Journal of Thermal Analysis and Calorimetry, Vol. 75 (2004) 205–219

CURING ADHESIVES OF UREA–FORMALDEHYDE TYPE WITH COLLAGEN HYDROLYSATES OF CHROME-TANNED LEATHER WASTE

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(Received August 10, 2003; in revised form September 16, 2003)

Abstract

Condensation of dimethylol-urea (DMU) mixed with urea (U) and collagen hydrolysate (H), obtained through enzymatic hydrolysis of chrome-tanned leather waste, without added acid curing agents in the solid phase was studied through DSC and TG techniques in a temperature interval up to 220°C. Among both techniques TG proved be more useful.

While the DMU+U mix produced methylene-oxide ($–CH_2–O–CH_2–$) and methylene ($–CH_2–$) bridges at a ratio of approx. 1:1, urea substituted for collagen hydrolysate increased the proportion of more stable methylene bridges to methylene-oxide bridges to a ratio of approx. 2:1. Methylene-oxide bridges are considered to be the main potential sources of formaldehyde emissions from cured urea–formaldehyde type adhesives, and thus the use of collagen hydrolysate in preparation of urea–formaldehyde adhesive types is a suitable way how to make such adhesives more environmental friendly.

Keywords: amino-resins, curing, formaldehyde emission, hydrolysates of chromed leather waste

Introduction

Adhesives based on urea–formaldehyde condensates (UF resins) are employed in the wood-processing industry as well as in a number of other industrial manufactures mainly for application from aqueous systems (non-inflammable systems with relatively low production costs), for easily adapting to various curing conditions, for their cured films possessing good thermal properties and lacking sharp coloration. Among their disadvantages is potential emission of carcinogenic formaldehyde from cured films, which grows with an increasing molar ratio of formaldehyde to urea in initial reaction mixture (e.g. [1]). Adhesives with a declared lower formaldehyde emittance are, therefore, usually produced in a lower molar ratio of formaldehyde to urea (approx. 1.2 :1) in

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1388–6150/2004/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

the reaction mixture and, moreover, a further addition of approx. 5% urea to the adhesive is recommended prior to actual curing of adhesive film [1, 2].

Most works dealing with problems of urea–formaldehyde type adhesives date from the second half of the 20th century and are more focused on the field of actual adhesive preparation (reaction of urea with formaldehyde, conducted in an alkaline environment in molar ratio of both reactants approximately ranging from 1:1.5 to 1:2) resulting in a mixture of oligomeric polycondensates of dimethylol-urea (DMU) with reactive methylol ($–CH_2–OH$) groups. Polycondensation in this stage follows formal kinetics of a second-order reaction and its activation energy was determined as 54 kJ mol^{-1}, activation energy of reverse reaction was determined as 79.5 kJ mol^{-1} [3–5]. Reaction heat associated with preparing methylol- and dimethylol-urea was later determined as 20.5 kJ mol^{-1} by Lundquist [6], who arrived at a value of 64.4 kJ mol^{-1} for the activation energy of primary addition reaction and to a value of 85.3 kJ mol^{-1} for the reverse reaction of N-methylol derivatives hydrolysing to urea and formaldehyde.

Problems of actual cure of such adhesive films have received attention practically only in last decade. Thermal behaviour of UF adhesives was followed by TG [7] and DSC [8], Schanzer and Bührer [9] employed thermogravimetric analysis for studying trimethylol-melamine condensation. They detected two clearly enough separated waves of mass decreases on TG curves. The first appeared in a temperature interval to about 120°C (corresponding to mass decrement $-\Delta m_1 \approx 6.39\%$), the second one in temperature interval at approx. 140°C (associated with mass decrement $-\Delta m_2 \approx 12.25\%$). As they had detected merely water among gaseous reaction products up to a temperature of 200°C through mass spectrometry and FTIR, they ascribed the first wave to condensation leading to production of methylene-oxide ($–CH_2–O–CH_2–$) bridges with splitting-off of water, and subsequently the second, ending at approx. 140°C and exhibiting a virtually twofold mass loss of sample, to release of water with formation of more stable methylene ($–CH_2–$) bridges. They detected further mass decrease of polycondensate above temperatures of 220°C, finding formaldehyde and ammonia among gaseous reaction products and even methanol (used for stabilising methylol derivatives of melamine). From such results they concluded that methylene-oxide bridges may be transformed to methylene bridges (with elimination of formaldehyde) above that temperature. A further increase in temperature above 250°C, after their finds, subsequently leads to deep thermal degradation of polycondensate.

