

DYNAMIC MECHANICAL PROPERTIES OF EPOXY/NOVOLAC SYSTEM MODIFIED WITH REACTIVE LIQUID RUBBER AND CARBON FILLER

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This paper reports on the work carried out to evaluate the frequency dependent viscoelastic properties of epoxy/novolac composites modified with a liquid reactive rubber and carbon filler. For epoxy systems modified with elastomer, three typical transitions were observed: the α -relaxation deeply related to the glass transition of epoxy, the β -transition of epoxy, and the glass transition of rubber appeared near to the β -relaxation of epoxy resin. Considering an Arrhenius equation, the activation energies of β -relaxation were estimated. In the region of glass transition and rubbery state the temperature dependence of the shift factor (a_T) was determined through Williams–Landel–Ferry (WLF) equation.

Keywords: activation energy of molecular relaxation, dynamic mechanical thermal analysis, epoxy resins, fillers, reactive rubber, WLF equation

Introduction

Epoxy resins are used as structural matrices for high performance composites as they are stiff at relatively high temperature [1–3]. The resins compounded with new or modified fillers offer excellent possibilities to produce matrices possessing special properties or new combinations of properties. Typical fillers such as: talc, calcium carbonate, silica, glass beads and powdered metals are usually used for this purpose [4–11]. The presence of finely ground filler well dispersed in polymer network can change its structural organization and physico-mechanical characteristics [2, 12]. The high heat-resistance of filled epoxies is one of the key factors making them an attractive matrix for high-tech composites. The disadvantage is that they are brittle and exhibit poor resistance to crack propagation and, consequently, low impact strength. For a long time, extensive use was made of the modification of epoxy polymers by introducing elastomeric materials. This provided satisfactory improvement and satisfied the major impact resistance requirements imposed on the matrix [6, 13]. The modification of epoxy resins with flexible copolymers like carboxyl- (CTBN) and epoxy-terminated butadiene acrylonitrile rubbers (ETBN) were found to improve the impact characteristics, but they reduced the thermal resistance and the resistance to absorption of moisture by the modified epoxy resins [13–20]. In our earlier reports [21–24] we described the effects of the

presence of both coal and rubber on the curing kinetics, morphology, viscoelastic, and mechanical properties of epoxy resins.

In this paper, we report on more properties of epoxy resins containing medium rank coal as organic filler. The frequency dependent dynamic mechanical properties of neat epoxy/novolac system are compared to those containing reactive rubbers and coal. The experimental values of the real and imaginary part of dynamic elastic moduli and loss tangent ($\tan\delta$) were obtained as functions of temperature and frequency. In the fully cured epoxies modified with rubber, three transition modes were observed, as also reported by other authors [14, 25–28]. At high temperature of ca. 150°C, a sharp peak of the α -relaxation was observed on the loss modulus and $\tan\delta$ curves that was attributed to the large scale rotational motions. The broad peak at low temperature (ca. –60°C) was identified as the β -transition of epoxy, which was associated with motions of small units: fragments of the type $-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{O}-$, unreacted epoxy groups and other free ends. The peak related to the glass transition of the randomly distributed rubber phase appeared near the β -relaxation of epoxy continuous phase, at ca. –30°C. The frequency dependence of the loss peak temperature over a broad range of frequencies provides an estimate of the activation energy (E_a) for molecular relaxations [25, 29, 30]. The magnitude of the potential barrier to molecular movement can be related to the chemical structure of the network.

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The simplest equation describing the temperature/frequency relationship for a transition is the Arrhenius equation. For β -transition processes obeying the Arrhenius theory, the plot is linear and E_a can easily be evaluated, but the formula has a straightforward meaning only when E_a is independent of temperature. In polymers, non-Arrhenius behaviour is often observed at and above glass transition (T_g) [25, 29–32]. Then, one obtains the so called apparent activation energy (E_{app}).

In this work, the Arrhenius formula was used to determine the potential barrier for β -transition in epoxy/novolac systems containing coal and rubber. In the region of glass transition, the temperature dependence of the shift factor a_T was determined by using the Williams–Landel–Ferry equation [29, 33–35].

