN/coal epoxy system (curve 5).

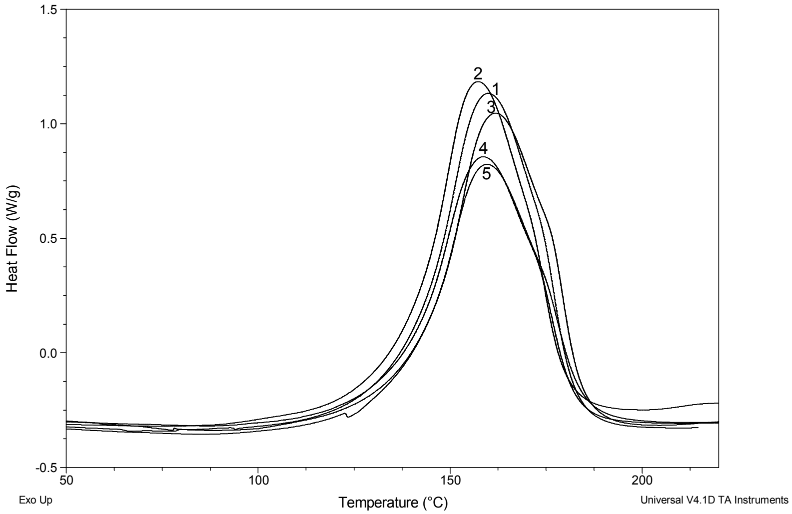


Figure 1. Heat flow as measured by DSC during the cure at 10°C min$^{-1}$ for 1: unfilled EP/NZ system; 2: EP/NZ with CTBN; 3: EP/NZ with ETBN; 4: EP/NZ with coal; 5: EP/NZ with coal and ETBN.

We observed only one peak in dynamic thermograms also at different heating rates, both when curing were carried out in neat epoxy/novolac system and in the system modified with rubber or/and coal. The reaction onset temperature and the exothermic peak temperature at 10°C min$^{-1}$ heating rate were found to be lower for the epoxy resin modified with 6 wt.% of CTBN. The peak temperature decreased from 160°C for the plain epoxy/novolac formulation down to 157°C for CTBN/epoxy system. The thermogram of a mixture containing 6 wt.% of ETBN is also shown in Figure 1 for the sake of comparison with the effect of the presence of CTBN. No visible shift of the peak temperature for epoxy/novolac sample modified with ETBN as compared to that of the non-modified system can be observed. The temperature of exothermic peak for coal-filled epoxy is also practically the same as for the unfilled epoxy/novolac composition.

The dynamically cured samples in the second heating run don't show any residual heat, only the inflection point of heat flow taken as the $T_g$ as it can be seen in Figure 2.

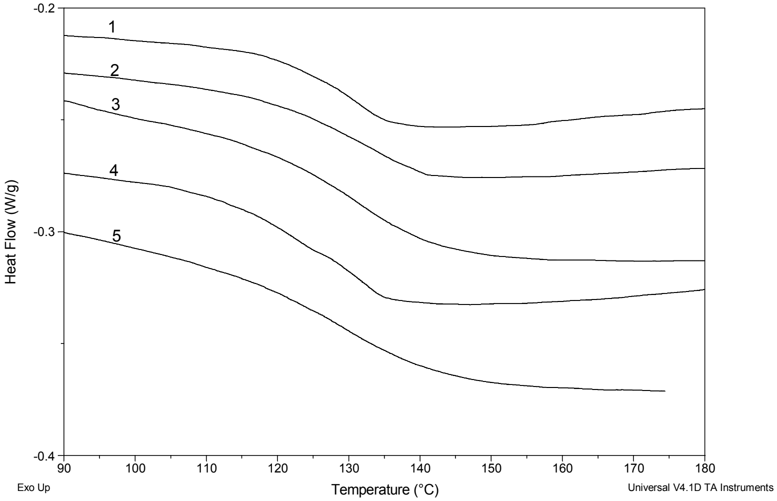


Figure 2. The heat flow during second runs at 10°C min$^{-1}$ for 1: unfilled EP/NZ system; 2: EP/NZ with CTBN; 3: EP/NZ with ETBN; 4: EP/NZ with coal; 5: EP/NZ with coal and ETBN.

By measuring the variations of temperature corresponding to the maximum of exothermic peak for different heating rates, one can calculate the apparent activation energy of curing. The temperature of peak, $T_{max}$, in DSC thermograms at different heating rates are compared in Table 2 for the epoxy/novolac systems studied.

