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Research Article

Modification of Crosslinked PVA by Grafting of Acryl Monomers for Getting Higher Thermal Stability

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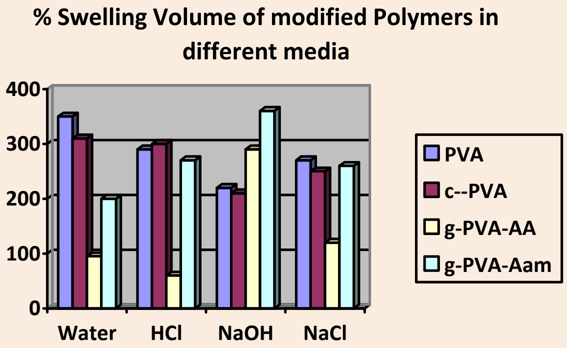
Abstract

In this study PVA was modified by simultaneous cross linking and grafting. Crosslinking was initiated in aqueous medium using benzoyl peroxide. Acrylic acid and acrylamide monomers were used for grafting. Reaction variables- time, temperature & concentrations were optimized for getting desired yield of modified polymer. Polymers were characterized by FT-IR & thermal analysis (TGA/DTA). Modified polymers were also examined for their swelling behavior in N/10 HCl, N/10 NaOH, N/10 NaCl electrolytes and neutral water. Grafted copolymer has shown good absorption capacity upto 350% in alkali & 250% in N/10 NaCl solutions. On the basis of thermo mechanical behavior and absorption capacities, polymers find applications in various fields like as hydrogel in contact lenses, controlled release of drugs, long lasting surgical and cosmetic implants.



Keywords: PVA, Cross linking, grafting, FT-IR & TGA/DTA

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Introduction

Poly (vinyl alcohol), PVA is one of the most important vinyl linear polymers. PVA has excellent film forming, emulsifying, resistant to oil, and adhesive properties. It is odorless and nontoxic. It has high tensile strength and flexibility, as well as high oxygen and aroma barrier properties. . The water, which acts as a plasticiser, reduces its tensile strength, but increases its elongation and tear strength. PVA is fully degradable and is a quick dissolver in water[1]. PVA has a melting point of 230°C and 180–190°C for the fully hydrolysed and partially hydrolysed grades. It decomposes rapidly above 200°C as it can undergo pyrolysis at high temperatures. PVA is an atactic material but exhibits crystallinity as the hydroxyl groups are small enough to fit into the lattice without disrupting it.An arrangement of substituents around the backbone, i.e. tacticity determines the degree of crystallinity[2]. Further Crystallinity depends on Size of side groups (smaller the group, larger the crystallinity) regularity of chain. Increased crystallinity enhances mechanical properties and increase in molecular weight increases physical properties; however, decreases processibility i.e., movement of particles in melt polymer decreases and motion ceases at “glass transition temperature(Tg)”. Depending on the crosslinking and additives used, the polymer component will be hard or soft. Polymers are hard and glassy below Tg while rubbery above Tg. Generally a crosslinked material is thermoset and cannot be reshaped. Due to recent advances in polymer chemistry, the exceptions to this rule are continually growing[3-4]. Crosslinking can be initiated by heat, chemical agents, irradiation, or a combination of these. Theoretically, any linear plastic can be made into a crosslinked plastic with some modification to the molecule so that the crosslinks form in orderly positions to maximize properties. It is conceivable that, in time, all materials could be available in both linear and crosslinked formulations. Properties of the modified polymer are dependent on crosslinking or grafting[5]. New functional group introduced and alteration in the original structure of the polymer change the physical & thermo mechanical properties like tensile strength, flexibility, glass transition temperature (Tg), softening point, thermal degradation, hydrolysing character, swelling behaviour etc and consequently modified polymers find wide applications in various fields[6-7].

Experimental:

Materials

PVA (M.wt- 72000), acrylic acid, acrylamide, benzoyl peroxide, toluene & methanol of “Merck” were used.

