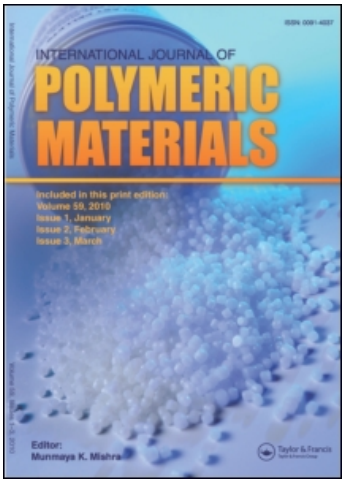

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Characterization and some properties of functionalized graft copolymer

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CHARACTERIZATION AND SOME PROPERTIES OF FUNCTIONALIZED GRAFT COPOLYMER

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The study involved investigation and characterization of membranes prepared by graft copolymerization of acrylonitrile (AN) and vinyl acetate (VAc) binary monomers onto low density polyethylene (LDPE) and isotactic polypropylene (IPP). The mutual γ-irradiation method was used as a grafting technique. 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. The effects of grafting and chemical treatments on the thermal properties and crystallinity of the prepared graft copolymer have been investigated using DSC, TGA and XRD.

Keywords: 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 separation processes and electrochemical applications [1–6]. 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 and also on the base polymer. 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 [6]. The crystallinity has been found to exert strong influence over the transport behavior of molecules through grafted films [7].

In the previous study, preparation of ion-exchange membrane by radiation grafting of (VAc/AN) binary monomers onto LDPE and IPP and the possibility of their practical uses in separation processes, was

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investigated [8]. In the present work, the physical properties of the prepared membranes were determined including melting temperature (T_m), heat of melting (ΔH) and decomposition temperature by DSC and TGA. XRD for the grafted and grafted treated copolymers was performed and compared with the base polymer to clarify their morphological structures and the changes caused by the grafting and chemical treatment.

EXPERIMENTAL

Materials

Low density polyethylene (LDPE) films of thickness 80 μm and Isotactic Polypropylene (IPP) films of thickness 30 μm 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

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

X-ray Diffraction Measurements (XRD)

XRD measurements were conducted on blank, grafted and those treated with KOH or NH_2OH. The diffractograms were obtained using Ni-filtered Cu k_α radiation ($\lambda = 1.54$ Å, at 40 kV and 28 mA) generated by a Philips Pw 1730 apparatus. The scanning speed was 2°/min.

Thermal Stability Measurements

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

RESULTS AND DISCUSSION

IR-Spectroscopy

Infrared analysis in Figure 1, was made for the grafted IPP films to confirm the formation of graft copolymer. The spectrum of IPP-g-P(AN/VAc) films

