

pH-Reversible Magnetic Gel with a Biodegradable Polymer

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ABSTRACT: Polymer gels that react to external stimuli, such as pH, temperature, and electromagnetic fields, are an important class of materials. Such materials have pharmaceutical, industrial, and biomedical applications. Our intention in this study was to synthesize a stimuli-responsive polymer gel with a biodegradable polymer. However, the chemical crosslinker, divinyl sulfone, which is most widely used for the crosslinking of this type of material, is highly toxic in nature. To overcome this problem, a reversible magnetic gel was synthesized with hydroxy propyl cellulose (HPC) and maghemite at pH 13 without with a chemical crosslinker. With a decrease in pH from 13 to 9, the gel formed a homogeneous dispersion of HPC particles with maghemite in it. This process was a reversible physical gelation where the crosslinks of the network had a physical origin (in this case, hydrogen bonding) and, therefore, were

sensitive to variations in pH. When this physically prepared gel was compared with the chemically crosslinked one, no significant differences in structural properties were noted. At higher pH values, the gel was formed due to weak intermolecular hydrogen bonding, as observed by the broadening of the IR band in both the magnetic and non-magnetic gels. Transmission electron micrographs also showed no significant difference in the gel morphology. Differential scanning calorimetry showed an increase in melting temperature for the gel sample compared to that of pure HPC. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3337–3341, 2004

Key words: magnetic polymers; gels; biodegradable; nanocomposites

INTRODUCTION

Polymer gels are unique in two respects. First, they have unique structure of a macromolecular network with a large amount of solvent in them, and second, they can be responsive to external stimuli, such as pH,^{1,2} temperature,^{3–5} and magnetic fields.⁶ These properties allow them to be used as sensors,^{7,8} actuators,⁹ and releasing or encapsulating agents.^{5,10} Polymeric gels are formed by chemical crosslinking or by physical entanglement. The latter process, or physical gelation, takes place in melt or in solution under certain conditions when the molecular weight (MW) of the polymer exceeds the critical MW by some weak interactions. This physically crosslinked polymeric network is reversible. In this study, we focused on the preparation of a reversible magnetic gel by changing the pH of the medium. Cellulose ethers, such as carboxy methylcellulose, hydroxy propyl cellulose (HPC), and hydroxy propyl methylcellulose, are biodegradable polymers and are extremely important for

their use as drug-delivery media^{11,12} and in the food industry.¹³

EXPERIMENTAL

We used HPC and maghemite ($\gamma\text{Fe}_2\text{O}_3$)¹⁴ to synthesize the magnetic gel.^{15,16} Different concentrations of HPC were made in a NaOH solution at pH 12. Initially, 1 g of HPC (MW = 370,000) was mixed with 300 mg (30 wt % of the polymer) of CTAB-modified $\gamma\text{Fe}_2\text{O}_3$ powder in 200 mL of sodium hydroxide solution (pH = 12). The solution was then sonicated at an amplitude of 50% for 30 s. When the solution became homogeneous, solid crushed pellets of NaOH were added to this solution and mixed thoroughly. During this process, the pH of the solution was continuously checked with a pH meter. A reddish brown gel was formed at pH 13 and was separated from the solution. With the decrease in pH (at pH 9), the gel broke down and formed a homogeneous dispersion of the HPC– $\gamma\text{Fe}_2\text{O}_3$ complex. This brown dispersion again transformed into a gel with an increase in the pH to 13. To compare the structural and other features of the HPC magnetic gel formed by changes in pH and formed by chemical crosslinking, we prepared a magnetic HPC gel by chemical crosslinking. HPC (1 g; MW

