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CURING OF UREA-FORMALDEHYDE ADHESIVES WITH COLLAGEN TYPE HYDROLYSATES UNDER ACID CONDITION

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Abstract

Condensation of dimethylol urea and its mixtures with urea or hydrolysate of chrome-tanned leather waste (mass fraction in mixture 0.05) in the presence of a variable quantity of phthalic acid, as acid curing agent (within mass fraction limits 0.01–0.1), was studied through TG technique. During condensation of sole dimethylol urea or of its mixture with urea, oxy-methylene as well as methylene cross-links are produced at a ratio of approx. 1:1, presence of leather waste hydrolysate reduces this ratio to approx. 1:2 in favour of more stable methylene bridges. Higher concentrations of phthalic acid (above mass fraction 0.05) lead to formation of a new TG mass decrement wave in the 150–180°C temperature interval, which probably relates to transition of more unstable oxy-methylene bridges to more stable methylene bridges, with splitting-off of formaldehyde. Oxy-methylene bridges may be regarded as a potential source of formaldehyde emissions by cured urea-formaldehyde adhesive films. Hydrolysate of chrome-tanned leather waste and a suitable concentration of acid curing agent distinctly reduce formaldehyde emission from cured urea-formaldehyde adhesive films.

Keywords: acid hardeners, chromed leather waste, condensation, collagen hydrolysates, dimethylol-urea

Introduction

The disadvantage of urea-formaldehyde-type adhesives, still being widely employed in the wood-processing industry, is a tendency of their cured adhesive films to emit formaldehyde, well-known for its carcinogenic effects [1]. Works dealing with aminoplast-type adhesives are focused in the main on reaction of urea with formaldehyde conducted in an alkaline environment, which is utilised when industrially producing adhesives and leads to methylol derivatives of oligomeric urea-formaldehyde compounds [2–4]. The condensation phase of the reaction (in practice, usually conducted in acid environment), coming into effect during cure of adhesive films, is merely a sporadic subject of more detailed studies [5–7].

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It was found that hydrolysate of chrome-tanned leather waste added to dimethylol urea, in absence of acid curing agents, clearly limits formation of relatively unstable oxy-methylene bridges which may be regarded as potential source of formaldehyde emissions [7]. Acid curing agents may also significantly participate in such limitation. Their influence was investigated in greater detail by TG technique. In conducted experiments, commercial urea-formaldehyde methylol oligomers were modelled (similarly to preceding study [7]) by dimethylol urea (DMU). In order to specify influence of urea and hydrolysate of chrome-tanned leather waste in the presence of an acid curing agent, investigated systems were based on sole DMU as well as on its mixtures with an 0.05 mass fraction of urea (U) or of hydrolysate of chrome-tanned leather waste (H). Acid curing agent was modelled by phthalic acid (PHA) (mass fraction levels in mixture 0.01–0.1), which is sometimes recommended for curing urea-formaldehyde adhesive films in industrial practice.

Experimental

Starting materials

Dimethylol-urea (DMU)

Sigma-Aldrich, Cat. No 205-444-0 – for laboratory use, dried (mol. mass 120.1, melt. point 126°C). In accordance with manufacturer´s recommendations, the preparation was kept in refrigerator at 0°C.

Urea (U)

Lachema, Brno, Cat. No 11058077 (mol. mass 60.055, melt. point 135°C)

Hydrolysate of chrome-tanned leather waste (H)

Obtained through enzymatic hydrolysis of chrome-tanned leather waste by a procedure described in detail [8, 9].

All materials are identical with products used in preceding experiments, and their TG and/or DSC characteristics are given in [7]. Basic analytical characteristics of hydrolysate of leather waste only are summarised in Table 1 to facilitate orientation.

Phthalic acid (PHA)

Sigma-Aldrich, Cat. No 40,291-5 (melt. point 205°C). Its TG and DSC characteristics are presented in Figs 1 and 2.

