

Functionalization of polyethylene by graft copolymerization for separation processes

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Abstract. Incorporation of polar functional moieties into polyethylene (PE) film has been achieved by graft copolymerization of polar monomers such as methacrylic acid (MAAc) and acrylamide (AAm) on to PE film, preirradiated with γ -rays from ^{60}Co source, using benzoyl peroxide (BPO) as initiator in aqueous medium. Percentage of grafting of MAAc and AAm was determined as a function of irradiation dose, monomer and initiator concentration, temperature, reaction time and amount of water. Maximum percentage of grafting of MAAc (1453%) and AAm (21.28%) was obtained at $[\text{MAAc}] = 235.3 \times 10^{-2} \text{ mol/L}$, $[\text{AAm}] = 23.4 \times 10^{-2} \text{ mol/L}$, $[\text{BPO}] = 5.5 \times 10^{-2} \text{ mol/L}$ and $16.5 \times 10^{-2} \text{ mol/L}$ at 80°C , 90°C in 180 min and 90 min respectively. The grafted PE films were characterized by FTIR, Thermogravimetric analysis (TGA) Scanning Electron Micrography (SEM) and X-ray diffraction methods. Some selective properties of grafted films such as swelling behavior, ion and metal uptake have been carried out. The biodegradation studies of the grafted PE films have also been investigated. The grafted films developed superior swelling behavior with maximum swelling (480%) in water as compared to pristine PE (13.55%), better thermal stability and ion and metal uptake studies showed promising results that can be effectively used for desalination of brackish water and separation of metals from the industrial effluents.

Keywords: polyethylene film; swelling; ion separation; metal uptake; biodegradation; desalination

1. Introduction

Synthetic polymeric membranes continue to derive their utility in separation science and therefore are the subject of intensive research. Polymers derived from hydrocarbon monomers due to their excellent physical properties and chemical inertness are being used in large amount in wide range of applications. However, the materials from these polymers are hydrophobic and lack functionalities and hence have restricted applications as membranes.

Membrane technology, using graft copolymerization to produce functionalized membranes, offer a much greater potential for the complete management of separation than that using individual polymer (Cabasso 1989). With grafted membranes one could revolutionize the biochemical, pharmaceutical and other chemical industries (Jiratananon 1997, Johnson and Tragardh 1990). Grafting of glycidyl methacrylate to polypropylene in an extruder, initiated with organic peroxide was carried out by Pesetskii and Makarenko (2002). UV induced graft copolymerization of Ar plasma pretreated PTFE and PVDF films was carried out by Yang *et al.*

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(2002). Strongly acidic membranes are commonly prepared by grafting of polystyrene branches onto polymer films and the resulted grafted films are subsequently sulphonated (Walsby 2001). Ion exchange membranes modified with sulphonic and phosphonic acid groups were prepared by radiation induced grafting of glycidyl methacrylate onto PE film and subsequent sulphonation and phosphonation of poly (GMA) graft chains by Choi *et al.* (1999). Grafting of 4-vinylpyridine (4-VP) and methacrylonitrile (MAN) onto Teflon- FEP film by preirradiation method in aqueous medium was carried out by Kaur *et al.* (2001). Salt rejection studies of PE films grafted with 4-VP and binary mixture of 4-VP and MAN were carried out by Kaur *et al.* (1997). Temperature stimuli responsive polymer, poly (N-isopropylacrylamide), PNIPAAm, was grafted into tubular- type porous PE membranes by the plasma induced graft copolymerization technique (Wang 2002). Gamma- radiation was used in every step of the synthesis of a sequential interpenetrating polymer net work made of two smart polymers i.e., polyacrylic acid and PNIPAAm, the later grafted onto PP with the aim of developing medicated coatings for medical devices (Munoz-Munoz *et al.* 2009). Zhang *et al.* (2008) prepared low dielectric constant porous films of HDPE grafted with maleic anhydride by thermally induced phase separation. Effectiveness of polyvinyl alcohol membranes selected for ultra filtration of synthetic oily water was evaluated by Wu *et al.* (2008). PE microfiltration films and composite nano filtration membranes were elaborated by Enyashovich *et al.* (2005). Electrical and mechanical properties of PE film grafted with methacrylic acid by mutual method were investigated by Omichi *et al.* (1986). Hegazy *et al.* (1989) studied the effects of different solvents on the radiation grafting of methacrylic acid on to PTFE films. Graft copolymerization of mixture of monomers such as acrylonitrile/acrylic acid, acrylonitrile/methacrylic acid and acrylonitrile/glycidyl methacrylate on to preirradiated PE films was studied by Choi *et al.* (2000). Recently radiation induced grafting of binary mixture of methacrylic acid and 4-VP on to Teflon-FEP films has been successfully carried out by Kaur *et al.* (2010) with the graft showing good ion separation behavior.

It is thus, observed from the literature that not much of work is reported on the grafting of methacrylic acid and acrylamide on to preirradiated PE film. Therefore, in the present studies commercial polyethylene film has been modified through graft copolymerization of vinyl monomers with polar functionalities that can impart both membrane properties and degradation behavior without disturbing the inherent properties of the pristine film. Monomers such as methacrylic acid (MAAc) and acrylamide (AAm) carrying carboxyl and amide as pendent functional groups are grafted onto peroxidized PE films using benzoyl peroxide as radical initiator thereby avoiding post grafting reactions to convert the groups into ionic moieties for further interactions. Optimum reaction conditions for affording maximum and homogenous grafting have been evaluated. The properties such as swelling, ion and metal uptake and biodegradable behavior of the grafted membranes were also evaluated.

2. Experimental

2.1 Materials and method

PE film (0.54 mm) was obtained through the courtesy of Prof. Nichole of CNRS Thiasis, Paris, France. Benzoyl peroxide (BPO) (S.D. fine, Mumbai), methacrylic acid (Merck) and acrylamide (Merck) were used as received. Distilled water was used as the reaction medium.

2.2 Irradiation of PE film

PE film was cut into small strips of size (2 cm x 4 cm), washed with methanol, dried and weighed. The film samples were irradiated with gamma rays from ^{60}Co source housed in Gamma chamber-900 at a constant dose rate of 2.052 kGy/h for different time periods.

2.3 Graft copolymerization

To the peroxidized and weighed PE film placed in a standard joint two necked flask was added a definite amount of water (2.5 ml-30 ml), known amount of monomer (MAAc/AAm) (5.9×10^{-2} mol/L- 58.83×10^{-2} mol/L) and the initiator, benzoyl peroxide (4×10^{-2} mol/L- 16.5×10^{-2} mol/L). The reaction mixture was refluxed for definite time periods, under constant stirring at a constant temperature (50°C - 90°C). After the reaction was over, the grafted film was washed with water to completely remove the homopolymer, poly (MAAc)/ poly (AAm). The grafted film, free from homopolymer, was dried till constant weight. Percentage of grafting (Pg) was calculated from the increase in the weight of pristine film as follows

$$\%Grafting = \frac{W_g - W_o}{W_o} \times 100$$

where W_o and W_g are respectively the weights of pristine film and grafted film after the complete removal of the homopolymer. Percentage of grafting was determined as a function of total dose, concentration of monomer and initiator, time, temperature and amount of water.

2.4 Biodegradation studies

Biodegradation of pristine PE and grafted PE i.e., PE-g-poly (MAAc) and PE-g-poly (AAm) was studied by soil burial method.

Garden soil freed from pebbles and unwanted matter was collected from the area of good plantation and measured its pH and moisture content. Soil of known moisture content (22.71%) and pH (7.85) was taken in different pots. A weighed amount of each of the samples i.e., pristine PE film, PE-g-poly (MAAc) and PE-g-poly (AAm), wrapped respectively in loose knitted synthetic net, were placed separately in the pots and care was taken that the samples were completely buried under the soil. Samples were removed after a specific number of days for assessment of change in the weight during the period. Percent weight loss, determined as a function of number of days, was calculated as follows

$$\%Wt.loss = \frac{W_0 - W}{W_0} \times 100$$

where W_0 and W respectively were the initial and final weights of the sample after a specific number of days (a gap 10 days was maintained).

