Chapter – IV

Modification of Pristine Copolymers, Chs-co-Chi and Chi-co-PVA, by Grafting of Binary Mixture of Acrylic acid and Acrylamide, (AAc +AAm) onto the Copolymer by Chemical Method
In the present Chapter, attempts have been made to modify the two copolymers, Chs-co-Chi and Chi-co-PVA, prepared and discussed in Chapter I and Chapter II, by grafting of binary mixture of acrylic acid and acrylamide, (AAc + AAm), through chemical method using ammonium persulfate as the radical initiator.

Chitin, a natural acetyl-amino polysaccharide, Chitosan, a deacetylated derivative of chitin and PVA, a synthetic water soluble poly hydroxy polymer, are well known for their non-toxic, biodegradable, non-carcinogenic and biocompatible properties and hence can be used in a variety of biomedical and pharmaceutical properties like, wound healing and dressing, tissue engineering, drug delivery etc. These can also be modified in the form of films and so can be used in applications like packaging to protect food supplements, in sunglasses etc. Therefore, copolymer of chitin with chitosan and chitin with PVA have been synthesized. The respective copolymers have been modified by grafting of AAc and AAm and discussed in Chapter II and III respectively.

Number of methods for grafting of hydrophilic monomers onto chitosan, chitin and PVA, individually or in combination with other monomers have been investigated. AAc grafted chitin based hydrogels have been used in wound dressing applications, removal of dyes from aqueous solutions and to fix magnetically aligned mesophase. Acrylonitrile, AAc, AAm and methyl acrylate were grafted onto chitin using ceric (IV) ion as redox initiator. Grafting of styrene has been carried out by different methods onto chitin and mercapto-chitin. El-Toony et al. synthesized foam-PVA/AAc hydrogels by gamma radiation and used these for the removal of Ca$^{2+}$, Mg$^{2+}$, reduction of turbidity and microbial count of Nile river. Al-qudah et al. copolymerized PVA with AAc using gamma irradiation and used the copolymer for the removal of Zn$^{2+}$, Co$^{2+}$ and Mn$^{2+}$ ions from their aqueous solutions. Singh and Pal synthesized hydrogels of sterculia cross-linked PVA and PVA-AAm and used it for wound dressing. The hydrogel synthesized was characterized by SEM, FTIR, TGA and swelling studies. Acrylic acid grafted chitosan had been developed and the graft copolymer synthesized had been used in waste water treatment for removal of toxic metal ions. When the grafted chitosan was cross-linked with montmorillonite or with Muscovite it was used as super adsorbent. Graft copolymer of chitosan, AAc and PVA and that of chitosan, AAc and sodium humate had also been synthesized and used as super adsorbents. Acrylamide had been grafted on to chitosan using radical
initiator and cross-linking agents by different methods which was then characterized using different analytical techniques.\cite{21-25}

A number of researches have been carried out to study the grafting of a variety of binary vinyl monomeric mixtures on different polymer backbones.\cite{26} As different monomers have favourable or opposite relations, therefore, graft copolymerization of mixture of monomers is a more complex phenomenon as compared to the grafting of the individual monomers. Michael et al.\cite{27} synthesized interpenetrated polymer network of Chitosan-poly(AAc-co-AAm) hydrogel by free radical polymerization method. The hydrogel was characterized by FTIR, micro structural techniques and compressive mechanical testing. Alka and Neeraj\cite{28} synthesized superparamagnetic nano-iron oxide loaded poly(AAc-co-AAm) hydrogel in situ conditions and characterize it by TEM, XRD and FTIR analytical techniques. They used the hydrogel for the removal of poisonous lead (Pb\(^{2+}\)) ions from aqueous solutions. Gupta et al.\cite{29} used atom transfer radical polymerization (ATRP) method of grafting of binary mixture of N-isopropylacrylamide (NIPAAm) and acrylic acid monomers onto multi-walled carbon nano-tubes. Chauhan and Harinder\cite{30} synthesized novel graft copolymers of cellulose-based hydrogels for water technologies using acrylic acid, acrylamide and their binary mixture as monomers, benzoyl peroxide as an initiator and glutaraldehyde as cross-linker. Binary mixture of AAm-AAc and acrylonitrile-acrylic acid has been successfully grafted onto polyester fibers using benzoyl peroxide as an initiator.\cite{31} Thermal and pH sensitivity of binary grafting of monomers NIPAAm and acrylic acid on to poly(tetrafluoroethylene) PTFE, had been carried out by Burillo et al.\cite{32}

Chauhan and Kaith\cite{33} has graft copolymerized cellulose fiber backbone of Serani by different vinylic monomer mixtures using CAN-nitric acid system as reaction initiator. Gupta\cite{34} had successfully carried out graft copolymerization of binary mixture of N,N'-diethyl acrylamide and AAc monomers onto cellulose using ATRP method. Sharma\cite{35} had grafted methyl methacrylate, 2-hydroxymethyl methacrylate and glycidyl methacrylate on to cellulose along with binary monomer mixture with AAm, AAc and acrylonitrile using benzoyl peroxide as initiator and studied their thermal properties. Graft copolymerization of binary mixture of AAc and AAm had been carried onto gelatin backbone using APS as reaction initiator. The optimization of grafting had been carried out through the varying the concentration of AAm, AAc, APS and gelatin and
reaction temperature. Sharma et al. modified fibers of *Hibiscus cannabinus* by graft copolymerization with AAc and binary mixture of AAc and AAm and characterized these using FTIR and SEM analytical techniques. The graft copolymers were used for removal of dyes from aqueous systems. Omer and Erdener have synthesized a ternary semi-interpenetrating polymer networks by the introduction of poly(ethylene glycol) into AAm/ sodium acrylate hydrogels. The hydrogels so formed have high water and dye sorption properties and hence can be used for dye removal from their aqueous solutions. Binary mixture of styrene and AAm was successfully graft copolymerized on to cellulose acetate by radiation-induced method. Hydrogels of poly(AAm-co-AAc), which behave as superabsorbent, had been prepared by a number of authors and were characterized by fast swelling, pH swelling dependence, composition and ionic strength. Wanjie Li et al. prepared poly(AAm-co-AAc) and used for slow-release of fertilizers.

