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# THE INFLUENCE OF IRRADIATED WOOD FILLER ON SOME PROPERTIES OF POLYPROPYLENE - WOOD COMPOSITES

**Abstract:** The problem of compatibility between the wood filler and thermoplastic matrix is of essential importance in composite production. Numerous methods have been developed for increasing this compatibility, which is still representing a challenging objective of composite research throughout the world. The research into these methods is primarily directed towards their efficiency from the viewpoint of the composite performance and their economical acceptability. The latter is of particular importance for the composite production in the developing countries with respect to the shortage of the corresponding funds. With this respect, the utilization of ionizing radiation might have considerable advantages. In this research, the beech wood flour was irradiated by a dose of 10 *kGy* of $^{60}$Co gamma rays for purpose of provoking the changes by the ionizing effect. The effects of ionizing radiation upon the properties of wood particles have been examined by IR spectroscopy and by determination of contents of hydroxyl groups in wood by acetylation as an indirect method. All these methods have been expected to reveal the chemical effects of the applied radiation treatment. The irradiated and the control wood flour were used in order to produce the samples of composite with polypropylene. The polypropylene-wood flour (PP-WF) composites were produced with 40% of wood particles having fraction size 0.3 *mm*. The melt-blended composites were modified with amido-acrylic acid (AMACA) as a new coupling agent synthesized for this propose in amount of 6 wt.% (based on wood filler) and successively with 0.05 wt.% (based on PP) of organic peroxide during mixing step. The composites containing coupling agents showed superior mechanical properties, compared to the untreated one. The highest extent of improvement of tensile was achieved in PP-WFl composites modified with AMACA coupling agent.

**Key words:** wood plastic composites, polypropylene, wood filler, radiation (γ- rays)

## УТИЦАЈ γ-ЗРАКА НА НЕКА СВОЈСТВА ПОЛИПРОПИЛЕН - ДРВНИХ КОМПОЗИТА

**Апстракт:** Проблем компатибилности између дрвног пуниоца и термопластичне матрице је од битне важности за призводњу композита. Бројне методе су

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развијене за повећање ове компатибилности и још увек представљају изазовне циљеве у истраживању композита широм света. Истраживања која се баве овим методама су првенствено усмерене на њихову ефикасност са аспекта квалитета композита и њихове економичности. Ово задње је од практичне важности за производњу композита у развијеним земљама с обзиром на све већу несташицу расположивих фондова. У складу са тим, употреба јонизованог зрачења може имати значајне предности. У овом истраживању дрвно брашно букве озрачивано је гама зрацима извора $^{60}$Co дозом од 10 *kGy* у циљу модификације путем јонизујућих ефеката. Утицај јонизујућег зрачења на дрвне честице испитиван је путем IR спектроскопије и помоћу одређивања садржаја хидроксилних група у дрвету ацетиловањем као индиректне методе. Од поменутих метода је очекивано да осветле хемијске ефекте примењеног зрачења. Озрачено и контролно дрвно брашно коришћено је у циљу производње узорака композита са полипропиленом. Полипропилен - дрвно брашно (ПП-ДБ) композити су произведени са 40% дрвних честица фракције величине 0,3 *mm*. Топло-мешани композити су модификовани помоћу амидо-акрилне киселине (AMACA) као новог везујућег агенса који је синтетизован за потребе овог истраживања, а у количини од 6 мас.% (рачунато на масу дрвног брашна) уз истовремено додавање 0,05 мас.% (рачунато на масу ПП) органског пероксида у току фазе мешања. Композити који садрже везујући агенс показали су боља механичка својства у поређењу са нетретиранима. Највеће побољшање затезне чврстоће је постигнуто код ПП-ДБ композита модификованих са AMACA куплујућим агенсом.

