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CURING OF UREA-FORMALDEHYDE RESINS ON A WOOD SUBSTRATE

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TG-DTA analysis method was used to study the curing behaviour of urea-formaldehyde (UF) adhesive resins in the presence of a wood substrate. The cure process was followed using a Setaram labsys^{TM} instrument in flowing nitrogen atmosphere by varying the ratio of resin and wood. Resin cure was catalysed with 2% of NH_4Cl. Curing tests were performed in the open standard platinum crucibles and in the sealed glass capsules. To characterise the reactivity of curing system, the peak temperatures in DTA curve and the mass loss values in TG curve were taken as the apparent indices. The main attention was paid to phenomena which actually take place in curing of UF resins during manufacturing of particleboards. Reactivity of the curing system depends mostly on methylol content of resin and can be adequetly evaluated by the maximum temperature of exothermic peak. The wood substrate has a substantial influence on the resin and water diffusion in system causing the changes in water/resin separation and water evaporation conditions. The water movement in curing adhesive joint was a confusing parameter in determining the peak positions. The rate of mass loss on a wood substrate is higher as compared to curing UF resin alone.

Keywords: *curing, particleboards, TG-DTA analysis, urea-formaldehyde resins*

Introduction

Urea-formaldehyde (UF) and phenol-formaldehyde resins are the most used polycondensation resins today for manufacturing particleboards, medium density fiberboard and plywood. The performance of all formaldehyde-based resins in their processing is greatly influenced by curing characteristics and is strongly dependent on the substrate on which resin cure takes place [1–6]. In order to understand their curing behaviour, wood should be used as a substrate for the studies. It would simulate more exactly the formation of a thermosetting adhesive joint such as occurs in manufacturing glue line as compared to the curing resin alone. Curing behaviour of thermosetting adhesives on a wood substrate has been studied by different methods, mainly using differential scanning calorimetry [1, 2], thermomechanical analysis techniques [3–6], and also regarding theoretical considerations [7]. These studies point out that a wood-induced catalytic activation on the reactions of hardening in the adhesive joint exists, and resin polymerisation and crosslinking proceed at a much faster rate when the resin is in contact with polymeric wood constituents [1]. The catalytic effect established is attributed mainly to cellulose [2] and is explained by the sum of a multitude of resin/substrate secondary force interactions [1]. The formation of covalent bonds at the interface of substrate between resin and wood was also supposed, but found to be small under wood adhesive application conditions [2]. It also has been shown that the cure process is influenced by a diffusion hindrance effect. This effect is explained both by growing resin molecules absorbed on the wood surface, and by the polymeric constituents of the substrate slowing relative molecular movement and thus hindering contact between resin reactive sites [2]. In the lower temperature region of curing process, the presence of water in adhesive appears to be the substantial factor causing the variations in behaviour of the system [3, 5, 6].

In the present work, the TG-DTA technique was used to follow curing behaviour of UF resins on a wood substrate dependent on the ratios of resin and wood. TG-DTA method makes it possible to simultaneously follow the heat flow and mass loss of the sample during curing. We focused on the industrial resin samples and wood chips, taking for experiments the raw materials used in the technological process of the particleboard manufacturing factory Pärnu Plaaditehas AS.

Experimental

Industrial UF resins of different conversion degree and prepared by different multistep reaction procedure were used, labelled as UF1, UF2 and UF3. In Table 1, the characteristics of resins determined by standard analysis methods are presented.

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Table 1 Standard analysis of used UF resins

Characteristics	UF1	UF2	UF3
Dry solids 105°C, 3 h/%	69.5	68.7	68.2
pH	8.6	9.1	8.4
Viscosity 25°C/mPas, Brookfield viscometry	322	427	480
Density 20°C/g cm^{-3}	1.286	1.278	1.286
Gel time 100°C/s, with 1% NH_4Cl	50	54	81
Free formaldehyde/%, sulphite method	0.15	0.15	0.1

These resins have been well-proved at Pärnu Plaaditehas AS for obtaining PB of low formaldehyde emission. It has been found earlier [8] that different UF resins show quite similar curing characteristics, presumably determined by close final molar ratio of all modern UF resins (formaldehyde to urea 1.03–1.08).

