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CROSS-LINKING EPOXIDE RESINS WITH HYDROLYSATES OF CHROME-TANNED LEATHER WASTE

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Differential scanning calorimetry was employed to investigate the reaction of diglycidyl ethers of bisphenol A (DGEBA) of mean molecular mass 348–480 Da, with collagen hydrolysate of chrome-tanned leather waste in a solvent-free environment. The reaction leads to biodegradable polymers that might facilitate recycling of plastic parts in products of the automotive and/or aeronautics industry provided with protective films on this basis. The reaction proceeds in a temperature interval of 205–220°C, at temperatures approx. 30–40°C below temperature of thermal degradation of collagen hydrolysate. The found value of reaction enthalpy, 519.19 J g^{-1} (=101.24 kJ mol^{-1} of epoxide groups) corresponds with currently found enthalpy values of the reaction of oxirane ring with amino groups. Reaction heat depends on the composition of reaction mixture (or on mass fraction of diglycidyl ethers in the reaction mixture); proving the dependence of kinetic parameters of the reaction (Arrhenius pre-exponential factor A (min^{-1}) and activation energy E_a (kJ mol^{-1})) did not succeed. Obtained values of kinetic parameters are on a level corresponding to the assumption that reaction kinetics is determined by diffusion.

Keywords: *collagen waste hydrolysates, curing, differential scanning calorimetry, epoxide resins*

Introduction

Epoxide resins are outstanding for their easy processing, low coefficient of thermal expansivity, high rigidity, elasticity and resistance to humidity and chemicals. Their more significant shortcomings include only (apart from rather high price) considerable brittleness that might be a hindrance in some industrial applications, and, maybe, not overly great burning resistance [1–4]. They are often used as bonding polymers for protective coatings in the automotive or aeronautics industries. Resistance of epoxide films to water and chemicals is welcome in surface treatment of parts but complicates recycling on termination of their life, particularly concerning plastic parts produced for the automotive and aeronautics industries.

Modifying inconvenient properties of epoxide resins is usually based either on building-in soft polymer segments into epoxide chains (for example, sulphones, compounds containing phosphorus, polyimido-polyesters, polyethylene-oxides, polymethyl-methacrylates, etc.) [5–9], or more often on appropriately selecting cross-linking agents and their relative concentrations. A higher proportion of oligomers having amino group ends in epoxide materials generally increases modulus of elasticity of the resultant polymer and, besides primary diamines with relatively short chains, other compounds usually recommended here are polyfunctional amines, aliphatic dicarbonic acids or their anhydrides, compounds of Mannich base type, dicyan-diamides [10, 11] as well as polyamides of nylon or caprolactam type [12]. Applying polyamides is often connected with solvent-free systems which further have the advantage of minimally polluting the environment [13].

Epoxide-polyamide systems (polyamide-6,6 or polyamide-6, often modified with formaldehyde to achieve solubility in ethanol) have received, lately in particular, considerable attention. Gorton [14] was probably the first to voice the opinion that polyamides are capable of cross-linking epoxides by reacting their amide nitrogen with oxirane ring of epoxides. Sprauer and Harrison [15] pointed out the connection between specific properties of such polymer films and their multi-phase character, given by limited compatibility of epoxides with polyamides. Wang and Chen [16] suppose that cross-link density is less important for properties of such films than mutual miscibility of both main components. These aspects are not quite clear yet as theoretical treatment of such systems is substantially more complicated than of those in which epoxide resin is cross-linked with low-molecular amines.

In manufacture of leather, substantial quantities of chrome-tanned collagen come off as waste in solid state. The waste has been so far disposed of by landfilling, which is not an optimum solution owing to the large content of environmentally controversial compounds of Cr^{3+} in such waste. Cr^{3+} compounds are

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quite easily eluted from dumped waste by acid rains and in their soluble form pass into ground waters. When these are processed into drinking water, the widely applied oxidising procedures lead to oxidation of Cr^{3+} compounds to Cr^{6+} compounds which are very potent carcinogens. In addition, the widely discussed problems of renewable raw material sources, for that matter biodegradabe polymers, support efforts to utilise the protein fraction of such waste as a secondary industrial raw material.

