

**Rad.C-10**      **Characterization and Some Properties of Functionalized  
Graft Copolymer**

El-Sayed. A. Hegazy, H. Kamal, N. A. Khalifa\* and Gh. A. Mahmoud

*National Center for Radiation Research and Technology,  
P.O. Box 29, Nasr City, Cairo, Egypt.*

*\*Faculty of Science, Helwan University, Helwan, Egypt.*

**ABSTRACT**

The study involved the investigation and characterization of membranes prepared by graft copolymerization of acrylonitrile (AN) and vinyl acetate (VAc) binary monomers onto lowdensity polyethylene (LDPE) and isotactic polypropylene (IPP). The mutual  $\gamma$ -irradiation method was used as a grafting technique. The effects of grafting and chemical treatments on the thermal properties and chrySTALLINITY of prepared graft copolymer have been investigated using DSC, TGA and XRD. IR spectra recorded before and after grafting and also for the chemically treated membranes to elucidate the structural changes occurred due to grafting and chemical treatments.

*Key Words : Radiation, Grafting, Thermal Stability, Crystallinity*

**INTRODUCTION**

Radiation- induced graft copolymerization of monomers onto different polymers have been widely studied to produce membranes for various purposes, such as in separation processes and electrochemical applications<sup>(1-5)</sup>. The various steps involved in the membrane preparation process may influence the overall structure of membranes depending upon the nature, amount, and distribution of the grafted chains. These changes may be in the form of a crystalline-amorphous ratio, lamellar defects, and domain formation of the grafted component in the membrane matrix<sup>(6)</sup>. The crystallinity has been found to exert strong influence over the transport behaviour of molecules through grafted films<sup>(7)</sup>.

In the previous study, preparation of ion-exchange membrane by radiation grafting of (AAc/AN) binary monomers onto PE and PP and the possibility of their practical uses in separation processes, was investigated<sup>(8)</sup>. In the present work, the physical properties of the prepared membranes were determined including melting temperature ( $T_m$ ), heat of melting ( $\Delta H$ ) and decomposition temperature by DSC and TGA. XRD of the grafted and the treated graft copolymers was performed and compared with the base polymer to clarify their morphological structures and the change caused by the grafting and chemical treatment.

## EXPERIMENTAL

### Materials:

Low density polyethylene (LDPE) films of thickness 80  $\mu\text{m}$  were provided by El-Nasr Co. for Medical Supplies, Egypt. Reagent grade acrylonitrile (AN) of purity 99.3 % (Merck) and reagent grade vinyl acetate (VAc) of purity 99 % (Merck) were used as received. Other chemicals, such as solvents, inorganic salts, acids and other reagents were reagent grade of BDH type.

### Infrared Spectrophotometry Measurement:

Analysis by IR spectrophotometry was carried out using a PYE Unicam 1100 infrared spectrophotometer (in the range 4000-400  $\text{cm}^{-1}$ ).

### X-Ray Diffraction Measurements (XRD):

XRD measurements were conducted on blanks, grafted samples at room temperature. X-ray diffraction pattern (intensity vs. diffraction angle plate) was recorded in the range of diffraction angle  $2\theta = 4 - 50^\circ$  using Phillips Pw 1730 x-ray generator equipped with a scintillation counter. The diffraction patterns were run with nickel filter (cuka),  $\lambda = 1.45 \text{ \AA}$ . The X-ray diffractograms were obtained using following experimental conditions:

Filament current = 28 mA  
Voltage = 40 kV  
Scanning speed = 20 mm/ min. or  $2^\circ$ / min.

### Thermal Stability Measurements:

Thermal gravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) curves for the investigated samples were performed under nitrogen atmosphere using a computerized Perkin Elmer 7-series thermal analysis system. A flow rate of pure nitrogen gas was 50 ml/ min. for both TGA and DSC. A heating rate was  $20^\circ\text{C}/\text{min}$ . from ambient up to  $600^\circ\text{C}$  for TGA and  $10^\circ\text{C}/\text{min}$ . from ambient to  $250^\circ\text{C}$  for DSC.

## Results and Discussion

### 1-IR-Spectroscopy:

Infrared analysis was made for the grafted IPP films to confirm the formation of graft copolymer. The spectrum of the IPP-g-P(AN/VAc) films shows a characteristic band of C=N group of PAN at  $2250 \text{ cm}^{-1}$ . A new absorption bands appeared around  $1740 \text{ cm}^{-1}$ ,  $1240 \text{ cm}^{-1}$  and  $1099 \text{ cm}^{-1}$  which correspond to C=O groups of VAc, C-O and O-C=O stretching of acetate, respectively. It is also noted that, the intensity of these absorption bands increases with increasing the graft percent (spectra 2, 3). The IR-spectra for  $\text{NH}_2\text{OH}$  and  $\text{KOH}$ -treated membranes, (spectra 4,5) showed that the absorbance at  $2250 \text{ cm}^{-1}$  disappeared and a broad absorption band appeared around  $3200\text{-}3600 \text{ cm}^{-1}$  and