Method of grafting of PVA

PVA (1gm) was dissolved in 20 ml of water and 1.0 ml of benzoyl peroxide solution (1.0gm in 100 ml of toluene) was added into it to initiate the free radical mechanism.0.5 gm of acrylic acid was added in to the solution and it was vigorously stirred. The solution was heated with stirring at 90°C for 90 minutes. Insoluble product was filtered, washed thoroughly with hot water, toluene and finally with hot water. The gel was shaken with methanol then filtered, dried and weighed The reaction was repeated by varying the time of reaction (30 to 120 minutes), amount of acrylic acid (0.25 gm to 1gm) , amounts of benzoyl peroxide solution (0.5 to 2.5 ml) and temperature (70 to 110 °C) for getting desired yield of modified polymer. Monomer acrylamide was taken in place of acrylic acid for the graft PVA with acrylamide and the same method as above described was followed.

Swelling Behaviour of different polymers

Swelling characteristics is important to know the behaviour of the polymer in different electrolytic solutions at different pH. For absorption capacity, the pre-weighed sample (1gm) was immersed in 25 ml of distilled water or N/10 HCl or NaOH or NaCl solution and allowed to swell for 24 hours. Swollen sample was separated and wiped with filter paper to remove droplets from the surface and weighed. The percentage swelling was calculated. Swelling behaviour was also detrmined by other researchers[8-9].

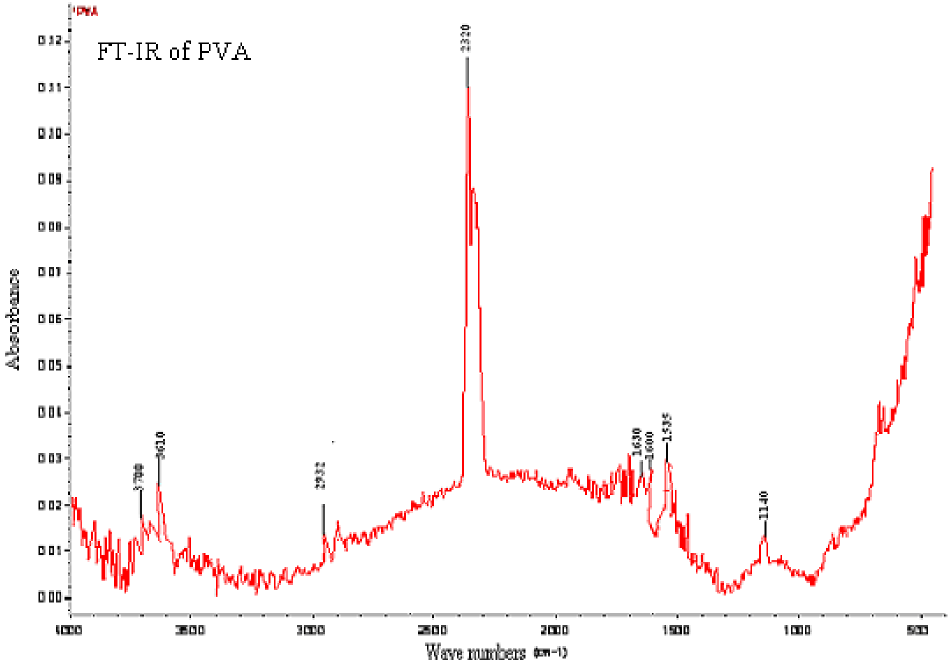

Figure 1 (FT-IR of PVA)

Characterization

All polymer samples including original and modified PVA polymers were characterized by FT-IR and TGA/DTA using Perkin-Elmer instrument of HNB Garhwal Central University Campus in Srinagar and Indian Institute of Petroleum-Dehradun. FT-IR i.e Fourier transform infrared spectroscopy has been widely used for the characterisation of different original and modified polymers.[10-11]. FT-IR spectra of original PVA is given in figure 1 while figure 2 and 3 are infra-red spectra of grafted PVA with acrylic acid(g-PVA-AA) and grafted PVA with acrylamaide(g-PVA-AAm) respectively. Figures 4, 5 & 6 are thermogravimetric analysis curves of original PVA, g-PVA-AA & g-PVA-AAm respectively.

