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Effect of γ-irradiation on the hydrolytic stability and thermo-oxidative behavior of bio/inorganic modified urea–formaldehyde resins

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ABSTRACT

In order to minimize emission of formaldehyde from urea–formaldehyde resins (UF) and to improve their thermo-oxidative behavior, the effect of low γ-irradiation on hydrolytic and thermo-oxidative stability of nano-silica modified UF resin, modified UF resin with wood flour (*Pinus silvestris* L.) as natural filler and modified UF resin with mixture of SiO_2/WF fillers were investigated. The hydrolytic stability of modified UF resins was determined by measuring the mass loss and liberated formaldehyde concentration of modified UF resins after acid hydrolysis. The studied modified UF resins have been irradiated (50 kGy) and effect of γ-irradiation was evaluated on the basis of percentage of liberated formaldehyde before and after irradiation. The minimum percentage (1.23%) of liberated formaldehyde and mass loss of a 25.35% were obtained in wood flour modified UF resin after γ-irradiation which indicate significant improvement in the hydrolytic stability compared to other modified UF resins. The effect of γ-irradiation was evaluated also on the basis of thermo-oxidative behavior of the same modified UF resins before and after irradiation. The thermo-oxidative behavior was studied by non-isothermal thermo-gravimetric analysis (TG), differential thermo-gravimetry (DTG) and differential thermal analysis (DTA) supported by data from IR spectroscopy. After γ-irradiation, the shift of DTA peaks a higher temperature indicates that thermo-oxidative stability of modified UF/SiO_2/WF is increase.

1. Introduction

Urea–formaldehyde (UF) resins, as the most popular type of the so-called amino plastic resins, are widely used in many manufacturing processes due to its useful properties [1]. The adhesive materials whose durability joint against environmental stress in order to gain good long-term performances for wood composites are required in wood panel industry. As a polymeric condensation product formed by chemical reactions between formaldehyde and urea, UF resin adhesive is most widely used for the manufacturing of wood-based composite panel such as plywood, particleboard, or medium density fiberboard. It is chosen as an adhesive resin due to its high reactivity, good performance in panel, water solubility and low price. Still, insufficient resistance to water limited UF resins to interior applications. Furthermore, the hydrolytic degradation process and formaldehyde emission from some urea–formaldehyde (UF) bonded wood products has been recognized for a number of years as a potential source of indoor air pollution and health problems [2–5]. The emitted formaldehyde causes from a free formaldehyde present in UF resins after synthesis and mostly from hydrolysis of UF resins under acidic and moisture conditions. Many studies have recognized the hydrolysis as a responsible factor in long-term formaldehyde emission of UF resin bonded wood panels [6–10]. Hence, the efforts were directed to the better understanding of resin hydrolytic degradation process and ways of minimization of the formaldehyde emission. The hydrolytic stability of UF resin could be enhanced if the structure of UF resins was modified by incorporating co monomers into the polymer chains and also incorporating some suitable modifiers and buffers into the resin that are capable of neutralizing the acid catalysts are used as curing agents [11–16]. Nevertheless, the improvement of the hydrolytic stability of UF resin in terms of formaldehyde emission is still very topical.

Modification of UF resins is perhaps one of the best possibilities to create stabilized UF resins which could exceed toxicological and other limitations in their application. By adding the selected

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materials in certain quantities as fillers, catalysts and hardeners it is possible to get UF resins with improved physical and chemical properties [16–19]. Radiolysis of polymers with gamma or electron irradiation is well-known technique for modification of polymers and already found its industrial applications [20–23]. Due to creation of altered branching and low-density cross-links between the chains polymers can achieve numerous desired properties. Radiochemical studies on cross-linking or degradation of polymers are important for designing new materials [24]. However, there is a lack of information about the gamma radiation induced effects and modification of polymer nanocomposites after their low dose irradiation.

Thermo-oxidative stability data has often been used to assess shelf life of polymers used in medicine and pharmacy [25,26]. TGA and DTA are two of the most widely used methods for studying thermo-oxidative stability of polymers. Thermo-oxidative stability is stability against degradation upon exposure to elevated temperatures in an oxidizing environment. Air, which contains oxygen molecules, is a typical example of an oxidizing environment [27]. The oxidative degradation of polymers involves free-radical chain reactions. A radical chain reaction results from a single initiation event. Degradation rates of polymers in air at temperatures below 150 °C depend on the reactivity of the peroxy radicals formed. Oxidative degradation of polymers typically follows a free-radical mechanism involving cross-linking and/or chain scission initiated by free radicals from peroxides (ROO∗) formed during the initial oxidation step. This high reactivity radical will promote the propagation of thermal degradation reaction [24].