Table 2. The non-isothermal DSC data at different heating rates for epoxy/novolac systems

| Epoxy system | Peak temperature (°C) | | | |
|---|---|---|---|---|
| | $q$= 2°C min$^{-1}$ | $q$= 5°C min$^{-1}$ | $q$= 10°C min$^{-1}$ | $q$= 15°C min$^{-1}$ |
| EP/NZ | 130.7 | 147.0 | 160.0 | 168.1 |
| EP/NZ /CTBN | 127.7 | 144.1 | 157.1 | 166.5 |
| EP/NZ /ETBN | 130.8 | 146.9 | 159.9 | 169.0 |
| EP/NZ /coal | 129.4 | 145.7 | 158.5 | 167.4 |
| EP/NZ/ETBN/coal | 129.2 | 146.4 | 159.8 | 167.8 |

As it is shown in Table 2, the peaks shift to higher temperature as the heating rate increases. It can be seen that the temperature of peak for each composition at respective heating rate do not much differ from each other, except for the epoxy/novolac composition modified with CTBN. In this case, the $T_{max}$ moves towards high temperature somewhat slower than the peaks for other compositions, apparently due to the presence of carboxyl groups.

By using the Kissinger approach [32] (eq. 2):

$$\frac{d[\ln q / T_{max}^2]}{d(1/T_{max})} = -\frac{E}{R} \tag{2}$$

and Flynn-Wall-Ozawa method [33, 34] (eq. 3):

$$\log q = \log\left[\frac{AE}{g(\alpha)R}\right] - 2.315 - \frac{0.457E}{RT_{max}} \tag{3}$$

the activation energy, $E$, was calculated from the temperatures of maximum peak at different heating rates. In these equations $T_{max}$ is the maximum peak temperature, $q$ is the heating rate, $R$ is the gas constant, and $A$ is the pre-exponential factor.

According to, the plot of $\ln(q/T_{max}^2)$ versus $1/T_{max}$ gives the activation energy without any specific the Kissinger equation assumption on the conversion level. The Flynn-Wall-Ozawa method provides the activation energies for different conversions, $\alpha$. In the present study, the latter method was applied only to the maximum rate where the peak appears. The values of activation energy for the epoxy systems studied as determined using the two models are presented in Table 3.

Table 3. The activation energies calculated using the Flynn-Wall-Ozawa and Kissinger methods for epoxy/novolac systems

| Epoxy system | Activation energy (kJ·mol$^{-1}$) | |
|---|---|---|
| | Flynn-Wall-Ozawa | Kissinger |
| EP/NZ | 76.2 | 73.1 |
| EP/NZ /CTBN | 72.6 | 69.4 |
| EP/NZ /ETBN | 74.7 | 71.6 |
| EP/NZ /coal | 75.1 | 72.1 |
| EP/NZ /coal/ETBN | 74.6 | 71.5 |

The activation energies determined by the Flynn-Wall-Ozawa method are higher than those obtained from the Kissinger model. A slight decrease in the activation energy calculated using both models was observed for CTBN-modified epoxy system. The carboxyl terminated rubber has an accelerating effect on the curing rate of the epoxy/novolac mixture. The activation energy for ETBN/epoxy system seems to be almost the same as that for non-modified epoxy. The energy of activation is also not affected by bituminous coal in filled epoxy/novolac formulation.

Further information about the curing kinetics was obtained by using the isothermal DSC measurements. The comparison of isothermal results should confirm the accelerating effect of carboxyl-terminated rubber. The curing in this latter epoxy system proceeds, as was mentioned above, through an autocatalytic mechanism with the maximum rate for the conversion region of 50-60%. To take into account the autocatalytic reaction with non-zero initial reaction rate, Kamal [35] proposed the generalized expression:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1-\alpha)^n \tag{4}$$

where $k_1$ and $k_2$ are the rate constants with two different activation energies and $m$ and $n$ are the reaction orders.

Figure 3 shows a series of isothermal reaction rate curves at 130°C as a function of time for the epoxy/novolac mixture without modifiers (curve 1) and in the presence of CTBN and ETBN (curves 2 and 3). The shapes of these plots are similar to those observed for other epoxy matrices and typical for an autocatalytic process, with the maximum rate of conversion after the start of the reaction The maximum of the peaks obtained for rubber-modified epoxy compositions were shifted to shorter time, especially for the system with CTBN.