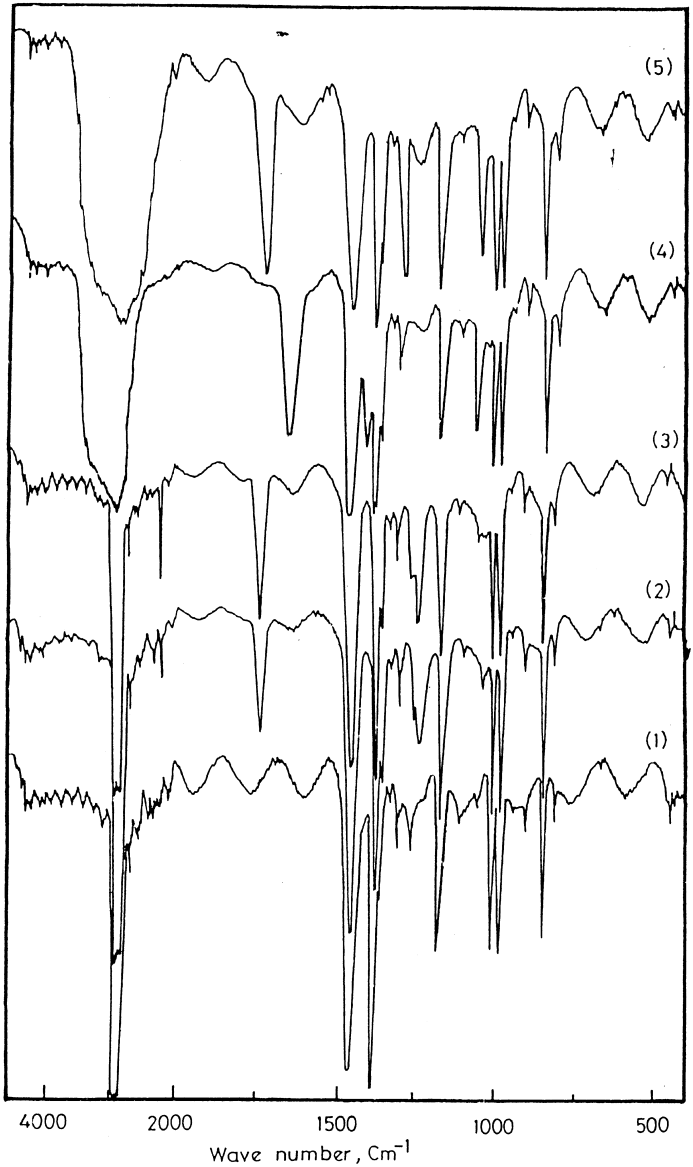

FIGURE 1 IR-Spectra of: (1) Original IPP, (2) IPP-g-P(AN/VAc; 9.5%), (3) IPP-g-P(AN/VAc; 14.1%), (4) 14.1% Treated with NH_2OH, (5) 14.1% Treated with KOH.

shows a characteristic band of C≡N group of PAN at 2250 cm^{-1}. New absorption bands appeared around 1740 cm^{-1}, 1240 cm^{-1} and 1099 cm^{-1} which correspond to C=O, C—O and O—C=O stretching of acetate

groups, respectively. It is also noted that the intensity of these absorption bands increases with increasing the graft percent (spectra 2, 3).

IR-spectra for NH_2OH and KOH-treated membranes (spectra 4, 5) showed that the absorbance at 2250 cm^{-1} disappeared and a broad absorption band appeared around 3200 – 3600 cm^{-1} and other peak at 1050 cm^{-1} which are assigned to OH and C—O of alcoholic groups, respectively. For KOH-treated films, new absorption bands appeared around 1711 cm^{-1} and 1290 cm^{-1} which are the characteristic bands of C=O and C—O streching of carboxylic groups. For NH_2OH-treated films new absorption bands appeared around 1425 cm^{-1} and 1650 cm^{-1} which are the characteristic bands of C—N and amidoxime groups. The appearance of broad band around 3170 – 3350 cm^{-1} was signed to N—H group of amidoxime that resulted from the treatment of nitrile group with NH_2OH – HCl [9].

