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Graft copolymerization of poly (vinyl alcohol) with acrylic acid & acrylamide using benzoyl peroxide to get hydrogel

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ABSTRACT

In this study, graft copolymer of PVA was synthesized 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 may find applications in various fields as hydrogel like in controlled release of drugs, long lasting surgical and cosmetic implants.

KEYWORDS

PVA;
Cross linking;
Acrylic acid;
Acryl amide;
Grafting;
Hydrogel;
FT-IR;
TGA/DTA.

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. 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. 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. 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. 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.

Materials used

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

Method of grafting of PVA

PVA (1g) was dissolved in 20 ml of water and 1.0 ml of benzoyl peroxide solution (1.0g in 100 ml of toluene) was added into it to initiate the free radical mechanism.0.5 g 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 g to 1g), 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 characteristics

Swelling characteristics is important to know the behaviour of the polymer in different electrolytic solutions at different pH. For absorption capacity, the preweighed sample (1g) 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.

CHARACTERIZATION

Polymer samples were characterized by Fourier transform-Infrared spectroscopy (FT-IR) and Thermogravimetric/Differential thermal analysis (TGA/DTA) methods using Perkin-Elmer instruments.

FT-IR- Infrared spectroscopy exploits the fact that molecules absorb specific frequencies that are characteristic of their structure. The term Fourier transform spectroscopy reflects that techniques, a Fourier transform is required to turn the raw data into the actual spectrum.

TGA-Thermogravimetric analysis is a type of analysis on samples that determines changes in weight in relation to change in temperature. While DTA or Differential thermal analysis is a thermoanalytic technique, similar to differential scanning calorimetry. In DTA, the material under study and an inert reference are made to undergo identical thermal cycles, while recording any temperature difference between sample and reference. This differential temperature is then plotted against time, or against temperature (DTA curve or thermogram). Changes in the sample, either exothermic or endothermic, can be detected relative to the inert reference. Thus, a DTA curve provides data on the transformations that have occurred, such as glass transitions, crystallization, melting and sublimation. The area under a DTA peak is the enthalpy change and is not affected by the heat capacity of the sample.

RESULTS AND DISCUSSION

Grafting and simultaneous crosslinking of PVA was done with acrylic acid or 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. Benzoyl peroxide was selected as the initiator which unlike several available water soluble redox initiators do not leave ionic by-products capable of binding to the resulting copolymers. 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.

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 (Figure 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 Figure 2. Similarly PVA was also modified by grafting of acrylamide in the same medium. From the Figure 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 Figure 4 to 6. Figures 5 & 6 are corresponding to thermograms of PVA-g-AA and PVA-g-AAm respectively. Thermal degradation of the polymers are 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 Figure 5 & 6.

TABLE 1 : Swelling characteristics (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%