In order to check the effect of nitrogenous compounds on the degradation of samples of PE film and PE grafts, the soil beds were also supplemented with organic fertilizer (6 gm of urea per kg of soil) to encourage an active microbial flora. All the samples as discussed were placed similarly under urea enriched soil and the loss in weight was noted. The loss in weight with time was

monitored by weighing the samples after a regular interval of time (10 days) and percent weight loss was determined as discussed above.

3. Evidence of grafting

3.1 Area change

The size of the film was found to increase upon grafting. Percent area change of the grafted films was determined from the increase in the area of the original film after grafting as follows

$$\text{Area change} = \frac{\text{Final area} - \text{Initial area}}{\text{Initial area}} \times 100$$

3.2 FTIR spectroscopy

FTIR spectra of pristine PE film, PE-g-poly (MAAc) and PE-g-poly (AAM) were obtained on Nicolet-5700 IR Spectrophotometer.

3.3 Thermo gravimetric analysis

Thermo gravimetric analysis of the pristine and grafted PE was carried out on Shimadzu DTA-60 H Thermal Analyzer.

3.4 Scanning electron micrography

Surface topology and homogeneity of PE film and grafted PE film i.e., PE-g-poly (MAAc) and PE-g-poly (AAM) was studied by scanning electron micrography (JEOL JSM 6100).

3.5 X-ray diffraction Studies

The X-ray diffraction (XRD) patterns of the samples were recorded on a Philips PANALYTICAL X'PERT PRO X-ray powder diffraction using Cu K α ($\lambda = 1.54060 \text{ \AA}$) radiation. The crystallite size of samples was measured from the X-ray line broadening analysis using Debye-Scherrer formula after accounting for instrumental broadening.

$$D_{XRD} = \frac{0.89\lambda}{\beta \cos \theta}$$

Where λ is the wavelength of X-ray used in \AA , β is the full width at half-maximum (FWHM) in radians in the 2θ scale, θ the Bragg angle.

3.6 Swelling studies

Dried and weighed pristine PE film and PE-g-poly (MAAc) of $2 \times 2 \text{ cm}^2$ size each were immersed in solvents of different polarity such as water, methanol, ethanol and benzene at 25°C for 24 h and 48 h. After the stipulated time period, the films were removed from the solvents and

dried between the folds of filter paper to remove the liquid adhering to the surface and weighed immediately. The percentage of swelling was calculated as

$$\text{Percentage of swelling} = \frac{W_s - W_d}{W_d} \times 100$$

where W_s and W_d are the weights of the swollen and dry films respectively.

3.7 Ion uptake studies

Ion uptake studies of pristine PE film and the grafted PE film samples, PE-g-poly (MAAc) and PE-g-poly (AAM) ($2 \times 2 \text{ cm}^2$ each) from 0.5% aqueous electrolytic solutions of NaCl, KCl, Na_2SO_4 and K_2SO_4 at 37°C were studied as a function of percentage of grafting. The samples of the pristine PE and grafted PE films were placed separately in 50 mL of 0.5% aqueous solutions of NaCl, KCl, Na_2SO_4 and K_2SO_4 for different time period. After the stipulated time of immersion, the films were removed from the solution and the conductance of the electrolytic solution was noted. In order to ascertain the ion uptake, the films were dried and immersed in the double distilled water for different time periods to leach out the ions. The conductance of water was taken before and after the immersion of the film.

3.8 Sorption of heavy metal ions

Grafted samples were used for the removal of the heavy metals ions such as Cu (II), Ni (II) and Fe (II) that generally exist in waste water, from their respective salt solutions. For accomplishing this purpose, separate 0.1 M aqueous solution of these metal ions were prepared and the standard curves were drawn at the characteristic wavelength of each metal ion solution (307, 392 and 248.3 nm) using UV-Vis spectrophotometer (Biochem 1100-1200).

For metal uptake studies, the pristine PE film and the grafted PE film ($2 \times 2 \text{ cm}^2$ each) were suspended separately in the metal ion solution (Cu^{+2} and Ni^{+2}) for different time periods (4 h, 8 h, and 24 h) and only for 1h in case of Fe^{+2} beyond which the oxidation to Fe^{+3} starts at 25°C . After the stipulated time, the films were removed from the metal solutions and the optical density (O.D.) of the residual metal solution was taken. The percent metal uptake was determined from the standard curve.

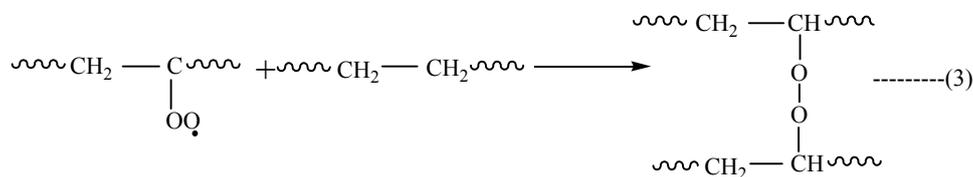
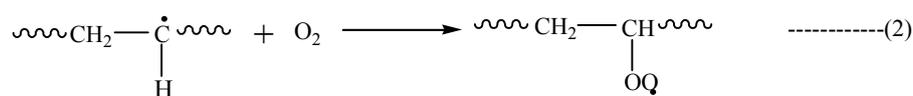
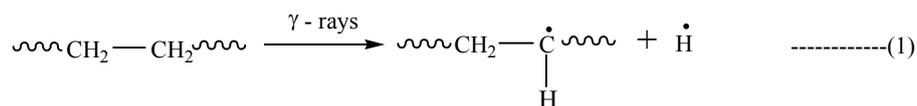
4. Results and discussion

4.1 Mechanism of grafting

Irradiation of PE film in air causes oxidation of PE film with the formation of peroxy linkages. The peroxidized PE film is subjected to graft copolymerization in the presence of monomers using BPO as initiator. Recently, it has been reported that gamma irradiation of PE also generates hydroperoxides groups onto PE with total dose of 150 kGy using lower dose rate (0.04 kGy/h) and the concentration of the hydroperoxides decreases with increasing the dose rate to 0.69 kGy/h (Buttafava 2007). In the present studies, since high dose rate of 2.052 kGy/h has been used and the total dose (49 kGy) given is less, the formation of hydroperoxides does not seem to be formed.

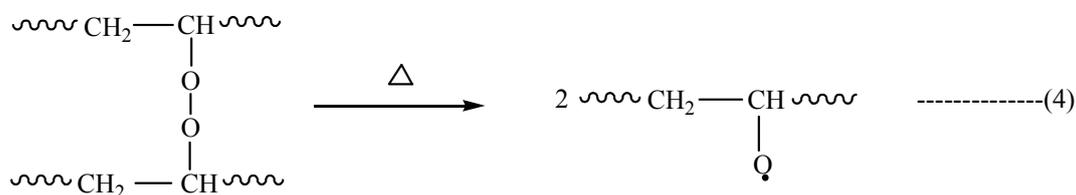
Therefore, the process of graft copolymerization of monomer onto peroxidized PE film by chemical method takes place by the following mechanism.

