

Enhancement the Properties of High and Low-Density Polyethylene Membranes by Radiation Grafting Process

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Abstract

In this work, trials have been made to prepare different graft copolymers by direct irradiation grafting technique and evaluating their reverse osmosis properties. The acrylic acid monomer was grafted onto two improper polymers (low and high-density polyethylene) by means of gamma-ray as a motivator. The optimum conditions of preparation were using acetone as a solvent, monomer concentration 30% (wt/wt), using anhydrous ferric chloride as an inhibitor with optimum concentration 0.1% (wt/wt) and irradiation dose 20 KGy. Mechanical, rheological and thermal properties of the prepared membrane were also investigated. The prepared grafted membranes showed significant results in RO desalination method using underground saline water from Abo Swear, Ismailia, Egypt. Copyright © VBRI Press.

Keywords: Gamma irradiation, grafting polymerizations, polyolefin, mechanical, rheological and thermal properties.

Introduction

Water is the secret of life for all livings, although its abundant nature gift, the danger of lack of water attracted large consideration during the last two decade [1, 2]. Due to the growth of rapid industrialization, cultivation, and growing population, man must pay enough care to the available natural water resources. Adapted, it is needed to adopt different desalination techniques converting saline water into water suitable for human demands [1, 3].

Among the different methods of desalination, reverse osmosis method is the largest method used in the world; this is due to its great advantages compared with the other methods of desalination as it provides effective removal for all types of contaminants and consumes low energy in the desalination compared with the other methods [1, 4]. The most critical part of RO process is the membrane. Reverse osmosis membranes are, most essentially, organized by the chemical and physical properties of the membrane used in the process. Properties of the perfect RO membrane are resistance to chemical and microbial attack, mechanical stability over long operating times, and have the preferred separation characteristics for each system [5, 6].

There are several methods to modify polymer properties (mechanical, electrical, swelling behavior, reverse osmosis *etc.*) such as: blending, grafting

and curing. Recently, the irradiation grafting copolymerization has received reputation in refining the performance of polymer [7]. This technique has several advantages compared to other methods, such as; economic and environment-friendly, where there is a waste, homogeneous distribution of the monomer on the grafted polymer [8]. A graft copolymer can be denoted as shown in (Fig. 1) where A is the main polymer chain, B_n and B_m are the side chains grafts initiated from the monomer B. The extent of polymerization in B_n and B_m grafts is called the degree of grafting (grafting yield) which is gravimetrically determined as the percentage of mass increase [9].

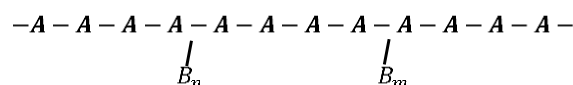
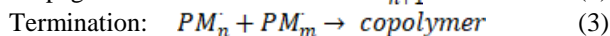
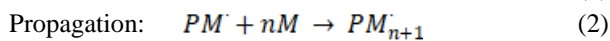
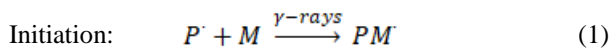


Fig. 1. Graft copolymerization process.

Both the backbone and side chain grafts can be either homopolymer or copolymer. Graft copolymerization happens due to the creation of active sites (free radicals or ionic chemical groups) on the polymer matrix. These active sites could initiate the chemical polymerization reaction [10]. The creation of active sites on the polymer matrix can be performed by numerous methods such as plasma treatment [11], ultraviolet (UV) light irradiation [12], decomposition of chemical initiator [13] and high energy irradiation [14].

Of all, high energy radiation-induced graft copolymerization method is preferred for membrane preparation because it presents bulk modification for polymer films [15]. However, the other methods such as; UV or plasma-induced graft copolymerization produces only a surface change in polymers [10]. The reaction mechanism of radiation-induced graft copolymerization comprises of three main steps that could be demonstrated by the subsequent chemical equations [16]:



where, P^{\bullet} the primary radical, M is the monomer unit and PM^{\bullet} is the initial chain, PM_n^{\bullet} and PM_m^{\bullet} are the graft growing chains. Any factor that affects one or more of the earlier steps causes a change in the degree of grafting. However, attention is essentially given to the first step where high energy irradiation is often considered as an alternative to other initiation methods [16]. Grafted copolymers could acquire new characteristics reliant on the chemical structure of the used monomer, such as water sorption [17], enhanced elasticity, hydrophobic/ hydrophilic character, ion-exchange [18, 19], dye adsorption capabilities [20, 21], heat resistance [22, 23], thermos-sensitivity [24, 25], pH sensitivity [26], antibacterial effect [27], endurance to microbiological raid... *etc.* [28, 29].

In this work, the synthesise 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. The effect of monomer and inhibitor concentrations, the type of solvent and the effect of irradiation dose. Moreover mechanical, rheological, thermal and FTIR spectra characterization for the prepared grafted membrane were carried out. Finally, the performance of the prepared grafted membranes for both HDPE and LDPE in small-scale RO desalination unit were studied using underground saline water from Abo Swear, Ismailia governorate, Egypt.

Experimental

Materials

Low/high-density polyethylene films were manipulated as polymeric substrates got from El Nasr Comp., Egypt. Acrylic Acid (AAc) (99 % purity) from Merck, Germany, and Ferric chloride anhydrous were used without further purification.

Graft copolymerization

High and low-density polyethylene sheets (20 × 20) cm² were washed with acetone and dried in vacuum oven at 50 °C. The sheets were weighed and immersed in monomer solution (AAc + solvent + anhydrous ferric

chloride). The mutual irradiation grafting method was used as a technique in which the films were subjected to gamma irradiation in the existence of a monomer/solvent solution. Glass tubes (vol. ~25 ml) that confined the films and solution were exposed to cobalt-60 gamma irradiation at a dose rate of 13.5 Gy/min. The grafting process was achieved after aerated nitrogen across the solution for (30 – 45) min. The grafted films were washed with distilled water to eliminate the residual monomer, and the adhesive homopolymer on the surface was extracted in water for 48 h. The grafted films were then dehydrated in a vacuum oven at 60 °C for 24 hours and were afterward weighed. The grafting yield was determined as a percent increase in the film weight as follows:

$$[(W_g - W_o) / (W_o)] \times 100 \quad (4)$$

where, W_g and W_o represent the grafted and un-grafted film weights, respectively. Factors affecting the preparation conditions such as the effect of solvent type, monomer concentration, inhibitor concentration and dose-effect were studied.

Swelling behavior

The clean dried grafted films of known weights were immersed in distilled water at 25 °C until equilibrium has been reached (24 hrs. in most cases). The membranes were then detached, dried between two filter papers to eliminate external water and swiftly weighed. The water uptake percentage was calculated as follows:

$$\text{Swelling percent (S \%)} = (W_s - W_g) / (W_g) \times 100 \quad (5)$$

where, W_g and W_s represent the weights of dry and wet grafted films, respectively.

Electrical measurements for the grafted membranes

The volume resistivity of the prepared samples 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 to indicate the grafting of AAc was bulk grafting and cause changes in the volume resistivity.

FTIR spectroscopic analysis

FTIR investigation was achieved by means of a JASKO 4100 FTIR spectrometer between 400 and 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 to determine the change in chemical composition due to grafting.