Siimer *et al.* [10] monitored using TG-DTA technique curing of various commercial adhesives based on urea formaldehyde polycondensates, and stated influence of curing conditions on cured resins properties. In connection with recycling problems of particle board, bonded by UF adhesives, Fleischer and Maruzky followed the behaviour of hardened UF resins under various hydrolysis condition and assessed the influence of pH and temperature on the hydrolysis process [11]. Hirata *et al.* [12] investigated UF resins pyrolysis using TG in He atmosphere and find out the process consisted from several steps directed by zero- and first order kinetics.

Various sources [13, 14] indicate that tanning industry produces 50–60% (based on raw hide mass) of proteinaceous waste with chrome tanned shavings representing the most problematic waste type. Recently developed biotechnological processes [15, 16] of that proteinaceous waste treatment, leading to proteinaceous hydrolysates of standard quality, were successfully applied in industrial practice.

Hydrolysates of chrome-tanned leather waste exhibit similar reactivity to aldehydes as urea (e.g. [17]) and may well make up a supplementary addition lowering formaldehyde emission of UF adhesives type. Possible effect of chrome tanned leather hydrolysates on UF resins curing process is subject of the presented work.

Experimental and results

Suitable techniques for observing the curing process of urea–formaldehyde type adhesives are methods of thermal analysis, chiefly of TG and differential scanning calorimetry (DSC). Both of them are applied in this work to behaviour of dimethylol-urea in a mixture with urea and also with hydrolysate of chrome-tanned leather waste which could well replaced it in industrial applications.

Starting materials

Dimethylol-urea (DMU) (by Sigma-Aldrich, Cat. No. 205-444-0), dried, for laboratory use, mol. mass 120.1, melt. point 126°C [18]). In accordance with manufacturer's recommendations, the preparation was kept in refrigerator at 0°C.

Urea (U) 99.5% (by Lachema, Brno, Cat. No. 11058077), mol. mass 60.055, melt. point 135°C [18].

Hydrolysate of chrome-tanned leather waste (H) was obtained in powder form through enzymatic hydrolysis of chrome-tanned leather waste from tanning by a procedure described in detail [15–17]. Its characteristics are presented for illustration in Table 1.

Table 1 Characteristics of enzymatic hydrolysate of chrome-tanned leather waste

Dry matter/%	9.04
Amide nitrogen in dry substance/%	15.65
Ash in dry matter/%	3.09
Cr content in dry matter/ppm	13.60
Primary amino groups in dry matter/mmol g^{-1}	0.24
Average mol. mass (Numer. mean, M_N)/kDa	19.80

Procedure

Condensation of DMU (usually catalysed in practice with acid or acid-releasing substances) was studied – for the sake of simplification – without addition of the mentioned agents – in mixtures with urea (U) or leather waste hydrolysate (H) in mass ratios covering interval 0–0.3 (with U) and 0–0.5 (with H). Reaction mixtures were prepared by weighing-in solid powdery reactants and homogenising them on a Perkin

Elmer vibrating mill usually employed in preparation of KBr tablets for IR spectrophotometry. The mass of homogenised solid reaction mixture for a milling capsule was around 0.5 g and homogenising efficiency was enhanced by inserting an agate ball (inert material) into the milling capsule. To minimise possible heating of the homogenised mixture, a short homogenisation time was selected – max. 3 s.

TG measurements were made using fully computerized thermogravimetric analyser TG Q 500 (TA Instruments, New Castle/De/USA) in nitrogen atmosphere, with heating rates 1 and 2°C min^{-1}, sample mass 1–6 mg in Pt sample pan and temperature intervals reaching from room temperature (cca 25°C) to 300°C. Calibration of the instrument followed the instrument software. The software algorithm enables computation of kinetic parameters (pre-exponential factor *A* (min^{-1}) and activation energy E/kT), according to ASTM E 1641 [19], provided at least two measurements at different heating rate are available. The waves of mass decrease on TG curves (measured sample mass decrease *vs*. temperature) were identified easily on the base of minima points of first derivatives TG curves.