Experimental

Materials

The epoxy resin was a commercial grade prepolymer of the diglycidyl ether of bisphenol A (EP) supplied by Shell Chemical Co., as Epikote 827, with an epoxide equivalent mass (EEW) of 181.8. Phenol-formaldehyde novolac (Novolac Z, NZ, $M_n = 570 \text{ g mol}^{-1}$) obtained from Chemical Plants in Nowa Sarzyna (Poland) was used as the curing agent. 2-ethyl-4-methylimidazole (0.3 mass%) was a catalyst. Two types of reactive liquid rubbers were used. The first was the carboxyl-terminated butadiene-acrylonitrile copolymer Hycar 1300X8 CTBN (BF Goodrich Chem.) having molar mass of 3550 g mol^{-1} and acrylonitrile content 18%. The mass fraction of CTBN rubber in epoxy mixture was varied from 0 to 16%. The second rubber was an epoxy-terminated copolymer (ETBN) prepared from CTBN and an excess of epoxy resin. The content of ETBN in the epoxy matrix (expressed in relation to that of CTBN) was 6 mass%. The medium rank mineral coal (83.6% of C) was used as organic filler (16 mass%). Finely powdered coal of particle size 20–90 μm was degassed and vacuum dried at 100°C.

Sample preparation

The stoichiometric amounts of novolac and epoxy resin, calculated according to their functionality, were heated up to 80°C and mixed together by stirring continuously until a clear mixture was obtained. After degassing the mixture, the catalyst was added. The cured materials for testing were obtained in the cycle: 6 h at 150°C and 4 h at 180°C [21, 22]. Rubber-modified samples were prepared by first dissolving the modifier in epoxy resin at approximately 80°C and then adding novolac and catalyst. The curing proce-

sure was similar to that applied for non-modified epoxy. Coal-filled epoxies were obtained by mixing the epoxy resin with filler for 2 h at 100°C. The rubber/coal/epoxy samples were prepared by first mixing the epoxy resin with coal at 100°C. The carboxyl- or epoxy-terminated rubber was then added to the coal dispersion in epoxy. Further operations were the same as for the neat EP/NZ system.

Methods

The dynamic mechanical analysis (DMA) was performed using DMA 2980 TA Instruments analyzer. The measurements were made for fully cured samples. The changes of the storage modulus (E'), loss modulus (E'') and loss factor ($\tan\delta$) were recorded as a function of temperature and frequency. The T_g of fully cured epoxies were taken to be the temperatures at the maximum of $\tan\delta$ peak at 1 Hz. The testing mode was the bending dual cantilever clamp with samples having a cross-section $12.7 \times 3.1 \text{ mm}$ and length of 60 mm. The samples were oscillated both at single frequency of 1 Hz (with oscillation amplitude 10 μm) and in multi-frequency mode. The mechanical spectra at 1 Hz were obtained using temperature scan rate of 3°C min^{-1} starting from -100°C and ending just above the glass transition temperature of epoxy samples. To determine the activation energies of molecular relaxations, the frequency was varied over 4 decades in the range from 0.1 to 100 Hz. Due to long time of data collection in the multi-frequency mode, the readouts were recorded using the step-and-hold method with 1°C as temperature increment. The isothermal frequency sweep method provides data at all ranges of temperature with good accuracy. The temperature used as reference one in WLF equation was taken as that of the loss modulus peak at 1 Hz. The data were shifted and the parameters in WLF equation evaluated using TA Instrument TTS Data Software.

Morphological studies were performed by using scanning electron microscopy (XL30 Philips SEM). Microphotographs of rubber-modified epoxy/novolac system filled with coal were taken on the fracture surface coated with gold. The polished surfaces of epoxies were observed also in Neophot 21 optical microscope.

Results and discussion

The effect of the type and content of reactive rubber on the viscoelastic characteristics at frequency of 1 Hz for rubber-modified EP/NZ compositions was reported in previous papers [22, 23]. The mass fraction of CTBN in epoxy mixture was changed from 0 to 16%. The storage modulus gradually decreased with increasing amount of liquid rubber in compari-

son to the corresponding neat EP/NZ sample. The T_g of CTBN and ETBN-modified epoxy systems containing up to 8.6 mass% of rubber was practically the same as for neat epoxy (150°C). However, the high content of rubber (16 mass%) resulted in reduction of T_g by about 10°C [23].

The functional groups present on the surface of coal particles are known to have an effect on the kinetics of curing as well as on the dynamic mechanical properties of the coal-filled epoxy systems [21, 22, 24]. The increase of filler content up to 29 mass% resulted in gradual increase of the storage modulus as compared to the neat EP/NZ system. The magnitude of loss factor was reduced with increasing content of coal. The T_g , on the other hand, was independent of the coal content, up to 29 mass%. Basing on these findings, the optimal contents of the epoxy resin modifiers were taken to be 6 mass% of rubber and 16 mass% of coal.

Completely cured epoxies modified with rubber, i.e. the compositions cured at 150 and post-cured at 180°C, consisted of a continuous epoxy phase with randomly distributed rubber particles of the size 0.5–3 μm . Figure 1 presents the morphology of the fractured surface of EP/NZ system with CTBN rubber, as observed by SEM.

