CROSS-LINKED BIO/INORGANICALLY MODIFIED UREA-FORMALDEHYDE RESINS: INFLUENCE OF γ-RADIATION ON FORMALDEHYDE CONTENT

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WHAT WE DID

The effect of γ–irradiation on hydrolytic stability of nano-silica, nano-titania, and wood flour (WF) modified urea-formaldehyde (UF) resins was investigated. Modified UF resin with wood flour-WF (*Pinus silvestris L.*) as natural filler and modified UF resin with a mixture of SiO_2/WF and TiO_2/WF fillers were synthesized. A total of five samples were synthesized, with the designations UF/SiO_2, UF/TiO_2, UF/WF, UF/SiO_2/WF, and UF/TiO_2/WF, under the same conditions. The content of free formaldehyde (FA) was determined by the bisulfite method. The hydrolytic stability of modified UF resin was determined by measuring the concentration of liberated FA of modified UF resins after acid hydrolysis (Figure 1). The studied modified UF resins have been irradiated with 50 kGy and the effect of γ–irradiation was evaluated on the basis of the percentage liberated FA before and after γ–irradiation..

MATERIALS AND METHODS

Materials: The following materials were employed in the study reported here: Urea $(NH_2)_2CO$ (Alkaloid-Skopje, North Macedonia); 35% Formaldehyde CH_2O (Unis-Goražde, Bosnia and Herzegovina); SiO_2 (particle size 12 nm) and TiO_2 (particle size 21 nm) (Sigma-Aldrich Chemistry, Germany) and wood flour (particle size 250-300 μm) (*Pinus silvestris L.*) as natural filler supplied by Tigar company. All the other materials and solvents used for analytical methods were of analytical grade.

Synthesis and modification of UF composites: Five samples (UF/SiO_2, UF/TiO_2, UF/WF, UF/SiO_2/WF, and UF/TiO_2/WF), of modified UF composite materials with formaldehyde to urea (F/U) ratio (0.8) were synthesised using the same procedure [1].

Resin hydrolysis and determination of liberated formaldehyde: The hydrolytic stability of modified UF composites was determined by measuring the mass loss and liberated formaldehyde (FA) concentration of modified UF composites after acid hydrolysis. The sulfite method [2,3] was used to the determined the percentage of free and liberated FA.

Reaction titration: $CH_2O + Na_2SO_3 + H_2O \rightarrow NaSO_3CH_2OH + NaOH$

The free and liberated FA (%) content was calculated from the equation:

$$FA(\%) = \frac{(V1 - V2)cE100}{1000\ a}$$

where V is volume of HCl (cm^3), c is the concentration of HCl (mol/dm^3), E is equivalent weight of formaldehyde, and a is weight of samples (g).

