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Thermal investigations of curing process of EPY® epoxy system

Summary — The curing, postcuring and additional postcuring of the EPY® epoxy system (applied for ship machine foundation chocks) have been examined by differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA). Parameters of curing have been determined by a dynamic variant of DSC at various heating rates. DMTA method has given an information on the epoxy system viscoelasticity. The crosslinking degree was calculated from the heat of the dynamic curing reaction. The influence of heating rate on curing parameters was shown. Glass transition temperatures of the postcured and additionally postcured epoxy systems was also determined. The results showed that the temperature range of softening of machine foundation chocks could be shifted beyond the range of their operating temperatures.

Key words: epoxy system, curing, postcuring, additional postcuring, dynamic mechanical properties, glass transition temperature, working temperature.

During the cure of an epoxy system a number of complex chemical and physical changes occur as the material turns from a viscous liquid to a highly crosslinked solid. All these changes are reflected in the cure kinetics and the characteristics of physical and chemical properties of the resin system making possible to determine the optimum parameters of the curing process, what in turn enables to work out a highly efficient technology of the production of the material of required utility properties [1, 2]. Such information can be obtained by thermoanalytical methods. According to International Confederation for Thermal Analysis and Calorimetry (ICTAC) the thermal analysis is defined as „the measurement of changes of physical properties as a function of temperature controlled by a determined program" [2, 3]. Most often applied methods of thermal analysis [4, 5] are: differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), thermomechanical analysis (TMA) and dynamic mechanical thermal analysis (DMTA).

The investigations of the curing reaction of the epoxy system are usually carried out by several thermoanalytical methods as the complex application of complementing methods such as *e.g.* DSC + DMTA ensures more complete quality and quantity picture of the process investigated. DSC is most often used for the examinations of the curing of the epoxy system and determination of kinetic parameters and thermal effects of the process [6] while DMTA that follows the changes in an internal molecular mobility is applied for examinations of the structure and viscoelasticity of the material (in the wide range of temperature changes and deformation frequency) [4, 7].

EPY® epoxy system — the object of the investigations presented in this paper — was worked out in the close cooperation with Polish shipbuilding industry and has been for many years applied for foundation chocks in seating of the ship machinery and installations and also the heavy land industrial machines (presses, machine tools, mining machines) [8, 9]. It obtained many approvals and quality certificates of respected in the world ship engine producers and classification societies supervising ship building and repairs [8, 9]. Recently the investigations on improvement of the material and extending its application in machine and appliances assembling in other fields of the techniques have also been carried out.

The general purpose of the investigations was the estimation of the possibility of the practical use of DSC and DMTA thermal examinations for the evaluation of the phenomena which occur during the cure EPY® epoxy material, depending on the process parameters, whereas the particular purpose was the examination of conditions of the occurrence and the course of the softening effect of the investigated material.

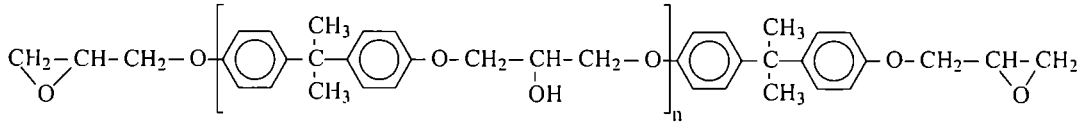
EXPERIMENTAL

Materials

The main components of the investigated material of trade name EPY® (from Marine Service Jaroszewicz) are: epoxy resin Epidian 6 (epoxy number 0.532 mole/100 g) produced by Chemical Works Organika-Sarzyna in Nowa Sarzyna and a curing agent Z-1 (triethylenetetraamine) from the same supplier. The resin and curing agent ratio is constant and equals 14 phr of the curing agent to 100 parts of the resin. The epoxy system is completed with additives bestowing the appropriate technological and utility properties upon the material.

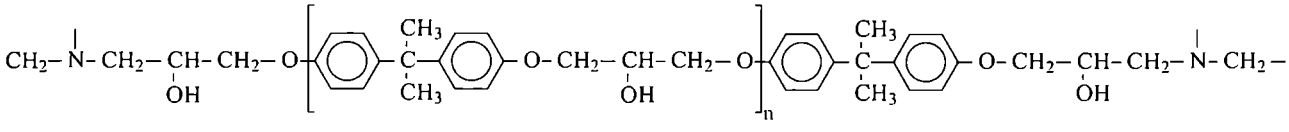
Sample preparation

In the examinations of the curing by DSC method, the system of samples prepared just before the measurement were used. The samples used for the postcuring investigations both by DSC and DMTA methods were cast in the metal forms in the shape of small rectangular bars (50×10×3 mm) and cured at 23 °C for 24, 48 and 168 h. Besides a few samples cured at 23 °C for 24 h were additionally postcured at 80 °C for 1 and 2 h.