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

Dry substance/%	9.04
Amide nitrogen in dry substance/%	15.06
Ash in dry substance/%	3.09
Cr content in dry substance/ppm	13.60
Primary amino groups in dry substance/mmol $–NH_2$ g^{-1}	0.24
Average molar mass (numerical mean M_N) kDa	19.80

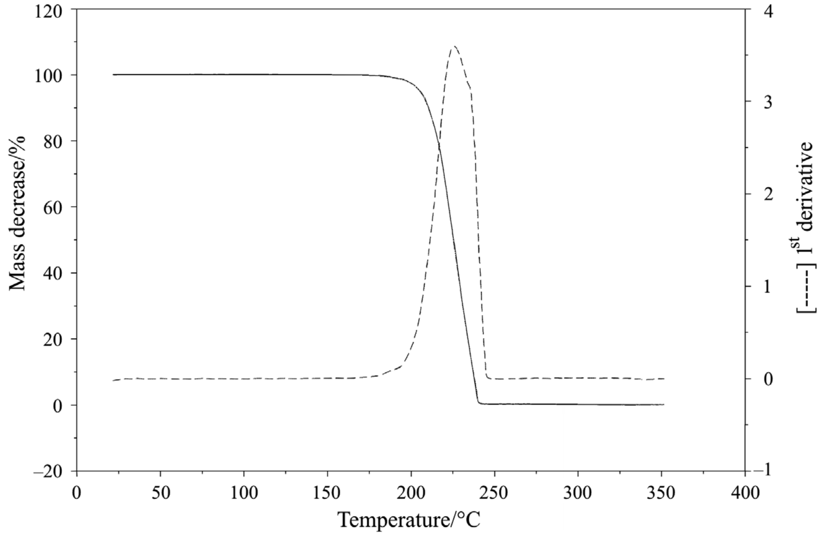

Fig. 1 TG curve of phthalic acid employed in experiments as acid curing agent. Weighed quantity 5.6825 mg, dT/dt=10°C min^{-1}

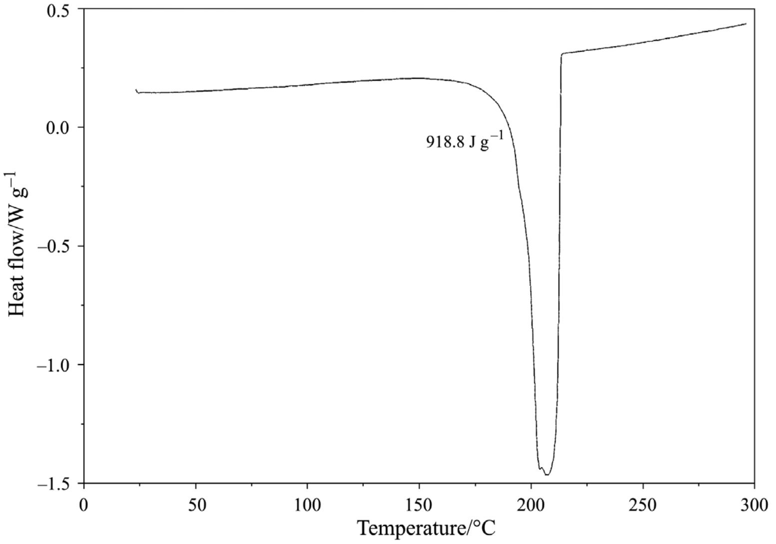

Fig. 2 DSC curve of phthalic acid employed. Weighed quantity 2.190 mg, dT/dt=2°C min^{-1}

Procedure and results

Thermogravimetric curves (together with their first derivatives) in a temperature interval ranging from room temperature (approx. 25°C) to 250°C, in some cases up to 300°C, of sole DMU and its blends with 0.05 mass fraction of U or of H were obtained applying current non-isothermal TG technique on a fully computerized TGA Q 500 instrument (TA Instruments Inc., New Castle, Del./USA) at a temperature increase of 1 or 2°C min^{-1}. In order to specify effect of acid curing agent on the reaction under study, reaction mixtures contained phthalic acid in various concentrations in mass fraction range 0.01–0.1.

Thermogravimetric curves of DMU mixed with a low mass fraction of phthalic acid (not exceeding 0.03) do not virtually differ from systems containing no phthalic acid.

If concentration of phthalic acid in the studied reaction mixture exceeds a mass fraction level of 0.03–0.05, TG curves in temperature interval 150.9–170.3°C reveal another wave of mass decrement which does not correspond to thermal degradation of phthalic acid (comp. Figs 1 and 2). This is illustrated by the TG curves of reaction mixture of DMU with mass fractions 0.03 and 0.05 of phthalic acid (Figs 3 and 4).

Similar behaviour is also displayed by mixtures of DMU with mass fraction 0.05 of U or H. Average values of temperature intervals for detected TG waves of mass decrements are essentially retained. Presence of hydrolysate in reaction mixture merely reduces the mass decrement of second TG wave ($-\Delta m_2$, % in Table 2) to the benefit of mass decrement on third TG wave ($-\Delta m_3$, % in Table 2) in the same manner as with reaction mixtures containing no acid curing agent. This fact together with the mass decrement of TG wave in 150–170°C temperature range ($-\Delta m_4$, %) is apparent in data of Table 2.