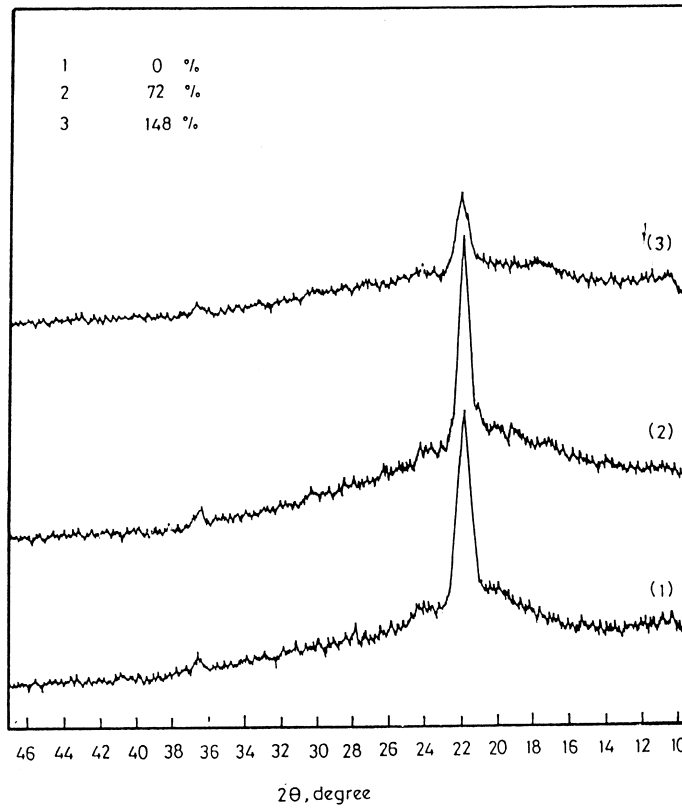

FIGURE 2 XRD-Patterns of blank LDPE and its graft copolymer with different degrees of grafting.

X-ray Studies (XRD)

X-ray diffractograms of various samples; the blank LDPE and IPP films, graft copolymers of different degrees of grafting and graft copolymer treated with KOH or alcoholic NH_2OH, are presented in Figures 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 occur 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 and 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 appears only due to dilution of crystalline fraction by the incorporation of the amorphous PAN and PVAc chains into the polymer matrix [7, 10].

It is obvious from Figures 4, 5 that the diffraction curves of the treated-graft copolymer recorded in the same region, and it does not show any new

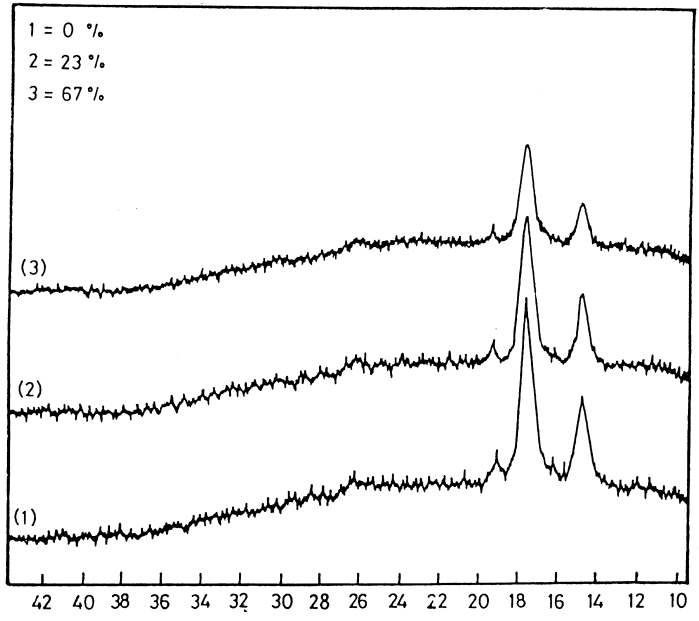

FIGURE 3 XRD-Patterns of blank IPP and its graft copolymer with different degrees of grafting.