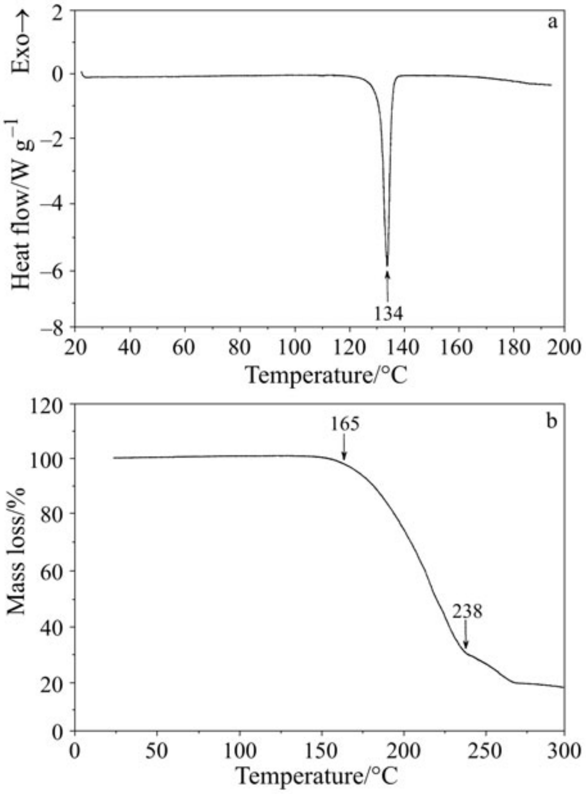

Fig. 1 DSC and TG curves of applied urea preparation (U). a – DSC curve of U: 25–200°C; weighed quantity: 2.0 mg, d*T*/d*t*=10°C min^{-1}; b – TG curve of U: 25–300°C; weighed quantity 2.0 mg, d*T*/d*t*=10°C min^{-1}

For DSC measurements computerized instrument DSC 2010 CE (TA Instruments, New Castle/Del/USA) was used with heating rate 1 or 2°C min^{-1}. Sample measured (1.0–5.5 mg) was weighed in a non-hermetic Al pan, and heat flow measurement followed using similar empty non-hermetic pan as blank. All DSC measurement were done using nitrogen as cell purge gas, in temperature range from room temperature (approx. 25°C) to about 300°C with heating rate usually 1 and 2°C min^{-1}.

Typical DSC and TG curves of sole DMU, U and their mixtures (mass fraction of U in mixture was 0.05) and/or H (mass fraction of H in mixture was 0.1) are shown for illustration in Figs 1–3. While in DSC records of sole U a single endothermic peak may be detected in the region of 134°C (ΔH=238.078 J g^{-1}), which corresponds to phase transition (melting) of urea (135°C), with DMU there are two well separated endothermic peaks, the first in the region of 105°C (ΔH=27.98±6.03 J g^{-1}), the second in the region of 127°C (ΔH=229.44±7.36 J g^{-1}). Thermal co-ordinates of the second DSC endo-peak are in quite good agreement with melting temperature of DMU (melt. point 126°C).

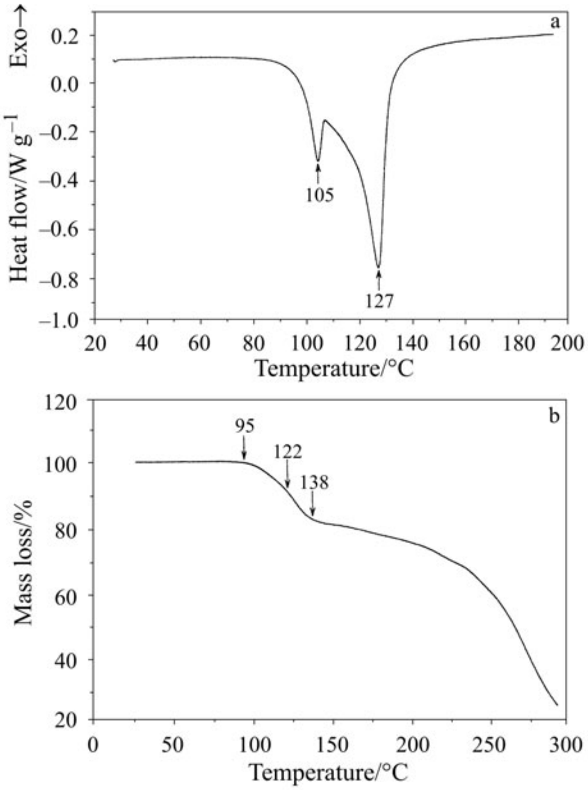

Fig. 2 DSC and TG curves of applied dimethylol-urea preparation (DMU). a – DSC curve of DMU: 25–200°C; weighed quantity 1.0 mg, $\mathrm{d}T/\mathrm{d}t$=1°C min^{-1}; b – TG curve of DMU: 25–300°C; weighed quantity 1.0 mg, $\mathrm{d}T/\mathrm{d}t$=1°C min^{-1}

TG curves of U exhibit a single wave of mass loss beginning at temperatures above 165°C and finishing around 238°C (Fig. 1b), corresponding to its thermal breakdown, while TG curves of DMU exhibit two more or less distinctly separated waves, the first in the temperature region of 100–121.8°C corresponding to a loss of 6.8% in mass of analysed sample, continuing in a second wave (in temperature interval of 121.85–137.72°C) with a characteristic mass loss of 15.8% (related to same basis). Both TG curves come within the same temperature regions as endothermic peaks of DSC curves. The shape of a typical TG record of DMU is presented in Fig. 2b.

