

Radiolysis of composite polypropylene/hemp fibers

Wojciech Głuszewski ^(D), Hanna Lewandowska ^(D), Rafał Malinowski ^(D), Oksana Krasinska ^(D)

Abstract. This paper presents the results of the research on the effects of ionizing radiation on the properties of a composite material consisting of polypropylene (PP) and hemp fibers (HFs). The radiolysis effects were investigated for the composites having HF contents in the amounts of 10, 20, 30, and 40% by weight, as well as for pure PP. Particular attention was paid to the protective effects the aromatic compounds contained in the HF had on the radiolysis of PP/HF composites. This phenomenon may explain the deviations that the irradiated composites displayed upon the addition of HFs and their dependency on the HF content. Both the granules and the standardized composite specimens were subjected to radiation treatment. The gas chromatography (GC) technique was employed to determine the yield of radiolytically generated hydrogen (GH₂) and absorbed oxygen (GO₂). The oxidation phenomenon was studied during irradiation, 24 h after irradiation, and after a 40-day aging period at room temperature. Changes in the melt flow rate (MFR) and the mechanical properties were also determined. It was described how the radiation treatment of the investigated composites accelerates their degradation. It was found that this effect applies to both HF and PP. It was also demonstrated that PP not only does not enhance the resistance of HF to oxidation but, on the contrary, accelerates the processes of their post-radiation degradation. It was further observed that the phenomenon of postradiation degradation can be controlled by changing the PP content in the composite, as well as the amount of aromatic compounds present in the HF. The amount of the absorbed dose allows us to control the degradation time of the PP/HF composites. This applies in particular to the chain oxidation of the PP matrix triggered by the ionizing radiation. It was also found that composites based on PP and natural fibers susceptible to radiation degradation may have significant implications for the use of easily degradable polymer materials in the environment.

Keywords: Composites • Degradation • Hemp fibers • Polypropylene • Radiolysis

Introduction

meric materials is usually to improve their thermal or mechanical properties by cross-linking their matrices. However, in some cases, cross-linking effects occur to a negligible extent, and the degradation phenomena predominate primarily. This is the case, for example, in polypropylene (PP). This polymer, in the presence of oxygen, does not undergo the process of radiation cross-linking, and the free radicals produced during this process initiate the process of chain oxidegradation [1-3]. As a result, PP rapidly reduces its functional properties [4, 5]. This undesirable phenomenon, which occurs, among others, during the sterilization of most medical devices, can be used to produce PP composites with natural fibers with accelerated decomposition time in the environment [6–9]. An example of such fibers is hemp fibers (HF) [10–12].

The purpose of radiation modification of poly-

In addition to nonradiation-resistant cellulose and hemicellulose, these fibers also contain extreme-

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W. Głuszewski[⊠], H. Lewandowska Institute of Nuclear Chemistry and Technology Dorodna 16 St., 03-195 Warsaw, Poland E-mail: w.gluszewski@ichtj.waw.pl

R. Malinowski, O. Krasinska Łukasiewicz Research Network – Institute of Engineering of Polymer Materials and Dyes, Toruń, Poland

Received: 2 October 2023 Accepted: 27 February 2024 ly radiation-resistant aromatic compounds such as lignin and cannabinoids. The presence of aromatic systems in these compounds has a significant impact on some of the effects of radiation treatment of polymeric materials that contain them. They are responsible, among other things, for the occurrence of the "protective effect" phenomenon [13–15]. In organic radiation chemistry, the protective effect of the aromatic compounds is known in relation to the aliphatic polymer matrix. Its extent depends on the form of contact between the aromatic compound and the polymer macromolecules. The effect involves absorption by the aromatic systems and the resonant scattering of part of the energy of the ionizing radiation absorbed by the polymer. The energy dissipation is made possible by the transfer of charge or energy from the ionization spur to the aromatic structure. In this work, we are limited to analyzing this phenomenon from the point of view of only mono-ionization spurs. However, it should be remembered that there are also multi-ionization spurs, which are estimated at 20% of the energy contribution, and which lead directly to the degradation of the polymer and the formation of small-molecule products. The protective phenomenon against multi--ionization spurs has already been studied by means of chromatographic analysis of low-molecular-weight products of the radiative degradation of PP (carbon monoxide and methane) [16, 17]. Hence, this particular aspect of radiolysis was not included in this work.