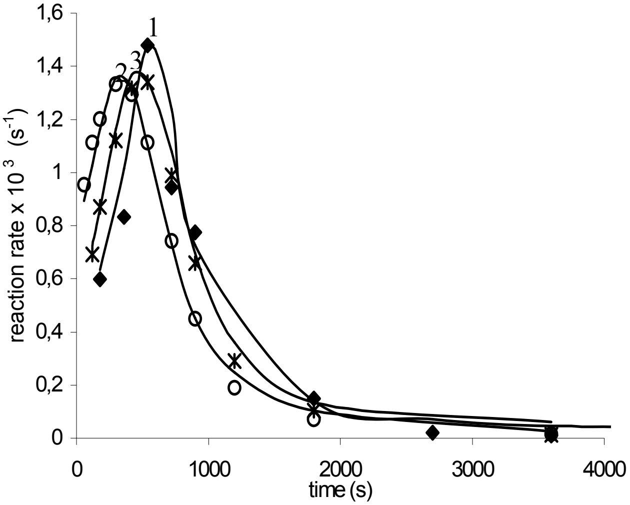


Figure 3. Isothermal reaction rate curves as a function of time at 130°C for 1: unfilled EP/NZ system; 2: EP/NZ with CTBN and 3: EP/NZ with ETBN.

The effect of the coal filler on the reaction rate as a function of time for epoxy/novolac system and system containing epoxy-terminated rubber is shown in Figure 4.

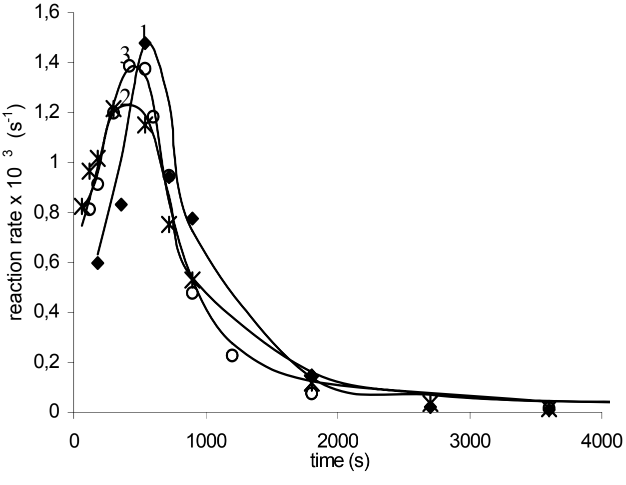


Figure 4. Isothermal reaction rate curves as a function of time at 130°C for 1: unfilled EP/NZ system; 2: EP/NZ system filled with coal and 3: EP/NZ system with ETBN and coal.

The maximum reaction rate for the coal/epoxy and ETBN/coal/epoxy system are shifted to the shorter time, in comparison to unfilled epoxy material. The magnitude of reaction rate peak decreases for epoxy/ETBN composition with coal as compared to the neat epoxy/novolac system.

The kinetic parameters were calculated by fitting the experimental data to eq. (4), depending on the composition and the curing temperature. The constant $k_1$ was graphically determined as the initial rate at time equal 0, given by the intercept of the reaction rate versus time plot. The rate constant, $k_1$ and $k_2$ were assumed to be constant at a given temperature and following an Arrhenius equation form. The resulting data are summarized in Table 4.

Table 4. Kinetic parameters of epoxy/novolac formulations following autocatalytic kinetic model

| Epoxy system | Temperature (°C) | $k_1 \cdot 10^3$ ($s^{-1}$) | $k_2 \cdot 10^3$ ($s^{-1}$) | $m$ | $n$ | Average $m$ value | Average $n$ value |
|---|---|---|---|---|---|---|---|
| EP/NZ | 100 | 0.05 | 1.25 | 1.5 | 1.4 | 1.5 | 1.3 |
| | 130 | 0.49 | 7.79 | 1.6 | 1.5 | | |
| | 150 | 2.64 | 13.65 | 1.3 | 1.1 | | |
| EP/NZ/CTBN | 100 | 0.17 | 0.75 | 1.1 | 1.2 | 1.1 | 1.1 |
| | 130 | 0.79 | 3.65 | 1.0 | 1.0 | | |
| | 150 | 3.89 | 9.13 | 1.1 | 1.1 | | |
| EP/NZ/ETBN | 100 | 0.06 | 0.48 | 1.1 | 1.2 | 1.1 | 1.1 |
| | 130 | 0.56 | 4.11 | 1.1 | 1.0 | | |
| | 150 | 2.87 | 8.52 | 1.2 | 1.1 | | |
| EP/NZ/coal | 100 | 0.09 | 1.65 | 1.5 | 1.4 | 1.5 | 1.3 |
| | 130 | 0.81 | 9.55 | 1.6 | 1.5 | | |
| | 150 | 3.71 | 16.62 | 1.3 | 1.1 | | |
| EP/NZ/coal/ETBN | 100 | 0.08 | 0.51 | 1.2 | 1.1 | 1.3 | 1.1 |
| | 130 | 0.64 | 4.21 | 1.3 | 1.1 | | |
| | 150 | 2.96 | 9.25 | 1.4 | 1.1 | | |