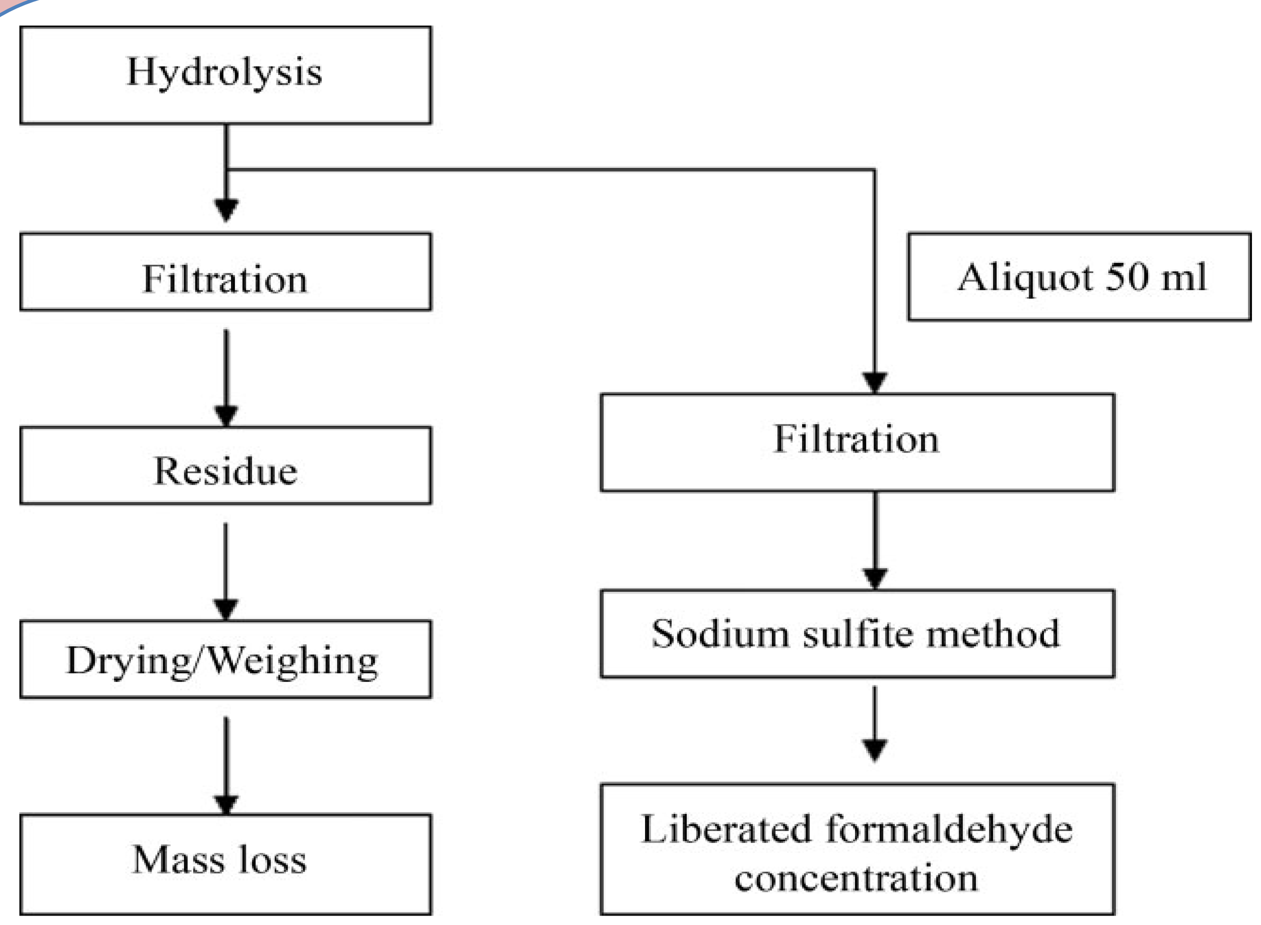

Figure 1. Schematic diagram of hydrolysis procedures for determination of content liberated FA in the modified UF composite.