Wood raw material (pine, spruce) with moisture content of 1.7% consisted mainly of sawdust (80%) and cutter chips (20%). In some cases fine powder wood flour was milled from the same material, which creates more favorable conditions for resinating than occurring on solid wood surface. Samples from the following systems were tested by TG-DTA analysis, the ratios represent the liquid UF resin content to wood substrate (mass/mass).

UF resin alone, 90 parts resin/10 parts wood, 80 parts resin/20 parts wood, 70 parts resin/30 parts wood, 60 parts resin/40 parts wood, 50 parts resin/50 parts wood, 30 parts resin/70 parts wood, 14.5 parts resin/100 parts wood, wood (W) alone.

14.5 parts of liquid resin per 100 parts of wood chips is the industrial level of resin content (about 10 parts of resin solids) in forming mat in particleboard manufacturing.

TG-DTA measurements were recorded with a Setaram labsys^{TM} instrument in dynamic heating conditions with the heating rate of 5 K min^{-1} in the stream of nitrogen (flow rate 40 mL min^{-1}) and measuring sensitivity 50 μV. The DTA temperature program ran from 30 to 500°C. The heat flow on DTA curves was expressed in μVs mg^{-1} as in original Setaram program. Open standard platinum crucibles of 100 μL were used, and the mass of the samples was 25 to 30 mg, depending on the mass ratio of resin and substrate. As exothermic curing peaks in DTA curves are often overlapped by the large water evaporation endotherms, the curing tests were also performed in the sealed glass capsules, and the mass of the samples was diminished to 10–20 mg. Experiments with UF1 and UF2 were performed in open crucibles, while UF3 as a resin of highest conversion degree and of more complex structure was tested mostly in sealed capsules. Resin cure was catalysed with 2% of NH_4Cl added as 20% water solution.

Three-layer particleboards of 9700·2650 mm dimensions and of thicknesses in the range of 6–28 mm at Pärnu Plaaditehas AS are produced. In the present study, the thicknesses of 11, 18 and 22 mm for general-purpose boards P1 were selected. After pneumatic spreading of wood particles, the core layer contains rather coarse particles and the surface layer contains rather fine particles. The core layer and surface layers were resinated separately by different compositions of the adhesive mixtures because a temperature gradient from the surface to the core of panels during hot-pressing process exists. At press plate temperature of 210°C and hot-pressing time of 8.0–9.5 s per mm, in the core layer of the panel a slow increase in temperature occurs and the final temperature remains lower than that in the surface layers. Depending on the density of the particleboards, the pressures of 210 bar (<700 kg m^{-2}) and 230 bar (>700 kg m^{-2}) were used. Physical and mechanical parameters were determined according to DIN 68763, formaldehyde emission was measured by the perforation method (EN 120). General-purpose boards should correspond to the requirements of EN 312-1 for use in internal conditions, and the content of free formaldehyde to the requirements of emission class E1. To fulfil the E1 requirements, urea (40% solution) as scavenger was added to adhesive mixture up to 7% of dry resin, as usual to core layer. Consumption of paraffin wax as hydrofobic agent was 0.4% of dry wood. The amount of catalyst NH_4Cl (25% solution) on the average of 2% of dry resin was used.

Results and discussion

During UF resin manufacturing, the final reaction products between urea and formaldehyde can range from the simple monomethylolurea to very complicated crosslinked structures. During resin curing, a three-dimensional network structure is built up. The formation of linear condensation products in cure process begins at lower temperature if the resin contains greater amount of reactive methylol groups [9]. The curing curves for UF1 and UF2 reveal the exothermic peak maxima at 80.8 and 81.1°C and the endothermic peak minima at 105.4 and 106.5°C, respectively. UF3 is less active due to high condensation degree in resin synthesis, and curing reactions take place at higher temperature region than in case of UF1 and UF2. In Fig. 1, the curve of UF3 resin cured with 2% of NH_4Cl is presented. It can be seen that DTA curve shows the complicated exotherm with a peak maxi-