Irradiation of PE film

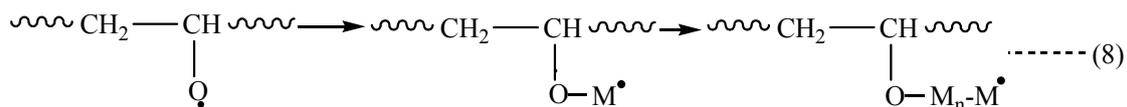
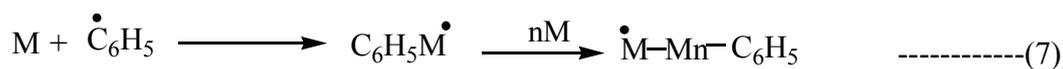
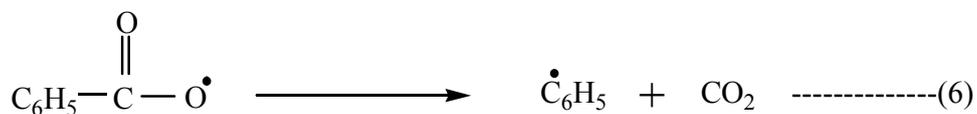
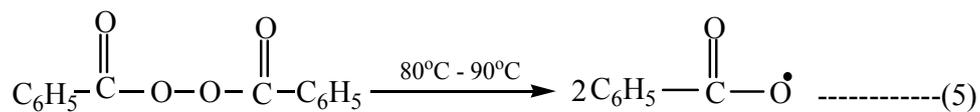


4.2 Initiation and propagation

The peroxidized PE film decomposes upon heating to generate macroperoxy radicals which offer the sites for grafting.



The decomposition of BPO also generates active radicals which activate the monomer.



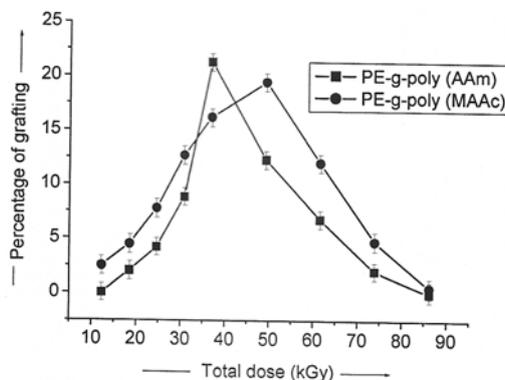
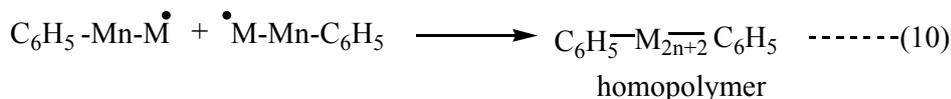
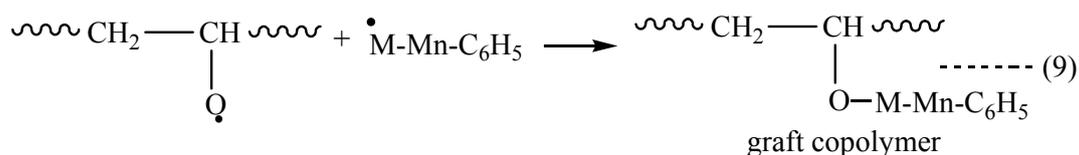


Fig. 1 Effect of total dose on percentage of grafting of AAm and MAAC onto PE film

Termination



Grafting of monomers take place by either grafting from (Eq. (8)) or grafting onto (Eq. (9)) processes, while simultaneously homopolymer formation also takes place according to Eq. (10).

4.3 Effect of reaction parameters

Optimum reaction conditions such as total dose, [MAAc], [AAm], [BPO], temperature, time and amount of water pertaining to maximum percentage of grafting of MAAC and AAm have been evaluated and the results are explained in the light of the mechanism.

4.4 Effect of total dose

Percentage of grafting of AAm and MAAC onto PE films was studied as a function of total dose and the results are presented in Fig. 1. It is observed from the Figure that the percentage of grafting of AAm and MAAC experiences a gradual increase in percentage of grafting with increasing total dose. Maximum grafting of AAm and MAAC (21.28%, 19.6%) was observed respectively at an optimum total dose of 36.94 kGy and 49.25 kGy beyond which it decreases continuously. With increasing total dose, formation of radicals takes place on the surface and the bulk of the film which offer active sites for grafting either by ‘‘Grafting onto’’ (Eq. (8)) or ‘‘Grafting from’’ (Eq. (9)) methods. Decrease in percentage of grafting beyond the optimum value may be due to the reason that at higher total dose some chain scission reactions also takes place thus lowering percentage of grafting. Similar observations were made during radiation induced grafting of acrylic acid onto rayon fiber (Kaur 2010).

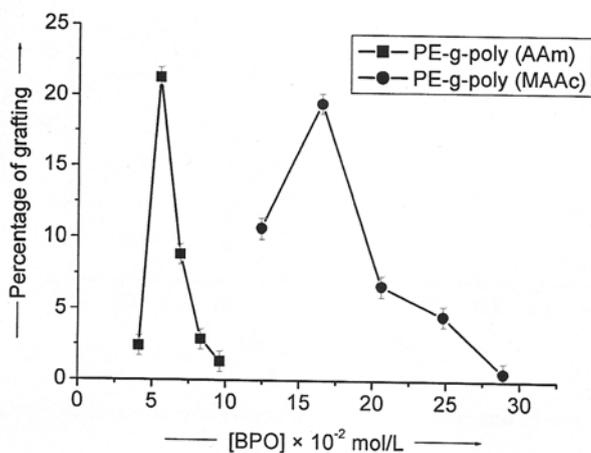


Fig. 2 Effect of initiator concentration on percentage of grafting of AAm and MAAC onto PE film

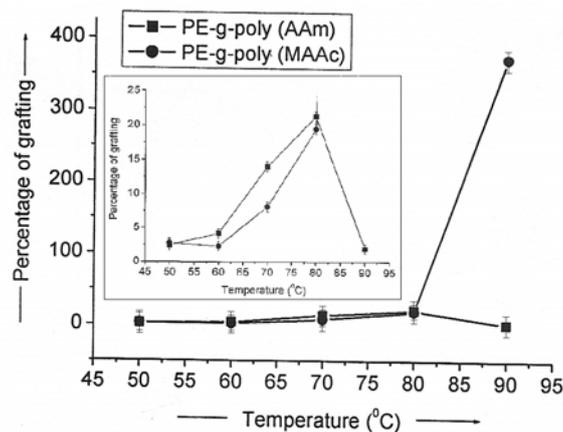


Fig. 3 Effect of temperature on percentage of grafting of AAm and MAAC onto PE film

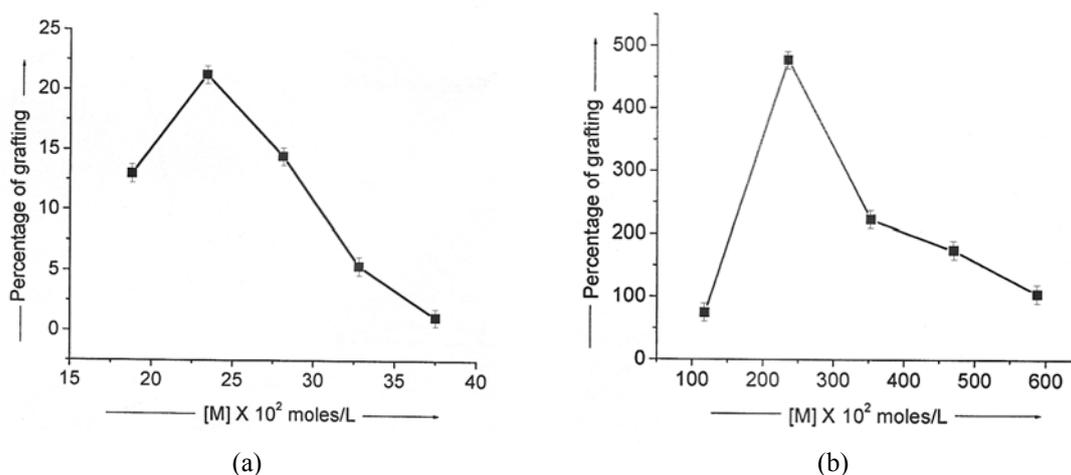


Fig. 4 Effect of monomer concentration on percentage of grafting of (a) AAm onto PE film (b) MAAC onto PE film

4.5 Effect of [BPO]

Fig. 2 represents the effect of concentration of BPO on percentage of grafting of AAm and MAAC onto PE film. It is observed from the Figure that percent grafting of both the monomers increases with increasing [BPO], giving maximum (21.28% and 19.46%) at [BPO] = 5.5×10^{-2} mol/L and 16.5×10^{-2} mol/L respectively. Further increase in [BPO] beyond the optimum value decreases percentage of grafting. Initial increase in the percent grafting is due to the increase in the number of free radicals due to increasing [BPO], which initiate the monomer that leads to graft formation. With increasing concentration of BPO, initiation of monomer with increased free radicals from BPO leads to preferential homopolymer formation leading to decrease in percent grafting. In addition, at higher concentration, BPO also undergoes induced decomposition (Misra 1979) leading to decrease in the initiator concentration lowering the radical concentrations that subsequently decrease percentage of grafting.