Mechanical properties

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

Rheological properties

The rheological test was performed for the prepared samples using a GEMINI-2 rheometer (Malvern, Bohlin Instruments, and Worcestershire, UK) with parallel-plate geometry (plate diameter 25 mm, gap 1.1 mm) to illustrate the changes in rheological properties due to grafting. Dynamic frequency sweep investigations were achieved over the frequency range of 0.01–10 rad/s at 200 °C.

Thermal Gravimetric Analysis (TGA)

Shimadzu TGA – 60, (Kyoto, Japan), was used in this study. In this test, (5–10) mg sample was weighted and heated from 35 to 750 °C with a heating rate of 10 °C/min. An inert atmosphere was maintained by the continuous flow of nitrogen at 50 ml/min.

Differential Scanning Calorimetry (DSC)

Shimadzu DSC calorimeter (Kyoto, Japan) coupled with a data station was used to examine the thermal characteristics of the grafted polyethylene (PE) membrane. The heating rate of 10 °C /min was adjusted from 25 °C to 200 °C under the nitrogen atmosphere. The weight of samples for the DSC analysis was (5–10) mg. The heat of fusion (ΔH_f) of grafted PE film was obtained from the area under the melting thermo grams.

Scanning Electron Microscopy (SEM)

The Morphology was examined using a scanning electron microscope type ZEISS Germany which consists of an electron optical column, vacuum system, and electronics. In this test, the samples cross-section was prepared by fracturing the corresponding films in liquid nitrogen. For focusing the electrons into a fine spot on the specimen cross section, three lenses (electromagnetic lenses) are used.

Reverse osmosis measurements

Fig. 2 shows the unit used in this study, it is a laboratory model DDS reverse osmoses system, model LAB-20, manufactured by Danish Sugar Corp. Ltd., Denmark. The maximum number/thickness of membranes that could be cast-off are 20 cm, the operative membrane area is 0.018 m², and the flow rate of the feed solution is 3 l / min. The salt rejection present (R_s) and water flux (J_{H_2O}) were calculated as follows:

$$R_s (\%) = (C_f - C_p) / (C_f) \times 100 \quad (6)$$

where, C_f and C_p represent the concentrations of feed and permeate water (product), respectively. J_{H_2O} is expressed in the weight of product in grams per unit membrane area in cm² and unit operation time in sec, i.e., $J_{H_2O} = \text{gm} / \text{cm}^2 \cdot \text{Sec}$. The salt concentration in water can be measured in ppm by using the TDS meter (4510 conductivity meter – Jenway, UK).

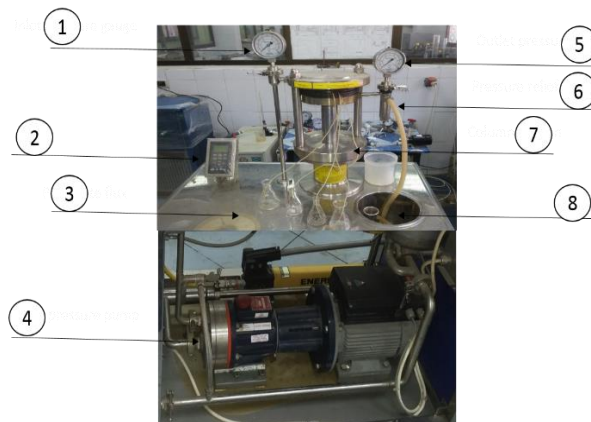


Fig. 2. DDS reverse osmoses system, model LAB-20 1- Inlet pressure gauge, 2-Operating control system, 3-Permeate flux, 4-High pressure pump, 5-Outlet pressure gauge, 6-Pressure relief valve, 7-Column section, 8-Inlet stream.

Results and discussion

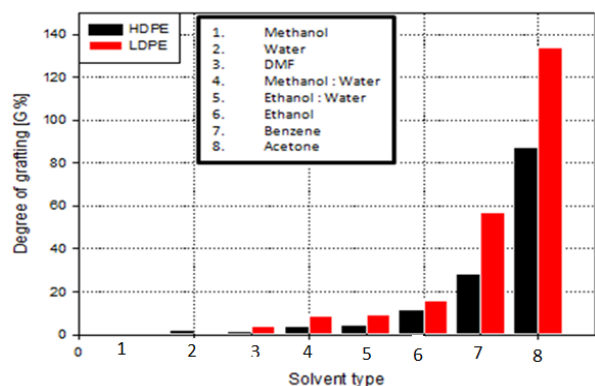
Parameters affecting on (G %) in the preparation of HDPE and LDPE

Fig. 3 shows the main different factors affecting on (G %) in the preparation of grafted HDPE and LDPE membranes. These factors are the effect of solvent type, monomer concentration, inhibitor concentration and doses.

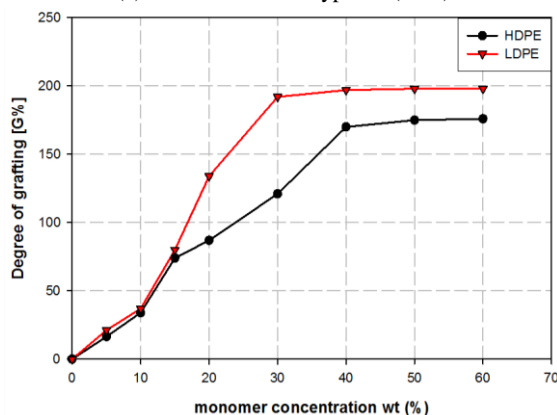
Effect of solvent type

In the irradiation graft procedure, solvents take a noteworthy influence on the swelling of the substrate to be grafted, liquifying the grafting mixture and chain transfer effect that can enhance grafting or homopolymerization [30]. In this part of the work, for obtaining the highest degree of grafting a set of preliminary experiments were conducted using a different type of solvents. **Fig. 3a** 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 high/ low-density PE. Alternatively, no grafting arises by means of pure methanol [21].

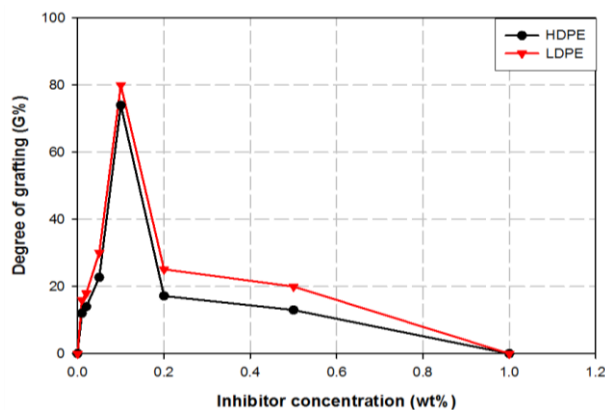
Commonly, improved degree of swelling can expand the rate of diffusion of monomer. The swelling proficiency of solvent is categorized by solubility parameter (δ), which favorable to be similar to that of the polymer [7]. The (δ) value of benzene (18.8), acetone (20.4), DMF (24.7), ethanol (25.9), methanol (29.6) and water (47.7) whereas, solubility parameter (δ) for polyethylene is (16.3 Mpa^{1/2}). Therefore, it is anticipated that benzene will display the best results, which is not the case consistent with our results that displayed acetone as the best solvent. This could be ascribed to the solubility of the grafting mixture in benzene is not as acetone. Consequently, when the grafting of acrylic acid chain start, this prevents benzene from diffusion into the bulk (surface grafting) and prevents active radicals on the substrate from grafting with monomer molecules.



