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Synthesis and Characterization of Acrylic acid Grafted Styrene- Maleic anhydride Copolymer

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ABSTRACT

Modification of Styrene-maleic anhydride copolymer, synthesized in toluene using benzoyl peroxide (BPO) as initiator, through graft copolymerization of hydrophilic monomer, acrylic acid, (AAc), has been carried out in aqueous medium by chemical and gamma radiation methods. Optimum conditions pertaining to maximum percentage of grafting were evaluated as a function of different reaction parameters. In case of chemical method, maximum percentage of grafting of AAc, (95%), was obtained using 14.56×10^{-3} *moles of AAc,* 12.38×10^{-4} *moles of BPO at* 70^0C *in 180 min. Gamma radiation induced grafting of AAc produced maximum grafting, (855%), at a total dose of 68.04 kGy using* 21.83×10^{-3} *moles of AAc. Swelling studies of the grafted styrene-maleic anhydride copolymers, SMA-g-poly (AAc), has been studied as a function of temperature, time and pH. Maximum swelling (3290%) was observed at* 37^0C *in 12h at 9 pH for the grafted sample prepared by radiation method. The graft copolymers have been characterized by FTIR, XRD and Thermo gravimetric analysis. From the XRD and TGA data, a correlation between crystallinity and thermal behavior of the grafted copolymer has been observed. The graft copolymer was used as a drug carrier and the release of an antibiotic drug, ampicillin, was studied at pH 3.5 and pH 7.5.*

Keywords: SMA, graft copolymerization, Thermal analysis, X-ray analysis, drug delivery, swelling behavior.

INTRODUCTION

Styrene–maleic anhydride copolymers (SMA) are well known commercialized polymers with diverse applications [1,2]. SMA copolymers with relatively high anhydride content have been used for various coating's additives and binder applications. Because of the presence of aromatic and anhydride functionalities, the molecular and segmental structures of SMA can be modified easily. One can modify its degree of hydrophilicity and other properties by adjusting the styrene–maleic ratio or by incorporating long hydrophobic alkyl chains or hydrophilic oxyalkylene moieties, these compounds can act as surfactants and demulsifiers in petroleum industry. Graft copolymers of cellulose acetate (CA, d.s.:2.45) with styrene- maleic anhydride random copolymers were synthesized by reacting the hydroxyls on CA backbone with the anhydride on SMA. The uniform dispersion of SMA in the CA matrix induced new properties to the grafting reaction products and the dimensional stability of the grafting products was better or comparable to cellulose triacetate [3]. Anchoring minute quantities of glucose, sucrose or lactose, onto functionalized polystyrene, (polystyrene-co-maleic anhydride copolymer), increases the rates of biodegradation of polyolefins significantly [4]. Long fatty alcohol grafts were synthesized by esterification of SMA with octanol, tetradecanol and octadecanol, respectively. SMA and the esters were used as surface modifiers to blend with high density polyethylene (HDPE). It was found that grafting of alcohols onto SMA can promote the enrichment of the modifiers on the surface of the blending film, and that the enrichment effect enhances when using shorter fatty alcohols [5].

Much attention has been directed in recent years to polyelectrolyte hydrogels that show different swelling behaviors in response to small variation in solution conditions such as temperature and pH [6-8]. These hydrogels are used in variety of novel applications, including controlled drug delivery [9], immobilized enzyme system [10, 11] and separation processes [12]. Much of the fundamental on the swelling behaviors of the hydrogels were investigated since Tanaka [13] has suggested the swelling theory that clarified the relation between the swelling behaviors and temperature of the swelling medium. Guderman and Peppas [14] reported on the synthesis and characterization of pH sensitive interpenetrating network of poly (vinyl alcohol) and monoprotic acrylic acid. Shan et al.[15] synthesized pH-sensitive hydrogels of acrylic acid /cyclodextrin based copolymer. They studied its swelling with respect to pH. Samchenko and coworkers [16] prepared a polymeric hydrogels of acrylic acid and acrylamide and studied their physicochemical properties. Swelling properties of poly (AAm/HPMA/MA), a terpolymer and its diffusion and absorption of bovine serum albumin (BSA) from aqueous BSA solution was studied by Oztop and coworkers [17]. Styrene- maleic anhydride copolymers with hydrophobic styrene moiety when grafted with hydrophilic monomer can give a product with properties of a hydrogel. In the present article we, therefore, report on grafting of a hydrophilic monomer, acrylic acid, on styrene- maleic anhydride copolymer both by chemical and radiation methods. Styrene-maleic anhydride copolymer was synthesized in the laboratory in toluene using BPO as radical initiator. Swelling properties of the pristine copolymer and the graft copolymer were measured at different time, temperature and pH values.

MATERIALS AND METHODS

2.1 Materials and Method

Styrene (Merck), maleic anhydride (S.D. fine Chem., Mumbai), benzoyl peroxide (S.D. fine Chem., Mumbai), acrylic Acid (Merck), ethylene diamine (S.D. fine Chem., Mumbai), toluene (Qualigens fine Chem., Mumbai) and petroleum ether (60-80^{0}C) (RFCL Ltd., N. Delhi) were used as received. Distilled water was used as the reaction medium for grafting reactions.

2.2 Synthesis of Styrene – Maleic anhydride Copolymer:

To a three necked round bottomed flask (500 mL), equipped with a reflux condenser, stirrer and a nitrogen gas inlet system, was added maleic anhydride (4.0 g) and styrene (3mL) dissolved in toluene (35 mL). A known amount of benzoyl peroxide and petroleum ether was then added to the flask and the reaction mixture was stirred at 60^{0}C for 120 min. After the stipulated time period**,** styrene – maleic anhydride (SMA) copolymer was recovered from reaction mixture by filtration as white precipitates. The precipitates were washed repeatedly with toluene followed by washings with benzene and CCl_4 respectively to remove free polystyrene and unreacted maleic anhydride. The product was dried in oven at 60^{0}C for 14h to a constant weight.

2.3 Graft Copolymerization:

2.3.1 By Chemical method

To a three necked round bottom flask (250 mL), charged with water (20 mL), was added a known amount of SMA (0.2g), BPO (8.26-14.45 × 10^{-4} moles), and acrylic acid (7.28-29.11 × 10^{-3} moles). The flask was placed in the water bath maintained at a constant temperature (50-80^{0}C) and the reaction was carried out under stirring for different time periods (90- 210min). After the completion of reaction, the reaction mixture was filtered and the residue, SMA-g-poly (AAc), was washed thoroughly with water to remove any homopolymer, poly (AAc), and dried at 60^{0}C in oven to a constant weight. Percentage of grafting was calculated from the increase in weight of the copolymer as follows:

$$\%\ \text{Grafting} = \frac{Wg - Wo}{Wo} \text{ X } 100$$

where W_0 and Wg respectively are the weights of SMA copolymer and SMA-g-poly (AAc) after complete removal of the homopolymer.