4.6 Effect of temperature

Effect of temperature on percentage of grafting of AAm and MAAC onto PE film was studied and the results are presented in Fig. 3. It is observed from the Figure that percentage of grafting of AAm rises continuously with increasing temperature giving maximum percentage (21.28%) at 80°C beyond which it decreases. However, in case of MAAC, it is observed that percentage of grafting remain constant up to 80°C beyond which it shoots to give maximum grafting (372.2%) at 90°C . Percentage of grafting was found to increase with further rise in temperature (the area of the film increases) but the film loses its strength.

Increase in grafting percentage with increasing temperature is attributed to the reason that higher temperature leads to (1) higher rates of BPO decomposition leading to more free radicals and (2) higher rates of monomer diffusion from the solution phase to the active sites. Decrease in percent grafting beyond optimum temperature is attributed to the occurrence of various chain transfer and other reactions such as thermal polymerization.

4.7 Effect of monomer concentration

Figs. 4(a) and (b) respectively represent the effect of concentration of AAm and MAAC on percentage of grafting of AAm and MAAC onto PE film. It is observed that the percentage of grafting of both the monomers increases with increasing monomer concentration giving maximum (21.28%, 478%) at [AAm] = 23.4×10^{-2} mol/L and [MAAC] = 235.3×10^{-2} mol/L respectively beyond which it decreases. The decrease in percentage of grafting beyond optimum monomer concentration is due to the preferential homopolymer formation.

4.8 Effect of reaction time

Graft copolymerization of AAm and MAAC onto PE film was studied as a function of reaction time and the results are presented in Fig. 5. It is observed from the Figure that percent grafting of AAm and MAAC increases with increasing reaction time giving maximum grafting percentage

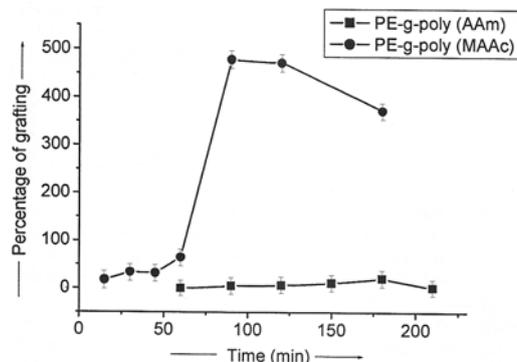


Fig. 5 Effect of time on percentage of grafting of AAm and MAAC onto PE film

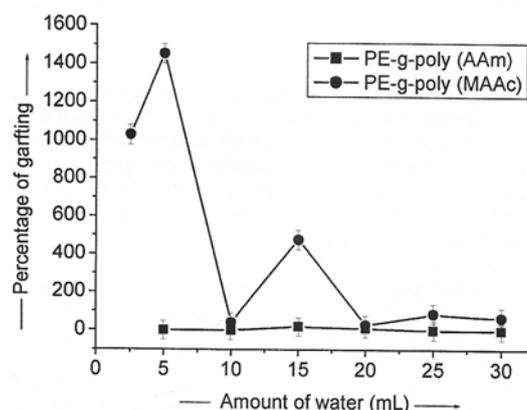


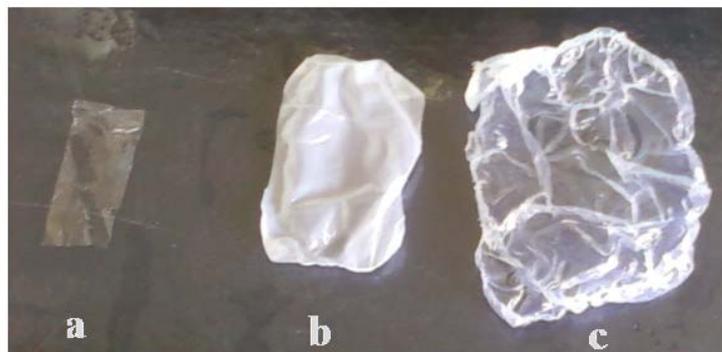
Fig. 6 Effect of amount of water on percentage of grafting of AAm and MAAC onto PE film

(21.28%, 478%) with in 180 min and 90 min respectively beyond which it decreases. The decrease in grafting may be due to induced decomposition of the initiator with increasing time of reaction which over all decreases the concentration of the initiator.

4.9 Effect of amount of water

Effect of amount of water on grafting percentage of AAm and MAAC onto PE film was studied and the results are presented in Fig. 6. Maximum percentage of grafting 21.28% and 1453% of AAm and MAAC was obtained using 15 and 5 ml of water respectively. Further increase in the amount of water decreases percentage of grafting of both the monomers. Acrylamide undergoes solvent transfer reaction with water. The reported C_s value for AAm with water is high ($C_s = 5.8 \times 10^{-4}$ at 40°C) (Kwang-Fu 1972), thus the monomer is wasted in the side reaction leading to decrease in grafting percentage of AAm. In case of MAAC, the accessibility of monomer is decreased to the active sites due to high solvation of the monomer.

5. Evidence of grafting



Percent area change of PE-g-poly (MAAc) as a function of percentage of grafting (a) Pristine PE film (b) PE-g-poly (MAAc) 174.5% and (c) PE-g-poly (MAAc) 223.3%

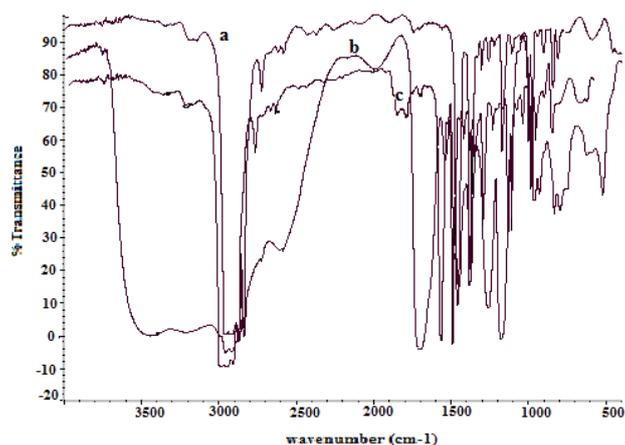


Fig. 7 FTIR of (a) pristine PE film, (b) PE-g-poly (MAAc) and (c) PE-g-poly (AAM)

Table 1 Percent area change of PE-g-poly (MAAc) as a function of percentage of grafting

S. No.	Sample	% Grafting	Area (Sq. cm)	% Area Change
1	PE-g-poly (MAAc) ^a	174.5%	12.60	57.50%
2	PE-g-poly (MAAc) ^b	223.3%	14.85	85.63%

5.1 Area change

When grafting was carried out onto PE film as a function of various reaction parameters, it was observed that the dimensions of PE film increased tremendously (Table 1).