This type of morphology was observed for the most of rubber-modified epoxy materials as described in detail in literature [14, 15–18]. The epoxy/novolac system filled with both coal and reactive rubber has more complex morphology. It is presented in Fig. 2. The optical and SEM micrographs for the coal-filled specimen in Fig. 2 show, that the particles of coal have irregular and angular shapes. In contrast to the filler, rubber separates in the form of spherical areas. The size and range of rubber particles distribution in the CTBN/epoxide differ from those in the coal/CTBN/epoxy system. Broad rubber particle size distribution is observed for CTBN/epoxy system filled with coal. The size of rubber in coal/epoxy matrix is of the order of 0.5–29 μm , therefore the diame-

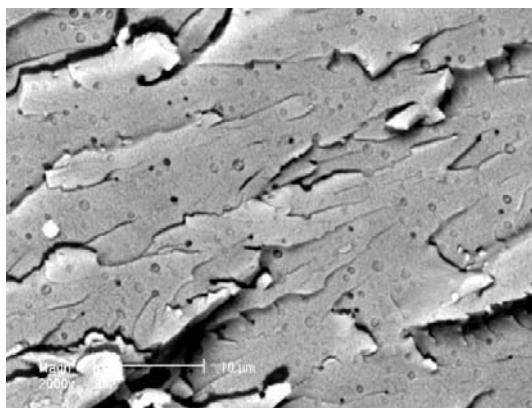


Fig. 1 SEM micrograph of epoxy/novolac matrix containing 6 mass% of CTBN

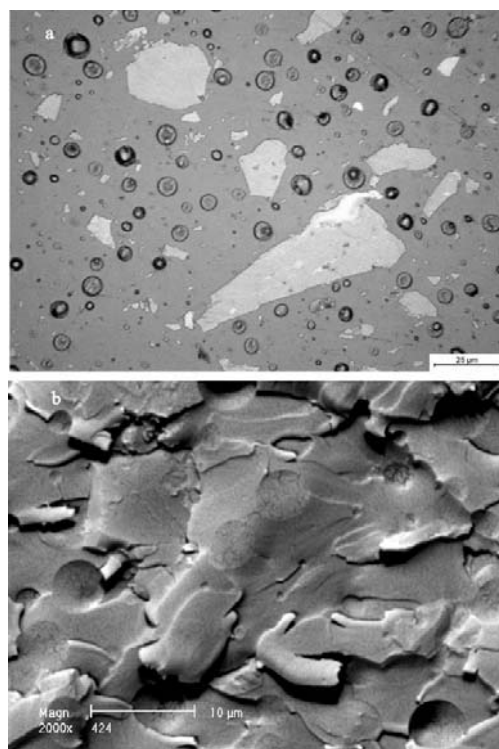


Fig. 2 a – Optical and b – SEM micrographs of epoxy matrix filled with 16 mass% of coal and 6 mass% of CTBN

ters of rubber in coal-filled epoxy are larger than in unfilled CTBN/epoxy system.

The neat EP/NZ system, both without filler and with coal, gives two peaks in the loss modulus and $\tan\delta$ curves: β -transition and glass transition of epoxy. For epoxy system modified with rubber, the third loss peak connected with the glass transition of rubber phase appears. At higher temperature, ca. 150°C occurs sharp peak of the α -transition for epoxy resin (Fig. 3). The T_g was observed as a large maximum in the $\tan\delta$ and a corresponding drop in the storage modulus. The temperature dependences of the storage modulus and $\tan\delta$ for CTBN-modified and coal-filled epoxy systems in relation to the EP/NZ specimen are shown in Fig. 3.

For each EP/NZ system, the modulus decreased as temperature was risen and as the material passed from the glassy to rubbery state. The storage modulus for the neat EP/NZ specimen at room temperature was 2630 MPa. The modulus decreased for the corresponding CTBN/epoxy mixtures. The presence of coal in the epoxy system resulted in an increase of modulus. The highest storage modulus was measured for EP/NZ sample filled with just coal.

The T_g that corresponded to the maximum of $\tan\delta$ peak for CTBN-modified and coal-filled epoxy specimen remained similar to that for the neat EP/NZ system and was found to be ca. 150°C. The epoxy materials containing coal and/or rubber give the tangent peak of smaller size than in the case of neat epoxy.

