



## Open Environment Degradability Study of CS/PVP/PNIPAm Hydrogel Film

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### ABSTRACT

Recent environmental regulations and societal concerns throughout the world have triggered renewed efforts in pharmaceutical industry to develop products which are compatible to the environment. This article reports the synthesis of CP1 hydrogel film and its nature of biodegradability in an open environment after 12 weeks. FTIR spectra of the hydrogel films (after biodegradation) show shift of peaks and change in peaks intensities, as for PVP characteristics peak at  $1678\text{ cm}^{-1}$  was totally diminished, which refer to the chemical change in the hydrogel film. From DSC study of CP1S,  $T_g$  shifted from  $57^\circ\text{C}$  to  $47^\circ\text{C}$  and exothermic peak observed at  $290^\circ\text{C}$  which was  $5^\circ\text{C}$  lower than CP1. In TGA, second weight loss of CP1S started  $50^\circ\text{C}$  less than CP1 and weight loss % was also decreased by 3%. CP1S has only one XRD peak at  $20.43$  and all the peaks were absent from their position it means that crystallinity of the sample reduced to minimal level by microbial degradation. Rod shaped fungus observed once the image of the film surface was scanned. So, variation in bonding, thermal properties and weight loss of the hydrogel films with time provide the direct evidence of environmental degradation of the hydrogel film.

**Keywords:** CS, PVP, PNIPAm, Degradation.

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### INTRODUCTION

Bio-based polymeric hydrogels for different applications have drawn the attention of researchers as an alternative approach to deal with the problem of disposal of waste [1]. With the recent increase in ecological consciousness, research has turned toward finding biodegradable materials. Biodegradation is a chemical degradation of materials by the action of microorganisms. According to the definition, a biodegradable polymer is “a degradable polymer wherein the degradation is through the action by microorganisms” [2]. Use of hydrogel films has been under attack for some time because lack of recyclability, renewability, biodegradability or incorporation of toxic drugs. Current trends indicate that steady growth will be needed in the use of biodegradable hydrogel films because of societal and legislative pressure [3].

CS, widely distributed in bacteria, fungi, and crustaceans, is the N-deacetylated chitin and received particular attention because it possesses good film-forming property [4, 5]. For example, films prepared by solution casting of nylon6/CS and PCL/CS were well studied and exhibited good biodegradabilities [6].

These efforts were made due to the serious environmental problems, mainly caused by plastics. These were irrecoverable and end up in landfill burial sites. Due to this reason, development of biodegradable material used as a wound dressing materials received more attention.

To improve some of these drawbacks, CS was often blended with some biodegradable synthetic polymers such as PCL, PLA, PVA, PVP and PNIPAm which could have good potentials for wound dressing applications. CS is a well known Material in the Wound Dressing field. CS has advantage over other polysaccharides due to its non-toxicity, biocompatibility and biodegradability. PVP, a synthetic polymer, has good biocompatibility. The miscibility of CS and PVP in the films has been reported, and it is considered that carbonyl groups in the pyrrolidone rings of PVP interact with amino and hydroxyl groups of CS by forming hydrogen bonds and produce materials with novel characteristics [7]. PNIPAm has been widely examined as a smart material due to its unique phase separation behavior upon external temperature changes. PNIPAm hydrogels are well known for their discontinuous phase separation near their lower critical solution temperature (LCST) 32°C. [8] These materials provide environmentally advantageous biodegradable alternatives to conventional non-biodegradable materials such as polyethylene (PE) for many applications.

Concerning the demand of consumers for high quality hydrogel films, and at the same time keeping in mind the issue of environmental pollution, the use of renewable resources to produce edible or biodegradable hydrogel films that can maintain product quality and reduce waste disposal problems are being explored. So, this study investigates the environmental degradability of CS/PVP/PNIPAm hydrogel film under aerobic conditions. In order to know the degradability of CS based hydrogel film, FTIR, DSC, TGA, XRD, and FESEM were employed to characterize the film.