Leather waste hydrolysate (H) displays on DSC curves (Fig. 3a) a marked endothermic peak with a minimum around 60°C which unambiguously corresponds to content of water present in hydrolysate and an indistinctive endothermic peak in the region of 137–147°C which had already been ascribed to cyclohexyl amine (<1 mass%) used to produce an alkaline environment in the enzymatic breakdown of chrome-tanned leather waste [17]. This endothermic peak becomes less distinct in time, probably due to a certain volatility of cyclohexyl amine. The course of TG curves of H (Fig. 3b) is consistent with the course of DSC curve.

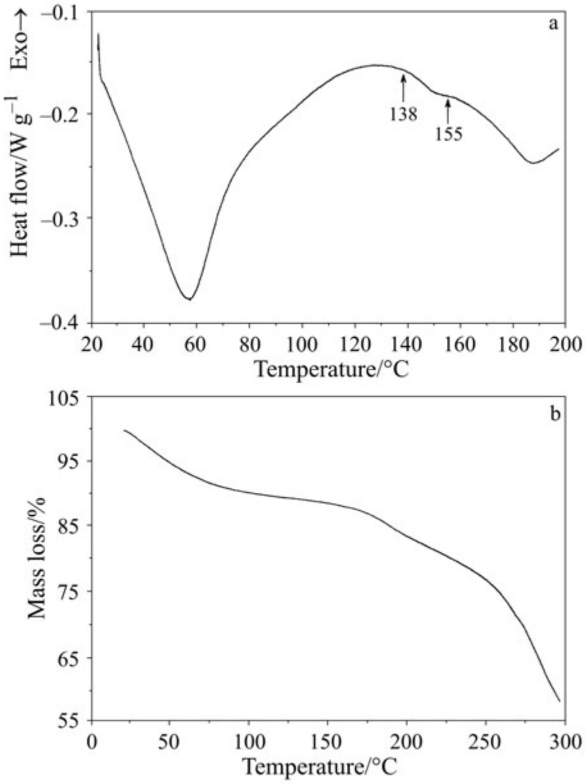

Fig. 3 DSC and TG curves of applied hydrolysate of chrome-tanned leather waste (H).
a – DSC curve of H: 25–200°C; weighed quantity 2.0 mg, dT/dt=2°C min^{-1};
b – TG curve of H: 25–300°C; weighed quantity 2.1 mg, dT/dt=2°C min^{-1}

DSC curves of mixtures of DMU with U and also H rather correspond to DSC curves of DMU itself (Figs 4a and b), and, in addition, another not too strongly developed endothermic peak of low energy content (ΔH=8.3±3.1 J g^{-1}) can be detected in the 60°C region with DMU+H mixtures (Figs 5a and b); this is most probably related to moisture bound to collagen hydrolysate.