The PP/HF composites may play an important role in many sectors, such as the automotive, aerospace, medical, arms, and the packaging industries. The fibers increase the strength of the polymer matrix, improve the thermal stability, and stabilize the processing conditions. Products made from such composites experience lower processing shrinkage. They can be especially important for the environment. On the one hand, the use of petroleum-derived PP is reduced, and on the other hand, the presence of natural fibers makes this type of material more environmentally friendly. Moreover, after radiation treatment, such composites should degrade even faster in the environment. The use in radiation treatment of a polymeric material that includes, on the one hand, degradable PP and, on the other, HF containing highly radiation--resistant lignin and cannabinoids but also nonresistant components such as cellulose could be the basis for developing a new type of material with hitherto unknown properties and applications. By appropriate selection of both the components and the irradiation conditions, the susceptibility of this type of material to degradation can be controlled to some extent, which can have a significant impact on its degradation in the environment. This aspect has inspired the authors of this work to perform a study of the effect of ionizing radiation on the properties of such composites. In this work, the protective effect of HF on radiation--modified PP was investigated. The protective effect of lignin in the radiolysis of cellulose is also known. This study was conducted in the context of radiation preservation of paper. However, we did not find any information about HFs. In the case of the PP/HF

composite, the protective effect applies to both cellulose and the PP matrix. This was determined based on the results of the radiolytic yields determined by the gas chromatography (GC) technique, changes in melt flow rate (MFR), and some mechanical properties of the PP composites containing 10–40 wt% of HF.

Experimental materials and methods

Materials

The radiolysis studies of PP/HF composites used both pellets and HF-containing moldings: 10, 20, 30, and 40 wt%. Pure PP and HF were also investigated. PP type Moplen HP 456J with MFR of 3.4 g/10 min (2.16 kg, 230°C) and density of 0.9 g/cm³ was supplied by Basell Orlen Polyolefins (Poland). Natural HFs, at 6 mm long, were purchased from the Institute of Natural Fibers and Medicinal Plants in Poznan (Poland).

Sample preparation

PP granules and PP composites were obtained using a type BTSK 20/40D corotating twin-screw extruder (Bühler, Germany). The extrusion process was carried out at cylinder heating zone temperatures of 180–190°C and a die-head temperature of 190°C. The screw speed was maintained constant (150 rpm). Before the composite-extrusion process, the HFs were dried at 110°C for 24 h. PP and HF were dosed into the feed zone of the extruder in such a way so as to obtain PP composites with HF contents of 10, 20, 30, and 40 wt%, respectively. The extrudate was cooled in a stream of cold air and then pelletized. The obtained granules were then dried $(70^{\circ}C, 24 h)$ to get rid of the residual moisture. Part of the granule samples thus obtained was destined for fundamental testing (GC, MFR), and part of it used for obtaining standardized test shapes. Samples in the form of barrels and dumbbells were produced in accordance with PN-EN ISO 527-2:2012 using a Battenfeld Plus 35/75 screw injection-molding machine (Battenfeld GmbH, Germany). The injection-molding process was carried out at the same temperatures and screw speeds as the composite-extrusion process.

Methods

The following experimental methods were employed for the characterization of the obtained composites:

Primary samples (PP and HF) and PP/HF composites were subjected to radiation treatment using a cobalt GC 5000 gamma-ray source (dose rate: 1.8–1.7 kGy/h) (Fig. 1) and the electron beam of an Elektronika 10/10 accelerator (dose rate: 14 000 kGy/h). The irradiations were conducted in an air atmosphere.