Percentage of grafting was determined as a function of concentration of SMA, monomer, initiator, time and temperature.

2.3.2 By Radiation method

To a 50mL beaker containing 5mL water was added SMA (0.2g) and acrylic acid ($7.28\text{-}29.11 \times 10^{-3}$ moles) and the beaker was placed in the gamma chamber. The reaction mixture was irradiated by γ-rays at a constant dose rate (1.89 kGy/h) under ambient conditions for different time periods. After irradiation, the product was collected and washed repeatedly with excess water to remove the homopolymer. The final product was dried in oven at 60^0C. Percentage of grafting was determined as a function of total dose and concentration of monomer and time and determined as above.

2.4 Swelling Behavior

Swelling of SMA, SMA-g-poly (AAc) was studied in water at different pH and different temperatures. A known amount of the sample was kept in water for 6h and 12h. After the stipulated time, the copolymer was removed from the water and the extra liquid was removed by blotting with soft filter paper and then weighed. Percent swelling was determined from the increase in the weight of the original sample as follows:

$$\%\ \text{Swelling} = \frac{\text{Ws} - \text{Wo}}{\text{Wo}} \text{ X } 100$$

where Ws and Wo respectively are the weights of swollen polymer and original polymer.

2.5 Drug Delivery Studies

Preliminary studies for use of the copolymer as a support for the drug and the release of the same has been under taken taking ampicillin as the model drug.

2.5.1 Drug uploading:

An aqueous solution of ampicillin (1.0g in 200mL) was prepared and its optical density (OD) was measured at 205nm. Weighed sample of acrylic acid grafted SMA (0.200g) was added to the drug solution (35mL). The pH and the temperature of the solution were maintained at 9 and 37^0C and the solution were kept for 24h undisturbed. The polymer was removed from the drug solution and dried. The weight of the loaded polymer was 0.250g.

2.5.2 Drug release

Known amount of the drug loaded polymer (0.100g) was placed in water (50mL) of pH 3.5 and 7.5 at 37^0C. The OD of the solution was measured after a duration of 20 min up to 160 min and finally at 6h and at 8h.

2.6 Characterization

(i) Spectroscopic Analysis: FTIR spectra of SMA copolymer and SMA-g-poly(AAc) graft copolymer were recorded on KBr disc using a Thermo-5700 Spectrophotometer. ^{1}H NMR spectra were recorded on Bruker Avance II 400 NMR Spectrometer at room temperature using DMSO.

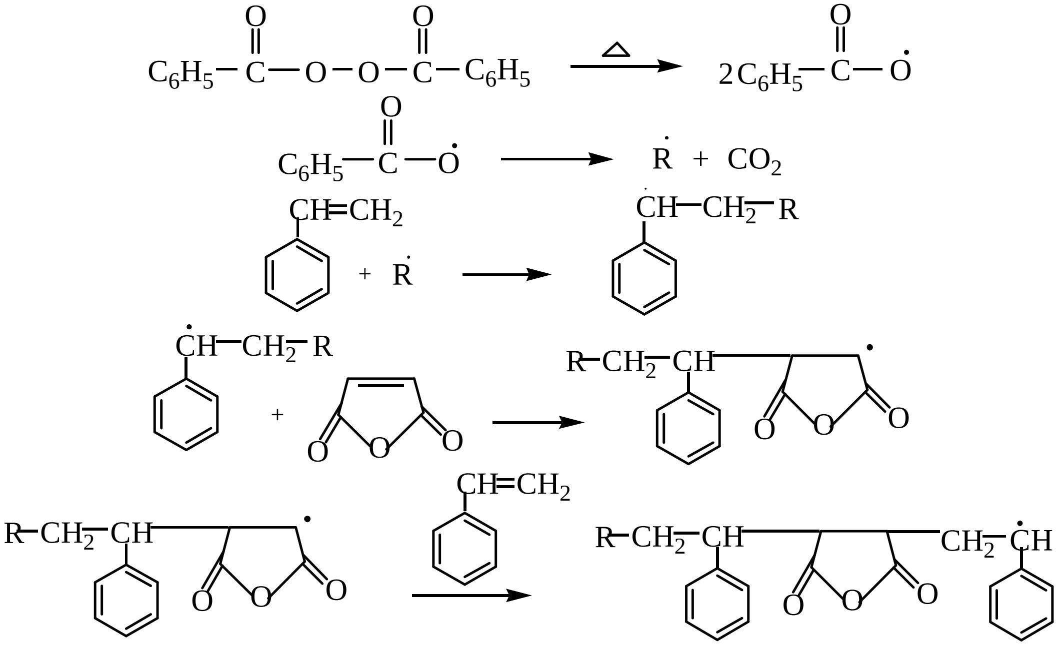
(ii) Thermo gravimetric analysis (TGA) of SMA and SMA-g-poly (AAc) was carried out in nitrogen atmosphere (200ml/min) at a heating rate of 10^0C/min on Shimadzu DTA-60 H Thermal Analyzer. The samples weights were kept within 5-8mg.

(iii) X-ray diffraction studies were performed under ambient conditions on X-ray diffractometer (Bruker-D8 advance model; IIT Roorkee, India) using Cu target and goniometer scanning range $0\text{-}70^0$C.

RESULTS AND DISCUSSION

Copolymerization of styrene and maleic anhydride is a well known reaction that gives a copolymer with alternate monomer units of styrene and maleic anhydride. In the present studies copolymerization has been carried out using benzoyl peroxide, BPO, a well known free radical initiator. The phenyl radicals generated from BPO have the ability to initiate the monomer or abstract hydrogen atom from the polymer thus, generating active sites on the polymeric backbone. Based on this, following are the various steps involved in the synthesis of the copolymer and the graft copolymer:

3.1 Copolymer Formation



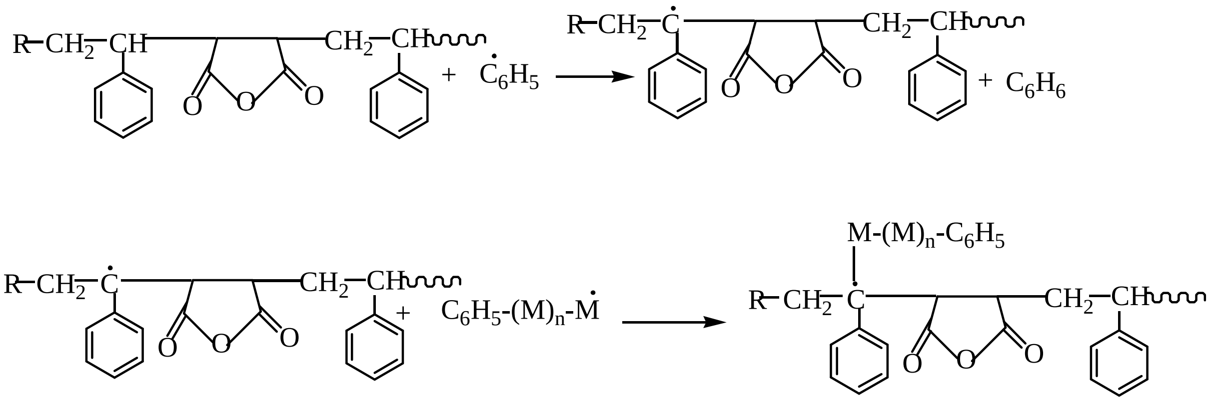
SMA Copolymer

3.2 Graft Copolymer Formation:

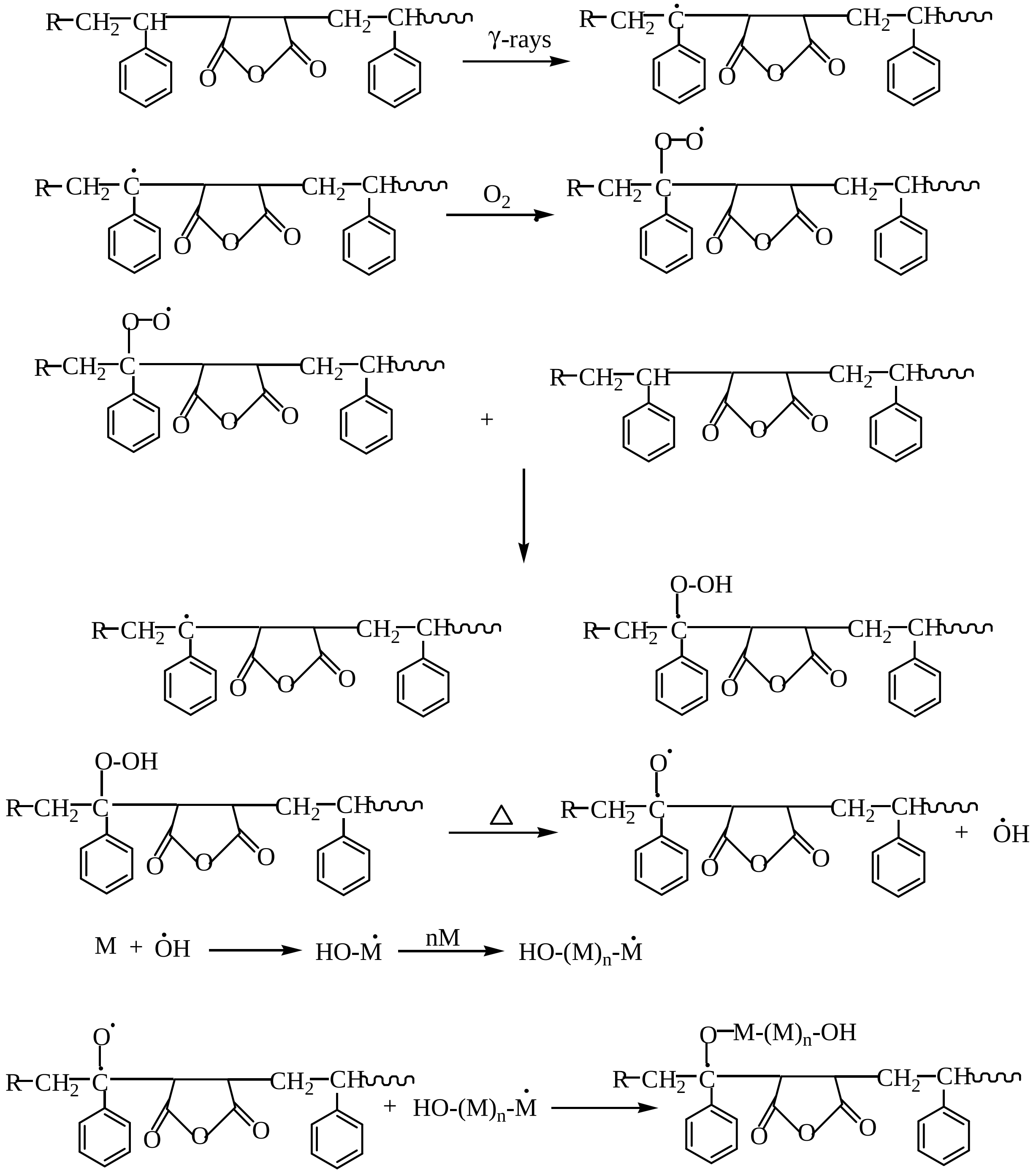
Phenyl radical from benzoyl peroxide generates active sites on the copolymer and also initiates the monomer. The reaction between the polymer growing radical and the active site on the copolymer gives the graft copolymer [18-20].

3.2.1 Grafting by Chemical Method:

$$\dot{C}_6H_5 + M \longrightarrow C_6H_5\text{-}\dot{M} \longrightarrow C_6H_5\text{-}(M)_n\text{-}\dot{M}$$



3.2.2 Grafting by Radiation Method:



3.3 Synthesis of SMA Copolymer

Percent copolymer formation (Pc) of styrene-maleic anhydride (SMA) copolymer was studied as a function of various reaction parameters. During optimization of reaction conditions it was observed that percent formation of SMA copolymer increased with increasing the amount of styrene giving maximum Pc (44%) using 26.18 × 10^{-3} moles of styrene thereafter it decreases and becomes constant. Varying the amount of maleic anhydride, percent formation of SMA copolymer initially remains constant and then increases to give maximum (56%) using 4.08 x 10^{-}

^{2}moles of MAn. The reactivity ratio of styrene to maleic anhydride is 0.02:0 [21] indicating the formation of alternating copolymer. The reactivity ratios further indicate that the growing radical of styrene preferably react with that of maleic anhydride and therefore, optimum amount of each is required to give the maximum copolymer formation. Percent copolymer formation, when studied as a function of amount of the initiator, maximum Pc (87%) was obtained using 10.32 x 10^{-4}moles of BPO which increases to 93%, on varying the amount of the solvent (30mL) of toluene. While the studying the effect of temperature and time of reaction on Pc, it was observed that both these factors also affect the formation of the copolymer. Percent copolymer formation increases to 98% in 120 min at 60°C using 5mL optimum amount of petroleum ether.

Maximum percent SMA copolymer formation (98%) thus, was obtained at the following optimum reaction conditions.

