

Synthesis and characterization of novel swollen cross-linked poly acrylic acid

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Abstract

A cross-linked poly acrylic acid super absorbent polymer has been successfully synthesized by reacting poly allyl sucrose, styrene and acrylic acid batch charging in aqueous medium under the occurrence of nitrogen atmosphere. This novel method is profitable in terms of reducing the toxicity and is fast and economical than available methods. The morphological structure of the synthesized polymer was studied by SEM which showed layered self-assembled structures.

Using FTIR, the characteristically involved functional groups of the functionalized polymers were identified. To analyze the thermal character of the prepared polymer in terms of their endothermic or exothermic behavior, TGA and DSC techniques were employed. The synthesized materials could be used as water-absorbing agents in the field of material science and technology.

Keywords: Poly allyl sucrose, styrene, acrylic acid, water-absorbing agent, particle size, copolymer composition, TGA, DSC, FT-IR, SEM.

Introduction

Superabsorbent polymers (SAPs) are cross-linked polymers which absorb and retain a great amount of water compared to its own mass. There are numerous types of SAP including poly (acrylic acid) (PAA), poly acrylamide (PAAm), starch-graft-poly acrylonitrile (PAN)¹ and cross-linked carboxymethyl cellulose². Universal SAP manufacture capability reached 3.5 million tons in year 2015³. At present, the major market of SAP is baby diapers and other hygiene products such as adult incontinence products, hygienic napkins and absorption pads for hospital uses. Additional applications of SAPs comprise soil moisture conditioning, aqueous waste treatment, cable water jamming and tangible additives etc.⁴

Excessively retentive polymers are cross-connected polymer contain network like a chain without dissolving and they can retain just as grip the enormous amount of water in the swollen structure. The retained fluid is barely removable still under certain powers⁵. Super sponges have perceived critical thought as a result of their impressive applications in few zones, for example, sterile products⁶⁻⁸, gardening⁹, squander

water treatment¹⁰ and prescription for medication-free strategy¹¹ while in a wide assortment of uses, about all of the super sponges utilized as dispensable particles depend on completely oil-based polymers with high creation cost and having genuine condition sway and along these lines, they have certain limits. In water, SAPs swell to a straightforward chewy gel and their mass can suck up and hold unforeseen extraordinary measures of water or fluid arrangement¹².

The making of the primary water-spongy polymer organized from acrylic acid (AA) and the cross-connecting agent styrene was thermally polymerized in a fluid medium and afterward the main development of hydrogels was shown up¹³. These hydro gels were generally found on hydroxy alkyl methacrylate and associated monomers with swelling ability up to 50%. In the present strategy, water is utilized as a dissolvable medium and K₂S₂O₈ as an initiator. This strategy is useful in completing the enormous number of polymer items in lesser time when contrasted with the ordinary strategies. Water is picked as dissolvable in this polymerization response to make blend greener way.

Material and Methods

Chemicals and equipments: Allyl sucrose, styrene, acrylic acid, ethanol and K₂S₂O₈ are of laboratory grade. Basic glass products like three-neck round bottom flask and gear like mechanical stirrer and Brookner FT-IR spectrophotometer were used.

Synthesis of salts of cross-linked poly acrylic acid: A nitrogen gas gulf tube and mechanical stirrer were fitted with a three necked round bottom flask of 1000 ml limit. 100 ml of dissolvable blend is moved into the flask and includes two little bits of porcelain. Gradually heat the dissolvable blend to 60 °C temperature and afterward pass the nitrogen gas to sparge the flask substance to power out the air. Allyl sucrose (1, 0.8, 0.6, 0.4, 0.2 g), a diverse measure of acrylic acid and styrene are added to the response blend and mixed. In the meantime, 1 % of an initiator (K₂S₂O₈) is added to start the polymerization and temperature is step by step expanded to 80°C. Jellified item is seen in 45 minutes. The gelis dried for 24 hours and then granulated for further assessment. The reaction mixture is employed is as described in table 1.

Swelling test: SAP (0.5 g) samples (W₀) are placed into a pre-weighed beaker. The polymers are dipped in an excess amount of water for overnight to reach the stability of swelling. Then the excess amount of water is removed until

no liquid was dropped off. The polymers are weighed (W_1) and the swelling capacity was calculated by equation:

$$\text{Swelling capacity} = \text{Wet/dry} \times 100\% = W_1/W_0 \times 100\%$$

Absorbance capacity of polymers is shown in table 2.

