

Behaviour of hydroxy propyl cellulose (HPC) hydrogel in the presence of the SDS surfactant: A rheological study

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HPC-iodine hydrogel was found to enhance the gelling process and further exhibited stronger hydrogel properties when incorporated with borax. There is a preferential occupation of active sites of the HPC by borax through di-diol complexation. Borax has shown a comparatively higher affinity towards HPC than SDS or iodine.

Keywords: Hydroxy propyl cellulose (HPC), borax, iodine, SDS, FT-IR, rheology, DSC.

Introduction

Hydroxy propyl cellulose (HPC) is a surface-active and water-soluble non-ionic cellulose derivative of a natural macromolecule¹. Due to its non-toxicity, biodegradable, bio-compatible nature, pH-dependent and temperature-sensitive, HPC and its composite materials are suitable for the food industry, pharmaceutical, cosmetic industry, adhesives, controlled drug release, etc., and thus becoming a potential green material². HPC undergoes hydration and dehydration phenomena at around LCST (i.e. 41°C aqueous solution)³ due to expanding and shrinking of the structure of the polymer material. This unique property is exhibited when there is hydrophilic interaction to form hydrogen bonding and hydrophobic interaction to cleave hydrogen bonding between different groups present in HPC polymer and surrounding water molecules at varied temperatures. This LCST can be manipulated from the addition of salt or by copolymerizing HPC with hydrophilic and hydrophobic monomer. HPC-based hydrogels have been studied for the formation of nano-gel and characterised for the self-supporting system despite its limited practical use due to low adsorption capacity⁴. It has also been a well-known fact that the rheological characterization of polymeric materials provides fundamental information to assess guality, storage stability, and sometimes consumer evaluation⁵. Many researchers have accounted for the rheological behaviour of HPC based materials i.e. elastic property at two distinct regions. The behaviour also increases with an increase in the irradiation dose of UV-radiation. The gel also has two relaxation times within the gelnetwork and enhanced gelation behaviour by the addition of SDS from 0.4 to 1.0 CMC. The rheological behaviour of the HPC-based system was found to have increased when an antimicrobial substance like erythromycin or magnolol, which influences drug delivery behavior, was present⁶. Interestingly, HPC-based gel formulated in propylene glycol (PG), water, ethanol was found to favour in the formation of a more-elastic gel with an increase in PG content⁷. The glassy, rubbery nature and viscous flow have also characterized the viscoelastic (relaxation) and phase behaviour of some polymer blends like HPC-PEG (polyethylene glycol) 400 and found phase equilibrium drastically change with the molecular mass of the oligomeric PEG. The concentration dependences of the melting temperature of PEG 1500 and the glass transition temperatures of blends complement the phase diagrams and vividly illustrate all relaxation and phase transitions characteristic of a given system. It is a fact that the rheological properties of HPC hydrogel continue to be of considerable interest in the last decades when incorporated with materials. However, no report till the date on rheological properties of HPC-iodine hydrogel was found during literature survey and hence the investigation in the present study.

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Experimental

Materials:

HPC polymer of Mw 100,000 was procured from Aldrich and used without further purification. Anionic surfactant, SDS, iodine (I₂) (extra pure), potassium iodide (KI) (over 99.5%) and borax (sodium tetraborate) were procured from Loba Chemie, Bombay. The surfactant SDS was purified following the standard procedure⁸. It was re-crystallized several times from hot methanol, refluxed in diethyl ether nearly for 72 h through Soxhlet Extractor and finally dried under vacuum. The crystalline iodine was also purified following the procedure mentioned elsewhere⁹. Solid sample of crystalline iodine was purified by heating the crystals in a porcelain basin on a water bath with a cold glass funnel held over it. The iodine crystals changed from a dark solid to a purplish vapour. The hot iodine vapour condensed and deposited directly to a crystalline solid on the cool surface of the funnel was carefully collected and stored in tightly sealed coloured glass container.

Preparation of the HPC-iodine complex:

Solution of iodine (0.2 mM)-potassium iodide (0.8 mM) in 4 mM SDS was prepared using iodine-potassium iodide (2:8 mM) stock solution by dilution method. Following the same procedure HPC (0.1%)-iodine (0.08 mM) complexes in the presence of 4 mM SDS and/or 0.3% borax were also prepared.

Preparation of the HPC hydrogel:

HPC polymer solution of about 5% w/v was prepared by dissolving the HPC polymer in double distilled water by dissolution for about 72 h. Different HPC-iodine gels in aqueous or in aqueous SDS solution were prepared by mixing adequate amounts of the HPC, I₂-KI solutions and SDS solution to give resultant gels containing 2% (w/v) HPC, 0.3% (w/v) borax, 1 mM iodine and 4 mM SDS. A good uniform gel was obtained after at least five rounds of heating and cooling between 60°C and 25°C. Then the gel was finally washed with distilled water for at least three times to remove excess materials and then dried at room temperature for future use.