The first step when processing chrome-tanned leather waste into a secondary industrial raw material is (usually enzymatic) hydrolysis [17]. Products of this hydrolysis were prepared on pilot-plant scale in a powdered form, and their adequate industrial application is getting under focused attention at present.

Collagen hydrolysate of chrome-tanned leather waste (virtually free of chromium compounds – Table 1) is similar to polyamides with its high content of amide nitrogen, and differs from them with a higher concentration of primary amino groups which react with the oxirane ring of epoxides more easily than secondary amino groups or even amido groups that are contrarily more represented in polyamides. Mean molecular mass of collagen hydrolysates is comparable to molecular mass of polyamides, but their molecular mass distribution is notably wider. Similarly to polyamides (modified or unmodified), collagen hydrolysates are miscible with current epoxide resins only to a limit, but their crystallinity is less marked than that of polyamides.

One of the industrial applications of collagen hydrolysates under consideration is their use in cross-linking of epoxide resins – best with solvent-free systems – that may lead to biodegradable epoxide films. These could considerably facilitate, for example, recycling of plastic parts surface-treated with lacquers on such a basis. The presented work is an introductory study of these problems.

Experimental

Starting materials

Comprised commercially available model epoxides based on bisphenol A, with oxirane rings at ends of molecule, and mean molecular mass in limits 348–480 Da:

- diglycidyl ether of bisphenol A (DGEBA 348)–poly(bisphenol A-co-epichlorohydrin)glycidyl end capped: Av. mol. mass 348, CAS No. 25036-25-3, Sigma/Aldrich Cat. 2005–2006, Product No. 406821 – solid substance, with *m.p.* 44.1° C and density=1.169 g cm^{-3} at 25°C
- diglycidyl ether of bisphenol A (DGEBA 355) – poly(bisphenol A-co-epichlorohydrin) glycidyl end capped: Av. mol. mass=355, CAS No. 20536-25-3, Sigma-Aldrich Cat. 2005–2006, Product No. 387703 – solid substance, with *m.p.* 41.7°C and density=1.168 g cm^{-3} at 25°C
- diglycidyl ether of bisphenol A (DGEBA 377) – poly(bisphenol A-co-epichlorohydrin) glycidyl end capped: Av. mol. mass=377, CAS No. 25036-25-3, Sigma-Aldrich Cat. 2005–2006, Product No. 405493 – viscous, colourless liquid, viscosity 100–150 Poise at 25°C and density=1.168 g cm^{-3} at 25°C
- diglycidyl ether of bisphenol A (DGEBA 480) – poly(bisphenol A-co- epichlorhydrin)glycidyl end-capped: Av. mol. mass=480, CAS No. 25036-25-3, Sigma-Aldrich Cat. 2004–2005, Product No. 40681-3 – viscous, colourless liquid, viscosity 150–180 Poise at 25°C and density=1.168 g cm^{-3} at 25°C.

These materials, apart from data given by manufacturer, were characterised by curves of differential scanning calorimetry (DSC curves) shown for illustration in Fig. 1.

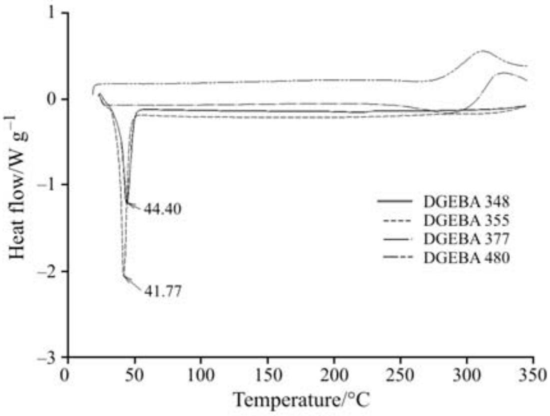

Fig. 1 DSC curves of employed diglycidyl ethers of bisphenol A (DGEBA) with varied mean molecular mass: $dT/dt=10°C\ min^{-1}$

Hydrolysate of chrome-tanned leather waste in powdered state was prepared by enzymatic hydrolysis of chrome-tanned leather waste by the procedure according to [17]. Its analytical characteristics are obvious from data in Table 1.

