

## THE INFLUENCE OF WOOD EXTRACTS ON THE RHEOLOGICAL PROPERTIES OF UREA-FORMALDEHYDE ADHESIVE DURING CURE

### **Mladjan POPOVIĆ**

Assist.prof.dr. - University of Belgrade - Faculty of Forestry  
Address: Kneza Višeslava 1, 11030 Belgrade, Serbia  
E-mail: [mladjan.popovic@sfb.bg.ac.rs](mailto:mladjan.popovic@sfb.bg.ac.rs)

### **Milanka DJIPOROVIĆ-MOMČILOVIĆ**

Assoc.prof.dr. - University of Belgrade - Faculty of Forestry  
Address: Kneza Višeslava 1, 11030 Belgrade, Serbia  
E-mail: [milanka.djiporovic@sfb.bg.ac.rs](mailto:milanka.djiporovic@sfb.bg.ac.rs)

### **Milan ŠERNEK**

Assoc.prof.dr. - University of Ljubljana - Faculty of Biotechnology  
Address: Rožna dolina, Cesta VIII/34, 1000 Ljubljana, Slovenia  
E-mail: [milan.sernek@bf.uni-lj.si](mailto:milan.sernek@bf.uni-lj.si)

### **Jasmina POPOVIĆ**

Assistant - University of Belgrade - Faculty of Forestry  
Address: Kneza Višeslava 1, 11030 Belgrade, Serbia  
E-mail: [jasmina.popovic@sfb.bg.ac.rs](mailto:jasmina.popovic@sfb.bg.ac.rs)

### **Ivana GAVRILOVIĆ-GRMUŠA**

Assist.prof.dr. - University of Belgrade - Faculty of Forestry  
Address: Kneza Višeslava 1, 11030 Belgrade, Serbia  
E-mail: [ivana.grmusa@sfb.bg.ac.rs](mailto:ivana.grmusa@sfb.bg.ac.rs)

### **Abstract:**

*Rheological analysis was used to evaluate the influence of the wood species of beech, fir and poplar on the gelation time of commercial urea-formaldehyde (UF). The UF adhesive samples were mixed with hot water extracts of selected wood species. Two series of samples were prepared, one without the catalyst addition and the other with the addition 0,2% of amonium chloride, per dry adhesive mass. Both series included the control UF adhesive samples, without the addition of wood extracts. Measurements of the visco-elastic properties of UF adhesive samples during cure were conducted at the temperature of 80°C, and at the constant frequency of 1Hz. The addition of wood extracts had a positive catalytic influence in the case of the UF adhesive samples without the catalyst addition. Contrary, wood extracts have retarded the curing of the UF adhesive samples with catalyst.*

**Key words:** UF adhesive; wood extracts; rheometry; gel time.

## INTRODUCTION

The catalytic effects of wood extracts on the gel time of urea-formaldehyde (UF) adhesive have been investigated earlier. It was found that the gel time of UF adhesive increases with the increase in the pH of wood extracts (Slay *et al.* 1980), and that the buffer capacity of the extracts presents another parameter that affects the UF adhesive cure (Johns and Naizi 1980).

In the more contemporary studies, the use of thermomechanical analysis (TMA) and dynamic mechanical analysis (DMA) have proved to be very appropriate tool for evaluation of thermoset adhesives curing behaviour, by monitoring the change in their visco-elastic properties.

TMA method has been used to investigate the gelation and vitrification temperatures, degree of curing reaction and the temperature maximum of the elastic deformation during cure of urea-formaldehyde (UF) and other amino resin systems (Yin *et al.* 1995). It was observed that the mechanical strength of bonded wood samples correlates well with the adhesive curing rate. The same method was used in the studies of the characteristic time-temperature-transformation (TTT) and continuous heating transformation (CHT) diagrams which illustrate the physical and chemical changes related to the adhesive curing process (Lu and Pizzi 1998a, Lu and Pizzi 1998b, Pizzi *et al.* 2001). Visco-elastic properties of the adhesive curing behaviour on wood substrates were also studied by DMA method (Umemura *et al.* 1996, Onic *et al.* 1998). The evaluation of parameters such as the gelation temperature, storage and loss modulus, viscosity and the loss factor, were also used to investigate the influence of formaldehyde to urea ratio on the curing behaviour UF adhesive systems (Park and Kim 2008, Halasz *et al.* 2000). As a part of the DMA method, the study of the visco-elastic properties on the liquid materials is also called the rheological analysis.

