RA-3

Radiation-induced graft copolymerization of vinyl monomer onto polyolefin polymeric substrate: preparation and characterization

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Abstract

In this work, the synthesis of graft copolymers containing a functional group (carboxylic group) through mutual radiation grafting method for acrylic acid monomer onto high/low density polyethylene substrate was investigated. The optimum conditions for radiation grafting were studied. In this regard, the effect of solvent type, monomer concentration, inhibitor concentration and irradiation dose on the grafting yield was determined. Some selected properties of the prepared graft copolymers were studied to illustrate the possibility of practical use in the industrial applications such as: water desalination, ion exchange, separation……etc. These properties were: water uptake, mechanical and electrical properties and the structure of the grafted membranes were investigated using Fourier transform infra-red (FTIR) analysis. The optimum conditions for mutual radiation grafting were achieved using acetone as a solvent, FeCl\(_3\) as inhibitor with concentration 0.1 \% (wt/wt), acrylic acid as monomer with concentration 30 \% (wt/wt) and irradiation dose 20 kGy.

Keywords: Gamma irradiation; Grafting; Polyolefin; Mechanical properties

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1. Introduction

Changing the properties of the polymeric materials to make it suitable for use in different applications is very important and has a large area in modern technology. There are several methods to modify polymer properties (mechanical, electrical, swelling behavior, reverse osmoses...etc.) such as: blending, grafting and curing. During recent years, the techniques of graft copolymerization and blending have acquired importance in improving the performance of materials (1-3). In this study we concentrate on the grafting technique, which could be achieved by several methods such as chemical, photochemical, enzymatic, radiation and plasma induced techniques[1].

Irradiation technology may serve as a tool, not only for grafting to improve polymers but also for reactive compatibility(5-7). The advantages of high energy application to polymeric modifications rather than the other methods are summarized as follows: i) Economically and environmentally clean technique, where there is no need to use initiators or temperature and no waste in case of post irradiation grafting. ii) It provides good distribution of the monomer on the surface of the grafted polymer [2].

Radiation grafting can be divided into two major categories according to the method of preparation: i) Simultaneous (direct or mutual) method: it is the simplest technique of radiation grafting in which the polymer backbone is irradiated in the presence of a monomer. The monomer could be used in different forms; vapor, liquid or in the bulk solution to form free radicals on both the polymer backbone and the monomer. ii) Pre-irradiation method: grafting is carried out in two steps; firstly the polymer backbone is irradiated either in vacuum or in air to form active free radicals, and then the monomer is added to the irradiated polymer [3].

Depending on the chemical structure of the monomer grafted onto a substrate, graft copolymers gain new properties such as water absorption [10], improved elasticity, hydrophilic or hydrophobic character, ion-exchange [11,12], dye adsorption capabilities [13, 24], heat resistance [15, 16], thermosensitivity [17,18], pH sensitivity [19], antibacterial effect [20], resistance to microbiological attack,….. etc. [21, 22].

In this paper, gamma irradiation and acrylic acid monomer were used to improve the properties of high and low density polyethylene membranes. In this regard, the effect of monomer and inhibitor concentrations, the type of solvent and the effect of irradiation dose, moreover mechanical, electrical, water uptake and FTIR spectracharacterization for the prepared grafted membrane were carried out.
2. Experimental

2.1 Materials

Commercial high-density polyethylene (HDPE) and low density polyethylene (LDPE) films were used throughout this work as polymeric substrates obtained from Exxon Mobil Chemical, USA. Acrylic Acid (AAc) (GC 99% purity) from Merck, Germany, was used without further purification. All other chemical reagents were of analytical grade and were used as received.

2.2 Graft copolymerization

The direct radiation grafting method was used as a mutual technique in which the films were exposed to gamma radiation in the presence of a monomer/solvent solution. Glass tubes (vol. ~25 mL) that contained the films and solution were subjected to cobalt-60 gamma radiation at a dose rate of (13.5) Gy/min. The grafting process was performed after bubbling nitrogen through the solution for (30) minutes. The grafted membranes were washed thoroughly with distilled water to remove the residual monomer, and the sticky homopolymer on the surface was extracted in water for 48 h. The membranes were dried in a vacuum oven at 50 °C for 24 h and were subsequently weighed. The grafting yield was determined as the percentage increase in the membrane weight as follows:

\[
\left(\frac{W_g - W_0}{W_0}\right) \times 100\% (1)
\]

Where

\(W_g\) and \(W_0\) represent the grafted and ungrafted film weights, respectively [23].