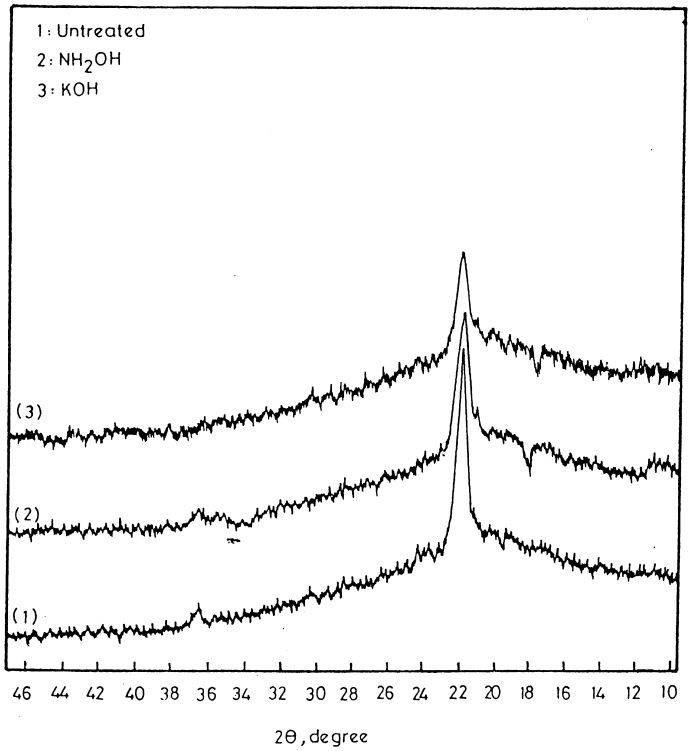

FIGURE 4 XRD-Patterns of untreated grafted LDPE (72%) and its treated form.

diffraction peak. It is also observed that the intensity of crystalline diffraction peak decreases if compared with that of the grafted 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 large decrease in crystallinity for KOH-treated membrane reflects the higher polarity of the carboxylic acid groups than the amidoxime ones.

Thermal Properties

Thermal Gravimetric Analysis (TGA)

TGA thermograms for the blank and the grafted LDPE and IPP films with various degrees of grafting are presented in Figures 6, 7, respectively. The ungrafted-LDPE and IPP showed stable thermograms up to a temperature of $\approx 400°C$, beyond which a smooth decrease in weight is observed. A single stage character of the degradation is evident from the curves and complete

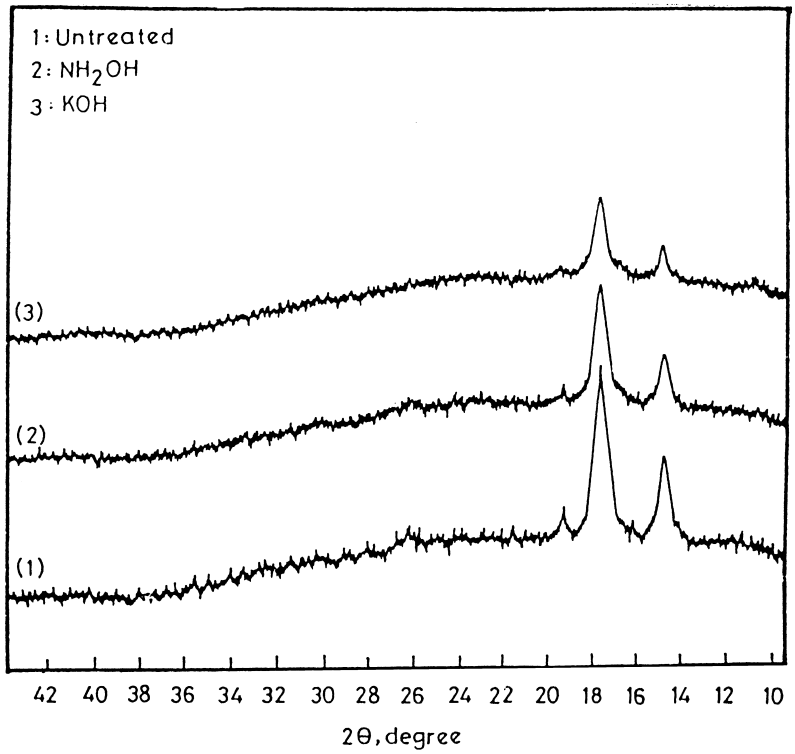

FIGURE 5 XRD-Patterns of untreated grafted IPP (23%) and its treated form.

depolymerization of the sample to monomer occurs at ≈ 500°C and ≈ 470°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°C may be attributed to the elimination of adsorbed moisture and side graft chains degradation [11]. The second decomposition stage, observed in the temperature ranges of 400–500°C for LDPE and 400–470°C for IPP, is due to extensive degradation of the polymer backbone chain leaving a residue. The residue from the grafted LDPE and IPP 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 probably due to the increase in crosslink formation with degree of grafting.

