Electron beam irradiation method to change polypropylene application: Rheology and thermo-mechanical properties

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Received: 13 July 2018, Accepted: 9 September 2018

ABSTRACT

Irradiation of polymers is one of the most effective and economical methods for modifying their properties and for changing their applications. In this study, an extrusion grade polypropylene (PP) was treated by electron beam irradiation to produce a PP suitable for injection molding. Irradiation was carried out at different doses (0-80 kGy) under atmosphere air and at ambient temperature. Melt flow index (MFI) measurements showed PP samples irradiated in the range of 10 to 40 kGy are suitable to use in injection molding. Electron beam irradiation decreased the viscosity and the shear thinning rheological behavior of PP. The differential scanning calorimetry (DSC) analysis revealed that electron beam irradiation increased the crystallinity percentage and temperature of PP, but decreased the melting temperature. Among all treated samples, the PP20, irradiated at the dose of 20 kGy, showed the highest impact resistance. It had higher Young’s modulus and tensile strength, but lower elongation-at-break in comparison with untreated PP. Polyolefins J (2019) 6: 53-61

Keywords: Polypropylene; electron beam irradiation; rheological properties; mechanical properties; thermal properties.

INTRODUCTION

In recent decades, irradiation of polymer materials, especially polyolefins, using ionizing beams, such as electron and gamma, with the different objectives consisting of crosslinking [1, 2], recycling [3-5] and modifying [5, 6] have attracted considerable attention from both scientific and industrial points of view.

Like other polyolefins, PP as a commodity polymer has a wide variety of grades different in the architecture and the molecular characteristics, and therefore, the physico-mechanical properties and application. However, serious efforts have continued for obtaining new grades of PP with desired properties and processing ability. Since the polymerization is known as a costly and complex method to produce the new grades of polymers, the modification of PP after polymerization and prior converting the product has been more interested in this area. For this purpose, the use of chemical agents, such as peroxides, through the reactive extru-
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Effects of electron beam and gamma irradiation on the rheological and crystallization properties of PP under different atmospheres of acetylene, hydrogen and nitrogen [12]. They reported that degradation was the major reaction in the initial step of irradiation no matter the atmosphere. But, the long chain branching (LCB) and crosslinking increased with time, due to the double bond formation in PP chain structure. The capability of PP crystallization increased after irradiation process and it was found that the melt strength of irradiated PP could increase because of the LCB formation. Auhl et al. investigated profoundly the electron beam irradiation influence under nitrogen atmosphere on PP structure using the shear and elongation rheological measurements [13]. They found that with increasing the irradiation dose, first, a reduction of molar mass takes place and, then, an increase in the number of LCBs occurs. From the rheological results interpenetration based on the zero-shear viscosity and the strain hardening elongation rheological behavior it was revealed that the length of LCBs becomes shorter at higher irradiation doses and the architecture changes from starlike to treelike branches at higher irradiation doses. Krause et al. modified isotactic PP using electron beam irradiation in nitrogen atmosphere and at different temperatures, in order to insert LCB in PP chains structure [14]. They reported that increasing irradiation temperature leads to a slight reduction in molar mass, an increment in LCB and crystallization temperature of irradiated PP. Gamma irradiation of a variety of linear homopolymer PP grades different in molecular weight and molecular weight distribution were performed under acetylene atmosphere by Yoshida et al. [1]. The results of gel fraction, and rheological and tensile mechanical properties showed that the presence of acetylene monomer promotes irradiation-induced crosslinking and branching for PP chains and these modifications are more marked for the PP grades with high melt flow index. Auhl et al. compared the effects of electron beam and gamma irradiation on molecular structure of PP [15]. According to the rheological analysis, it was found that gamma irradiation leads to higher degrees of long-chain branching and a high molecular weight tail. They reported that electron beam and gamma-irradiation effects in polypropylene do not follow the same reaction kinetics and, thus, generate different structures of long-chain branching.

Corresponding to the literature, more research works about the irradiation of PP were related to investigation of the irradiation effects on the architecture of PP chains using the melt rheological experiments and there is a little work in using the irradiation to change the grade of PP and study of its influences on the mechanical properties, especially impact resistance, of PP. Irradiation-induced change in the PP grade from extrusion to injection after blending an extrusion grade PP with elastomers having relatively high viscosity has been known as a proper method to achieve the PP/elastomer blends with a fine morphology stable during the injection molding [16-23]. Although it has been reported that electron beam irradiation under specific conditions, for example at high temperatures, overcomes some drawbacks of this technique, such as trapped radicals and post treatment reactions [18-23], applying EB irradiation treatment under ambient conditions for some objectives similar to controlled degradation of PP chains, as is the main aim of this work, is more convenient and interesting from practical point of view.