The course of a typical DSC curve of collagen hydrolysate is shown in Fig. 2. The wide exothermal peak with a minimum at 49.3°C relates most probably to humidity contained in powdered hydrolysate. In the temperature range of 219–235°C (mean: 226.4°C), a glass transition region may be detected, followed by a second endothermal peak (temperature range 253–293°C) which was ascribed to melting of hydrolysate, immediately followed by its thermal degradation.

Table 1 Characteristics of employed chrome-tanned leather waste hydrolysate

Dry substance/%	92.99
Amide nitrogen in dry substance/%	14.85
Ash in dry substance/%	4.94
Cr content in dry substance/ppm	28.15
Ca content in dry substance/ppm	27456.62
Mg content in dry substance/ppm	4798.00
Primary amino groups in dry substance/ mmol NH_2 g^{-1}	0.216
Av. molecular mass (numerical mean M_N)/kDa	17.75

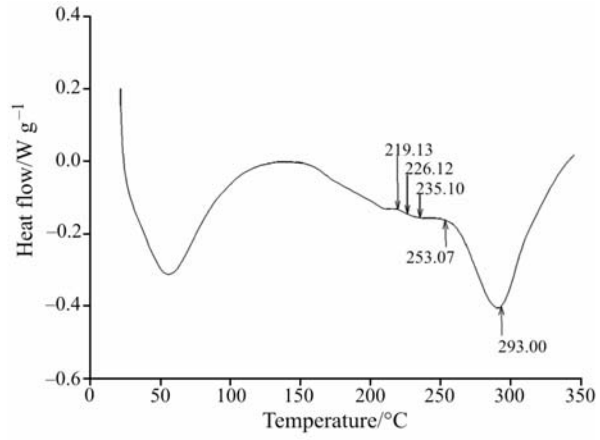

Fig. 2 DSC curve of chrome-tanned leather waste hydrolysate, dT/dt=10°C min^{-1}

Working procedure

Limited compatibility of DGEBA with hydrolysate of chrome-tanned leather waste favours work in solvent-free systems. Most similar studies are conducted in a stoichiometric ratio of both participating groups (oxirane ring:amino groups). However, collagen hydrolysate can react with oxirane ring of DGEBA through various functional groups, including hydroxo groups generated on the opening of oxirane ring. For this reason, particular reaction mixtures were prepared by homogenising air-dry hydrolysate with quantities of particular DGEBAs corresponding to their mass fractions of 0.05–0.33. Homogenisation of reaction mixtures was performed in a mortar.

Thermal behaviour of homogenised reaction mixture in weighed quantities of 2–7 mg was analysed by differential scanning calorimetry (Differential Scanning Calorimeter DSC 2050, TA Instruments, New Castle DE, USA) in an atmosphere of nitrogen, in temperature interval 25–300°C, at rate of temperature increase dT/dt=10°C min^{-1}.

On DSC curves of these reaction mixtures we may detect, apart from a prominent endothermal peak in the region around 58°C which undoubtedly relates to moisture contained in hydrolysate, a marked exothermal peak in the range of 205–220°C which was ascribed (in accord with finds by other authors) to the reaction of amino groups of hydrolysate with oxirane ring of DGEBA. This exothermal peak is followed quite closely by the glass transition region of hydrolysate (detected in temperature interval 219–235°C), which may complicate to some extent calculation of reaction heat, or of kinetic parameters of the condensation reaction.

A typical DSC records of reaction mixtures of investigated DGEBAs with collagen hydrolysate are shown in following Fig. 3.