Poly(AAc-co-AAm) grafted chitosan had been synthesized by Mahdavinia et al. The effect of the buffer solution, ionic strength and concentration of cross-linker on the swelling properties of these systems had been studied. Gamma-ray induced graft copolymerization of binary monomer mixture of n-butyl acrylate and styrene on poly(ethylene terephthalate) film had been carried out by Ping et al. Temperature responsive character of binary photo-grafted mixture of AAc and NIPAAm onto cellulose had been carried out by Wen. Modification of delignified Grewia optiva, a waste biomass, has been carried out by Graft copolymerization of methyl methacrylate as principal monomer in a binary monomer mixtures of ethyl methacrylate and ethyl acrylate using ascorbic acid/ H_2O_2 as initiator under microwave irradiation. Grafiting of binary monomers onto silk fiber using ceric ammonium nitrate as redox initiator has been carried out by Sunil et al. and the graft copolymer was characterized by FTIR, TGA and SEM analytical techniques. The binary graft copolymer so synthesized was used for uptake of gentian violet dye.

In the light of above discussion, it was thought to modify pristine copolymers, Chs-co-Chi and Chi-co-PVA through grafting with binary mixture of hydrophilic monomers, AAc and AAm, using ammonium persulfate as radical initiator. The swelling properties of each of the graft copolymer, prepared as a function of different reaction parameters, have been investigated and compared with the pristine copolymers.
4.1. EXPERIMENTAL

4.1.1. Materials and Method:

The copolymers, Chs-co-Chi and Chi-co-PVA prepared in Chapter II and III respectively have been used as base polymers. Ammonium persulfate (APS) (S.D. Fine, Mumbai), a free radical initiator, acrylic acid (AAc) and acrylamide (AAm) (Merck, India) were used as received. Distilled water was used throughout the study as the reaction medium.

4.1.2. Graft copolymerization of binary mixture of Acrylic acid, Acrylamide (AAc + AAm) onto Chs-co-Chi and Chi-co-PVA copolymers: Synthesis of (Chs-co-Chi) g-poly(AAc-co-AAm) (Chi-co-PVA)-g-poly(AAc-co-AAm) graft copolymers:

Graft copolymerization of binary monomer mixture onto Chs-co-Chi and Chi-co-PVA has been carried out by chemical method using ammonium persulfate as radical initiator.

A known weight of the copolymer Chs-co-Chi/ Chi-co-PVA (1.0 g), in the form of the monolith, and a known amount of APS (0.73 x 10^{-1} - 3.65 x 10^{-1} mol/L), binary mixture (AAc + AAm), taken in definite proportions, ([AAm] = 2.34 x 10^{-1} - 11.72 x 10^{-1} mol/L; [AAc] = 4.86 x 10^{-1} - 43.76 x 10^{-1} mol/L) were taken in a test tube containing water (3mL). The reaction mixture was placed in a water bath maintained at a constant temperature (50-90°C) and the reaction was allowed to proceed for different time periods (2-6 h). After the stipulated time period, the graft copolymers, (Chs-co-Chi)-g-poly(AAc-co-AAm)/ (Chi-co-PVA)-g-poly(AAc-co-AAm), was removed from the test tube and suspended in excess amount of water for some time so as to eliminate the residual monomers and homopolymer/ copolymer, if present. The graft copolymer, free from homopolymer/ copolymer was dried at 50°C till constant weight was obtained.

4.1.3. Swelling behaviour:

Swelling behaviour of each of the (AAc + AAm) grafted Chs-co-Chi/ Chi-co-PVA copolymers, (Chs-co-Chi)-g-poly(AAc-co-AAm), (Chi-co-PVA)-g-poly(AAc-co-AAm), prepared under different reaction conditions, has been studied at room temperature as a function of time.

4.1.4. Swelling studies of (AAc + AAm) grafted Chs-co-Chi/ Chi-co-PVA copolymers in water:

Accurately weighed (0.100 g) samples of (Chs-co-Chi)-g-poly(AAc-co-AAm)/ (Chi-co-PVA)-g-poly(AAc-co-AAm) graft copolymers were separately immersed in 30 mL of
distilled water. The beakers were covered and placed undisturbed at room temperature. The work up and measurement of percentage was carried out as per procedure described in Chapter II.

4.1.5. Swelling studies of (AAc + AAm) grafted Chs-co-Chi/ Chi-co-PVA copolymers in buffer solutions:

Dried sample (0.100 g) of graft copolymers, (Chs-co-Chi)-g-poly(AAc-co-AAm) and (Chi-co-PVA)-g-poly(AAc-co-AAm), were separately immersed in 30 mL of citrate buffer of pH 2.8 and 30 mL of phosphate buffer of pH 7.2 in separate beakers. The beakers were covered and kept undisturbed at 37°C. The swelling percentage was measured by the procedure described in Chapter II.

4.1.6. Swelling studies of (AAc + AAm) grafted Chs-co-Chi/ Chi-co-PVA copolymers in salt solutions:

Dried samples (0.100 g) of (Chs-co-Chi)-g-poly(AAc-co-AAm) and (Chi-co-PVA)-g-poly(AAc-co-AAm) graft copolymers were separately immersed in known amount (30 mL) of 0.9% NaCl solution in separate beakers. The beakers were covered and kept undisturbed at 37°C. The swelling percentage was measured by the procedure described in Chapter II.