+

$$H_2N-CH_2-CH_2-NH-CH_2-CH_2-NH-CH_2-CH_2-NH_2 \quad (1)$$



Methods

DSC measurements

The courses of the curing and postcuring reactions of the epoxy system were investigated using a differential scanning calorimeter DSC-7, from Perkin-Elmer, applying the dynamical method. DSC measurements were carried out immediately after mixing the components of the system using 10 mg samples in 50 μL aluminum pans with covers. The samples were heated at the temperature range from -20 to 180 °C in the nitrogen atmosphere at various heating rates: 1, 3, 5 and 10 °C/min. In the postcuring examinations the measurements were carried out using approximately 30 mg samples cut out from the middle of the bars cured the way described above. The samples were heated with the rate of 10 °C/min from 5 to 200 °C and then cooled to 5 °C and reheated to 200 °C with the same rate. This was done so as to check if the exothermic effect occurs. This might reveal the incomplete curing of the system during the first heating cycle in DSC.

DMTA measurements

DMTA apparatus MK II from Polymer Laboratories was used for the examinations of viscoelasticity of the material. The measurements were carried out using the bars prepared the way described, under a three-point bending mode called „dual cantilever" at the deformation frequency 1 Hz. The measurements were performed at the temperature range -20 to 220 °C in the nitrogen atmosphere and heating rate 3 °C/min.

RESULTS AND DISCUSSION

Effect of curing rates during DSC examination

The epoxy resin, the main component of EPY® system, reacts with a curing agent forming a crosslinked structure according to equation (1) [10].

The curing reaction of the epoxy resin in the presence of additives in the system was examined by DSC at four various heating rates. The DSC thermograms are shown in Fig. 1. The variation of the conversion as a function of the temperature and time of curing at various heating rates of the tested system are presented in Figs. 2a and 2b, respectively.

The basic parameters of the DSC examinations taken into consideration to reach some information about the curing reaction [11, 12] are collected in Table 1.

With increasing heating rate, the mobility of chains increases and the process can proceed with higher rate. This is revealed by a distinct shift of both exothermic peaks of the curing reaction (Fig. 1) and conversion

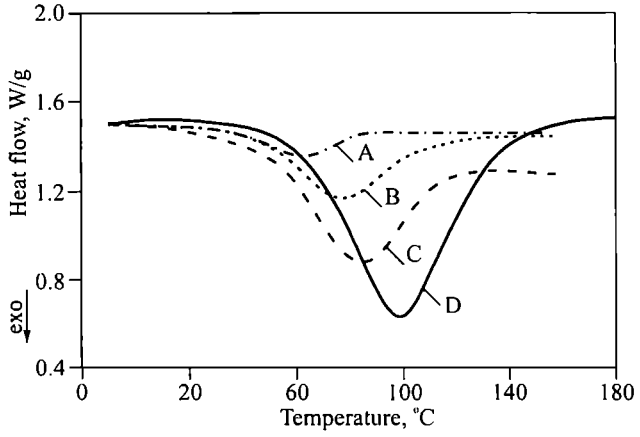


Fig. 1. DSC thermograms of epoxy system for various heating rates (°C/min): A — 1, B — 3, C — 5, D — 10