Table 1 represent the weight loss percent at different decomposition temperatures for LDPE and IPP grafted with P(VAc/AN). From the quantitive comparison of weight loss in the temperature range of 50–400°C,

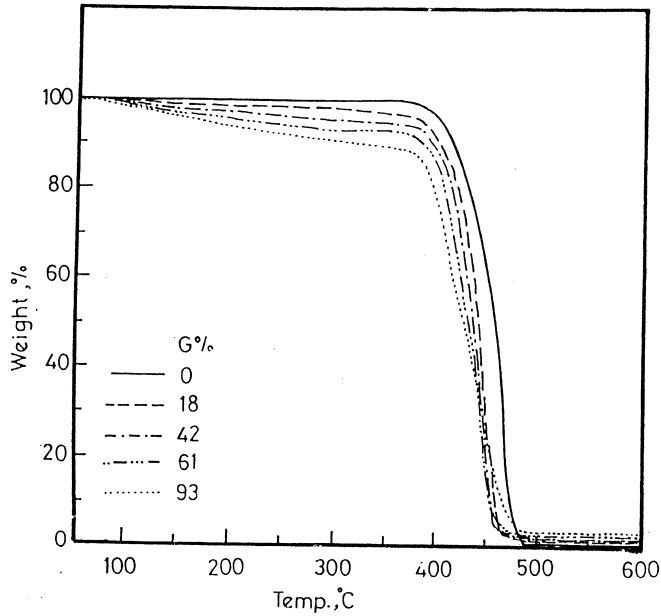

FIGURE 6 TGA thermal diagram for a series of LDPE g-P(AN/VAc).

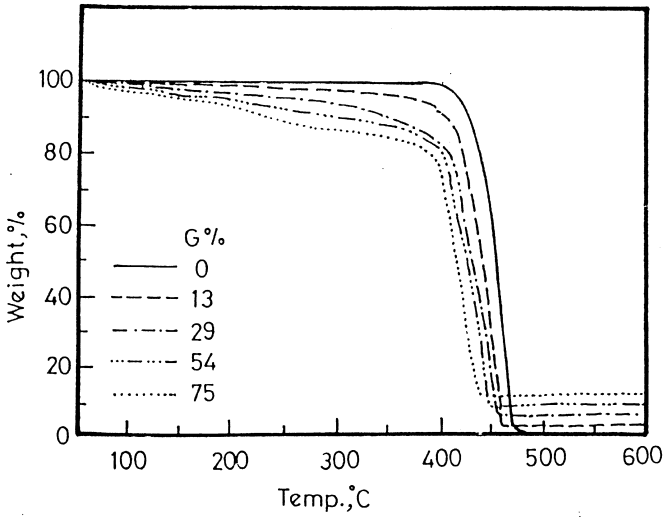

FIGURE 7 TGA thermal diagram for a series of IPP g-P(AN/VAc).

TABLE 1 The weight loss of grafted LDPE and IPP membranes as a function of temperature

	Degree of grafting (%)							
	Weight loss (%)							
	LDPE				*IPP*			
Temp. (°*C*)	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	1.0	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

it is observed that the weight loss increases with increasing grafting percent. Such increment in weight loss with grafting 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 grafted-untreated and treated membranes by either KOH or alcoholic NH_2OH. 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_2OH does not introduce a new decomposition temperature. For the KOH-treated membranes, 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 base polymer.

The high value of the initial weight loss in the case of KOH-treated membranes compared to the NH_2OH-treated ones is due to the higher hydrophilicity of these membranes and consequently higher absorbed moisture than for those NH_2OH-treated ones. Table 2 shows that the thermal stability for the grafted-untreated is higher than NH_2OH and KOH-treated membranes.