Sty x 10^3 mol	**[MAn] x 10^2 mol**	**[BPO] x 10^4 mol**	**Amt. of Toluene (mL)**	**Time (min.)**	**Temperature (°C)**	**Amt. of Pet ether (mL)**	**% Conversion**
26.18	**4.08**	**12.38**	**30.0**	**120**	**60**	**5.0**	**98.00**

3.4 Effect of Reaction variables on Grafting of AAc onto SMA:

3.4.1 Effect of amount of SMA copolymer:

Percentage of grafting of AAc onto SMA polymer was studied as a function of amount of the copolymer and the results are presented in Fig.1. It is observed from the figure that percent grafting increases initially giving maximum (85%) using 0.2g of the copolymer, beyond which it decreases constantly and drops to around 14% with 0.35 g of the copolymer. The decrease in the grafting percentage is due to the reason that the ratio of the number of active sites to the concentration of the monomer used is higher and as such remains unused and the excess radicals instead trigger the chain scission leading to decrease in the percentage of grafting.

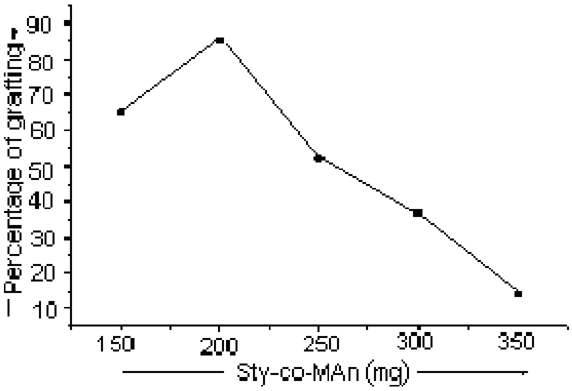


Fig.1 Effect of amount of SMA on percent grafting of AAc

3.4.2 Effect of amount of monomer:

Grafting percentage was studied as a function of amount of acrylic acid and the results are presented in Fig.2. It is observed that after the initial increase in Pg, maximum grafting (85%) was obtained using 14.56 × 10^{-3}moles of AAc beyond which it decreases sharply to 30% at 21.83 × 10^{-3} moles of AAc. At higher amount of the monomer, homopolymer formation becomes the preferred process since the growing polymeric chains react with the monomer units lying close in the vicinity. The homopolymer, poly (AAc), thus formed, being soluble in water increases the viscosity of the medium their by restricting the mobility of the growing polymeric chains to the active sites leading to decrease in grafting percentage.

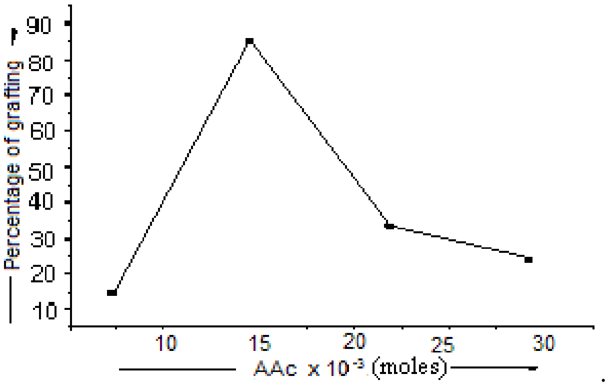
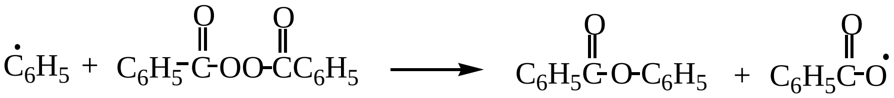


Fig.2. Effect of amount of AAc on percent grafting of AAc

3.4.3 Effect of [BPO]:

Fig.3 depicts the effect of amount of BPO on percentage of grafting of AAc onto SMA copolymer. It is observed from the figure that Pg increases with increasing amount of BPO, giving maximum (85%) using 12.38 × 10^{-4} moles of BPO beyond which it decreases slightly. As the amount of BPO increases, generation of active sites on the SMA copolymer and initiation of monomer toward polymerization takes place that leads to increase in percent graft copolymer formation. Further increase in the amount of BPO leads to induced decomposition reaction leading to decrease in radical concentration and hence the overall grafting reaction.



$$\dot{C}_6H_5 + C_6H_5\text{-}\overset{O}{\overset{\|}{C}}\text{-}OO\text{-}\overset{O}{\overset{\|}{C}}C_6H_5 \longrightarrow C_6H_5\overset{O}{\overset{\|}{C}}\text{-}O\text{-}C_6H_5 + C_6H_5\overset{O}{\overset{\|}{C}}\text{-}\dot{O}$$

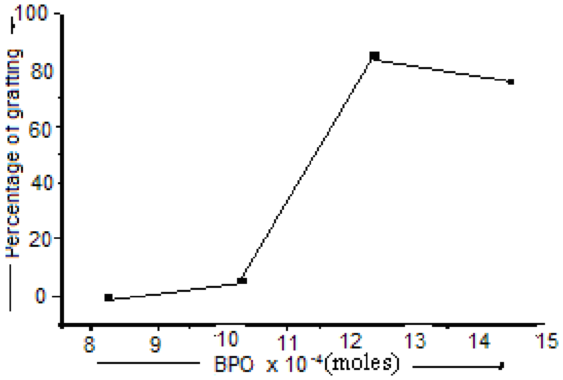


Fig.3. Effect of amount of BPO on percent grafting of AAc

3.4.4 Effect of liquor-ratio:

Percentage of grafting of AAc was studied as a function of amount of water and the results are presented in Fig.4. It is observed from the figure that percentage of grafting increases when the amount of water was increased from 10 to 20 ml, where maximum grafting (85%) was observed. Percentage of grafting remains constant with further increase in the amount of water.

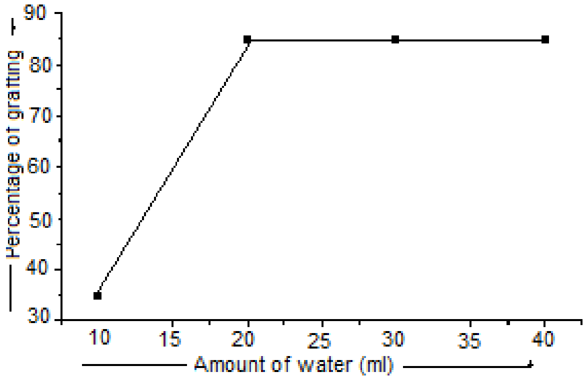


Fig.4. Effect of amount of water percent grafting of AAc

3.4.5 Effect of reaction time and temperature:

Figures 5 & 6 respectively represent the effect of reaction time and temperature on percent grafting of AAc. It is observed from Fig.5 that Pg increases with increasing time of reaction giving maximum (85%) in 180 min beyond which it decreases while with increasing temperature, maximum grafting (95%) was obtained at 70°C beyond which it decreases. Decrease in Pg beyond the optimum value is due chain scission, various chain transfer processes and thermal polymerization.