Results and Discussion

FT-IR spectra: The Fourier Transform Infrared (Brooker FT-IR spectrometer alpha Model) Spectroscopic technique

is used for characterization of polymers by preparing KBr pellets of the materials. The representative IR spectrum of the polymer is displayed in figure 1. The spectra exhibit the characteristic IR peak at 3010 cm^{-1} ($-\text{C}=\text{C}-\text{H}$ stretching) of CH_2 scissoring and the strong peak at 1696 cm^{-1} for $-\text{C}=\text{O}$ stretching of inter-molecular hydrogen bonding of acrylic acid. The absorption band at 1188 cm^{-1} is recognized for $-\text{C}-\text{O}$ stretching of ether bending vibration. The peak at 1395 cm^{-1} is accredited to $\text{O}-\text{H}$ bending vibration.

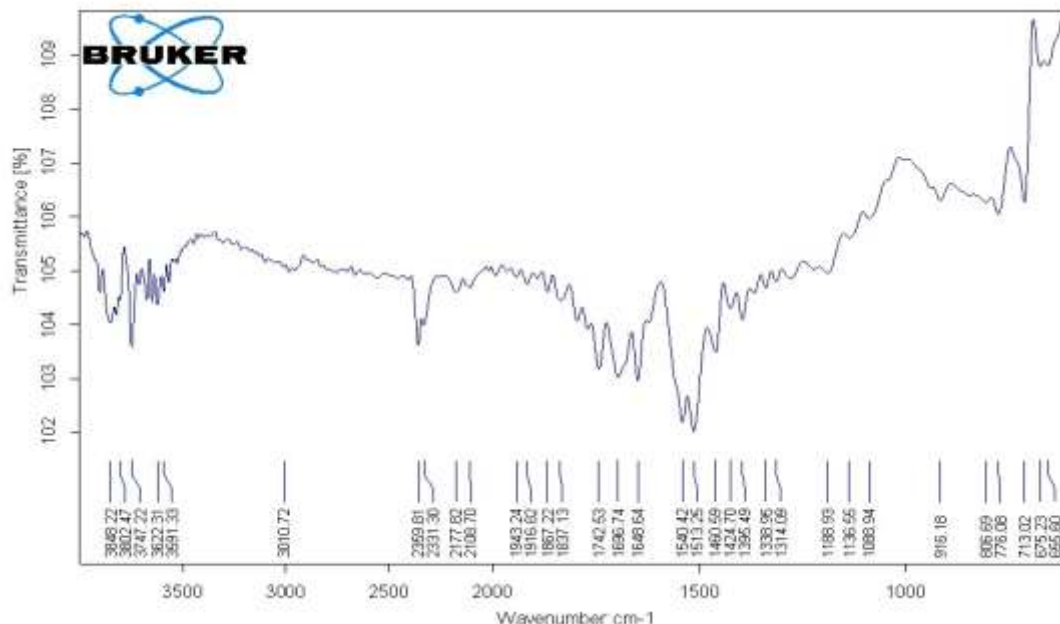


Fig. 1: FT-IR of cross-linked polymer

Table 1
Amount of reagents

CHEMICALS	AMOUNT (2.1)	AMOUNT (2.2)	AMOUNT (2.3)	AMOUNT (2.4)	AMOUNT (2.5)
Allyl sucrose	1 gm	0.8 gm	0.6 gm	0.4 gm	0.2 gm
Styrene	56 gm	56.1 gm	56.2 gm	56.3 gm	56.4 gm
Acrylic acid	43 gm	43.1 gm	43.2 gm	43.3 gm	43.4 gm
Ini - $\text{K}_2\text{S}_2\text{O}_8$	1 gm	1 gm	1 gm	1 gm	1 gm
Sol. - $\text{H}_2\text{O} + \text{C}_2\text{H}_5\text{OH}$	490 + 10 ml	490 + 10 ml	490 + 10 ml	490 + 10 ml	490 + 10 ml
Neut. - NaOH	7 pH	7 pH	7 pH	7 pH	7 pH