It is observed from the Table and the figure above that the size of the PE film increases gradually with increase in percent graft level. The enhancement of the area of the grafted film following grafting indicates that the grafting reaction also involves the diffusion of the monomer into the bulk of the film to give graft copolymer. The size of the film was much increased in case of grafting higher than 223.3%. The homopolymer was removed from the film during solvent treatment and also no homopolymer could be seen adhering to the surface of the film.

5.2 FTIR Spectroscopy

On comparison of IR spectra of PE film, PE-g-poly (MAAc) and PE-g-poly (AAM), (Fig. 7) it is observed that the additional peaks at 1705.4 cm^{-1} due to $\nu_{C=O}$ str and broad peak at 3413.7 cm^{-1} due to the associated ν_{O-H} str of the carboxylic groups of grafted MAAc and a minor peak at 3353.4 cm^{-1} due to ν_{N-H} str, peaks at 1698.6 cm^{-1} due to amide I and 1600 cm^{-1} due to amide II of the amide group of grafted AAm are observed. All these peaks are absent in the unmodified PE film. The presence of additional peaks due to the grafted polymeric chain confirms the formation of graft copolymer.

5.3 Thermo gravimetric analysis

Thermogravimetric analysis (TGA) of pristine PE film, PE-g-poly (MAAc) (87.09%) and PE-g-poly (AAM) (2.03%) was carried out in nitrogen atmosphere at a heating rate of $20^\circ\text{C}/\text{min}$ and the respective primary thermograms are presented in Fig. 8. The initial decomposition temperature, (IDT), final decomposition temperature, (FDT) and decomposition temperature, (DT) at every 10% wt. loss are presented in Table 2.

Table 2 Thermogravimetric analysis of PE and PE grafted samples

Sample	IDT ($^\circ\text{C}$)	FDT ($^\circ\text{C}$)	DT ($^\circ\text{C}$) at every 10% wt. loss										% Residue left
			10%	20%	30%	40%	50%	60%	70%	80%	90%	100%	
Pristine PE	316.10	447.78	353.8	377.8	391.0	400.9	409.1	415.9	422.2	427.9	433.8	440.3	0
PE-g-poly(MAAc)	210.56	516.09	242.4	264.9	277.5	288.6	300.1	313.2	328.8	346.9	370.2	405.7	0
PE-g-poly(AAm)	330.88	476.52	335.2	372.4	389.3	401.4	411.9	421.3	429.4	436.6	443.2	450.5	0

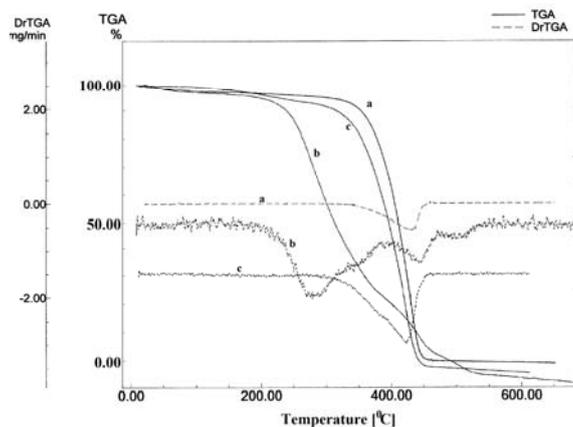


Fig. 8 Thermogram of (a) pristine PE film, (b) PE-g-poly (MAAc) and (c) PE-g-poly (AAM)

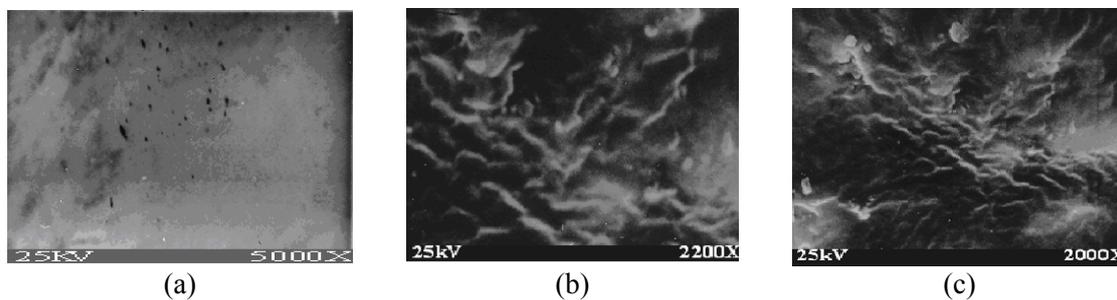


Fig. 9 SEM of (a) Pristine PE film, (b) PE-g-poly (AAM) and (c) PE-g-poly (MAAc)

The thermograms of PE film and PE-g-poly (AAM) show single stage decomposition whereas PE-g-poly (MAAc) shows two stages of decomposition. Comparing the initial and final decomposition of pristine and grafted PE films, it is observed from the Table that IDT of PE-g-poly (AAM) grafted film (330.88°C) is higher than both PE-g-poly (MAAc) (210.56°C) and pristine PE film (316.10°C). The FDT, on the other hand, of both AAM and MAAC of grafted films is higher (464.71°C , 449.95°C) than pristine PE film (441.18°C).

After the start of initial decomposition, all the films continue to decompose with rising temperature. The decomposition temperature at every 10% wt. loss of pristine PE film is higher than either of the grafted films but the temperature difference between each 10% wt. loss of PE film is very small indicating a fast rate of decomposition of PE. The DT values of PE-g-poly (AAM) are lower up to 30% wt. loss but increases beyond 40% wt. loss in comparison to pristine PE film, whereas in case of MAAC grafted PE film, these values are lower all through the decomposition as compared to PE film and also PE-g-poly (AAM) films.

The temperature difference between each 10% wt. loss, however, is higher in case of the grafted PE films which indicates a slow decomposition rate. Between AAM and MAAC grafted PE films, the temperature difference between each 10% weight loss is much higher for MAAC grafted films. The higher temperature difference between each 10% wt. loss is attributed to the reason that in case of the grafted films, the pendant amide groups and carboxylic acid groups form imide and anhydride linkages after the loss of ammonia and water from respective grafted polymeric chains that provides thermal stability to the film.

In DTG curve, the decomposition curve shows maximum decomposition rate of 0.36 mg/min, which is less than that of pristine PE film (0.53 mg/min.) indicating that the decomposition rate slows down upon grafting with acrylamide.

The DTG curve of PE film grafted with methacrylic acid shows two endothermic peaks, the first peak indicating the rate of decomposition as 0.08 mg/min, which lowers at higher temperature, the second peak to 0.03 mg/min. This may be due to the reason that once anhydrides are formed, the film becomes stable, leading to slower rate of decomposition.

Higher FDT values of the grafted PE, higher temperature difference between every DT values and lower rate of decomposition of the grafted PE films indicate that better thermal stability is achieved upon grafting.

5.4 Scanning electron microscopy

The respective scanning micrographs of pristine PE film, PE-g-poly (MAAc) (87.09%) and PE-g-poly (AAM) (2.03%) are presented in Figs. 9(a)-(c) respectively. It is observed from the Figure that PE film represents the unstained substrate with smooth surface, while the grafted sample becomes heterogeneous because of considerable deposition of polymer on the surface of PE film. The effect of AAM grafting upon surface morphology of PE film was investigated with SEM micrographs at magnification 25 kV X 2200 and that of PE-g-poly (MAAc) at magnification 25 kV X 2000 respectively. This range gives a good idea about the geometry and appearance of the micro-particles. Rough appearance in SEM is most related to the site of graft initiation, which would occur most frequently in the amorphous as opposed to crystalline surface regions of the film (Cohn 1984). As expansion of the grafted film occurs, stress produced in the surface of grafted film causes fissures to appear. Through such fissures, fresh monomer can diffuse into the available free volume of PE film to continue the grafting process.