## MATERIALS AND METHODS

**Materials:** All salts and reagents used were of analytical degree. PVP supplied from Sigma–Aldrich Chemical (Milwaukee, Wisconsin, USA) with molecular weight  $MW = 1400-1600 \text{ g mol}^{-1}$ . CS (Aldrich Chemical) powder, medium molecular weight,  $MW = 161,000 \text{ g mol}^{-1}$ , degree of deacetylation,  $DD = 75.6\%$ , 200–400 mPa.s and (3% (w/v) of polymer in aq. acetic acid solution) were used without further purification. PNIPAm was purchased from sigma-Aldrich Chemical (USA). Soil of pH 7.9 arranged from PUSA (New Delhi, India). Composition of Soil are sand 60.8%, clay 20.5%, silt 18.7%, Carbon 0.5%, Nitrogen 55.72 mg  $\text{Kg}^{-1}$ , and ammonium nitrogen 5.6 mg  $\text{Kg}^{-1}$ . CA was purchased from sigma-Aldrich Chemical.

**Preparation of CS/PVP/PNIPAm hydrogel film:** We separately prepared 3% solutions of CS and PVP. Quantities from 3% solutions of CS and PVP were mixed into the CP molar ratios of 4:1. The mixtures were kept under stirring for 1 hr at 25°C until the PVP and CS completely formed a clear solution then, 2% v/v solution of PNIPAm slowly added by pipette under constant stirring. The final concentration of PNIPAm in each hydrogel solution was 10% v/v of the polymeric solution. Further in the sequence, the solution was poured into plastic moulds/Petri dishes and allowed to dry for 72–120 h at room temperature. After peeling it off from Petri dish transfer it into the desiccator then test the degradability in an open environment.

**Fourier Transform Infra Red Spectroscopy:** FTIR was used to characterize the presence of specific chemical groups in the hydro gels film. The instrument was of BROOKER VORTEX V70. FTIR spectra were obtained in the range of 4000 to 650  $\text{cm}^{-1}$ . FTIR spectra were normalized and major vibration bands were identified associated with the main chemical groups.

**Differential Scanning Calorimetry:** The DSC analysis was used to characterize the thermal behavior of the polymer powders and the interactions between the polymers in the films. DSC was performed on a

calorimeter (NETZCH Instruments, 204 DSC) to determine the melting endotherm of dry and drug loaded samples, respectively. All samples were equilibrated at 30°C, in sealed aluminum pans and then scanned up to 400°C with a heating rate of 20°C min<sup>-1</sup> under nitrogen flow.

**Thermogravimetric analysis:** Thermogravimetric analyses were carried out by a PERKIN ELMER THERMAL ANALYSIS. About 5-10 mg samples were positioned in silica pans, and the samples were heated at 20°C min<sup>-1</sup> from ambient temperature to 600°C. Thermal analyses were performed under the nitrogen flow (10 mL min<sup>-1</sup>).

**X-Ray Diffraction:** To study the crystalline nature of the composite films by XRD-PW 1700 was employed to obtain the wide X-ray diffraction patterns. In this study, the WAXD patterns were obtained under the condition of 40 kV and 15 mA with a continuous scan mode at the speed of 5.00 deg min<sup>-1</sup> from 3° to 90°.

**Field Emission Scanning Electron Microscopy:** Morphology of hydrogel films obtained by FESEM. The instrument was of NOVA NANO SEM 450, FEI. The images were obtained using an accelerating voltage of 10–15 kV.

## RESULTS AND DISCUSSION

**Fourier Transform Spectroscopy:** In the figure 1 the appearance of peaks at 1678cm<sup>-1</sup> and 1291cm<sup>-1</sup>[9] were correspond to di-substituted amid absorption and the other band is also characteristic of PVP. Peak at 1582cm<sup>-1</sup> was of amide I of CS or PNIPAm. Peak at 3525cm<sup>-1</sup> was of -OH and -NH stretching. Furthermore, it can be seen that in CP1S the height of amid peak of PVP at 1678 cm<sup>-1</sup> (characteristic peak for amid group in pure PVP) is totally diminished. This is most probably due to influence of polysaccharide to amid group of PVP. Characteristic peaks of PVP at 1678cm<sup>-1</sup> and 1291cm<sup>-1</sup> also diminished in height and slightly shifted to lower frequency in case of CP1S. Peak at 3525cm<sup>-1</sup> was of -OH and -NH stretching goes slightly to higher frequency in case of CP1S. We observed that all the peaks of CP1 were as such but the peak height and peak position got decreased or increased in case of CP1S which were resulted from decreased in bonding among the functional groups of polymers. This decrease in bonding may be due to growth of bacteria and fungus on the hydrogel film to degrade the sample.

