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UREA-FORMALDEHYDE RESINS CHARACTERIZED BY THERMAL ANALYSIS AND FTIR METHOD

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Urea-formaldehyde (UF) resins are the most used polycondensation resins today, in manufacturing particleboards. UF resins possess some advantages such as fast curing, good performance in the panel, water solubility and low price. However, the main chemical bonds of the UF resins macromolecules are hydrolysis sensitive. This causes low water and moisture resistance performance and subsequent formaldehyde release from the UF-bonded panels. A multitude of pathways have been explored for the improvement of UF resins' behavior relating either to their synthesis procedure or application parameters during panel manufacture. In this study, two UF resins (a conventional and an innovative one produced at very low pH and temperature conditions) were analyzed for their specifications and characterized with TG-DTA technique in dynamic heating conditions and FTIR measurements both in their pre-polymer and cured state.

Keywords: *DSC, FTIR, TG-DTA, urea-formaldehyde (UF) resin*

Introduction

Urea-formaldehyde resins are preferred by the wood-based panels industry due to their high reactivity and cost efficiency. Nevertheless, their main disadvantage is the low tolerance to humid conditions, which brings on progressive degradation of the ether bridges existed in the network of the resin and consequently persistent formaldehyde release from the UF-bonded wood panels. Various characterization methods have been applied for the detection of their thermal behavior, like differential scanning calorimetry [1–5] and thermogravimetry [6–11], targeting to the location of the critical parameters during their synthesis procedure, like pH, mole ratio and the sequence of the various production steps, which could be proved effective for the improvement of the resin's performance.

In this study, urea-formaldehyde resins of low formaldehyde to urea mole ratio were produced by CHIMAR Hellas, following two different synthesis procedures and investigated with application of Fourier transform infrared spectroscopy (FTIR) and thermogravimetry (TG-DTA).

Experimental

Urea-formaldehyde (UF) resins are thermosetting polymers, which result from the reaction of urea (U) and formaldehyde (F). This reaction is basically a two-step process, comprising of the methylolation and condensation stage. Methylolation refers to the addition of up to three molecules of the bifunctional formaldehyde to one molecule of urea to give the so-called methyloureas. The formation of methylol groups mostly depends on the F/U molar ratio, with higher molar ratios increasing the tendency to form highly methylolated species. The UF polymer builds up in the acid condensation stage. The methylols, urea and formaldehyde still present in the system, react to give linear and partly branched molecules with medium and even higher molar masses. The urea molecules are bonded with methylene ether bridges ($–CH_2–O–CH_2–$) and methylene bridges ($–CH_2–$). Their ratio of methylene to methylene ether bridges formed depends on the temperature and pH conditions used. Ether bridges can rearrange to methylene bridges by splitting off formaldehyde. One ether bridge needs two formaldehyde molecules and it is not as stable as a methylene bridge.

The resins are delivered in liquid or powder form (after spray drying) to the industry for the production of various wood-based panels. During this stage (hardening reaction), the resin cures completely and a more or less three-dimensional network is build up.

CHIMAR Hellas produced two UF resins following different synthesis procedures. The first one was a conventional resin, whose synthesis procedure included an alkaline methylolation followed by a mild acid condensation step, while the second resin was produced according to an innovative CHIMAR technology, which included acid methylolation followed by strong acid condensation stages. The dry solids for the conventional and innovative resins were 65.6 and

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Table 1a Standards for PB evaluation–dry properties

a–a	Dry properties	Unit	Test method	Remarks
1	IB (internal bond)	N mm^{-2}	EN 319	–
2	Density	kg m^{-3}	ISO/DIS 9427	–
3	MOR (modulus of rapture)	N mm^{-2}	EN 310	–

Table 1b Standards for PB evaluation–wet properties

a–a	Wet properties	Unit	Test method	Remarks
1	TS (dimensional stability)	%	EN 317	24 h, 20°C
2	Moisture content of board	%	EN 322	–
	FF (free formaldehyde)	mg(100 g atro)$^{-1}$	EN 120	perforator method

65.8%, respectively in the pre-polymer and 62.79 and 62.97%, respectively in the cured resins. Both resins had final formaldehyde to urea (F:U) mole ratio 1.07.