The reaction orders were determined by averaging values estimated of all isothermal experiments. The results presented in Table 4 show the rate constants to be affected both by the presence of reactive rubber and coal filler. The parameter $k_1$ is associated with both the noncatalytic and catalytic reactions because of the presence of functional groups in the initial formulations. Here, the effect of carboxyl groups becomes evident. The initial rate of cure for CTBN/epoxy/novolac formulation is higher by a factor of two as compared with that for non-modified epoxy/novolac system. However, $k_2$ of the CTBN-modified composition was lower due to formation of CTBN phase dispersed in continuous epoxy matrix.

In the experiments on the similar composition, but with CTBN rubber pre-reacted with epoxy groups to yield ETBN rubber, the curing rate was not much changed as compared to that for unmodified system, what is very important from viewpoint of later processing. Naturally, the reaction rate constants are sensitive to temperature. As expected, the kinetic constants $k_1$ and $k_2$ increase as the reaction temperature rises.

The presence of coal in epoxy system alters the reaction rate at the initial part of cure. The active groups existing on the surface of coal seem to catalyze the reaction. The parameter $k_1$ for the coal-filled epoxy system increases as compared to the unfilled one. Probably, like other hydrogen-bond donors, the groups on coal surface participate in the opening of epoxy rings. As already shown, epoxy monomers could be grafted on the surface of coal, but the extent of grafting depends on the coal rank, and reaction conditions [26,27,30].

The thermal properties of coal were characterized by dynamic DSC carried out for neat powdered filler. Figure 5 shows the first and second DSC runs for the grinded coal. The exothermic peak observed in the first scan disappeared from the second scan. Some volatile matter might be released during heating and coal might pass through structural rearrangement. Thus, it was found that coal used in this study did not show any transition up to 250°C.

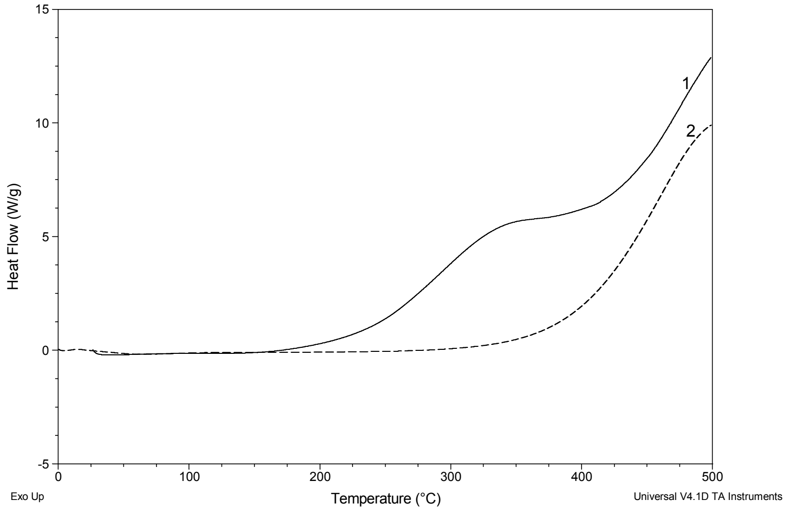


Figure 5. DSC thermograms of bituminous coal used as a filler to epoxy resin; 1: first scan at 10°C $min^{-1}$, 2: second scan at 10°C $min^{-1}$.

Two activation energies representing curing reactions were determined from the kinetic rate constants, $k_1$ and $k_2$ using the Arrhenius plot. The activation energies, $E_1$ and $E_2$, as well as the pre-exponential factors, $A_1$ and $A_2$ associated with the constants $k_1$ and $k_2$ for the plain epoxy/novolac system and its mixtures with rubber and coal are presented in Table 5.