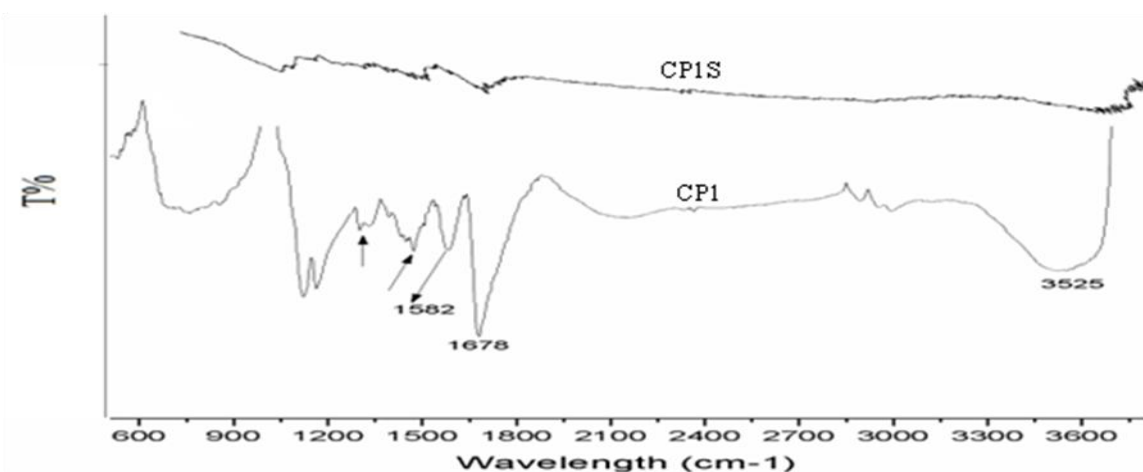
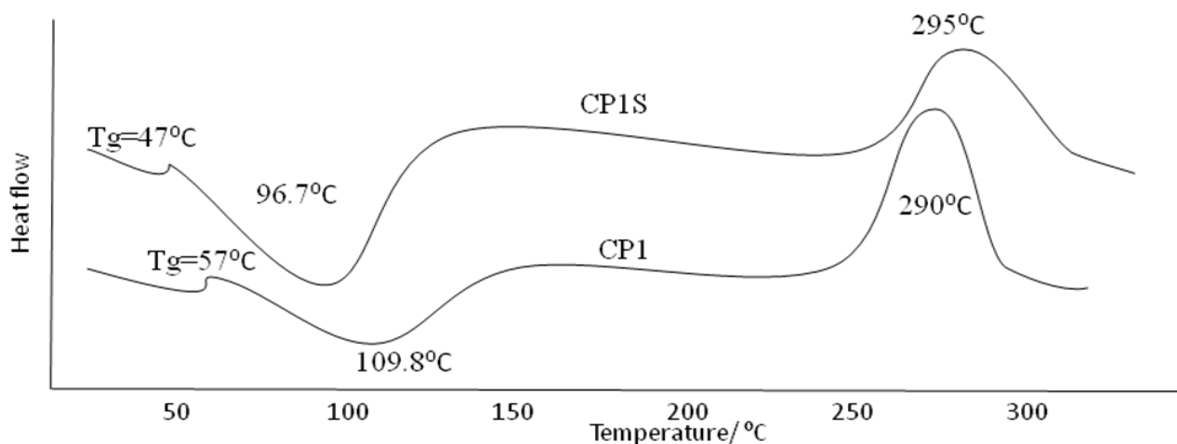