TG curves obtained at two different heating rates (1 and 2°C min^{-1}) allow to calculate kinetic parameters of respective reactions, as pre-exponential Arrhenius factor (A/min^{-1}) and activation energy ($E/\text{kJ mol}^{-1}$), using Q 500 instrument's soft-

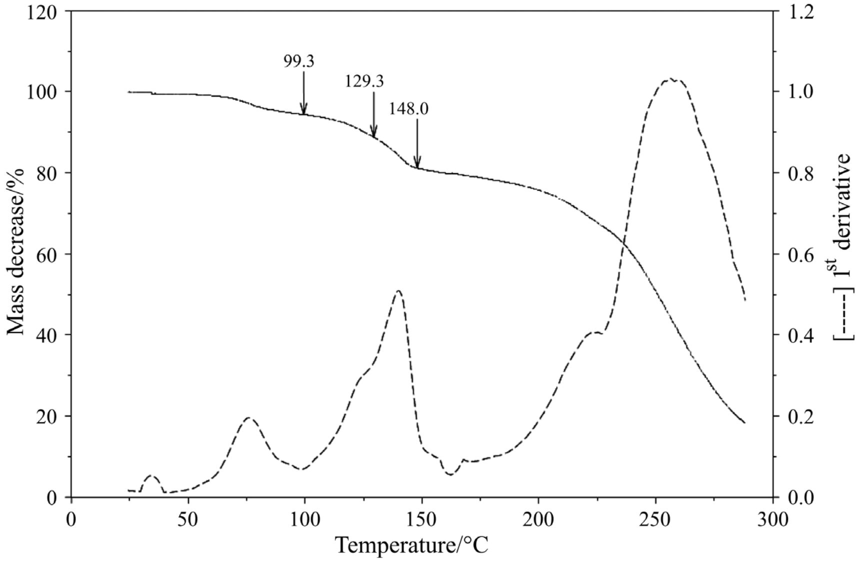

Fig. 3 TG curve of mixture DMU+phthalic acid (acid mass fraction 0.03)

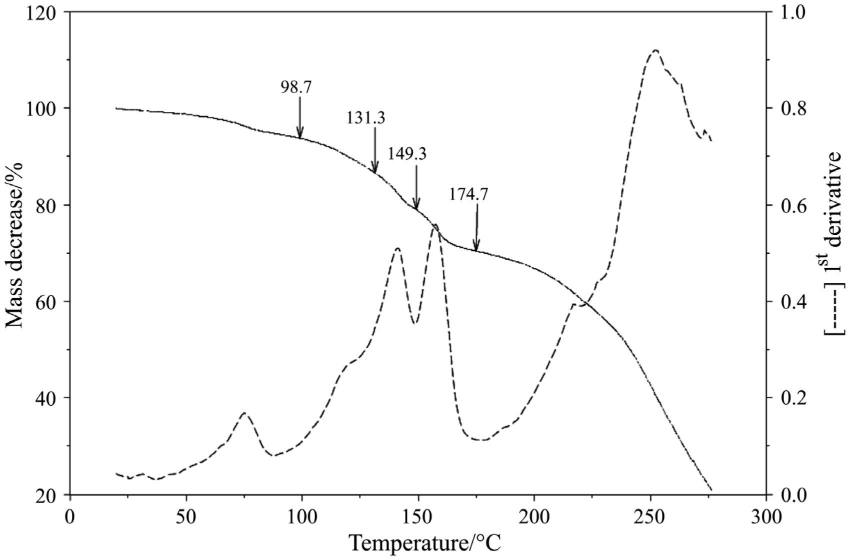

Fig. 4 TG curve of mixture DMU+phthalic acid (acid mass fraction 0.05)

ware applying ASTM E 1641 technique [10]. Experimentally determined values of such kinetic parameters, in dependence on reaction mixture composition, are presented in Table 3.

Discussion

TG curves of mass decrements in dependence on temperature, at low concentrations of acid curing agent, exhibit three waves: the first (TG_1 – in an interval from almost room temperature to approx. 94.2°C) is typical by substantial fluctuation of values (average 15–20%, comp. Table 2), which is somewhat greater with samples where a longer time elapsed between their preparation and TG measurement. Fluctuation also increases with samples containing hydrolysate of chrome-tanned leather waste which alone (comp. Table 1) contains about 10% moisture. Mass decrements detected in this wave are not related to mass decrements of TG waves at elevated temperatures, it may be assumed that the first TG wave of mass decrements is related to content of water bound by measured sample the reference (compare Table 1).