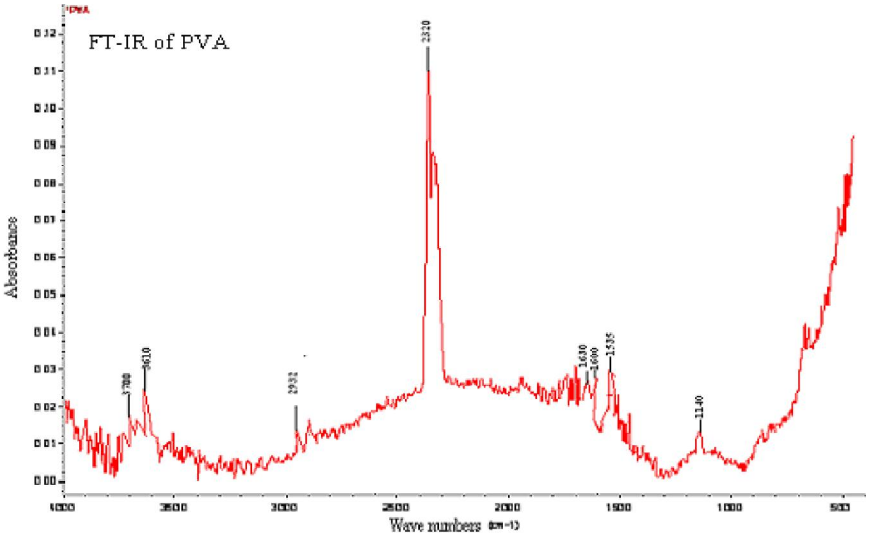

Figure 1 : FT-IR of PVA

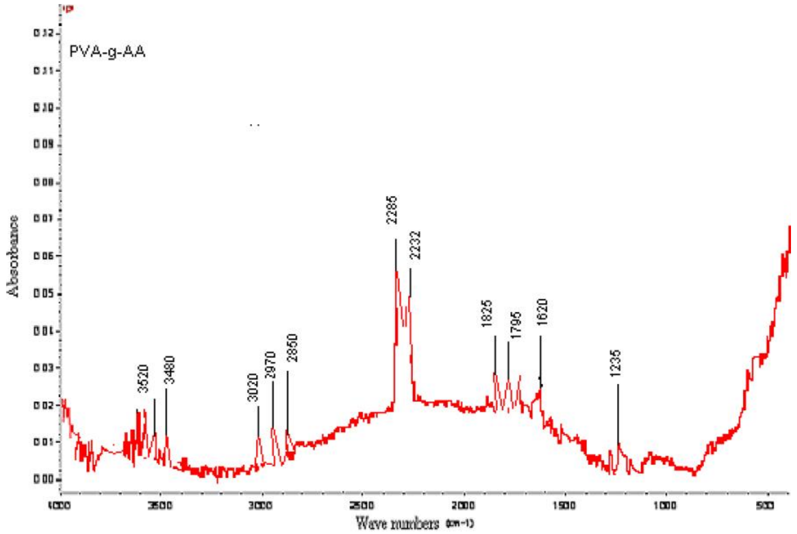

Figure 2 : FT-IR of PVA-g-AA

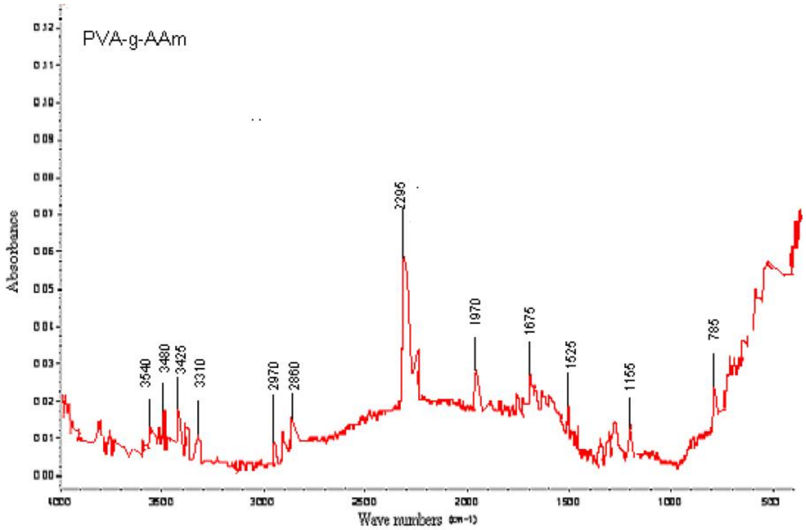

Figure 3 : IR of PVA-g-AAm

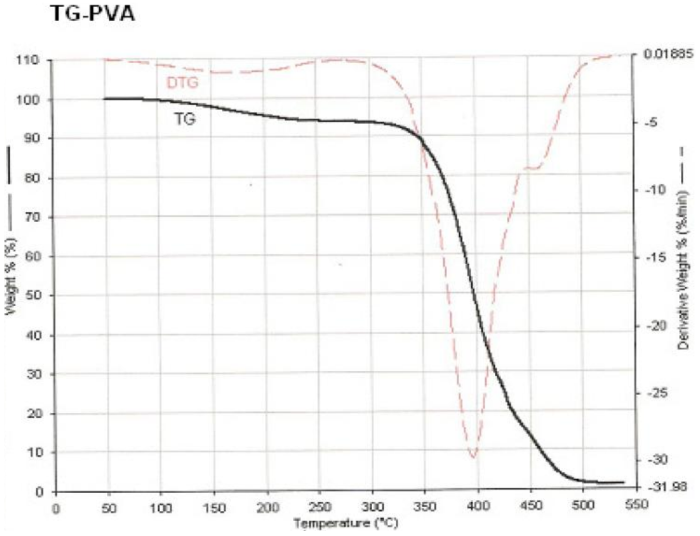

Figure 4 : TGA of PVA

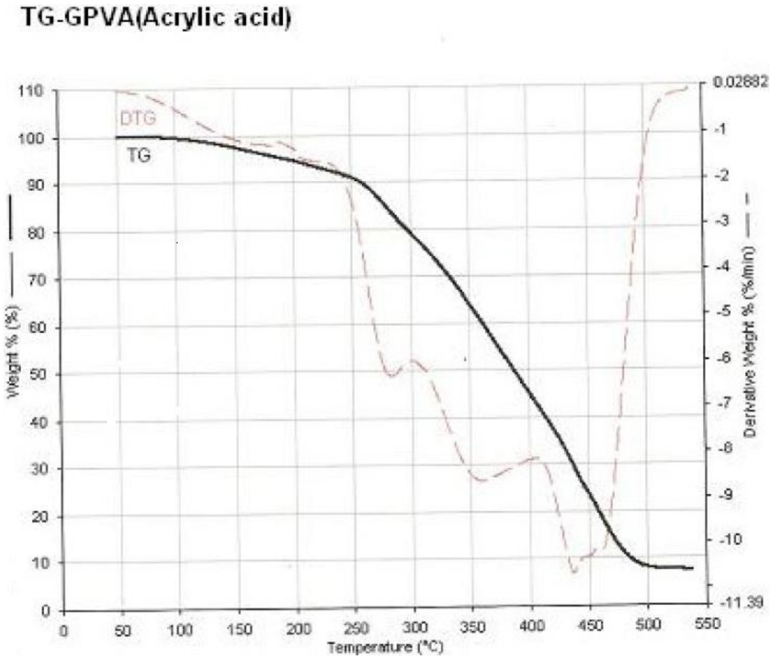

Figure 5 : TGA/DTG curve of PVA-g-AA

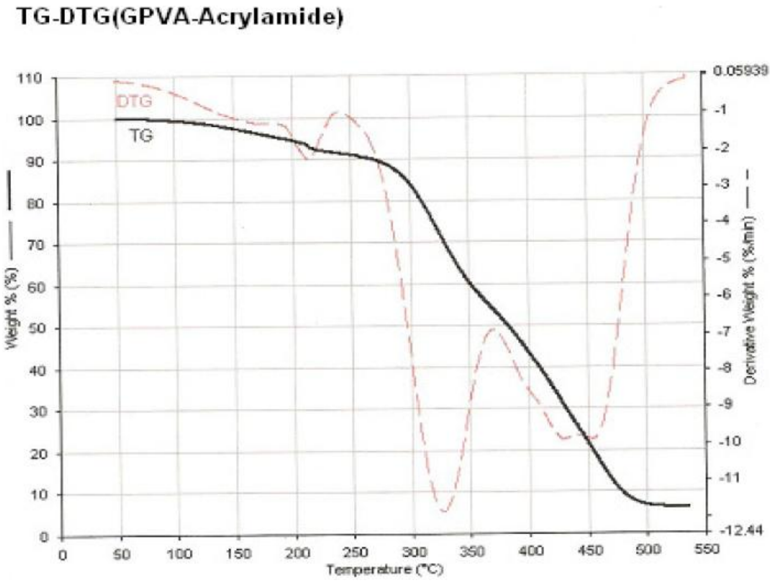

Figure 6 : TGA/DTG curve of PVA-g-AAm

Swelling characteristics

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, as a water-soluble film useful for packaging, as fiber reinforcement in concrete, as a surfactant for the formation of polymer encapsulated nanobeads, used with polyvinyl acetate to make Elmer’s glue, used in eye drops and hard contact lens solution as a lubricant, used in protective chemical-resistant gloves, used as a fixative for specimen collection, when doped with iodine, this polymer can be used to polarize light, as an embolization agent in medical procedures etc.

REFERENCES

[1] R.B.Seymour, C.E.Carraher; Polymer Chemistry, 3rd Edition, Marcel Dekker, New York, 30-38 **(1996)**.