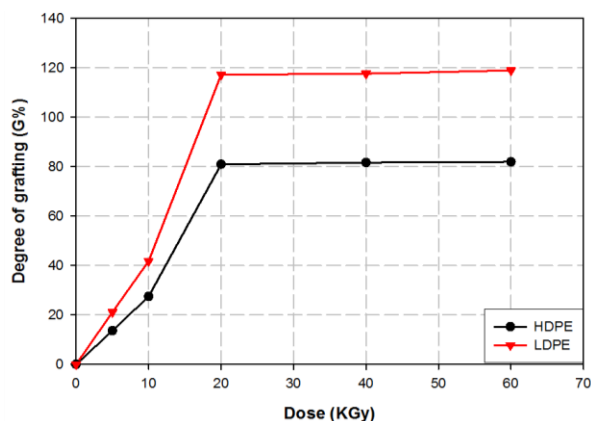
(a) Effect of solvent type on (G %)



(b) Effect of monomer concentration on (G %)



(c) Effect of inhibitor concentration on (G %)



(d) Effect of doses on (G %)

Fig. 3. Factors affecting on (G %) for membrane preparation, a) Effect of solvent type, b) Effect of monomer concentration, c) Effect of inhibitor concentration and d) Effect of doses.

Effect of the inhibitor concentration

For a solvent grafting system without an inhibitor, homo-polymerization takes place at the beginning of the reaction. Acrylic acid is one of the speediest monomers to be polymerized by radiation; this produces a considerable reduction in the monomer accessible for the grafting progression. In addition, intensive homo-polymerization leads to a high viscosity of the grafting solution, which makes an obstacle to the movement of the monomer to the interior film and decreases the degree of grafting [31]. For this reason, only homo-polymerization 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 [21]. **Fig. 3c** shows the effect of using anhydrous ferric chloride as an inhibitor. The results showed that using FeCl_3 as an inhibitor in the range (0: 0.1) wt % increases the degree of grafting (G %) of both high and low-density polyethylene. However, by increasing FeCl_3 concentration greater than 0.1 wt % the degree of grafting (G %) decreases. This may be attributed to the dissemination of ferric ions inside of the film structure which constrains the active radicals formed on its surface, therefore decreases the possibility of the acrylic acid species to be grafted onto HDPE and LDPE [32].

Effect of monomer concentration

Fig. 3b shows the relation between monomer concentration (AAc) wt % and the degree of grafting (G %). The results revealed that as the concentration of acrylic acid (wt %) increases the degree of grafting (G %) increased for both (HDPE) and (LDPE). On the other hand, G % varied with monomer concentration. As the (AAc) wt % increases up to 30 %, the G % increases. Nevertheless, the degree of grafting appears to be constant past 30 % monomer concentration. This may be related to the following; at a lower concentration of acrylic acid (AAc) a few free radicals are formed in the species of the monomer which make the opportunity for formation of homopolymer decreases. Consequently, the chance of grafting occurrence increases and the amount of homopolymer formed decrease and the rate of G % increased. On the other hand, at higher concentration of AAc greater than 30 wt % many active free radicals are formed in AAc and the chance to combine with each other to form homopolymer increases, thus the viscosity of the grafting blend increased. This hindered diffusion of the monomer (AAc) towards the polymer backbone, which makes the rate of G % decreased [31, 33].

Effect of irradiation doses

Fig. 3d 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), 24-hour reaction time and (AAc) 30% (wt %). The result revealed that by increasing the irradiation dose G %

increased rapidly for both HDPE and LDPE until it reaches dose 20 KGy. For irradiation doses greater than 20 KGy, the rate of increase in G % is very small, that we can consider this increase is neglected. This phenomenon can be explained as follows for irradiation doses less than 20 KGy 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 grow rapidly, so the rate of increase in G % is high [17]. On the other hand at irradiation doses greater than 20 KGy, the number of active free radicals formed were high and the distance between them was 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 G % was very small [31].

Finally, from the previous discussion we can notice that, in all the main parameters affecting on G % (solvent type, monomer concentration, inhibitor concentration and doses), the value of G % for HDPE is lower than that of LDPE. This variation in the value of G % is due to the difference in structure between LDPE and HDPE, as the fraction of the crystalline content in HDPE is higher than LDPE thus, the opportunity of the monomer to be grafted on LDPE is easier than HDPE.

Characterization of the grafted polyethylene

FT- IR analysis

Membranes of un-grafted PE and grafted PE were subjected to IR analysis at room temperature to determine the changes in the structure of PE due to the grafting process and the chemical treatment process. The FT-IR spectra of un-grafted and grafted LDPE and HDPE with different grafting yields of AAc are shown in (Fig. 4 and Fig. 5) respectively. The IR spectrum of the un-grafted PE shows an absorption band at about (2700-3000) cm^{-1} due to the stretching of the -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 [21].

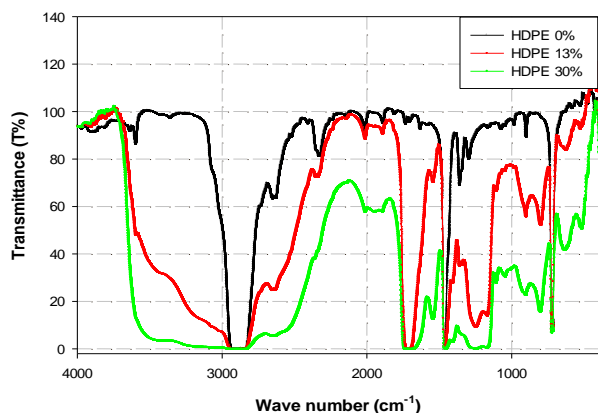


Fig. 4. IR spectra of the un-grafted HDPE and that grafted with different ratios of AAc.

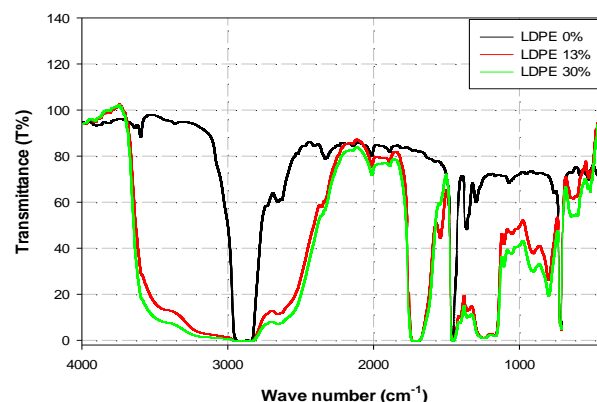


Fig. 5. IR spectra of the un-grafted LDPE and that grafted with different ratios of AAc.