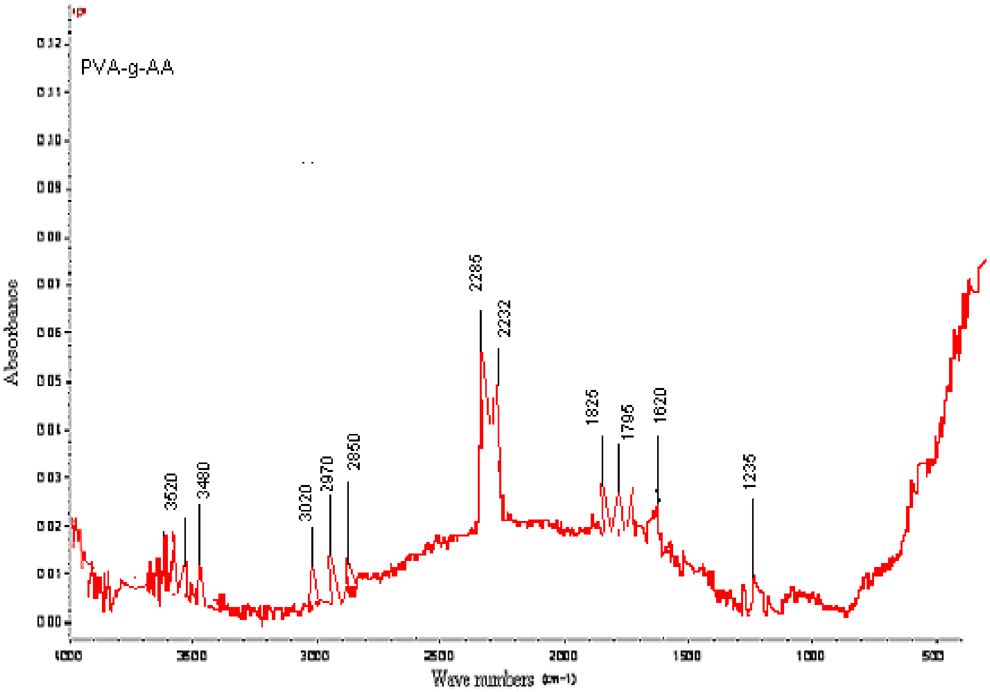

Figure 2 (FT-IR of PVA-g-AA)

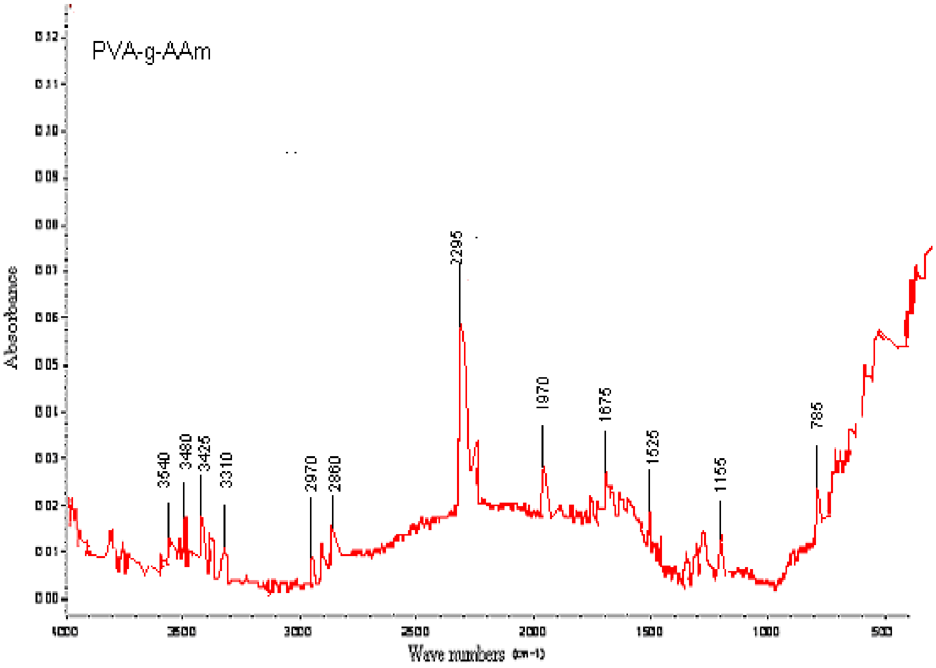

Figure 3 (FT-IR of PVA-g-AAm)