4.2. Characterization:

The graft copolymers, (Chs-co-Chi)-g-poly(AAc-co-AAm) and (Chi-co-PVA)-g-poly(AAc-co-AAm) have been characterized by the following methods:

4.2.1. Fourier Transform Infrared Spectroscopy (FTIR):

FTIR spectra of (Chs-co-Chi)-g-poly(AAc-co-AAm) and (Chi-co-PVA)-g-poly(AAc-co-AAm) were obtained by Nicolet-5700 Spectrophotometer.

4.2.2. Scanning Electron Microscopy (SEM):

Surface topology and homogeneity of the graft copolymers, (Chs-co-Chi)-g-poly(AAc-co-AAm) and (Chi-co-PVA)-g-poly(AAc-co-AAm) was studied by Scanning Electron Microscope of model LEO 1430 VP.

4.2.3. X-Ray Diffraction Studies (XRD):

The X-ray diffraction patterns of (Chs-co-Chi)-g-poly(AAc-co-AAm) and (Chi-co-PVA)-g-poly(AAc-co-AAm) were recorded on a Philips PAN ANALYTICAL X’PERT PRO X-ray Powder Diffractometer.
4.2.3. Measurement of particle size

Average Crystallize Size (D) in the sample was calculated from peak widths $\Delta 2\Theta_{1/2}$ in the characteristic diffraction peaks using the Debye–Scherrer’s equation:

$$D = \frac{0.89 \lambda}{(\Delta 2\Theta_{1/2}) \cos \theta_b}$$

where $2\Theta_b$ is the position of a peak in the diffractogram from a specific crystallographic plane (hkl).

4.2.4. Particle size analysis:

Particle size analysis of (Chs-co-Chi)-g-poly(AAc-co-AAm) and (Chi-co-PVA)-g-poly(AAc-co-AAm) were performed on Navowavetrac Particle Size Analyzer (Metrohm, US).

4.2.5. Thermogravimetric Analysis (TGA):

Thermogravimetric analysis (TGA) of graft copolymers (Chs-co-Chi)-g-poly(AAc-co-AAm) and (Chi-co-PVA)-g-poly(AAc-co-AAm) was carried out on Thermal Analyzer (EXSTAR TG/ DTA 6300) in air at a heating rate of 10°C per min with temperature range of 20 to 820°C.

4.3. Results and Discussion:

4.3.1. Mechanism of Graft Copolymerization of (AAc + AAm) onto Chs-co-Chi/Chi-co-PVA:

Both the sulphate ion radicals and hydroxyl radicals, from APS, initiate the process by generating free radicals on the backbones of pristine copolymers and also initiate the monomers to give growing polymer chains. The interaction of the active sites on the copolymer and active growing polymeric chains leads to the formation of the graft copolymer. Based on this, the mechanism of grafting of (AAc + AAm) onto Chs-co-Chi/Chi-co-PVA is proposed as follows (Scheme I):
Optimization of the reaction condition for graft copolymerization of (AAc + AAm) onto Chs-co-Chi/Chi-co-PVA copolymer has been based on swelling characteristic of the graft copolymer in water and the results are explained in the light of the mechanism.

4.3.1.1. Effect of monomer concentration:

Grafting of binary monomer mixture, (AAc + AAm) onto Chs-co-Chi and Chi-co-PVA copolymer has been studied as a function of their respective concentrations and their effect on the swelling behaviour of the respective graft copolymers, (Chs-co-Chi)-g-poly(AAc-co-AAm), (Chi-co-PVA)-g-poly(AAc-co-AAm) has been investigated. Optimization of monomer concentration has been carried out on the basis of effect of concentration of each monomer, AAc and AAm individually in the monomer mixture and the results are presented in Figs. 4.1 (a-d respectively).

Keeping the concentration of AAc fixed at $34.03 \times 10^{-1}$ mol/L, (since at this concentration, maximum swelling was exhibited when AAc was grafted individually on Chs-co-Chi copolymer) concentration of AAm was varied. It is observed from Fig. 4.1a that the percentage of swelling of each of the sample, prepared at varying [AAm], increases gradually with time reaches maximum and then becomes constant. Maximum swelling (172.73% in 120 min) was observed for the sample prepared at lower [AAm] =
4.69 × 10⁻¹ mol/L beyond which it decreases. Taking optimum [AAm] (4.69 × 10⁻¹ mol/L), the concentration of AAc in the binary mixture was varied. Swelling percentage increases with increase in [AAc] giving maximum (172.73% in 120 min) for the graft copolymer prepared by using higher concentration of AAc (34.03 × 10⁻¹ mol/L) beyond which percent swelling decreases.

Fig. 4.1a  Percent swelling of (Chs-co-Chi)-g-poly(AAc-co-AAm) as a function of time: Effect of [AAm]

Reaction Conditions: Chs-co-Chi = 1.0 g, [AAc] = 34.03 × 10⁻¹ mol/L, [APS] = 1.46 × 10⁻¹ mol/L, reaction temperature = 70°C, reaction time = 4 h

Fig. 4.1b Percent swelling of (Chs-co-Chi)-g-poly(AAc-co-AAm) as a function of time: Effect of [AAc]

Reaction Conditions: Chs-co-Chi = 1.0 g, [AAm] = 4.69 × 10⁻¹ mol/L, [APS] = 1.46 × 10⁻¹ mol/L, reaction temperature = 70°C, reaction time = 4 h
On comparing percent swelling of individual monomers, AAc and AAm, it is observed from the results (Chapter II) that AAc grafted Chs-co-Chi copolymer produces higher swelling (271.43% in 60 min) as compared to AAm grafted copolymer (140% in 240 min) but when the two are used as a binary monomer mixture, percent swelling decreases to (172.73% in 120 min) from (271.43%) that of AAc grafted copolymer indicating that AAm as a second component, decreases the swelling behaviour. Thus, it is evinced that poly(AAc) grafted chains provides better swelling properties due to the pendent carboxylic groups but when AAc is copolymerized with AAm, the pendent amide groups, because of low hydrophilic characteristics, decreases percentage of swelling.