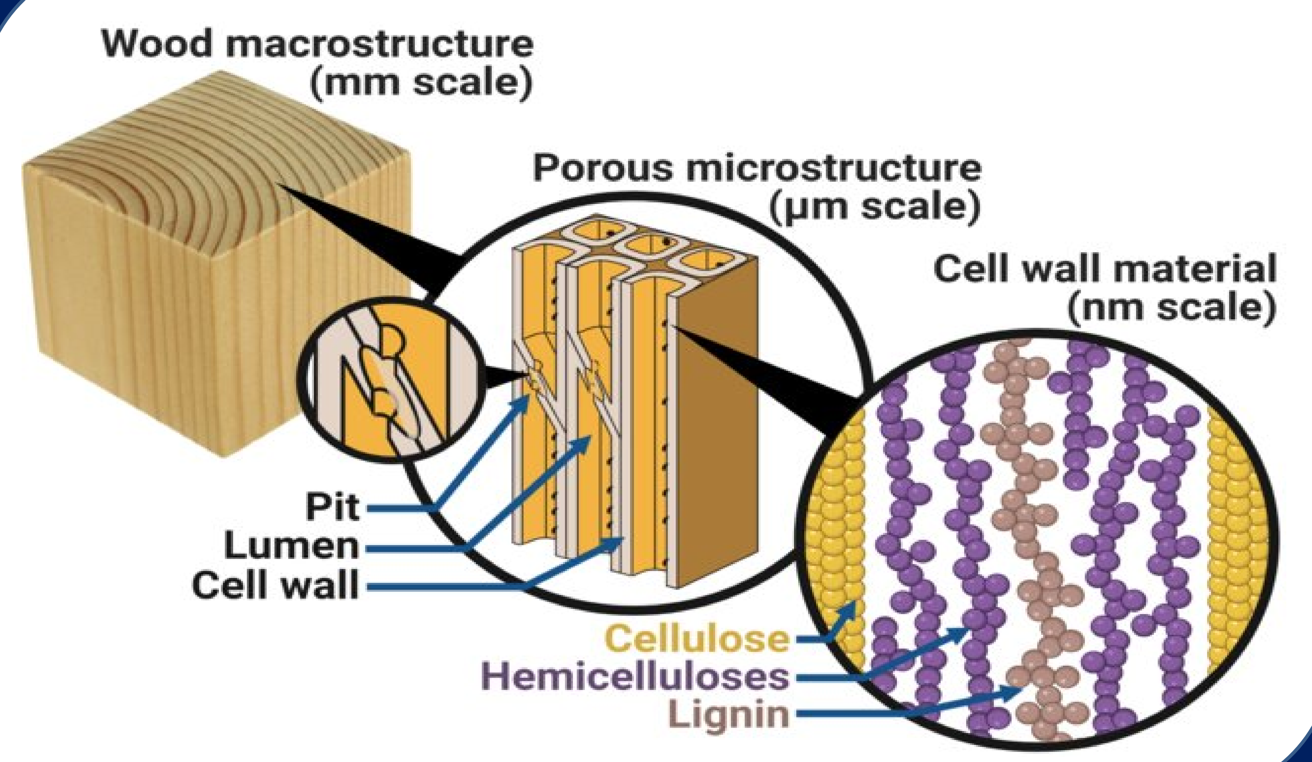

Figure 2. *Simplified overview of wood structure on different length scales [4].*