**Кључне речи:** дрвно пластични композит, полипропилен, дрвни пунилац, γ-зрачење

## 1. INTRODUCTION

The ever-increasing shortage of high-quality wood with the resulting price increases as well as the environmental protection issues both emphasize the importance and benefits from waste wood utilization (Điporović *et al*., 1997, 2002). The composite production can be a very profitable utilization of this waste, with the recently noticed trend of combining wood particles with thermoplastic matrices. In the automotive industry, mainly in Europe, components previously made with glass fiber composites that do not require high load-bearing capabilities are now being replaced with hemp, flax and other natural fiber composites. Wood flour and rise husks are commonly used as reinforcing materials for plastic composite decking boards and railing systems in North America (80% of the approximately $3.2 billion market). The market for WPC decking is growing rapidly. Market share grew from 2% of the decking market in 1997 to 8% in 2000 (Smith, 2001), and it is expected to more than double by 2005 (Mapleston, 2001).

Low density, renewability, recyclability, low energy consumption, biodegradability, low abrasion to tools, low health risk when inhaled and low cost make this material environmentally, economically and socially friendly (Wambua *et al*., 2003). Some drawbacks of the natural fiber plastic composites are: poor compatibility with hydrophobic thermoplastic matrix, poor thermal stability above 220°*C*, hygroscopicity, low bulk density and poor dispersion with ordinary plastic matrix (Điporović *et al*., 2002).

However, in the wood particles polar and hydrophilic substances prevail, as opposed to the nonpolar and hydrophobic thermoplastic matrix as a polypropylene (PP). Therefore one of the major issues to be tackled in production of such composites is the issue of compatibility. Different modifications known to increase the compatibility of the wood particles and the thermoplastic matrix include acetylation (Điporović, 1990), grafting (Kokta et al., 1986, Điporović *et al*., 1996), plasma (Young *et al*., 1994) and radiation (Czvikovsky *et al*., 1982) treatments, etc. The methods of acetylation and plasma treatment with appropriate adjustments to conditions of our research have been already investigated (Điporović *et al*., 1996/a, 2002/a, Todorović *et al*., 1996), and it was only logical to investigate the effect of the radiation treatment. Furthermore, also applicable as the reason for this research, is the need for increased competitiveness through improved product quality.

In this research ionizing radiation was used for preliminary wood particles modification. Further, such particles were used for composite production. The effects of ionizing radiation upon the properties of wood particles were examined by IR spectroscopy, and by determining content of acetyl groups. The compatibility of irradiated wood particles and polypropylene (PP) matrix was followed by changes of mechanical properties of composites.

## 2. EXPERIMENTAL

Materials: The following materials were used for production of polypropylene - wood composites:

- POLYPROPYLENE (PP) powder, MFR.3 *g*/10 *min*; density 0.905 $g\cdot cm^{-3}$; stress at break 23 *MPa*; elongation 570%; elasticity modulus 1,180 *MPa*; IZOD impact resistance (notched) 34,6 $J\cdot m^{-1}$. Produced by HIPOL, Odzaci.
- ADDITIVES

– neutralizer, Ca stearate (HICI Chemical);

– initiator, organic peroxide TRIGONOX 7.5P (AKZO Chemie), 7.5% peroxyde carrier on PP powder;

– antioxidants: IRGANOX RA1010, IRGANOX PS802, ULTRANOX 626 (CIBA);

- COUPLING AGENT

– Amidoacrylicacid(AMACA)-3-[6-(3-carboxy-acryloylamino)-hexylcarbamoyl]-acrylic acid (bruto formula $C_{14}H_{20}N_2O_6$, density 1,259 $g\cdot cm^{-3}$, melting temperature 158°*C*), synthesized for this use;

- WOOD FILLER, dried wood flour (WFl) of beech (*Fagus moesiaca*) fraction size 0.30 *mm* (passed through 40 mesh sieve and retained on 50 mesh sieve).

**Radiation treatment**. In this research, the WFl was treated by the absorption dose of 10 *kGy* of $^{60}$Co gamma rays, for purpose of provoking the changes due to the ionizing effect. The irradiation was performed at the Institute of Nuclear Sciences "Vinca" Gamma Laboratory.

IR spectrography and Acetylation metdods were described in previous study (Điporović *et al*., 1996/a).