Similarly, in case of the grafting of the binary monomer mixture onto Chi-co-PVA, optimization has been carried out on the basis of effect of concentration of each monomer, AAc and AAm individually (Fig. 4.1c and Fig. 4.1d respectively). Keeping the concentration of AAc fixed at $14.58 \times 10^{-1} \text{ mol/L}$, (since at this concentration, maximum swelling was exhibited by AAc grafted (Chi-co-PVA)-g-poly(AAc) copolymer) concentration of AAm was varied. It is observed from the figure the percentage of swelling of each of the sample, prepared at varying [AAm], increases gradually with time reaches maximum and then becomes constant. Maximum swelling (216.13% in 480 min) is observed for the sample prepared at [AAm] = $9.38 \times 10^{-1} \text{ mol/L}$ beyond which it decreases. Taking optimum [AAm] ($9.38 \times 10^{-1} \text{ mol/L}$), the [AAc] in the binary mixture was varied. Swelling percentage is found to increase with increasing [AAc] giving maximum (271.05% in 390 min) for the graft copolymer, prepared by using $24.31 \times 10^{-1} \text{ mol/L}$ concentration of AAc beyond which percent swelling decreases.

![Graph](image)

**Fig. 4.1 (c) Percent swelling of (Chi-co-PVA)-g-poly(AAc-co-AAm) as a function of time: Effect of [AAm]**

Reaction Conditions: Chi-co-PVA = 1.0 g, [AAc] = $14.58 \times 10^{-1} \text{ mol/L}$, [APS] = $1.46 \times 10^{-1} \text{ mol/L}$, reaction temperature = $70^\circ \text{C}$, reaction time = 4 h
On comparing percent swelling of individual monomers, AAc and AAm, it is observed from the results (Chapter III) that AAm grafted Chi-co-PVA copolymer produces higher swelling (427.59% in 90 min) as compared to AAc grafted copolymer (186.67% in 480 min) and when the two are used as a binary monomer mixture, percent swelling (271.05% in 390 min) is higher than the AAc grafted copolymer but lower than the AAm grafted copolymer.

From the results, it is interesting to note that when grafting of AAc and AAm is carried out on to the two structurally different copolymers, Chs-co-Chi and Chi-co-PVA, contradictory results are observed. In the former, higher swelling percentage is observed for AAc grafted copolymer while in the latter, AAm grafted copolymer gives the maximum swelling percentage. These observations can be explained considering the interactions of the functional moieties of the copolymers with the pendent groups of the grafted polymer chains. Higher number of NH₂ and lesser OH groups in Chs-co-Chi copolymer, enter into inter-molecular H-bondings with the pendent amide groups of the grafted poly(AAm) in comparison to the carboxylic groups of grafted poly(AAc) chains which are connected through intra-molecular H-bonds while opposite situation is experienced with Chi-co-PVA where the number of OH groups are higher in comparison to NH₂ in the copolymer which enter into inter-molecular H-bondings with the pendent carboxylic groups of the grafted poly(AAc) in comparison to the amide groups of grafted poly(AAm) chains which are poorly connected through intra-molecular H-bonds. Intra-
molecular H-bonded moieties interact with water more than the inter-molecular H-
bonded moieties giving the respective swelling behaviour.

The increase in swelling behaviour of graft copolymer with increasing monomer
concentration is attributed to an increase in the diffusion of monomer and the growing
polymeric chains to the active sites of the copolymer backbones resulting in higher graft
formation. Higher grafting percentage results in the increased number of pendant
carboxylic acid/ amide groups that enhance the hydrophilicity of the copolymer through
interaction with water molecules leading to increased swelling capacity.

The decrease in the swelling percentage after a particular concentration of the respective
monomers may be due to the self annihilation of the polymeric chains leading to the
preferential homopolymer/copolymer formation over graft copolymerization thus
affecting swelling capacity of the graft copolymer. The larger number of graft chains
may also hinder the water molecules to diffuse into the hydrogel matrix thereby
decreasing swelling percentage.

4.3.1.2. Effect of [APS]:

Effect of [APS] on graft copolymerization of (AAc + AAm) on to Chs-co-Chi and Chi-
co-PVA and on swelling behaviour of the respective graft copolymers, (Chs-co-Chi)-g-
poly(AAc-co-AAm) and (Chi-co-PVA)-g-poly(AAc-co-AAm) was studied and the
results are presented in Fig. 4.2a and Fig. 4.2b.

It is observed from Fig. 4.2a that swelling capacity of each of the graft copolymer, (Chs-
co-Chi)-g-poly(AAc-co-AAm), prepared by varying [APS] increases gradually with time
reaches maximum and decreases thereafter. Maximum swelling (172.73% in 120 min) is
observed for the sample prepared at lower [APS] = 1.46 × 10^{-1} mol/L beyond which it
decreases. However, in case of grafting of (AAc + AAm) onto Chi-co-PVA, percentage
of swelling increases continuously, reaching maximum and then becomes constant.
Maximum swelling (271.05% in 390 min) has been observed for the sample prepared at
the same lower APS concentration (1.46 × 10^{1} mol/L). Increase in [APS], beyond the
optimum decreases percent swelling in both the cases. The reduction of swelling beyond
the optimum [APS] may be attributed to an increase in homopolymer/ copolymer
formation affecting grafting and hence swelling characteristics. Degradation of the
copolymer structure in the presence of excess of APS also affects the grafting and
swelling behaviour.
Fig. 4.2a Percent swelling of (Chs-co-Chi)-g-Poly(AAc-co-AAm) as a function of time: Effect of [APS]