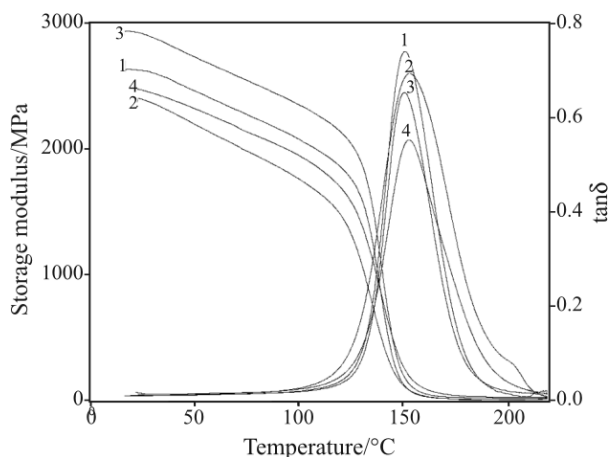


Fig. 3 Storage modulus and $\tan\delta$ at 1 Hz for cured specimens: 1 – EP/NZ, 2 – EP/NZ+6 mass% of CTBN, 3 – EP/NZ+16 mass% of coal, 4 – EP/NZ+16 mass% of coal+6 mass% of CTBN

The decrease of the loss tangent magnitude seems to be a result of restricted molecular mobility related to the presence of modifier and filler.

Table 1 shows the $\tan\delta$ peak width at half of peak height ($S_{1/2}$) and area under $\tan\delta$ peak ($A_{\tan\delta}$) vs. CTBN mass fraction in EP/NZ system. The results for epoxy modified with 6 mass% of ETBN and for coal filled material are also presented.

The broadening of $\tan\delta$ peak with increasing CTBN content can be related to the possibility that α -relaxation of network fragments having different cross-link density in rubber-modified epoxy appears in slightly different temperature range than for neat epoxy. The area under $\tan\delta$ peak also gradually increases with increasing amount of CTBN in relation to the neat epoxy. $S_{1/2}$ and $A_{\tan\delta}$ for coal/epoxy system are close to the results for unfilled EP/NZ system.

The broad peak at lower temperature (ca -60°C) was identified to be β -transition of epoxy, which is associated to the motions of short-chain segments: glyceryl-like fragments, glycidyl groups, other free ends and monomer or impurities. Additionally, for

Table 1 $\tan\delta$ peak width at half of peak height ($S_{1/2}$) and area under $\tan\delta$ peak ($A_{\tan\delta}$) for EP/NZ systems modified with CTBN or ETBN and filled with coal

Epox system	$S_{1/2}/\text{K}$	$A_{\tan\delta}/\text{K}$
EP/NZ	26.8	7.3
EP/NZ/CTBN (3 mass%)	31.2	8.8
EP/NZ/CTBN (6 mass%)	37.8	9.6
EP/NZ/CTBN (8.6 mass%)	40.4	9.7
EP/NZ/ETBN (6 mass%)	39.3	8.6
EP/NZ/coal (16 mass%)	25.7	6.5
EP/NZ/coal (16 mass%)/CTBN (6 mass%)	32.7	6.7

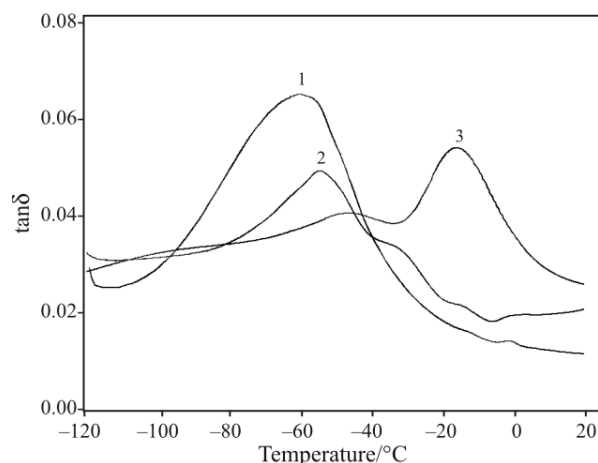


Fig. 4 Low temperature region of the $\tan\delta$ spectrum at 1 Hz for the cured specimens: 1 – EP/NZ, 2 – EP/NZ+6 mass% of CTBN, 3 – EP/NZ+16 mass% of CTBN

EP/NZ material modified with rubber, near the β -transition of the epoxy, the other relaxation peak appeared in the loss factor curve at ca -30°C , assigned to the glass transition of the rubber. The magnitude of the peak increased with rising rubber content. The low temperature region of loss tangent spectrum is shown in Fig. 4.

The dynamic mechanical properties described above were measured at single frequency. By using the frequency sweep, it is possible to determine the activation energy of β -relaxation for epoxy modified with rubber and coal. The changes in loss modulus at various frequencies are shown in Fig. 5. For the epoxy system without any additives, the loss modulus peaks at lower (Fig. 5a), and higher temperature region (Fig. 5b), which correspond to β - and glass transitions, respectively. Naturally, the temperature positions of the relaxation peaks are shifted towards higher temperature as the frequency increases.