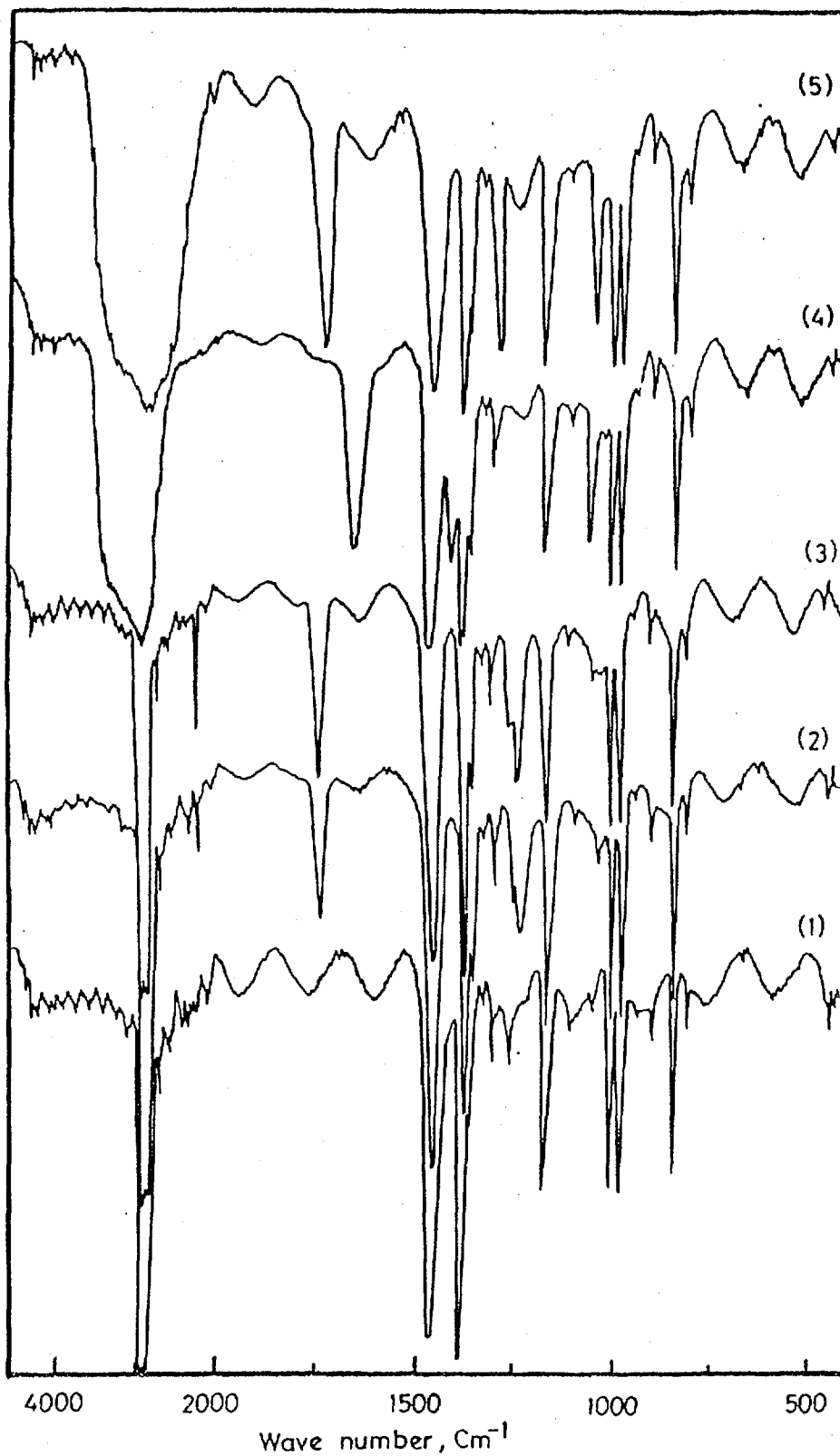


Fig. 1: IR-Spectra of: (1) Original IPP;  
(2) IPP-g-P(AN/VAc; 9.5% (3) IPP-g-P(AN/VAc; 14.1%  
(4) 14.1% Treated with NH<sub>2</sub>OH (5) 14.1% Treated with KOH

other peak around  $1050\text{ cm}^{-1}$  which are assigned to OH and C-O alcoholic groups, respectively. For KOH-treated films, new bands appeared around  $1711\text{ cm}^{-1}$  and  $1290\text{ cm}^{-1}$  which are the characteristic bands of C=O and C-O stretching of carboxylic groups. For  $\text{NH}_2\text{OH}$ -treated films new absorption bands around  $1425\text{ cm}^{-1}$  and  $1650\text{ cm}^{-1}$  which are the characteristic bands of C-N and amidoxime groups. The appearance of broad band around  $3170\text{-}3350\text{ cm}^{-1}$  assigned to N-H group of amidoxime that resulted from the treatment of nitrile group with  $\text{NH}_2\text{OH-HCl}$  <sup>(9)</sup>.

## 2-X-ray Studies (XRD):

X-ray diffractograms of various samples; the trunk LDPE and IPP films, graft copolymers of different degrees of grafting and graft copolymer treated with KOH or alcoholic  $\text{NH}_2\text{OH}$ , are presented in Figs. (2 - 5). Since the crystalline reflections in the diffraction patterns of the grafted samples occurs at identical diffraction angles as in LDPE and IPP and no additional diffraction peak occurs in the grafted samples. It appears that, PVAc and PAN are present as an amorphous phase and the crystalline regions are contributed by LDPE and IPP sequence. It is also observed that, as the degree of grafting increases the intensity of crystalline diffraction peaks decreases. These results suggest that the inherent crystallinity of the backbone polymer (LDPE & IPP) is not impeded by the graft copolymerization of AN and VAc and the grafting occurs only in the amorphous areas. The decrease in the overall crystallinity of LDPE and IPP then appears only due to dilution of crystalline fraction by the incorporation of the amorphous PAN and PVAc chains into the polymer matrix <sup>(10, 11)</sup>.

It is obvious from Figs. (4,5) that, the diffraction curves of the treated-graft copolymer recorded in the same region, and it does not show any new diffraction peak. It is also observed that, the intensity of crystalline diffraction peak decreases if compared with that of the grafted and untreated ones and the decrease in crystallinity is more in the KOH- treated grafted film, for both LDPE and IPP. The decrease in crystallinity in the alkali-treated grafted films may be due to the incorporation of polar groups by alkaline treatment. The decreasing in crystallinity in KOH treated membrane reflects the high polarity of the carboxylic acid groups than the amidoxime groups.

## 3-Thermal Properties:

### 1-Thermal Gravimetric Analysis (TGA):

TGA thermograms for the ungrafted and the grafted LDPE and IPP films with various degrees of grafting are presented in Figs. (6, 7), respectively. Ungrafted LDPE and IPP showed a stable thermograms up to a temperature of  $\approx 400\text{ }^\circ\text{C}$ , beyond which a smooth decrease in weight is observed. A single stage character of the degradation evident from the curves and complete depolymerization of the sample to monomer occur at  $\approx 500\text{ }^\circ\text{C}$  and  $\approx 470\text{ }^\circ\text{C}$  for LDPE and IPP, respectively. TGA curves of LDPE-g-P(VAc/AN) and IPP-g-P(VAc/AN) with various degrees of grafting reveal that there are two distinct steps of weight loss: The first step of weight loss in the range of  $50 - 400\text{ }^\circ\text{C}$  may be attributed to the elimination of adsorbed moisture and side graft chains degradation <sup>(11)</sup>. The second decomposition stage observed in the temperature ranges of  $400 - 500\text{ }^\circ\text{C}$  for LDPE and  $400 - 470\text{ }^\circ\text{C}$  for IPP due to extensive degradation of the