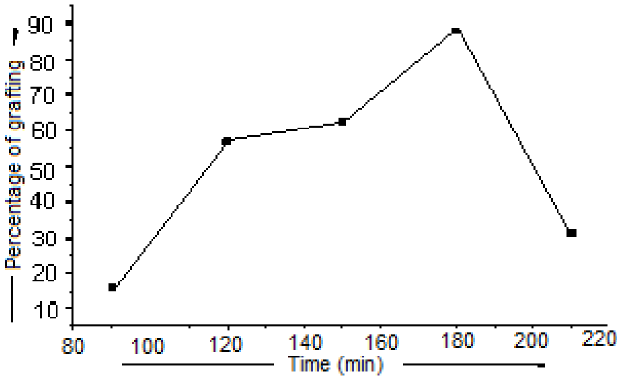


Fig.5. Effect of Time percent grafting of AAc

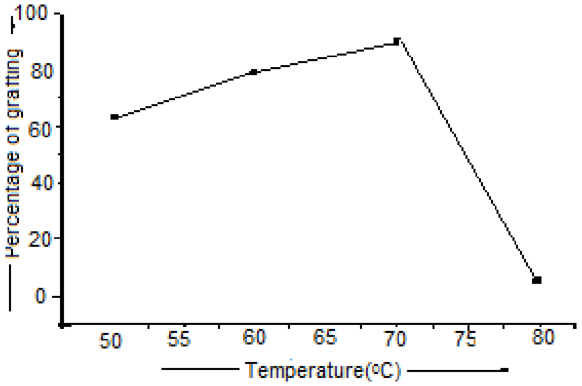


Fig.6. Effect of Temperature percent grafting of AAc

3.5 Grafting of AAc by Radiation method:

Gamma radiation induced grafting of AAc onto SMA copolymer was studied as a function of amount of monomer and the time of irradiation i.e. total dose. The results are presented in Fig.7. It is observed from the figure that at lower amount of AAc (7.28 $\times 10^{-3}$moles), Pg decreases with increasing total dose. Maximum grafting (600%) was observed at total dose of **45.36 kGy**. With increase in the amount of AAc, Pg was found to increase with increasing total dose giving maximum (855%) using 21.83 $\times$ 10^{-3} moles of AAc at an optimum total dose of **68.04 kGy** and decreases thereafter. Decrease in percentage of grafting beyond the maximum in each case is due to the preferable homopolymer formation.

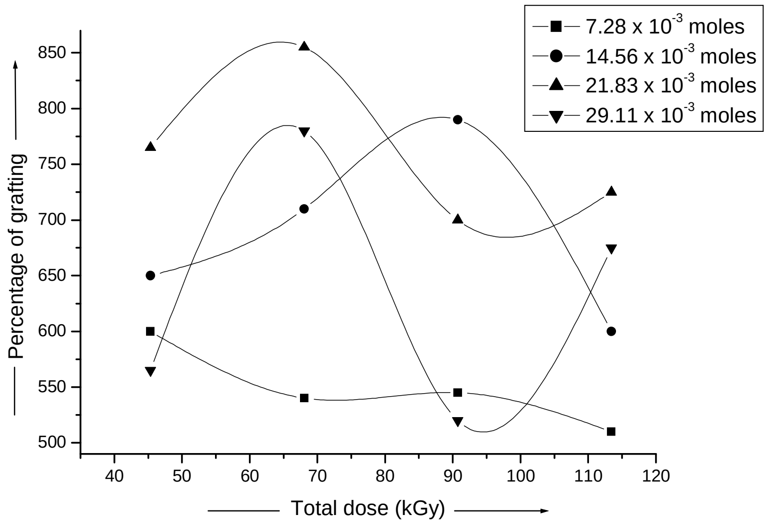


Fig.7. Effect of Total dose percent grafting of AAc

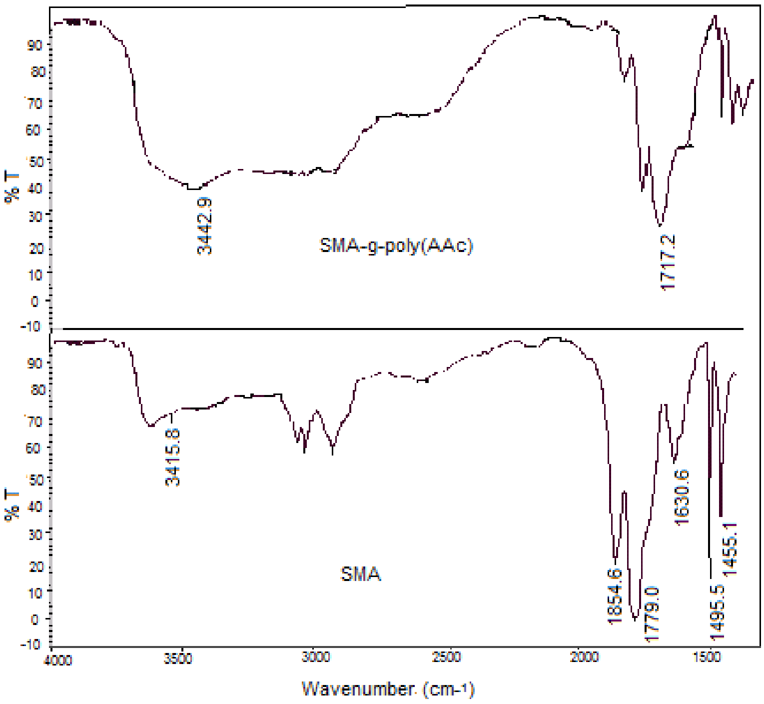


Fig.8. FTIR of SMA andSMA-g-poly(AAc)

3.6 Characterization of Graft copolymer

SMA and SMA-g-poly (AAc) copolymers have been characterized by IR, ^{1}HNMR, TGA and XRD analytical methods.

3.6.1 FTIR Spectroscopy: IR spectra of SMA and SMA-g-poly (AAc) are presented in Fig.8. IR spectrum of pure SMA shows bands at 3415.8 cm^{-1}due to associated –OH group, while bands at 1854.6 cm^{-1} and 1779.0 cm^{-1} are due to >C=O of anhydride group. Aromatic ring of styrene shows bands due to $\upsilon_{C=C}$ stretching and deformation at 1630.6, 1495.5 and 1455.1 cm^{-1} respectively.

The peaks due to >C=O of anhydride group and the >C=O of the grafted acrylic acid appears as a combined broad peak at 1717.2 cm^{-1} in the IR spectra of the grafted SMA copolymer and the peak due to associated hydroxyl groups of the pendent carboxylic groups of the grafted poly acrylic acid appears at 3442.9 cm^{-1}.