The multifrequency DMA results differ from those obtained at single frequency. The differences both in the values of dynamic moduli and in the appearance of spectrograms were observed, especially for the rubber-modified samples. In the temperature below 0°C , the β -transition of the epoxy and glass transition of the rubber are visible at single-frequency runs. At several frequencies, a peak connected to the glass transition of rubber is observed only at the lowest frequencies (0.1, 0.5 and 1 Hz). Figure 6a shows the low temperature region of the loss modulus for the CTBN/epoxy, while Fig. 6b presents the peaks for the same modified epoxy system at temperature range from 50 up to 200°C .

The loss modulus vs. temperature curves for rubber/epoxy specimen filled with coal at the whole temperature range look like those for the rubber/epoxy system without coal. At temperature below 0°C

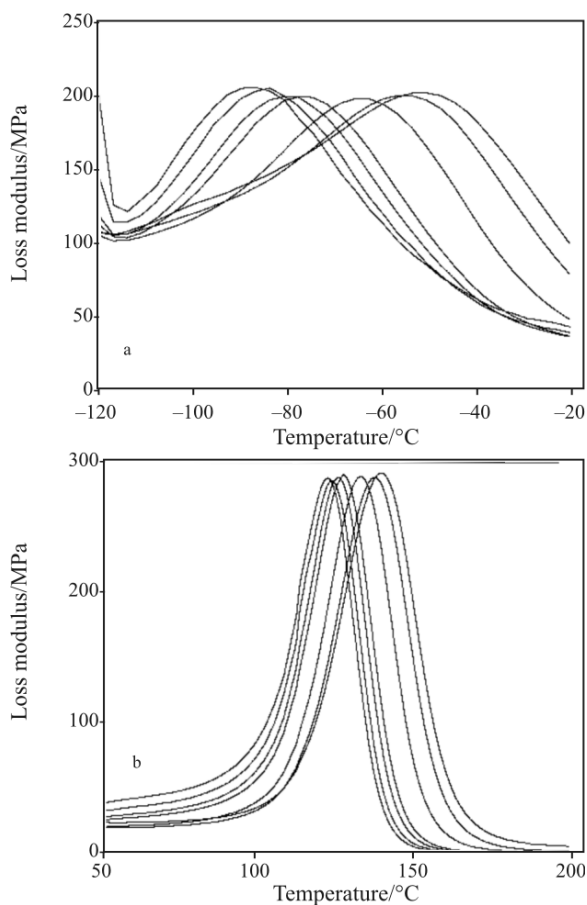


Fig. 5 Loss modulus as a function of temperature in multi-frequency mode for neat EP/NZ specimen in a – β -transition region and b – glass transition region

(Fig. 6a), β -transition peak for epoxy resin overlaps the α -transition peak for rubber. These two transitions differ considerably in their response to different frequencies as reflected by changes in slopes of the $[\ln(\text{frequency})]$ vs. $[1/T_{\text{max}}]$ plots (where T_{max} is temperature at the maximum of loss peak).

Consider the Arrhenius equation for the relaxation process [29]:

$$E_a = -R \frac{d \ln f}{d(1/T_{\text{max}})}$$

where T_{max} is the absolute temperature which corresponds to the peak maximum of loss modulus at the frequency f . The activation energies of the β -relaxation process in epoxy materials determined from the slope of $[\ln(\text{frequency})]$ vs. $[1/T_{\text{max}}]$ plot are presented in Table 2. The β -transition of EP/NZ is characterized by the activation energy equal to 66 kJ mol⁻¹. Berstein [25] found the activation energy for β -transition in an epoxy resin cured with metaphenylene amine somewhat higher, namely 90 kJ mol⁻¹. Apparently, in the presence of rubber, the mobility of short fragments in cross-linked epoxy changed and the potential barrier