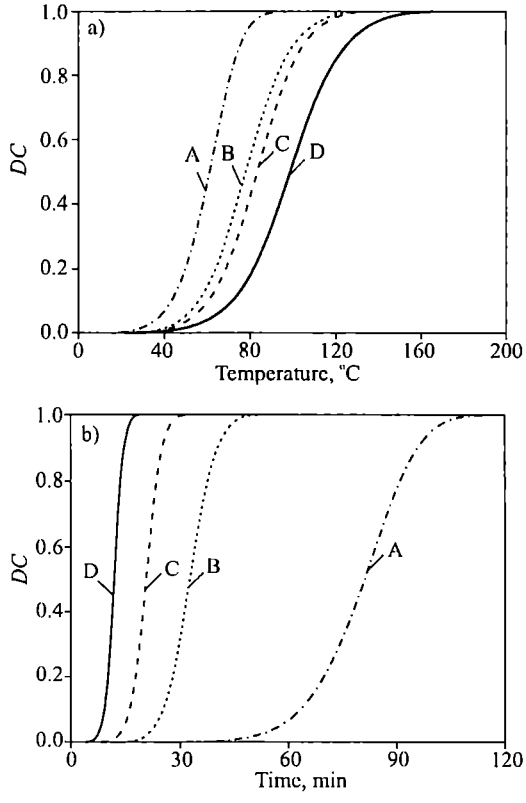


Fig. 2. Dependence of degree of conversion (DC) of epoxy system an temperature (a) and time (b) for various heating rates. For curves symbols see Fig. 1

Table 1. Curing characteristics of epoxy system, evaluated from DSC thermograms recorded for various heating rates*)

Heating rate °C/min	T_i °C	T_{min} °C	T_f °C	ΔH_T J/g	$T_f - T_i$ °C	t_c min
1	15.7	62.1	96.7	211.4	81.0	81.0
3	21.8	77.9	140.5	233.5	118.7	39.6
5	22.0	83.9	140.0	246.2	118.0	23.6
10	22.1	97.9	166.2	256.7	144.1	14.4

*) T_i — initial temperature, T_{min} — minimum peak temperature, T_f — final temperature, ΔH_T — total enthalpy of the reaction, t_c — curing time.

degree (Fig. 2a) towards higher temperatures when heating rates are risen.

A typical response of the epoxy system to the increment in the heating rate appears not only in ΔH_T of the curing increase but also in continuous increase in the characteristic values (T_i, T_m, T_f) and temperature range (T_f-T_i) (Table 1), as well as decrease in t_c (Fig. 2b). Such a behaviour results from the interaction of numerous factors [11], especially physical ones (the influence of the viscosity on the mobility of chains).

Postcuring

The courses of the samples postcuring examined by DSC method are presented in Fig. 3. Glass transition temperatures of the system reached in the first (T_{g1}) and second (T_{g2}) DSC heating cycle, characteristic temperatures of the postcuring (T_i, T_m and T_f) and values of its residual enthalpy (ΔH_{res}) are presented in Table 2.

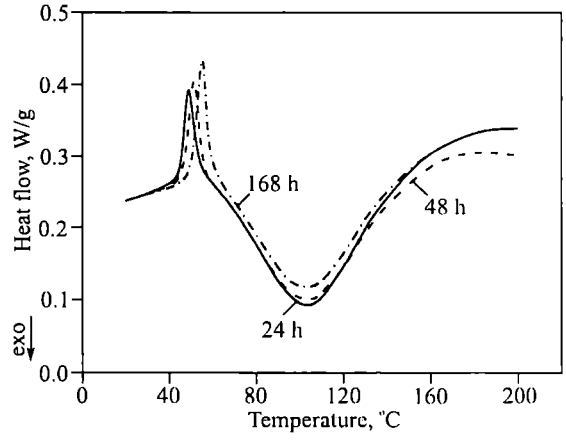


Fig. 3. DSC thermograms of epoxy system postcured at 23 °C for 24, 48 and 168 h

Table 2. Postcuring characteristics of epoxy system at 23 °C*)

Postcuring time, h	T_{g1} °C	T_i °C	T_{min} °C	T_f °C	ΔH_{res} J/g	T_{g2} °C	$T_f - T_i$ °C
24	44.3	57.6	104.2	173.4	65.2	111.3	115.8
48	50.1	57.9	105.1	171.8	60.3	112.3	113.9
168	52.4	61.0	105.6	166.2	56.1	112.9	105.2

*) T_{g1}, T_{g2} — glass transition temperature in the first and second heating cycle, respectively; ΔH_{res} — residual enthalpy of reaction; for T_{min}, T_i and T_f see Table 1.

Figure 3 presents the typical DSC thermograms of the postcured epoxy system (23 °C) where after a distinct relaxation peak attributed to the glass transition temperature a spacious exothermic minimum is observed. Its appearance might reveal the presence of non-reacted functional groups. It implies the necessity of annealing of the material what is essential in the case when an

application for machine foundation chocks is considered.