**Preparation of composites**. In the first step, the dry mixtures of ingredients in the following quantities were used:

- 60% PP powder stabilized with additives: 0.67% TRIGONOX 7.5P (corresponds to 0.05% pure organic peroxide) + 0.05% Ca stearate + 0.15% IRGANOX RA1010 + 0.25% IRGANOX PS802 + 0.15% ULTRANOX 626;
- 40% wood flour (irradiated WFl-γ or control WFl);
- 0% and 6% of coupling agent: AMACA calculated on the weight of wood flour.

**Conditions of test specimens preparation**. In the second step dry mixtures were melt-mixed in intensive mixer „RHEOMIX 600" under following conditions:

• Temperature . . . . . . . . 210°*C* • Time/rotation frequency . . 7 *min*/70 *rpm*.

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The samples for mechanical tests were prepared by press molding under the following conditions:

| Press molding process | Cooling process |
|---|---|
| • Temperature ......................... 230°*C* | • Temperature . . . . decreasing up to 20°*C* |
| • Time . . . . . . . . . . . heating up 4-5 *min*, press molding 3-4 *min* | • Time . . . . . . . . . . . . . . . . . . . . . . 7 *min* |
| • Specific pressure . . . . . . . . . . . 3.1 *MPa* | • Specific pressure . . . . . . . . . . . 3.1 *MPa*. |

**Mechanical tests**. Tensile properties were measured by INSTRON 4204 testing equipment according to ASTM D 638 standard method, using speed of 50 $mm \cdot min^{-1}$ for testing tensile strength and elongation, and 5 $mm \cdot min^{-1}$ for testing modulus of elasticity. The elongation testing was carried by extension-meter. Notched IZOD impact resistance was tested according to ASTM D 256 standard by ZWICK 5101 testing pendulum. Mechanical properties were presented as the statistical averages of 6-9 measurements. The coefficients of variation were for tensile strength about 7.4%, for elongation about 49%, for modulus of elasticity about 14.6% and for impact resistance (Izod - notched) about 4.9%. The high variation coefficient is the consequence of the material heterogeneity. The number of measurement does not decrease this coefficient significantly.

## 3. RESULTS AND DISCUSSION

The IR spectra for irradiated and control WF were presented in the previous study (Điporović *et al*., 1996/a). It was found that the presented spectra had similar shapes within the entire scan and that there were no new peaks appearing or the old ones disappearing, with the introduction of radiation treatment. However, it was found that a quantitative difference in the peak heights existed, indicating changes in quantitative ratio of molecular groups. It was noted that the ratio of the relative heights of peaks ascribed to hydroxyls and alcanes decreased due to radiation treatment.

The effect of irradiation is also evident in the results of applying acetylation both to the irradiated and the control samples which were presented in the previous study (Điporović *et al*., 1996/a). It was noted that the acetyl yield was reduced (about 10.1%) by the radiation treatment. Generally, wood flour irradiation to the sufficient absorbed dose value results in chemical modification of the wood tissue (most probably due to changes regarding the hydroxyl groups).

The results of mechanical properties of PP-WF composites produced with 40% nonirradiated and irradiated wood flour and by AMACA agent addition of 0-6 wt.% are presented in Figures 1-4. The AMACA agent addition of 6% wt. (based on wood filler) was chosen as optimal amount in composites in earlier study (Điporović *et al*., 2003)

From Fig. 1 it can be noticed that TS values of control composites (PP+WF) are lower than TS values of the original PP matrix. It was expected because of the incompatibility of wood flour with PP matrix, resulting in the absence of adhesion on the surface filler/matrix. By ionizing pretreatment, the hygrophobicity of the wood flour increase. At the same time its better compatibility produces a significant improvement of TS of PP+WFγ composites. Futhermore, it was noticed an obvious improvement of TS composites with 6% of AMACA addition as a coupling agent. It was achieved an improvement