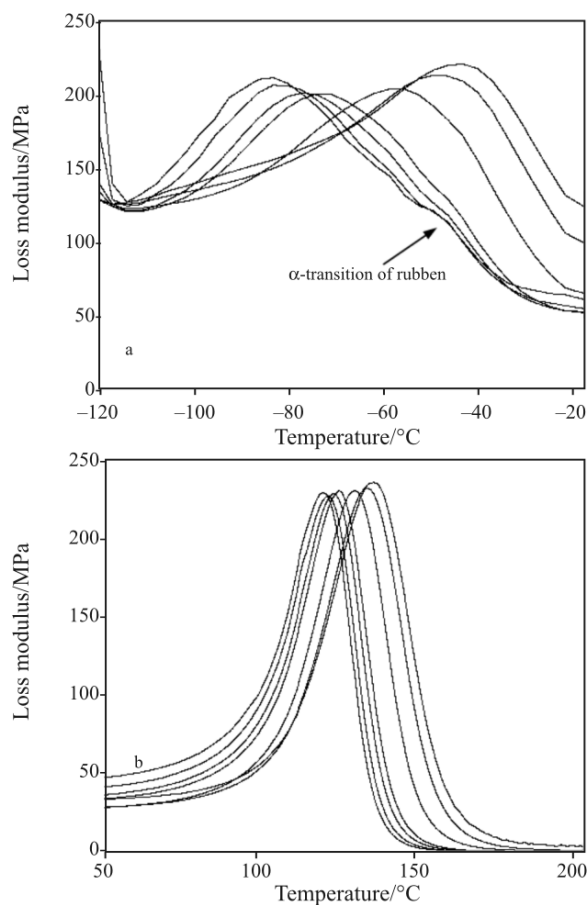


Fig. 6 Loss modulus as a function of temperature in multifrequency mode for coal-filled EP/NZ sample with 6 mass% of CTBN at a – β -transition region and b – glass transition region

of this transition in EP/NZ system with CTBN or ETBN was lower than that in neat EP/NZ. The decrease of E_a for β -transition in rubber/epoxies can be a result of change in the nature of interactions. The value of activation energy for the rubber/epoxy system filled with coal was noted to be the same as in neat epoxy.

The glass transition is known to be a non-Arrhenius process, but in many papers, the Arrhenius relation was applied to describe relaxation phenomena at and above glass transition [25, 29–31]. In this work,

Table 2 Activation energies in β -transition region for neat, rubber/epoxy, and rubber/coal/epoxy systems

Epoxy system	$E_a/\text{kJ mol}^{-1}$
EP/NZ	66.3
EP/NZ/CTBN (3%)	64.5
EP/NZ/CTBN (6%)	61.0
EP/NZ/CTBN (8.6%)	55.2
EP/NZ/ETBN (6%)	58.7
EP/NZ/coal (16%)/CTBN (6%)	65.5

the WLF equation was used to describe the time-temperature behaviour of epoxies in the T_g region [29, 33]:

$$\lg a_T = \lg(\tau_T/\tau_{T_0}) = -C_1(T-T_0)/(C_2+T-T_0)$$

where τ_T and τ_{T_0} are the relaxation times (viscosity or dynamic modulus) at temperature T and the reference temperature T_0 , C_1 and C_2 are constants for a given polymer.

The dynamic mechanical data at glass transition region were collected by performing frequency sweep experiments as was shown above in Figs 5 and 6. The plots show the loss moduli as a function of temperature at various frequencies. The loss modulus isotherms at various temperatures were constructed for all epoxy systems and, after selecting a reference temperature, they were shifted with respect to time (or frequency). A master curve can thus be generated extending outside the range of frequency or time easily accessible by experiment.

Figure 7a shows the resulting loss modulus master curve for the CTBN/epoxy system. An attempt of generating the master curve for coal/ETBN is presented in Fig. 7b.

The reduction of the viscoelastic properties to the glass transition temperature proceeded with good accuracy in the case of neat and rubber-modified epoxies. For the coal-filled epoxy materials, it worked only in a limited temperature range. The interactions between polymer and filler particles together with the tendency of powdered coal to agglomerate complicate the dynamic mechanical spectra. When the master curve was compiled for the coal/epoxy system, many points of loss modulus branched off from the master curve particularly at low frequencies. The interpretation of master curve at its ends becomes unclear. Hence, only the medium range of frequency seems to be reliable from the practical point of view. The multi-component thermosets with coal do not behave as simple rheological liquids and the use of the horizontal shift factor a_T for all isotherms of loss modulus might not be sufficient to produce a correct master curve.

The master curves displayed in Fig. 7 demonstrate that the data collected over 4 decades of frequency can be transformed to cover sixteen and even twenty decades. The shift factor, a_T was used to displace each isotherm to the reference temperature and to determine the constants in WLF equation. The plots of a_T vs. T for all samples over the temperature range from 120 to 160°C are presented in Fig. 8.