Reaction Conditions: Chs-co-Chi = 1.0 g, [AAc] = 34.03 $\times 10^{-1}$ mol/L, [AAm] = 4.69 $\times 10^{-1}$ mol/L, reaction temperature = 70°C, reaction time = 4 h

Fig. 4.2b Percent swelling of (Chi-co-PVA)-g-poly(AAc-co-AAm) as a function of time: Effect of [APS]

Reaction Conditions: Chi-co-PVA = 1.0 g, [AAc] = 24.31 $\times 10^{-1}$ mol/L, [AAm] = 9.38 $\times 10^{-1}$ mol/L, reaction temperature = 70°C, reaction time = 4 h

4.3.1.3. Effect of reaction temperature:

Fig. 4.3a and Fig. 4.3b represents the percentage swelling of (Chs-co-Chi)-g-poly(AAc-co-AAm) and (Chi-co-PVA)-g-poly(AAc-co-AAm) graft copolymer samples respectively, prepared as a function of time at different temperatures (50–90°C). It is observed from the figures that swelling percentage of each of the samples prepared at different temperatures increases with time gives maximum, decreases slightly and then
becomes constant. Maximum percentage swelling (172.73% in 60 min) is obtained for the (Chs-co-Chi)-g-poly(AAc-co-AAm), prepared at 70°C and (288% in 180 min) is obtained for (Chi-co-PVA)-g-poly(AAc-co-AAm) grafted samples, prepared at 60°C. Grafting reactions carried out at lower temperatures does not completely generates active radicals from the initiator and hence on the copolymer thus affecting grafting reaction and swelling capacity of the graft copolymer. At higher temperature than the optimum homopolymer/ copolymer formation may affect the grafting and swelling behaviour of the graft copolymer.

Fig. 4.3a Percent swelling of (Chs-co-Chi)-g-Poly(AAc-co-AAm) as a function of time: Effect of reaction temperature:

Reaction Conditions: Chs-co-Chi = 1.0 g, [AAc] = 34.03 × 10⁻¹ mol/L, [AAm] = 4.69 × 10⁻¹ mol/L, [APS] = 1.46 × 10⁻¹ mol/L, reaction time = 4 h

Fig. 4.3b Percent swelling of (Chi-co-PVA)-g-Poly(AAc-co-AAm) as a function of time: Effect of reaction temperature

Reaction Conditions: Chi-co-PVA = 1.0 g, [AAc] = 24.31 × 10⁻¹ mol/L, [AAm] = 9.38 × 10⁻¹ mol/L, [APS] = 1.46 × 10⁻¹ mol/L, reaction time = 4 h
4.3.1.4. Effect of reaction time:

Reaction time is one of the important factors that controls the kinetics of the graft copolymerization. Therefore the effect of reaction time on grafting of (AAc + AAm) onto Chs-co-Chi and Chi-co-PVA copolymers and on swelling behaviours of the respective graft copolymers was studied as a function of time and the results are presented in Fig. 4.4a & Fig. 4.4b respectively.

It is observed from Fig. 4.4a, that percentage of swelling of all the (Chs-co-Chi)-g-poly(AAc-co-AAm) copolymers, prepared at varying time of reaction, increases continuously with a constant rate reaches maximum and then becomes constant, after experiencing a small decrease. However, the graft copolymer, prepared in 4h of reaction time, shows increase in percent giving maximum (172.73% in 120 min), decreases thereafter and becomes constant.

Similar observation is made during grafting of binary mixture (AAc + AAm) onto Chi-co-PVA, the percent swelling increases gradually with time, reaches maximum and then becomes constant. Maximum percent swelling (288% in 180 min) is observed for the graft copolymer synthesized in a reaction time of 4 h.

Lower swelling percentage observed for both the graft copolymers, prepared in 2 h and 3 h of reaction time, may be attributed to the reason that the reaction time is insufficient to completely activate the copolymers and the monomers which further affects the formation of graft copolymers and swelling properties. The lower percentage of swelling of the graft copolymers synthesized in reaction time beyond optimum may be due to chain scission reactions, through backbiting processes, affecting the copolymer structures and hence swelling characteristics.

![Fig. 4.4a Percent swelling of (Chs-co-Chi)-g-Poly(AAc-co-AAm) as a function of time: Effect of reaction Time](image)

**Fig. 4.4a** Percent swelling of (Chs-co-Chi)-g-Poly(AAc-co-AAm) as a function of time: Effect of reaction Time

Reaction Conditions: Chs-co-Chi = 1.0 g, [AAc] = 34.03 x 10^{-1} mol/L, [AAm] = 4.69 x 10^{-1} mol/L, [APS] = 1.46 x 10^{-1} mol/L, reaction temperature = 70°C
4.3.2. Effect of pH on swelling behaviour of (AAc + AAm) grafted Chs-co-Chi/ Chi-co-PVA copolymers:

An acidic and alkaline medium have an effect on swelling properties of the copolymers and establishes a significant role in biomedical applications. Therefore, the swelling properties of graft copolymers, (Chs-co-Chi)-g-poly(AAc-co-AAm), (Chi-co-PVA)-g-poly(AAc-co-AAm) have been studied in acidic pH 2.8 and alkaline pH 7.2 at 37°C and the results are presented in Fig. 4.5a & Fig. 4.5b respectively.