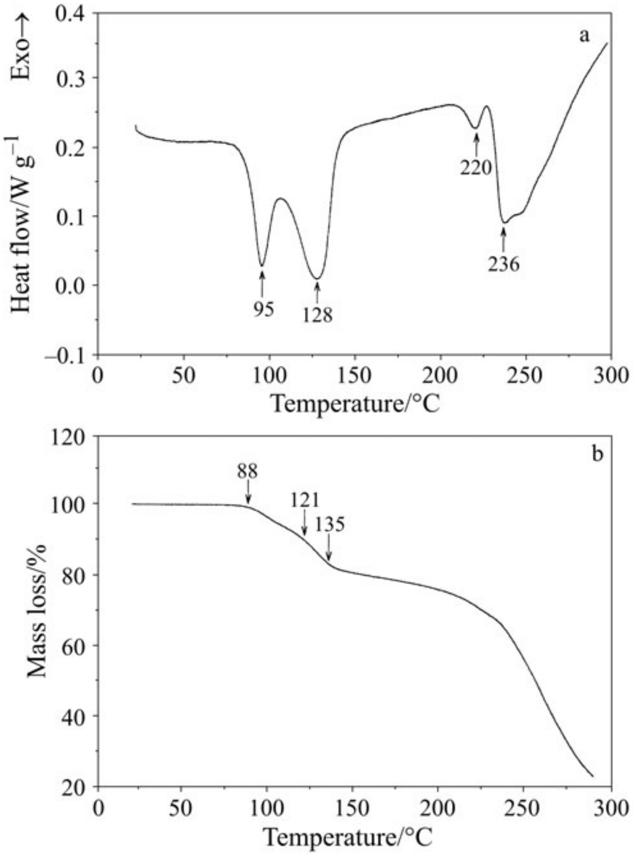

Fig. 5 Typical DSC and TG curves of mixture dimethylol-urea (DMU)+hydrolysate of chrome-tanned leather waste (H). a – DSC curve of reaction mixture DMU+H, mass fraction of H=0.01, weighed quantity 2.01 mg, temperature interval 25–300°C, dT/dt=1°C min^{-1}; b – TG curve of reaction mixture DMU+H, mass fraction of H=0.05, weighed quantity 6.30 mg, temperature interval 25–300°C, dT/dt=1°C min^{-1}

With both marked, well defined endothermic peaks there occurs a shift of the temperature co-ordinates of their minimum, and to a notably lesser extent also that of their energy content, when content of U and/or H is changed. Average values of both characteristics in dependence on U and/or H are obvious from data of Table 2.

Table 2 Temperature co-ordinates and energy contents of endothermic DSC peaks of dimethylol-urea with mass fraction of urea (or hydrolysate) in mixture

Mass fraction of urea or hydrolysate in mixture		First endo-peak		Second endo-peak	
		Av. value T_{min}/°C	Av. value of ΔH/J g^{-1}	Av. value T_{min}/°C	Av. value of ΔH/J g^{-1}
Urea	0.00	104.2±1.1	27.92±6.03	126.0±1.9	229.44±7.36
	0.01	101.8±1.3	25.125±1.89	125.9±1.9	237.42±12.51
	0.03	97.0±1.5	22.903±0.29	125.0±2.3	241.50±0.29
	0.05	94.1±2.2	17.985±1.26	124.9±1.4	243.92±8.07
	0.08	97.3±1.0	11.890±1.19	121.8±1.5	224.50±1.84
	0.10	84.5±1.4	20.730±8.89	120.4±1.4	202.38±5.57
	0.30	75.5±0.4	30.24±0.12	124.3±7.1	224.35±3.72
	1.0	–	–	133.5±1.3	237.45±2.94
Hydrolysate	0.01	96.9±1.8	68.98±8.04	128.1±0.3	179.78±8.94
	0.05	91.8±1.6	93.43±6.19	138.9±3.1	174.43±11.14
	0.10	87.4±1.8	105.38±2.27	141.0±0.7	172.63±31.82
	0.50	83.5±2.9	58.37±20.24	136.6±1.3	120.50±10.12

Similarly, the content of U in mixtures with DMU affects the temperature interval in which both mass-decrease waves of TG curves and pertaining loss in mass can be detected. These data are summarised in following Table 3.

In addition, TG curves of DMU-H mixtures exhibit (for that matter, in accord with curves of DSC measurements) 3 waves of mass loss in sample. The first ends at temperatures above 85–87°C and corresponds to a small loss in sample mass ($-\Delta m \approx 2$–3%); it may be attributed to hydrolysate-bound moisture. It is not too distinctly separated from the second wave which corresponds by its temperature co-ordinates to the first TG wave of DMU itself (or of DMU-U mixture), and the corresponding loss in mass is clearly lower. The third TG wave then practically corresponds in both parameters (temperature interval and mass loss) to the second TG wave of DMU.

TG analysis of DMU and of its blends with U and/or H was conducted at different rates of heating and corresponding values of pre-exponential factor A (min^{-1}) and activation energies E/kT (kJ mol^{-1}) were calculated, applying official ASTM method [19] for both TG waves which were obviously related to condensation of DMU alone and/or also in the presence of U or H. Such results are summarised in Table 4 for combination DM+U and in Table 5 for DM+H.