The results of measurements collected in Tables 1 and 2 confirm that increasing of curing rate distinctly shifts T_i value towards higher temperature and widens the temperature range of (T_f - T_i). Yet, the prolongation of postcuring time (from 24 to 168 h) does not cause such distinct effects — a diminishing of exothermic peak at the temperature range from about 57 °C till about 170 °C with postcuring time prolongation (so decrease in ΔH_{res} from 65.2 to 56.1 J/g) as well as endothermic peak shift so as T_g value towards the higher temperature — in the temperature range (T_f - T_i). However, with prolongation of postcuring time the T_{g1} value increases and ΔH_{res} value decreases (Table 2). The effects presented in DSC thermograms (Fig. 3) are the consequence of the gradual conversion of functional groups and an increase in crosslinking density [13]. However, an increase in crosslinking degree (α) of the system with postcuring time (23 °C) prolongation from 24 to 48 and 168 h is rather insignificant and equal to 0.75, 0.76 and 0.78, respectively. The values were calculated according to the formula [1, 5]:

$$\alpha = \frac{\Delta H_T - \Delta H_{res}}{\Delta H_T} \quad (1)$$

where: ΔH_{res} — *residual enthalpy of the partially cured system*, ΔH_T — *total enthalpy of cure reaction* (ΔH_T = 256.7 J/g).

The lack of the distinct increase in the α value and thereby the improvement of mechanical properties of the material indicates that precuring time prolongation is inexpedient if further thermal operations are planned.

As known, additional postcuring increases the crosslinking degree of the resin causing T_g increment. Additional postcuring of the investigated material at 80 °C for 1 and 2 h results in an increase in its T_{g1} value from 44.3 (without additional postcuring) to 97.5 or 99.8 °C, respectively; T_{g2} value changes after postcuring at these conditions from 113.3 °C to 117.2 °C or 118.6 °C.

Viscoelasticity

Figure 4 shows the temperature dependence of the storage modulus E' of the system cured (at 23 °C) for 24, 48 and 168 h. The values of E' for temperature 23 and 60 °C are collected in Table 3. The temperature 23 °C is

T a b l e 3. Effects of postcuring time on dynamic mechanical properties of epoxy system (tgδ, E') at 23 °C or 60 °C (working temperature) and on T_g value resulting from tgδ$_{max}$

Postcuring time, h	T_g, °C	tgδ$_{max}$	Temperature 23 °C		Temperature 60 °C	
			E', MPa	tgδ	E', MPa	tgδ
24	56.7	1.571	2181.0	0.027	25.2	1.508
48	62.3	1.424	2477.1	0.015	57.1	1.361
168	65.3	1.328	2644.3	0.011	122.3	1.071

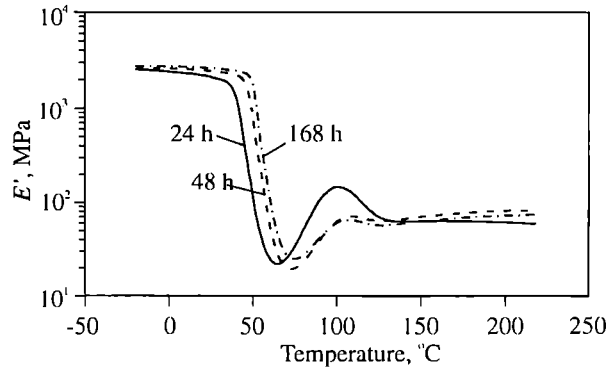


Fig. 4. Storage modulus (E') versus temperature of epoxy system postcured at 23 °C for 24, 48 and 168 h

the temperature of casting and curing of the samples, while 60 °C is a presumable working temperature of machine foundation chocks of ship engines [14]. Table 3 collects also the data concerning the effects of postcuring time on loss factors values (tgδ) at temp. 23 °C and 60 °C as well as on the value of maximal tgδ (tgδ$_{max}$). The positions of tgδ$_{max}$ values on DMTA plots correspond with the alfa transformation temperature assumed thereafter as the T_g.

The courses of DMTA curves (Fig. 4) and the data collected in Table 3 indicate that curing time prolongation (from 24 to 168 h) at 23 °C does not shift considerably, *i.e.* beyond the working temperature (20—60 °C) of the machine foundation chocks, both the temperature range in which the decrease (approx. 2 orders) in E' value and the increase in tgδ occur. Thus, to reach an effective shift of the temperature range in which softening is observed requires an additional postcuring of the system.