Swelling behavior of grafted membranes

From the practical point of view, the grafted membranes, as well as treated films, should exhibit a 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 Fig. 6. The result revealed that water uptake improved with increasing the degree of grafting and tend to stabilize at more grafting. These results indicated that the grafting of AAc onto PE membranes enhanced the hydrophilic properties of such polymer. This performance could result from the steric hindrance consequence produced by the development of hydrogen bonds between acidic (COOH) groups [34]. This process eventually impedes the absorption of water molecules. The higher water uptake by grafted PE may allow better interaction with aqueous solutions [35].

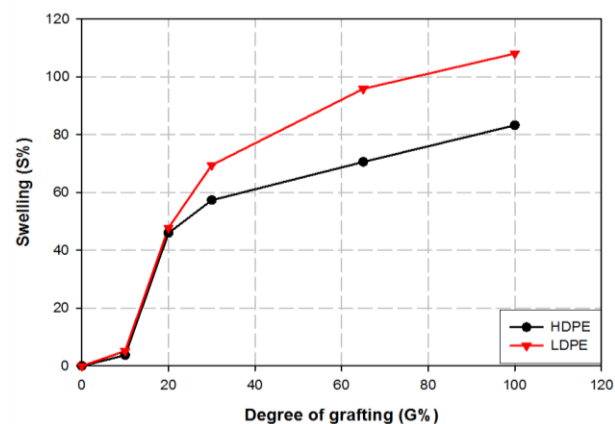


Fig. 6. Water uptake of un-grafted PE and that grafted with different ratios of AAc for 24hr.

Electrical measurements for grafted membranes

The electrical resistivity of the grafted PE membranes with AAc content was evaluated as a function of the degree of grafting as shown in Fig. 7. The figure clarifies that the electrical resistivity of PE grafted copolymer decreased by increasing the degree of grafting of AAc. The core factors influencing the electrical resistivity are the number of charge carriers

and their motion 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. 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 [36].

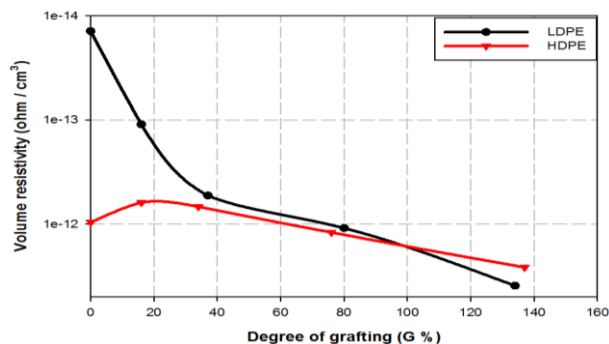


Fig. 7. Volume resistivity of un-grafted and grafted PE with a degree of grafting

Mechanical properties

Mechanical assets could be thought as the greatest important property of polymers for various applications. It is well known that polymers are classified into three types according to their stress-strain curves brittle, tough and elastomer. At high (G %) for grafted polyethylene, it tends 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 Fig. 8 and Fig. 9. However, the increase of AAc grafting in the membrane increases the brittleness properties. Commonly, at minimal G %, the mechanical properties of grafted membranes were greater than those of polyethylene. Usually, mechanical properties are controlled by three morphological factors, the number of tie molecules, lamellar thickness and molecular chain entanglement [37].

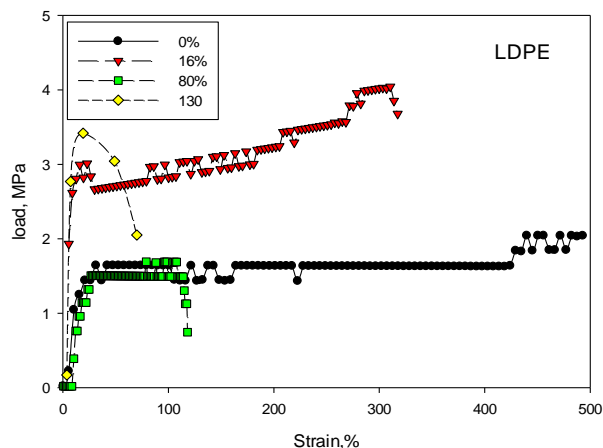


Fig. 8. Stress-Strain curves for LDPE grafted with acrylic acid at different grafting percentage.

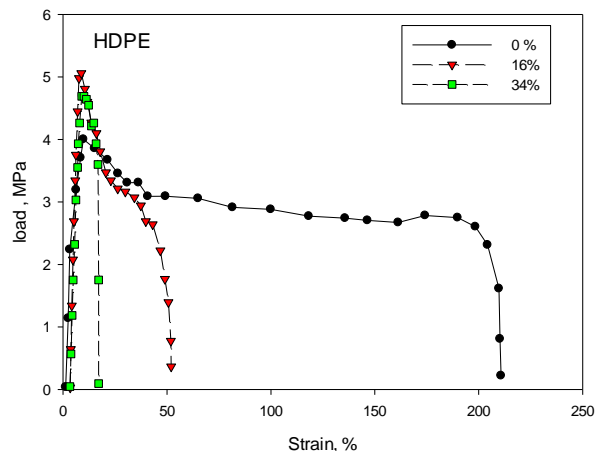


Fig. 9. Stress-Strain curves for HDPE grafted with acrylic acid at different grafting percentage.

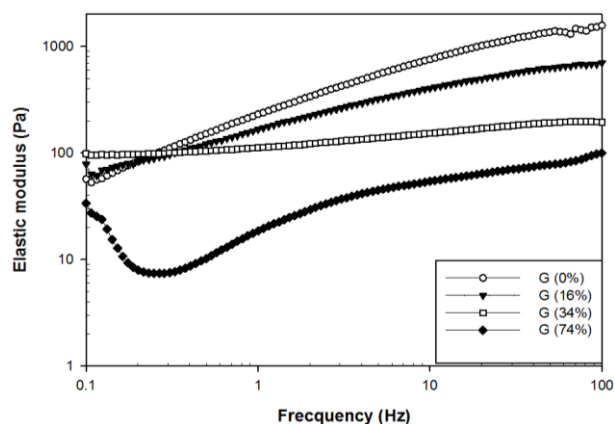


Fig. 10. Effect of grafting percent on elastic modulus for un-grafted and grafted HDPE with different (G %).

Rheological measurements

The melt rheology is an important property to understand the structure-property relationship in thermoplastics and their process ability [17]. Fig. 10-15 show the elastic modulus (storage modulus) (G') (i.e. energy that is stored and can be recovered), viscous modulus (G'') (loss modulus, i.e. energy that cannot be recovered) and the complex viscosity (μ) for un-grafted HDPE and LDPE and their grafted copolymers with different G % that measured at 200 °C respectively. From Fig. 10-13 all stated properties (G' and G'') were increased with increasing the frequency for both grafted and un-grafted HDPE and LDPE. At low frequency, this increase is due to that enough time which is available to unfold chains and they relax slowly, which decrease the G' and G'' values. In addition, at high frequency, the polymer chains were deformed, and the entangled chains had less time for re-orientation that leads to increases of the moduli (G' and G''). Normally presence of crosslinks between polymer chains increased the elastic modulus (G') than viscous modulus (G'') and indicated the high interaction between polymer chains. The degree of grafting can affect the values of G' , G'' and complex viscosity (μ) due to the energy values that occur during shear processing and

dependent on the mutual interactions between polymer interphases. Correspondingly, G' and G'' increased with growing the frequency. Furthermore, their values decreased with increasing the G %. This reduction in G' and G'' may be attributed to two factors taking place during grafting process:

- Formation of numerous short grafted chains of acrylic acid that didn't hinder the movement of polyethylene chains with frequency at elevated temperature (200 °C).
- Presence of homo-polymer molecules between polyethylene chains which facilitate the movement of chains with frequency.