The resins evaluated at particleboard production that is a wood product of wide use. The boards were produced at CHIMAR's lab-scale wood-based panels production plant, according to the usual industrial practice. The resin (in liquid form) was admixed with hardener, paraffin and water for the preparation of the glue mixture. The glue mixture was sprayed on particles from pine having moisture content ca. 4%. The particles were blended with the glue mix and formed in mat with dimensions of 44x44x1.8 cm. The boards were pressed at high temperature for a certain time sufficient enough to achieve the total curing of the resin (hardening) and the maximum development of the polymer's network. The produced boards were sanded and proper samples of them were subjected to evaluation for their wet and dry properties as well as for their formaldehyde emissions. All test, were carried out according to the relative European standards, which are cited in Tables 1a and 1b.

The specifications of the resins were determined according to the conventional lab analysis, as well as FTIR spectroscopy and TG-DTA technique in dynamic heating conditions.

The FTIR spectroscopy, in transmittance mode, was used for the characterization of the functional group of the resins. For the liquid samples, a drop of the material was put between two KBr pellets (sandwich) while for the solid samples, KBr pellets with 1 mass% of the powdered material were produced. The spectra were obtained in the spectral area 4000–400 cm^{-1}, with a resolution of 2 cm^{-1} and 32 scans. A FTIR microscope (i-series, Perkin-Elmer) was used for the characterization of the particle board. Small pins of the wood were removed from the specimens and placed on a freshly prepared KBr pellet. The spectra were obtained in transmittance mode with an aperture of 100 μm.

Thermal analysis was carried out with a Setaram Setsys TG-DTA 1750°C. Samples (5.5±0.2 mg) were placed in alumina crucibles. An empty alumina crucible was used as reference. Samples were heated from ambient temperature to 500°C in a 50 mL min^{-1} flow of N_2. A heating rate of 5°C min^{-1} was used and continuous records of sample temperature, sample mass, its first derivative and heat flow were taken.

Results and discussion

The specifications of the resins are reported in Table 2 while the properties of boards, determined according to the respective European standards, are cited in Table 3.

Table 2 Specifications of resins

Properties of pre-polymer	Unit	Conventional resin	Innovative resin
pH at 25°C		8.0	8.3
Brookfield viscosity at 25°C	cP	320	365
Hardening time at 100°C	s	50	49
Water tolerance (resin/water) at 25°C	mL mL^{-1}	1/2.5	1/4.3
Surface tension	mN m^{-1}	71	72
Dry solids	mass/mass %	65.6	65.8
Free formaldehyde	%	0.06	0.07
Buffer capacity (measured with 0.1 N H_2SO_4)	mL	11.0	8.0

Table 3 Particleboard evaluation

Properties of particleboards	Unit	European standard	Conventional resin	Innovative resin
Internal bond (IB)	N mm^{-2}	EN319	0.37	0.56
Modulus of rupture (MOR)	N mm^{-2}	EN310	18.3	18.59
Thickness swelling (24 h)	%	317	31.6	19.7
Free formaldehyde content	mg(100 g atro)$^{-1}$	EN120-perforator method	7.83	7.6

Comparing the specifications of the two UF resins, it is obvious that the new process developed by CHIMAR gave a product of very low buffer capacity and increased compatibility with water (water tolerance). These properties are very important for the industry, as the low buffer capacity indicates the potentiality to reduce or even eliminate the use of acid for the hardening of the resin, while the increased water tolerance renders good wash down properties to the product and allows the easy cleaning of the apparatus used for the uncured product. All the other specifications of the resins are similar, which means that no special treating of the resin is required for its application in board production.

Above that, the procedure developed by CHIMAR facilitates the production of resins having remarkable clarity when freshly prepared, while the conventional resins of this low mole ratio F:U are opalescent and more usually thick white liquids. To make such resins as clear transparent liquids, allows an instant visible means of checking that the resin made by this process has been supplied and that contamination by other materials has not taken place.

These advantages can be achieved with no loss of strength in the resin. As it is obvious from the properties of particleboards (Table 3) made with this innovative UF resin, both the internal bond (IB) and the thickness swelling (TS) of boards have been drastically improved, while the formaldehyde emissions remained comparable to the values of the conventional resin.

The absorbance spectra of the pre-polymer and the cured resin of the conventional one are presented in Fig. 1. The spectra of the conventional and the innovative resins are almost identical and the peaks revealed could be attributed to the characteristic functional groups of the resin such as amide I, II and C=O at 1650–1550 cm^{-1} and CH_2OH, CH_3 and CN at 1400–1360 cm^{-1}, etc. The most characteristic difference between the pre-polymers and the cured resins is at the spectral area 3700–3000 cm^{-1}. The broadening of the band of the pre-polymer at ~3440 cm^{-1}, could be attributed to pre-polymer's byproducts, such as water and excess formaldehyde, which allow hydrogen bonding with the reactive functional groups such as CH_2OH, NH_2 and NH [12]. The sharpening and the shifting at 3350 cm^{-1} of this band after curing, indicate the formation of bonded NH group.

