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Document heading doi: 10.21276/apjhs.2019.6.1.30 **Research Article**

Modified PVA by Grafting and Blending and study on Biodegradation

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Abstract

PVA is widely used industrial vinyl polymer which is used in different biomedical applications like for blood carrying bags, syringes etc. It is biodegradable in its unmodified form but when it is modified and by crosslinking and grafting techniques then its degradability decreases but thermal stability increases. In this study PVA was modified by grafting and blending using acrylic acid and acryalamide monomers . Blended and grafted PVA has shown greater thermal stability but biodegradability was found to be slightly decreased for grafted polymer while blended polymers have shown better biodegradability.

Key words: PVA, grafting, biomedical application, biodegadability.

Introduction

Polyvinyl alcohol(PVA) is one of the most important vinyl polymer which is used in many industries like adhesive industry, biomedical, paints etc. PVA is used for making glue, gums in adhesive Industry and syringes, blood carrying bags in biomedical field(1). PVA has scope for modification by crosslinking and grafting. Cross-linking product is formed by using free radical initiator. In the condition of inter-crosslinking of polymer chains dehydration occurs with elimination of water molecules and chain are interlinked and when reacted with acrylamide or acrylic acid then amide linkage also occurs and new modified polymer obtained. Blends of PVA with starch and cellulose were also prepared. Blended polymers also have good stability and can be used in different field. Blended polymer also has scope of biodegradability.

Modification of Poly (vinyl alcohol) by crosslinking & grafting techniques

First PVA was modified in the presence of organic peroxide , for which I g of polymer was dissolved in 20 ml of water and 1.0 ml of benzoyl peroxide solution (0.5% w/v of toluene) and it was vigorously stirred. The solution was heated with stirring at 50°-60°C to for 1.5 to 3 hrs time. Insoluble crosslinked PVA (c-PVA) was filtered ,washed thoroughly with hot water , toluene and finally with hot water. So obtained modified polymer was obtained in gel form which was shaken with methanol and filtered and dried to modified polymer. Further polymer was modified by grafting of acrylic monomer for grafting purpose acrylic monomer 25 to 50% (w/w) of PVA was also dissolved along with peroxide 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 and filtered, dried and weighed. The reaction was repeated by varying the time of reaction amount of acrylic acid and acrylamide (20 to 70% w/w) , amounts of peroxide solution (0.5 to 2.5 ml) and temperature (60 to 110 °C).Vinyl polymers have been modified successfully by crosslinking and grafting by many researchers(2-3)

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Blending of PVA with starch and Cellulose

PVA (1gm) was taken along with 1 gm of starch in 50 ml water in a beaker and dissolved with stirrer for 30 minutes.2 ml of Benzoyl peroxide(1% solution in toluene) was added slowly with stirring to get blended polymer at 60-80°C in 1-2 hrs time. Similarly another blended polymer with cellulose was prepared in same conditions. Blended polymer was formed in gel form which was treated with methanol and filtered and dried.

Thermal characterization (TGA/DTA)

Thermal stability of a polymer is best shown by Thermal gravimetric analysis. TGA/DTA analysis of Polymer samples were done from Indian Institute of Petroleum (CSIR), Dehradun using Perkin-Elmer Thermal Analyzer .