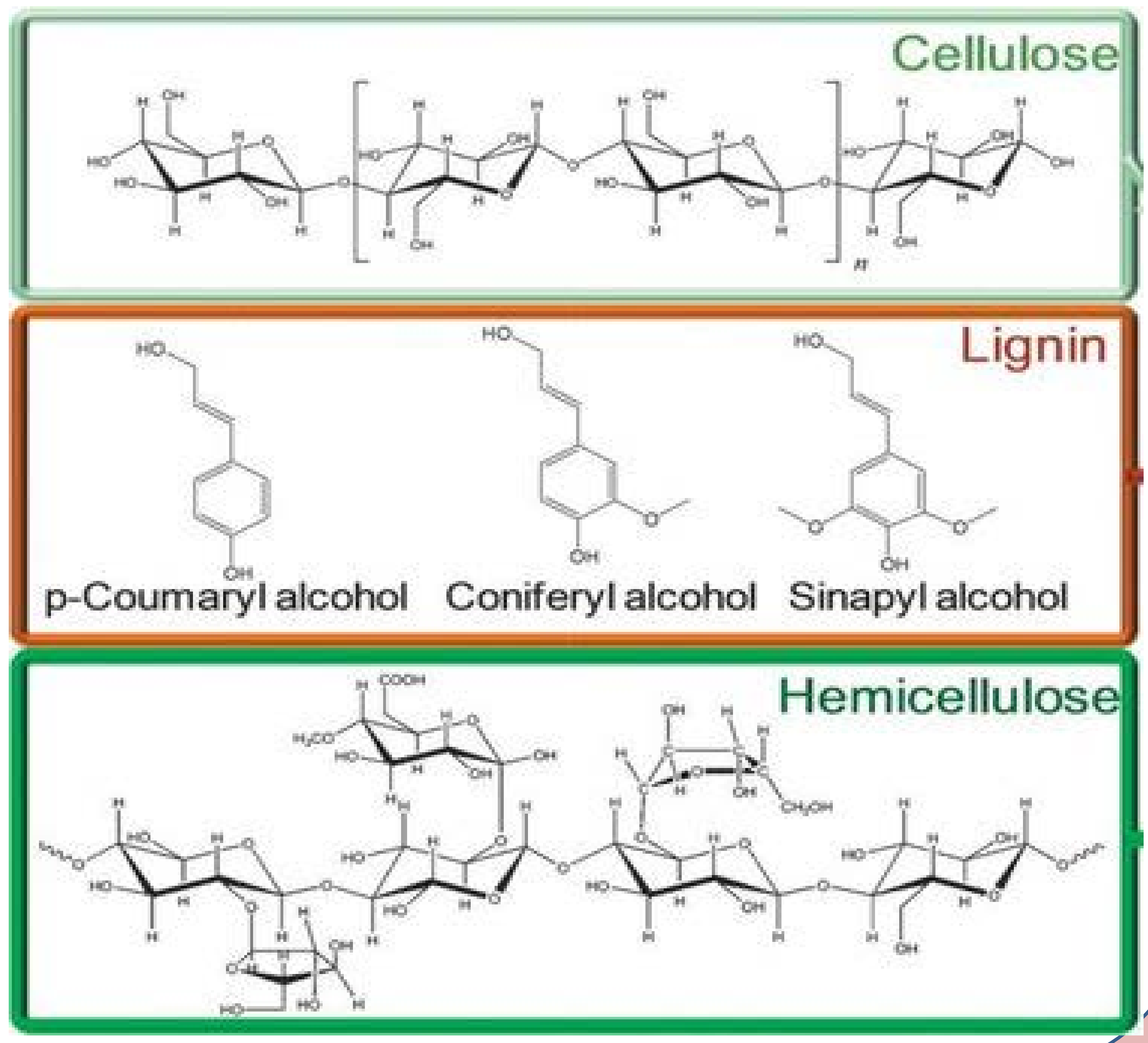

Figure 3. *Structure of cellulose, hemicellulose, and lignin.*

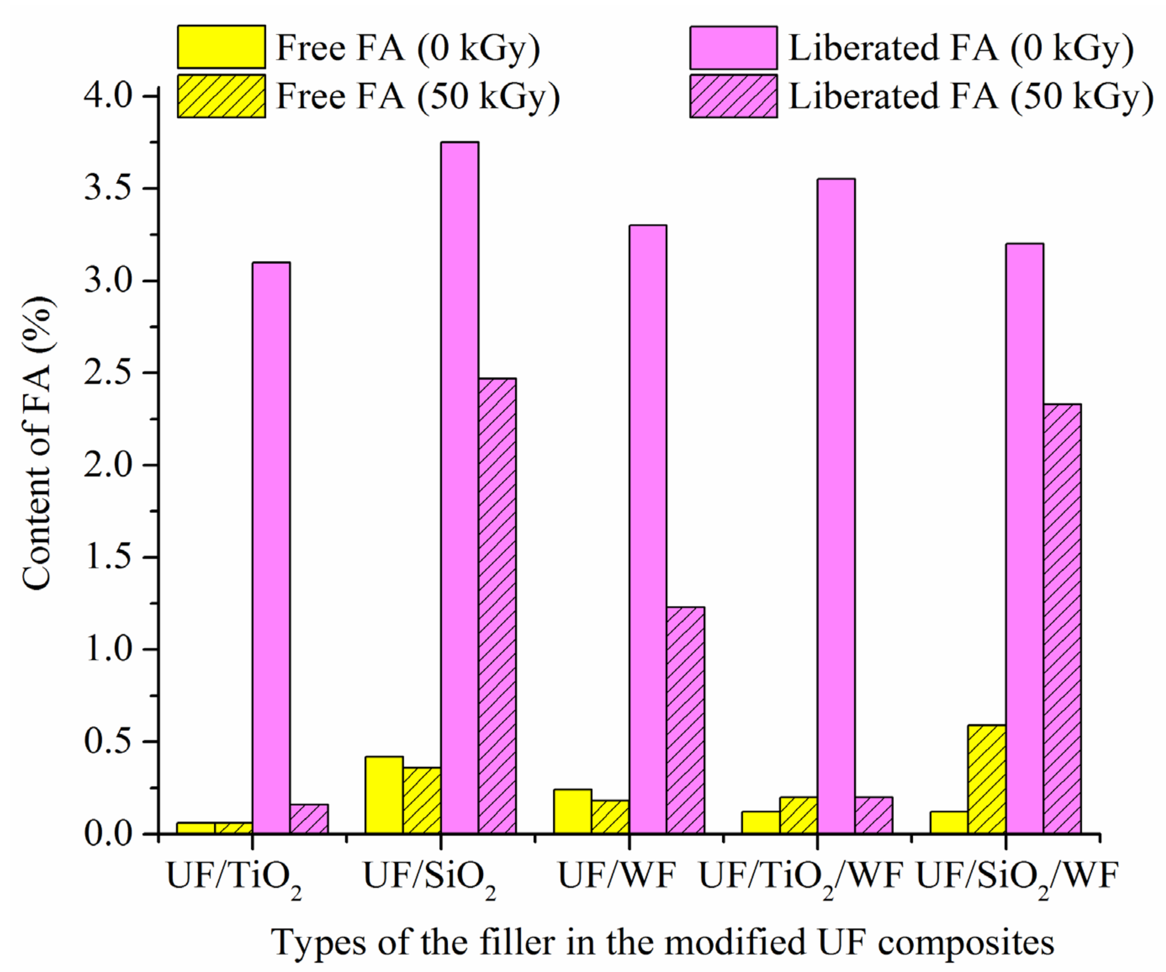

Figure 4. *FA content in cross-linked modified UF composites before and after γ–irradiation depending on the filler used.*

RESULTS AND DISSCUSION

SiO_2, as well as TiO_2, have a characteristic structure and relatively small particles and thus a large specific surface area and the particles themselves have the ability to adsorb certain substances on the surface due to the large number of OH-groups that are potentially active sites for binding the formaldehyde. Due to its natural acidity, wood, like other celluloses, can absorb FA from UF resins and become emitters of the same FA. On the other hand, WF containing cellulose, hemicellulose and lignine (Figure 2 and 3), and many OH-group can react with free FA from UF resin.

The amount of free FA after irradiation was lower in TiO_2 modified UF composite (0.06%) (Figure 4) while the amount of liberated FA (3.1%) was found lower in all cases. The minimum percentage (0.16%) of liberated FA (Figure 4) was obtained in UF/TiO_2 composite after γ–irradiation which indicates a significant improvement in the hydrolytic stability compared to other modified UF resins. The reason for that could be extensive bonding most probably between the hydroxyl/metilol groups of the matrix and OH-groups of the inorganic reinforcement, resulting in a strong structure.

After acid hydrolysis and γ–irradiation, it is evident that the content of released FA is drastically reduced (Figure 3). This leads to the conclusion that γ–irradiation promotes additional cross-linking of UF resins. The largest change is recorded in UF/TiO2 and UF/TiO_2/WF composites where the content of released FA decreases from 3.13% to 0.16% and from 3.55% to 0.2%, respectibility.

CONCLUSIONS

- The minimum percentage of free FA (0.06%) and liberated FA (3.1% and 0.16%) were obtained in UF/TiO_2 composite before and after γ–irradiation which indicates a significant improvement in the hydrolytic stability compared to other modified UF resins.
- γ–Irradiation causes additional cross linking of UF resin, which rapidly decreases the content of liberated FA after acid hydrolysis

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