UV-Visible spectrophotometric measurement:

UV-Visible scanning spectrophotometer (Shimadzu UV-2456) was used to record the absorption spectra of polymeriodine complexes for both the aqueous and aqueous SDS solution in the wave-length range from 300 to 600 nm by maintaining at 30°C from the thermostated water circulating the sample solution.

FTIR spectrophotometric measurement:

The IR spectra of the semi-solid and semi-liquid polymer gel samples were measured with the help of a Fourier Transform Infrared Spectrophotometer (FTIR-8400S Shimadzu) having effective measuring wave number ranges between 7800–500 cm⁻¹.

DSC measurement:

Perkin-Elmer DSC-2 was used to take DSC scan of the HPC gels in between $37-170^{\circ}$ C at a heating rate of 10° C/min following the standard procedure of the instrument. The solidus and the liquidus temperatures were estimated from peak temperatures in the thermogram. The transition temperatures were also determined using pure standards of *p*-nitro-toluene and naphthalene.

Viscoelastic measurement:

AR500 Rheometer (TA instruments UK) was used for rheological measurement of the different prepared HPC-iodine gels. An equilibration time of 30 min was allowed before taking each measurement at 30°C and appropriate inertial corrections were taken care of in angular frequency range 0 to 100 rad/sec.

Results and discussion

The FT-IR spectra of different HPC gels are shown in Fig. 1. The broad bands around 3430–3440 cm⁻¹ for all the gel systems indicate the presence of intermolecular hydrogen bonding¹⁰. The sharp peak observed around 1650 cm⁻¹ corresponds to the bound water molecules or absorption of water in the gel network¹¹. The presence of iodine in the HPC polymer showed a large broadening of the O-H bond which is an indication of the formation of stronger H-bonding. The presence of SDS (at 4 mM) also leads to further broadening of the O-H band¹². However, presence of borax appears to disturb H-bonding of the HPC network system, perhaps due to a different predominant aggregating behaviour of borax in the polymer network. The disappearance of a sharp band *ca.* 2330 cm⁻¹ in case of HPC-iodine gel on the addition of borax or SDS was observed further broadening



Fig. 1. FT-IR profile of HPC and HPC-iodine gel in presence of SDS (4 mM), borax and borax and SDS (4 mM).

of the band around 3500 cm⁻¹ thereby suggesting a strong indication of participation by the remote hydroxyl group present in the hydrophobic site of the polymer chain in the intermolecular hydrogen bonding in the presence of borax or SDS. The presence of borax along with SDS in the HPC-iodine gel has shown nearly identical spectra with pure HPC polymer. The effect of SDS in the network formation of the polymer system appears to be neutralized or suppressed by abstracting the iodine from gel network and leaves the HPC polymer as the major component of the gel network system.

The rheograms showing the behaviour of elastic (G') and viscous modulii (G") against the angular frequency, ω /(rad/ sec) for the HPC-iodine gel systems are shown in Fig. 2 at 30°C. The response of G' against ω /(rad/sec) for different HPC-iodine gels are also separately compared in Fig. 3. The gel system demonstrates Newtonian liquid-like behaviour with the G" higher than G' up to 31/(rad/sec) and beyond this value, G' increases and becomes larger than G" in Fig. 2a and the frequency around $\omega = 31/(rad/sec)$ is therefore called the cross-over frequency¹³. Thus, the HPC-iodine mixture starts to behave the gel-like system beyond this frequency^{13,14}. The presence of SDS (at 4 mM) in the HPCiodine system decreases the cross-over to $\omega = 17/(rad/sec)$ (Fig. 2b), which is an indication of the fact that SDS enhanced in the production of more intriguing network structure due to mixed micelle formation in the system. On the other hand, the addition of borax into the HPC-iodine system has shown viscous nature and showing no crossover between G' and G" in the entire frequency range (Fig. 2c), a behaviour exhibited very differently from the other HPC-iodine gels which could suggested that borax have disturbed the HPC-iodine linkage. This observation shows that even if the polymer shows a strong affinity towards borax rather than iodine or SDS, as suggested from FT-IR observation, the system comprising HPC and borax could not form a solidus structure as it was a predominant behaviour when HPC is interacting with iodine. However, the HPC-iodine system again when incorporated with both SDS (4 mM) and borax decreases the crossover frequency to lower value i.e. at about $\omega = 13.7/(rad/$ sec) as shown in Fig. 2d. It is apparent from the above observation that the addition of SDS (4 mM) or SDS (4 mM) along with borax in the HPC-iodine system enhances to attain gel-like behaviour at a lower frequency, ω . The increased in the elastic modulus, i.e. the gel-like character of the HPCiodine gel on the addition of SDS or SDS along with borax as shown in Fig. 3 is due to increase cross-linking of the HPC polymer chains by the addition of SDS or SDS along with borax in the network structure of the system^{13,14}. The HPCiodine gel in the presence of both SDS (4 mM) and borax have shown a very similar G' curve with that of HPC-iodine gel in SDS (4 mM) up to the frequency, $\omega = 55/(rad/sec)$. The gel system has larger G' beyond the frequency, $\omega = 55/$ (rad/sec). The presence of borax in the HPC-iodine gel has large G' values up to a frequency, $\omega = 38/(rad/sec)$ but the gel shows a distinct plateau at a higher frequency beyond ω = 38/(rad/sec). This effect of borax of showing the plateau in G' curve can neither be observed when the gel is present with SDS nor SDS along with borax. It also shows that there is predominant character of borax while forming the network structure could no longer replaced by SDS monomers. The exhibition of such a plateau in G' curve is the characteristic of the presence of a network structure in the system¹⁵.