The rheometer instruments are very sensitive to the molecular shifting in the sample. In that way it is possible to detect certain transitions in the macromolecules, such as the gelling and vitrification temperatures, as well as to monitor the mechanical changes in the material influenced by the chemical reactions (Haines 2002, Menczel and Prime 2009).

In this research the rheological analysis was used to evaluate the effects of the wood extracts from the selected species on the curing behaviour of the UF adhesive.

During its cure the UF adhesive, as the most of the formaldehyde based thermosets, will pass through the certain transition phases, between the liquid, non-gelled rubber, gelled rubber and gelled glass states of the material (Pizzi *et al.* 2001). Those transitions will induce the changes in the visco-elastic behaviour of the adhesive, which will be recorded by the rheometer instrument. Usually, the controlled parameter in the rheometry tests is the strain, applied in the oscillatory shear mode; while the measured value is the resulting stress. The oscillatory character of the strain reflects in the same oscillatory character of the stress.

In the case of the oscillatory shear stress, the complex shear modulus can be expressed with the following equation:

$$G^* = G' + iG'' \quad (1)$$

$G'$  - storage modulus, in N/mm<sup>2</sup>

$G''$  - loss modulus, in N/mm<sup>2</sup>

$i$  - imaginary number

The real component  $G'$  represent the ideal elastic solids, and the imaginary component  $G''$  represent the liquid (viscous material). The visco-elastic materials are characterised by both components. When subjected to the controlled oscillatory load, such materials will induce a certain lag between the strain and inflicted stress, defined by the phase angle ( $\delta$ ). This can be expressed as the loss factor ( $\tan\delta$ ) by the following equation:

$$\tan \delta = \frac{G''}{G'} \quad (2)$$

Assuming that the oscillatory character of the applied shear stress does not influence in the adhesive curing reaction, it is possible to monitor its visco-elastic behaviour in regard to the temperature and time. The adhesive transition from the liquid into the gel phase is defined by the gelation point or the gelation time ( $t_{gel}$ ). There are several criteria in the rheological analysis used for detection of gelation time, such as the intersection of  $\tan\delta$  curves obtained at multi-frequency sweeps or the extrapolation of reciprocal value of zero share viscosity to the zero value. One of the widely used method is to determine the intersection between the  $G'$  and  $G''$  curves, which is the point when  $\tan\delta$  equals zero value (Halasz *et al.* 2000, Mravljak and Sernek 2011).

There are also several methods for determination of vitrification point. This can be detected as the maximum value of  $G''$  at the frequency of 1Hz, maximal value of  $\tan\delta$  at the frequency of 1Hz, or at the onset or the end of the frequency dependance of  $G'$ .

## MATERIALS AND METHODS

Hot water extracts were obtained from the three selected wood species growing in Serbia: beech (*Fagus moesiaca* / Domin, Maly/Czeczott.), poplar (*Populus x Euroamericana* 'I-214') and fir (*Abies alba* / Mill). The fraction of wood flour of 0.5-1.0mm was used for the 2h extraction at the boiling water temperature. Samples for the rheology measurements were further treated in lyophilization process in order to obtain dry extract.

UF adhesive used in this research was a commercial adhesive supplied by the company Petrohem (Lendava, Slovenia). The supplied adhesive emulsion had a molar ratio of F/U = 1.12, with the following characteristics: dry matter content = 67.54% (SRPS EN 827); density = 1303kg/m<sup>3</sup> (SRPS EN 542); viscosity = 505mPa·s (SRPS EN 12092) and pH value = 8.16 (SRPS EN 1245). For all of the visco-elastic measurements, the adhesive samples were used diluted to the concentration of 50%. The control adhesive samples were prepared without the addition of extracts. UF adhesive mixes with extracts were prepared with the addition of 1% of the relevant wood extracts (based on the dry adhesive mass). Before mixing with the supplied UF adhesive, the extracts were dissolved into distilled water in the ratio needed to adjust the UF adhesive concentration to 50%.