Swelling properties of polymer samples-

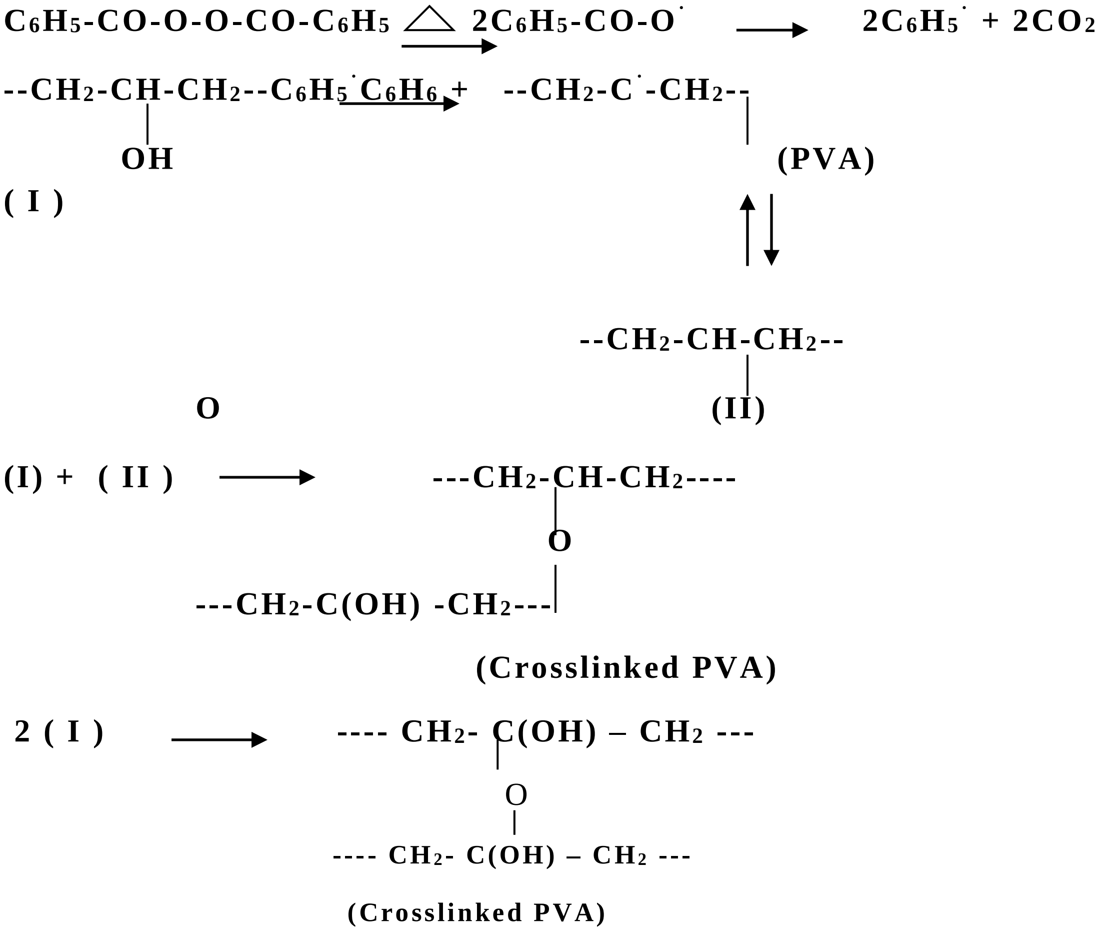
For the polymers swelling characteristics is an important property for biomedical application. Knowledge of the behavior of a polymer in acidic, basic or salt solution at different pH and depending upon the swelling, the polymer can be used as a hydrogel or similar purposes. For absorption capacity, the pre weighed sample (1gm) was immersed in 25 ml of distilled water or 0.1 N HCl or 0.I N NaOH or 0.IN NaCl salt solution and was kept undisturbed for 24 hrs to 48 hrs at room temperature. The swollen sample was removed and wiped with filter paper to remove droplets on the surface and weighed. The percentage swelling and swelling ratio was calculated. Swelling properties were also obtained by Singh A(4).

Swelling Percentage = $(W_2-W_1) \times 100/W_1$

(Where, W_2=Weight of swollen sample, W_1=Weight of dry sample)

Result Discussion

PVA was crosslinked in aqueous solution with benzoyl peroxide solution. Peroxide generates highly reactive phenyl radicals which abstract hydrogen from PVA. The free radicals so formed on the PVA are responsible for the creation of crosslinked network. Similarly modification of PVC was done by SinghA and his coworkers in 2010 (4).Some probable reactions of formation of crosslinked PVA with free radical given below



$$C_6H_5\text{-CO-O-O-CO-}C_6H_5 \xrightarrow{\triangle} 2C_6H_5\text{-CO-O}^{\cdot} \longrightarrow 2C_6H_5^{\cdot} + 2CO_2$$

$$\text{--}CH_2\text{-}\underset{\substack{|\\ OH}}{CH}\text{-}CH_2\text{--} \; C_6H_5^{\cdot} \longrightarrow C_6H_6 + \text{--}CH_2\text{-}\underset{|}{C^{\cdot}}\text{-}CH_2\text{--}$$

(I) (PVA)

$$\rightleftarrows$$

$$\text{--}CH_2\text{-}\underset{|}{CH}\text{-}CH_2\text{--}$$

O (II)

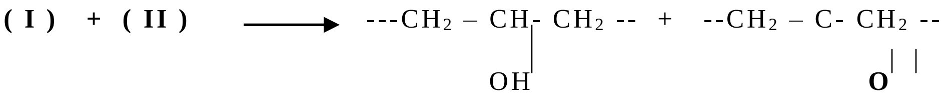
$$(I) + (II) \longrightarrow \begin{array}{c} \text{---}CH_2\text{-}CH\text{-}CH_2\text{----} \\ | \\ O \\ | \\ \text{---}CH_2\text{-}C(OH)\text{-}CH_2\text{---} \end{array}$$