2.3 FTIR spectroscopic analysis

IR analysis was performed using a JASKO 4100 FTIR spectrometer over the range of 400–4000 cm\(^{-1}\) at a resolution of 4 cm\(^{-1}\). Spectra with a high signal-to-noise ratio were obtained through the collection of 100 scans for each sample.

2.4 Swelling behavior

Swelling behavior of PE membranes grafted with acrylic acid were investigated by immersing them in distilled water for (24) h, then measuring the water uptake percentage of the swollen films from the following equation:
\[
\frac{(W_S - W_g)}{(W_g)} \times 100 \tag{2}
\]

Where, \( W_S \) and \( W_g \) represents the swollen and grafted film weights, respectively.

2.5 Mechanical properties

Mechanical testing was carried out at room temperature using tensile testing machine (Mecmesin, United Kingdom) MultiTest 25-I model, at crosshead speed 50 mm / min. Samples were cut out from the sheets as dumbbell-shaped using a steel die of standard width (4 mm). A benchmark of 1.5 cm was made on the working part of each test specimen for elongation estimation.

2.6 Electrical properties

The volume resistivity was measured according to the ASTM D257 specification using the Kethey electrometer (high resistance system) Model 6517 connected with Kethey 8009 resistivity test fixture, USA.

3. Results and Discussion

3.1 Effect of solvent type

Solvent plays an important role in the radiation graft process which can be summarized as follows: i) Swelling of the substrate to be grafted. ii) Dissolving the grafting mixture. iii) Chain transfer effect that can enhance grafting or homopolymerization [4]. A set of preliminary experiments were carried out using different solvents to obtain the highest degree of grafting. Figure (1) shows that among eight different solvents (methanol, ethanol, DMF, benzene, acetone, water, methanol 70% and ethanol 70%) acetone gave the highest percentage of grafting yield for both (HDPE) and (LDPE), while using pure methanol, no grafting occurs [5]. Greater extent of swelling can enhance the rate of diffusion of monomer. The swelling efficiency of solvent is characterized by solubility parameter (\( \delta \)), which should be similar to that of polymer [25]. The (\( \delta \)) value of benzene (18.8), acetone (20.4), DMF (24.7), ethanol (25.9), methanol (29.6) and water (47.7) whereas, solubility parameter (\( \delta \)) for polyethylene is (16.3 Mpa\(^{1/2} \)). Thus, it is expected that benzene will show the best results, which is not the case according to our results that showed acetone as the best solvent.
This could be explained as follows: the solubility of the grafting mixture in benzene is not as acetone, so when starting the grafting of acrylic acid chain it prevents benzene from diffusion into the bulk (usually surface grafting) and prevents active radicals on substrate from grafting with monomer molecules. Gamma photons produce radical sites on the PE backbone, where grafting occurs, whereas homopolymerization is initiated by H* and OH* radicals formed during the radiolysis of water[26].

\[
P^* + M \rightarrow P-M \text{ graft copolymers} \quad (3)
\]

\[
OH^* + M \rightarrow M-M \text{ homopolymer} \quad (4)
\]

3.2 Effect of the inhibitor concentration

For a solvent grafting system without an inhibitor, large homopolymerization can take place from the beginning of the reaction, because AAc is one of the fastest monomers to polymerize by radiation initiation this causes a significant reduction in the monomer available for the grafting process. In addition, intensive homopolymerization leads to a high viscosity of the grafting solution, which makes the movement of the monomer to the interior of the film difficult and decreases the grafting yield [23]. For this reason, only homopolymerization was observed even at very low monomer concentrations. It has been reported that addition of certain inorganic salts such as Mohr’s salt, Cu^{2+}, Fe^{2+} and Fe^{3+} inhibits the formation of the homopolymer [27]. Figure (2) shows the effect of using anhydrous ferric chloride as inhibitor. In the range (0: 0.1) wt% increased the grafting yield (G %) increased on both high and low density polyethylene. Above (0.1) wt % FeCl₃ the (G %) decreased by increasing the inhibitor concentration. This could be due to the diffusion of ferric ions to the interior of the film backbone which inhibits the active radicals formed on its surface, thus decreases the possibility of the acrylic acid species to be grafted onto (HDPE) and (LDPE)[6].

