GAMMA IRRADIATION – A METHOD OF RECYCLING POLYMERIC MATERIALS

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DOI 10.56082/annalsarscieng.2024.1.47

Rezumat. *Procesarea cu radiații a polimerilor are multe avantaje tehnice și de mediu. Poluarea scăzută și consumul redus de energie necesare procesarii cu radiatii a polimerilor, împreună cu potențialul său în reciclare, o face o tehnologie verde. Modificarea structurii polimerice a materialului plastic poate fi adusă fie prin mijloace chimice convenționale, fie prin expunerea la radiații de ionizare. În timpul procesului de iradiere se produc urmatoarele fenomene: ramificarea lanțului polimeric, reticularea, degradarea sau clivajul. Aceste fenomene coexistă și depind de mai mulți factori precum structura moleculară inițială și morfologia polimerului și mediul de iradiere i.e. doza de iradiere, debitul dozei de iradiere, prezența sau absența oxigenului. Această lucrare oferă o privire de ansamblu asupra posibilităților de reciclare a polimerilor folosind iradierea gamma.*

Abstract. *Radiation processing of polymers has many technical and environmental advantages. The low pollution and low energy consumption of radiation processing of polymers, along with its potential in polymer recycling makes it a green technology. Modification in polymeric structure of plastic material can be brought either by conventional chemical means or by exposure to ionization radiation. During the irradiation process the following phenomena occurs: chain branching, cross-linking, degradation or cleavage. These phenomena coexist and depend on several factors such as the initial molecular structure and morphology of the polymer and the irradiation environment i.e. irradiation dose, irradiation dose rate, presence or absence of oxygen. This paper provides an overview of the polymer recycling possibilities using gamma irradiation.*

Keywords: gamma radiation, recycling, polymers, degradation

1. Introduction

During the irradiation process the following phenomena occurs: chain branching, cross-linking, degradation or cleavage. These phenomena coexist and depend on several factors such as the initial molecular structure and morphology of the polymer and the irradiation environment i.e. irradiation dose, irradiation dose rate, presence or absence of oxygen. Different polymers have different responses to radiation, especially when it comes to crosslinking vs. chain scission. “G” value notation is used to quantify the chemical yield resulting from the radiation

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processing of the materials. G(x) is used for crosslinking outcomes and G(s) is used for scission outcomes. Materials with G(x):G(s) ratios above 1 are favored for crosslinking as materials with G(x):G(s) ratios below 1 tend to undergo degradation more. Materials whose G(x) and G(s) values are both low are more resistant toward radiation. Examples of radiation effect on some polymeric materials are shown in table 1 The radiation process was carried out at room temperature without the presence of oxygen, a factor that predisposes materials to crosslinking [1].

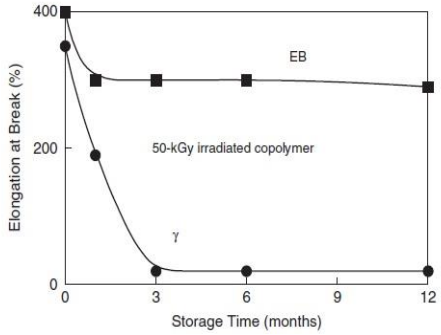
Table 5. Materials and radiation effects

No.	*Material*	*G(x)*	*G(s)*	*G(s)/G(x)*
1.	Low-density polyethylene	1.42	0.48	0.34
2.	High-density polyethylene	0.96	0.19	0.20
3.	Polytetrafluoroethylene	0.1–0.3	3.0–5.0	10
4.	Isotactic polypropylene	0.16–0.26	0.29–0.31	1.1–1.5
5.	Butyl rubber	<0.5	2.9–3.7	>6
6.	Polymethylmethacrylate	<0.50	1.1–1.7	>2
7	Polyvinylacetate	0.1–0.3	0.06	0.2
8	Nylon 6,6	0.5–0.9	0.7–2.4	1.4

It is known that when chain scission occurs the molecular weight decreases. When the radiation dose increases, the molecular weight involving G(x) and G(s) can be summarized having 3 possibilities: 1) When G(x) is much greater that G(s), the molecular weight continuously increases due to continuous crosslinking, but the molecular weight will level off because G(s) will increase faster; 2) when G(x) is greater, but not much greater than G(s), G(s) will eventually catch up with G(x), and the molecular weight will show a turning point, with the overall reaction changing from crosslinking to degradation; 3) continuous degradation will occur when G(s) is greater than G(x) [1].