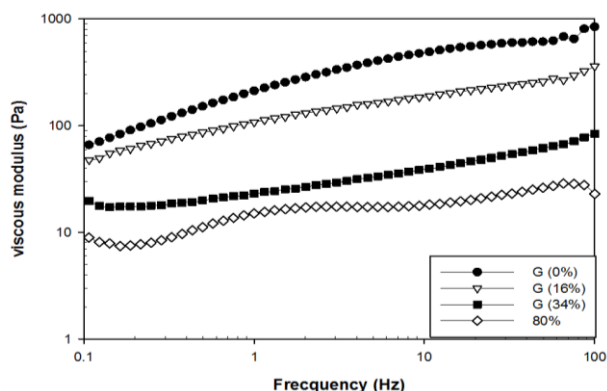


Fig. 11. Effect of grafting percent on viscous modulus for un-grafted and grafted HDPE with different (G %).

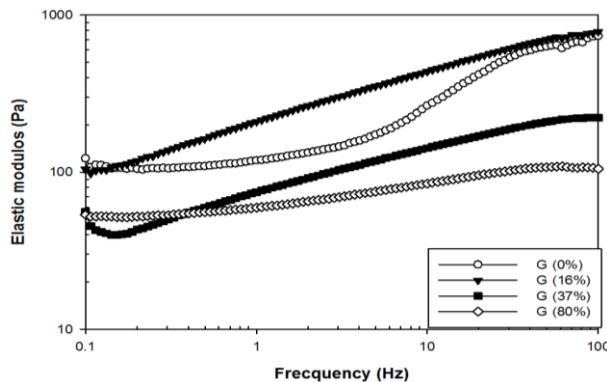


Fig. 12. Effect of grafting percent on elastic modulus for un-grafted and grafted LDPE with different (G %).

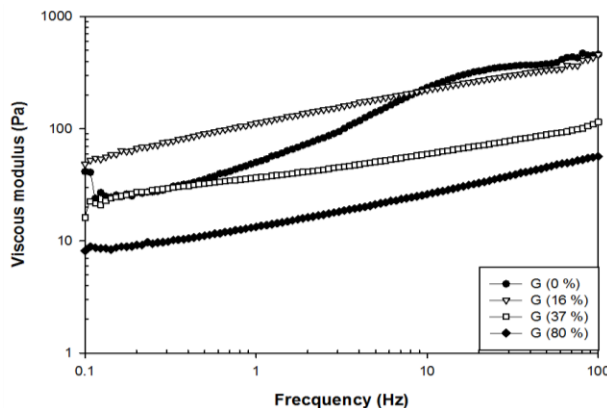


Fig. 13. Effect of grafting percent on viscous modulus for un-grafted and grafted LDPE with different (G %).

Fig. 14 and **Fig. 15** show the complex viscosity of HDPE and LDPE respectively. The results reveal that the viscosity was decreased with frequency. This behavior may be related to the stretching of entangled chains onto oriented chains (i.e. shear thinning behavior) [38]. The viscosity also decreased with increasing the AAc grafting percent in both HDPE and LDPE. Also, diffused homo-polymer or molecules enhance the shear thinning behavior of polyethylene [39].

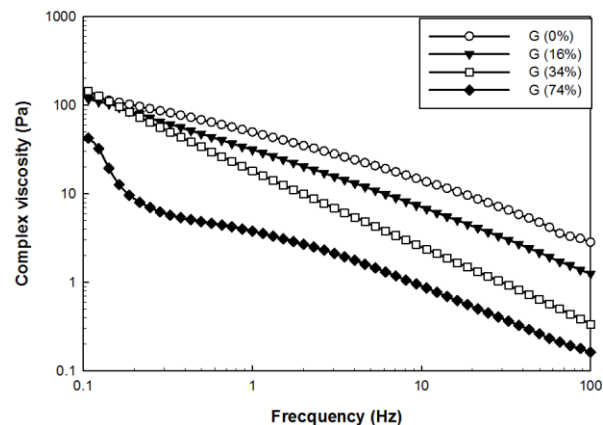


Fig. 14. Effect of grafting percent on complex viscosity for un-grafted and grafted HDPE with different (G %).

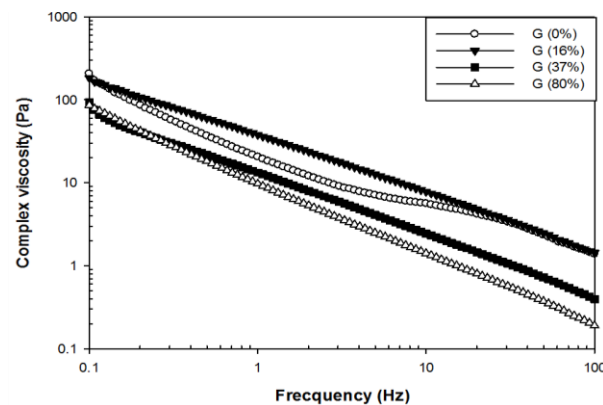


Fig. 15. Effect of grafting percent on complex viscosity for un-grafted and grafted LDPE with different (G %).

Fig. 16 and **Fig. 17** show the plots of $\log G'$ versus $\log G''$ (Cole-Cole plots) for un-grafted and grafted HDPE and LDPE with different AAc graft ratios. The plot describes the relation between the amount of energy stored and amount of energy dissipated per unit volume of the melt under test. This property depends on the molecular characterization and chemical structure of the melt. Incidentally, Cole-Cole plot is convenient in examining the consequence of molecular parameters (e.g. molecular weight, molecular weight distribution, the degree, and length of chain branching) and chemical structure of polymer on the fluid elasticity. When the penetrated polymer chains are not bonded to substrate molecules, the associated Cole-Cole plot will be deviated from linearity due to the ease of chain movement in the presence of homo-polymer molecules without any hydrogen bonding at (200 °C) [17].

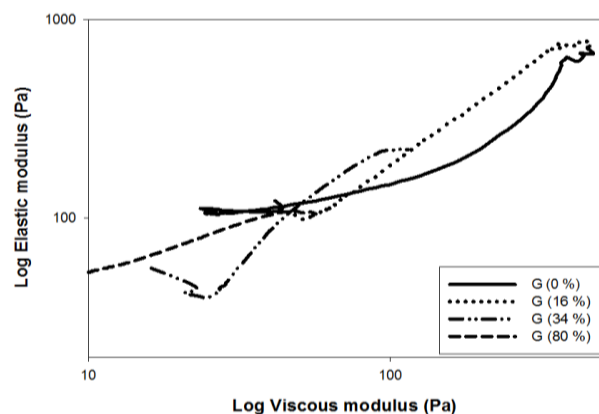


Fig. 16. Log G' versus Log G'' for un-grafted and grafted HDPE with different (G %).