[2] P.W.Manders; Modern Plastics Encyclopedia, **71(12)**, 95-98 **(1990)**.
[3] N.M.Bikales; Encyclopedia of Polymer Science and Technology, Section V, Vinyl Alcohol Polymers., John Wiley & Sons, **14**, 149-239 **(1971)**.
[4] M.Muthukumar; Macromolecules, **22**, 4656 **(1989)**.
[5] C.A.Finch; Poly (vinyl alcohol), 3rd Edition, Wiley, New York, 535-538 **(1985)**.
[6] J.C.Pinto; J.Vinyl Technology, **12(1)**, 7 **(1990)**.
[7] M.O.David, Q.T.Nguyen, J.Neel; J.Membr.Sci., **73**, 129-130 **(1992)**.
[8] R.Gref, Q.T.Nguyen, R.Clement; Colloid.Polym.Sci., **271**, 1143-1145 **(1993)**.
[9] K.Behari, A.Srivastava; A.Journal of Macromolecular Science, **44**, 451-460 **(2006)**.
[10] R.R.Blanchard; In Handbook of plastic Material and Technology, J.Wiley & sons, New York, Ed, 110-114 **(1990)**.
[11] M.Fabin, et al; Polymer, **35(10)**, 2201-2204 **(1994)**.
[12] T.W.Greene; Protective Groups in Organic Synthesis, Wiley- Interscience, New York, 124-127 **(1981)**.
[13] F.W.Billmeyer; Text book of polymer Science, 3rd Edition, Viley, 300-305 **(1984)**.
[14] C.A.Finch; Poly (vinyl alcohol), 3rd Edition, Wiley, New York, 535 **(1985)**.