Figure 2 presents the dependence of mass loss and heat flow on the temperature, for both the pre-polymer and the cured polymer of a conventional UF resin. The curing of the resin is extended in a wide temperature area, while any exothermic peak is totally covered by the endothermic curve of the water evaporation reaction. The water comes up either by the quantity added during the synthesis of the resin, or results from the condensation reactions. No obvious thermal incident is observed in the area of temperatures beyond the water evaporation and up to 210°C, while a small mass loss observed corresponds to the free formaldehyde's slow release. The endothermic peak with minimum at 232–237°C is attributed by many authors to the degradation of methylene-ether bridges in the resin's network. The comparative results of the pre-polymer

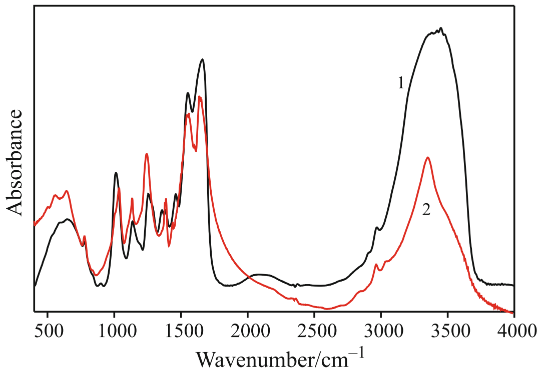

Fig. 1 Absorbance spectra of the conventional resin 1 – the pre-polymer and 2 – the cured resin

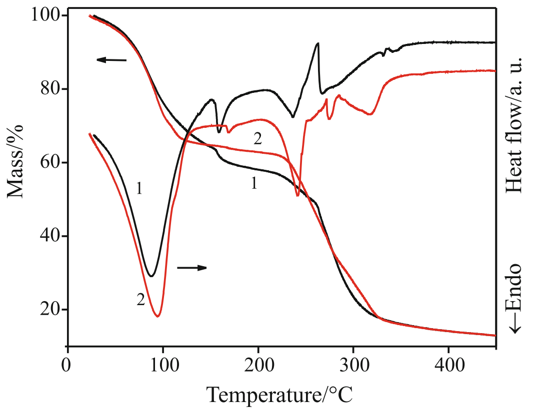

Fig. 2 Mass (%) and heat flow *vs*. temperature for the conventional resin 1 – the pre-polymer and 2 – the cured resin

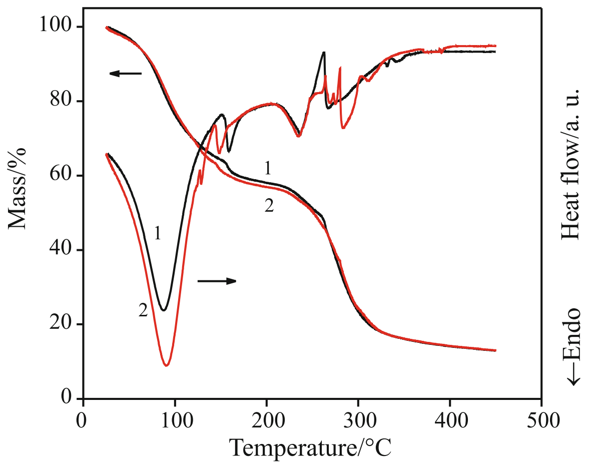

Fig. 3 Mass (%) and heat flow *vs*. temperature for the pre-polymer resin 1 – the conventional resin and 2 – innovative resin

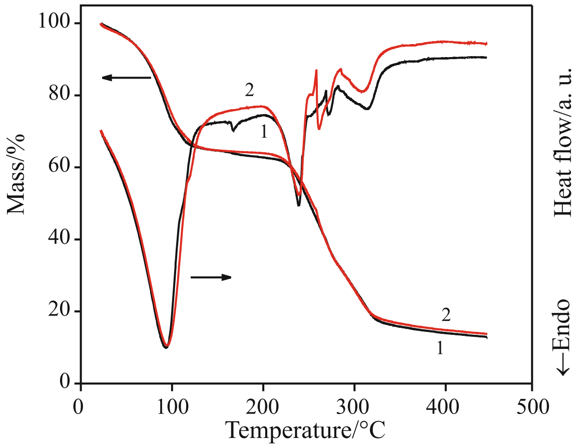

Fig. 4 Mass (%) and heat flow *vs*. temperature for the totally cured resin 1 – the conventional resin and 2 – innovative resin