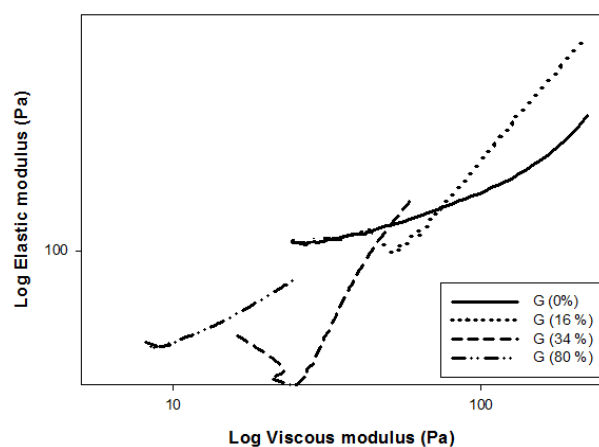


Fig. 17. Log G' versus Log G'' for un-grafted and grafted LDPE with different (G %).

Differential scanning calorimetry

DSC was used to investigate the effect of AAc grafting as thermal properties of HDPE and LDPE[40]. **Fig. 18** and **Fig. 19** summarized in **Table 2** which show the DSC thermograms of un-grafted and grafted HDPE and LDPE respectively. These figures reveal that an endothermic peak owing to the crystalline melting temperature. As expected the T_m for un-grafted HDPE (130 °C) was higher than that of LDPE (123 °C). Also, the grafting process for polyethylene slightly decreases the thermal parameters, for both HDPE and LDPE as can be seen in **Table 2** and this decrease was shifted down by increasing the grafting percent.

Table 2. Thermal parameters for ungrafted and grafted HDPE and LDPE at different (G %).

Sample type	G%	ΔH (J/g)	T_{onset} (°C)	T_{endset} (°C)	T_m °C
HDPE	0	+165.7	122	139	130.5
	34	+105.8	122.3	137	129.6
	80	+70.6	122.5	135	128.8
LDPE	0	+58.7	114.3	127.3	123.0
	34	+47.9	113.2	127.8	120.3
	80	+32.6	112.1	125.6	119.6

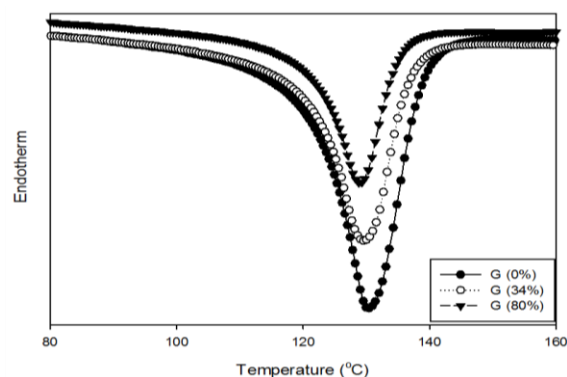


Fig. 18. DSC thermograms for un-grafted and grafted HDPE with different (G %).

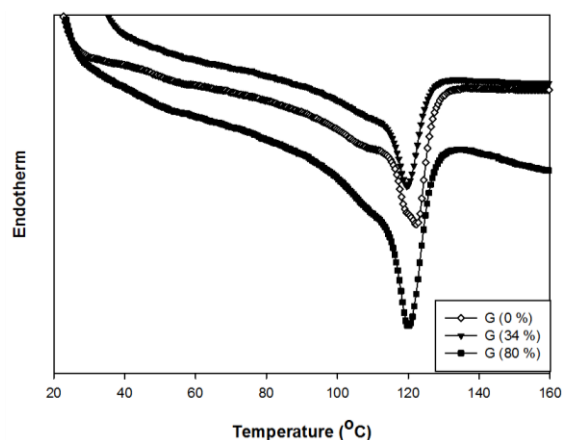


Fig. 19. DSC thermograms for un-grafted and grafted LDPE with different (G %).

The decrease in T_m and ΔH for grafted films with increasing (G %) may be due to the grafting process that carried out at temperature not more than (40 °C) that's far below the T_m of HDPE and LDPE, which has low tendency to swell at this temperature and consequently the monomer solvent diffusion occurs at amorphous part of polyethylene and no swelling in crystalline part[41]. The AAc grafts enter the amorphous region and the surface of crystallites; this behavior increases the amorphous content which exerts a dilution effect on the crystalline structure of the films without any significant disruption to crystallites [16, 42].

Thermal Gravimetric Analysis (TGA)

TGA primarily used to determine the composition of the material and to predict its thermal stability upon elevated temperature [43]. The weight loss outline is studied at a specified temperature. The amount of the residual at a final temperature and the temperature of various degradation steps were also investigated. The bond dissociation energy in polyethylene and acrylic acid have been reported to be 414, 347, 749, 351 and 464 KJ/mol for C-H, C-C, C=O, C-O, and O-H respectively [44]. According to these values, it can be predicted that the average bond dissociation energy for PE and AAc are (338 and 473) KJ/mol respectively.

From these values, it can be predicted that grafting of AAc onto PE will increase the thermal stability of PE. Also, the limited molecular chain mobility in polymer matrix due to irradiation and/or grafting is expected to increase the thermal stability.

The normal TGA thermograms for un-grafted LDPE, HDPE and their grafted samples at different grafting percent were shown in **Fig. 21** and **Fig. 23**. From these figures, the chain decomposition process was started at about (350 – 450 °C) depending on the composition ratio. However, the grafted LDPE and HDPE were started earlier than un-grafted LDPE and HDPE. This earlier start in thermal decomposition is due to water removal from two acrylic acid molecules. Also, it can be noticed that no weight loss in the temperature range up to 200 °C, indicating the complete drying of the films during the (G %) measurements. The water removal occurs in temperature range (200 – 320) °C may be due to water removal from adjacent two acid molecules described by **Fig. 20**. The loss percent at this range of temperature was about (12.5 %) which supported the proposed mechanism of removal of molecule cyclization of two acid groups; that was confirmed by the results obtained from **Fig. 22** and **Fig. 24** which represent the rate of decomposition reaction versus temperature. From those figures, the thermal decomposition process in PE and grafted PE is similar in the main degradation process and there is one inflection in the degradation rate curves; that indicated the degradation occurs in one step over the decomposition temperature range.

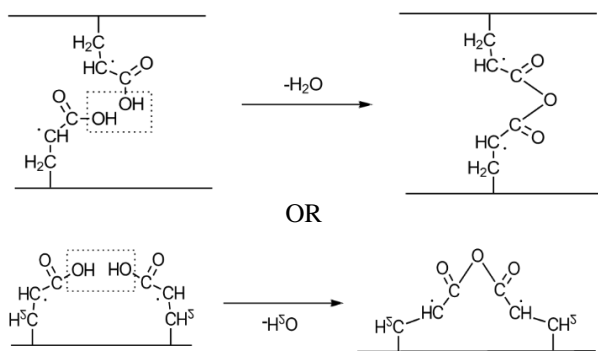


Fig. 20. Mechanism of water removal from two AAc molecules.