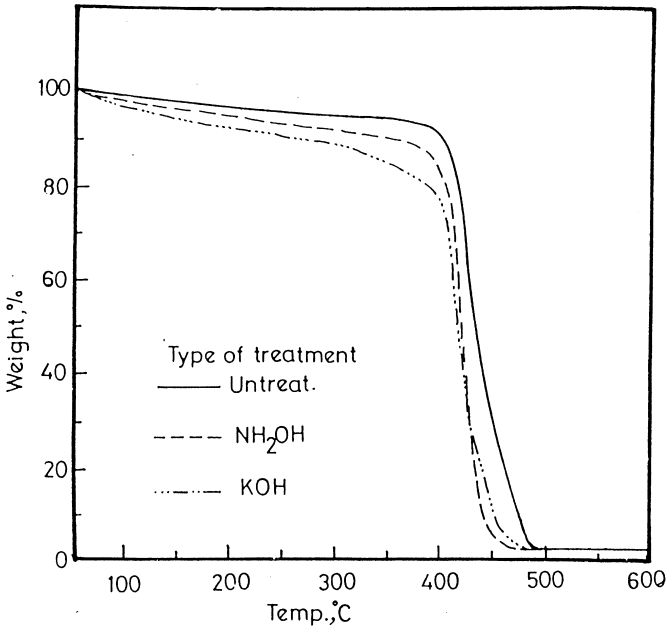

FIGURE 8 TGA thermal diagram for treated grafted LDPE (42%).

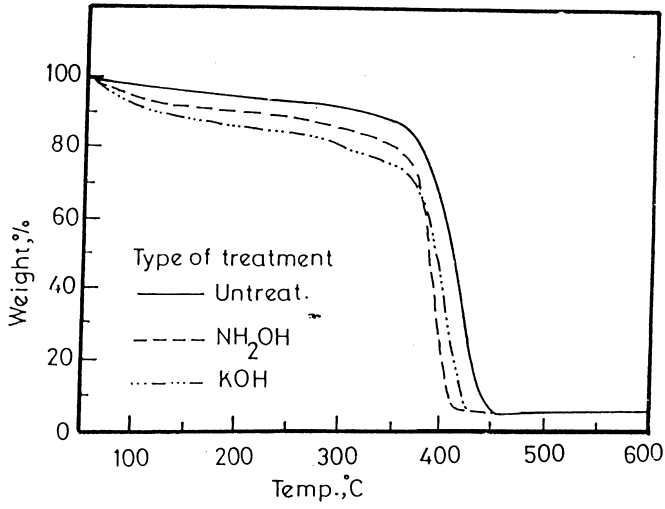

FIGURE 9 TGA thermal diagram for treated grafted IPP (29%).

TABLE 2 The weight loss of the treated and untreated grafted LDPE (42%) and IPP (29%) membranes as a function of temperature

	Weight loss (%)					
	LDPE membrane			*IPP membrane*		
Temp. (°C)	*Untreated*	NH_2OH	*KOH*	*Untreated*	NH_2OH	*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

Changes in Thermal Parameters

Changes in thermal parameters for the prepared grafted membranes were masured by DSC which is mainly used for studies of physical transitions. Figures 10, 11 show the DSC thermograms of ungrafted and grafted LDPE

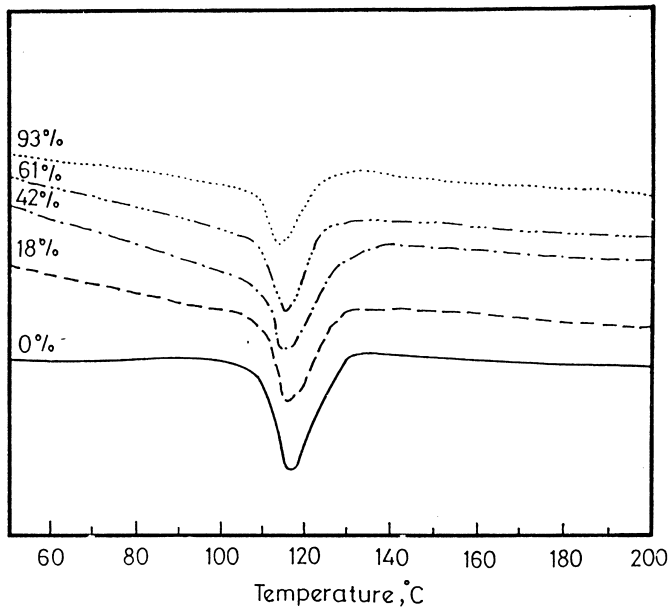

FIGURE 10 DSC thermogram for a series of LDPE g-P(AN/VAc).