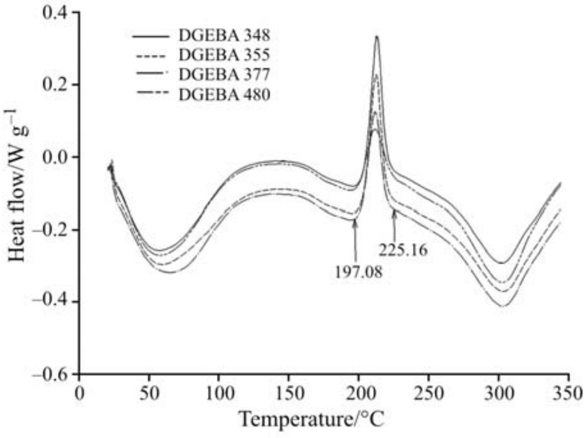

Fig. 3 Typical DSC record of reaction mixture of DGEBA with chrome-tanned leather waste hydrolysate: dT/dt=10°C min^{-1}, mass fraction DGEBAs in reaction mixtures: 0.1667

Results of performed experiments (reaction heat, Q (J g^{-1}), logarithm of the Arrhenius pre-exponential factor, log$A$ – A (min^{-1}) and activation energy, E (kJ mol^{-1}) – calculated by the method after Borchard–Daniels [18]) are then arranged for easy survey in Table 2.

Results and discussion

Collagen hydrolysate contains a number of functional groups capable of reacting with the oxirane ring of DGEBA. Admittedly, most significant among those are supposedly primary amino groups, but secondary amino groups can react similarly, and Zhong and Guo [12] even proved potential participation of amide groups in such a reaction. Besides, especially at higher concentrations of DGEBA in the reaction mixture, even a reaction of oxirane ring with hydroxyl groups of hydrolysate cannot be excluded, or with hydroxyl groups generated during homopolymerization of oxirane end groups of DGEBA. On the other hand,

Table 2 Reaction heat, Q (J g^{-1}), log of Arrhenius pre-exponential factor, log$A$ (A (min^{-1})) and activation energy E_a (kJ mol^{-1}) for the reaction of collagen hydrolysate with some diglycidyl ethers of bisphenol A

Composition of reaction mixture			Q/J g^{-1}	Arrhenius kinetic parameters of reaction	
DGEBA/g	Hydrolysate/g	DGEBA mass fraction		log$A$ (A/min^{-1})	E_a/kJ mol^{-1}
		DGEBA, av. molecular mass – 348 Da			
0.3007	6.0140	0.0476	7.76	65.94	620.5
0.3545	3.5450	0.0901	14.65	67.30	598.2
0.5749	2.8750	0.1667	22.20	65.66	610.4
0.5082	1.6940	0.2287	36.51	62.16	579.1
0.5783	1.4460	0.2857	84.87	68.16	719.3
0.5930	1.1860	0.3333	105.38	61.06	655.5
			Mean:	65.047±2.98	630.50±52.89
		DGEBA, av. molecular mass – 355 Da			
0.3581	7.1620	0.0476	2.74	70.47	681.5
0.3905	3.9050	0.0901	9.00	65.16	581.9
0.5225	2.6130	0.1667	21.84	63.10	604.3
0.4873	1.3240	0.2308	37.13	63.52	590.2
0.5514	1.3790	0.2856	53.46	75.21	691.4
0.6358	1.2720	0.3333	67.65	55.91	519.8
			Mean:	65.562±6.97	611.517±68.14
		DGEBA, av. molecular mass – 377 Da			
0.2987	5.9740	0.0476	1.67	62.01	590.2
0.3823	3.8230	0.0901	5.82	67.14	659.5
0.5084	2.5420	0.1667	16.77	76.46	690.9
0.5274	1.7580	0.2308	35.63	68.76	636.4
0.5422	1.3560	0.2856	44.25	59.68	554.4
0.6831	1.3660	0.3333	54.68	55.63	518.1
			Mean:	64.947±7.78	608.257±68.99
		DGEBA, av. molecular mass – 480 Da			
0.2674	5.3480	0.0476	1.56	74.66	634.25
0.3663	3.6630	0.0901	5.80	64.73	690.9
0.5043	2.5220	0.1667	20.61	78.48	714.5
0.4581	1.5270	0.2308	40.28	73.14	670.1
0.5237	1.3090	0.2857	62.19	63.83	587.6
0.6456	1.2910	0.3334	86.02	61.21	564.4
			Mean:	69.342±7.33	643.625±62.03

steric accessibility of functional groups of hydrolysate may have a far-reaching effect on their reactivity.