Using the GC technique, we determined the yields of radiolabeled hydrogen (GH₂), which are proportional to the number of initially formed



Fig. 1. Laboratory gamma radiation source (a) and industrial installation with a 10 MeV, 10 kW electron accelerator (b).

macroradicals. A relatively simple analytical system with a packed column and a thermal-conductivity detector was used. The carrier gas was argon. In the same measurement, the yield of radiolytically absorbed oxygen was also analyzed, which made it possible to determine the oxidation yield of the samples in parallel (GO₂). Sample preparation for GC measurements was carried out according to the procedure detailed in the work of Głuszewski [18]. Each measurement point is the arithmetic mean of three analytical determinations. Analytical precision is determined by the accuracy of the radiation dose delivery. In the case of an electron beam (10 MeV), this value was estimated at 5%. The estimate was made on the basis of the depth dose distribution using a dosimetric PVC foil. In aging studies, nonirradiated and irradiated samples were sealed tightly in GC bottles and aged for 40 days at room temperature. After this time, the loss of oxygen in the bottles was determined. Aging tests were performed after 1 h and after 40 days on various samples. Detailed dosimetric tests showed that they were irradiated with doses of 30 kGy and 28 kGy. The MFR was measured according to the PN-EN ISO 1133:2006 standard (190°C, 2.16 kg). A capillary plastometer, type LMI 4003 (Dynisco, USA), was applied for the determination of the MFR value.

Tensile strength (σ_M), longitudinal modulus of elasticity (E_t), and elongation at break (ε_B) were evaluated according to the PN-EN ISO 527-1:2012 standard, using the extension rate of 10.0 mm/min. A tensile testing machine, type TIRAtest 27025 (TIRA Maschinenbau GmbH, Germany), was used to examine the mechanical properties under static tension.

The impact strength (a_{cN}) was evaluated according to the PN-EN ISO 179-1:2010 standard. The pendulum impact tester, type IMPats-15 (ATS FAAR, Italy), was intended for the determination of the Charpy impact strength.

Results and discussion

Taking into consideration the point of view of the protective phenomena, the results of the tests typical for radiation chemistry were compared with practical tests for mechanical properties.

Radiolysis

The radiative yield of hydrogen, the main gaseous product of the radiolysis of natural and artificial polymers, gives an estimate of the number of initially formed free radicals that initiate secondary chemical processes of oxidation, double-bond formation, or cross-linking. The study shows that this yield for PP is about twice as high as that for HPs (Fig. 2). The dependency of the hydrogen-radiation efficiency on the fiber content indicates a clear protective effect of the aromatic compounds contained in the HFs. Moreover, this effect is almost the same regardless of which type of radiation is used (EB or gamma). This is due to the fact that almost all the energy is transferred to the polymer by secondary electrons. A measure of the observed protective phenomenon is the deviation of the curves from additivity (Fig. 2). Even relatively small amounts of HFs (10%) were found to reduce the hydrogen evolution yield by 22%. This is a relatively large decrease, considering the content of aromatic compounds in HFs, which is estimated at about 6% (lignin and cannabidiol). The exponential trend of the changes in the radiative hydrogen yield as a function of the HF content in the composite clearly indicates the protective effect of HF.

Another aspect relates to the reaction of the free radicals, with oxygen being the reason for the post-radical degradation processes of polymer plastics. In the case of the studied materials (PP, HF, and PP/HF), it was found – as expected – that the HFs, as natural raw materials, undergo oxidegradation.



Fig. 2. Radiolytic hydrogen evolution yields after EB and gamma radiation (γ) irradiation.



Fig. 3. Radiolytic oxygen-uptake efficiencies during irradiation and in postirradiation phenomena after 24 h. EB, 30 kGy.



Fig. 4. Radiolytic oxygen-uptake capacities during irradiation and in postradiation aging phenomena.