### The measurements of pH value and buffer capacity

Before the titration, the pH meter (ISKRA) with glass electrode was calibrated with standard buffer solutions of pH 4 and pH 7. The amount of 50ml of each wood extract solution was used for the initial pH measurements and for the subsequent titration. The acid buffer capacity was defined as the amount of 0.025N H<sub>2</sub>SO<sub>4</sub> needed to reach the pH 3 of the extract solution. In the same way, the amount of 0.025N NaOH consumed during titration until the pH 8 of the extract solution defined the alkaline buffer capacity. Difference between the acid and the alkaline buffer capacities presented the absolute acid buffer capacity.

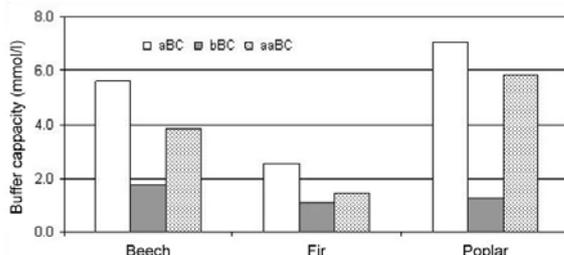
### Rheologic measurements

The measurements of the visco-elastic properties of the UF adhesive samples were obtained on the rheometer Ares G2 (TA Instruments, USA) with the dynamic stress control. The parallel plates were 25mm in diameter and the gap between them was 0.3mm. All the measurements were performed in the oscillatory shear stress mode with the small strain of 1% and the angular frequency of 6rad/s (at 1Hz). Sinusoidal character of the strains has allowed for the monitoring of storage modulus ( $G'$ ) and the loss modulus ( $G''$ ), as well for the determination of the loss factor ( $\tan\delta$ ).

All of the UF adhesive samples (with and without the addition of wood extracts) were divided into two series. The first series was used with the addition of NH<sub>4</sub>Cl as the catalyst in the amount of 0.2% (based on the adhesive dry mass). The relevant amount of the ammonium chloride was dissolved into distilled water used for the dilution of adhesive. The second series of UF adhesive samples was used without the catalyst addition. Each sample was prepared in the ambient condition and immediately after placed between the testing plates inside the heating chamber. Since the instrument could not compensate for the thermal expansion of the UF adhesive samples at the temperatures above 100°C, all of the measurements were performed at 80°C.

## RESULTS AND ANALYSIS

The fir extracts had the lowest pH value of 4.88, while the pH of beech and poplar was 5.46 and 5.59 respectively. The results for the buffer capacities of the selected wood species are shown graphically in the Fig. 1.

