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RADIATION STABILITY OF HYBRID COMPOSITES BASED UREA-FORMALDEHYDE RESIN MODIFIED WITH MICRO- AND NANO-TiO₂

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ABSTRACT

The thermal stability of organic-inorganic composites prepared by a two-stage polymerization of urea-formaldehyde resin (UF) with micro- and nano-TiO₂ before and after irradiation has been investigated. Composites of urea-formaldehyde and particles of TiO₂ of different size were synthesized, namely: *Composite 1* (UF+ micro-TiO₂) and *Composite 2* (UF + nano-TiO₂). The thermal stability of obtained materials was studied by non-isothermal thermo-gravimetric analysis (TG), differential thermal gravimetry (DTG) and differential thermal analysis (DTA). Hybrid composites based on UF resin have been irradiated (50 kGy) and after that their radiation stability was evaluated on the basis of thermal behavior. DTG peaks of both composites are shifted to a higher temperature after irradiation, but *Composite 1* after irradiation shows less change in thermal behavior than *Composite 2*.

INTRODUCTION

As a typical amino resin, UF resin adhesive possesses some advantages, such as fast curing, good performance in the panel, water solubility, the non toxicity of resin and resin products, the environmental compatibility of resin bonded products and lower price [1]. High-energy radiation is a well-known technique for modification of polymers. Radiation stability-resistance is the ability of the polymer to retain irradiation despite initial chemical and physical properties, macrostructure and microstructure, i.e. to avoid crosslinking and/or degradation. However, little work concerning the effects of γ -irradiation on the thermal properties of modified UF resins has been done. The goal of this work was to determine the radiation stability of the synthesized micro- and nano-TiO₂-based urea-formaldehyde composites

based on their thermal behavior. The thermal behavior of two types TiO₂-based UF hybrid composites (unirradiated and irradiated) was investigated using non-isothermal TGA, DTG and DTA.

EXPERIMENTAL

The following materials were used in the study reported here: Urea (Alkaloid-Skopje, FYR of Macedonia); 35% formaldehyde (Unis-Goražde, Bosnia and Herzegovina); micro- and nano-TiO₂ (Sigma-Aldrich, Germany). Two types of TiO₂-based UF hybrid composites with formaldehyde-to-urea (F/U) ratio of 0.8 were synthesized using the same procedure [1]. Irradiations were performed in air in the Co-60 radiation sterilization unit with the dose rate of 10 kGy⁻¹ and the total absorbed dose of 50 kGy. The thermal stability was investigated by non-isothermal thermogravimetry (TG, DTA) using a Setaram Setsys Evolution 1750 instrument (France). Samples (6±0.2 mg) were placed in alumina crucibles. An empty alumina crucible was used as a reference. The samples were heated from 30 to 600°C in a 20 cm³/min flow of argon atmosphere with a heating rate of 10°C/min. The temperatures at maximum decomposition rate were determined from the peak maxima of the DTG curves.

RESULTS AND DISCUSSION

The thermal behavior of unirradiated and irradiated hybrid composites based on UF resins occurs in three and four main stages (Figure 1 and 2). The mass loss at different temperatures is summarized in Table 1. The rate of the thermal decomposition reaction before and after irradiation, shows more than one maximum rate with temperature is increasing. This behavior indicated that thermal decomposition of these resin passed through multiple stages, depending on the state of decomposition and not on the components [2, 3].

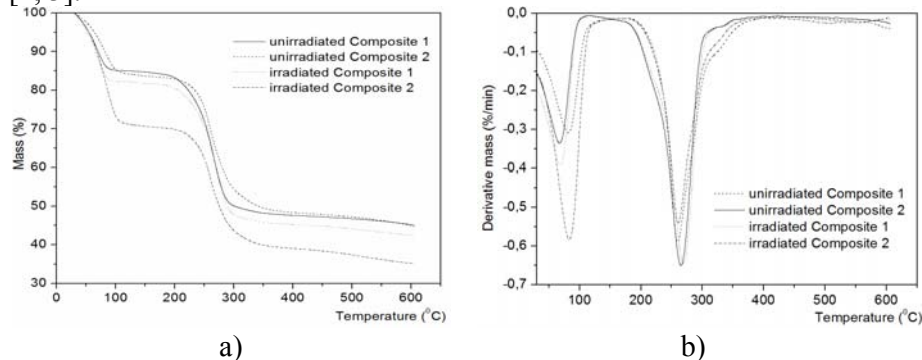


Figure 1. TGA (a) and DTG (b) curves of unirradiated and irradiated hybrid composites based on UF resin.