In this contribution, we aim to investigate the feasibility of change in the grade of PP from extrusion to injection via the electron beam irradiation method. For this propose, the electron beam irradiation of an extrusion grade PP is performed under ambient conditions and at different doses and the effects of irradiation are studied on the rheological and thermo-mechanical properties of PP.

EXPERIMENTAL

Materials
An extrusion grade of homopolymer PP HP550J (MFI=2.3 g/10min; 230 °C, 2.16 kg) from Jam Petrochemical Company, Iran, was used as received.

Samples preparation
Considering use of data of this research for another research work with the aim of preparing PP/elastomer...
blends irradiated after blending in a twin screw extruder (Brabender DSE, Germany), first, PP was processed by the twin screw extruder at 215 °C and was cut into granules. Then, irradiation of PP granules in air atmosphere and at a room temperature was carried out by an electron accelerator (TT200 Rhodotron at Radiation Processing Center, Yazd, Iran) at an acceleration voltage of 10 MeV and 10 mA current. Irradiation doses were 10, 20, 40 and 80 kGy and the dose per pass was 10 kGy. The average absorbed doses and the dose uniformity (the ratio of maximum adsorbed dose to minimum one within the sample palette) were measured by the cellulose triacetate (CTA) film. Irradiation doses along with the sample codes are listed in Table 1. Finally, PP granules were compression molded into sheets with 2 mm thickness in a DR Collin (25 MPa) laboratory hot press at 200 °C for 5 min under 10 MPa pressure and the sheet samples were cooled by cast under 10 MPa pressure for 2 min.

Samples characterization
Melt Flow Index (MFI)
In order to determine irradiation impact on flowability of PP, MFI of modified PP samples in granular form was measured by a MFI apparatus (Zwick 4100, Germany) at a temperature of 230 °C using a weight of 2.16 kg and according to ASTM D1238-04c.

Gel content measurement
To clarify the possibility of irradiation-induced cross-linking for PP, the gel fraction of irradiated PPs was determined by extraction of soluble components in xylene with 0.3 wt.% antioxidant (Irganox 1010) at 140 °C for 12 h. After extraction cycle, the remaining insoluble sample was dried in a vacuum oven at 150 °C to a constant weight. The gel content was calculated by Equation (1):

\[
\text{Gel content (\%) = } \frac{w_f}{w_0} \times 100
\]

where \(w_f\) is the final weight and \(w_0\) is the initial weight of the sample. Three samples were used to measure the gel content of each sample.

Rheological study
Melt linear viscoelastic rheological properties of the samples under oscillating shear flow were measured by a MCR501 rheometer equipped with parallel plate geometry (d=25 mm, gap=1 mm). Frequency sweep measurements were performed in a frequency range of 0.05-500 rad/s under nitrogen atmosphere at 190 °C and at a strain amplitude of 1 % to get the response of samples in the linear viscoelastic regime.

Differential Scanning Calorimetry (DSC)
Thermograms of the samples were determined by using a differential scanning calorimeter (Mettler TOLEDO DSC, Switzerland) in nitrogen atmosphere. A sample of about 5 mg was heated at a heating rate of 10 K/min from room temperature to 180 °C and kept for 2 min in order to remove the thermal history. Then, it was cooled at a cooling rate of 10 K/min to room temperature and finally reheated at the same heating rate to 180 °C. Equation (2) is used to calculate the crystallinity percentage of the samples:

\[
\text{Crystallinity (\%) = } \frac{\Delta H_f}{\Delta H_{f,100}}
\]

where \(\Delta H_f\) is the fusion heat obtained from the surface area under the melting curve of the sample and \(\Delta H_{f,100}\) is the one of 100 % crystalline sample. \(\Delta H_{f,100}\) of PP is 209 J/g [24].

Mechanical experiments
Tensile tests were carried out by HIW 200 and according to ASTM D638 at a crosshead speed of 50 mm/min at room temperature. For each sample, the average of 3 dumbbells was drawn. An impact device (ZWICK 5102, Germany) was used to measure Izod impact resistance of the samples. Impact tests were performed by a 1 J pendulum at room temperature and according to ASTM D256 standard. Five trials were done for each sample and the average values were reported.