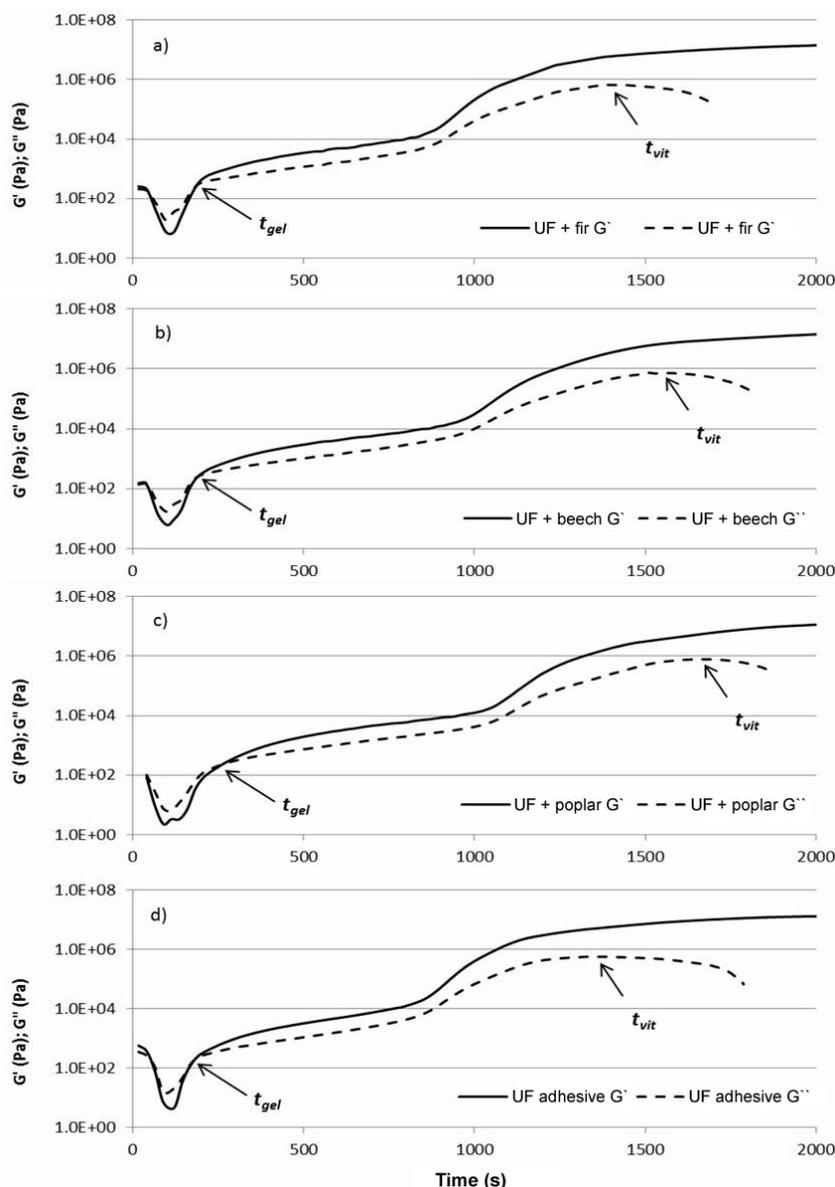


**Fig. 1**

**Buffer capacities of the beech, fir and poplar hot water extracts:**  
**aBC - acid buffer capacity; bBC - base (alkaline) buffer capacity; aaBC - absolute acid buffer capacity.**

The fir extracts had the lowest values for the acid buffer capacity of 2.64mmol/l, which is approximately 2.15 times less in regard to beech extracts and 2.7 times less then for poplar extracts. Since the alkaline buffer cappacity of extracts have resulted in relatively low values for all of the selected wood species, then the resulting absolute acid buffer cappacities have followed the similar trend of the acid bufer capacities of the extracts. The absolute acid buffer capacity was 1.46mmol/l for the fir extracts, 3.83mmol/l for the beech extracts, and has resultet in the highest value of 5.81mmol/l for the poplar extracts. The results of the titration are given in the Fig. 1, suggest that the fir extracts posses the highest catalytic potential in regard to all the selected wood species.

Characteristic diagrams in the Fig. 2 present the visco-elastic behaviour of the UF adhesive samples with the  $\text{NH}_4\text{Cl}$  addition (0.2% per adhesive dry mater). In general, it could be noticed that the all of the adhesive samples containing catalyst are characterised by both the gelation and vitrification transitions.



**Fig. 2**

**The change in the storage modulus ( $G'$ ) and loss modulus ( $G''$ ) during cure of the UF adhesive samples at the temperature of  $80^\circ\text{C}$ , and with the addition of 0.2%  $\text{NH}_4\text{Cl}$ :  
a - UF + fir extracts; b - UF + beech extracts; c - UF + poplar extracts and d - control UF adhesive.**

The gelation point was determined at the intersection between the  $G'$  and  $G''$  curves (the zero value of  $\tan\delta$ ), while the vitrification point was determined as the maximum value of the loss modulus  $G''_{max}$ , and the relevant results for the UF adhesive samples, with the addition of catalyst, are presented in the Table 1.