From Fig. 4.5a, it is observed that swelling percentage of (Chs-co-Chi)-g-poly(AAc-co-AAm) in acidic medium (pH 2.8) increases with a fast rate in first 60 min, after that with a slow rate, reaches maximum (187.5% in 1230 min) and then becomes constant. However, from Fig. 4.5b it is observed that in alkaline medium (pH 7.2) the percent swelling of the copolymer increases slowly with constant rate, attains maximum swelling (262.96%) in lesser time (330 min) beyond which it becomes constant. The swelling percentage of (Chs-co-Chi)-g-poly(AAc-co-AAm) in both low and high pH media is higher as compared to that observed in aqueous medium (172.73% in 120 min). This may be due to the reverse effect of the carboxylic and the amide groups in the respective pH. When compared with the percentage swelling of the pristine copolymer, Chs-co-Chi copolymer (182.86% in 1230 min at pH 2.8 and 264.52% in 330 min at pH 7.2) (Chapter II), it is observed that there is slight increase in swelling of binary grafted copolymer in acidic pH and slight decrease in alkaline pH.
In case of swelling percentage of binary graft copolymer, (Chi-co-PVA)-g-poly(AAc-co-AAm) it is observed from Figs. 4.5a and 4.5b, that, swelling percentage increases with fast rate both in the acidic (pH 2.8) and in alkaline (pH 7.2) media, reaches maximum (119.23% in 150 min and 239.13% in 180 min respectively) and then becomes constant. The swelling percentage of the binary monomer grafted copolymer is lower, in both low and high pH media, as compared to (288% in 180 min) of binary grafted Chi-co-PVA copolymer in aqueous medium. In comparison to the swelling of the pristine Chi-co-PVA, in the acidic (113.64% in 150 min) and basic (163.64% in 1230 min) media, percent swelling of the binary grafted Chi-co-PVA copolymer is higher in both pH media.

Fig. 4.5a Percent swelling of (Chs-co-Chi)-g-poly(AAc-co-AAm) and (Chi-co-PVA)-g-poly(AAc-co-AAm): Effect of pH 2.8 buffer

Fig. 4.5b Percent swelling of (Chs-co-Chi)-g-poly(AAc-co-AAm) and (Chi-co-PVA)-g-poly(AAc-co-AAm): Effect of pH 7.2 buffer
4.3.3. pH sensitivity and pulsative behaviour:

The pulsative behaviour of (Chs-co-Chi)-g-poly(AAc-co-AAm) and (Chi-co-PVA)-g-poly(AAc-co-AAm) copolymers as a function of swelling in different pH (2.8 and 7.2) has been studied at 37°C for exhibiting reproducible swelling-deswelling cycles. Swelling measurements were made after every 15 min in the medium of each pH up to 120 min before switching to the next pH. The studies were continued till 720 min and the results are presented in Fig. 4.5c.

Percentage of swelling of (Chs-co-Chi)-g-poly(AAc-co-AAm) and (Chi-co-PVA)-g-poly(AAc-co-AAm) in pH 7.2 medium increases with increasing time of swelling giving maximum (96.77% and 146.67% respectively) within 120 min after which the sample was shifted to the medium of pH 2.8. Percentage of swelling of both the graft copolymers was found to start decreasing and reaches the minimum value (61.29% and 100% respectively) in next 120 min. This cycle was repeated with shifting the samples to pH 7.2 where increase in swelling is observed giving maximum swelling (129.03% and 206.67% respectively) in 120 min. However, when the sample is next shifted to lower pH 2.8, the decrease in swelling is not high and sharp (119.35% and 170% respectively) and as the process of switching to alternate pH continues, it is observed that the change in swelling percent does not vary much till 720 min takes place.

![Fig. 4.5c Pulsative behaviour of (Chs-co-Chi)-g-poly(AAc-co-AAm) and (Chi-co-PVA)-g-poly(AAc-co-AAm) in pH 2.8 and 7.2 buffers](image)

4.3.4. Effect of counter ion on swelling percentage of (Chs-co-Chi)-g-poly(AAc-co-AAm) and (Chi-co-PVA)-g-poly(AAc-co-AAm) copolymers:

In order to investigate the utility of (Chs-co-Chi)-g-poly(AAc-co-AAm) and (Chi-co-PVA)-g-poly(AAc-co-AAm) grafted copolymers in biomedical applications the effect of
counter ion on the swelling behavior of the copolymer was been investigated in 0.9% aqueous solution of NaCl at 37°C and the results are presented in Fig. 4.5d.

It is observed from the figure that percentage of swelling of (Chs-co-Chi)-g-poly(AAc-co-AAm) and (Chi-co-PVA)-g-poly(AAc-co-AAm) increases with time giving maximum (120.83% and 96.97% in 150 min) and then becomes constant. The swelling in case of binary grafted (Chs-co-Chi)-g-poly(AAc-co-AAm) copolymer is found to be higher than its pristine (Chs-co-Chi) copolymer in salt solution (90% in 150 min) while (Chi-co-PVA)-g-poly(AAc-co-AAm) graft copolymer shows lower percent swelling than the pristine copolymer Chi-co-PVA (108% in 150 min) in salt solution.

However, in both the cases, percent swelling of the graft copolymers in salt solution is lower than that observed in water. It decreases from 172.73% to 120.83% in case of (Chs-co-Chi)-g-poly(AAc-co-AAm) and from 288% to 96.97% in case of (Chi-co-PVA)-g-poly(AAc-co-AAm). It is known that hydrophilic copolymers do not swell appreciably in the presence of electrolyte salts due to ex-osmosis due to the loss of hydrophilic-hydrophobic balance of the networks in the presence of electrolyte salts. The swelling ratios of 2451 and 119 g/g of gel have been reported in distilled water and in 0.9% NaCl solution respectively for the polymers prepared in an aqueous solution using acrylamide and 2-acrylamido-2-methylpropanesulfonic acid using KPS and NMBA. \[49\]

![Fig. 4.5d Percent swelling of (Chs-co-Chi)-g-poly(AAc-co-AAm) and (Chi-co-PVA)-g-poly(AAc-co-AAm): Effect of salt solution](image-url)
4.4. Characterization of (AAc-co-AAm) grafted Chs-co-Chi and Chi-co-PVA copolymers:

4.4.1. FTIR spectroscopy:

FTIR spectra of binary grafted (Chs-co-Chi)-g-poly(AAc-co-AAm) and (Chi-co-PVA)-g-poly(AAc-co-AAm) copolymers are presented in Fig. 4.6.