3.3 Effect of monomer concentration

Figure (3) shows the relation between monomer concentration (AAc) wt% on the grafting yield percentage (G %). It is clear that grafting yield (G %) increased for both (HDPE) and (LDPE) as the concentration of acrylic acid (wt %) was increased. Also the rate of increase of the grafting yield percent is high from the range of monomer concentration varies between (0-30) wt %, after this the rate of increase in (G %) decreased. This could be explained as follows at lower concentration of acrylic acid (AAc) the number of free
radicals formed in the species of the monomer is low, so the opportunity of formation of homopolymer is low and the chance for grafting occurrence is high and the amount of homopolymer formed is low, so the rate of grafting yield (G%) increased rapidly. On the other hand at higher concentration of acrylic acid (AAc) greater than 30 wt % the number of active free radicals formed in (AAc) was high and the chance to combine with each other to form homopolymer was high, so viscosity of the grafting mixture increased, which make the diffusion of the monomer (AAc) towards the polymer backbone was difficult, so the rate of increase in grafting yield (G %) decreased\[4, 7\].

3.4 Effect of irradiation dose

Figure (4) shows the percentage of acrylic acid (AAc) grafted on both (HDPE) and (LDPE) as a function of irradiation dose, at dose rate (13.5 Gy/min), reaction time (24h) and monomer concentration 30 (wt %). From the figure it is clear that by increasing the irradiation dose grafting yield increased rapidly for both (HDPE) and (LDPE) until it reaches dose (20 K Gy). For irradiation doses greater than (20 K Gy), the rate of increase in (G %) is very small, that we can consider this increase is neglected\[8\]. This phenomenon can be explained as follows for irradiation doses less than (20 K Gy) the number of free radicals formed were small and distributed far apart from each other, so the branched chains of monomer didn’t overlap with each other and grows rapidly, so the rate of increase in (G %) is high. On the other hand at irradiation doses greater than (20 K Gy), the number of active free radicals formed were high and the distance between them were very small and distributed close to each other, so the branched side chains overlapped with each other and hinder the growth of the branched chains, so the rate of increase in grafting yield were very small\[4\].

3.5 Characterization of the grafted polyethylene

3.5.1 FT-IR Analysis

Membranes of ungrafted PE and grafted PE were subjected to IR analysis at room temperature in order to determine the changes in the structure of PE due to the grafting process and the chemical treatment process. The FT-IR spectra of ungrafted and grafted LDPE and HDPE with different grafting yields of AAc is shown in Figures (5,6) respectively and the assignments of these peaks are summarized in Table (1). The IR spectrum of the ungrafted PE shows an absorption band at about (2700 – 3000) cm\(^{-1}\) due to the stretching of the \(-\text{CH}\) group present in all organic compounds. The presence of grafted chains could be confirmed from the appearance of the characteristic bands at
(3300 -3500) cm\(^{-1}\) and a strong band at (1710) cm\(^{-1}\) due to hydroxyl and carbonyl groups of acrylic acid grafted chains respectively.