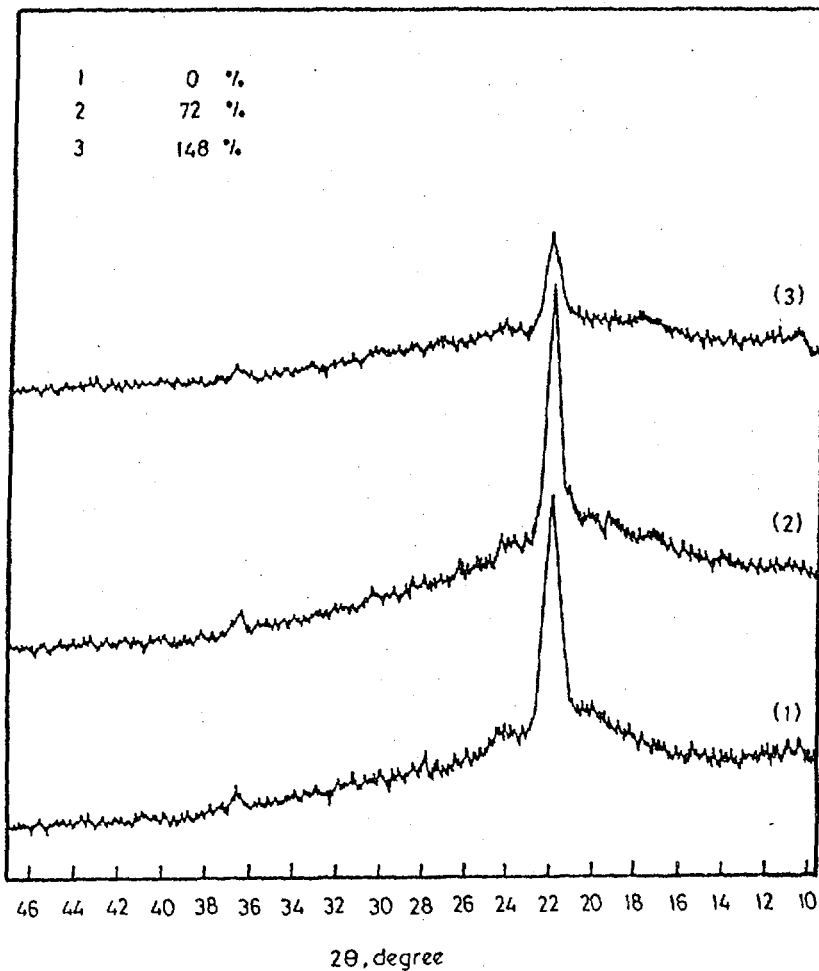


Fig. 2: XRD-Patterns of blank LDPE and its graft copolymer with different degrees of grafting.

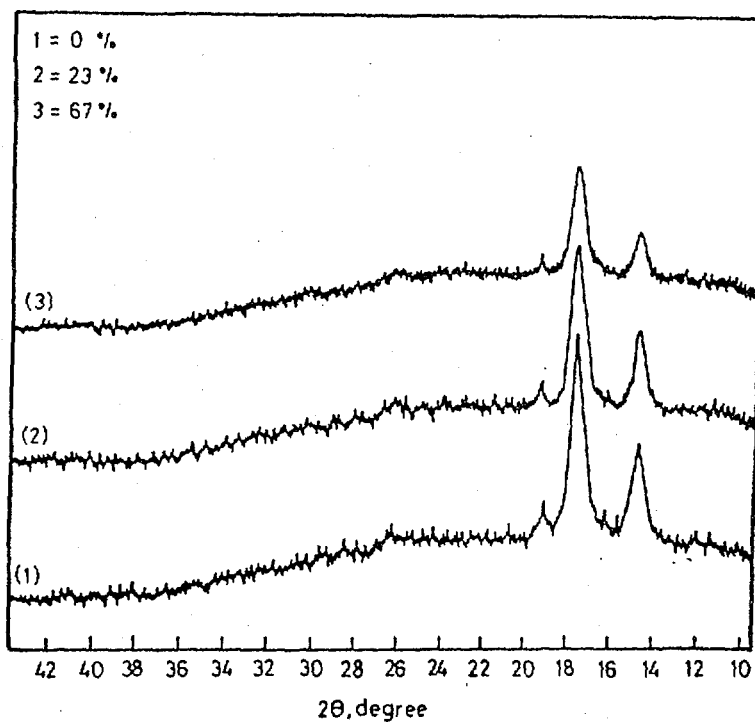


Fig. 3: XRD-Patterns of blank IPP and its graft copolymer with different degrees of grafting.