The goal of this work was to examine the effect of low γ-irradiation on hydrolytic stability and thermo-oxidative behavior of synthesized nano-silica and wood flour modified UF resins. The hydrolytic stability of modified UF resins before and after irradiation was determined by measuring the mass loss and liberated formaldehyde concentration of modified UF resins after acid hydrolysis. The thermo-oxidative behavior of two types of nano-silica modified UF resins (original and irradiated) was investigated using non-isothermal thermo-gravimetric analysis (TG), differential thermo-gravimetry (DTG) and differential thermal analysis (DTA) supported by data from IR spectroscopy.

2. Experimental

2.1. Materials

The following materials were employed in the study reported here: Urea $(NH_2)_2CO$ (Alkaloid–Skopje, FYR of Macedonia); 35% Formaldehyde CH_2O (Unis-Goražde, Bosnia and Herzegovina); Nanoparticles of SiO_2, a product of Degussa Co., Germany, were used as nano-filler for this work. The average diameter, density and specific surface of the silica nanoparticles were 12 nm, 0.37 g/cm^3 and 200 ± 25 m^2/g, respectively, and wood flour (WF) (*Pinus silvestris* L.) as filler with particle size 250–300 mm supplied by Tigar corporation (Serbia). All the other materials and solvents used for analytical methods were of analytical grade.

2.2. Synthesis of modified UF resins

Five samples of modified urea–formaldehyde (UF) resins with formaldehyde to urea (F/U) ratio (0.8) with different loading of filler were synthesized using the same procedure. Synthesis procedure was as follows: 60 cm^3 of distilled water and 0.1 mol of urea are mixed into reaction vessel with magnetic stirrer. Other components, such as different type of fillers (7.25 g SiO_2, 3.625 g SiO_2: 3.625 g WF and 7.25 g WF for composites marked as UF/SiO_2, UF/SiO_2/WF and UF/WF, respectively), 0.12 mol 35% formaldehyde and 0.6 cm^3 of concentrated sulfuric acid were added into the reaction mixture according to following order. The pH value is lowest of 6. Reaction mixture is mixed for 3 h. 0.22 mol of sodium hydroxide dissolved in 6 cm^3 of distilled water and added to reaction mixture before the stirring was done. The modified UF resins were cured at 110 °C for 2 h in a convective drying oven.

2.3. Determination of pH

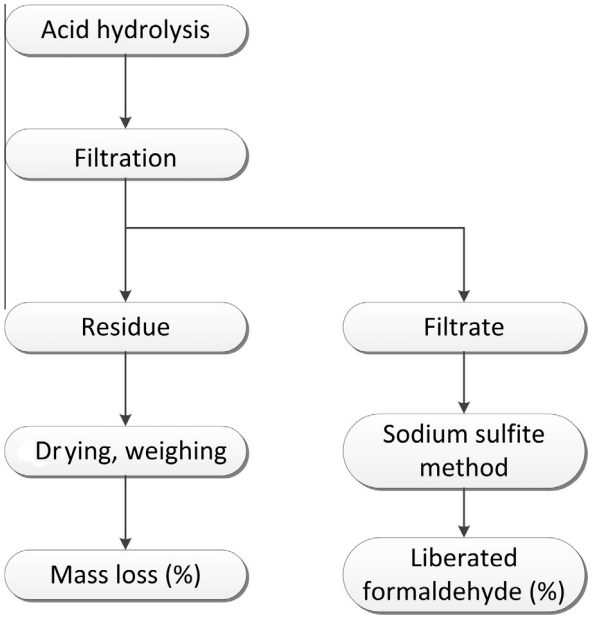
The modified UF resins were ground into particles and 2 g of each resin was topped with 10 ml of distilled water and mixed. After 48 h, the mixture was stirred and the pH was measured by pH meter. The same procedure was used for irradiated UF resin samples.

2.4. Determination of free formaldehyde

The percentage of free formaldehyde (FA) was determined by the sulfite method [28]. 0.5 g of the grounded resin was mixed with 25 ml of distilled water. After adding 4–5 drops of thymolphthalein, mixture was carefully neutralized by titrating with 0.1N sodium hydroxide. Then, 15 ml of 0.5 M sodium sulfate were added to the solution. The solution was stirred for 5 min; then, the mixture was slowly titrated with 0.1 M hydrochloric acid. The results were calculated. All measurements were performed at least as duplicates. To determine the blank, the solution without resin was determined according the same procedure and result was taking account in calculations.

2.5. Resins hydrolysis

The modified UF resins were ground into particles and prepared by adding 0.5 g of the each resin into 250 ml beaker and 50 ml of 0.1 M HCl. Then, the mixture was hydrolyzed by continuously and vigorously stirring with a magnetic bar, at 50 °C for 90 min (two replications for each sample). To determine the blank, 0.5 g of the same sample were extracted in 250 ml water for 90 min at room temperature. Scheme 1 shows the flow diagram of the hydrolysis and further analysis.



Scheme 1. Schematic diagram of hydrolysis procedures to determine the mass loss and liberated formaldehyde concentration of modified UF resins.