3.6.2 ^{1}HNMR: ^{1}HNMR spectra of SMA and SMA-g-poly (AAc) are presented in Fig.9 (a-b) respectively. SMA copolymer show peaks due to methylene, methine and aromatic proton. Methine protons of maleic anhydride moiety and styrene chain respectively appear at 3.857ppm and 3.474ppm while the methylene protons appear between 2.582-2.564ppm. The aromatic ring protons appear between7.448- 7.995ppm.

Grafting of acrylic acid takes place on the carbon directly attached to benzene ring after removing the tertiary hydrogen. The ^{1}HNMR spectra of SMA-g-poly (AAc), therefore, show a single peak at 3.380ppm due to the methane protons of maleic anhydride moiety with the methylene protons appearing between 2.557-2.548 ppm. In addition to the aromatic protons appearing7.587-7.784ppm downfield shift is observed with peaks between 8.035 – 8.061ppm of the aromatic protons due to the combined electron withdrawing effect of the maleic anhydride moiety and the carboxylic group of the grafted acrylic acid.

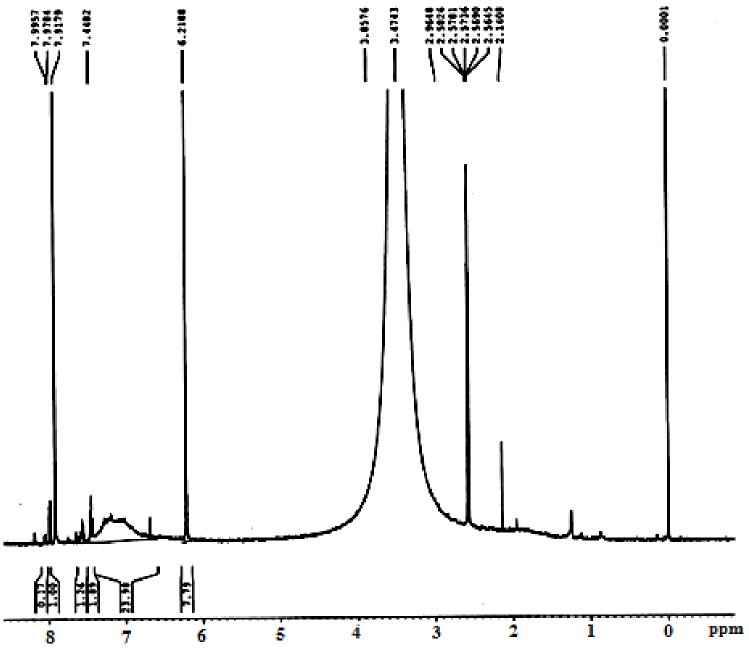


Figure.9(a). NMR of SMA

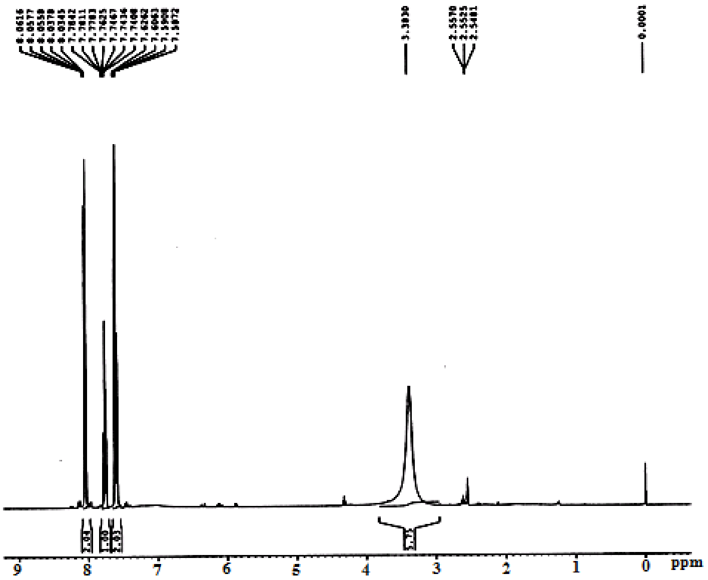


Figure.9(b). NMR of SMA-g- poly (AAc)

3.6.3 X-ray Diffraction Studies:

The X-ray diffraction pattern of SMA (Fig.10) shows broad peaks at 12^o and 21^o on 2θ scale with 1500 counts indicating that styrene-maleic anhydride copolymer is an amorphous material. Grafting of acrylic acid onto SMA, on the other hand, changes the character of SMA from amorphous to crystalline, sharp peaks at 21^o and 27^o on 2θ scale with increased intensity (3000 counts) are observed. The increase in the crystallinitty upon grafting is explained on the basis that during grafting the growing polymeric chains get chemically bound to SMA copolymer that provides fixed and arranged structure to the polymer. The particle size of the grafted polymer is 44 nm as calculated from the Scherrer's equation.

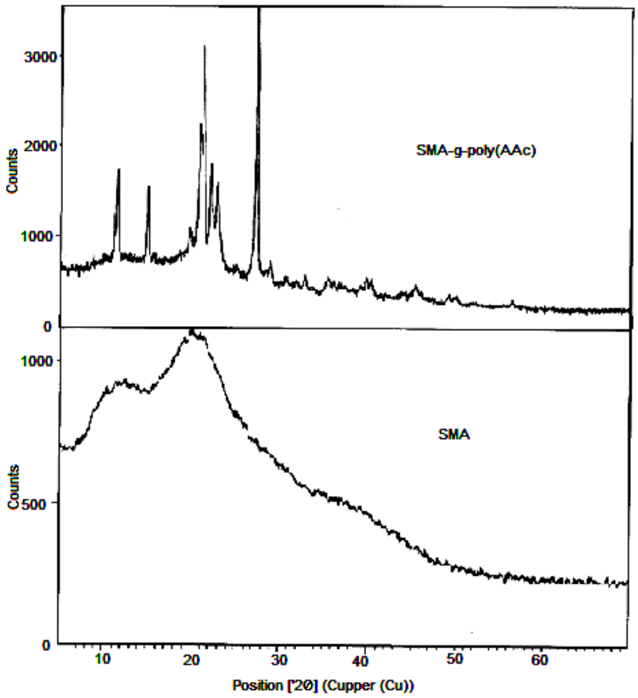


Fig. 10. XRD of SMA and SMA-g- poly (AAc)

3.6.4 Thermogravimetric Analysis:

Thermogravimetric Analysis, (TGA), of SMA and SMA-g-poly (AAc), was carried out and the respective thermograms are presented in Fig.11. Initial decomposition temperature (IDT), final decomposition temperature (FDT) and decomposition temperature (DT) at every 10% wt. loss of respective samples are presented in Table 1.