2. Polypropylene

Polypropylene is prone to radiation-induced oxidative degradation when irradiated in air. Tensile elongation is the most affected property of the material. In fig. 3 it is shown the radiation processing effect of gamma radiation and electron beam radiation regarding the shelf life [2]. Gamma irradiation induces a higher degradation effect after irradiation, effect which increases after a period of 3 months when irradiated at 50 kGy [3]. Electron beam irradiation degrades less the polypropylene including the shelf life. This effect is caused by the free radicals induced by radiation processing. In fig. 1 it is shown the irradiation effect on elongation parameter. In fig. 2 it is presented the effect of the radiation dose on the tensile strength; it decreases starting from a low dose of radiation (8 kGy) [4].



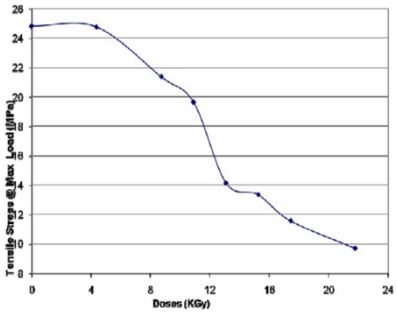


Fig. 1: Elongation at break decrease in months **Fig. 2** Tensile strengh vs radiation dose

Oxidative degradation can and it is used in order to increase the melt flow rate of the polymer. It increases with the radiation dose along with the reduction of molecular weight. A lower melt flow rate improves the processability of the material like injection molding, known as "visbreaking" [5]. Chemical visbreaking" is applied using substances that degrade the material e.g organic peroxides. This method has two major disadvantages: high cost of peroxides and hazardous or toxic residues of the decomposition products of the peroxides [1].

3. Teflon (PTFE)

PTFE is a widely used material that has great characteristics of anticorrosion, low and high temperature stability, electrical insulation, flame retardancy, and low friction surface. Regarding radiation, even its G(s) is not very high (between 3 and 5) it looses 54% of its tensile strength and 87% of its elongation if the irradiation takes place in air if irradiate at a relatively low dose of 10 kGy If irradiated in vacuum it still loses 17% of its tensile strength and 44% of its elongation [6]. In fig 3 and 4 it is shown the stres and strain behaviour for gamma irradiation in air on various doses up to 12 kGy [7]. Degradation of PTFE by radiation is used to transform it in powders. Even row PTFE powder can be irradiated because of its initial characteristics toughness, doughiness and slippery to grind, in order to be transformed into fine particles or micronized powders. The PTFE micro powders produced by radiation processing can be used in a wide range of industrial applications, including lubricants for motor oils, additives for inks and coatings and fillers for composites [1]. The radiation doses are rather high, between 500 and 1000 (kGy) but can be adjusted according to its final use [8]. The price for scrap PTFE powders can be as low as $1–4/kg, and the price for PFTE micropowders can be $8–20/kg (although it fluctuates significantly with economy), so the profit margin is high [1]. More than half (60–70%) of the total volume of the world's PTFE micropowders is processed by toll irradiation service providers using electron beam irradiators [1]. Gamma irradiation can deliver the

same results with lower doses due to oxygen involvement into the process. One problem of radiation processing of PTFE is the emission of hydrogen fluoride gas that in contact with moisture can be transformed into hydrofluoric acid which is toxic for human and corrosive for materials. This requires adaptation of irradiation facility and higher equipment costs.