RESULTS AND DISCUSSION
The most important characteristics of extrusion and injection grade PPs making them different in terms of processability are their flowability and their rheological properties. An injection grade PP has a zero-shear vis-

<table>
<thead>
<tr>
<th>Sample</th>
<th>Irradiation Dose (kGy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP&lt;sub&gt;p&lt;/sub&gt;</td>
<td>0</td>
</tr>
<tr>
<td>PP&lt;sub&gt;p1&lt;/sub&gt;</td>
<td>10</td>
</tr>
<tr>
<td>PP&lt;sub&gt;p2&lt;/sub&gt;</td>
<td>20</td>
</tr>
<tr>
<td>PP&lt;sub&gt;p3&lt;/sub&gt;</td>
<td>40</td>
</tr>
<tr>
<td>PP&lt;sub&gt;p4&lt;/sub&gt;</td>
<td>80</td>
</tr>
</tbody>
</table>
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Viscosity, and therefore, an MFI (usually between 8 and 35 g/10 min at 230 °C and 2.16 kg) significantly lower than that of an extrusion grade. The rheological differences between the various grades of PP originate from their different molecular characteristics, such as molecular weight, molecular weight distribution and molecular architecture. On the other hand, the molecular characteristics considerably influence the thermo-mechanical properties of PP being very important in its practical application. In this research with the aim of changing an extrusion grade of PP to a grade suitable for injection molding using irradiation method, firstly, the effect of electron beam irradiation on the rheological properties and, then, on the thermo-mechanical properties of the extrusion grade PP is investigated.

Gel content and rheological properties

Three reactions including crosslinking, long-chain branching and degradation could happen for PP chains during electron beam irradiation process. Since, for the PP samples irradiated at the different doses, gel content could not be measured, it was concluded that crosslinking was a neglectable reaction for them.

Figure 1 depicts MFI value against irradiation dose for the PP samples. These results indicate that irradiation increases MFI of polypropylene and the trend of its change with dose is approximately linear. The effect of irradiation on the MFI of PP is due to degradation of PP chains. The noteworthy is that the MFI values of PP samples irradiated at the doses of 10 and 20 kGy are in the range of the MFI values of commercial PPs applied for the injection process.

But, it should be mentioned that by considering the mechanical properties, especially the impact resistance, of the irradiated PP samples reported in the continuation of this work, PP, with the best performance was chosen to perform further experiments, including rheology and DSC.

Figures 2 and 3 show the linear viscoelastic shear rheological properties, complex viscosity, storage and loss moduli, as a function of frequency for PP and PP samples. Although, both the samples show a power law rheological behavior in all range of frequency, irradiation causes an attenuation of the shear thinning rheological behavior (Figure 2). Also, due to the irradiation, the slope of storage and loss modulus curves at low frequencies, known as the terminal zone, increases (Figure 3). This implies PP chains relaxation is facilitated by irradiation. These observations, besides significant reductions of complex viscosity and storage and loss moduli at all the frequencies after irradiation of PP, also confirm that degradation of PP chains is dominant phenomenon during the PP irradiation. It has been stated that the formation of long chain branches on PP chains could be also occurred by irradiation at the doses more than 1 kGy [1, 15, 25, 26]. Of course, the number of irradiation-induced LCBs on the PP chains depends on the irradiation conditions, especially the dose and the atmosphere of irradiation, as explained in introduction [13, 15, 25]. Yoshiga et al. [1] reported that LCB formation on the PP chains, as a prevailing phenomenon during the irradiation process in acetylene atmosphere, results in a decrease in MFI and an increase in viscosity at low frequencies due to the entanglements of LCB with the neighbor chains [27]; an intensification of the shear thinning rheological behavior [1] because of a decrease in the hydro-

![Figure 1](image1.png)

**Figure 1.** MFI value against irradiation dose for PP samples.

![Figure 2](image2.png)

**Figure 2.** Complex viscosity of un-irradiated PP and irradiated PP at 20 kGy.
dynamic volume of the chains with LCB [27] and a difficulty in the stress relaxation of the chains [1] because it is controlled by LCB retraction for branched polymers, rather than chain reputation [28]. These results are in contradiction with the ones obtained from rheological studies in this work, since the degradation of PP chains is dominant reaction rather than LCB formation on them during the irradiation process. On the other hand, Auhl et al. [13] applied the plot of the phase angle ($\delta = \tan^{-1}$ (Storage modulus / Loss modulus)) vs the complex shear modulus, $|G'(\omega)|$ known as Van Gurp-Palmen (vGP) plot, to detect LCB on PP chains irradiated in nitrogen atmosphere. The results showed that LCB formation on irradiated PP chains leads to a shift of $\delta$ to smaller values at relatively low values of $|G'(\omega)|$, indicating an increase of their elastic behavior, although PP chains degradation due to the irradiation was also confirmed by the viscosity and the molecular weight measurements [13]. The vGP plots for PP$_0$ and PP$_{20}$ samples are shown in Figure 4. The $\delta$ values of PP$_{20}$ are higher than those of PP$_0$ at all the values of $|G'(\omega)|$ and imply that LCB formation on irradiated PP chains is inconsiderable. In fact, in comparison to the neutral atmospheres such as nitrogen, irradiation of PP in air atmosphere could intensify irradiation-induced degradation of PP due to the presence of oxygen [10, 12].