However, this process is accelerated when HF is irradiated together with PP (PP/HF composite). This is due to the fact that in the composites studied, the main phase is the easily degradable PP. Therefore, the presence of PP accelerates the oxidation efficiency of the composite as a whole, which is indicated by a deviation from a linear relationship. It is also worth noting the high efficiency of postradical oxidation processes after 24 h (Fig. 3). A similar situation occurs in the analysis of the oxidation phenomenon during the aging process, where the oxidation is significantly more efficient in the presence of PP. Due to the oxidation process becoming highly efficient after a 40-day period (Fig. 4), it can be speculated that the free radicals regenerated in the chain oxidation of PP are partially transferred to cellulose or hemicellulose, which are easily degradable. This is especially likely considering that



Fig. 5. Oxygen-uptake efficiencies determined 1 h after EB and gamma irradiation. Dose of 28 kG.

cellulose and hemicellulose contain heteroatoms in their cyclic rings.

Figure 5 shows the variation of the oxidation– radiation efficiency as a function of the HF content and takes into consideration the two types of radiation used. The figure clearly shows the significant effects of irradiation time on the oxidation processes of the composites. The use of gamma radiation, which exposes the materials for longer compared to the EB radiation, results in significantly higher oxidation efficiency of the investigated composites. At a gamma radiation dose rate of 1.8 kGy/h, the oxidation efficiency is at least three times higher than for an electron beam with a dose rate of 14 000 kGy/h. Moreover, Fig. 5 clearly shows the protective effects of HF, manifested by the lack of linearity, in both gamma radiation and electron beam irradiation.

The confirmation of the protective effects of aromatic compounds in the processes of radiolysis of polymers, demonstrated by experimental results, makes it necessary to verify many previous works in which this aspect was completely disregarded. Comparison of the protective effects at the stage of the formation of macroradicals as a result of hydrogen atom detachment with the effects of reducing postradical oxidation suggests that it is the ionic phenomena (reduction in the number of macroradicals) that dominate over the secondary scavenging of free radicals.

Melt flow rate

Figure 6 shows the results of the MFR of PP and its composites before and after treatment with gamma radiation (30 kGy dose). The study shows that in the case of nonirradiated materials, an almost straightline decrease in MFR values is observed with an increase in HF content. This is a natural situation if an increasing amount of nonflow filler is added to the polymer matrix. A decrease in the value of MFR with an increase in the HF content is also observed in irradiated materials. However, in this case, the relationship is not rectilinear, but has an exponential form. In addition, all irradiated samples show higher MFR values compared to nonirradiated ones. First of all, note the very large (about 20-fold) increase in MFR values for pure PP after irradiation. Compared to the other samples, this increase is the



Fig. 6. The melt flow rate of the studied polypropylene and its composites.

largest and confirms the high susceptibility of PP to radiation degradation. As the mass fraction of HF increases, the ratio of MFR values between irradiated and nonirradiated samples decreases. This is mainly due to the observed protective effect of aromatic compounds present in hemp. Moreover, the results of MFR studies show that the protective phenomena occur mainly at the stage of ionic products of radiolysis.

Mechanical properties

The effects of the combined action of gamma radiation (with a dose of 30 kGy) and HF, including the protective effect of aromatics contained in HF, are also evident in some of the mechanical properties of the studied composites. This is most clearly seen in the change in the relative elongation at break $(\varepsilon_{\rm B})$ (Fig. 7), and thus in the strain of the modified samples. The expected observation is that the value of ε_B decreases with the increase of the proportion of HF in the tested samples regardless of whether they were irradiated or not. This is a known change due to the use of long fibers limiting the deformation of the material. A more significant change in our observations is the difference ($\Delta \epsilon_B$) occurring between nonirradiated and irradiated samples. It is greatest in the case of pure PP. On the other hand, as the HF content increases, this difference decreases, indicating the presence of a protective effect of HF.

Figure 8 shows the results of the tensile strength tests ($\sigma_{\rm M}$). In most cases, no significant changes are observed in the values of σ_M , which is mainly due to the large confidence intervals of the individual results. This refers to both pure PP as well as PP/HF composites. For the composite with the lowest HF content, a slight reduction in material strength is observed, regardless of whether that material was irradiated or not. This may be due to poor HF protection both at the extrusion stage of the composite (neutralizing free radicals formed by thermo-mechanical-oxidative degradation of PP) and after irradiation. The changes seen in Fig. 8 may also be due to other reasons, and include partial cross-linking, changes in the degree of polydispersity or the degree of crystallinity and crystallographic structure.