It is observed from the primary thermogram of SMA (Fig.11 curve-a) that initial decomposition of SMA begins at 274.3^{0}C after losing about 10-15% wt. due to the water desorption. There after the decomposition continues slowly up to 363.2 ^{0}C with 40% wt. loss and the temperature difference between each 10% wt. loss lying between 24^{0}C to 140^{0}C. With further rise in temperature, the rate of decomposition increases indicated by lowering of temperature difference to 9.8^{0}C between 60-70% wt. loss. Between 80-90% wt. loss, the difference increases to 31^{0}C. Final decomposition begins beyond 90% wt. loss at 445^{0}C which continues till 600^{0}C leaving 3 % residue.

Perusal of thermogram and thermal data of AAc grafted SMA show a very different decomposition behavior. SMA-g-poly (AAc) decomposes with an abrupt wt. loss of 42% at 121.37^{o}C beyond which the decomposition proceeds with a slow rate as indicated by a large temperature difference (31^{0}C-171.3^{0}C) between each 10% wt. loss. Final decomposition begins from 464.2^{o}C beyond it continues leaving behind 4.3% residue.

From the thermal behavior of the copolymer and grafted copolymer reveals that grafting has an impact on the thermal behavior of the copolymer and it has also been revealed from the XRD studies that the grafting increases the crystallinity of the copolymer. Thus from the results it can be inferred that the change in crystallinity seems to be responsible for the change in the thermal behavior. The observation indicates towards a correlation between crystallinity and thermal behavior of the copolymer.

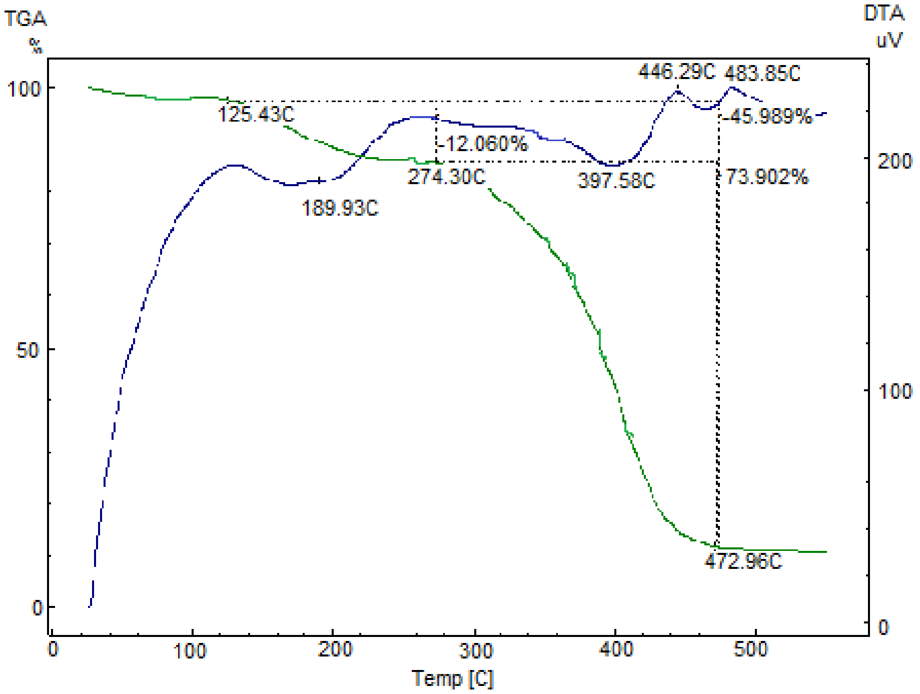


Fig.11(a).TGA of SMA

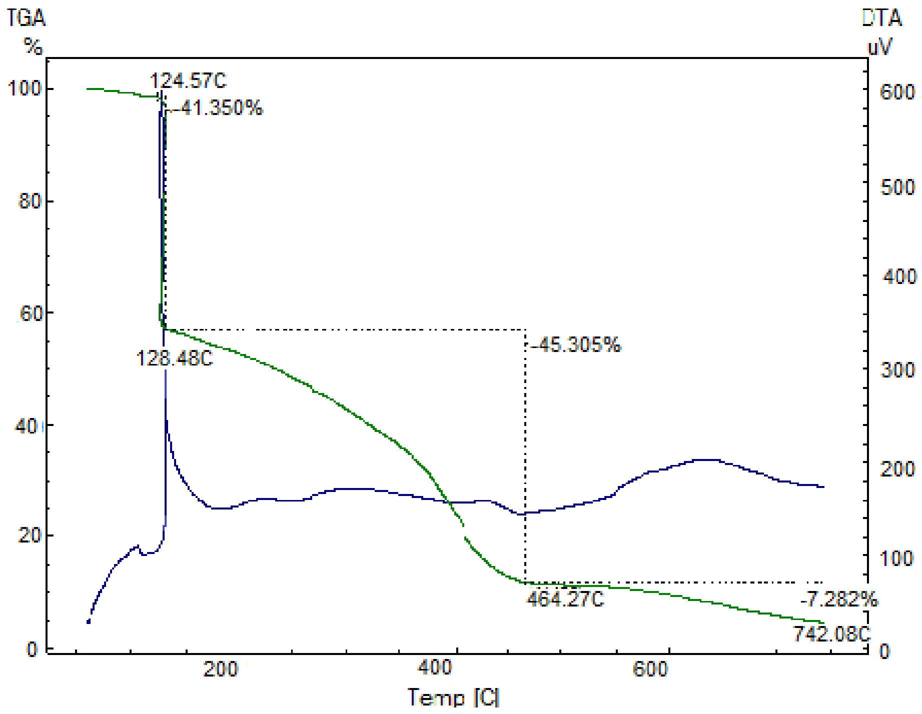


Fig.11(b). TGA of SMA-g- poly (AAc)

Table 1. Thermogravimetric Data of SMA and SMA-g-poly (AAc)

Sample	IDT (^{0}C)	FDT (^{0}C)	DT (^{0}C) at every 10% wt. loss									% Res. left
			10%	20%	30%	40%	50%	60%	70%	80%	90%	
SMA	274.3	445.0	160.3	300.0	339.7	363.2	376.8	387.2	397.0	409.7	440.7	3.0
SMA-g-poly (AAc)	124.5	464.2	132.6	130.8	129.4	127.6	233.4	319.3	380.3	411.6	582.9	4.3

3.7 Swelling Studies

Swelling studies of SMA and SMA-g-poly (AAc) in water were carried out in pH varying from acidic to basic and different temperatures in 6 and 12 h. The results are presented in Table 2. The pristine styrene-maleic anhydride copolymer remains suspended in water without undergoing any change while the graft copolymer prepared by the chemical method loosens and get suspended in water so much that it was difficult to effectively measure the swelling parameter.