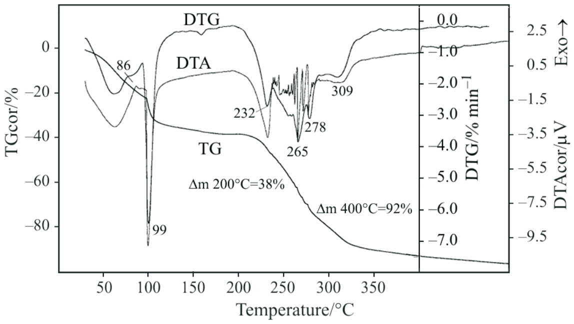

Fig. 1 TG, DTG, DTA curves of UF3 curing with 2% NH_4Cl

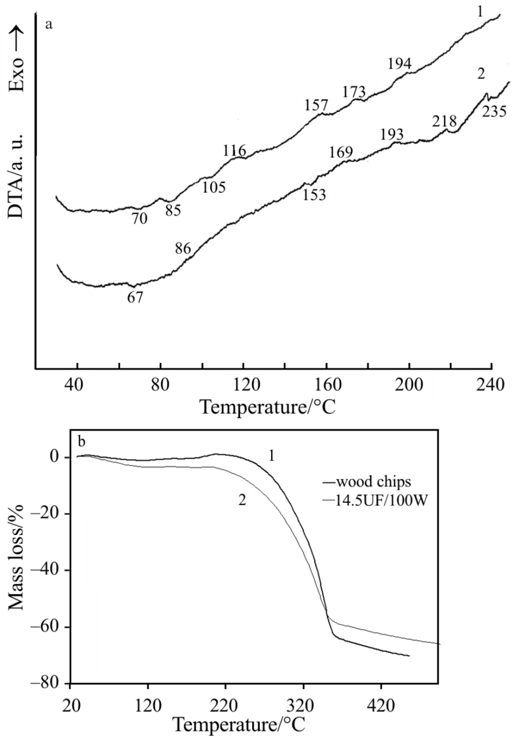

Fig. 2 a – DTA and b – TG curves of wood chips alone and resinated wood chips sample: 1 – wood chips alone; 2 – resinated with UF1 wood chips from production glue line

mum at 86°C and the sharp water evaporation endotherm with a minimum at 99°C.

The peak temperatures and mass loss values are the apparent indices to characterise the reactivity of curing resin while the exoeffect is not exactly determined due to large water evaporation endotherm. Despite that, it can be noticed that the reaction heat evolved is close in case of UF1 and UF2 consisting about 44 to 47 J g^{-1}. The exotherm in the DTA curve of UF3 shows smooth transition to endotherm and the value of the heat of curing reaction can be estimated as 37 J g^{-1} only roughly.

In the curing systems on a wood substrate the values of thermal effects is not clearly determinable due to overlapping peaks. In Fig. 2, DTA and TG curves for raw wood material and resinated wood chips obtained directly from the industrial glue line are shown. According to PB manufacturing recipe, 100 parts of wood chips were resinated with 14.5 parts of liquid UF1 (equal to 10 parts of resin solids) catalysed by 2% of NH_4Cl.

As can be seen from Fig. 2a, in the temperature range up to 210°C, the wood substrate alone and resinated with UF1 (UF/W 14.5/100) exhibits only weakly noticeable exothermic effects in DTA curve. The mass loss curves in Fig. 2b show that raising the temperature over 220°C, the degradation of wood substrate with mass loss begins to take place. Apparent destruction of wood is noticed in the 220–240°C range, and becomes more remarkable at higher temperatures. According to [2], in the temperature range up to 240°C, the evident transformation of the wood substrate does not occur. The miniexotherms in the DTA curve of wood (Fig. 2a) may be attributed to the internal effects in the lignocellulosic structure. In the DTA curve at about 220°C and higher, the changes in the wood substrate itself are more important than the

Table 2 Physical and mechanical properties of industrial UF-bonded particleboards

Thickness/ mm	Resin	Dry resin/ PB, kg m^{-3}	Scavenger/dry resin/%		Density/ kg m^{-3}	Bending strength/ MPa	IB strength/ MPa	Free F/ mg/100 g PB
			surface	core				
10	UF1	68.8	0	6.5	671	13.0	0.43	5.8
	UF2	69.1	0	7.0	687	14.3	0.50	5.5
	UF3	68.3	0	1.5	683	13.6	0.31	5.1
18	UF1	63.7	0	5.5	669	14.0	0.37	5.7
	UF2	63.1	0	5.6	657	13.5	0.46	5.5
	UF3	63.2	0	1.5	668	13.6	0.29	4.9
22	UF1	55.8	0	6.0	625	12.5	0.31	5.5
	UF2	56.1	0	6.5	631	13.0	0.32	4.9
	UF3	58.1	0	4.0	644	12.2	0.38	5.0

small changes occurring in the resin, so they dominate the whole complex system of the adhesive joint [4]. At the temperatures below 210°C, the changes observed in the mass loss values are only due to the resin. In addition to water evaporation, mass loss of resin during the cure arises from formaldehyde emission depending on methylol and dimethylene ether group content in resin [9].