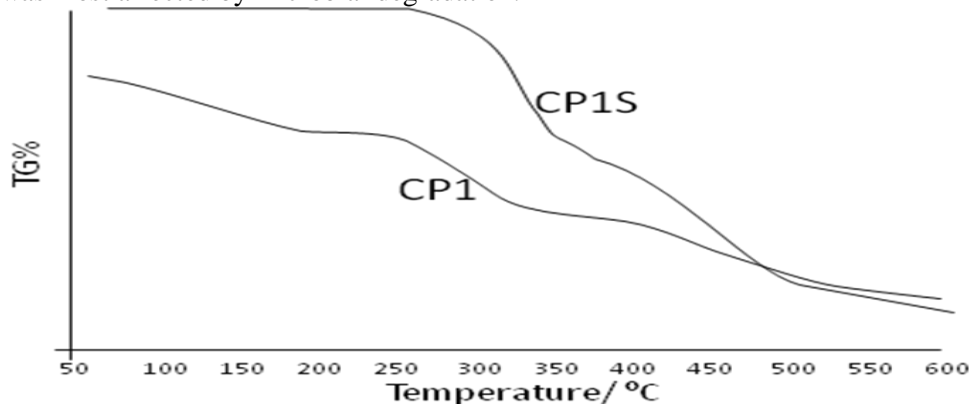
Figure 1. FTIR spectra of CP1 as developed material and CP1S as a soil buried material

**Differential Scanning Calorimetry:** Figure 2 showed the DSC peaks of CP1 and CP1S. On development of CP1  $T_g$  observed at 57°C. CP1 and CP1S showed peaks at 109.8°C and 96.8°C were of water evaporation [10]. The exothermal degradation peak of CP1 was at 295°C. These exothermal peaks were attributed to thermal stability in which heat released after the macromolecules became closely packed. This result demonstrates that the PVP and PNIPAm provide the thermal stability to CP1. In the same figure we found distinctive changes in case of CP1S.  $T_g$  shifted from 57°C to 47°C and exothermic peak observed at 290°C which was 5°C lower than CP1. Decrease in  $T_g$  and change in position of exothermic peak, showed degradation of CP1S by bacteria and fungus feeding on the film. Less heat and less temperature required for the degradation of sample because bacteria and fungus break the cross linking which provide the strength to the hydrogel film.



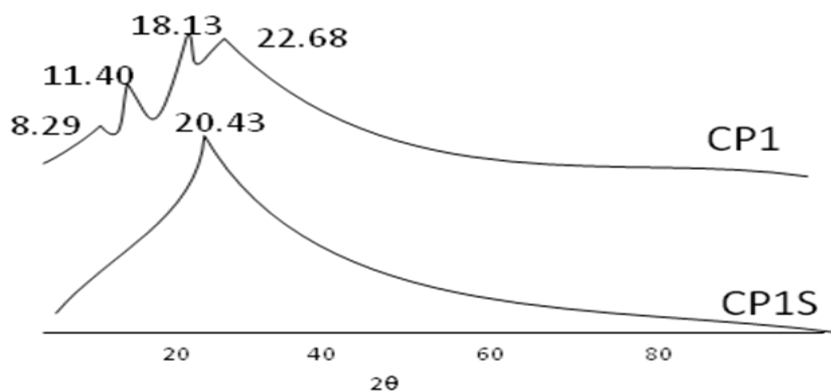
**Figure 2.** DSC results showed the differences in peak position of CP1 and CP1S

**Thermogravimetric analysis:** Figure 3 shows the TGA curves of CP1 and CP1S. First weight loss range of CP1 was 45°C-100°C. Second weight loss range was 275°C-350°C and weight loss % was 35%. Third weight loss started from 360°C to 595°C. In the same figure only two weight losses were found in the case of CP1S: first started from 222°C to 392°C and second started from 392°C to 593°C. Weight loss % also varied: at first stage it was 38% and at second stage it was 30%. First weight loss was not found in case of CP1S may be water was not present but main difference was of second weight loss and third weight loss. Second weight loss started 50°C less than CP1 and weight loss % was also varied by 3% as it was 38%. Third weight loss started 32°C higher than CP1. It may be added amount of released metabolites by feeding bacteria and fungus on CP1S. So TGA of CP1S showed only two step decomposition in which second step was most affected by microbial degradation.