The graft copolymer, SMA-g- poly (AAc) prepared by radiation method, on the other hand, showed excellent swelling behavior which may be due to the reason that some cross linking during radiation process takes place that holds the structure of the polymer. It is observed from the Tables that swelling percentage increases with increase in the pH from acidic to basic value. The higher value in the basic media is attributed to the fact that the anhydride moieties get hydrolyzed and the carboxyl functions exit as anions or as salt with properties of a polyelectrolyte. In either case repulsion between the negative charges on the carboxyl groups widens the net work leading to increased diffusion of the water molecules and interaction with groups to give high percent swelling. Swelling was also found to increase with increasing temperature and increasing time of swelling, both helping in widening of the network and diffusion of the solvent. Maximum swelling 2920% in 6h and 3290% in 12h was obtained at 37^{0}C and 9 pH. The high swelling behavior indicates that the graft copolymer can be utilized in applications such as water management, drug delivery etc. where swelling properties are required.

Table 2. Swelling percentage of SMA graft as a function of Time, Temperature and pH

S.No	Swelling Time (h)	Temperature (°C)	pH		
			4	7	9
1	6h	29	345	455	965
2		33	335	580	1190
3		37	720	2470	2920
4		43	525	775	1475
5	12h	29	415	675	1570
6		33	455	825	2240
7		37	1080	3060	3290
8		43	630	1025	2640

3.8 Drug delivery studies

Drug release generally involves simultaneous absorption of water and desorption of drug via a swelling controlled mechanism. The drug release from the polymer loaded with the drug was studied by measuring the OD of the water solution carrying the loaded sample as a function of time, pH and the results are presented in Fig.12. It is observed from the figure that the release of the drug increases with increase in the time up to 100 min beyond which it becomes almost constant.

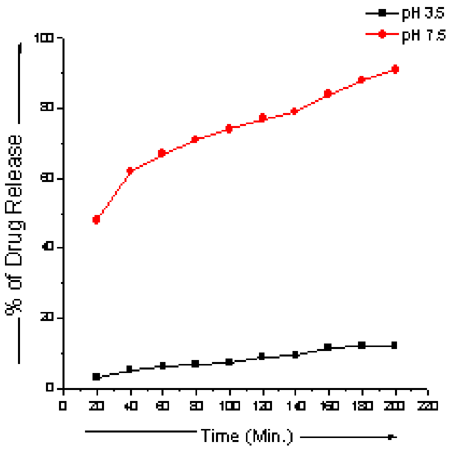


Fig.12.Drug release from SMA-g-poly (AAc)

To investigate more precisely the effect of polyampholytic formation on the release of ampicillin, the results were analyzed according to the following equation:

$$D = Mt/M = kt^n$$

where D or Mt/M is the amount of ampicillin (%) released at time (h); *n* is a diffusional exponent and k is the apparent release rate (%/h).

Ampicillin loaded hydrogels shows a non Fickian release with n value 0.566 and K=0.57 at pH 3.5, (From fig.13(a)) due to strong H-bonding interaction between carboxylic groups and amide groups, which present within the network due to presence of acrylic acid and ampicillin. These H-bonding interactions result in the formation of a compact or tight structure which dose not permit much movement of polymeric segments within the hydrogel network. This results in minimum swelling of hydrogel. Such type of explanations which accounts for minimum swelling at lower pH have also been offered elsewhere.[22]

However, in medium of pH 7.5 the almost complete ionization of –COOH group results in the extensive chain relaxation among similarity charged-COO^- groups presents along the macromolecular chain. Moreover, dissociation also causes an increase in ion osmotic swelling pressure. These two factors are thus responsible for higher degree of swelling in the medium of pH 7.5. At pH 7.5 hydrogel shows non fickian drug release with n value 0.255 and k

23.19 (from fig. 13(b)). The ionic strength in the neutral swelling medium is smaller than that in acidic media, therefore having the higher swelling capacities [23, 24].

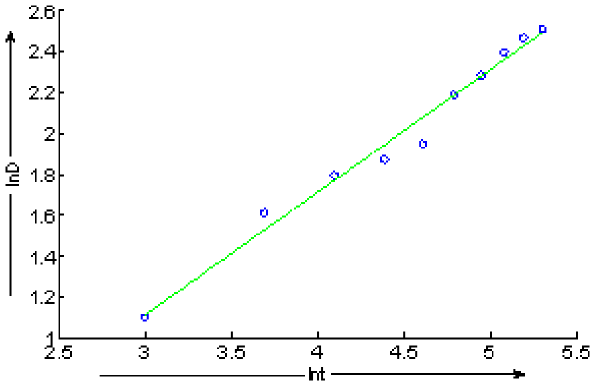


Fig.13(a) Plot of lnD vs. ln *t* for drug release of SMA-g-AAc hydrogel at 3.5pH

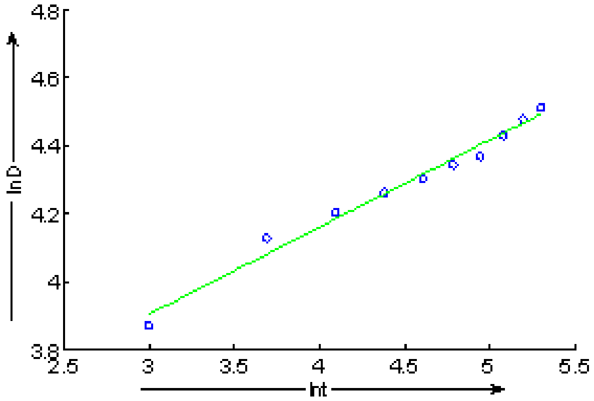


Fig.13(b) Plot of lnD vs. ln *t* for drug release of SMA-g-AAc hydrogel at 7.5pH

The increased release of the drug during the early period followed by the constant release of drug is beneficial for the effective drug action. The observed results, therefore, indicate that the SMA grafted with acrylic acid provides a vehicle for the drug that can be released in slow and sustained manner.

CONCLUSION

The synthesis of styrene-maleic anhydride copolymer and grafting of hydrophilic monomer, acrylic acid on to the copolymer has been successfully carried out both by chemical and radiation methods. The copolymer and the graft copolymer have been characterized by spectral, thermal and diffraction methods. An important correlation with crystallinity and thermal behavior of the copolymer has been observed. The radiation induced graft copolymer shows excellent swelling behavior indicating that the graft copolymer can be used in applications where swelling is an important criteria. The drug delivery is a suitable option for such type of polymer. The drug release from the polymer shows the effectiveness (swelling, pH responsiveness, functional groups of polymer etc.) of the polymer to be used as a vehicle for drug loading and drug delivery.

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