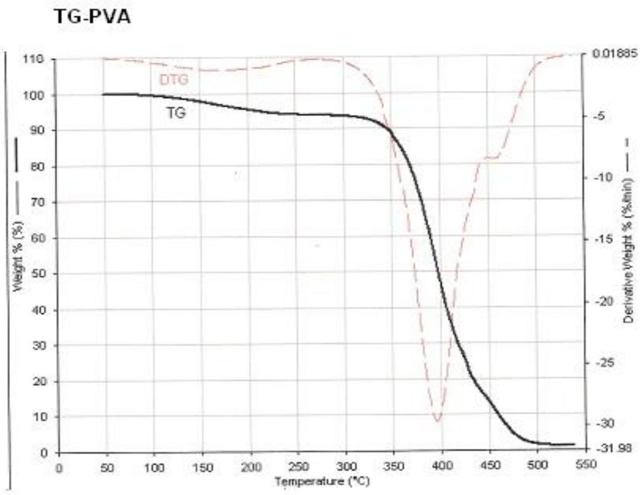

Figure 4 (TGA of PVA)

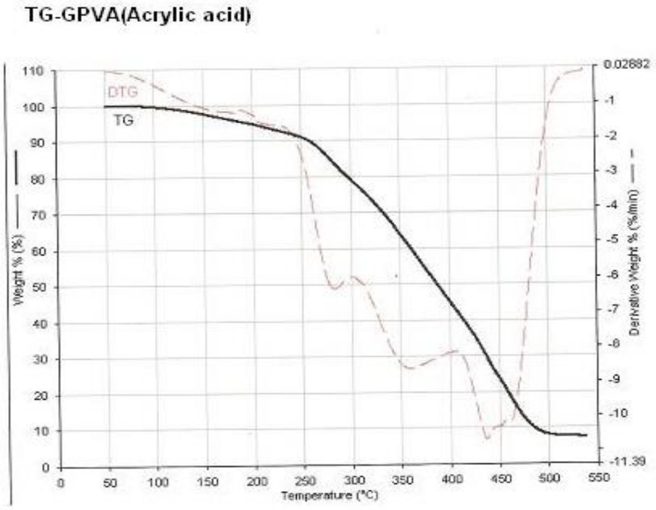

Figure 5 TGA/DTG curve of PVA-g-AA

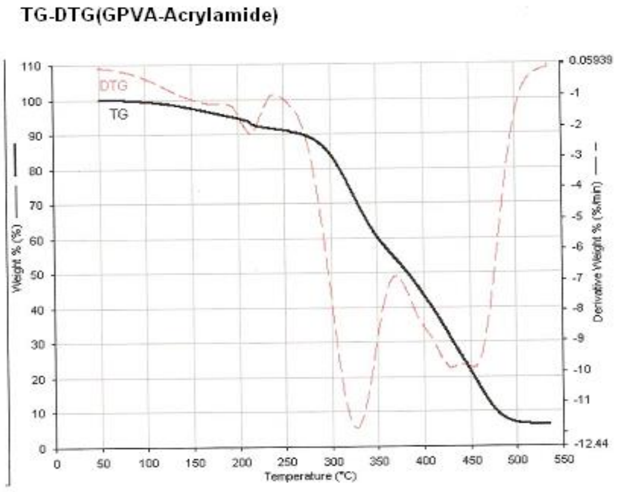

Figure 6 TGA/DTG curve of PVA-g-AAm

Results and Discussion

Grafting and simultaneous crosslinking of PVA was done with acrylic acid and acrylamide monomers in aqueous medium using benzoyl peroxide. These monomers as well as the polymers derived from them are soluble in water and therefore, the grafted and crosslinked PVA copolymers are expected to display excellent swelling behaviour in aqueous media and give potentially useful hydrogels. Other researchers also modified the polymer and observed the swelling behaviour as a main characteristic for showing hydrogels[12]. Benzoyl peroxide was selected as the initiators which unlike several available water soluble redox initiators do not leave ionic by-products capable of binding to the resulting copolymers. Benzoyl peroxide plays the role of free radical initiator in many reactions.[13] Modified polymer, PVA-g-AA is the PVA grafted with acrylic acid and another polymer PVA- g-AAm is grafted with acrylamde. A good yield of 85-90% of modified polymer was obtained by heating for about 1.5 hours at 90-100°C with stirring. Product was soft & crystalline but as the concentration of monomer acrylic acid or acrylamide was increased; product became harder and more adhesive. Similar observation was also observed by other researchers that on increasing the concentration of monomer durirng polymerisation, hardness of polymer increases [14].