(Crosslinked PVA)

$$2(I) \longrightarrow \begin{array}{c} \text{----}\; CH_2\text{-}\; C(OH) - CH_2 \;\text{---} \\ | \\ O \\ | \\ \text{----}\; CH_2\text{-}\; C(OH) - CH_2 \;\text{---} \end{array}$$

(Crosslinked PVA)

Mutual abstraction of hydrogen takes place occasionally leading to the generation of ketonic group on PVA, the presence of which has been reported.



$$(I) + (II) \longrightarrow \text{---}CH_2 - \underset{OH}{\underset{|}{CH}} - CH_2 \text{--} + \text{--}CH_2 - \underset{O}{\underset{||}{C}} - CH_2 \text{--}$$

(III)

The ketonic group facilitates the abstraction of a hydrogen atom from the adjacent carbon atom, thus creating alternative sites for branching/crosslinking. High yield of crosslinked polymer requires sufficient concentration of free radicals and hence of organic peroxide for the reaction.

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Characterization of modified PVA by FT-IR- The extent of modification in the polymer PVA could be established by the FT-IR characterization(5-6). FT-IR of PVA and c-PVA and grafted PVA are shown in figure (1), (2) and (3) respectively.

In The IR spectra (fig-1) of PVA, bands around 3650-3700 cm-1 are characteristics of stretching O-H vibrations ,bands around 1530-1600 cm-1 might be due to C-C stretching vibrations, band at around 1640 cm-1 might be corresponding to secondary O-H group in the polymer chain and band at 1140 cm-1 appears to be corresponding to C-O (alcoholic). Appearance of various characteristics bands in figure-II, PVA indicate the modification of PVA. Absorption bands at around 1115 cm-1 might be characteristics of C-O-C new bonds formed in the polymer as a result of crosslinking due to benzoyl peroxide which could be created through cross linkage while bands at around 3600 cm-1, 1080 cm-1 and 1610 cm-1 appears to be same as in IR spectra of PVC corresponding to hydroxy, C-O(alcoholic) and C-OH(secondary) respectively. Similarly in figure 2 , indicates the presence of C-NH bending vibration in the range of 3400-3500 cm-1 which are characteristics of amide linkages present in grafted modified PVA with amide. Similarly characterizations was done by others (7-8).

Thermal characterization -Thermal analysis curves of PVA and modified PVA are shown in figure 4,5 and6.Thermal stability as temperature raised upto 300°C,was higher in the modified PVA as compared to that of the original polymer which may be attributed due to crosslinking in the polymer.Thermal analysis curve of PVA modified by grafting/crosslinking of acrylic monomer is shown in figure 3 & 4 respectively. By the thermogram it is clear that the modified polymer looses 10% weight around 250°C while at 500°C only 10% undecomposed material is left. Complexity formed in the polymer due to crosslinking and grafting is confirmed by DTG curve.

***Swelling Characteristic*s for biomedical application**

Results of swelling capacity are presented in table 1.PVA is soluble in water hence the crosslinked polymer has excellent water absorption capacity, which is about 3-4 times of its weight. The crosslinked PVA exhibits high swelling characteristics (about 300%of its weight)in 0.1 N HCl, basic and NaCl solutions. The modified polymer formed by grafting of acrylic monomer was found to have good water retention ability (about 300-350 %) in 0.1N alkali solution and about 250% in salt solution Blended Polymer with starch and cellulose both have shown good swelling properties in all types of solutions. PVA -starch blended polymer have shown about 400% swelling in neutral salt solution while 300% by cellulose-PVA blended polymer in alkaline solution. The modified polymer was found to have very good swelling characteristics in aqueous media also. Biodegradation study was conducted by burial test method. Biodegradation of a polymeric material is chemical degradation brought by the action of naturally occurring microorganisms such as bacteria and fungi via enzymatic action into metabolic products of microorganisms (e.g., H_2O, CO_2, CH_4, biomass etc.)(9).We exposed these blends in soil, in natural condition for 3 to 6 months. In these samples soil along with sludge sewage from municipal water treatment plant and fermented garbage compost were added. We determined the loss in weight for checking of its degradability also confirmed by infra-red spectroscopy.

Results show (table-) that PVA was degraded by microorganism upon soil exposure, whereas when it blend with natural polymers like starch and cellulose then small decrease in degradation was observed.. The weight loss of PVA/natural polymer blends increases with the duration of sample exposure in soil and depends on both the nature & content of the natural polymer used.