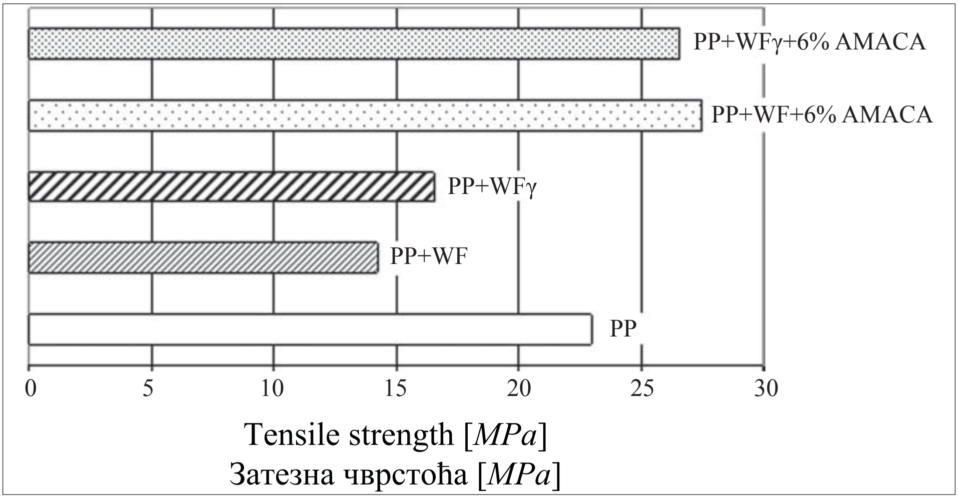


**Figure 1.** The influence of γ-rays and addition of AMACA as a coupling agent on tensile strength (TS) of PP composites filled with 40% beech wood flour

**Слика 1.** Утицај γ-зрака и додатка AMACA као везујућег агенса на затезну чврстоћу ПП композита испуњених са 40% буковог дрвног брашна of about 90%, of TS composite with noniradiated wood flour (PP+WF+6% AMACA) and about 60% of composites with irradiated wood flour (PP+WFγ+6% AMACA).These results prove that AMACA improved the adhesion between wood particles and polymer matrix. The higher values of TS of both composites, comparing to PP show that the addition of 6% AMACA agent resulted in reinforcement of the matrix, which was the aim of the research. The combination of AMACA agent and irradiated wood flour produced less improvement of TS PP composites due to chemical modification of wood tissue affected by γ-rays. The recorded reducing of hydroxyl groups of carbohydrate component and lignin cause lower reactivity of wood particles, which is necessary for achieving the adhesion in presence of any coupling agents.

However, we have to note that the irradiated wood particles, in combination with AMACA agent, significantly improve the elongation of composites (PP+WFγ+6% AMACA) (Fig. 2). This effect can be a consequence of both the achieved adhesion between filler and matrix and probably better surface wetting of wood particles which, due to irradiation, became similar to matrix polymer and in that way affected better homogenization during hot mixing in presence of AMACA agent. The elongation of other PP composites was similar.

The influence of γ-rays and addition of AMACA agent on modulus of elasticity of PP composites was not significant, which could be seen in Fig. 3. However, it was obvious that all the composites had significantly higher values of E comparing to PP, which was the aim of the research. The addition of 40% beech wood flour improved this property approximately by 144%. Similar values of E of all PP composites show that the addition of wood