Figures 5 and 6 and Table 4 present the results of DMTA examinations of the system additionally postcured at 80 °C for 1 and 2 h. For comparison, the results of examinations of the non-additionally postcured system are shown in the same Figures. Though it is observed that the additionally postcured system (in conditions given above) appears to have also a significantly

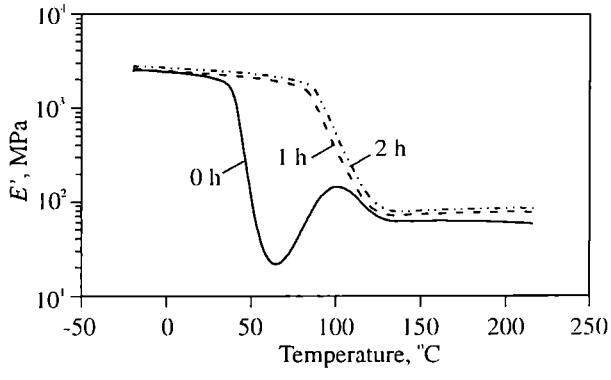


Fig. 5. Storage modulus (E') versus temperature of epoxy system additionally postcured at 80 °C for 0, 1 and 2 h

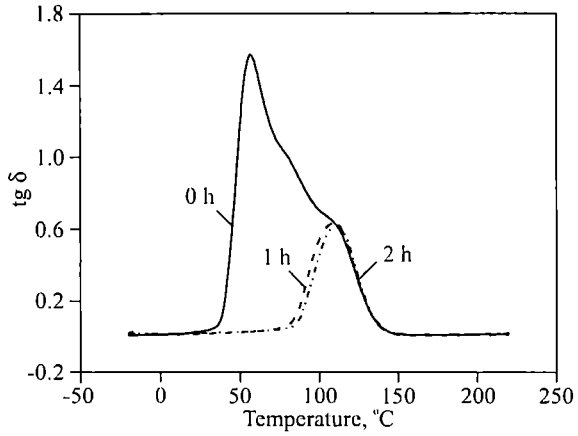


Fig. 6. Loss factor (tgδ) versus temperature of epoxy system additionally postcured at 80 °C for 0, 1 and 2 h

Table 4. Effects of additional postcuring time on dynamic mechanical properties of epoxy system (tgδ, E') at 23 °C or 60 °C (working temperature) and on T_g value resulting from $tg\delta_{max}$

Postcuring time, h	Tg, °C	$tg\delta_{max}$	Temperature 23 °C		Temperature 60 °C	
			E', MPa	tgδ	E', MPa	tgδ
0	56.7	1.571	2181.0	0.027	25.2	1.508
1	109.3	0.632	2328.2	0.022	2015.3	0.031
2	111.2	0.623	2534.5	0.021	2230.8	0.029

decreased value of the storage modulus *E'* (Fig. 5) in the temperature range of 85—135 °C, therefore significantly above the working temperature of machine foundation chocks, but it is distinctly smaller in comparison with non-postcured system. Also lowering of loss factor tgδ is observed beyond this range (Fig. 6), by the same diminishing of the ability to dissipation of mechanical energy what is caused by an increase in crosslinking degree. Undesirable softening of the material used for foundation chocks caused by an increase in chain mobility due to the temperature rise which is dangerous during exploitation of the machines and ship machineries can be restricted by additional postcuring.

CONCLUSIONS

The practice shows that the investigated EPY® epoxy system applied for machine foundation chocks shows good exploitation properties at working temperatures not exceeding 40 °C when 24 h of curing at 23 °C is used [9]. However, the rise of foundation chocks temperatures to 60 °C may cause the damages resulting from softening of the material that happens — as revealed by DSC and DMTA examinations — in temperature range, from 35 to 60 °C. It is possible to shift this range towards higher temperatures by additional postcuring of the system. Carrying out of the additional postcuring at 80 °C, *i.e.* at a boundary of working temperature of foundation chocks of ship engines [14], results in shift of the softening effect to the temperature range 85—135 °C, what in practice means a failure-free working. However, such additional postcuring, especially in the case of large objects (*e.g.* ship engines foundation chocks), is rather troublesome and costly in practice. Therefore the efforts are made to minimize the effect of the material softening in other way than additional postcuring with the use of external sources of heat.

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