The symbols in the plots of the shift factor a_T correspond to the experimental data. The line presents the best fit to the WLF equation. The constants C_1 and C_2 were determined from the fit. As can be seen, the WLF equation holds very well for neat and rubber-modified epoxy. When the epoxy is filled with

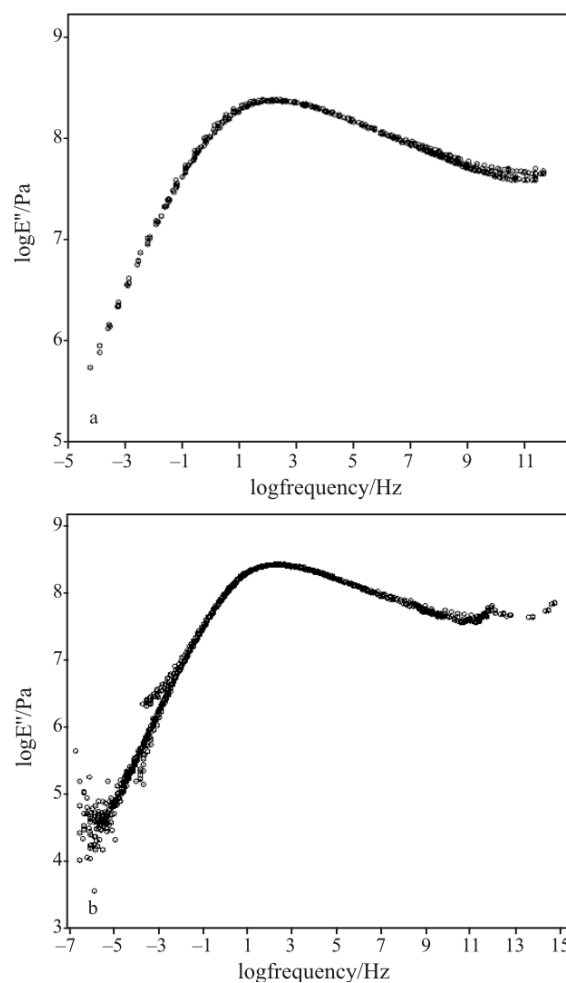


Fig. 7 Loss modulus master curve for epoxy resins: a – EP/NZ, b – EP/NZ+16 mass% of coal +6 mass% of CTBN

coal, a departure from WLF relation is observed, rendering impossible the determination of reliable C_1 and C_2 parameters.

The constants in the WLF equation can in principle be predicted from the free-volume theory ($C_1=17.4$ and $C_2=51.6$, using $T_0=T_g$) [29, 34]. The authors of the WLF model, advised against the use of ‘universal constants’ obtained as average values for several polymers, to determine the real constants for each system. The effect of CTBN content in EP/NZ system on the values of C_1 and C_2 was examined. The data obtained for neat EP/NZ material and that modified with rubber are presented in Table 3. The reference temperature was taken as the maximum in the loss modulus (E''), coupled with the inflection in the storage modulus (E') vs. temperature curve resulting from DMTA tests at 1 Hz, and was adopted to construct the master curves. The T_g can be measured with high sensitivity by monitoring the response of either the E' , E'' , or loss tangent ($\tan\delta$) as a function of temperature. The most commonly used is that corresponding to the peak in a $\tan\delta$ vs. T plot, but it is also taken as the peak tempera-

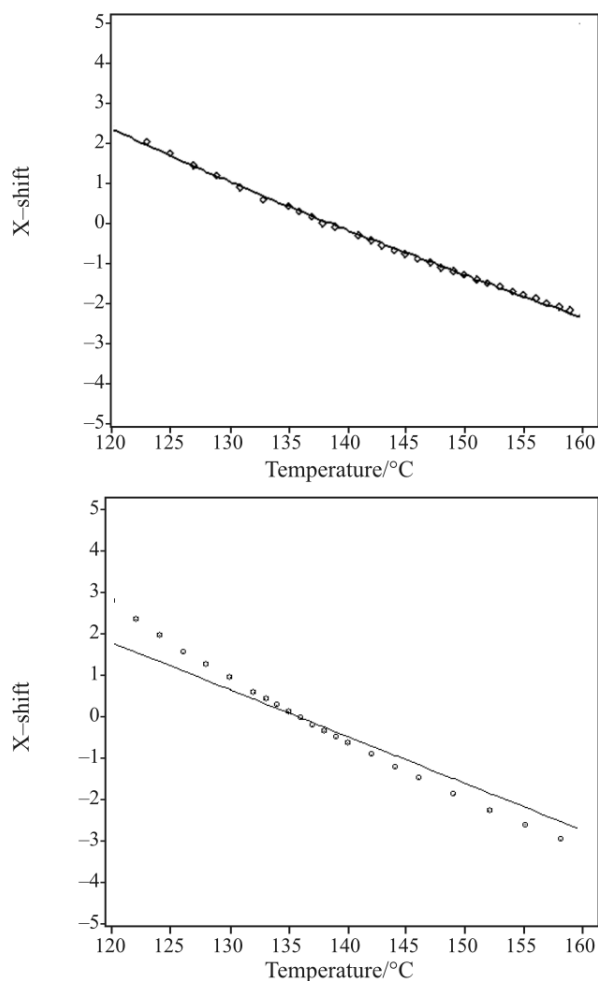


Fig. 8 The horizontal shift factor a_T as a function of temperature ($T_0=T_g$) for the systems: a – EP/NZ+6 mass% of CTBN, and b – EP/NZ+16 mass% of coal+6 mass% of CTBN

ture in a E'' vs. T plot; however, this temperature is lower than that corresponding to the $\tan\delta$ peak. This last temperature is very close to that of the E' inflection point decrease and therefore it was used as reference temperature in the WLF equation.