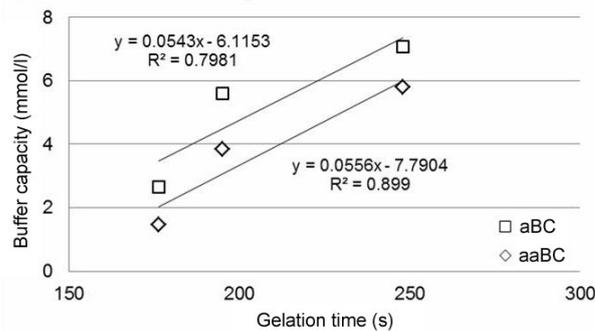
Table 1

**Gelation time ( $t_{gel}$ ) and vitrification time ( $t_{vit}$ ) of the control UF adhesive sample and the UF adhesive mixes with the extracts of beech, fir and poplar ( $NH_4Cl = 0,2\%$ ;  $T = 80^\circ C$ )**

Property	UF adhesive	UF + beech	UF + fir	UF + poplar
$t_{gel}$ (s)	<b>187</b>	<b>195</b>	<b>177</b>	<b>248</b>
st. dev.	11.2	12.7	17.7	25.5
$t_{vit}$ (s)	<b>1375</b>	<b>1464</b>	<b>1412</b>	<b>1671</b>
st. dev.	5.9	26.9	21.2	46.7

The gelation time of the UF adhesive control sample with the addition of 0.2%  $NH_4Cl$  and at the temperature of  $80^\circ C$  was 187.2 s (Table 1). Halasz *et al.* (2000) have recorded the lower gelation time of the commercial UF adhesive ( $122 \pm 2s$ ), yet it was obtained at the lower testing temperature ( $62^\circ C$ ), but at the higher level of catalyst ( $NH_4Cl$ ) addition (1%).

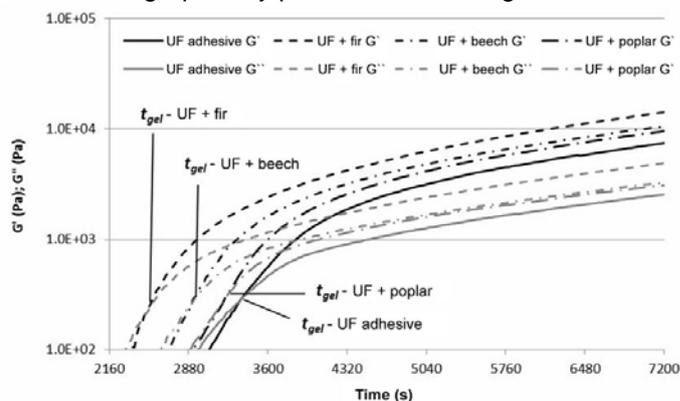
Concerning the UF adhesive sample series with the addition of catalyst, the presence of fir and beech extracts have not showed the significant effect on the gelation time of the UF adhesive. However the gelation time of the UF adhesive mix with fir extracts was lower in regard to the UF adhesive mix with beech extracts, suggesting that fir extracts might produce slightly catalytic effect on the UF adhesive cure. The results of the vitrification time have showed slightly retarding effect for both fir and beech extracts. The addition of poplar extracts resulted in approximately 32% higher gelation time and 21% higher vitrification time in regard to the control UF adhesive sample. The highest values of both gelation and vitrification time for the UF adhesive mix with poplar extracts, imply to the significant retarding effect of the poplar species. Obtained results correlates well with the acid and absolute acid buffer capacities of selected wood species, and the appropriate dependences are presented in the Fig. 3.



**Fig. 3.**

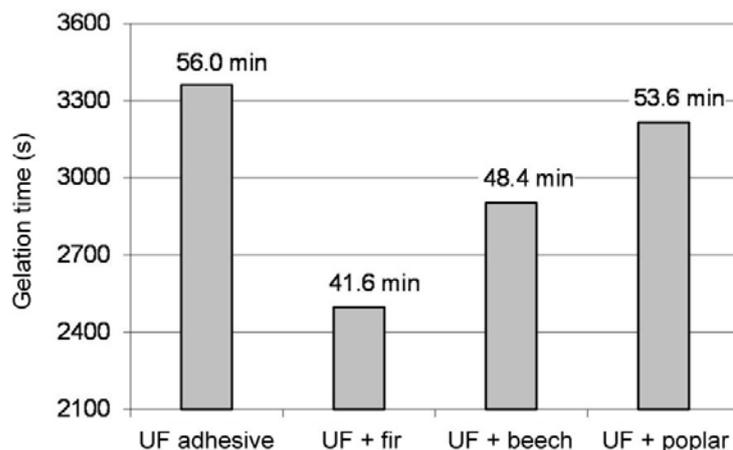
**The influence of the acid (aBC) and absolute acid buffer capacity (aaBC) on the gelation time of the UF adhesive with the 1% addition of beech, fir and poplar extracts (test temperature of  $80^\circ C$ ; catalyst addition of 0.2%)**