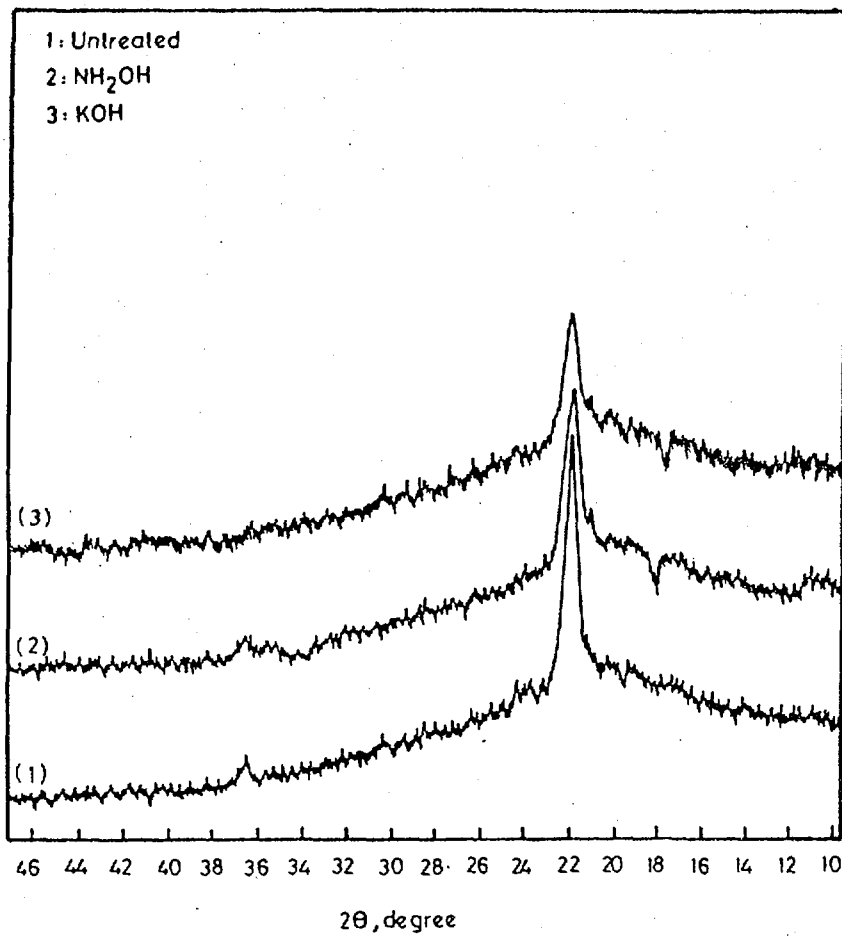


Fig. 4: XRD-Patterns of untreated grafted LDPE (72%) and its treated form

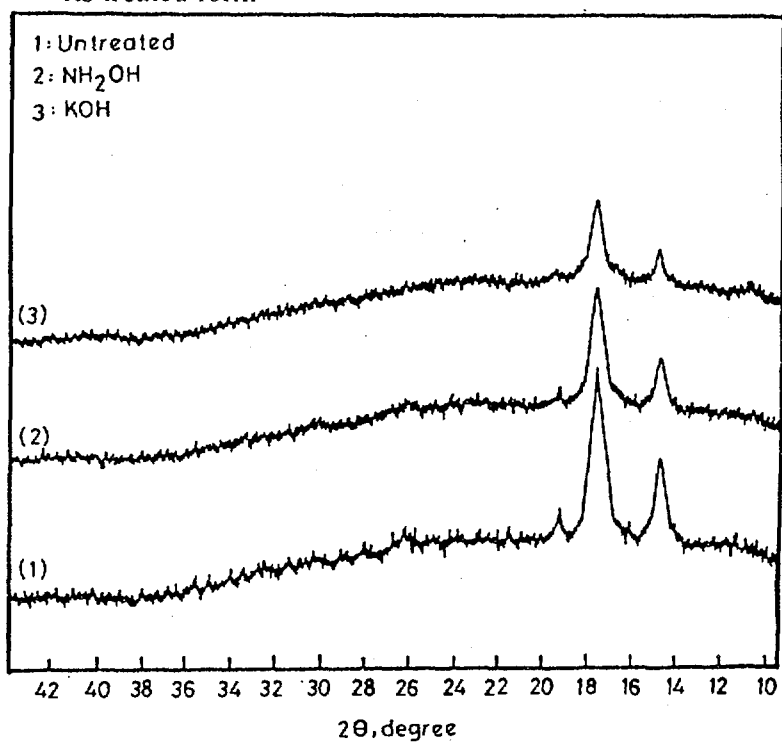


Fig. 5: XRD-Patterns of untreated grafted IPP (23%) and its treated form

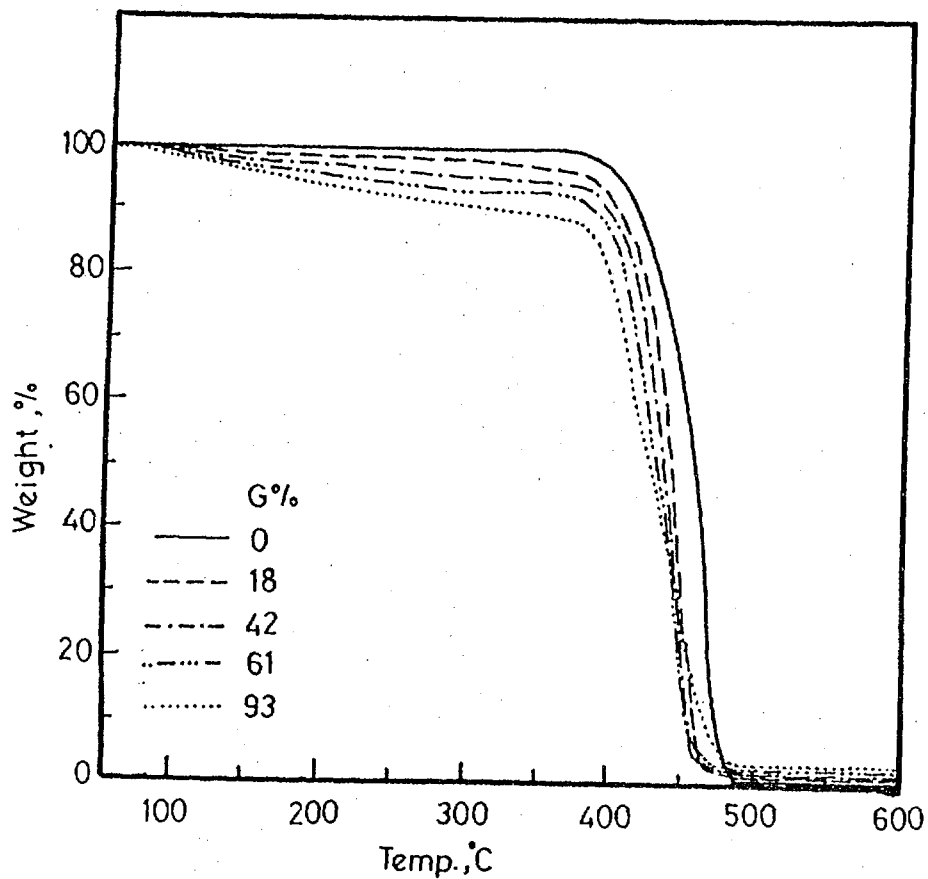


Fig. 6: TGA thermal diagram for a series of LDPE g-P (AN/VAc)

