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EFFECTS OF IONIZING RADIATION ON THE MOLECULAR STRUCTURE OF POLYETHYLENE

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Abstract – This study investigates the effects of gamma irradiation (^{60}Co) at doses of 100 and 300 kGy on HDPE composites reinforced with 17 wt% glass fiber. The aim is to evaluate structural and thermal modifications induced by irradiation for potential use in high-demand industrial environments. Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), Heat Deflection Temperature (HDT), Vicat Softening Temperature, X-ray Diffraction (XRD), and Scanning Electron Microscopy (SEM) were employed to characterize changes in the material. Results showed slight decreases in melting temperature and minor changes in crystallinity. However, improvements were observed in HDT and Vicat values, indicating enhanced thermal resistance. SEM images revealed good fiber dispersion and fracture surface morphology, although signs of interfacial incompatibility were still present. These findings support the application of gamma-irradiated HDPE composites in conditions involving thermal and mechanical stress.

Keywords: *HDPE, gamma irradiation, thermal properties, SEM, crystallinity*

Introduction

High-density polyethylene (HDPE) is a semicrystalline thermoplastic polymer widely used in structural and packaging applications due to its high mechanical strength, chemical stability, and radiation resistance [1, 2]. Its morphology consists of crystalline and amorphous regions, with the proportion between these phases directly influencing the material's physical and chemical properties. The typical crystallinity degree of HDPE, ranging from 60% to 80%, contributes to its high melting temperature (125–135 °C), dimensional stability, and solvent resistance. Ionizing radiation is a well-established technique for chemically modifying polymers, applicable in sterilization, surface functionalization, or enhancement of structural performance [3]. Among the most common sources, cobalt-60 (^{60}Co) is notable for emitting high-energy gamma irradiation (~1.17 and 1.33 MeV), capable of deeply penetrating polymeric matrices [4]. This irradiation promotes the formation of free radicals, which can trigger chain scission, crosslinking, or oxidation reactions, depending on the polymer structure and the exposure atmosphere [5, 6]. For HDPE, exposure to doses between 10 kGy and 300 kGy predominantly promotes intermolecular crosslinking, enhancing thermal resistance as evidenced by increased HDT and Vicat values, despite a slight reduction in melting temperature (Tm) [7, 8]. Crystallinity may be slightly affected due to the disruption of crystalline domains and the formation of crosslinked networks [9]. The incorporation of glass fibers (typically 10% to 30%) into the HDPE matrix is an effective strategy for improving stiffness, thermal creep resistance, and mechanical stability under severe temperature and load conditions. Radiation can further enhance the interaction between matrix and reinforcement, although the absence of compatibilizers may compromise interfacial adhesion [10, 11]. Characterization techniques such as Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), Heat Deflection Temperature (HDT), and Vicat Softening

Temperature are commonly used for analyzing radiation-induced changes in polymers. Complementary techniques such as X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) provide deeper insights into structural and morphological alterations [12, 13]. This study aims to investigate the effects of gamma irradiation (^{60}Co) at doses of 100 and 300 kGy on HDPE composites containing 17% glass fiber, evaluating their thermal stability, molecular structure, and morphological behavior after processing, targeting applications in demanding industrial environments such as leather degreasing processes.

Experimental

Materials

This study evaluated HDPE composites reinforced with 17% glass fiber under three conditions: non-irradiated, irradiated with 100 kGy and 300 kGy doses of gamma irradiation from cobalt-60 (^{60}Co). Samples were subjected to a series of thermal and structural characterization tests in accordance with standard protocols. Images of three different samples are shown in Fig 1.

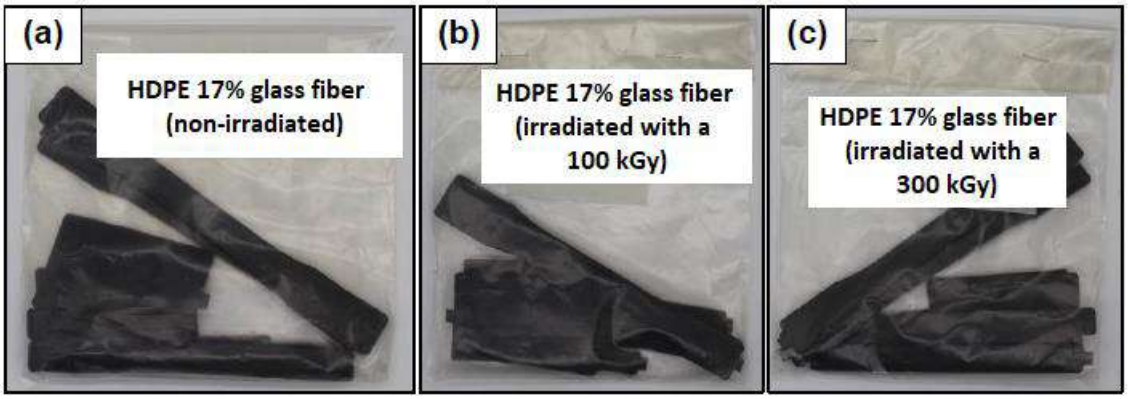

Figure 1: Sample Images - (a) HDPE 17% glass fiber, non-irradiated; (b) HDPE 17% glass fiber, irradiated with a 100 kGy dose; and (c) HDPE 17% glass fiber, irradiated with a 300 kGy dose.