5.5 X-ray diffraction studies

X-ray diffraction pattern of pristine PE film and grafted films is presented in Fig. 10. XRD pattern of pristine PE film shows two peaks at 14.53° and 20.91° at 2θ angle with total counts 2086.16 and 1129.53 respectively. Broad peak area between 2θ values of $11.30^\circ - 30.66^\circ$ shows semi crystalline nature of PE film. Upon grafting with MAAc, the XRD pattern shows four peaks

Table 3 Swelling behavior of PE film and grafted PE films in different solvents after 24 and 48 h

Samples	Percent grafting	% Swelling							
		H ₂ O		EtOH		MeOH		Benzene	
		24 h	48 h	24 h	48 h	24 h	48 h	24 h	48 h
PE film		13.55	10.18	08.11	11.11	12.50	04.75	00.00	00.00
	42.00	60.70	37.10	50.00	40.00	17.09	21.50	25.20	11.60
PE-g-poly (MAAc)	105.0	480.0	300.0	57.14	14.30	131.9	28.57	54.06	26.05
	206.0	222.0	150.0	144.5	100.9	33.33	50.00	21.60	13.45
	461.0	228.6	138.6	135.0	95.00	59.91	43.92	14.00	22.22

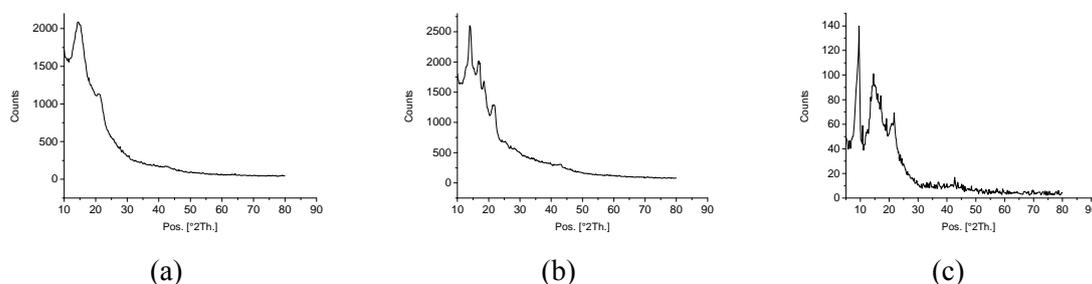


Fig. 10 XRD pattern of (a) Pristine PE film, (b) PE-g-poly (MAAc) and (c) PE-g-poly (AAM)

at 14.03° , 16.85° , 18.54° and 21.66° on 2θ scale with higher counts (2597.75, 2006.74, 1670.79 and 1281.88 respectively) as compared to pristine PE indicating small crystalline changes in the film.

However, when the film was grafted with AAm, a drastic change in the structure was observed. Distinct peaks appear covering a broad area between $5.22^\circ - 30.84^\circ$ with very low counts (139.73) indicating a shift to amorphous structure. Similar finding have been reported by Maziad *et al.* (2005) during grafting of AAm onto LDPE.

It was further observed that the d-spacing increases in case of MAAC grafted film from 4.96110 of pristine PE to 5.16047 while in case of acrylamide grafted film the d-spacing decreases to a lower value 0.2460.

5.6 Swelling behavior

Swelling behavior of pristine PE film and PE-g-poly (MAAC) was studied in polar and non-polar solvents such as H_2O , MeOH, EtOH, and benzene with decreasing order of dielectric constants 78.35, 33, 24.30 and 2.3 respectively as a function of percentage of grafting in 24 h and 48 h and the results are presented in Table 3. It is observed from the Table that PE film shows poor swelling in H_2O , MeOH, EtOH with no swelling in benzene while PE-g-poly (MAAC) shows good swelling percentage in 24 h and 48 h. However, percent swelling was found to be lower in 48 h. Decrease in swelling percent is explained invoking swelling-deswelling which is an equilibrium phenomenon. Initially the rate of swelling is faster than the deswelling and after attaining maximum, the rate of deswelling becomes slightly faster than the forward process of swelling resulting in small decrease in swelling percent. During swelling the solvents diffuses in to the polymer matrix and interacts with the functionalities through H-bonding leading to swelling and opening of the overall polymer structure. With increase in the length of suspension time in the solvent, after attaining maximum value, the solvent molecules start diffusing out from the swollen polymer matrix to attain self assembled solvent structure leading to decrease in swelling percentage. Maximum percentage of swelling of the grafted films was observed in water and minimum in benzene, a non-polar solvent. Increased percent swelling suggests that water interacts with the pendent carboxylic group of the grafted poly (MAAC). The order of solvents towards swelling of the grafted films i.e., PE-g-poly (MAAC) with respect to maximum swelling in each

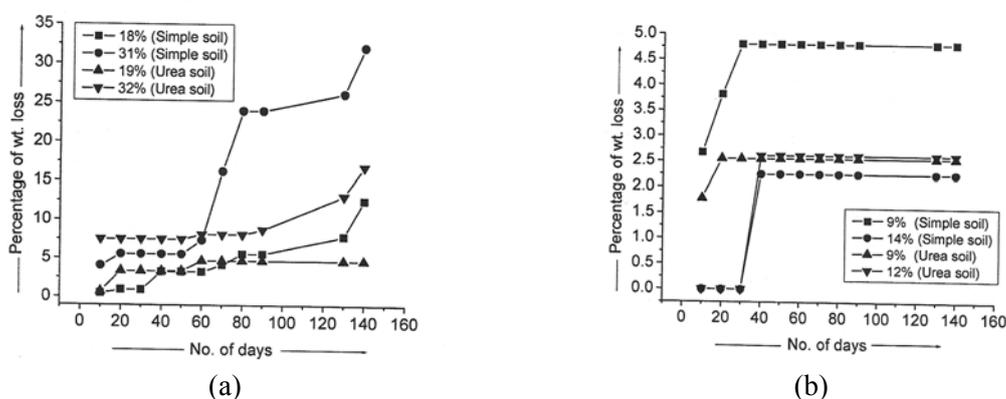


Fig. 11 Biodegradation behavior of (a) PE-g-poly (MAAC) and (b) PE-g-poly (AAM) in simple soil and urea soil

solvent was observed as follows: (Maximum swelling percentage is written in brackets below each solvent)

$$\text{H}_2\text{O} > \text{EtOH} > \text{MeOH} > \text{Benzene}$$

$$(480\%) \quad (144.54\%) \quad (131.86\%) \quad (54.06\%)$$

5.7 Biodegradation studies

Biodegradation of pristine PE film and the grafted PE film samples, PE-g-poly (MAAc) and PE-g-poly (AAm) with different levels of percent grafting was carried out in simple and urea enriched garden soil. The results are presented in Figs. 11(a) and (b). It was observed that in case of degradation of PE grafted with methacrylic acid (Fig. 11a) the sample with 32% grafting buried in urea enriched soil after showing 7.5% wt. loss in first 10 days remains almost constant with

Table 4 Conductance of aqueous electrolyte solutions (mS) and Distilled water (μS) after suspension of PE film, PE-g-poly(MAAc) and PE-g-poly (AAm) in 0.5 % electrolyte solutions and distilled water thereafter at 37°C