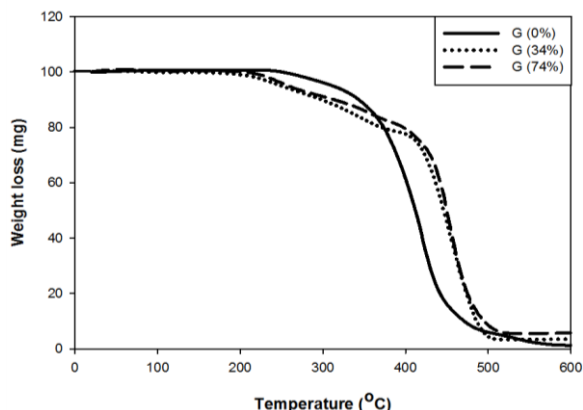


Fig. 21. TGA thermograms for ungrafted HDPE and grafted HDPE with different (G %).

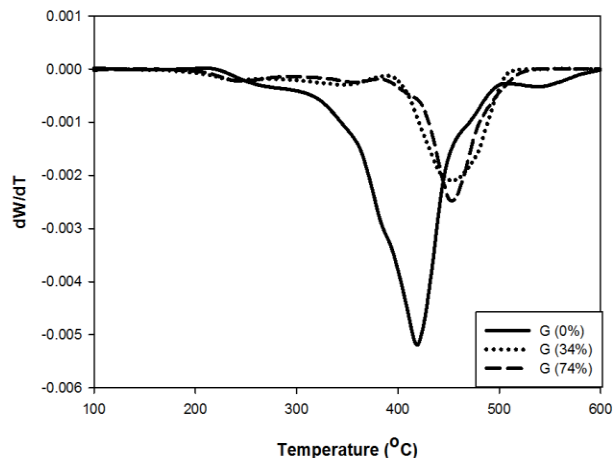


Fig. 22. The differential thermal analysis versus temperature for un-grafted HDPE and grafted HDPE with different (G %).

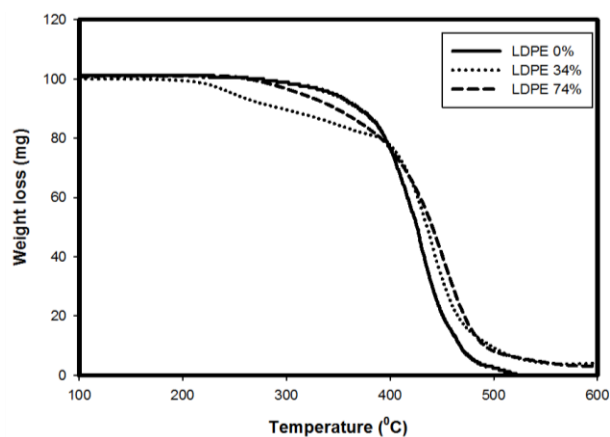


Fig. 23. TGA thermograms for un-grafted LDPE and grafted LDPE with different (G %).

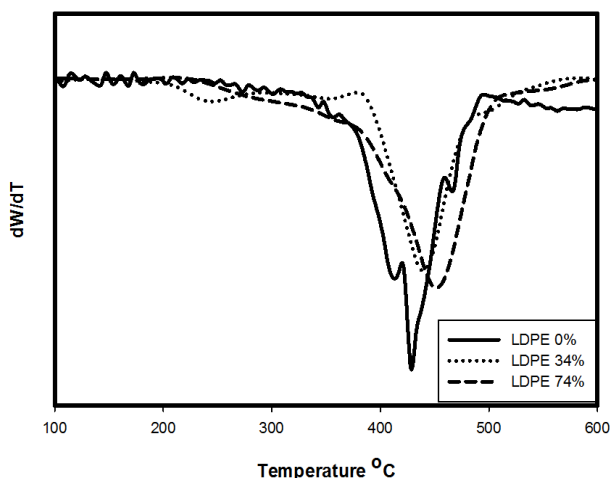


Fig. 24. The differential thermal analysis versus temperature for ungrafted LDPE and grafted LDPE with different (G %).

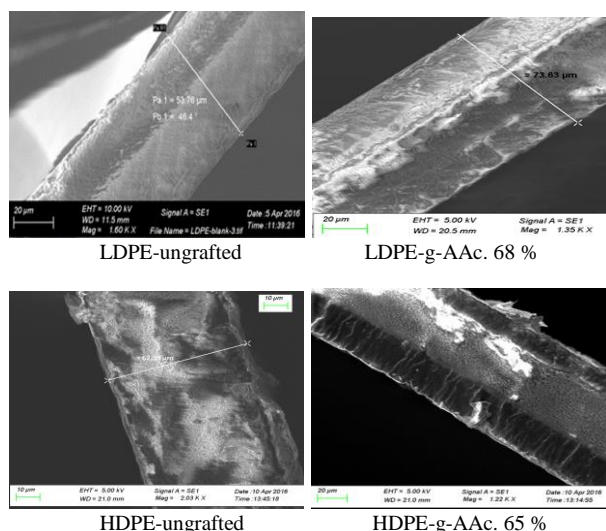
Table 3 shows some parameters obtained from the decomposition rate curves. The increase in T_{max} (the temperature at which highest rate of deformation occurs) was in accordance with the predicted thermal stability improvement obtained from a range bond dissociation energy for AAc (473) and PE (338) KJ / mole.

Table 3. The rate of thermal decomposition reaction parameters for ungrafted and grafted HDPE and LDPE with different (G %).

Sample Type	T _{Onset} (°C)	T _{Endset} (°C)	T _{max} (°C)
HDPE	254.66	479.22	420
HDPE-g-AAc (34%)	185.22	491.5	452
HDPE-g-AAc (74%)	100.38	513.5	458
LDPE	294.5	469.5	429
LDPE-g-AAc (34%)	268.2	516	443
LDPE-g-AAc (74%)	250.7	525	452

Scanning Electron Microscopy (SEM)

SEM pictures of ungrafted and grafted PE having different ratios of AAc are shown in **Fig. 25**. The result shows that the ungrafted PE micrographs had some protuberances with nearly single domains. As AAc grafted to PE, the grafted AAc (65 %) had a larger protuberance near the surface with a non-inner thickness of LDPE (less crystalline) than HDPE (higher crystalline). Also, different domains started to appear which may be due to different components in the matrix; (PE, PE-g-AAc, and PAAc). Rising the grafting percentage was accompanying with greater grafting layer and different domains. This figure was supported our explanation of the mechanical properties and (Cole-Cole plot).

**Fig. 25.** SEM micrograph for HDPE and LDPE (a) LDPE (0 %), (b) LDPE (68 %), (c) LDPE (190 %), (d) HDPE (0 %), (e) HDPE (65 %), (f) HDPE (90 %).

Reverse osmosis measurements

Membranes manufactured by the irradiation-induced grafting in aqueous AAc solution, onto HDPE and LDPE films, followed by alkaline treatment with KOH solution to confer ion characters, were studied to clarify the possibility of their practical use as reverse osmosis membranes. It is recognized that the economics of (RO) for desalination are determined by the properties of the membrane material, high water flux, and good salt rejection. In this work, the grafted membranes of HDPE and LDPE having various degrees of grafting were studied for reverse osmosis desalination of saline water.