Table 5. Activation energies and pre-exponential factors calculated from Arrhenius plots for epoxy/novolac systems

| Epoxy system | $E_1$ (kJ·mol$^{-1}$) | $E_2$ (kJ·mol$^{-1}$) | ln$A_1$ | ln$A_2$ |
|---|---|---|---|---|
| EP/NZ | 98.2 | 65.8 | 21.9 | 14.6 |
| EP/NZ /CTBN | 80.9 | 61.0 | 17.3 | 13.8 |
| EP/NZ /ETBN | 99.6 | 74.7 | 22.4 | 16.5 |
| EP/NZ /coal | 98.1 | 64.0 | 22.2 | 14.4 |
| EP/NZ /coal/ETBN | 94.5 | 69.2 | 21.0 | 15.0 |

The epoxy/CTBN system exhibits somewhat lower activation energy, particularly at the initial step of curing ($E_1$). The activation energies at the initial stage for the ETBN/epoxy and coal/epoxy systems are almost the same as for the unfilled epoxy composition. The values of activation energy related to the late stage of curing ($E_2$) for ETBN/epoxy material increase as compared to the non-modified epoxide.

The disaccord in the values of activation energies determined for isothermal and non-isothermal cure of epoxy/novolac systems can be attributed to the difference in temperature conditions in the two procedures. Similar differences between activation energies obtained in isothermal and dynamic curing were described in literature [36,37] for epoxy systems cured using different agents.

## Appendix

The rigid particles of filler usually induce an increase in thermal resistance of polymeric materials. The thermal stability of coal/epoxy considerably increased, especially at high temperature [27], but we observed typical fracture behaviour as for other particulate filled materials. The coal-filled epoxy matrix became more stiff and brittle. The Charpy impact behaviour of fully cured epoxy/novolac systems modified with different liquid rubbers used as toughening agent was examined earlier [29] and it was confirmed that rubbers improve the fracture properties of epoxies. To determine the influence of powdered coal on fracture energy, the Charpy impact tests were carried out according to ASTM D 256–88 for epoxy and ETBN/epoxy filled with coal. The single-edge notched samples (cured 6h at 150°C and 4h at 180°C) with dimensions of approximately: 80, 10 and 4 mm were tested using Charpy hammer with 1J pendulum. The impact energy to break for neat epoxy was 1.8 kJ $m^{-2}$ and that for ETBN/epoxy was equal 4.4 kJ $m^{-2}$. The impact resistance of for coal-filled epoxy decreased to 1.2 kJ $m^{-2}$. The introduction of liquid rubber improves the fracture properties of epoxy/coal material to a certain degree. The impact strength for hybrid ETBN/coal/epoxy was found to be 2.2 kJ $m^{-2}$.

## Conclusions

The effect of both elastomer, used as an impact strength modifier and coal as an organic filler on the curing behaviour of epoxy/novolac system was investigated by using dynamic scanning calorimetry technique. The autocatalytic kinetic model was used to calculate kinetic parameters of curing. For the non-isothermal curing the analysis was performed using two models: the Kissinger and Flynn-Wall-Ozawa ones. The results show, that modification of epoxy/novolac system with carboxyl functionalized liquid rubber does indeed affect the kinetic parameters of cure as compared to those for the plain epoxy mixture. Differences were observed in curing behaviour of CTBN and ETBN-modified systems. A clearly pronounced effect of CTBN content was noted. The initial rate of curing increased by a factor of two, as compared to that of unmodified epoxy/novolac system, whereas the rate constant $k_2$ of the CTBN-modified epoxy system was reduced due to formation of CTBN domains. From point of view of later processing is very advantageous that the reaction rate observed for ETBN/epoxy/novolac mixture was almost the same, as in non-modified system. The functional groups on the coal surface seem to affect the kinetic parameters of the cure of coal-filled system. It was shown that coal accelerates the epoxy-novolac reactions at early stages. The reaction rate for coal-filled epoxy composition slows down at further stages, but the $T_g$ of completely cured epoxy/coal system was unchanged in comparison to that of plain epoxy network. The apparent activation energies of cure reactions were found almost the same for unfilled and coal-filled epoxy matrix. A smaller activation energy as determined using both isothermal

(Arrhenius plot) and non-isothermal (the Kissinger and Flynn-Wall-Ozawa models) curing was observed for CTBN/epoxy/novolac series. On the contrary, the activation energy for ETBN-modified epoxy composition at the early stage of curing was almost the same, but at the later stages some increase of activation energy was noted both in relation to the non-modified epoxy system. The $T_g$ of completely cured hybrid epoxy system was not affected by modification with both coal and reactive rubber in comparison to that of non-modified epoxy/novolac material. Impact measurements show that the introduction of liquid rubber significantly improves the fracture resistance.

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