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Effect of γ-irradiation on the thermo-oxidative behavior of nano-silica based urea–formaldehyde hybrid composite with 4-chloro-3-nitro-2*H*-chromen-2-one

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ABSTRACT

Two types of nano-silica based urea–formaldehyde (UF) hybrid composite materials with formaldehyde to urea (F/U) ratio (0.8) were synthesized without (UF + SiO_2) and with coumarin (UF + SiO_2 + 4-chloro-3-nitro-2*H*-chromen-2-one). Nano-silica based UF hybrid composites have been irradiated (50 kGy) and effect of γ-irradiation was evaluated on the basis of thermo-oxidative behavior before and after irradiation. The thermo-oxidative behavior of materials 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 temperature values for selected mass loss to a higher temperature indicates that thermo-oxidative stability of modified nano-silica based UF resin with coumarin 4-chloro-3-nitro-2*H*-chromen-2-one is increase.

1. Introduction

Urea–formaldehyde (UF) resins are the most important type of the so-called amino plastic resins. Amino resins are often used to modify properties of other materials. These resins are added during the processing of products, such as textile fabrics to impart permanent press characteristics; automobile tires to improve the bonding of rubber to the tire cord; paper to improve its tear strength, especially of wet paper; and alkyds and acrylics to improve their curing properties. Amino resins are also used for molding products, such as electrical devices, jar caps, buttons and dinnerware, and in the production of countertops. As a typical amino resin, UF resin adhesive possesses some advantages, such as fast curing, good performance in the panel, water solubility, and lower price [1].

Coumarins, or benzo-α-pyrones, are a very large and important family of compounds. A lot of coumarins have been identified from natural sources, especially green plants. Their defining structure consists of fused pyrone and benzene rings, with the pyrone carbonyl group at position 2; this structure is illustrated in Scheme 1 for the coumarin parent molecule (IUPAC name: 2*H*-chromen-2-one, and also known as 1-benzopyran-2-one) [2].

The coumarins have long been recognized to possess anti-inflammatory, antioxidant, antiallergic, hepatoprotective, antithrombotic, antiviral, and anticarcinogenic activities. The hydroxycoumarins are typical phenolic compounds and, therefore, act as potent metal chelators and free radical scavengers. They are powerful chain-breaking antioxidants. The coumarins display a remarkable array of biochemical and pharmacological actions [3].

Coumarin polymers possessing antimicrobial activity have not received considerable attention in the literature. However the reported coumarin polymers possess variety of functions and appear to be interesting. Although there is large number of reports on monomeric coumarin derivatives, there are only a few reports on coumarin polymers.

Filler have a modifying effect on the properties of UF resin. But the fillers formerly used are all particles with sizes above micron grade, which have only small modifying effect. Nano-particles are presently considered to be high-potential filler materials for the improvement of mechanical and physical polymer properties. Chemical activities of nano-particles are excellent [4]. These new materials, called nano-composites or organic–inorganic hybrids, afford to combine both the advantages of the organic material as lightweight, flexibility and good moldability, and of inorganic materials such as high strength, heat-stable and chemical resistance [5,6]. While the reinforcement aspects of nano-composites are the primary area of interest, a number of other properties

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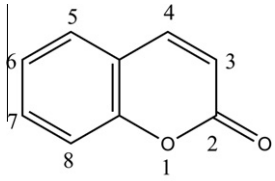


2*H*-chromen-2-one or
1-benzopyran-2-one

Scheme 1. Structure of coumarin.

and potential applications are important including flammability resistance, electrical/electronic properties, gas permeability, and thermal resistivity [7–9].

Interest in the development of new organic/inorganic nanocomposites has grown in recent years due to a wide range of potential use of these materials. These hybrids constitute a class of advanced composite materials with unusual properties, which can be used in many fields such as optics, electronics, mechanics etc. Today, attention has been focused on the nano-composites, especially those obtained from layered silicates [10,11] in thermoplastic or thermosetting matrices [12] since they demonstrated a noticeable improvement in thermal and mechanical properties with respect to micro-composites [13].

TGA and DTA are two of the most widely used methods for studying thermo-oxidative stability of polymers. Thermo-oxidative stability data has often been used to assess shelf life of polymers used in medicine and pharmacy [14,15].