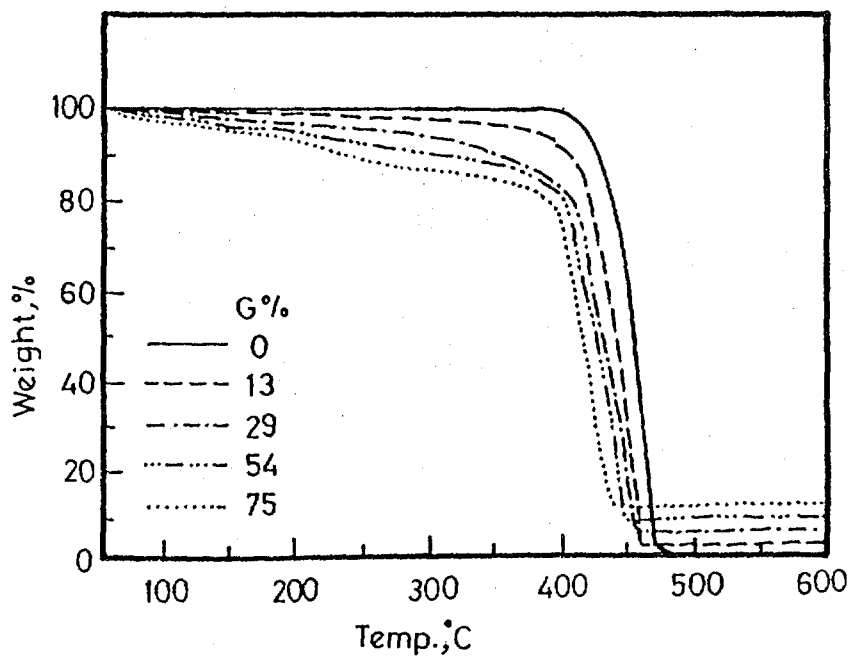


Fig. 7: TGA thermal diagram for a series of IPP g-P (AN/VAc)

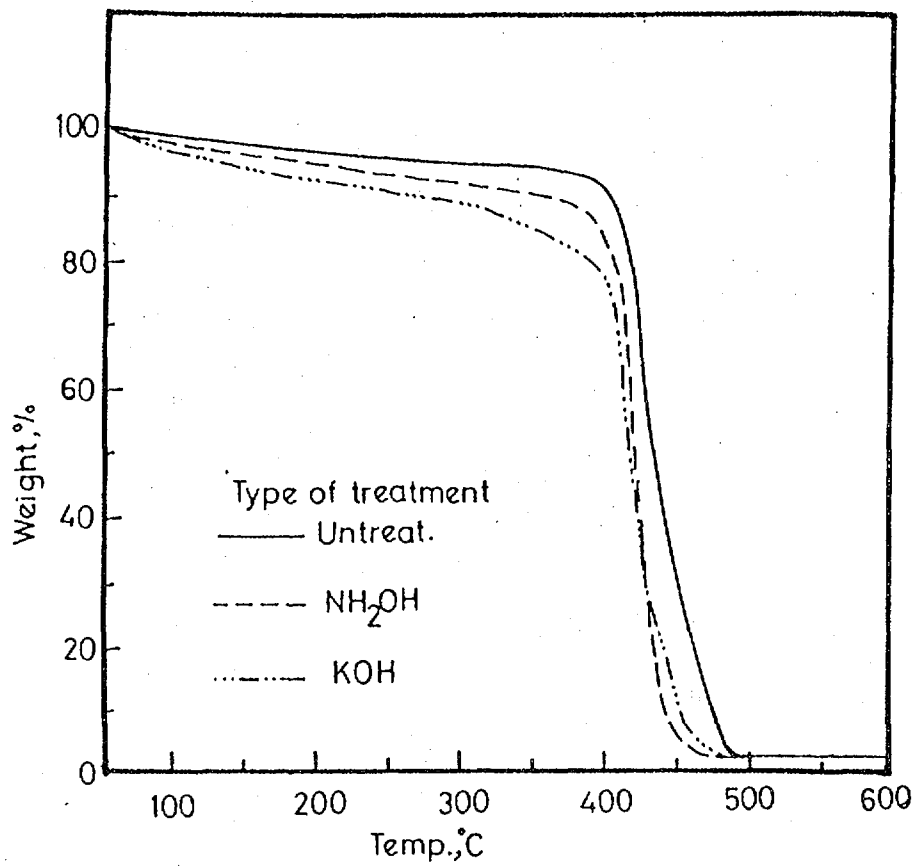


Fig. 8: TGA thermal diagram for treated grafted LDPE (42 %)

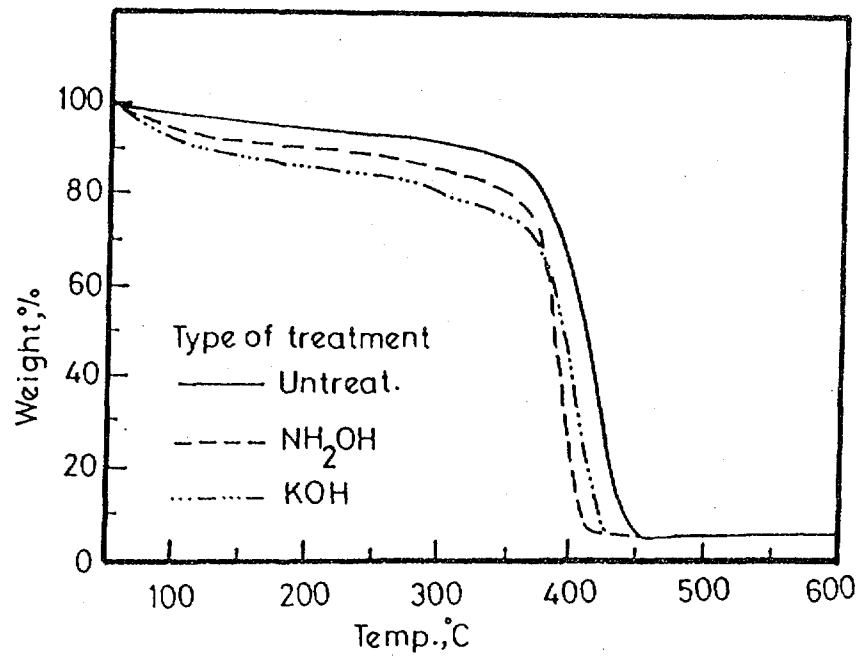


Fig. 9: TGA thermal diagram for treated grafted IPP (29 %)



polymer backbone chain leaving a residue. The residue from the grafted PE and PP left behind the final decomposition temperature is 4% for 93 graft percent in LDPE and 13% for 75 graft percent in IPP. It is also observed that, the left residue increases with increasing grafting degree due to the increase in crosslinking formation with degree of grafting.