Samples	% grafting	Electrolyte solution (0.5 %)	Conductance of aqueous electrolytic solution (mS) after					Conductance of Distilled water (μS) after				
			2 h	4 h	24 h	48 h	72 h	2 h	4 h	24 h	48 h	72 h
Pristine PE film		NaCl	10.99	10.83	10.71	10.11	10.83	3.82	3.84	3.93	4.53	5.20
		Na ₂ SO ₄	7.89	7.86	7.82	7.56	8.00	4.12	4.14	4.47	5.91	6.79
		KCl	8.72	8.65	8.38	8.27	9.16	5.7	6.3	6.7	7.00	7.3
		K ₂ SO ₄	7.22	7.14	7.08	7.01	7.38	4.2	5.8	5.9	6.0	6.7
PE-g-poly(MAAc)	37.6	NaCl	11	10.92	10.89	10.76	10.72	5.85	6.10	9.17	10.64	15.95
	166.6		10.12	10.69	10.45	10.34	9.81	9.82	8.39	12.18	13.23	14.91
	223.3		9.88	10.47	10.53	10.02	9.79	16.28	16.20	19.99	23	24
	37.6	KCl	11.06	10.90	10.74	10.69	10.57	5.04	5.25	5.37	5.55	6.97
	166.6		10.93	10.80	10.66	10.66	10.53	5.21	5.62	5.65	5.78	15.7
	223.3		10.72	10.67	10.62	10.36	10.30	23.1	23.5	23.5	23.6	24.3
	37.6	Na ₂ SO ₄	8.57	8.46	8.69	8.96	8.94	5.43	6.06	7.87	8.96	9.71
	166.6		7.75	7.12	7.07	7.44	6.83	18.1	20.6	19.3	21.3	13.87
	223.3		7.50	7.14	7.09	7.74	6.86	5.06	6.81	9.61	11.92	23.5
	37.6	K ₂ SO ₄	8.44	8.43	8.20	8.19	8.04	5.79	5.97	6.08	6.11	6.35
	166.6		8.43	8.43	8.19	8.16	7.93	7.39	8.20	8.24	8.59	9.17
	223.3		8.36	8.34	8.17	8.04	7.76	21.9	22.0	22.2	22.7	23.7
PE-g-poly(AAm)	13	NaCl	9.86	11.13	10.24	10.20	9.87	6.94	6.85	7.95	8.36	9.29
		KCl	11.19	10.87	10.48	10.40	10.49	4.99	4.70	4.42	4.43	4.66
		Na ₂ SO ₄	7.54	7.36	7.00	7.37	7.07	3.24	3.46	3.33	4.28	4.63
		K ₂ SO ₄	8.48	8.29	8.00	7.95	7.91	4.58	4.80	5.03	5.13	5.23

Conductance of original aqueous electrolytic solution of 0.5% NaCl = 11.15mS, Na₂SO₄= 8.05 mS, KCl = 9.68 mS, K₂SO₄= 7.46 mS and Distilled H₂O = 3.74 μS at 37°C.

Table 5 Conductance of aqueous electrolyte solutions (mS) and Distilled water (μS) after suspension of PE film, PE-g-poly(MAAc) and PE-g-poly (AAM) in 1 % electrolyte solutions and distilled water thereafter at 37°C

Samples	% grafting	Electrolyte solution (1 %)	Conductance of aqueous electrolytic solution (mS) after					Conductance of Distilled water (μS) after				
			2 h	4 h	24 h	48 h	72 h	2 h	4 h	24 h	48 h	72 h
Pristine PE film		NaCl	19.79	19.78	19.65	18.72	17.89	11.13	11.90	12.96	16.46	19.3
		KCl	19.17	18.83	18.67	18.40	17.58	5.20	5.86	6.71	9.04	10.92
		Na ₂ SO ₄	14.42	14.34	14.13	13.86	12.30	7.49	8.79	9.95	11.56	14.63
		K ₂ SO ₄	14.66	14.63	14.37	14.19	13.36	5.49	7.26	8.47	10.52	12.73
PE-g-poly(MAAc)	29.5	NaCl	18.26	17.98	17.71	17.39	17.19	8.18	9.55	9.92	10.50	12.57
	269		18.01	17.77	17.53	17.17	17.04	15.9	18.5	19.99	20.2	23.5
	478		17.07	16.82	15.97	15.71	14.42	32.3	34.6	34.7	35.1	36.5
	29.5	KCl	17.59	17.18	16.92	16.72	16.58	7.10	7.34	7.42	8.77	8.83
	269		17.37	17.13	16.82	16.64	16.32	15.3	17.8	19.36	19.40	20.9
	478		16.78	16.71	16.60	16.50	16.23	25.3	26.8	27.8	28.1	28.4
	29.5	Na ₂ SO ₄	12.60	12.29	12.24	11.68	11.64	7.50	7.82	7.82	8.09	15.0
	269		12.35	12.17	11.87	11.68	11.64	21.6	22.9	23.0	23.6	24.4
	478		12.17	12.02	11.82	11.65	11.46	22.9	22.9	27.4	29.2	31.7
	29.5	K ₂ SO ₄	13.28	12.56	12.50	12.17	12.04	5.56	6.00	6.29	6.61	10.93
	269		12.67	12.54	12.09	12.09	11.77	15.40	17.4	19.5	19.5	22.3
	478		12.34	12.32	11.98	11.94	11.63	16.44	20.5	21.8	22.0	22.9
PE-g-poly(AAM)	12.87	NaCl	18.67	17.88	17.74	17.30	17.29	4.72	5.39	5.75	10.42	11.35
		KCl	17.59	16.97	16.95	16.91	16.69	6.52	7.00	7.24	7.64	7.76
		Na ₂ SO ₄	12.69	12.19	12.05	11.98	11.73	3.97	4.73	4.30	10.32	10.94
		K ₂ SO ₄	12.92	12.51	12.32	12.19	11.99	5.39	5.82	6.21	6.49	6.70

Conductance of original aqueous electrolytic solution of 1% NaCl = 18.42 mS, Na₂SO₄ = 13.03 mS, KCl = 17.53 mS, K₂SO₄ = 13.06 mS and Distilled H₂O = 3.74 μS at 37°C.

negligible increase in percent wt. loss up to next 50 days beyond which it shows a marginal increase giving maximum 9% of wt. loss. The sample with equivalent graft level (31%) buried under simple soil shows 4.9% wt. loss in first 10 days which increase constantly till next 50 days beyond which a sharp increase in % wt. loss is observed giving maximum 24% wt. loss in 90 days. The lower % graft level (19%) sample shows lower percent wt. loss in first 10 days which increases to 3.36% in next 10 days and remain constant up to 50 days beyond which it again increases to 4.697% and remains constant there after. The sample (18% graft level) buried under simple soil shows 0.47% wt. loss in first 10 days, which increase up to 40 days showing 3.26% wt. loss. This remains constant for next 20 days and increases thereafter showing maximum 5.58% wt. in 90 days.

In case of PE grafted with acrylamide (Fig. 11b) different trend was observed. Loss of weight was observed during the early phases. The sample with lower percentage of grafting (9%) buried under simple and urea enriched soil respectively show 2.67% and 1.76% wt. loss in the first 10 days which increases to 4.8% and 2.55% in next 20 days and 10 days respectively and remain constant till 90 days burial period. The samples with 12% and 14% grafting, initially did not show

any loss in wt. up to 30 days beyond which 2.67% and 2.25% maximum % wt. loss is observed on the 40th day, that remains constant thereafter. Physically the film completely lost its strength and was broken into small pieces.

After 90 days of monitoring the degradation, all the samples were left undisturbed under next 50 days. Weight analysis after 50 days showed that except for the PE sample grafted with MAAC which showed some wt. loss giving maximum of 32.10% wt. loss in total, no other sample showed any further loss in weight.

5.8 Ion uptake studies

The conductance of the electrolytic solutions of sodium (NaCl), potassium chloride (KCl), sodium sulphate (Na₂SO₄) and potassium sulphate (K₂SO₄) was taken after specified period (2, 4, 24, 48 and 72 h) of immersion of the film and the results are presented in Tables 4 and 5.

Pristine PE, PE-g-poly (MAAc) and PE-g-poly (AAM) film suspended in electrolyte aqueous solution of NaCl, KCl, Na₂SO₄ and K₂SO₄ for 2, 4, 24, 48 and 72 h were removed and dried. The dried films were suspended in distilled water of known conductance for 2, 4, 24, 48 and 72 h. The conductance of the residual solution of the distilled water with suspended films was measured and the results are tabulated in Tables 4 and 5.