Irradiating composites with increasing HF content causes the difference (ΔE_t) between nonirradiated and irradiated samples to increase (Fig. 9). In the case of PP and the composite with the lowest HF content (10%), the differences are not yet significant. However, in irradiated composites containing at least 20 wt% HF, the E_t values are already higher than those for nonirradiated composites. This is partly consistent with the results of $\varepsilon_{\rm B}$, since usually a reduction in strain is associated with an increase in material stiffness. Moreover, as it follows from Fig. 9, the E_t values of the irradiated samples increase faster with the rise in the HF content compared to the nonirradiated samples. This proves that the material that contains higher amounts of HF is subjected to less radiation degradation. Thus, the protective effect of HF is visible.



Fig. 7. Elongation at break (ϵ_B) of the studied PP and its composites.

% hemp fibers



Fig. 8. Tensile strength (σ_M) of the studied samples before and after radiation treatment.



Fig. 9. Variations in the longitudinal modulus of elasticity (E_t) in the studied samples upon radiation treatment.

A slightly different situation is observed during the dynamic testing of mechanical properties. In contrast to static tensile testing, the protective effect is practically not visible in the impact test (Fig. 10).



Fig. 10. Impact strength (a_{cN}) of the studied PP and its composites.

Here, the effects of radiation degradation, especially of HF-containing composites, occur primarily. Considering that the impact strength of PP after irradiation virtually does not change, and the greatest changes occur in irradiated composites containing HF, it can be assumed that this is due to the presence of the fibers themselves in the composite. The significant weakening of the impact strength may be due either to the radiation degradation of cellulose and/ or hemicellulose or, more likely, to deterioration of the adhesion at the interface by which the transfer of dynamic impact energy from the polymer matrix to the dispersed phase is impaired. This effect is particularly visible in dynamic investigation. It should be noted that the tests were performed immediately after irradiation. It can be assumed that some of the free radicals from PP were transferred to cellulose and aromatic compounds. Such an effect was observed in chromatographic studies. This would explain the relatively small change in PP impact strength after irradiation. Despite this, PP/HF composites after radiation still show good impact strength. The same can be said for the other mechanical parameters tested. Some of them have even improved (e.g., E_t).

Conclusions

A variety of effects can be observed as a result of radiation modification of the PP/HF composites. One of them is the protective effect caused by the presence of aromatic compounds in HF. This effect is clearly visible, especially in the results of chromatographic studies. Radiative yields of hydrogen evolution and oxidation clearly show the protective effect of HF. This effect is also confirmed in the MFR studies. Although to a lesser extent, it is evident in some of the results of mechanical properties studies also. Some of the results of the mechanical properties studies also show the possibility of other processes, including degradation (of both PP and HF), cross-linking, or changes in the crystallinity of the materials studied. In general, the effects of radiolysis of systems composed of components interacting very differently with radiation are complex. Depending on the composition of the material, the amount of aromatic and alicyclic compounds it contains, its structure, irradiation conditions, and including the type of radiation source, very different radiolytic effects can be obtained. In this work, attention was mainly paid to the protective effect of aromatic compounds contained in the fibers. They affect both the postradiation degradation processes of PP and cellulose. Significant changes can be observed as soon as 10% HF is added. The use of PP susceptible to radiation degradation in composites with natural fibers may have important application significance for the use of easily degradable polymer composites in the environment. In addition, by changing the composition of the composite and the irradiation conditions, the "lifetime" of such composites can be controlled to some extent. The ability to exert such control may play a key role in environmental protection.

ORCID

- W. Głuszewski [] http://orcid.org/0000-0002-0825-5580
- O. Krasinska 💿 http://orcid.org/0000-0002-3257-8531
- H. Lewandowska D http://orcid.org/0000-0002-1960-1071
- R. Malinowski 回 http://orcid.org/0000-0001-7762-5875

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