Discussion

Dimethylol-urea polycondensates, which may be generally regarded as the structural prototype of urea–formaldehyde adhesives, are known for certain formaldehyde

Table 3 Characteristics of TG curves (final temperature *T*, mass decrement $-\Delta m/\%$) of mixtures of dimethylol-urea (DMU) with urea (U) and/or collagen hydrolysate of chrome-tanned leather waste (H)

Reaction mixture	TG_0 $T/°C$	TG_0 $-\Delta m_0/\%$	TG_1 $T/°C$	$TG_1/$ $-\Delta m_1/\%$	TG_2 $T/°C$	$TG_2/$ $-\Delta m_2/\%$
DMU	99.8±5.1	0	121.9±4.4	8.3±2.6	135.6±6.1	17.2±3.6
DMU+0.01U	97.0±3.3	0	121.4±2.4	8.4±0.9	135.8±2.9	17.1±1.2
DMU+0.03U	89.9±3.9	0	117.1±2.3	8.0±0.8	132.3±2.7	16.7±1.8
DMU+0.05U	87.9±	0	117.0±4.8	7.3±0.8	134.0±5.6	16.0±1.0
DMU+0.08U	82.9±	0	116.5±2.7	7.2±1.6	130.5±2.8	15.3±1.0
DMU+0.10U	88.5±	0	116.5±5.7	7.1±0.8	137.8±3.3	15.1±1.4
DMU+0.30U	79.1±2.1	0	105.1±3.7	6.9±1.6	145.5±3.5	15.0±1.8
DMU+0.01H	87.8±1.9	1.2±0.9	123.7±2.4	5.8±2.1	135.6±2.6	16.8±2.9
DMU+0.10H	77.7±2.8	2.3±0.2	125.9±2.4	5.8±1.3	140.2±5.5	15.7±1.2
DMU+0.30H	83.4±4.7	2.3±0.2	126.2±2.8	5.9±1.5	143.7±3.2	13.4±4.5
DMU+0.50H	85.9±2.9	3.5±0.3	121.8±4.8	4.8±1.1	144.5±3.5	11.0±5.5

Table 4 Average values of Arrhenius kinetic parameters: pre-exponential fractor *A* (min^{-1}) and activation energy *E* (kJ mol^{-1}) for first and second mass-decrease waves of TG curves for mixtures of dimethylol-urea with various mass fractions of urea

Mass fraction of urea in mixture with dimethylol-urea	Mass decrease wave 1 Average temperature interval 100–116°C		Mass decrease wave 2 Average temperature interval 118–135°C	
	A/min^{-1}	$E/\text{kJ mol}^{-1}$	A/min^{-1}	$E/\text{kJ mol}^{-1}$
0	18.35±2.12	245.19±5.46	21.22±8.11	254.77±9.07
0.01	18.24±2.45	200.00±5.13	16.15±1.48	253.22±6.36
0.03	22.58±8.45	192.48±11.22	31.78±4.16	249.80±8.92
0.05	25.98±2.41	193.71±5.11	31.01±3.55	245.75±4.87
0.08	24.78±5.29	194.07±3.47	31.01±3.55	238.96±3.20
0.10	26.99±1.77	195.01±9.70	30.65±0.94	234.49±9.67
0.30	25.95±4.75	187.78±10.75	20.66±4.61	169.62±8.64

emission which is usually associated with their hydrolysis. In order to limit formaldehyde emission it is usually recommended to reduce the ratio of formaldehyde:urea, when producing oligomeric dimethylol-ureas, below the 2:1 level (molar ratio) or perhaps to add approx. 5% urea to the adhesive closely before application. A positive effect is usually supported with results of customary tests, their results, however, often vary to a large extent.

When studying potential applications for enzymatic hydrolysates of chrome-tanned leather waste from tanning [16, 17], an opinion was voiced, among others, that such hydrolysates can be applied to advantage when formulating urea–formaldehyde type adhesives of lower formaldehyde emission.

Nevertheless, DSC technique applied to this problem did not prove too successful. Two endothermic peaks (situated at temperatures $T\approx100°$, or 125°C – Table 2), detectable both during condensation of sole dimethylol-urea (DMU) and of its mixture with urea (U) as well as with hydrolysate of chrome-tanned leather waste (H), are most probably related to the course of condensation reaction but it is somewhat problematic to find how much they are subject to influence of water absorbed in some components of the reaction mixture (first DSC peak – Table 2) or to phase transition of DMU (melt. point DMU≈126°C≈second peak, Table 2).

Increasing the mass fraction of U in the mixture with DMU shifts temperature co-ordinates of minimums of both endothermic DSC peaks and also their enthalpies toward lower values. With the first peak, these changes correspond to changed characteristics of the first TG wave in dependence on this parameter of the reaction mixture, which supports the concept that the first DSC endothermic peak is more strongly associated with the course of water released by condensation reaction than to water possibly adsorbed by some component of the reaction mixture (compare data of Tables 2 and 3).