It is observed from the Table that the conductance of the aqueous solutions of all the electrolytes decreases with increase in the time of immersion (except in 0.5% KCl and K₂SO₄) and also with increase in percentage of grafting in case of PE-g-poly (MAAc) and PE-g-poly (AAM).

In order to rule out that any change in the conductance of the electrolyte solution or distilled water after suspension of films is due to any homopolymer adhered to the surface of film or unfolding of the grafted chain releasing the entrapped homopolymer, the pristine PE, grafted films were directly suspended in distilled water of known conductance and it was found that to the maximum, the conductance of water remains unchanged except in case of PE-g-poly (MAAc) with 223.3% graft level where increase in conductance was observed. This is due to the rapid exchange of proton of carboxylic group with the hydrogen bonded structure of water. From Table it is observed that the conductance of 0.5% aqueous solution of NaCl and Na₂SO₄ decreases while the electrolyte solution of potassium shows an increase in conductance than the original conductance values of the respective solutions. In 1% solution, the conductance of all the electrolyte solutions decreases. Same trend is observed for the PE-g-poly (AAM) films.

The decrease in conductance of the electrolyte solution after the films were suspended in these solutions indicates that there is an interaction of the ions from the electrolyte solutions with the pendant group of the grafted PE films during which the ions are adsorbed onto the films surface due to these interactions (Scheme I). The decrease in the total ion content in the electrolyte solution thereby leads to decrease in conductance.

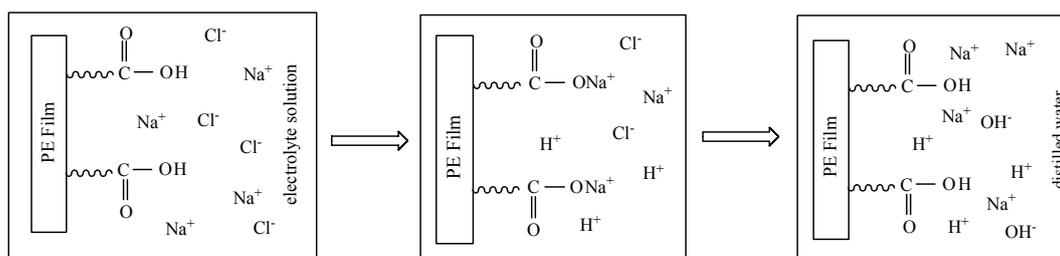
This was further corroborated by suspending the films in distilled water for different time periods (2, 4, 24, 48 and 72 h) and it is observed from the table that the conductance of water increases with increasing time of immersion. These observations indicate that the ions adsorbed on the surface of the film are dispensed in water, thereby increasing conductance of water.

The increase of conductance in case of KCl and K₂SO₄ in 0.5% solution may be attributed to the fact that the adsorption of potassium ion is less in comparison to sodium ion because of the size and therefore the hydrogen ions from the pendant carboxylic groups released also add to the total conductance of this solution.

The change in the conductance of the electrolytic solution of sodium and potassium salts and consequent increase of conductance of distilled water is attributed to the fact that the numbers of ions in 0.5% concentration are less in comparison to 1% solution. The barrier imposed by the film to the flow of the ion affects the conductance of the solution. Very few ions remain physically adhered to the surfaces that are dispensed in distilled water increasing the conductance to a small extent.

5.9 Metal uptake studies

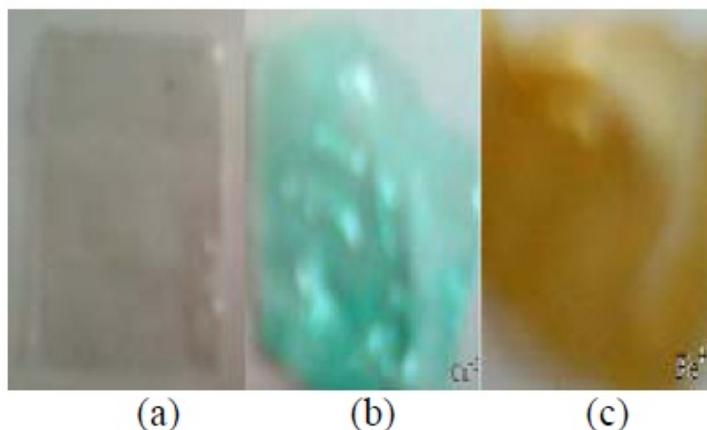
The efficiency of polymeric substrates for up taking metal ions can be determined from the time required to absorb the maximum capacity of metal ions by chelation or adsorption with its functional groups. Nurkeeva *et al.* (2002) studied the efficiency of prepared PE films radiation grafted with vinyl monomers for Cu^{+2} ion uptake. Trong *et al.* (2002) studied the Cu^{+2} ion uptake by Chitosan-g-poly (vinylacetate) copolymers and found that the specific adsorption is proportional to the degree of grafting.



Scheme 1 Schematic representation of exchange of ions with the pendent carboxylic groups of grafted PE film in NaCl solution and distilled water

Table 6 Metal-uptake studies of PE and grafted PE film

S. No.	Samples	% grafting	% metal adsorbed						
			Cu^{+2}			Ni^{+2}			Fe^{+2}
			4 h	8 h	24 h	4 h	8 h	24 h	1h
1.	PE film	0.00	0.24	0.00	0.00	0.00	0.00	0.00	0.00
2.	PE-g-poly (MAAc)	16.22	1.42	1.77	0.73	1.00	1.83	1.16	1.01
		27.00	2.04	2.04	0.24	1.35	3.01	1.49	1.55
		111.00	7.38	6.28	2.53	1.35	2.16	1.16	0.85
3.	PE-g-poly (AAm)	4.80	1.42	0.73	0.00	1.49	1.83	0.00	0.00



Metal uptake studies of (a) Pristine PE film, (b, c) PE-g-poly (MAAc) treated with CuSO_4 and FeSO_4 solution

In the present work, metal ion uptake (%) for different metal ions using pristine PE, PE-g-poly (MAAc) and PE-g-poly (AAM) are presented in Tables 6.

It is observed from the table that in case of PE-g-poly (MAAc) percent metal uptake of Cu^{+2} ions increases with increase in percentage of grafting, giving maximum uptake of 7.38% in 4 h for 111% graft level. But as time of immersion increases up to 24 h, % metal uptake for Cu^{+2} ions decreases. In case of Ni^{+2} metal ions, % metal uptake increases with increasing Pg and also with time of immersion. Maximum uptake of Ni^{+2} ions (3.01%) was observed in 8 h for the sample with 27% graft level. Within one hour only 1.55 % Fe^{+2} was absorbed by the film.

From the table following trend was observed for PE-g-poly (MAAc) w.r.t. metal ion uptake.

$$\text{Cu}^{+2} > \text{Ni}^{+2} > \text{Fe}^{+2}$$

$$(7.38\%) \quad (3.01\%) \quad (1.55\%)$$

PE-g-poly (AAM) with very low Pg level (4.80%) on the other hand, shows poor affinity for Cu^{+2} (1.42%), Ni^{+2} (1.83) and zero percent for Fe^{+2} ions. No absorption of any metal ion was observed for pristine PE film.

It is interesting to mention that the grafted film immersed in Cu^{+2} , Ni^{+2} and Fe^{+2} solutions attained blue, light green and brown color respectively which was stable even after several washings supporting the binding of these metal ions onto grafted chains of the grafted PE films.

6. Conclusions

PE films have been successfully grafted with polar functional groups. Grafting improves the thermal and swelling behavior of PE film and these properties further makes the film to be utilized as a membrane in ion and metal ion separation studies. The property of biodegradation imparted to the film upon grafting is additional and thus can be used as environment friendly polymeric membrane.

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