The effect of degree of grafting and operation time on salt rejection and water flux were examined. The used water in the application part (RO) desalination was underground saline water obtained from Abo Swear region in Ismailia governorate, Egypt with TDS concentration 2070 ppm.

Effect of operation time on water flux and salt rejection

Fig. 26 show the effect of operation time on water flux (J_{H_2O}) for grafted membranes of HDPE and LDPE respectively. The membranes having different degrees of grafting under an applied pressure of 40 atm and salt concentration 2070 ppm at room temperature (25 °C). J_{H_2O} increases as the operation time increases. Moreover, the higher the degree of grafting the higher the water flux obtained, at a given operating time for both HDPE and LDPE [37].

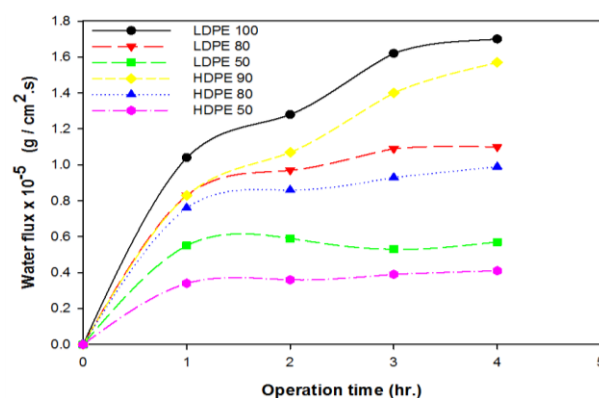
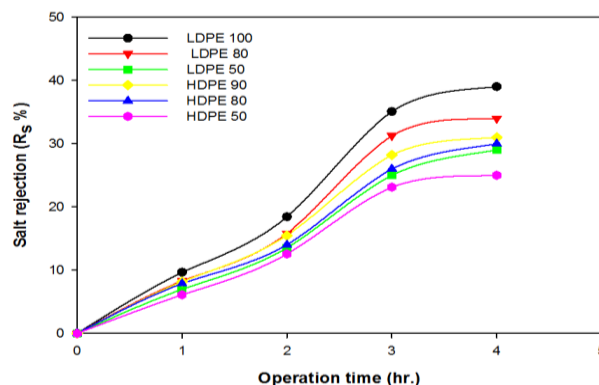
**Fig. 26.** Effect of operation time on water flux for HDPE and LDPE with different degrees of grafting at operating pressure 40 bar and feed concentration 2070 ppm.

Fig. 27 shows the effect of operation time on salt rejection (R_s %) for membranes of HDPE and LDPE having different degrees of grafting under an applied pressure of 40 atm and water concentration 2070ppm at room temperature (25°C). R_s % increases as the operation time increases. Moreover, the higher the degree of grafting the higher the salt rejection obtained, at a given operating time for both HDPE and LDPE [37].

**Fig. 27.** Effect of operation time on salt rejection for HDPE with different degrees of grafting at operating pressure 40 bar and feed concentration 2070 ppm.

Effect of degree of grafting on water flux and salt rejection

Fig. 28 and **Fig. 29** show the effect of degree of grafting (G %) on water flux (J_{H_2O}) and salt rejection (R_s %) for membranes of HDPE and LDPE respectively. The conditions of the experiment were; the applied pressure of 40 atm, salt concentration 2070 ppm at room temperature (25°C) and operation time 4h. It can be seen that both water flux (J_{H_2O}) and salt rejection (R_s %) were increased as the degree of grafting increases for both HDPE and LDPE [37]. This phenomenon could be explained as follows, when water molecules are introduced into grafted PE, they concentrate in the amorphous regions and become associated by hydrogen bonding due to grafting with AAc in PE, thereby filling the voids with bound water. In a structure such as this, it is proposed that the hydrogen bonding forms a network which facilitates diffusion of water molecules through it. On the other hand, it repels the diffusion of the ions, this difference in the rate of water and ion migration is the main concept causes the desalination [45]. Also, this mechanism showed the role of the structure of the membrane, as the higher the amorphous content, the higher salt rejection, and water flux. **Fig. 28** and **Fig. 29** indicated that water flux and salt rejection were higher in LDPE than HDPE because the amorphous content in LDPE was greater than that of HDPE. Also, from the melt rheology measurements and SEM micrographs we expected that a trace of homopolymer was formed between polyethylene chains, these traces of formed homopolymer, increases the intermolecular distances between the chains which support increasing of water flux with increasing grafting percent [46].

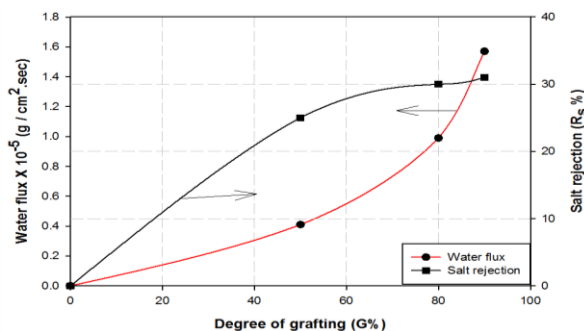


Fig. 28. Effect of degree of grafting on water flux and salt rejection for HDPE at operating pressure 40 bar, operation time 4h and feed concentration 2070 ppm.

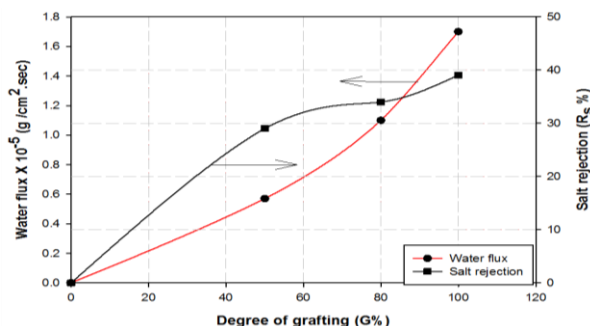


Fig. 29. Effect of degree of grafting on water flux and salt rejection for LDPE at operating pressure 40 bar, operation time 4h and feed concentration 2070 ppm.

Conclusion

A graft copolymer from polyolefin (high and low density polyethylene with acrylic acid could be prepared using gamma irradiation in a direct irradiation technique. The optimum conditions of preparation were using: acetone as a solvent; monomer concentration (30%) wt; anhydrous FeCl_3 as an inhibitor with concentration (0.1 %) wt and irradiation dose (20) kGy. Correspondingly, the properties of the prepared irradiation grafting of low and high-density polyethylene displayed that; by increasing degree of grafting more than 80 % the polyethylene changed from tough to the brittle polymer. The degree of grafting can affect the values of G' (storage modulus), G'' (viscous modulus) and complex viscosity (μ) due to the energy values that occur during shear processing and dependent on the mutual interactions between polymer interphases. The electrical resistivity of PE grafted copolymer decreased by increasing the degree of grafting of AAc. Water uptake improved with increasing the degree of grafting and tend to stabilize at more grafting. Melt rheology investigation revealed that a chemical crosslink was performed among PE chains at 200 °C. In addition, a trace of homopolymer was developed in the matrix. The thermal stability was increased by increasing grafting percent. Finally, grafted PE showed suitable results in RO desalination and by increasing operation time and degree of grafting, water flux and salt rejection were increased.

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