Table 1: Characteristic FT-IR peaks for ungraftedPE

<table>
<thead>
<tr>
<th>Wave number Cm(^{-1})</th>
<th>Intensity</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>720</td>
<td>Very strong</td>
<td>CH(_2) rocking</td>
</tr>
<tr>
<td>731</td>
<td>Very strong</td>
<td>CH(_2) rocking</td>
</tr>
<tr>
<td>888</td>
<td>Very weak</td>
<td>CH(_3) rocking, Vinlydene groups</td>
</tr>
<tr>
<td>890</td>
<td>Very weak</td>
<td>CH(_3) rocking, Terminal vinyl groups</td>
</tr>
<tr>
<td>908</td>
<td>Medium</td>
<td>CH(_3) rocking, Terminal vinyl groups</td>
</tr>
<tr>
<td>964</td>
<td>Very weak</td>
<td>Trans double bond, Terminal vinyl groups</td>
</tr>
<tr>
<td>990</td>
<td>Weak</td>
<td>CH(_2) twisting</td>
</tr>
<tr>
<td>1,050</td>
<td>Very weak</td>
<td>CH(_2) wagging, CH(_3) symmetrical bending</td>
</tr>
<tr>
<td>1,176</td>
<td>Weak-medium</td>
<td>CH(_3) symmetrical bending</td>
</tr>
<tr>
<td>1,375</td>
<td>Very weak</td>
<td>CH(_3) asymmetrical bending</td>
</tr>
<tr>
<td>1,457</td>
<td>Very weak</td>
<td>CH(_2) symmetrical stretching</td>
</tr>
<tr>
<td>1,463</td>
<td>Very strong</td>
<td>CH(_2) bending</td>
</tr>
<tr>
<td>1,473</td>
<td>Very strong</td>
<td>CH(_2) symmetrical stretching</td>
</tr>
<tr>
<td>2,850</td>
<td>Very strong</td>
<td>CH(_2) symmetrical stretching</td>
</tr>
<tr>
<td>2,857</td>
<td>Very strong</td>
<td>CH(_2) symmetrical stretching</td>
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<tr>
<td>2,874</td>
<td>Weak</td>
<td>CH(_3) symmetrical stretching</td>
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<td>2,899</td>
<td>Very strong</td>
<td>CH(_2) asymmetrical stretching</td>
</tr>
<tr>
<td>2,924</td>
<td>Very strong</td>
<td>CH(_3) asymmetrical stretching</td>
</tr>
<tr>
<td>2,960</td>
<td>Weak</td>
<td>CH(_2) asymmetrical stretching</td>
</tr>
</tbody>
</table>
3.5.2 Mechanical Properties.

Mechanical properties can be considered as the most important property of polymers for most applications. It is well known that polymers are classified into three types according to their stress-strain curves [31]. In brittle polymers such as polystyrene, the stress-strain curves are linear up to the fracture point. Tough polymers such as polyethylene exhibit a yield point followed by extensive elongation at almost constant stress (cold draw). The third type of stress-strain curve is exhibited by elastomers such as polyurethane, in which a nonlinear curve up to break point, and the elongation percentage may be of the order of several hundred percent [31].

At high (G %) for grafted polyethylene, ittends to be brittle-type polymer behavior with a linear relationship between stress and strain, whereas PE and PE-graft polymeric films with low (G %)behaved like tough polymers as shown in Figures(7,8). However, the increase of AAc grafting in the membrane increases the brittleness properties. In general, the mechanical properties of grafted membranes(at low G %) were higher than those of PE. Usually, mechanical properties are controlled by three morphological factors, the number of tie molecules, lamellar thickness and molecular chain entanglement.

The radiation grafting process would eventually cause changes in the mechanical properties of the substrate due to the added polymeric chains. The change in tensile strength and elongation percentage ofLDPE and HDPE with different grafting yields of AAc were shown in Figures. (9–11). From Figure(9), it is obvious that the tensile strength increased with the increase of the grafting degree to reach a maximum value at grafting degree around (50-70) % for LDPE and (25-40) % for HDPEand thereafter, it tends to decrease. The incorporation of grafted chains in grafted PE resulted in increasing its tensile strength and decreasing its tendency to flow (decreases its elongation).