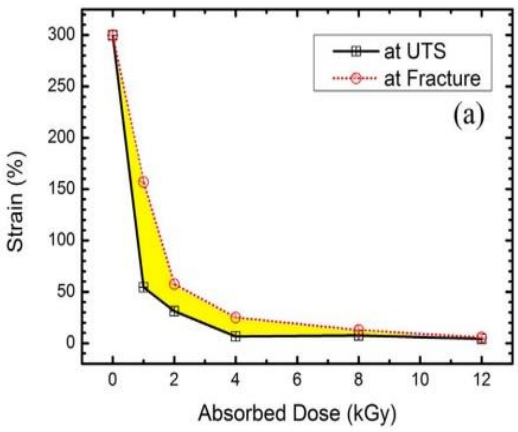


Fig. 3 Strain vs radiation dose

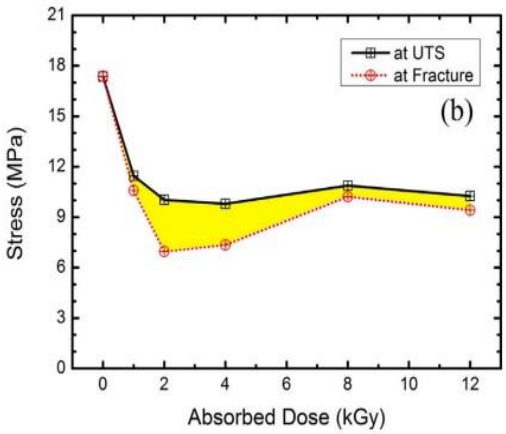


Fig. 4 Stres vs radiation dose

4. Butyl rubber (IIR)

IIR is very used in the tire industry. The G(s)/G(x) of IIR is 10–25 in air and 5.5–7.2 in nitrogen, depending on the grade of rubber and dose rate [9]. The irradiation was conducted with gamma rays. In fig. 5 it is shown the molecular weight decrease and saturation increase along with the increase in irradiation dose [10,11]. In fig 6 it is shown the decrease in tensile strengh and elongation starting fom 25 kGy [12].

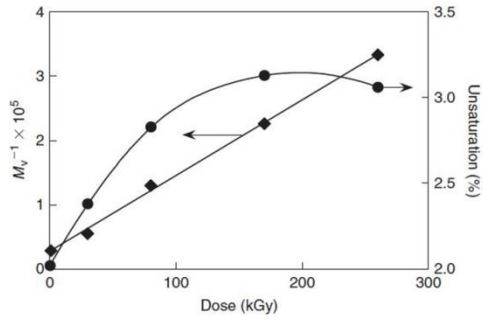


Fig. 5 Radiation effects on MW and saturation

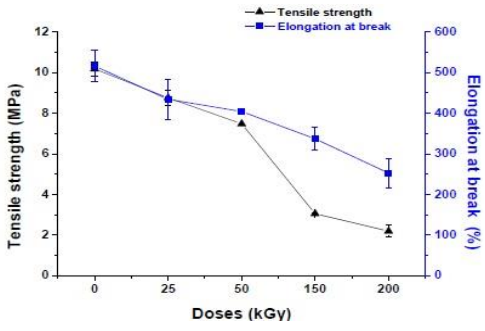


Fig 6. Dose dependent degradation

The irradiation also afects the vulcanization of the rubber which makes possible the recycling and re-utilization of material as a new one. Another advantage is that it improves the moldability of the blend [10, 11]. The recycled IIR have shorter vulcanization time, better tear resistance and better thermal stability [13]. In comparison to the traditional process it has a lower cost of production lower energy consumption and lower pollution than the conventional reclamation methods like microwaving, milling, and ultrasonic devulcanization [14].

Conclusions

Conclusion (1). Irradiation of polymers allows both the improvement of physicochemical characteristics and their degradation and recycling;

Conclusion (2). Gamma irradiation tends to degrade polymers due to low dose rates and the presence of oxygen;

Conclusion (3). Recycling of polymers can be done by incorporating them into virgin materials or into a mixture of other polymers leading to a new finished product;

Conclusion (4). Irradiation of polypropylene improves its processing properties.

Conclusion (5). The price of recycled teflon powder is very advantageous compared to virgin material;

Conclusion (6). Butyl rubber exhibits similar properties to virgin material while other properties are improved.

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