Table 2
Absorbance capacity of polymer

Wt. of cross-linking agent	Weight of sample (g)	Weight of swelled polymer (g)	Swelling capacity %
1.0 g	0.500 g	11.760	2252.13
0.8 g	0.500 g	26.119	5123.81
0.6 g	0.500 g	1.4280	185.612
0.4 g	0.500 g	44.255	8750.97
0.2 g	0.500 g	20.903	4080.69

Thermal analysis: The thermo gravimetric analysis (TGA) of the polymers indicates (Figure 2-6) that degradation of a polymer starts around 150°C and degrades completely above 200°C to 260°C. So, the polymers are thermally stable up to 150°C. The canyons (converse peaks) are due the fact that polymer has started to degrade and heat is liberated during degradation.

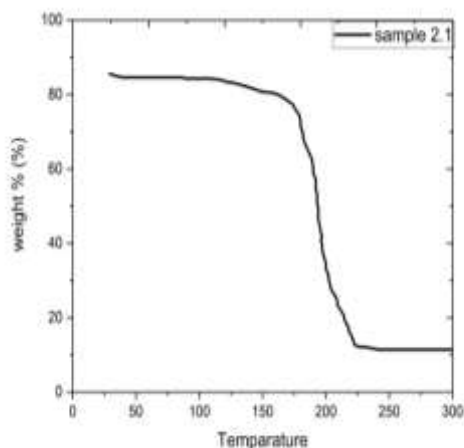


Fig. 2: TGA of cross-linked polymer (2.1)

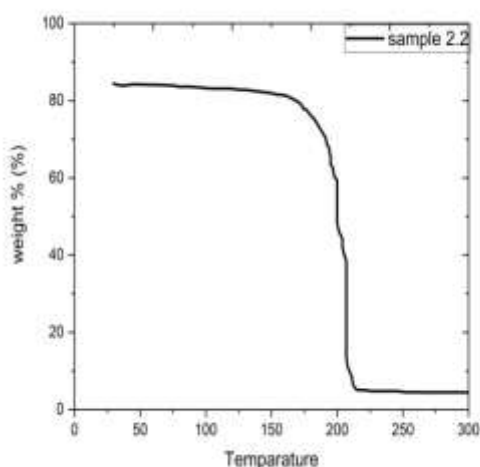


Fig. 3: TGA of cross-linked polymer (2.2)

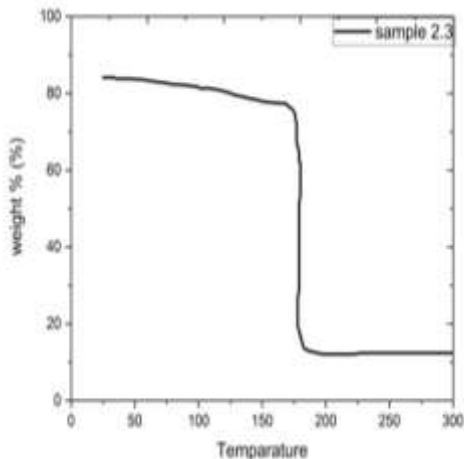


Fig. 4: TGA of cross-linked polymer (2.3)

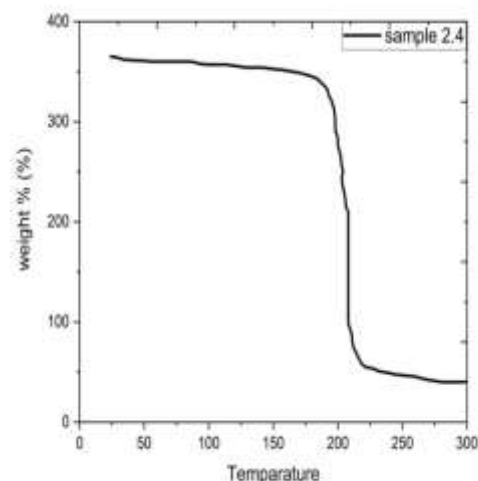


Fig. 5: TGA of cross-linked polymer (2.4)