For the reason mentioned above, no constants for the coal/epoxy systems are presented. The C_1 and C_2 values for all epoxy systems are generally higher as compared with the ‘universal constants’ predicted from the free-volume theory. C_1 seems to be independent of the content of reactive rubber, but C_2 decreases with increasing amount of CTBN.

Combination of the Arrhenius equation in the form: $E_a=Rd\ln\tau/d(1/T)$ and the WLF equation yields [29]:

$$E_a = 2.303RC_1C_2T^2/(C_2+T-T_g)^2$$

This relation can be interpreted as providing the apparent activation energy of stress relaxation at the glass transition region. These apparent activation en-

Table 3 WLF constants (C_1 and C_2) for neat and rubber-modified EP/NZ system

Epoxy system	T_0/K	WLF constants	
		C_1	C_2
EP/NZ	412	22.2	133.4
EP/NZ/CTBN (3%)	412	21.7	107.6
EP/NZ/CTBN (6%)	408	20.0	93.8
EP/NZ/CTBN (8.6%)	405	19.3	91.3
EP/NZ/ETBN (6%)	409	21.6	99.3

Table 4 Apparent activation energy of α -transition for neat and rubber-modified EP/NZ system

Epoxy system	$E_a/kJ\ mol^{-1}$
EP/NZ	541
EP/NZ/CTBN (3%)	655
EP/NZ/CTBN (6%)	680
EP/NZ/CTBN (8.6%)	664
EP/NZ/ETBN (6%)	687

ergies at the temperature taken as the maximum of the loss modulus peak are listed in Table 4.

The potential barrier of stress relaxation at the glass transition region for the neat EP/NZ network is equal to $541\ kJ\ mol^{-1}$. The high activation energy at T_g corresponds to the cooperative, complex motions over a broad range of frequency. The presence of rubber influences the potential barrier to the large scale motions in the modified EP/NZ system. The increase of E_a can be explained by the possible existence of additional junction points in the networks, resulting from intermolecular hydrogen bonds involving rubber end-capping functional groups (carboxyl or epoxy).

Conclusions

We have tested coal as a filler and rubber as an impact modifier for the processing of modified epoxy materials. The presence of elastomer and finely grinded coal dispersed in epoxy matrix changes the characteristics of the dynamic mechanical properties of the material. The storage modulus becomes smaller in the epoxy formulations with liquid rubber as compared to non-modified EP/NZ system. The epoxy matrix with coal is characterized by the highest storage modulus. The glass transition observed for the CTBN-modified (6 mass%) and coal-filled (16 mass%) multi-phase epoxy system remains similar to that for the neat epoxy.

The activation energy of β -relaxation obtained for unmodified EP/NZ material is equal to $66\ kJ\ mol^{-1}$. The potential barriers for the secondary transition of epoxy matrix containing rubber were lower as com-

pared with those for non-modified epoxy system. The higher activation energy for coal-filled rubber/epoxy composition was noted in relation to the neat epoxy.

Determination of the glass transition of rubber phase from the loss tangent curve was complicated due to its coincidence with the secondary relaxation of the epoxy.

The rubber and coal affect the constants in the WLF equation. Parameter C_1 seems to be independent on the content of reactive rubber, but C_2 decreases with increasing rubber amount. When the epoxy system was filled with coal, a departure from WLF relation was observed, rendering impossible the determination of reliable WLF constants. Many points deviate from the master curve for the coal/epoxy system making determination of WLF parameters difficult, particularly at low frequencies. The coal/rubber/epoxies show complex rheological behaviour and hence the use of the horizontal shift factor a_T for all isotherms of loss modulus might be insufficient to generate a correct master curve.

The stress relaxation activation energy at the glass transition temperature for the neat EP/NZ system estimated by means of WLF equation equals to 541 kJ mol⁻¹. The presence of rubber phase influences the potential barrier to segmental motions in epoxy system. The activation energies at T_g for rubber/epoxies increase relative to E_a value for non-modified epoxy.

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