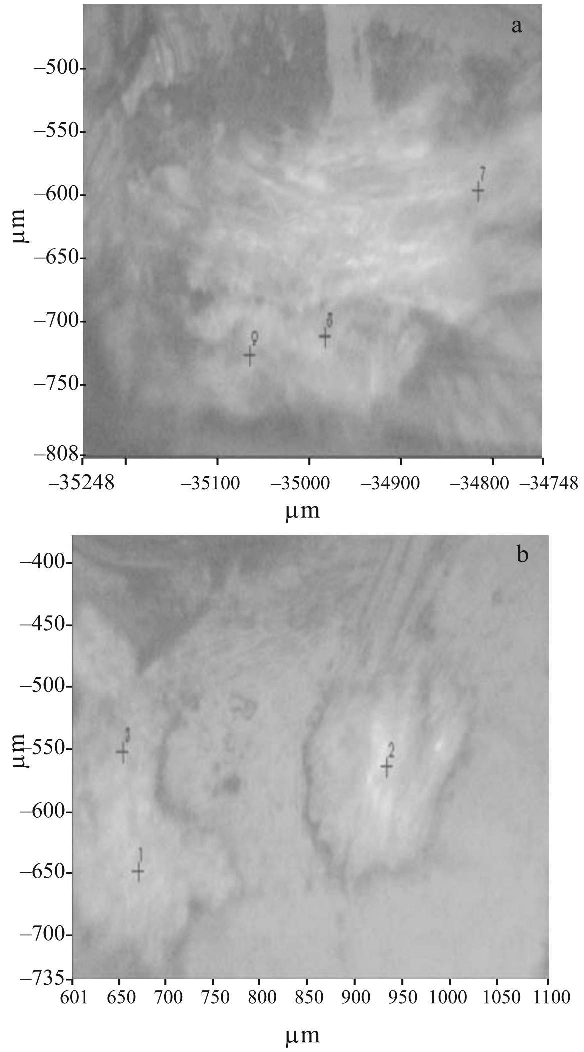

Fig. 5 Optical photos of particle board from the FTIR microscope a – pure wood and b – wood with resin

and cured polymer for both the conventional and innovative resins are presented in Figs 3 and 4. These figures show up that the minimum of the endothermic peak attributed to methylene-ether bridges comes about to lower temperatures at the pre-polymer than the cured resin. For the conventional resin this shifting is observed from 236.6±0.5 to 241.6±0.5°C, while the innovative resin performs a greater transposition from 234.6±0.5 to 242.0±0.5°C.

The study of particle boards with the FTIR microscope was done at small pins of pure and resin modified wood. The optical images of these specimens are presented in Figs 5a and b respectively, with the crosses indicating the positions where the spectra were obtained. In Fig. 6, representative FTIR absorbance spectra obtained from small areas (100 µm) of the above specimens, are compared with the spectrum of the resin. As it can be seen, the spectrum of resin modified wood, beyond the characteristic peaks of the resin, presents peaks attributed to the functional groups of pure wood, such as O–H (3600–3200 $\mathrm{cm^{-1}}$), C=O acetyl in xylans (1735 $\mathrm{cm^{-1}}$) and aromatic ring (1508, 1423, 1340–1315 $\mathrm{cm^{-1}}$) [13].

The system wood-resin was studied also with thermal analysis. In Figs 7 and 8 there is a comparative presentation of the mass loss and the heat flow towards the temperature for the wood chips, the innovative resin in cured state, and the wood chips blended with the same innovative resin. Referring to the chips, the first area of mass loss is completed close to 140°C and corresponds to the loss of the water-humidity of the chips. The second mass loss area starts at around 210 and extends up to 405°C, but without stabilization of the mass loss until the temperature of 450°C is reached. The area of 210 to 405°C corresponds to wood degradation. The above-mentioned temperature limits of mass loss are the same for both the wood chips and the cured resin. The only difference is that the water loss is greater at the first stage. Thus, it is of no surprise that the curve of the mass loss of the chips blended with resin has the same course with that of the pure raw materials. All of the above results advocate to the conclusion that a safe temperature threshold for the production of wood based panels with urea formaldehyde resins, could be considered the temperature of 200°C.