In the FTIR spectrum of (Chs-co-Chi)-g-poly(AAc-co-AAm), in addition to the peaks due to pristine copolymer, Chs-co-Chi peaks due to the grafted copolymer are observed. Peaks at 1660.20 cm\(^{-1}\) due to >C=O group of poly(AAc), peak at 1624.20 cm\(^{-1}\) due to amide group of poly(AAm) and a peak at 1560.21 cm\(^{-1}\) due to amide II are observed in the binary (AAc + AAm) graft Chs-co-Chi. Also a peak at 670.26 cm\(^{-1}\) due to (AAc-co-AAm) moieties\(^{[50]}\) was observed in the graft copolymer indicating successful grafting of (AAc + AAm) on to the Chs-co-Chi backbone.

In the FTIR spectrum of (Chi-co-PVA)-g-poly(AAc-co-AAm) graft copolymer, a broad peak between 3700 cm\(^{-1}\) to 3000 cm\(^{-1}\) is present which is due to the \(v_{(O-H)}\) stretching and extension of vibrations of \(v_{(N-H)}\) stretching of acrylamide. The appearance of peaks due to pendant carboxylic groups of poly(AAc) and amide groups of poly(AAm), at 1664 cm\(^{-1}\) and 1626.21 cm\(^{-1}\) along with a peak at 1559.22 cm\(^{-1}\) due to >C=O group and amide I & II respectively indicates successful grafting of binary monomer mixture (AAc + AAm) on to Chi-co-PVA backbone.

![FTIR spectra](image)

Fig. 4.6 FTIR spectra of (a) Chs-co-Chi)-g-poly(AAc-co-AAm) and (b) (Chi-co-PVA)-g-poly(AAc-co-AAm) graft copolymers
4.4.2. Scanning Electron Microscopy:

The Scanning Electron Micrographs, SEMs, of Chs-co-Chi, (Chs-co-Chi)-g-poly(AAc-co-AAm), Chi-co-PVA and (Chi-co-PVA)-g-poly(AAc-co-AAm) are presented in Figs. 4.7 (a-d respectively) to assess the surface topology and homogeneity of the copolymers.

Fig. 4.7a and Fig. 4.7b present scanning micrographs of pristine Chs-co-Chi copolymer and (Chs-co-Chi)-g-poly(AAc-co-AAm) graft copolymer at three different magnifications (500X, 1000X and 1500X). Pristine copolymer, Chs-co-Chi, exhibits a thick dense and porous structure with small cavities distributed on the entire surface of copolymeric matrix (Fig. 4.7a). Grafting of (AAc + AAm) onto Chs-co-Chi changes the surface topology of the graft copolymer. The surface of the graft copolymer becomes more heterogeneous due to the anchored grafted polymer. The porosity of the graft copolymers is also increased and can be well observed due to the presence of large pores on the surface of the graft copolymers (Fig. 4.7b).

Fig. 4.7c and Fig. 4.7d present scanning micrographs of pristine Chi-co-PVA copolymer and (Chi-co-PVA)-g-poly(AAc-co-AAm) graft copolymer respectively at three different magnifications (500X, 1000X and 1500X). It is observed that the pristine copolymer, Chi-co-PVA, exhibits a thick, dispersed, dense, porous and less heterogeneous structure with small cavities distributed over the entire surface (Fig. 4.7c) while the surface of the graft copolymer shows the distribution of the grafted polymer throughout with pores within evincing successful grafting of the monomer binary mixture (Fig. 4.7d).
4.4.3. X-Ray Diffraction Studies:

X-ray diffraction studies of (Chs-co-Chi)-g-poly(AAc-co-AAm) and (Chi-co-PVA)-g-poly(AAc-co-AAm) were carried out and the respective diffractograms are presented in Figs. 4.8a and Fig. 4.8b respectively.

XRD pattern of (Chs-co-Chi)-g-poly(AAc-co-AAm) copolymer (Fig 4.8a) shows a strong peak at 19.40° covering the region between 11° and 32° on the 2θ scale with intensity of 21666.67 counts, two small peaks due to chitin shift were also observed at 23.13° (9611.11 counts) and 26.57° (7500 counts) indicating crystalline nature of the copolymer.

XRD pattern of (Chi-co-PVA)-g-poly(AAc-co-AAm) copolymer (Fig. 4.8b) also shows a single peak at 19.17° covering the region between 13.33° and 31.67° with intensity of 13615.38 counts, a small peak at 26.67° covering a region between 25° and 27.5° with a peak intensity of 7923.08 counts indicating crystalline nature of the binary graft copolymer.
4.4.4. Particle Size Distribution: Crystallite size and particle size

Distribution of the crystallite size and particle size of the graft copolymers, (Chs-co-Chi)-g-poly(AAc-co-AAm) and (Chi-co-PVA)-g-poly(AAc-co-AAm) has been determined from the XRD data applying Scherer’s equation to FWHM and particle size analyzer (Figs. 4.8 a-b and Figs 4.9a-b respectively) and results are presented in Table 4.1.