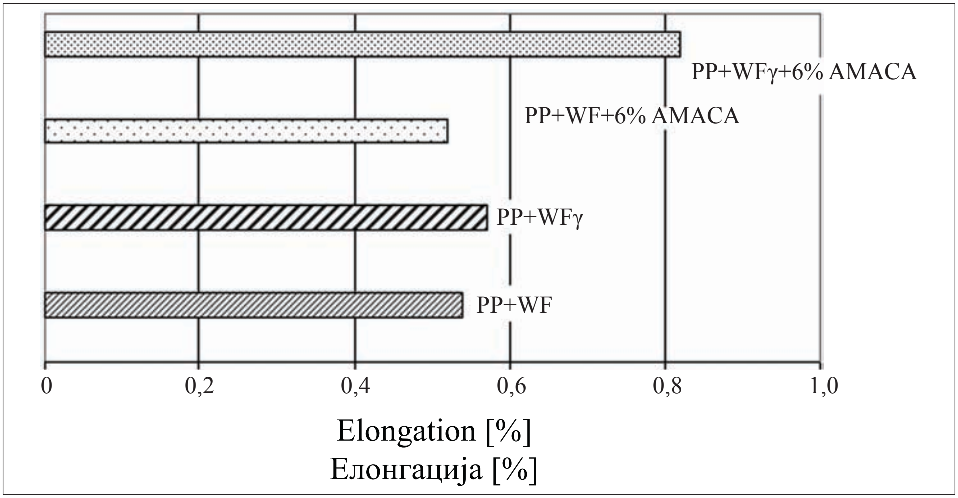


**Figure 2.** The influence of γ-rays and addition of AMACA as a coupling agent on elongation (ε) of PP composites filled with 40% beech wood flour

**Слика 2.** Утицај γ-зрака и додатка AMACA као везујућег агенса на елонгацију (ε) ПП композита испуњених са 40% буковог дрвног брашна

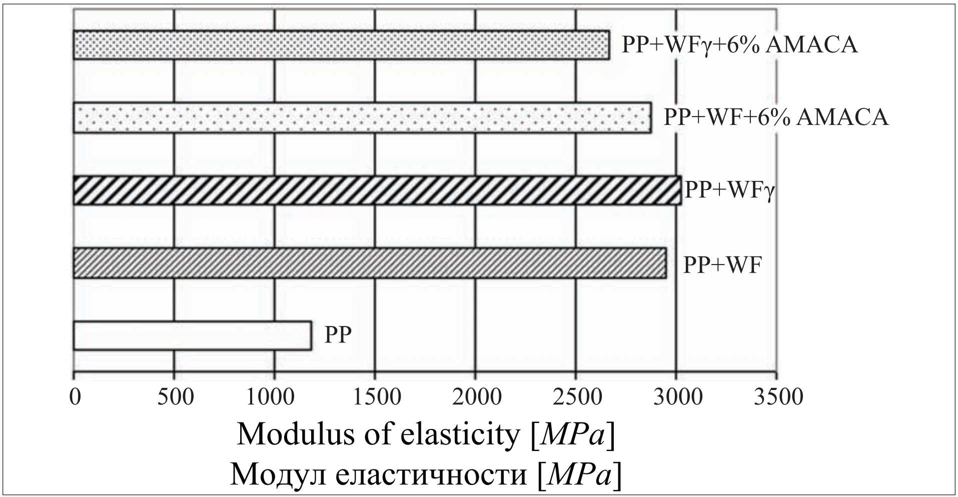


**Figure 3.** The influence of γ-rays and addition of AMACA as a coupling agent on modulus of elasticity (E) of PP composites filled with 40% beech wood flour

**Слика 3.** Утицај γ-зрака и додатка AMACA као везујућег агенса на модул еластичности ПП композита испуњених са 40% буковог дрвног брашна

filler is responsible for this property, which was proved in previous studies (Điporović *et al*., 1997, 2002).

The results of the impact resistance of PP composite illustrated in Fig. 4 show that the addition of wood flour in amount of 40% in composite improves toughness of PP composites. This effect can be a consequence of better impact resistance of wood particles as filler. The modification of wood particles by γ-rays has negative effects on this property. Therefore, the values of impact resistance of PP composite with irradiated wood flour were lower than those for composite with nonirradiated wood particles. We have to say that this effect is more emphasized in PP composites with AMACA agent (PP+WFγ+6% AMACA). These results suggest that chemical modification of wood tissue by γ-rays may leave consequence on the structure and internal bonds of carbohydrate components and lignin making the wood brittle and more breakable. The addition of AMACA agent could not neutralize the negative effect of γ-rays. Therefore, the composites with nonirradiated wood flour (PP+WF+6% AMACA) and this agent showed the best impact resistance.