The identification of the HDPE samples and their respective irradiation doses are summarized in Table 1.

Table 1 - Identification of Samples

Sample	Identification
(a)	HDPE 17% glass fiber, non-irradiated (0 kGy)
(b)	HDPE 17% glass fiber, irradiated with a 100 kGy dose
(c)	HDPE 17% glass fiber, irradiated with a 300 kGy dose

Note: Irradiation doses refer to total absorbed gamma irradiation.

Characterization methods

To assess thermal transitions, Differential Scanning Calorimetry (DSC) was performed using a PerkinElmer DSC-6000. Each sample underwent two heating cycles from 23 °C to 300 °C at a rate of 10 °C/min under a nitrogen atmosphere, with cooling steps in between. Melting temperatures (Tm) were recorded to compare the influence of irradiation. For thermal degradation behavior, Thermogravimetric Analysis (TGA) was conducted on a Shimadzu TGA-50. Samples were analyzed in nitrogen and oxygen atmospheres over the range of 25 °C to 800 °C, allowing evaluation of mass loss stages and residual content. Mechanical performance at elevated temperatures was evaluated using Heat Deflection Temperature (HDT) and Vicat Softening Temperature tests. HDT was measured under loads of 0.455 MPa and 1.82 MPa using silicone oil as the heat transfer medium, following ASTM D648. Vicat temperature was assessed using a 50 N load and a heating rate of 120 °C/h in accordance with ISO 306. Structural analysis was carried out through X-ray Diffraction (XRD) using a PANalytical Empyrean diffractometer with Cu Kα radiation. Crystallinity was quantified using peak area integration methods described by Canevarolo Jr. [13]. Morphological features were examined via Scanning Electron Microscopy (SEM) on a FEI Inspect S50. Both cryo-fractured surfaces and original sample surfaces were observed. Micrographs revealed fiber distribution, the presence of voids, and signs of interfacial incompatibility, especially in irradiated specimens.

Results and Discussion

Table 2 summarizes the main results obtained from thermal and structural analyses performed on HDPE composites reinforced with 17% glass fiber, under three conditions: non-irradiated (0 kGy), and irradiated with a 100 kGy and 300 kGy doses of gamma irradiation.

Table 2 – Summary of thermal and structural test results

Property	Method	Unit	0 kGy	100 kGy	300 kGy
Melting temperature (Tm)	DSC	°C	130.10	128.63	127.93
Crystallinity	XRD	%	54	55	54
Residue at 800 °C	TGA	%	17.17	17.84	17.95
HDT (0.455 MPa)	ASTM D648	°C	84.40	86.65	89.20
HDT (1.82 MPa)	ASTM D648	°C	51.95	54.65	56.20
Vicat Softening Temperature	ISO 306	°C	72.97	75.77	78.63

Note: All analyses were conducted under standardized conditions.

The data show that gamma irradiation induced relevant changes in the thermal behavior of HDPE composites. The slight decrease in melting temperature (DSC) with increasing dose (from 130.10 °C to 127.93 °C) is attributed to partial disruption of crystalline domains caused by crosslinking between molecular chains [7, 8]. However, crystallinity values measured by XRD remained nearly unchanged (54–55%), indicating that crosslinking occurred primarily in the amorphous regions [9, 14]. Thermogravimetric analysis (TGA) revealed a slight increase in residue at 800 °C as irradiation dose increased. This behavior has been previously reported and may be linked to the formation of thermally stable crosslinked structures [3, 15]. The HDT and Vicat results demonstrated consistent improvements in thermal resistance. The HDT reached 89.2 °C and the Vicat softening point increased to 78.63 °C at 300 kGy, indicating restricted molecular mobility due to crosslinking, consistent with increased matrix rigidity [6, 10, 16]. Scanning Electron Microscopy (SEM) images showed good fiber dispersion and brittle fracture patterns with random fiber

orientation. Interfacial voids and signs of microfibrillation were observed in the irradiated samples, suggesting internal stresses and limited matrix–fiber interaction, possibly worsened by the absence of compatibilizing agents [11, 13, 17]. Overall, the results confirm the potential of gamma irradiation as a structural modification tool that enhances thermal performance without significantly affecting the crystalline structure of the material.

Conclusions

Gamma irradiation at doses of 100 and 300 kGy led to significant improvements in the thermal properties of HDPE composites reinforced with 17% glass fiber. Increases in HDT and Vicat temperatures indicate the formation of stable crosslinked networks, despite minimal changes in crystallinity. Thermal stability was also enhanced, as evidenced by the slight increase in residual mass at high temperatures (TGA). SEM analysis showed adequate fiber distribution but also revealed interfacial limitations, highlighting the need for compatibilization strategies. The findings demonstrate the potential of gamma irradiation for enhancing the performance of HDPE-based composites in thermally demanding industrial environments.

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