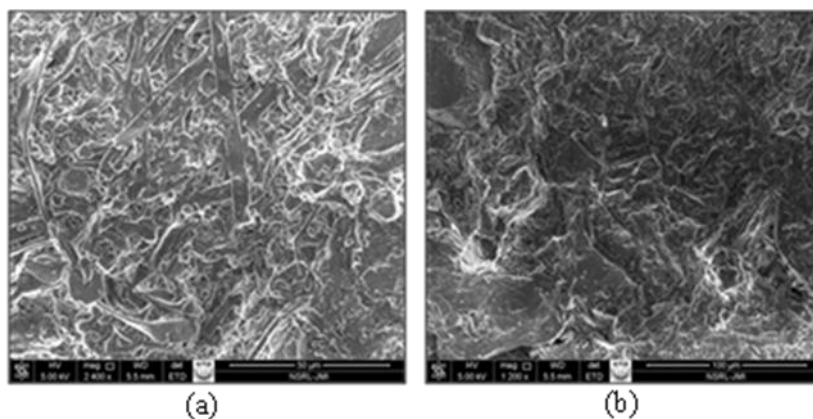
**Figure 3.** TGA results showed the weight loss changes of CP1 and CP1S

**X-Ray diffraction:** In figure 4 X-Ray diffraction peaks of CP1 were at 8.29, 11.40, 18.13 and broad peak at 22.86 showed a crystallinity level. The addition of PNIPAm into the CS and PVP generate interactions among component polymer to facilitate rearrangement of chain segments into ordered position for crystallization. Such intermolecular interactions were evident from FTIR, DSC and TGA results in which PNIPAm and PVP interacted with CS through their amide groups. This interaction would disrupt the inherent hydrogen bonding formation among CS molecules and among PNIPAm molecules which generate the crystallinity. In the same figure CP1S has only one peak at 20.43 and all the peaks were absent from their position it means that crystallinity of the sample reduced to minimal level by microbial degradation. This reduction in crystallinity level is believed to be mixing of component polymers or transformation of component polymer in to amorphous form [11].



**Figure 4.** X-Ray analyses of CP1 and CP1S

**Field Emission Scanning Electron Microscopy:** After 3 months in figure 5(a, b) irregularities can be observed on the hydrogel film surface, which means that the internal structure of CP1S has started to degrade. CP1S surface becomes more irregular, with some depositions (most probably deposition of microorganisms). Thus, the FESEM evaluation of the CP1 before and after degradation supports that CP1S are biodegradable. The major part of CP1 hydrogel film is made up of CS, which provide nutrient to the microbes. This may lead to the degradation process faster.



**Figure 5.** FESEM results showed degradation images before and after; (a, b) CP1S

## APPLICATIONS

Use of Hydrogel films day by day in wound dressing may affect the environment on soil burial sites. Degradation study of hydrogel films may help to design environment friendly products.



## CONCLUSIONS

The objective of this research work was to develop a hydrogel film which do not caused any danger to the environment. This hydrogel film is non-toxic as prepared with PVP, CS, and PNIPAm. Moreover, the experimental results obtained show that CP1 hydrogel film was thermally stable, flexible and showed crystallinity (before degradation) but, same hydrogel film showed major changes after 12 weeks when degradation study conducted in open an environment. The distinguishable differences occurred among the peak positions and the peak intensities of FTIR spectra, major change in weight loss of the hydrogel film before and after degradation, almost total loss of crystallinity in X-ray analysis, and the difference in external morphologies obtained through FESEM prove that CP1S hydrogel film is biodegradable. So, these materials show a broad range of physical properties and other advantageous characteristics at an acceptable cost and biodegradation rate and can be employed in a wide range of applications. To further improve the degradability of CP1S, incorporation of some other polymer starch, guar gum, cellulose can be apply.

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