It was interesting to observe the results of the rheometry tests performed on the UF adhesive samples without the addition of catalyst. In general, none of the UF adhesive samples have passed through the vitrification transition. After reaching the limit of 2h (7200s), which marked the applied test duration, all of the UF adhesive systems have remained in the gelled rubber state (Fig. 4). Therefore, only the results of gelation time are obtained, which are graphically presented in the Fig. 5.



**Fig. 4**

**The change in the storage modulus ( $G'$ ) and loss modulus ( $G''$ ) during cure of the UF adhesive samples at the temperature of  $80^\circ C$ , and without the catalyst addition.**



**Fig. 5**

**Gelation time for the the UF adhesive samples at the temperature of 80°C and without the catalyst addition.**

The results on the gelation time of UF adhesive sample series without the addition of catalyst, have showed the general catalytic effects of the wood extracts. However, the addition of poplar extracts did not have significant influence and have decreased the gelation time of the relevant adhesive mix for nearly 4.5%. On the other hand, the addition of beech extracts have decreased the gelation time of the UF adhesive for 15.7%. The catalytic effect of the fir extracts was even stronger, resulting in the 34.6% decrease in the gelation time of the relevant UF adhesive mix.

Here we can assume that the acid buffer capacity of wood extracts was the main factor which governed the curing reaction of the relevant UF adhesive samples and the gelation time obtained during rheometry tests.

## CONCLUSIONS

The pH and acid buffer capacity values for all the selected wood species have showed the lowest values for the fir extracts. Contrary, the poplar extracts exhibited the highest acid and absolute acid buffer capacity, even though its pH level was similar to pH of beech extracts.

The results of the rheological analysis are presented as the values of gelation and vitrification time, resulting from the visco-elastic behaviour during UF adhesive cure:

- The addition of 1% of the wood extracts in the **UF adhesive catalyzed systems** (0.2%  $\text{NH}_4\text{Cl}$ ) have showed negligible effects for the fir and beech wood species. However, the UF adhesive mix with fir extracts resulted in significantly lower gelation time in regard to the UF adhesive with the addition of beech extracts (approx. 10%), which might suggest on slightly catalytic effect of the fir species.

- The poplar wood species have showed significantly retarding effect on the UF adhesive cure. The addition of poplar extracts have influenced in approximately 21% higher values for both gelation and vitrification times of the relevant UF adhesive mix in regard to the UF adhesive control sample.

- The gelation time of the UF adhesive systems correlates well with the acid and absolute acid buffer capacities. Having in mind that the buffer capacity is the measure of the resistance toward the change in the pH of the extracts, it depends on the chemical composition and concentration of the extraneous material which may have the retarding effect on the adhesive cure. Therefore, it could be expected that the UF adhesive systems will show better performance when applied with the wood species of lower acid buffer capacity.

- The rheometry tests on the UF adhesive systems, **without the catalyst addition**, have showed that the effect of the wood species have changed and have been characterized by dominantly catalytic nature. This suggests that the acidity of the extraneous material in wood extracts has governed the curing reaction of UF adhesive. The highest catalytic effect has been achieved with the addition of fir extracts. The relevant UF adhesive mix has resulted in 35% decrease of the gelation time in regard to the UF adhesive control sample.

- However, in the case of non-catalyzed adhesive systems, the vitrification transition has not been observed during the whole test period of 2h. Therefore the gelation time was the only parameter for evaluation of the influence of wood species on the UF adhesive cure.

Observing the results of this paper in general, we could conclude that the wood species with lower acid buffer capacity, such as the fir wood, are more suitable for manufacturing of wood based panels. We should

also have in mind the subtle influence of wood extracts on the UF adhesive cure, which emphasize the necessity for evaluation of the acidity of wood species before its application with UF adhesive systems.

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