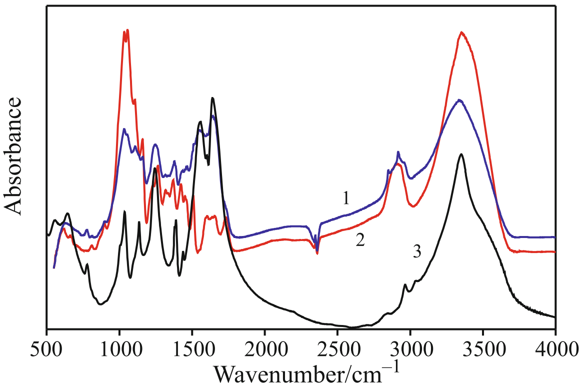

Fig. 6 FTIR absorbance spectra from the: 1 – particle board, 2 – pure wood and 3 – resin

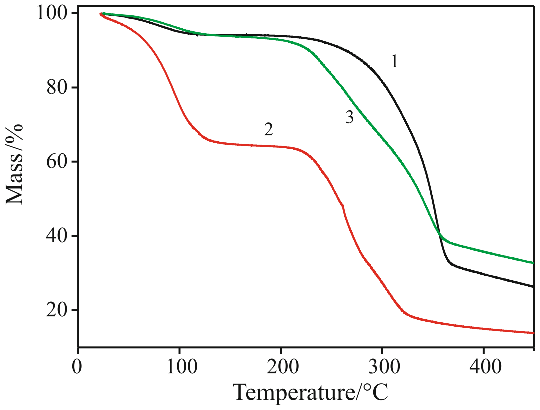

Fig. 7 Mass (%) *vs*. temperature for 1 – wood chips, 2 – cured innovative resin and 3 – wood chips blended with the cured conventional resin

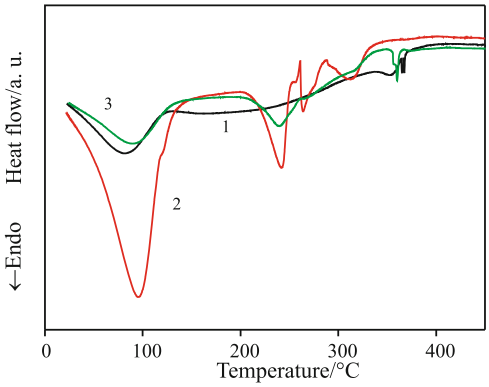

Fig. 8 Heat flow *vs*. temperature for 1 – wood chips, 2 – cured innovative resin and 3 – wood chips blended with the cured conventional resin

Conclusions

The innovative process developed by CHIMAR is suitable for the production of low F:U mole ratio urea-formaldehyde resins. Such a resin is capable of producing particleboards and fibreboards effective for many applications, without changing the usual industrial production procedure. Even though the analysis of the resins with TG-DTA technique in dynamic heating conditions and FTIR didn't bring to light any significant differences proclaiming the superiority of the new process, both the specifications of the pre-polymer and the properties of the boards manifest the advantageous properties and improved bonding ability of the innovative resin. This can be attributed to the synthesis parameters employed during the manufacture of the pre-polymer that allowed the development of a network with different structure and chemical bonds, while the terminal or pendant chemical units remained qualitatively the same.

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References

1 R. O. Ebewele, J. Appl. Polym. Sci., 58 (1995) 1689.
2 B.-D. Park, E.-C. Kang and J. Y. Park, J. Appl. Polym. Sci., 100 (2006) 422.
3 C. Xing, J. Deng, S. Y. Zhang, B. Riedl and A. Cloutier, J. Appl. Polym. Sci., 98 (2005) 2027.
4 M. Dunky, Int. J. Adhes. Adhes., 18 (1998) 95.
5 B.-D. Park, E. C. Kang and J. Y. Park, J. Appl. Polym. Sci., 101 (2006) 1787.
6 K. Siimer, T. Kaljuvee and P. Christjanson, J. Therm. Anal. Cal., 72 (2003) 607.
7 G. Camino, L. Operti and L. Trossarelli, Polym. Degrad. Stab., 5 (1983) 161.
8 S. Zeman and L. A. Tokareva, Thermochim. Acta, 202 (1992) 181.
9 K. Siimer, T. Kaljuvee, P. Christjanson, T. Pehk, J. Therm. Anal. Cal., 80 (2005) 123.
10 K. Siimer, T. Kaljuvee, P. Christjanson and I. Lasn, J. Therm. Anal. Cal., 84 (2006) 71.
11 K. Siimer, T. Kaljuvee, P. Christjanson, T. Pehk and I. Saks, J. Therm. Anal. Cal., 91 (2008) 365.
12 S. S. Jada, J. Appl. Polym. Sci., 35 (1988) 1573.
13 M. G. S. Yap, Y. T. Que and L. H. L. Chia, J. Appl. Polym. Sci., 43 (1991) 2083.

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