High-energy radiation is a well-known technique for modification of polymers. However, little work concerning the effects of γ-irradiation on the thermo-oxidative properties of modified UF resins has been done. Radiochemical studies on cross linking or degradation of polymers are important for designing new materials.

The goal of this work was to determine the effect of γ-irradiation synthesized nano-silica based urea–formaldehyde (UF) composite materials based on their thermo-oxidative behavior. The thermo-oxidative behavior of two types of nano-silica based urea–formaldehyde (UF) composite materials (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); 4-Hydroxycoumarin (Merck, Germany) and nano-SiO_2 (Merck, Germany) with specific surface 200 ± 25 m^2/g. All the other materials and solvents used for analytical methods were of analytical grade.

2.2. Synthesis of coumarin

4-Hydroxycoumarin was nitrated using 72% HNO_3 in glacial AcOH according to a published procedure, [16] to afford 4-hydroxy-3-nitrocoumarin. The starting compound, 4-chloro-3-nitrocoumarin, was prepared from 4-hydroxy-3-nitrocoumarin following the modified method by Kaljaj et al. [17]. The preparation was carried out in the following manner: *N*,*N*-dimethylformamide (DMF, 2 cm^3) was cooled to 10 °C in an ice bath. With stirring, $POCl_3$ (4 g, 0.026 mol) was added dropwise, and the obtained mixture was stirred for an additional 15 min. Then, the ice bath was removed and the reaction was left to proceed at room temperature for a further 15 min. Finally, the solution of 4-hydroxy-3-nitrocoumarin (5.4 g; 0.026 mol) in DMF (12.5 cm^3) was added drop wise. After 15 min of stirring, the reaction was stopped by adding cold water (15 cm^3). The precipitated solid was collected by filtration and washed with saturated sodium-bicarbonate solution and water. Recrystallisation from the mixture of benzene-n-hexane (1:1 volume ratio) yielded yellow crystals of 4-chloro-3-nitro-2*H*-chromen-2-one (5.1 g; 0.0226 mol) in 87% yield, m.p. 162–163 °C. Structures of 4-chloro-3-nitro-2*H*-chromen-2-one are shown in Scheme 2.

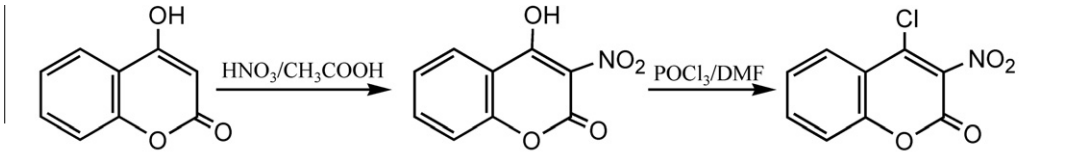
2.3. Synthesis of nano-silica based UF hybrid composites

Two types of nano-silica based urea–formaldehyde (UF) hybrid composite materials with formaldehyde to urea (F/U) ratio (0.8) were synthesized (UF with SiO_2-noticed as Resin 1, UF + SiO_2 + 4-chloro-3-nitro-2*H*-chromen-2-one-noticed as Resin 2) 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. Then, 0.015 mol of 4-chloro-3-nitro-2*H*-chromen-2-one (Resin 2) are added. Other components such as 7.25 g SiO_2, 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 resin was cured at 110 °C for 3 h in a convective drying oven. The pH value of cured resin was: 8 for Resin 1 and 4.5 for Resin 2. The content of dry solid was: 26.5% for Resin 1 (10.17 g) and 32.0% (14.11 g) for Resin 2. The content of coumarine in Resin 2 was 12%.

2.4. Techniques

2.4.1. γ-Irradiation

Irradiations of prepared samples were performed in air in the Co-60 radiation sterilization unit at the Vinca Institute of Nuclear Sciences. The Radiation Unit of the Vinca Institute has been described in more detail else where [18], the facility core is Co-60 gamma irradiator with wet storage working in batch mode (CEA, France). The samples were irradiated by gamma rays at room



4-Hydroxy-2*H*-chromen-2-one

4-Chloro-3-nitro-2*H*-chromen-2-one

4-Hydroxy-3-nitro-2*H*-chromen-2-one

Scheme 2. General reaction scheme for synthesis of coumarin (4-chloro-3-nitro-2*H*-chromen-2-one).