FT-IR spectra of PVA and modified polymers (PVA-g-AA & PVA- g-AAm) are shown in figure 1 to 3 and corresponding TGA/DTA analysis (Thermograms) are shown in figure 4 to 6.Swelling characteristics are given in table-1. Various absorption bands in the FT-IR spectra confirm the Modification of polymer, which could be understood by the comparative study of FT-IR spectra. The FT-IR spectrum (Fig-2) indicates about the modifications attempted in the polymer (PVA) through grafting of acrylic acid. The bands at 1710 cm^{-1} might be corresponding to C=O stretching vibrations, bands in the range of 1350-1250 might be due to O-H (carboxylic) in plane bending vibrations and bands in the range of 3400-3550 cm^{-1} appear due to C-OH (alcoholic). Some bands in the range of 2850-3000 cm^{-1} are corresponding to C-C vibrations in fig-2. Similarly **PVA** was also modified by grafting of acrylamide in the same medium. From the fig-3, we observe the characteristic bands in support of grafting of acryl amide in the polymer. The bands in the region of 3500-3400 cm^{-1} might be due to N-H stretching vibrations in the amide linkage while bands around 1650 cm^{-1} & 1630 cm^{-1} might be due to C=O stretching of amides and N-H in plane bending vibrations respectively, this double band is highly characteristics of amides.

Thermal behaviour of the modified polymers can be explained by TGA/DTA curves given in fig.4 to 6. Figures 5 & 6 are corresponding to thermograms of g-PVA--AA and g-PVA--AAm respectively. Thermal degradation of the polymers is changed slightly. Initial degradation rate upto 10% loss in weight is almost same in all polymers. It is clear that the modified polymers loose 10% weight around 250°C while at 500°C only 10% undecomposed material is left. Thermal stability of the graft polymer appears to be decreased slightly. Complexity formed in the polymers due to modification is further confirmed by two-three downward peaks in DTG curves at different temperatures shown in fig.5 & 6.

Swelling Characteristics Original PVA and modified PVA samples were tested for swelling behavior in different mediums like aqueous (Water), neutral salt medium(NaCl), acidic(HCl) and alkaline(NaOH). Their results are given in table 1.

Table 1 Swelling characteristics of original PVA & modified PVA Polymers (24 Hrs)

Polymer(sample)	Water	0.1 N HCl	0.1 N NaOH	0.1 N NaCl
PVA	340-350 %	280-290%	220-220%	260-270%
C-PVA (Peroxide) With out any other monomer	300-310%	290-300%	200-210%	240-250%
g-PVA-AA (Acrylic acid)	90-95%	55-60 %	280-290%	110-120%
g-PVA-AAm (Acrylamide)	190-200 %	260-270%	350-360%	250-260 %

The modified polymer, g-PVA-AA has shown good absorption capacity of about 300% in the N/10 NaOH solution, 120% in N/10 NaCl solution. Second modified polymer has shown good water retention capacity in all electrolytic solutions. Maximum 350% absorption was observed in the alkali solution followed by 270% in N/10 HCl solution and then 260% in salt solution. This graft polymer was observed to have better absorption capacity and adhesive nature. On the basis of thermo-mechanical and swelling characteristics polymers might be used in various applications like in adhesive and thickener material in latex paints, paper coatings, hairsprays, shampoos , glues , textile sizing agent ,Carbon dioxide barrier in polyethylene terephthalate (PET) bottles ,carotid phantoms for use as synthetic vessels in doppler flow testing ,as a mold release because materials such as epoxy do not stick to it .PVA has been used as a water-soluble film for packaging , as fiber reinforcement in concrete , as a surfactant for the formation of polymer encapsulated nanobeads similarly on the basis of observing swelling and thermal behaviour modified PVA by grafting of acrylic monomers can be used with polyvinyl acetate to make Elmer's glue or can be used in eye drops and hard contact lens solution as a lubricant further these modified PVA polymers may find application in making protective chemical-resistant gloves or fixative for specimen collection.

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