Table 1: Swelling characteristics of PVA Polymers (24h)

S.No	Polymer	Water	0.1N HCl	0.1N NaOH	0.1N NaCl
1.	PVA	340-350	280-290	220-230	260-270
2.	c-PVA	300-310	290-300	200-210	240-250
3.	c-PVA-g- AAm	190-200	260-270	330-350	250-260
4.	PVA-Str	210-230	280-320	300-340	350-380
5.	PVA-Cel	180-200	160-180	280-310	190-220

c-PVA – crosslinked, AAm- Acrylamide ,str-starch, cel- cellulose.

Table 2: weight Loss study of polymer

S. No.	POLYMER	Blended with	BLEND %	DEGRADATION MEDIUM	Loss in wt (%)
1.	PVA	-	0	Soil environment (including activated sludge	40%
2	PVA	Starch	Starch 25%	Soil environment (including activated sludge	30%
3	PVA	Starch	Starch 50%	Soil environment (including activated sludge	36%
4	PVA	Cellulose	25% cellulose	Soil environment (including activated sludge	26%
5	PVA	Cellulose	50%	Soil environment (including activated sludge	35%

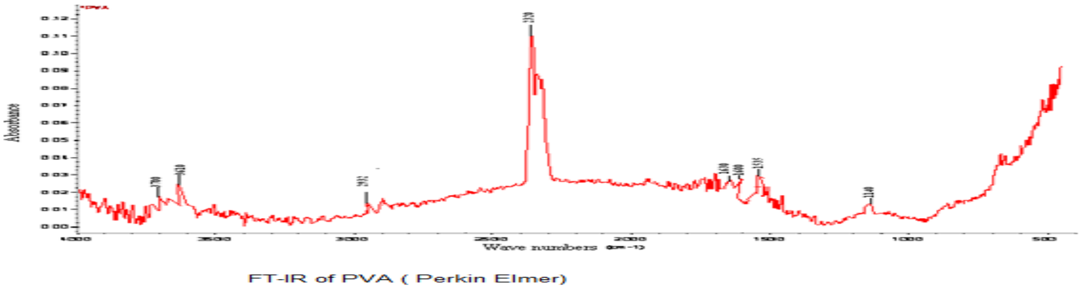

Fig 1:IR of PVA

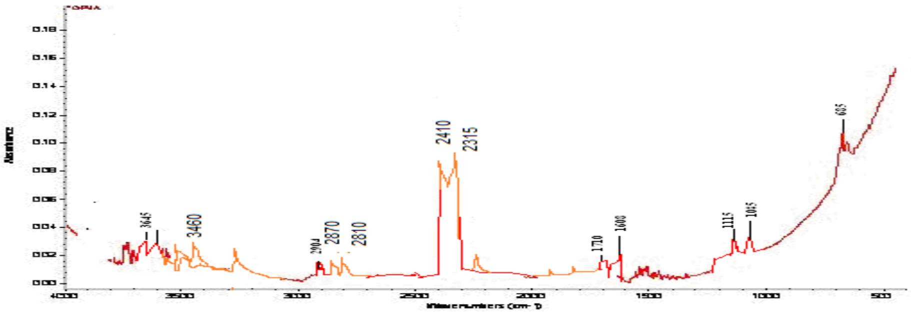

Fig 2: FT-IR of grafted modified PVA

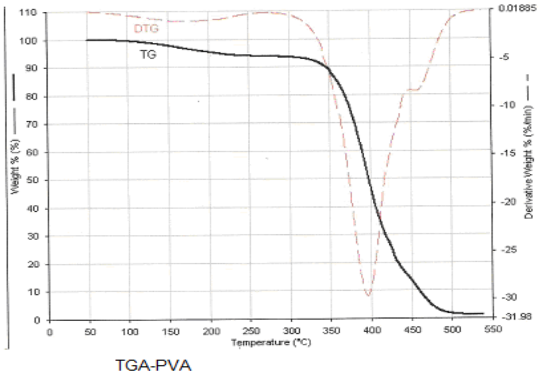

Fig 3: TGA of PVA

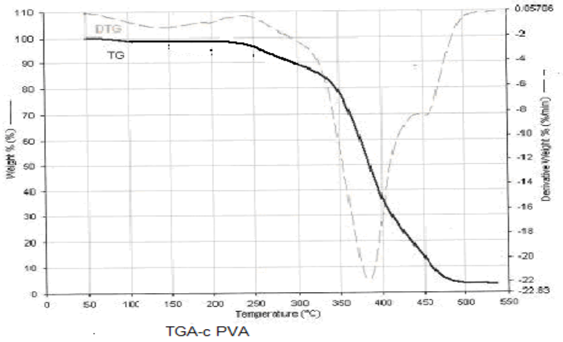

Fig 4: (TGA of modified grafted PVA)

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