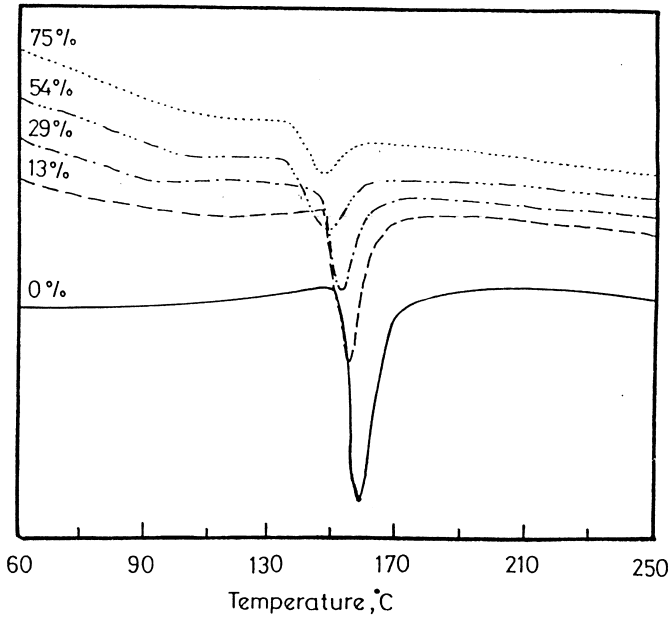

FIGURE 11 DSC thermogram for a series of IPP g-P(AN/VAc).

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_m) of the 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 membranes.

Tables 3, 4 show the thermochemical features as calculated from the crystalline melting transition behavior of the first DSC scans of LDPE and IPP before and after grafting. It can be seen that T_m 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% P(AN/VAc) into LDPE and 29% PAN/PVAc into IPP a depression in T_m of 1.6°C for LDPE and 6°C for IPP and a decrease in ΔH of 24.1 J/g for LDPE and 9.5 J/g for

TABLE 3 DSC Data for LDPE-g-P(AN/VAc)

Degree of grafting (%)	T_m (°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)

Degree of grafting (%)	T_m (°C)	ΔH (J/g)
13	154	47.1
29	152	43.4
54	148	35.7
75	146	29.3

IPP occurred. A further increase in the graft yield up to 93% for LDPE causes a decrease in T_m by 2.8°C and a significant drop in ΔH by 44.3 J/g.

However, the introduction of 75% P(AN/VAc) into IPP causes a depression of 12°C in T_m and a decrease in ΔH of 23.6 J/g. The observed depression in T_m and ΔH with grafting indicated that crystalline distortion may have occurred as a result of grafting of P(AN/VAc) onto LDPE and IPP films. Reduction of ΔH with grafting occurred also due to the amorphous nature of the incorporated P(AN/VAc) grafts. Such decrease in ΔH of the graft copolymer may, therefore, be due to the cumulative 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, shows a new