Considering the conditions of the industrial application of resins, it would be sufficient to record the DTA curves only up to 200°C. During particleboard hot-pressing at constant plate temperatures of 210°C, the temperature in the center of the board core only reaches 100–105°C as the times for curing are very short. From the point of view of research, attention was concentrated on that temperature region in which obvious differences appear between the curing resin alone and the resin on a wood substrate. The TG curves for wood chips in Fig. 2b clearly show that the possible maximum pressing temperature in manufacturing PB should not exceed 220°C.

The properties of wood-based boards are in principle determined by three parameters: wood component, resin and manufacturing technology. Using the constant composition of the mix of wood species and close PB processing parameters, the actual value of used UF resins becomes apparent.

The curing reaction in glue line may be regarded as the continuation of the acid condensation stage in the resin synthesis. During the hot-press cycle, the hardening of the resin and possible reactions of the adhesive with the wood substrate take place. For finished boards, the internal bond (IB) strength is the most sensitive physical characteristic, determined mainly by the nature and amount of applied resin. IB strength (tensile strength perpendicular to the board surface) depends on the structure advancement of the resin during synthesis and on the crosslinking density of cured resin network.

In Table 2, physical and mechanical properties of particleboards (PB) bonded with UF1, UF2 and UF3 for selected thicknesses of boards are presented.

Comparing the mechanical properties of boards bonded with these resins, it is seen that at thicknesses 10 and 18 mm, IB strength shows the highest values in case of resin UF2. In resin processing, optimum viscosity is an important factor. In case of low viscosity, a great part of resin might penetrate into the wood, causing starved adhesive bond. On the other hand, in case of high viscosity, slower wetting may occur with very low penetration into the wood surface and hence giving poor mechanical locking. At a certain solid content, the viscosity of adhesive mix mainly depends on the degree of the conversion in manufacturing. Evidently, the high conversion degree of UF3 expressed in high viscosity of resin (Table 1) causes lower strength values. Only at the thickness of 22 mm, UF3 reveals higher IB value compared to the other resins. Due to longer press time in case of great thickness of board, the advanced condensation of resin during synthesis may gain effect. As UF1 has lower condensa-