The network structure is formed through di-diol complexation by crosslinking between HPC and borax as shown in the reaction Scheme 1, similar to the case of PVA-borate complexation¹⁶. Such di-diol complexation disturbs the interaction between HPC and iodine and reduces the stiffness of HPC-iodine gel. It is also evident from Fig. 4 that SDS monomers cannot exhibit its influences of enhancing complexation between HPC and iodine when borax is incorpo-



Fig. 2. Visco-elastic properties showing frequency dependence of HPC-iodine gel (a) in presence of SDS (4 mM), (b) borax, (c) and SDS (4 mM) and borax (d).



Fig. 3. Frequency dependence of storage modulus (G') for HPC-iodine gel in presence of SDS (4 mM), borax and borax and SDS (4 mM).



Fig. 4. Absorption spectra of iodine (I₂-KI) solution, HPC-iodine complex in the presence of borax, SDS (4 mM) and both in SDS (4 mM) and borax at 30°C.

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Scheme 1. Di-diol complexation between two diol units of HPC with borate ion.

rated. Thus the addition of borax in the iodine complexes of HPC brings about a reduction in the absorbance of the triiodide complex band below than HPC-iodine complexes and the complex even in the presence of the SDS. This is an indication about the preferential interaction of the borate ion of borax with OH groups of the polymer chain to undergo the di-diol complexation thereby minimizing a number of aggregating spaces for the formation of I2 species. Such preferential interaction of OH groups with borate ions would lead us to the suggestion that HPC polymer has better interaction with borax than SDS as is evident from the rheograms of the gel systems. The extent of reduction for the absorbance of the tri-iodide complex is also so appreciable that absorbance is much below from that of the tri-iodide reference band of $I_2/$ KI solution. It may be mentioned from the literature survey that this behaviour of the HPC-iodine system in the presence of borax has not been reported elsewhere or available to compare with our results. However, a similar polymer-iodine complex of PVA was reported by Ohishi et al.¹⁷ where complexation process was found to enhance in the presence of boric acid, a phenomenon which is just an opposite behaviour shown by that of the HPC-iodine complex. The decrease in absorbance of the HPC-iodine complex, while the addition of borax, may be due to enhancement of the microgel formation during complexation. The microgel formation arises from intriguing network of intermolecular or intramolecular hydrogen bonds, through many junction points, leads to reduced aggregate spaces¹⁸. Fig. 5 shows the DSC profile of different HPC based hydrogels in the presence of SDS or/and borax. DSC measurements are used to observe the change in transition temperature of the gel systems. Endothermic peaks at 365 K and 356 K show the temperatures at which the gel systems melt. The gel melting point is a physical parameter used to identify the nature of the substance and its degree of purity¹⁹. The addition of borax to HPC-iodine gel has shown endothermic peak at around, 356 K while that of HPC-iodine gel appeared at around 365 K. The higher melting temperature of HPC-iodine indicated that a high amount of thermal energy was needed in order to disturb the system and the lower melting temperature has Singh: Behaviour of hydroxy propyl cellulose (HPC) hydrogel in the presence of the SDS surfactant



Fig. 5. DSC profile of different HPC and HPC-iodine gels in the presence of SDS (4 mM) or/and borax.

showed the gel melting point at a lower temperature as observed in Fig. 5.

Conclusions

Presence of borax in the HPC-iodine complex resulted in the lowering of the absorption values thereby suggesting a greater formation of the microgel in the system. Borax has higher affinity towards HPC when comparing with SDS or iodine, and therefore has the preferential occupation of aggregated spaces of the polymer chain through a different binding mode of di-diol complexation. It is apparent from the above observation that the addition of SDS (at 4 mM) only or SDS (at 4 mM) along with borax in the HPC-iodine system enhances to achieve gel-like behaviour at a lower frequency,



Scheme 2. Schematic representation showing the effect of SDS (4 mM), borax and both borax and SDS (4 mM) in HPC-iodine network.

shown less thermal stability of the HPC-gel in presence of borax due to decreasing cross-linking in the gel system²⁰. It is also observed that the addition of borax to the HPC-iodine gel does not disturb the biphasic nature of the gel²¹. This behaviour also supports the contention that borax has the preferential occupation of active sites of the polymer making available minimum aggregation spaces for the iodine molecules to enter. This preferential occupation of active sites also, on the other hand, leads to decreasing the stiffness of the HPC-iodine gel. The addition of both borax and SDS in HPC-iodine gel does not show any biphasic behaviour but

 ω . A proposed model showing the effect of SDS, borax or both SDS and borax in the HPC-iodine gel network is shown in Scheme 2.

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