Table 4.1: Comparison of size particles in XRD and particle size analyzer (nm)

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>(Chs-co-Chi)-g-poly(AAc-co-AAm)</th>
<th>(Chi-co-PVA)-g-poly(AAc-co-AAm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XRD</td>
<td>5.64 nm</td>
<td>2.53 nm</td>
</tr>
<tr>
<td>Particle Size</td>
<td>2594 nm</td>
<td>1587 nm</td>
</tr>
</tbody>
</table>

Fig. 4.9 Particle size of (a) (Chs-co-Chi)-g-(AAc-co-AAm) and (b) (Chi-co-PVA)-g-(AAc-co-AAm) graft copolymer
4.4.4. Thermogravimetric Analysis:

Thermogravimetric analysis (TGA) of (Chs-co-Chi)-g-poly(AAc-co-AAm) and (Chi-co-PVA)-g-poly(AAc-co-AAm) was carried out in air at a heating rate of 10°C/min and the respective primary thermograms are presented in Fig. 4.10a and Fig. 4.10b. The initial decomposition temperature (IDT), final decomposition temperature (FDT) and decomposition temperature (DT) at every 10% weight loss are presented in Table 4.2.

It is observed from Fig.4.10a that (Chs-co-Chi)-g-poly(AAc-co-AAm) shows single stage of decomposition. Initially the graft copolymer loses about 10% of weight due to water desorption between 100-150°C. The decomposition begins at 211.70°C, the initial decomposition temperature, which it continues up to 464°C losing almost 75% of the weight. Beyond this a sharp decrease in weight (losing about 20%) is observed with further rise of temperature to 515°C from where begins the final decomposition which continues to leave no residue. The DT values at every 10% weight loss are higher than those observed for the pristine copolymer (Chapter II, Table 2.2). It is also observed that the temperature difference between DT values at each 10% weight loss is also higher till 50% weight loss beyond which it becomes lower in comparison to that of pristine copolymer.

The DTG curve shows two exothermic peaks at 476°C and 506°C with 1.82 mg/min and 2.10 mg/min rate of decomposition respectively. In the DTA curve, two exothermic peaks at 480°C (0.354 μV) and at 515°C (0.698 μV) are observed with total 3.53 J/mg of energy release.

It is observed from Fig. 4.10b that (Chi-co-PVA)-g-poly(AAc-co-AAm) shows two stages of decomposition. First stage of decomposition of the (AAc-co-AAm) grafted Chi-co-PVA copolymer begins at 204.09°C after losing almost 10% of the weight due to water desorption. Beyond this decomposition continues up to 282°C losing 40% of weight from where starts the second stage of decomposition. It continues losing up to 30% of weight till 442°C. When the temperature is further increased till 484°C, a sharp decrease in weight loss is observed (23%) beyond which starts the final stage of decomposition that continues leaving 2.06% of residue. The DT values at each 10% weight loss of the graft copolymer are lower in comparison to the pristine copolymer, Chi-co-PVA (Chapter III, Table 3.2). The temperature difference between DT values at
each 10% loss is also low except for the weight loss between 40% to 60% where the temperature difference is high depicting variable rate of decomposition. The variable rate of decomposition is also depicted in the DTG curve. The decomposition begins with a slow rate of 0.53 mg/min (225°C) which decreases to 0.50 mg/min at 264°C. The decomposition continues and increase in rate of decomposition is observed, 2.63 mg/min (473°C) that decreases to 1.69 mg/min at 487°C corroborating the TG analysis. The DTA curve shows a sharp single exothermic peak at 486°C (0.486 mV) with 4.83 J/mg of energy release.

Thus, from the thermal data of (AAc + AAm) grafted Chs-co-Chi and Chi-co-PVA graft copolymers, it is observed that grafting of the binary monomer mixture onto Chs-co-Chi copolymer further improves the thermal behaviour of the copolymer with higher IDT, DT values at every 10% weight loss and higher temperature difference between DT values at each 10% weight loss. However, in case of grafting of the binary monomer mixture onto Chi-co-PVA copolymer, thermal property of the graft copolymer is not improved as is indicated by the lower IDT, FDT and DT values at each 10% weight loss and lower temperature difference between DT values at every 10% weight loss in comparison to the pristine copolymer.

Fig. 4.10a Primary Thermogram of (Chs-co-Chi)-g-poly(AAc-co-AAm)
Fig. 4.10b Primary Thermogram of (Chi-co-PVA)-g-poly(AAc-co-AAm)

Table 4.2: Thermogravimetric Data of (Chs-co-Chi)-g-poly(AAc-co-AAm) and (Chi-co-PVA)-g-poly(AAc-co-AAm) graft copolymers

<table>
<thead>
<tr>
<th>Sample</th>
<th>IDT (°C)</th>
<th>FDT (°C)</th>
<th>DT (°C) at every 10% weight loss</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>(Chs-co-Chi)-g-poly(AAc-co-AAm)</td>
<td>211.70</td>
<td>495.76</td>
<td>187.74</td>
</tr>
<tr>
<td>(Chi-co-PVA)-g-poly(AAc-co-AAm)</td>
<td>204.09</td>
<td>484</td>
<td>206.27</td>
</tr>
</tbody>
</table>

Conclusion:

Pristine copolymers, Chs-co-Chi and Chi-co-PVA have been successfully modified through graft copolymerization with binary mixture of hydrophilic monomers, AAc and AAm, using ammonium persulfate as radical initiator. The modified graft copolymers have shown good swelling properties. The characterizations such as FTIR, SEM, XRD
and TGA also confirm the grafting of (AAc + AAm) onto Chs-co-Chi and Chi-co-PVA copolymers. The FTIR consists of all the additional peaks due to AAc and AAm. SEM depicts the change in the topology of the surface on grafting of monomers onto the copolymeric base. The pristine copolymers, Chs-co-Chi and Chi-co-PVA, upon grafting of vinyl monomers has either improved or retained thermal stability. XRD and Particle Size Analysis detail out the nano structure of the pristine and grafted copolymers.
References


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