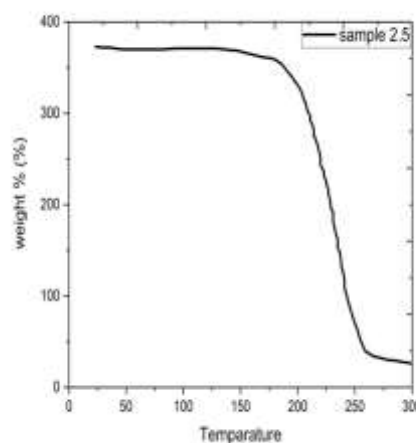


Fig. 6: TGA of cross-linked polymer (2.5)

Differential Scanning Calorimetric (DSC) analysis: The cross-linking is also characterized by DSC analysis as shown in figure 7-11. DSC of SAP cross-linked shows a weight loss within two stages. Essentially, acrylic acid has the glass-transition temperature (T_g) about 106°C, but due to cross-linked with styrene, there may be slightly change in T_g . DSC thermograms designate that T_g of the polymer increases by about 115°C and is independent of the amount of allyl sucrose. There is the hump in the bend and fix the midpoint in each curve as T_g . The initial stage shows weight loss between 40°C and 125°C which may be due to the loss of absorbed and bound water. The next stage of mass loss started at 225°C and continued to 275°C during which weight loss may due to the degradation of the cross-linker.

Morphological Analysis: To investigate surface morphology of the synthesized polymer, SEM analysis was carried out for the sample. Figure 12a shows the clear surface morphology of the synthesized sample at different scale. Figure 12 scanned at 200 μm shows a fiber like amorphous structures including semi solid particles. The higher resolution of the analyzed image indicates multilayer

polymeric structures having random particles which may be present due to the presence of acrylic acids and sucrose molecules (figure 12 b). However, figure 12c shows randomly distributed polymeric nonporous structures which are finely scattered with same morphology.

Conclusion

It is well observed that the allyl sucrose and acrylic acid are hydrophilic, but styrene is hydrophobic which is fundamentally used in our reported work. Polymer segments of acrylic acid/styrene form one phase and ally sucrose with acrylic acid form another immiscible phase. In this work, by using this method clear rubbery gel is achieved. DSC of SAP cross-linked with AS shows a weight loss.

The predictable super absorbent polymer synthesized from acrylic acid and cross-linking agent has a solid smooth nonporous surface. The cross-linking was also supported by DSC analysis.

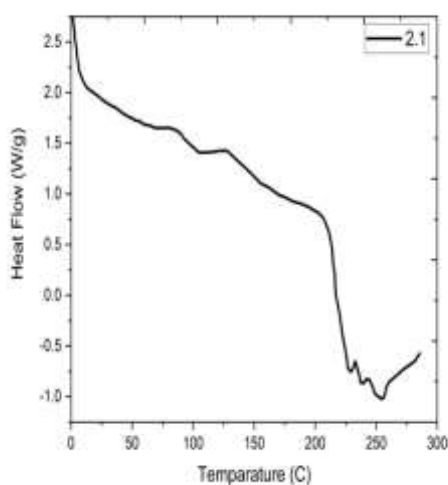


Fig. 7: DSC of cross-linked polymer (2.1)

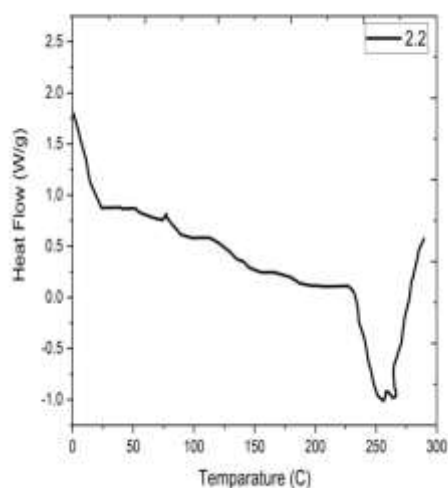


Fig. 8: DSC of cross-linked polymer (2.2)

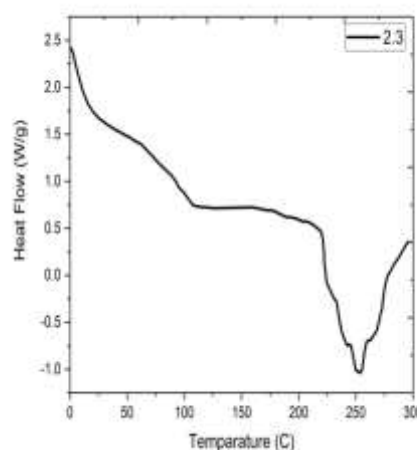


Fig. 9: DSC of cross-linked polymer (2.3)