The mechanisms of irradiation-induced degradation of PP chains in a neutral and in air atmosphere are shown in Scheme 1(a, b) [29]. However, as mentioned before, PP irradiation in air atmosphere is preferred for some objectives, like decrease in the molecular weight of PP was achieved in this research. Moreover, it should be noticed that irradiation of PP under ambient conditions is more convenient and inexpensive.

![Figure 3](image1.png)

**Figure 3.** Storage and loss moduli of un-irradiated PP and PP irradiated at 20 kGy.

![Figure 4](image2.png)

**Figure 4.** Phase angle ($\delta$) vs complex modulus for un-irradiated PP and PP irradiated at 20 kGy.

![Scheme 1](image3.png)

**Scheme 1.** Mechanisms of PP chains degradation induced by irradiation in a neutral atmosphere (a) and in air atmosphere (b) [29].
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**Thermo-mechanical studies**

The DSC heating and cooling curves obtained for PP₀ and PP₂₀ samples are presented in Figures 5. The crystallinity percentage, the crystallization and melting temperatures of the samples are given in Table 2. The amount of crystallinity for PP₂₀ is more than that of PP₀. This is in agreement with the decrease of the molecular weight of PP after irradiation, since it is easier for the PP chains with lower molecular weights to make the crystalline structure [12]. Both PP samples exhibit two melting temperatures (Figure 5), which could imply the existence of crystalline structures with different lamella sizes. On the other hand, due to the lower molecular weights of irradiated PP chains, both melting temperatures are lower for PP₂₀ compared to PP₀ (Table 2).

**Figure 6** presents the results of the impact strength of PP samples irradiated at the different doses. These results indicate a dual effect of irradiation dose on the impact resistance of PP, so that PP₂₀ and PP₈₀ samples have the highest and the lowest impact resistance, respectively. This dual effect could be related to the irradiation impacts on the structure characteristics, the molecular weight and the crystallinity of PP. According to the results of the rheological studies, the molecular weight of PP is reduced by irradiation, which could in turn lead to an increase in the PP crystallinity as evidenced by the DSC results. Both of these irradiation-induced structural changes of PP could have a negative effect on its impact strength [12]. But, the highest impact strength for PP₂₀ sample reveals that in addition to the effect of irradiation on increasing of the crystallinity which negatively influences the impact resistance of PP, another positive effect should be considered. This could be PP chains with very low molecular weights formed during the irradiation process. These chains could play the plasticizer role and facilitate the mobility of PP chains with high molecular weights and, therefore, improve the impact resistance of PP. Considering the results of impact resistance (Table 3), it would appear that the irradiation-induced positive effect, due to the formation of very low molecular weight PP chains, on the impact resistance of PP is only prevailed at the irradiation dose of 20 kGy. In the other words, the negative effects of molecular weight decreasing and crystallinity percentage increasing of PP after irradiation on its impact resistance are dominant for PP₁₀, PP₄₀ and PP₈₀.

**Figure 7** displays the tensile mechanical behavior of PP samples irradiated at the various irradiation doses. The tensile mechanical properties of these samples have been also reported in Table 3. The samples of PP₀, PP₁₀ and PP₂₀ show a ductile mechanical behavior, so that well-known mechanical performances in-

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**Table 2.** Melting ($T_{m1}$ and $T_{m2}$) and crystallization ($T_c$) temperatures, heat of fusion ($ΔH_m$) and crystallinity percentage of un-irradiated PP (PP₀) and PP irradiated at 20 kGy (PP₂₀).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{m1}$ (°C)</th>
<th>$T_{m2}$ (°C)</th>
<th>$T_c$ (°C)</th>
<th>$ΔH_m$ (J/g)</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP₀</td>
<td>166</td>
<td>148</td>
<td>110.7</td>
<td>93</td>
<td>44.5</td>
</tr>
<tr>
<td>PP₂₀</td>
<td>163.5</td>
<td>145</td>
<td>112</td>
<td>102</td>
<td>48.8</td>
</tr>
</tbody>
</table>

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**Table 3.** Tensile test results for PP samples irradiated at different doses.