Table (1) represent the weight loss percent at different decomposition temperatures for LDPE and IPP grafted with PVAc and PAN.

**Table 1.** The Weight Loss of Grafted LDPE and IPP Membranes as a Function of Temperature

Temp. , °C	Weight loss, (%)							
	Degree of grafting, (%)							
	LDPE				IPP			
	18	42	61	93	13	29	54	75
50	----	----	----	----	----	----	----	----
100	0.9	1.9	2.8	3.1	----	1.0	2.6	3.1
150	1.4	2.1	3.1	4.2	0.1	2.0	4.8	5.2
200	2.1	2.9	4.3	6.1	0.3	2.2	5.1	7.1
250	2.2	3.4	5.2	7.0	0.8	3.3	7.2	10.0
300	2.3	4.1	5.9	8.5	1.1	5.1	8.9	12.5
350	2.7	5.1	6.1	10.2	2.4	8.6	11.1	14.2
400	6.2	9.3	12.3	20.7	7.0	16.3	18.3	21.7
450	70.3	74.4	80.6	75.3	69.9	80.4	90.0	86.3
500	98.6	98.3	97.1	96.0	97.0	94.1	90.1	87.0

From the quantitative comparison of the weight loss in this temperature range 50 - 400°C, it is observed that, the weight loss increases with increasing grafting percent. Such increment in weight loss may be due to tacticity and sequence distribution of the comonomer AN/ VAc in the graft copolymer which affect the thermal behavior beside the nature of the comonomer.

Figures (8, 9 ) show the thermal stability of untreated and treated membranes by either KOH or alcoholic NH<sub>2</sub>OH. It is observed that, the introduction of carboxylic acid groups by the alkaline treatment of the graft copolymer with KOH changes the overall degradation pattern, while the introduction of amidoxime groups into the graft copolymer by treatment with NH<sub>2</sub>OH does not introduce a new decomposition temperature. For the KOH-treated membranes, there are three stages of decomposition appear in TGA curves. The first stage of weight loss at (50 - 300°C) is attributed to moisture desorption and elimination of water from the side groups. The second stage of weight loss in the temperature range 300 - 400°C is attributed to graft chain degradation. The last stage of decomposition is depolymerization of the backbone polymer.

The high value of the initial weight loss in the case of KOH-treated membranes compared to the NH<sub>2</sub>OH-treated ones due to the higher hydrophilicity of these membranes and consequently higher absorbed moisture than that for those NH<sub>2</sub>OH-treated ones. Table (2) show that the thermal stability for the grafted untreated > NH<sub>2</sub>OH and KOH - treated membranes.

**Table 2.** Weight loss of the treated and untreated grafted LDPE (42%) and IPP (29%) membranes as a function of temperature,

Temp , °C	Weight loss, (%)					
	LDPE membrane			IPP membrane		
	Untreated	NH <sub>2</sub> OH	KOH	Untreated	NH <sub>2</sub> OH	KOH
50	-----	-----	-----	-----	-----	-----
100	1.9	2.6	3.4	1.0	1.2	2.9
150	2.0	3.0	6.9	2.0	2.9	3.4
200	2.9	5.1	7.1	2.2	3.0	5.0
250	3.4	6.6	9.5	3.3	4.3	6.2
300	4.1	7.9	10.0	5.1	6.0	8.1
350	5.1	9.2	14.5	8.6	9.2	12.2
400	9.3	17.0	23.0	16.3	18.0	20.5
450	74.4	84.0	88.0	80.4	85.1	90.7
500	98.3	98.3	98.3	94.1	94.1	94.1

## 2-Changes in Thermal Parameters of Prepared Membranes:

Changes in thermal parameter for the prepared grafted membranes were measured DSC which is mainly used for studies of physical transitions.

Figures (10, 11) show the DSC thermograms of ungrafted and grafted LDPE and IPP, respectively. All samples show endothermic transition in the temperature range of 100 - 130°C and 130 - 170°C for LDPE and IPP, respectively. The melting temperature (T<sub>m</sub>) of graft copolymer is slightly reduced as compared to the ungrafted ones. The shape of the thermograms under the melting peak remain almost the same for all the membranes.

Tables (3, 4) show the thermochemical features as calculated from the crystalline melting transition behavior of the first DSC scans of LDPE, IPP before and after grafting. It can be seen that, (T<sub>m</sub>) and heat of melting (ΔH) of the ungrafted LDPE and IPP are 117°C, 158°C, 76 J/g and 52.9 J/g, respectively. However, due to the introduction of 42% PAN/ PVAc in LDPE and 29% PAN/ PVAc in IPP a depression of 1.6°C for LDPE and 6°C for IPP in the T<sub>m</sub> and a decrease in (ΔH) of 24.1 J/g for LDPE and 9.5 J/g for IPP were occurred. A further increase in the graft yield up to 93% for LDPE causes a decrease in T<sub>m</sub> by 2.8°C and a significant drop in (ΔH) by 44.3 J/g is resulted.