## 3. CONCLUSIONS

Based on the results of the mechanical properties of PP - WF composites, it can be stated that:

1. Beech wood flour irradiated by a dose of 10 *kGy* of $^{60}Co$ γ-rays can be used for production of polypropylene (PP) composites, having improved elongation charasteristics;

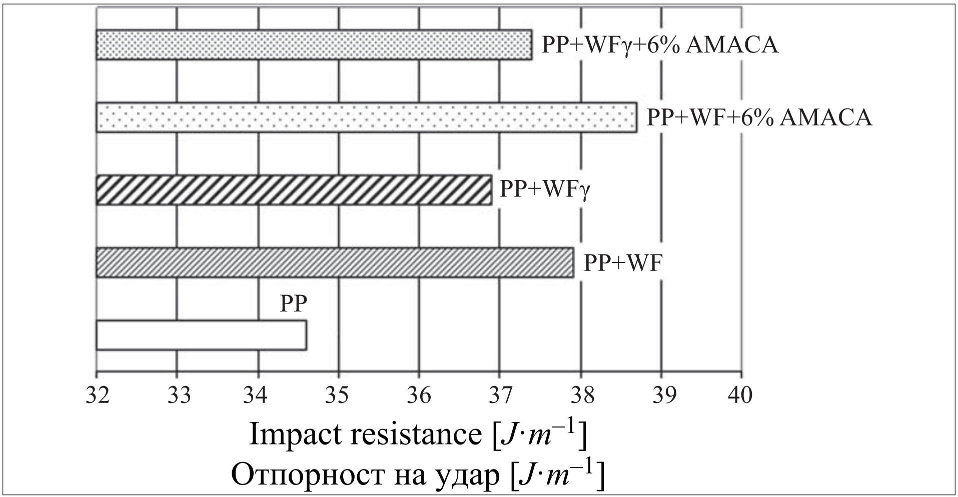


**Figure 4.** The influence of γ-rays and addition of AMACA as a coupling agent on impact resistance (Izod-notched) of PP composites filled with 40% beech wood flour

**Слика 4.** Утицај γ-зрака и додатка AMACA као везујућег агенса на отпорност на удар ПП композита испуњених са 40% буковог дрвног брашна

2. The irradiated wood particles of beech wood flour in amount of 40% in PP composites have a positive effect on tensile strength of composite without coupling agents added. This is probably due to chemical modification of wood tissue, caused by ionizing effect during the pretreatment;
3. However, irradiation of the some wood flour could not improve tensile strength of these composites having coupling agent;
4. Somehow, irradiated wood flour interfere full coupling effect of AMACA agent. Thus, interaction of irradiated wood filler with AMACA coupling agent, need further investigation.

**Напомена:** Истраживања изнета у овом раду финансирало је Министарство за науку и технологију у оквиру пројекта BTN-361005A.

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**УТИЦАЈ γ-ЗРАКА НА НЕКА СВОЈСТВА ПОЛИПРОПИЛЕН-ДРВНИХ КОМПОЗИТА**

**Резиме**

Резултати механичких својстава композита на бази дрвног брашна и полипропилена добијени у овом раду, указују да се буково брашно озрачивано гама зрацима извора $^{60}Co$ дозом од 10 *kGy* може користити за прозводњу побољшаних полипропиленских композита. Озрачене честице дрвног брашна у количини од 40% у композиту позитивно утичу на затезну чврстоћу полипропиленских композита због хемијске модификације дрвног ткива изазване јонизујућим ефектом током предтретмана зрачивања.

Додатак амидо-акрилне киселине (АМАСА), као везујућег агенса, у количини од 6 мас.% (рачунато на масу дрвног пуниоца) значајно ојачава полипропиленске композите испуњене са 40% дрвног брашна, захваљујући побољшању адхезије на контактној површини пунилац/матрица.

Озрачивањем, као предтретманом, дрвног брашно показује боље ефекте на својства полипропиленских композита када се користи самостално, јер озрачене честице због своје умањене хемијске реактивности ометају потпуни адхезивни ефекат АМАСА, као агенса спајања.