The increase in tensile strength with decreasing of elongation could be explained on the basis that graft copolymerization would reduce the degree of crystallinity, decreases spherulitic morphology and shifts the glass transition temperature (T_g). The combined effects of these factors is to decrease elongation percentage and increase tensile strength. Moreover, at higher grafting degree, the incorporated grafted chains produce a stress between the PE chains which weaken the overall tensile strength. The mechanism of crosslinking along with grafting was due to the chain transfer to the backbone polymer as follows, forming a ketone structure which is responsible for crosslinking as shown in the following scheme: this crosslinks increases the tensile and decreases the elongation properties.
3.5.3 Swelling Behavior of Grafted membranes

From the practical point of view, the grafted membranes as well as treated films should exhibit suitable hydrophilic property. Hydrophilic properties of grafted PE films with AAc were investigated by measuring water uptake percentage of the swollen films as shown in figure (12). The figure shows that water uptake increased with increasing grafting yield and tends to level off at higher grafting degree. These results indicated that the grafting of AAc onto PE membranes enhanced the hydrophilic properties of such polymer. The relatively low water uptake content observed at higher grafting yield, compared to that at lower grafting yield, could be attributed to the steric hindrance effect caused by formation of hydrogen bonds between acidic(OH) groups. This behavior eventually impede the absorption of water molecules. The higher water uptake by grafted PE may allow better interaction with aqueous solutions [32].

3.5.4 Electrical Resistivity of grafted membranes

The electrical resistivity of the grafted PE membranes with AAc was evaluated as a function of grafting yield as shown in Figure (13). It is clear that the electrical resistivity of PE grafted copolymer decreased by increasing the grafting yield of AAc. The main factors affecting the electrical resistivity are the number of charge carriers and their mobility within the bulk of the polymer. These parameters could be related to the chemical composition and morphology of the polymer. The charge carriers may be electrons or positive holes [33]. The decrease in electrical resistivity of the grafted films could be due to the introduced polar groups (OH and C=O) with their lone pair of electron and the subsequent increase in the amorphous fraction in the polymer matrix due to grafting.
4. Conclusions

Synthesis of grafted substrate (polyolefin) can be processed using mutual irradiation method. A graft copolymer from polyolefin (high and low) with acrylic acid was prepared using gamma irradiation in a mutual method. The optimum conditions of preparation were: using acetone as a solvent; monomer concentration (30 %) wt; anhydrous FeCl$_3$ inhibitor concentration (0.1%) wt and irradiation dose (20) kGy. The chemical composition, mechanical and electrical properties of the prepared membranes is investigated. The results showed that the swelling properties were increased with increasing grafting percentage and level off at about 100%. Also, FT-IR spectra showed the characteristic bands for acrylic acid (1740, 3000-3500 Cm$^{-1}$). On the other hand, by increasing (G%) more than 80% the polyethylene changed from tough to brittle polymer.

5. References


[31] Nielsen, L. E. Landel, R. F. Stress strain behavior and strength. In Mechanical properties of polymers and composites; Marcel Dekker, New York, 1994; Chap. 5.


Fig. 1 Effect of solvent type on radiation grafting yield of AAc on to HDPE and LDPE: monomer concentration 20 %wt, irradiation dose (20KGY), inhibitor concentration 0.1 wt% FeCl₃.

Fig. 2 Effect of inhibitor concentration on radiation grafting yield of AAc on to HDPE and LDPE: monomer concentration 20 %wt, irradiation dose (20KGY) and acetone as a solvent.
Fig. 3. Effect of monomer concentration on the grafting yield (G %) of AAc onto HDPE and LDPE: inhibitor concentration 0.1 wt% FeCl₃, irradiation dose (20 KGY) and acetone as a solvent.

Fig. 4. Effect of dose on the grafting yield (G %) of AAc onto HDPE and LDPE: Inhibitor concentration 0.1 wt% FeCl₃, monomer concentration 30 wt% and acetone as a solvent.
Fig 5. IR spectra of the ungrafted HDPE and that grafted with different ratios of AAc.

Fig 6. IR spectra of the ungrafted LDPE and that grafted with different ratios of AAc.
Fig 7. Stress-Strain curves for LDPE grafted with acrylic acid at different grafting percentage.

Fig 8. Stress-Strain curves for HDPE grafted with acrylic acid at different grafting percentage.
Fig 9. Tensile strength of PE with different ratios of AAc.

Fig 10. Elongation percentage of PE with different ratios of AAc.
Fig 11. Tensile strength at 100% strain of ungrafted PE and that grafted with different ratios of AAc

Fig 12. Water uptake of ungrafted PE and that grafted with different ratios of AAc for 24 h.
Fig 13. Volume resistivity of ungrafted PE and that grafted with different ratios of AAc.