In experiments immobilising proteins by means of bis-oxiranes, it is usually necessary, because of the relative stability of oxirane ring, to remove unreacted oxirane rings on termination of the reaction [19]. Hence, a lower fraction of DGEBA in the reaction mixture with collagen hydrolysate may obviously simplify the investigated process to some extent. For that reason, experiments were conducted at individual concentrations of DGEBAs corresponding to their mass fractions of 0.05–0.33 in reaction mixtures with collagen hydrolysate.

Reaction heat, Q (J g^{-1}) (Table 2) exhibits quite marked dependence on the mass fraction of DGEBA in the reaction mixture. Similar dependencies were already observed earlier (e.g. [20]), and De Bakker *et al.* [21] for example approximated them when first approaching a linear dependency. In systems we investigated such a dependency is better depicted by log–log function

$$\log Q = 2.71533 + 1.84501 \log X$$

where Q – reaction heat (J g^{-1}), X – mass fraction of DGEBA in reaction mixture, which shows a 99.15% determination coefficient for investigated DGEBAs (heedless of their mean molecular mass). The graphic picture of such approximation, together with points corresponding to particular experiments performed with DGEBAs of various molecular mass (Table 2), is shown in Fig. 4.

Limit value Q of this approximation function (for $X_{\mathrm{DGEBA}} \rightarrow 1$) attains value 519.19 J g^{-1}, which corresponds to value of enthalpy ΔH=101.24 kJ mol^{-1} after conversion per mol oxirane ring. Taking into account different molecular mass of studied DGEBAs, values that can be arrived at for employed DGEBAs (different mean molecular mass) are 90.34 for DGEBA$_{348}$, 92.16 for DGEBA$_{355}$, 97.87 for DGEBA$_{377}$ and 124.61 kJ mol^{-1} for DGEBA$_{480}$.

Data by earlier authors (e.g. [22]) on enthalpy of the reaction of diglycidyl ethers of bisphenol A type

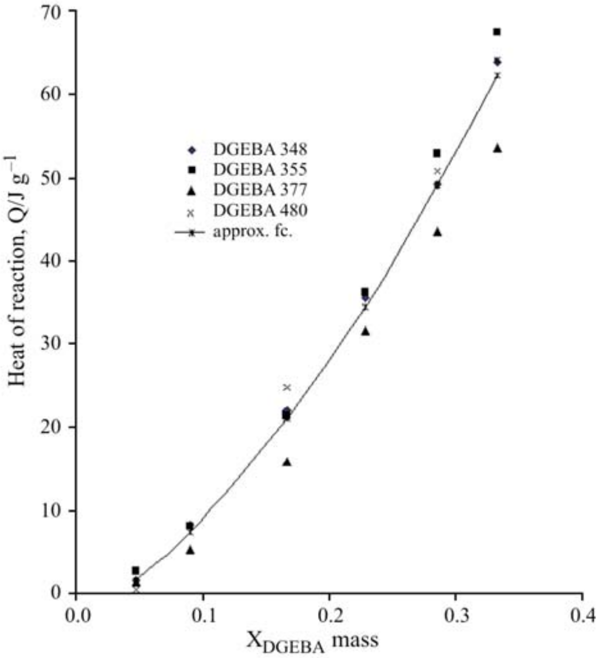

Fig. 4 Dependency of reaction heat on mass fraction of DGEBA in reaction mixture; approximation function: $\log Q=A+B\log X_{\mathrm{DGEBA}}$