<table>
<thead>
<tr>
<th>Sample</th>
<th>E(MPa)</th>
<th>$σ_y$(MPa)</th>
<th>$ε_{y50}$</th>
<th>$σ'_b$(MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP₀</td>
<td>240±2</td>
<td>28.9±0.2</td>
<td>650±10%</td>
<td>23±0.1</td>
</tr>
<tr>
<td>PP₁₀</td>
<td>253±1</td>
<td>28.7±0.3</td>
<td>635±10%</td>
<td>22.8±0.2</td>
</tr>
<tr>
<td>PP₂₀</td>
<td>256±1.3</td>
<td>28.8±0.2</td>
<td>620±15%</td>
<td>24.3±0.2</td>
</tr>
<tr>
<td>PP₄₀</td>
<td>275±2.7</td>
<td>29.5±0.3</td>
<td>15 ±3%</td>
<td>20.5±0.5</td>
</tr>
<tr>
<td>PP₈₀</td>
<td>274±3.1</td>
<td>-</td>
<td>11±1.6%</td>
<td>27±0.7</td>
</tr>
</tbody>
</table>
cluding elasticity, yield, strain softening, cold drawing and strain hardening, are observed in the stress-strain curves of the samples (Figure 7). The tensile mechanical properties, exception the modulus, of PP$_{10}$ are near to that of PP$_{0}$. But, considering the slope of the stress-strain curves in the strain hardening region, it is more for PP$_{20}$ than for PP$_{0}$. This is in agreement with the decrease in the molecular weight of PP after irradiation, as Meijer et al. have well explained that the strain hardening phenomenon is weakened for semi-crystalline polymers with increasing the molecular weight [12]. As revealed by the mechanical properties results (Table 3), it would appear that the higher ability of PP$_{20}$ to perform the strain hardening phenomenon could compensate the negative effect of its lower molecular weight on the tensile strength, so that it is even slightly higher for PP$_{20}$ in comparison to PP$_{0}$. But, irradiation-induced lower average molecular weight causes somewhat less elongation-at-break of PP$_{20}$. Due to the increased crystallinity of PP after irradiation, as evidenced by the DSC results, the Young modulus of PP$_{10}$ and PP$_{20}$ samples is higher than that of PP$_{0}$ (Table 3). On the other hand, the yield stress values of the irradiated PP samples and PP$_{0}$ are approximately equal. Considering that the yield stress of semi-crystalline polymers is affected by both the crystallinity and lamellar thickness [12], the absence of change in the yield stress of PP after irradiation could be attributed to the opposite impacts of irradiation, crystallinity increasing and lamellar thickness decreasing on PP crystallization, and therefore, on its yield stress.

But, according to the results shown in Figure 7, irradiation of PP at doses higher than 20 kGy has led to change its mechanical behavior, so that PP$_{40}$ has a semi-ductile mechanical behavior and PP$_{80}$ shows a brittle one (Figure 7). These observations are related to an intensified decrease of PP molecular weight with increasing irradiation dose.

CONCLUSION

In order to change the grade of PP from extrusion to injection, the electron beam irradiation of an extrusion grade PP was performed under ambient conditions at different doses (0-80 KGy) and the effects of irradiation on the rheological and thermo-mechanical properties of PP were investigated. According to the gel content measurements, no crosslinking reaction was confirmed for PP chains after irradiation. The MFI results showed that the increase in MFI value of polypropylene was intensified with the irradiation dose and PP samples irradiated at the doses of 10 and 20 kGy had appropriate MFI values suitable for the application in injection molding process. From the melt linear viscoelastic rheological properties, it was found that the predominant phenomenon during irradiation of PP under ambient conditions was degradation of PP chains and no evidence was observed for LCB formation in PP chains structure. The DSC results revealed that the irradiation of PP resulted in an increment in its crystallinity percentage and a reduction in its melting temperature. Depending on the irradiation dose, irradiation had a dual influence on the impact resistance of PP and the sample irradiated at the dose of 20 kGy (PP$_{20}$) showed the best impact resistance. Young’s modulus and tensile strength were higher, but elongation-at-break was lower for PP$_{20}$ sample in comparison with untreated PP. Irradiation of PP at the doses higher than 20 kGy changed its tensile mechanical behavior from ductile to semi-ductile or brittle.

REFERENCES