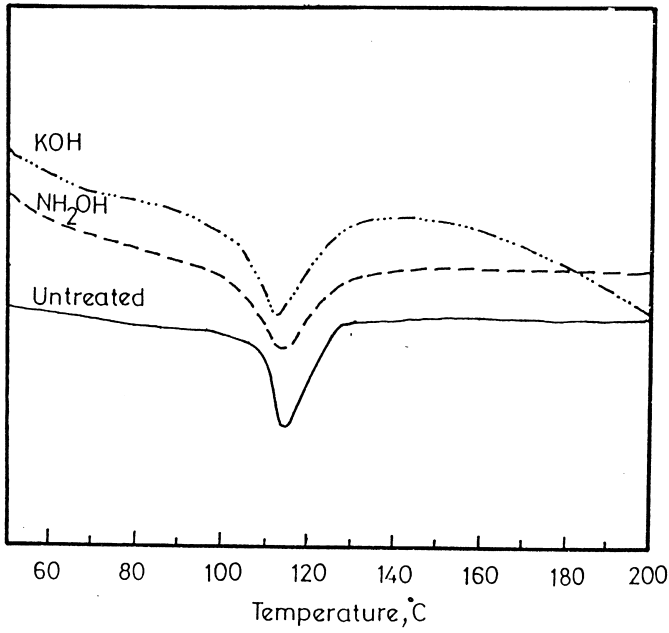

FIGURE 12 DSC thermogram for grafted treated and untreated LDPE (42%).

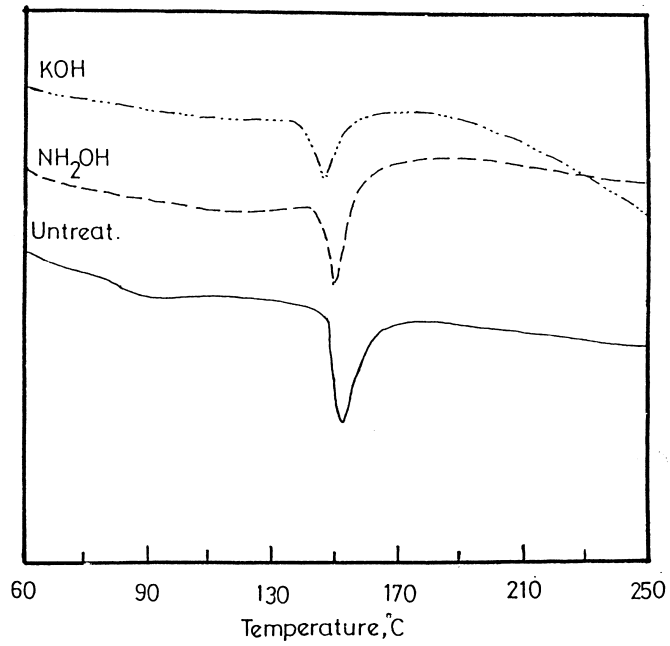

FIGURE 13 DSC thermogram for grafted treated and untreated IPP (29%).

endothermic transition above 170°C, which may be due to dehydration reaction as reported by many authors for poly (acrylic acid) and its copolymers [12, 13]. It is also observed that the beginning of the thermograms for the grafted membranes, especially for the alkali-treated ones, shows a different shape 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 is 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 and IPP before and after treatment with NH_2OH or KOH.

TABLE 5 DSC data for untreated and treated grafted LDPE having 42% graft

Degree of grafting (%)	T_m (°C)	ΔH (J/g)
Untreated	115.4	51.9
NH_2OH	114.2	42.2
KOH	112.4	34.6

TABLE 6 DSC data for untreated and treated grafted IPP having 29% graft

Degree of grafting (%)	T_m (°C)	ΔH (J/g)
Untreated	152	43.4
NH_2OH	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 T_m and a decrease in ΔH 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 ΔH by 9.7 J/g and 4 J/g for LDPE and IPP, respectively. These results indicate that the type of treatment, too, affects the crystalline structure of the grafted LDPE and IPP. The above results revealed that, the crystal size domains in the grafted LDPE and IPP decreased by treatment process leading to a reduction in T_m and ΔH values. Such decrement in T_m and ΔH is larger when the grafted membranes were 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.

CONCLUSION

The structural changes are dependent on the nature of the base polymer as well as the 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 possess physical attributes that make them appear attractive as support in ion-exchange separation processes.

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