with curing agents of diamine type (related per mol oxirane) as a rule fluctuate in dependence on diamine structure. Thus, Khurana *et al.* [7], when curing DGEBA with aromatic amines containing silicon, arrived at enthalpy of such a reaction at the value of ΔH=72.9–103.9 kJ mol^{-1} and suppose the found values are associated with structure of employed diamines. Lee *et al.* [23], when cross-linking epoxides based on 4,4'-biphenyls with diamino-diphenyl sulphones and diamino biphenyl esters, arrived at value ΔH=127 kJ mol^{-1}, and Barral *et al.* [24] give the value of reaction heat Q=313 J g^{-1} for the reaction of curing DGEBA with diamines derived from bis-aminocyclohexane. When cross-linking DGEBA with various imidazoles, Ooi *et al.* [25] found ΔH values fluctuating within limits 70.4–102.8 kJ mol^{-1} and think fluctuation of these values is not associated only with type of applied imidazole but also with rate of temperature increase ($\mathrm{d}T/\mathrm{d}t$) during DSC measurements. All authors more or less agree that the value of enthalpy of reaction of oxirane ring with various diamines lies in range 102–105 kJ mol^{-1} (per mol oxirane ring) [26, 27].

De Bakker *et al.* [21] tend to the opinion that this currently accepted value of total enthalpy of the reaction of oxirane ring with functional groups considered for curing epoxide resins with usual curing agents (primary and secondary amino groups, or hydroxyl groups), i.e. $\Delta H\approx105$ kJ mol^{-1} oxirane ring, is slightly exaggerated because it is based on assumed minimum differences in enthalpy of the reaction of considered functional groups with oxirane ring. According to their finds, enthalpy of the reaction of 1 mol oxirane ring with primary amino groups ΔH_{prim}=83±2 kJ mol^{-1}, with secondary amino groups ΔH_{sec}=131±9 kJ mol^{-1}, and with hydroxyl groups ΔH_{OH}=65±6 kJ mol^{-1}, so that the average enthalpy of usual curing reactions of epoxide resins is closer to value ΔH=92±1 kJ mol^{-1} – again per mol oxirane ring. Considering the potentially varied proportions of discussed functional groups in collagen hydrolysate, we may assume the found limit values of reaction heat (or calculated average values of enthalpy of its reaction with various DGEBAs) are in good accord with finds by authors mentioned above.

In cross-linking reactions executed in the solid phase, some authors also noticed dependency of reaction kinetic parameters (pre-exponential factor, A (min^{-1}) and activation energy, E (kJ mol^{-1})) on the concentration of oxirane rings, or on ratio of oxirane rings and amino groups in the reaction mixture. In the executed experiments cross-linking DGEBA by means of collagen hydrolysate (Table 2), a like dependency could not be detected. Both kinetic parameters admittedly exhibit certain fluctuation in particular experiments, characterised with individual DGEBAs by a 95% reliability interval of average value around 10%, but this may be regarded as a reasonable scatter of experimental results when taking into account the usual reliability of analogous calculations. A plausible explanation for the observed fact may also be the considerable preponderance of groups able to react with oxirane ring of DGEBA, provided for in the reaction mixture by a higher hydrolysate concentration (its mass fraction in reaction mixture X_{Hydr}=0.95–0.67).

Based on values of reaction heat, Q (J g^{-1}), on its dependency on concentration of DGEBA in reaction mixture and on values of kinetic parameters of the reaction, we may assume that collagen hydrolysates, when curing epoxide resins, behave similarly to polyamides PA6 or PA6,6. This also corresponds to the temperature interval (200–220°C) in which cure of studied DGEBAs proceeds. Thermal degradation of collagen hydrolysates occurs (in nitrogen) only at temperatures at least 30°C higher, and obtained values of kinetic parameters of the cross-linking reaction also agree with the concept that the mechanism determining kinetics of such a reaction, by the way similar to most like reactions conducted in solvent-free systems, is diffusion.

Preliminary results of laboratory experiments, which have not been completely finished yet, suggest that epoxides cured with collagen hydrolysates may be quite readily degraded into soluble components by proteases, of bacterial origin above all, which are economically well available. Hence, the assumption that such systems are biodegradable is well justified. From both an economic as well as ecological point of view, this property may be interesting for a number of practical applications (for example, using similar systems as bonding polymers for coating materials, recycling automobile plastic parts, disposing of printed wiring base plates, etc.).

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