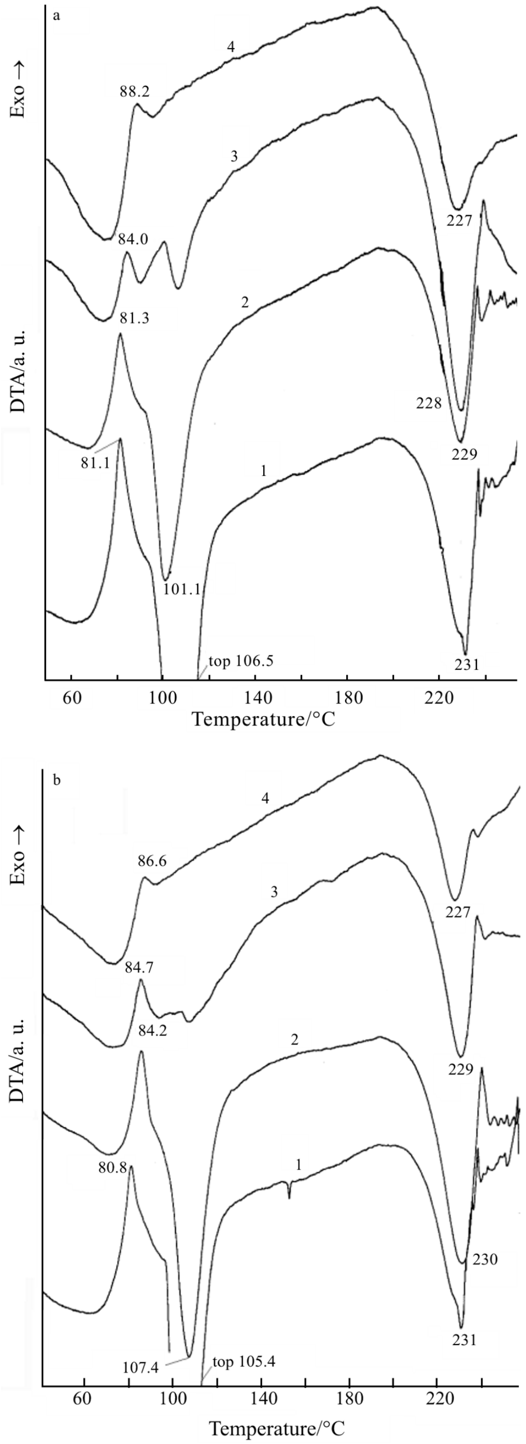

Fig. 3 DTA curves of a – UF1 and b – UF2 curing on a wood substrate: 1 – resin alone; 2 – UF/W 90/10; 3 – UF/W 80/20; 4 – UF/W 70/30

tion degree, more time to attain the same crosslinking degree is necessary. It should be mentioned that the mechanical properties in all cases surpass the requirements for general purpose boards P1 (IB strength 0.28 MPa, bending strength 12.5 MPa). The content of free F was minimised with additional urea as scavenger, and it satisfied the requirements of E1 standard (a rotating half-year F emission level is less than 6.5 mg F/100 g particleboard). Storage of resins in technological acceptable limits of viscosity maintained the physical and mechanical properties in accordance with the technical requirements.

In the following, the behaviour of resin cure on a wood substrate for the case when the resin content in mix is higher as compared to the industrial level, is examined.

In Fig. 3, the exothermic peak temperatures depending on ratio UF/W were followed.

DTA curves from different samples show that increasing the content of wood in the system, the exothermic peak maxima are shifted to increasingly higher temperatures, until disappearing at the ratio 60/40, where resin curing exotherms appear to be gradually buried under thermal effects related to wood substrate and a variety of diffusion effects. The decreasing endoeffects refer to water diffusion in wood material.

Mass loss curves for the same systems (Fig. 4) are located in presumed order – with decreasing content of resin in the UF/W system the amount of evaporated water diminishes. From the data the catalytic effect of wood substrate cannot be deduced.

In Fig. 5, the mass loss values are presented in relation to resin content in temperature region of exoeffects where wood destruction still does not take place.

Mass loss curves show that when the resin cures alone (curve 1), the sharp mass loss begins at higher temperature as compared to curing on a wood substrate. Increasing the part of wood, the amount of evaporated water in the observed temperature ranges calculated to resin content rises due to changed conditions for diffusion and water release from the curing system.

For following the DTA curves in exothermic region, sealed glass capsules were also used. In Fig. 6, the DTA curve of UF3 curing in exothermic region is shown. It can be seen that the position of exothermic peak maximum at about 86°C is the same as in case of open crucible (Fig. 1), and therefore does not depend on vessel used. But heat flow curves and the corresponding heat effects are different. In open crucible, due to water evaporation, part of exothermic peak

