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Research Article

OPTIMIZED MODIFICATION OF CROSSLINKED PVA BY GRAFTING FOR APPLICATION IN BIOMEDICAL FIELD AS HYDROGEL

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ABSTRACT

PVA (Polyvinyl alcohol) is one of the most widely used industrial vinyl polymer. It is biodegradable in its unmodified form but when it is modified by crosslinking and grafting techniques then its thermal stability was found to be increased but degradability decreases.In this study, PVA was crosslinked by using benzoyl peroxide solution and grafting of acryl monomers in different conditions to get maximum yield of modified polymer. Parameters of Temperature, time, amount of crosslinking agent were optimized. Time of about 1 hr at heating temperature of 80°C with 0.5 % benzoyl peroxide was found to be optimum for getting better yield of grafted modified polymer. Crosslinked and grafted PVA have shown greater stability but biodegradability was found to be decreased. So formed modified PVA may find application in Biomedical field like hydrogel formation as it has also shown good absorption behavior and sweeling properties.

KEYWORDS: *Polyvinyl alcohol, Crosslinking, Grafting, Biodegradability, Optimized conditions.*

INTRODUCTION

Polyvinyl alcohol (PVA) is one of the most important vinyl polymer which is used in many industries like adhesive industry, biomedical, paints etc (Sperling 1974). PVA is used for making glue, gums in adhesives Industry and syringes or blood carrying bags in biomedical applications. PVA has scope of modification by elimination of water molecules in optimum condition and simultaneously suitable monomer like acrylic acid or acrylamide can be used for grafting. Crosslinking and grafting are used for modification of different polymers (Phillip1978). In this study PVA has been modified by using above mentioned techniques in different conditions to get more stable polymer which can find application in biomedical field.

EXPERIMENTAL

Materials Used:

PVA, acrylic acid, acrylamide, benzoyl peroxide, HCl, NaOH and NaCl (A.R grade) of Rankem were used.

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Method for modification:

PVA was cross linked in aqueous solution with benzoyl peroxide solution, 1 g of PVA was dissolved in 25-100 ml of water at 50°C in water bath with stirring then 5-10 ml of 1 % solution of benzoyl peroxide was added and after one hour it was filtered and dried. For grafting of PVA, 1 gm of it was taken in dissolved form in water and then peroxide solution added (with varying the concentration)and 0.1 to 1 g of acrylic acid and acrylamides were added with stirring. After 2 hrs methanol was added to get insoluble grafted polymer which was filtered, dried and weighed.

Optimization of variables:

Reaction variables for the crosslinking of PVA with benzoyl peroxide through a free radical mechanism were optimized. Organic peroxide has been used by many researchers for polymerization through free radical formation (Grohens 2001; Han 2002). Parameters for this reaction such as temperature, concentration of monomer and time of heating were altered in separate experiments for obtaining the cross linked product in a good yield. The results of the optimization of crosslinking of PVA are presented in tables 1 to 6.

RESULTS AND DISCUSSION

In this study PVA was successfully moderately modified by crosslinking and grafting techniques. Grafting of acrylic acid and acrylamide was done in the presence of organic peroxides. 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 cross linked network. Different parameters were optimized by varying the concentration, temperature, time etc. Results are shown in table 1 to 5. Table-1 shows the optimization of time for preparation of high yield of modified PVA, which was obtained in time of about one hour. From Table-2, it is clear that temperature of 80°C is optimum for getting good yield of modified polymer.Table-3 indicates the optimization of dosage of grafting monomer i.e. acrylic acid. About 0.5 g of acrylic acid (50% w/w of PVA)is sufficient to get better yield of grafted PVA with acryl monomer. Swelling characteristics are very important for use in biomedical field. For getting Swelling behavior, 1g of polymer was dipped in 50 ml of water, N/10 HCl, N/10 NaOH and N/10 NaCl solution in 24 hrs time. Weights of polymer before and after dipping in different solutions were taken and percentage swellings were determined, these results are shown in table-5. From the results it is clear that original polymer was having maximum swelling about 3 to 3.5 times in aqueous solution. Some modified polymers have shown very good absorption behavior in different acidic to alkaline medium from 2 to 4 times. The swelling behavior was also studied by Singh et al 2010.

Cross linked PVA has shown maximum swelling behavior in N/10 HCl acidic. Grafted PVA with acrylic acid (c-PVA-g-AA) has shown maximum absorption in N/10 alkaline solution, i.e about 340 to 380%, while PVA grafted with acrylamide also has shown maximum absorption in alkaline medium about 380 to 400% which makes it suitable for use as hydrogel in biomedical application. It has also shown good absorption in neutral N/10 NaCl solution.

Table No. 1: Optimization of time for preparation of cross linked PVA

S.No.	Time of Heating (min.)	Yield (mg)
1	30	325
2	60	580
3	90	650
4	120	710, tight & dark colour

(PVA 1g, water 50 mL, benzoyl peroxide solution 0.5%, temp.70°C)

Table No. 2: Optimization of temperature for cross linking of PVA

S. No.	Time of Heating (min.)	Yield (mg)
1	60	330
2	70	540
3	80	660
4	90	705
5	100	710
6	110	720, brownish and tight

(PVA 1g, water 50 mL, time of heating 60 min, benzoyl peroxide solution 0.5%)

Table No. 3: Modification of poly (vinyl alcohol) by grafting of acrylic acid (c-PVA-g-AA)

S.No.	Monomer (Acrylic acid) (g)	BPO Soln (0.5%. (ml)	Time (hrs)	Yield %
1	0.20	1.0	1	25
2	0.25	1.0	1.5	30
3	0.50	1.0	1.0	52
4	0.50	1.0	1.5	70
5	0.50	1.5	1.5	74
6	1.00	1.5	1.5	84, slightly sticky
7	1.00	1.5	2	86, sticky solid

BPO= 0.5% in toluene, temperature=80°C, PVA=1g in 50 ml of water

Table No. 4: Modification of poly (vinyl alcohol) by grafting of acrylamide (c-PVA-g-AAm)

S. No.	Monomer Acrylamide (g)	BPO Solution (ml)	Time (hr)	Yield (%)
1	0.25	1.0	1	30
2	0.25	1.0	1.5	34
3	0.50	1.0	1	48
4	0.50	1.0	1.5	80
5	0.50	1.0	2.0	85
6	1.00	1.5	1.5	90
7	1.00	2.0	2	92, Sticky solid

BPO solution= 0.5% in toluene. Temperature=80°C, PVA=1.0 g in 50 ml water

Table No. 5: Swelling characteristics of PVA Polymers (24h)

S. No	Polymer	Water	0.1N HCl	0.1N NaOH	0.1N NaCl
1	PVA	350-370	290-310	210-230	280-290
2	c-PVA-BPO	280-310	305-330	210-230	260-280
3	c-PVA-g-AA	120-140	60-80	340-380	120-140
4	c-PVA-g-AAm	190-220	250-270	380-405	260-280

(Polymer -1g, electrolytic solution 25 ml & swelling time 24hrs)
BPO-benzoyl peroxide; AA- Acrylic acid; AAm- Acrylamide; c-cross linked; g- graft

CONCLUSIONS

Polyvinyl alcohol is usually biodegradable in its pure and unmodified form. In the present study, this polymer has been changed by crosslinking and grafting methods. A high yield of modified polymer was obtained at optimized conditions but the biodegradability of polymer reduced due to stability of modified forms.

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