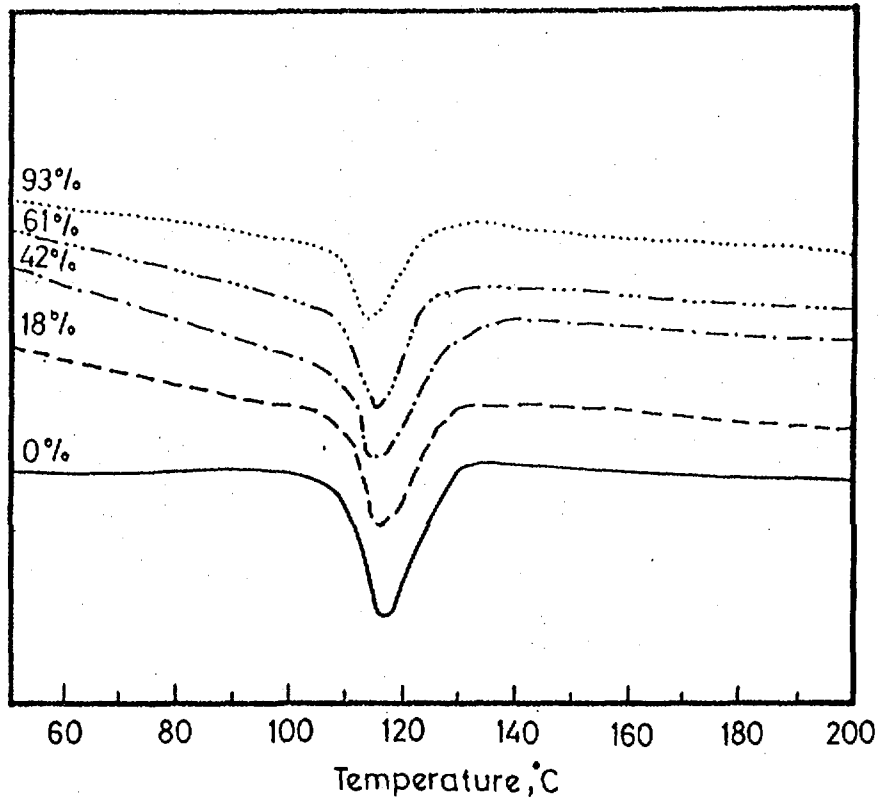


Fig.10: DSC thermogram for a series of LDPE g-p (AN/VAc)

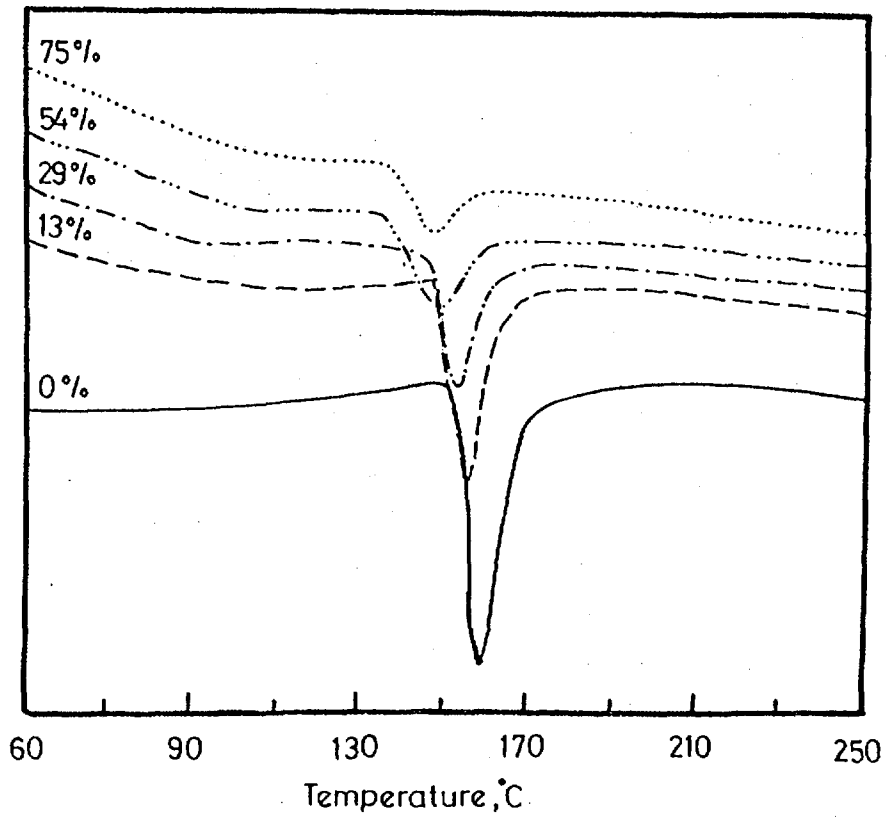


Fig.11: DSC thermogram for a series of IPP g-p (AN/VAc)

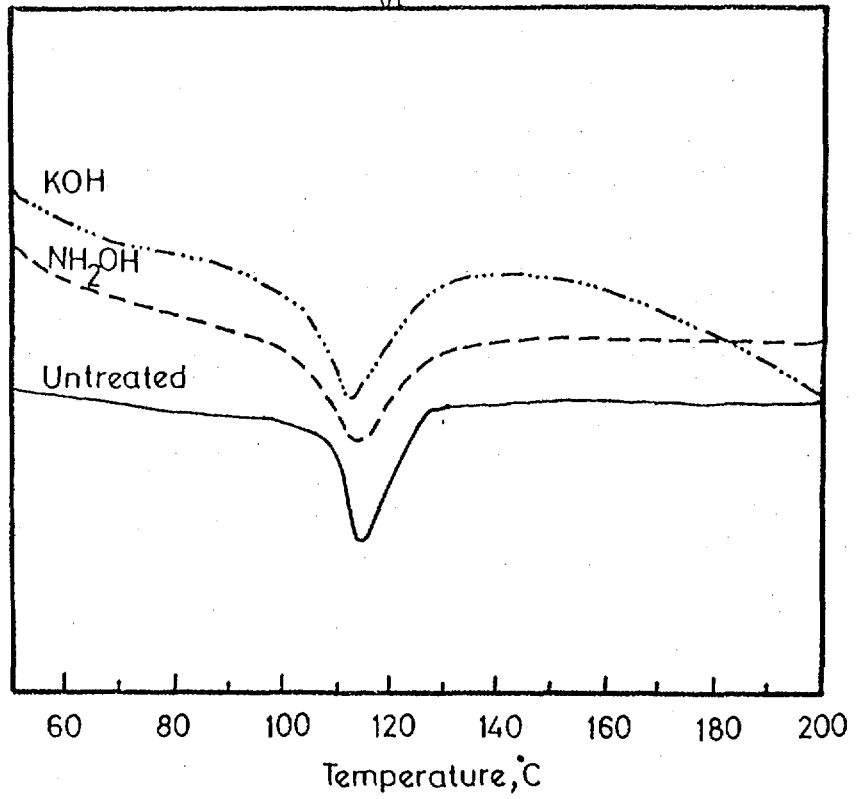


Fig.12: DSC thermogram for grafted treated and untreated LDPE (42 %)