Table 5 Average values of Arrhenius kinetic parameters (pre-exponential factor *A* (min^{-1}) and activation energy *E* ($\mathrm{kJ\ mol}^{-1}$) for mass-decrease waves of TG curves for reaction mixtures of dimethylol-urea with different mass fractions of chrome-tanned leather hydrolysate

Hydrolysate mass fraction in mixture with dimethylol-urea	Mass decrease wave 1 Average temperature interval 25–87°C		Mass decrease wave 2 Average temperature interval 100–125°C		Mass decrease wave 3 Average temperature interval 127–141°C	
	A/min^{-1}	$E/\mathrm{kJ\ mol}^{-1}$	A/min^{-1}	$E/\mathrm{kJ\ mol}^{-1}$	A/min^{-1}	$E/\mathrm{kJ\ mol}^{-1}$
0.00	–	–	18.35±2.12	245.19±5.46	21.22±8.11	254.77±9.07
0.01	18.56±1.90	160.26±4.32	20.66±6.34	160.96±13.65	33.42±1.12	273.41±4.68
0.05	16.11±2.43	124.20±6.21	18.47±6.36	145.83±14.49	31.00±9.11	244.92±17.24
0.10	21.41±1.87	153.36±11.0	19.40±0.65	226.67±12.63	30.48±5.37	251.08±9.82
0.30	21.13±5.79	124.52±11.73	20.84±1.03	230.67±48.60	31.05±4.16	244.28±44.22
0.50	23.87±6.35	147.49±9.60	22.57±3.74	232.66±35.57	33.36±2.93	267.08±9.72

Correspondence of the second detected DSC endo-peak (T_{min}=125.96°C, ΔH=229.44 J g^{-1}) with temperature co-ordinates of the second TG curve (compare again data of Tables 2 and 3) is somewhat worse and the influence of phase transition (melting) of DMU seems to be greater than the influence of condensation reaction. Provided this view is accepted, a phase diagram of the system can be constructed based on temperature co-ordinates of this endo-peak for DMU mixtures containing different mass fractions of U. Such a diagram, for the sake of interest, is shown in Fig. 6. In the light of results obtained it is not clear whether the condensation reaction runs parallel to phase transition of DMU or whether the reaction is conditioned by this phase transition. In addition, its practical significance is complicated by the fact that conditions of pressure and temperature during industrial applications range in quite different dimensions (120–160°C, 1.5–9.8 MPa).

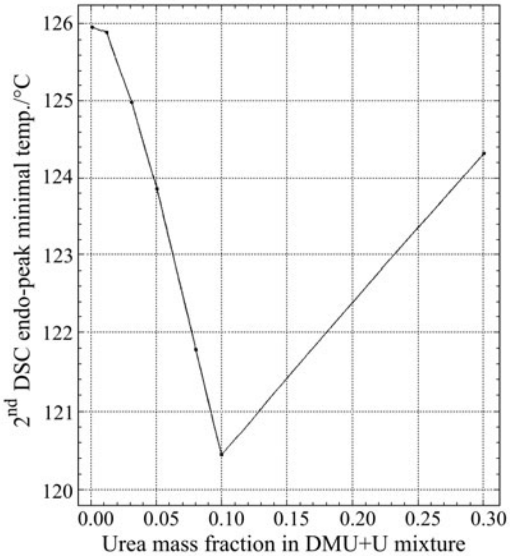

Fig. 6 Influence of mass fraction of DMU in reaction mixture with U on the temperature of minimum of endothermic DSC peak 2

TG curves (temperature dependence of mass decrease) of DMU and its mixtures with U and/or H provide results similar to those obtained by Schanzer and Bührer (comp. [9]) with methylol derivatives of melamine. Water absorbed by hydrolysate of chrome-tanned leather waste [17] is released within temperature interval 80–90°C, and in the case of sole DMU and its mixtures with U is practically absent. The mass decrease of the TG curve with a typical mass decrement of 8.3%, associated with the course of DMU polycondensation, can be detected in the case of DMU itself in temperature interval 100–120°C. With an increasing mass fraction of U in reaction mixture, the temperature interval of the curve is shifted to somewhat lower temperatures, and when mass fraction of U>0.03, even the mass decrement associated with this curve is reduced. In association with finds by Schanzer and Bührer [9] and with a view to the detected mass decrement, this TG wave may be attributed to the formation of methylene-oxide (–CH_2–O–CH_2–) bridges. The mass decrease of TG curve in the region of approx. 130–140°C, (attributed to methylene bridges formation) corresponds in the case of DMU to mass decrement 17.17% and clearly tends to decrease when the mass fraction of urea in the mixture increases above 0.05. Based on the ratio of mass decrements of both reactions it may be assumed that the ratio of methylene-oxide (–CH_2–O–CH_2–) and methylene (–CH_2–) bridges formed during condensation of DMU (in absence of acid curing agents) approximately reaches the level of 1:1 (48.5:51.5%), and this ratio is altered only slightly as the mass fraction of U in the reaction mixture increases. This find is graphically documented by the dependencies of mass decrements of both TG curves on the mass fraction of urea in the mixture (Fig. 7).