The first-step degradation occurs in the temperature region around 30–140°C for all samples; and with a DTG peaks observed around 68–81°C and 81–84°C for unirradiated and irradiated modified UF composites, respectively, indicating water and formaldehyde evaporation.

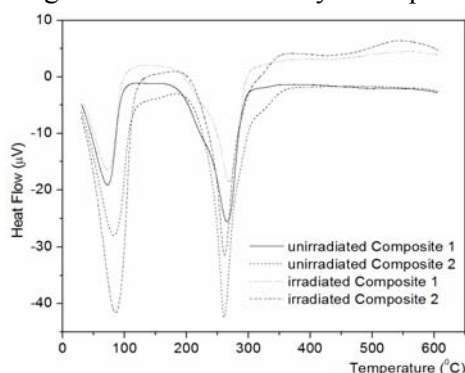


Figure 2. DTA curves of unirradiated and irradiated hybrid composites based on UF resin

Table 1. DTG, DTA data of peak values, and total mass loss for unirradiated and irradiated hybrid composites based on UF resin.

Samples	Dose of γ -irradiation (kGy)	DTG peak values (°C)	DTA Endothermic peak values (°C)	Total mass loss (%)
Composite 1	0	67.9	71.9	54.8
		218.9*	219.7*	
		265.0*	264.9*	
	50	335.8	327.7	57.6
		68.5	72.8	
		217.3*	222.4*	
Composite 2	0	269.1*	269.3*	55.2
		339.8	324.2	
		441.1	441.1	
	50	81.4	82.5	64.5
		259.5*	260.4*	
		334.4*	330.4*	
		83.8	85.2	
		260.4*	261.4*	
		331.9*	323.3*	
		507.0	456.1	

*overlapping peaks

The minimum of the endothermic peak attributed to water evaporation which comes to lower temperatures for *Composite 1* than *Composite 2*. Main mass loss happened in the second stage. In this stage degradation occurs in the temperature region around 164–395°C for all samples. In Figure 1 can be notes that the second and third degradation regions are overlapped for all hybrid composites based on UF resins. In the DTA measurements (Figure 2) the endothermic peak with minimum at 264.9, 260.5 for unirradiated UF resin composites and at 269.3, 261.4°C for irradiated UF resin composites, respectively, is attributed to the degradation of methylene ether bridges into methylene bridges and cross linking reactions in the resins network [3]. Degradation of cured resin composite begins the liberation of formaldehyde from dimethylene ether groups. This kind of destruction can be regarded as post curing of resin composite, as released formaldehyde participates in further reaction, finally giving more stable methylene group.

The *Composite 1* showed lower values for total mass loss (54.8 and 57.6%) than *Composite 2* (55.2 and 64.5%) before and after irradiation, respectively.

CONCLUSION

1. DTG peaks of both composites are shifted to a higher temperature after γ -irradiation.
2. After irradiation, *Composite 1* shows minor changes in the thermal properties compared with *Composite 2*, which indicates that the *Composite 1* has more resistant to the effect of γ irradiation than *Composite 2*.
3. The total mass loss for *Composite 1* is less than that of *Composite 2*.

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REFERENCES

- [1] S. Samaržija-Jovanović, V. Jovanović, S. Konstantinović, G. Marković, M. Marinović-Cincović, *J Therm Anal Calorim.*, 2011, 104, 1159–1166.
- [2] B. D. Park, SM. Lee, JK. Roh, *Eur. J. Wood Prod.*, 2009, 67, 121-123.
- [3] K. Siimer, T. Kaljuvee, T. Pehk, I. Lasn, *J Therm Anal Calorim.*, 2010, 99, 755–762.