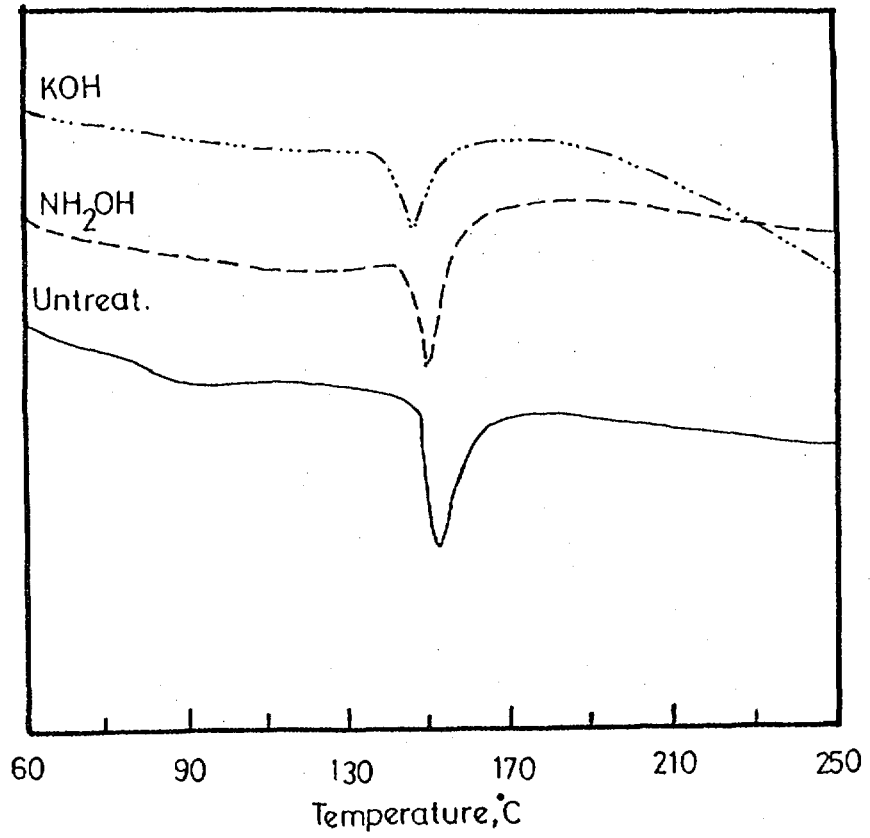


Fig.13: DSC thermogram for grafted treated and untreated IPP (29 %)

**Table 3.** DSC Data For LDPE-g-P(AN/VAc) Copolymer

Degree of grafting(%)	T <sub>m</sub> (°C)	ΔH (J/g)
Blank	117.0	76.0
18	116.2	63.1
42	115.4	51.9
61	115.0	44.2
93	114.2	31.7

**Table 4.** DSC Data For IPP-g-P(AN/VAc) Copolymer

Degree of grafting(%)	T <sub>m</sub> (°C)	ΔH (J/g)
Blank	158	52.9
13	154	47.1
29	152	43.4
54	148	35.7
75	146	29.3

However, the introduction of 75% PAN/ PVAc into IPP causes a depression of 12°C in the T<sub>m</sub> and a decrease in the heat of fusion of 23.6 J/g. The observed depression in T<sub>m</sub> and ΔH with grafting indicated that the crystalline distortion occurred as a result of grafting PAN and PVAc onto LDPE and IPP films. Reduction of ΔH with grafting occurred also due to the amorphous nature of the incorporated (PAN/PVAc) grafts. The decrease in the (ΔH) of the membrane is therefore, due to the accumulative influence of the “dilution effect” and “crystal disruption” in the LDPE and IPP films.

Figures (12 , 13) show the DSC thermograms for untreated and treated membranes. The thermogram of KOH-treated membrane, show a new endothermic transition above 170°C, which may be due to dehydration reaction as reported by many authors for poly (acrylic acid) and its copolymers<sup>(9,10)</sup>. It is also observed that, the beginning of the thermograms for the grafted membranes, especially, for the alkali-treated ones shows a different shapes as compared to the ungrafted polymers. This endothermic reaction around 50 - 100°C represents the loss of absorbed moisture. The absence of prominent endothermic peak in this region for the blank as observed for the grafted copolymer may be due to the lower initial moisture content of the sample.

Tables (5,6) show the thermochemical features as calculated from the crystalline melting transition behavior of the first DSC scans of LDPE, IPP before and after treatment with NH<sub>2</sub>OH or KOH.

**Table 5.** DSC data for untreated and treated grafted LDPE having Grafting, 42%.

Degree of Grafting(%)	T <sub>m</sub> (°C)	ΔH (J/g)
Untreated	115.4	51.9
NH <sub>2</sub> OH	114.2	42.2
KOH	112.4	34.6

**Table6.** DSC data For untreated and treated grafted IPP having Grafting, 29%.

Degree of grafting(%)	T <sub>m</sub> (°C)	ΔH (J/g)
Untreated	152	43.4
NH <sub>2</sub> OH	150	39.4
KOH	146	36.1

From Tables (5 , 6) it can be seen that the treatment with KOH causes a depression of 3°C and 6°C in the  $T_m$  and a decrease in the  $\Delta H$  of 17.3 J/g and 7.3 J/g, for LDPE and IPP, respectively. While the treatment with  $NH_2OH$  decreases the  $T_m$  by 1.2°C and 2°C and also, a depression in  $\Delta H$  by 9.7 J/g and 4 J/g for LDPE and IPP, respectively. These results indicated that, the type of treatment also affects the crystalline structure of the grafted LDPE and IPP. These results revealed that, the crystal size domains in grafted LDPE and IPP decreased by treatment process leading to a reduction in  $T_m$  and  $\Delta H$  values. Such decrement in  $T_m$  and  $\Delta H$  is larger when the grafted membranes was treated with KOH due to the more amorphous nature of the incorporated carboxylic acid groups which easily forms a crosslinked network structure, i.e .higher amorphous content is formed. This leads to the decrease in both  $T_m$  and  $\Delta H$ .

### Conclusion

The structural changes are dependent on the nature of the base polymer as well as the monomer, functional groups introduced into the graft copolymer by chemical treatment and also dependent on the extent of graft copolymerization. These membranes have been found to show a good thermal stability as evaluated by TGA in combination with DSC and can be used under variety of conditions of temperature. Such grafted treated membranes of physical attributes that makes them appear attractive as a support in ion - exchange separation processes.

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