Further waves of mass decrements (TG_2 in temperature region 95.3–130.4°C, and TG_3 in temperature region 127.2–158.9°C) exhibit a distinct connection with proceeding condensation. Mass decrements in practically same temperature intervals were registered during condensation of other amino-methylol derivatives, and are associated with release of water during formation of oxy-methylene (temperature interval 95.3–130.4°C) and methylene (temperature interval 127.2–158.9°C) cross-links (e.g., [11, 12]). Detected waves are not quite ideally separated, so their quantitative evaluation (including calculation of kinetic parameters) is somewhat more compli-

Table 2 Mass decrement, $-\Delta m_x$ in particular TG waves

x*	Heating rate/ °C min^{-1}	$-\Delta m_1$/% T=25–94.2°C	$-\Delta m_2$/% 65.3–130.4°C	$-\Delta m_3$/% 127.2–150.9°C	$-\Delta m_4$/% 150.9–170.3°C
		Reaction mixture: DMU+phthalic acid			
0.01	1.0	4.15	5.71	8.21	0
	2.0	3.41	5.98	7.02	0
0.3	1.0	2.98	4.71	7.15	1.21
	2.0	3.50	5.83	7.46	1.82
0.05	1.0	5.66	5.84	8.80	4.85
	2.0	3.50	5.83	7.46	5.19
0.10	1.0	4.77	5.68	8.77	8.65
	2.0	3.72	5.94	7.12	9.30
		Reaction mixture: DMU+0.05U+phthalic acid			
0.01	1.0	5.31	6.44	7.03	0
	2.0	6.25	6.25	6.66	0
0.03	1.0	5.67	5.41	6.05	0
	2.0	4.31	5.35	5.51	0
0.05	1.0	4.20	5.93	7.95	0.16
	2.0	4.40	5.76	6.11	0.34
0.10	1.0	4.23	7.63	7.83	3.87
	2.0	3.05	5.76	6.09	6.45
		Reaction mixture: DMU+0.05H+phthalic acid			
0.01	1.0	7.45	4.07	8.14	0
	2.0	6.20	3.80	7.24	0
0.03	1.0	5.71	4.49	8.16	0
	2.0	5.30	4.49	8.57	0
0.05	1.0	4.48	4.49	10.62	1.63
	2.0	4.06	5.43	7.79	5.09
0.10	1.0	4.89	4.49	9.80	3.68
	2.0	4.06	3.39	9.81	8.36

*x – Mass fraction of phthalic acid

cated. Average mass decrements of both waves, to some extent, depend on reaction mixture composition (i.e. sole DMU, DMU+0.05 mass fraction of U or H), however, proving their dependence on concentration of acid curing agent in the reaction mixture was unsuccessful.

Mass decrements of wave, detected at higher concentrations of acid curing agents in temperature range 150.9–170.3°C (TG$_4$ – Table 2), on the contrary display quite a clear dependence on concentration of acid curing agent. The origin of this mass

Table 3 Values of pre-exponential factors (A/min^{-1}) and activation energy (E/kJ mol^{-1}) of detected condensation reactions of dimethylol urea in presence of phtalic acid of various concentrations

Mass fraction of phthalic acid in mixture, x	Wave TG$_2$ T=95.3–130.4°C		Wave TG$_3$ T=127.2–150.9°C		Wave TG$_4$ T=150.9–170.3°C	
	A/min^{-1}	E/kJ mol^{-1}	A/min^{-1}	E/kJ mol^{-1}	A/min^{-1}	E/kJ mol^{-1}
Reaction mixture composition: DMU+phtalic acid						
0.01	11.17±2.84	98.03±18.89	36.14±2.90	290.70±22.72	–	–
0.03	9.55±2.78	95.11±28.10	28.21±16.07	284.87±28.39	8.45±0.70	87.83±3.53
0.05	32.10±4.59	235.42±36.20	35.16±3.84	285.25±30.42	13.33±1.23	125.44±14.88
0.10	29.51±6.38	225.38±46.37	29.49±0.96	146.55±8.45	14.46±1.02	128.66±6.96
Reaction composition: DMU+0.05U+phtalic acid						
0.01	13.01±0.80	111.40±4.40	21.35±9.63	179.47±71.56	–	–
0.03	25.67±5.72	198.00±40.66	20.38±2.77	211.49±53.83	–	–
0.05	29.35±5.81	223.82±41.68	25.04±6.85	253.50±55.14	14.13±1.07	126.82±8.99
0.10	35.06±1.62	263.84±10.86	36.85±1.59	298.43±12.54	17.46±1.25	151.96±11.97
Reaction composition: DMU+0.05H+phtalic acid						
0.01	15.05±6.35	121.60±49.56	22.31±2.66	189.60±17.86	–	–
0.03	21.30±7.05	168.78±48.29	31.11±2.05	256.38±13.08	–	–
0.05	25.88±3.26	199.66±10.53	32.65±6.03	258.62±41.85	20.59±2.09	182.06±17.26
0.10	32.77±2.90	247.62±20.88	25.46±6.06	297.70±73.66	21.43±0.60	192.38±7.96