Addition of U immediately before actual cure of urea–formaldehyde adhesive films can thus scarcely dramatically reduce the proportion of forming methylene-oxide bridges which, due to their well-known poorer stability, may be regarded as a potential source of formaldehyde emissions from these adhesives.

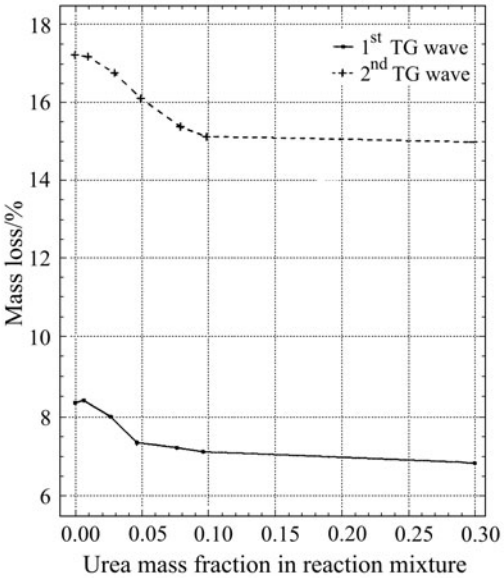

Fig. 7 Influence of mass fraction of urea (U) in reaction mixture with dimethylol-urea (DMU) on mass decrement of both detected TG waves

This conclusion also corresponds with a very small difference in activation energies of reactions leading to methylene-oxide (–CH_2–O–CH_2–) and methylene (–CH_2–) bridges, as were determined by evaluating TG curves by the ASTM E 1641 method [19] (Table 4). Urea added immediately prior to cure of such adhesive films can, perhaps, fulfil the function of a certain ‘catcher’ of formaldehyde released through gradual breakdown of methylene-oxide bonds, which are with great probability the potential source of formaldehyde emissions. The achieved reduction of formaldehyde emissions from such adhesive films is thus rather tied to a lower molar ratio of formaldehyde to urea in the starting reaction mixture. Possibly increasing the molar fraction of urea additionally added to adhesives of this type, above a value of 0.05, seems to be somewhat counterproductive when regarding values of activation energies of both reactions (drop in total mass decrement dependently on growth of mass fraction of U, obvious from Table 4).

TG curves of systems containing hydrolysate of chrome-tanned leather waste (DMU+H – compare data of Table 3) display three more or less well separated waves of mass decreases. The first (ending at T≈80–85°C) is associated with a minimum mass decrement ($-\Delta m_1$=1.2–2.3%) and corresponds with great probability to release of water absorbed by hydrolysate [1]. The second wave, approximately situated in temperature region 85–126°C, may be associated with formation of methylene-oxide ($-CH_2-O-CH_2-$) bridges. Compared to DMU+U reaction mixtures, its mass decrement is correspondingly lower ($-\Delta m_{av.}$≈5.5%). The third detected mass decrease wave, associated in the DMU+U system with formation of methylene ($-CH_2-$) bridges, is somewhat shifted toward higher temperatures (123–145°C) in the case of DMU+H systems. If mass fraction of H exceeds 0.05, corresponding mass decrement tends to shift to lower values. However, if mass fraction of H in mixture with DMU does not exceed the value of mass fraction as mentioned, the ratio of mass decrements in both reactions (associated with formation of methylene-oxide ($-CH_2-O-CH_2-$) and methylene ($-CH_2-$) bridges) corresponds to a more favourable ratio (approx. 1:2 in favour of more stable methylene bridges). Relative production of methylene-oxide bridges (potential source of formaldehyde emissions) is hence somewhat suppressed through this replacement, which may be characterised as a positive effect of hydrolysate application.

Owing to higher molecular mass of hydrolysate, mechanical properties of adhesive bonds may be expected to be affected rather positively by such a replacement. Certain influence can be exerted by catalysing condensation of methylol derivatives in such adhesives with acid curing agents. Solutions to problems indicated are not quite simple and they will receive attention in further works.

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The authors wish to thank the Ministry of Education of the Czech Republic for financial support to this work, executed under MSM Grant No. 265 2002/14.

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