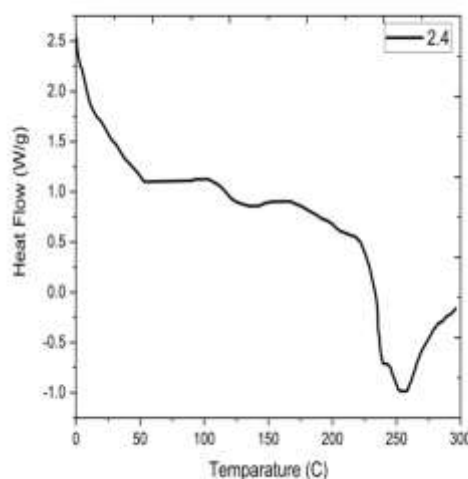


Fig. 10: DSC of cross-linked polymer (2.4)

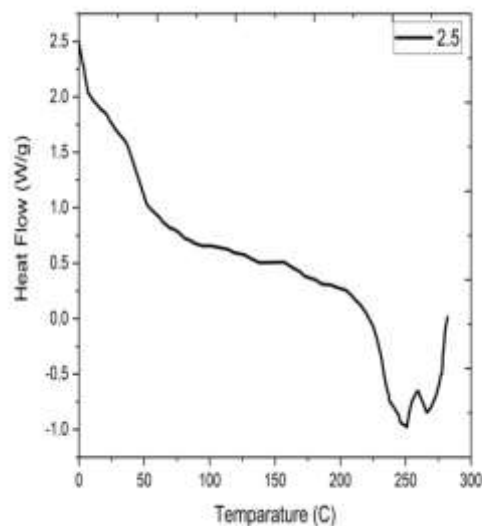


Fig. 11: DSC of cross-linked polymer (2.5)

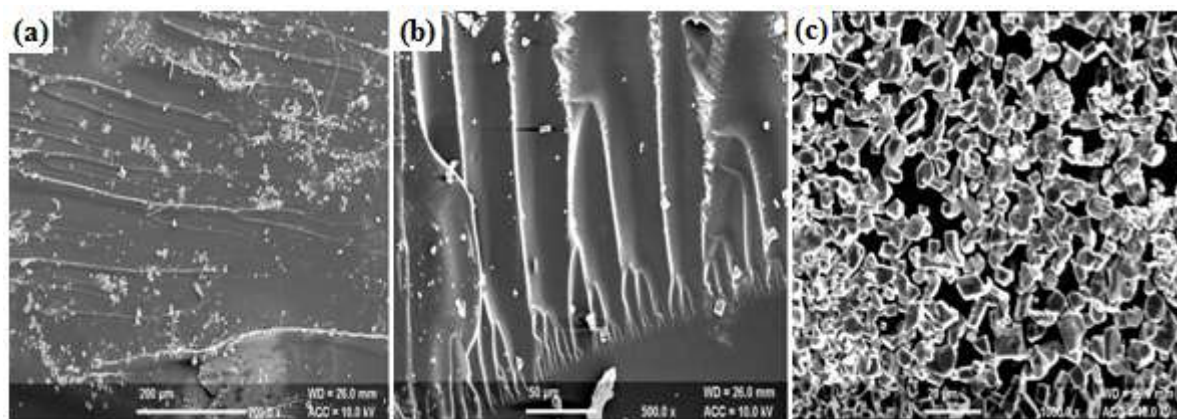


Fig. 12: SEM micrographs of prepared SAP's show superabsorbent polymer cross-linked with PAA-AS and styrene with different micro sizes

Hydrophilic networks reactive to some molecules can be used in drug systems and in controlled release drugs¹⁰. Super absorbent polymers were also employed in various applications such as absorbent paper products, bandages and surgical pads, wound dressings and as chemical absorbents. Additionally, they are applicable in food packaging¹⁵. From the swelling analysis, it is investigated that the newly invented polymers absorbed higher amount of water content.

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