decrement wave is conditioned by a certain minimal concentration of acid curing agent (with sole DMU – mass fraction of phthalic acid 0.03, with mix of DMU+0.05 mass fraction of U or H – concentration corresponding to mass fraction 0.05). These facts are graphically represented in Fig. 5.

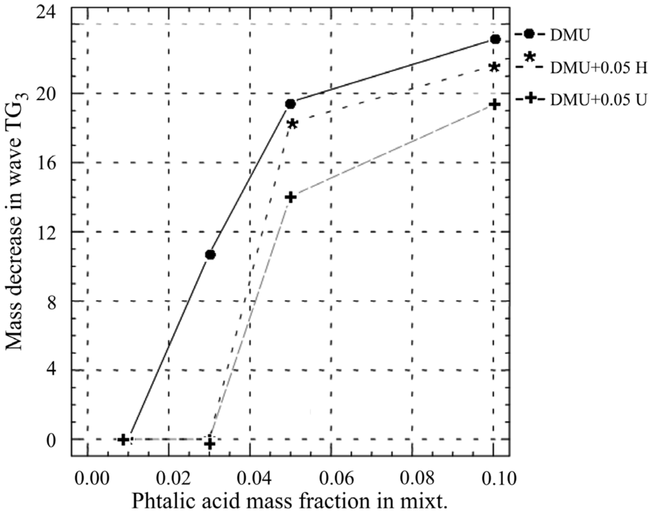

Fig. 5 Dependencies of mass decrements on/in wave TG$_4$ (interval 150.9–170.3°C) on mass fraction of acid curing agent in reaction mixture of different composition. 1 – sole DMU; 2 – mixture DMU+0.05U; 3 – mixture DMU+0.05H

When studying behaviour of methylol oligomers of other amino compounds through TG, some authors detected formaldehyde in gaseous products in the 150–180°C temperature range [11, 12]. Together with a strong influence exerted on mass decrement on this TG wave (TG$_4$ in Table 2) by concentration of acid curing agent in reaction mixture, it supports the opinion that this mass decrement is related to transition of more unstable oxy-methylene cross-links to more stable methylene cross-links associated with elimination of formaldehyde.

The temperature interval in which this mass decrement can be detected corresponds with the temperature interval generally recommended for curing urea-formaldehyde adhesive films. Observed facts are in agreement with conclusions of some previous authors according to whom curing adhesive films of oligomeric methylol-amino derivatives in the presence of urea requires higher concentration of acid curing agents (e.g. [13, 14]).

From values presented in Table 2 it may be concluded that oxy-methylene and methylene links are produced in reaction mixtures containing sole DMU and/or DMU+mass fraction 0.05U at an approximate 1:1 ratio (42:58 with DMU, 47.8:52.2 with DMU+0.05U) regardless of possible presence of acid curing agent. However, mass fraction 0.05 of hydrolysate of chrome-tanned leather waste added to DMU brings about a lowered ratio of oxy-methylene bonds to methylene bonds in favour of

Table 4 Average mass decrement of TG waves in condensation of dimethylol urea in presence of mass fraction 0.01–0.10 phthalic acid, with their 95% confidence intervals

Reaction mixture	$-\Delta m_1$/% T=25–94.5°C	$-\Delta m_2$/% 95.3–130.4°C	$-\Delta m_3$/% 127.2–150.9°C	$-\Delta m_4$/% 150.9–170.3°C
DMU	4.01±0.60	5.61±0.37	7.75±0.62	3.88±3.10
DMU+0.05 U	4.68±0.895	6.11±0.72	6.65±0.74	1.35±2.05
DMU+0.05 H	5.27±1.12	4.33±0.50	8.77±0.98	2.35±2.61

more stable methylene bonds, at a ratio of about 1:2 (or ratio 33:66) also heedless of possible presence of acid curing agent the reference (compare Table 4). The positive effect of hydrolysate on formation of more stable cross-links, as detected during condensation in a neutral environment, stays thus retained also in the presence of acid curing agents.

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