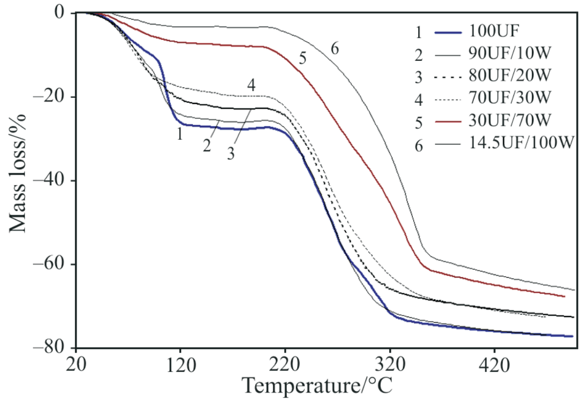

Fig. 4 TG curves of system UF1/W

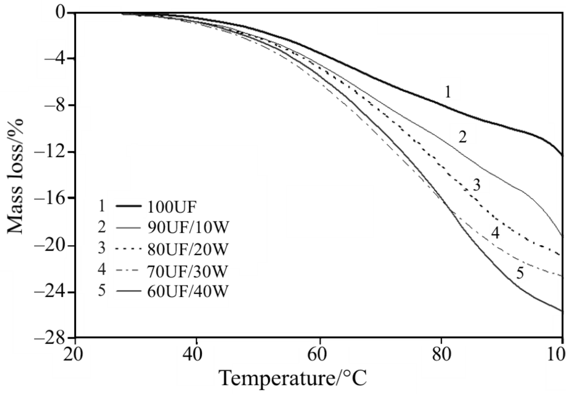

Fig. 5 TG curves in relation to resin content in systems UF1/W

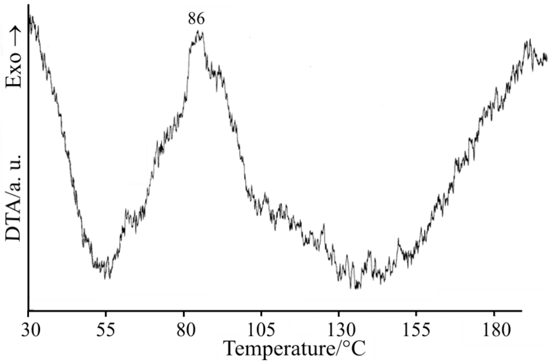

Fig. 6 DTA curve of UF3 curing with 2% NH_4Cl in sealed capsule

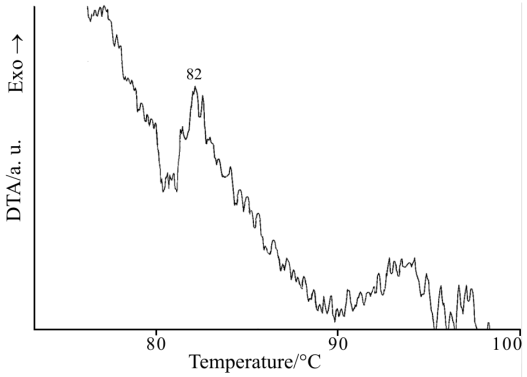

Fig. 7 DTA curve of system UF3/W 14.5/100 from production glue line

area is overlapped by large endotherm and calculated heat effect was lower.

In Fig. 7, the DTA curve for industrial wood sample resinated with UF3 is presented. Comparing the exothermic peak positions in Figs 6 and 7, the shift of exothermc peak of about 3–4°C can be observed. As compared to the curing temperature of resin alone, it can be concluded that the influence of wood substrate as promotor on resin curing process seems to be remarkable. But the heat flow evolved, calculated by area under exotherm is too low and does not relate to the resin content in the system.

In Fig. 8, DTA curves for system UF3/wood 50/50 are presented both for wood chips and fine wood flour. In case of wood flour, the effect is observed presumably under more favorable conditions than in curing on solid wood surface [2]. Figures show different behaviour of systems dependent on the size of wood particles. Hence, the different movement of water in adhesive joint reveals in different slope of curves, although the opposite shape of curves would be expected, corresponding to the higher surface of wood flour. In both cases, catalytic effect of the substrate is noticeable, shifting the exothermic peak to the temperature range of 81–83°C.

Increasing the ratio of resin to wood substrate, the increase in amount of water in system also takes place, reducing the rate of curing process. Diffusion problems become evident, and the exothermic reaction peaks reveal at higher temperature. In Fig. 9a, the curing exotherm of system UF3/wood 70/30 obtained with sealed capsule is shown. As compared to curing the resin alone (Fig. 6), a noticeable shift of exothermic peak to higher temperature is observed. Curing the resin alone, diffusion problems only occur at the end of the reaction [2].

Decrease in the curing rate at higher ratios of resin/wood is observed in curing with open crucible. In DTA curve of system UF3/wood (Fig. 9b), the exothermic peak maximum is shifted from 86 (Fig. 1) to 89°C. The large endothermic peak of water evaporation with a minimum at 112°C partly overlaps the curing exotherm. The evolved heat flow is considerably lower as compared to curing resin alone due to absorption of resin on the substrate and has the value in relation to resin content in system approximately of 15 J g^{-1}.

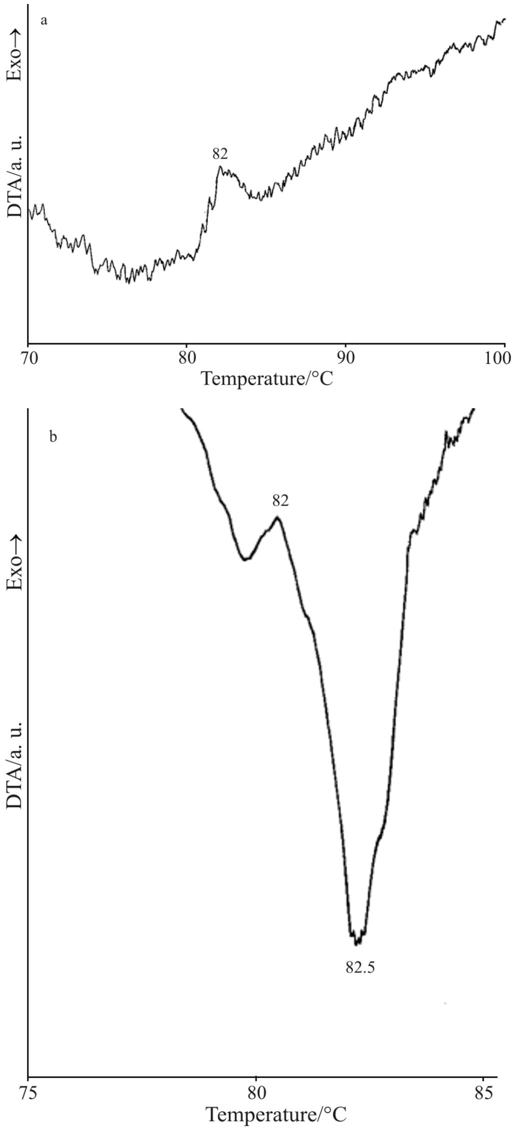

Fig. 8 DTA curve of system UF3/W 50/50: a – wood chips; b – wood fluor

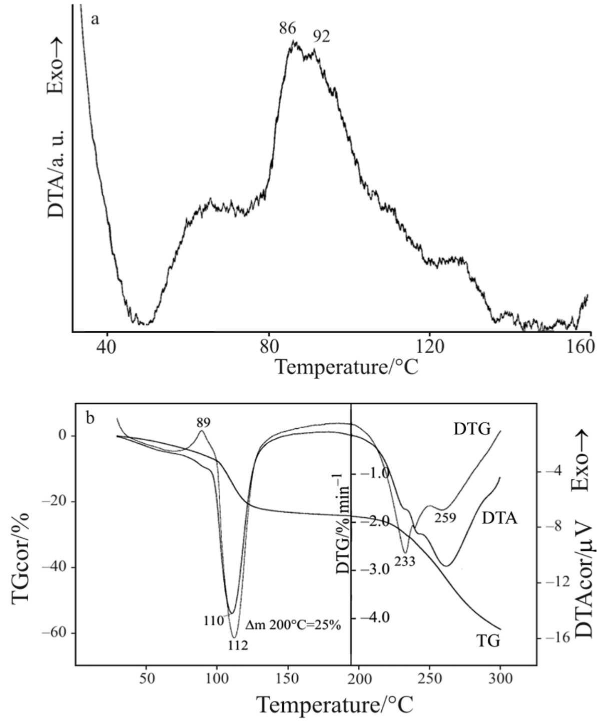

Fig. 9 TG, DTG and DTA curves of system UF3/W 70/30: a – in sealed capsule; b – in open crucible

Conclusions

The behaviour of UF resin cure on a wood substrate is different as compared to curing the resin alone. Wood substrate changes the water and resin diffusion characteristics in curing adhesive joint essentially. Considering the complexity of the curing system, the following conclusions can be drawn:

Water presence in the curing system is the most confusing parameter in determining the relative positions of exothermic and endothermic peaks in the DTA curves. In open crucible, the exothermic peaks shift to higher temperature, according to the decrease in the UF/W ratio. Due to evaporation of water from system, the resin molecules are less mobile and the polymeric constituents of the substrate slow down the contact between reactive sites of the resin. Calculated to resin content, the rate of mass loss is higher in case of the increase in the amount of wood substrate. If curing is recorded in sealed capsule, the rate of curing and the reactivity of the resin on a wood substrate is higher as compared to curing resin alone, and exothermic peaks reveal at lower temperature.

Results of this work should be of certain applied interest as they comprise the behaviour of UF adhesive curing under conditions similar to those used in the manufacturing of UF-bonded particleboards.

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