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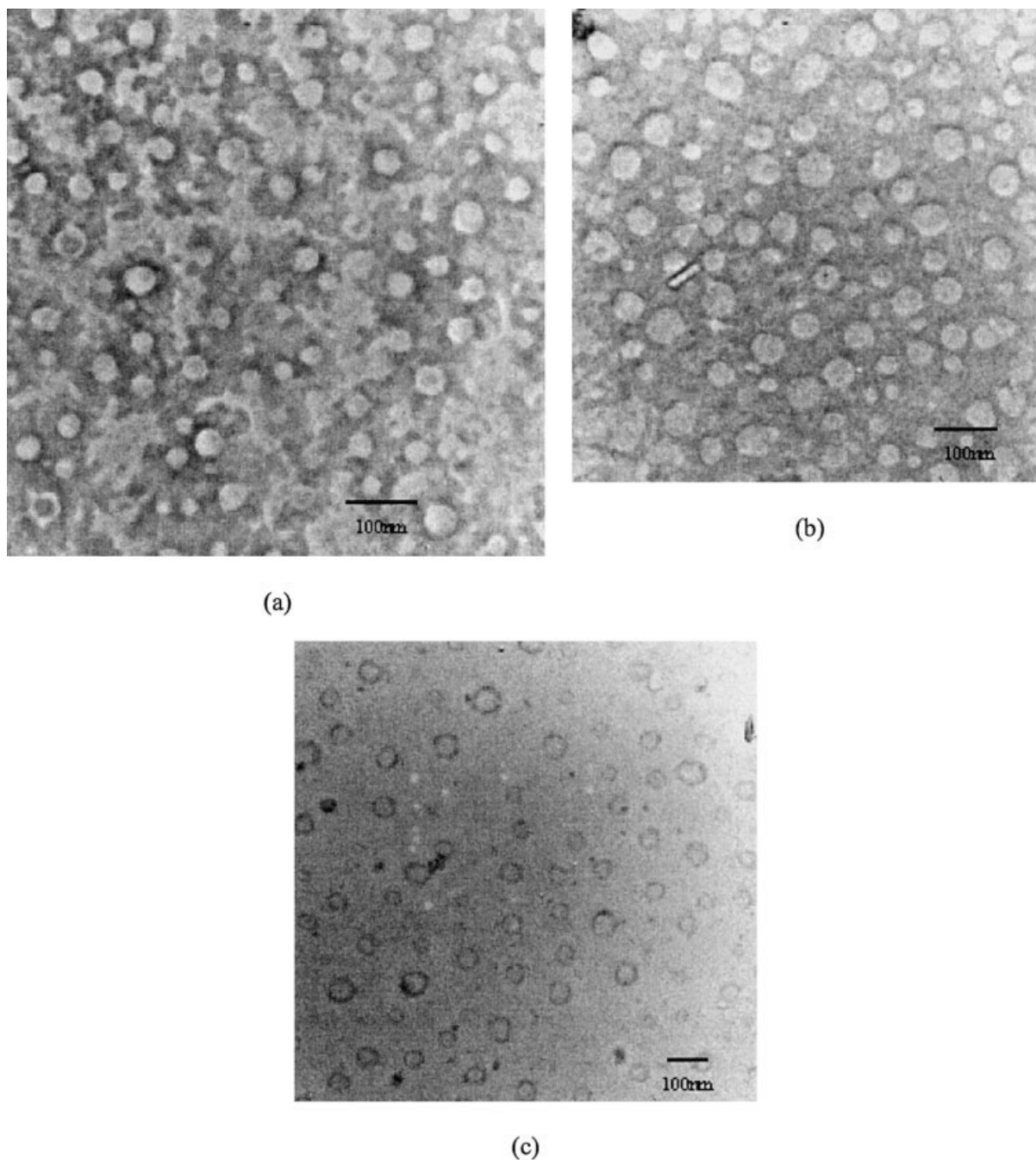


Figure 1 TEM micrographs for the HPC gels formed by (a) physical and (b) chemical gelation and (c) HPC dispersion at pH 9.

= 370,000) was mixed with 300 mg (30 wt % of the polymer) of CTAB-modified $\gamma\text{Fe}_2\text{O}_3$ powder in 200 mL of a sodium hydroxide solution (pH = 12) and was sonicated at an amplitude of 50%. The mixture was mixed at a speed of 200 rpm at 65°C for 1 h. Divinyl sulfone (4 wt % of the polymer) was added to mix. This procedure of the formation of a HPC gel by chemical crosslinking was partly adapted from the work of Hu et al.¹⁷

RESULTS AND DISCUSSION

Transmission electron microscopy (TEM)

Figure 1(a,b) shows the TEM micrographs (with a Jeol TEM 2010) for the gel samples formed by physical and chemical gelation, respectively. No significant difference in the gel structures was observed. Both had a network structure formed by the HPC nanoparticle (with iron oxide in them). Figure 1(c) shows the TEM

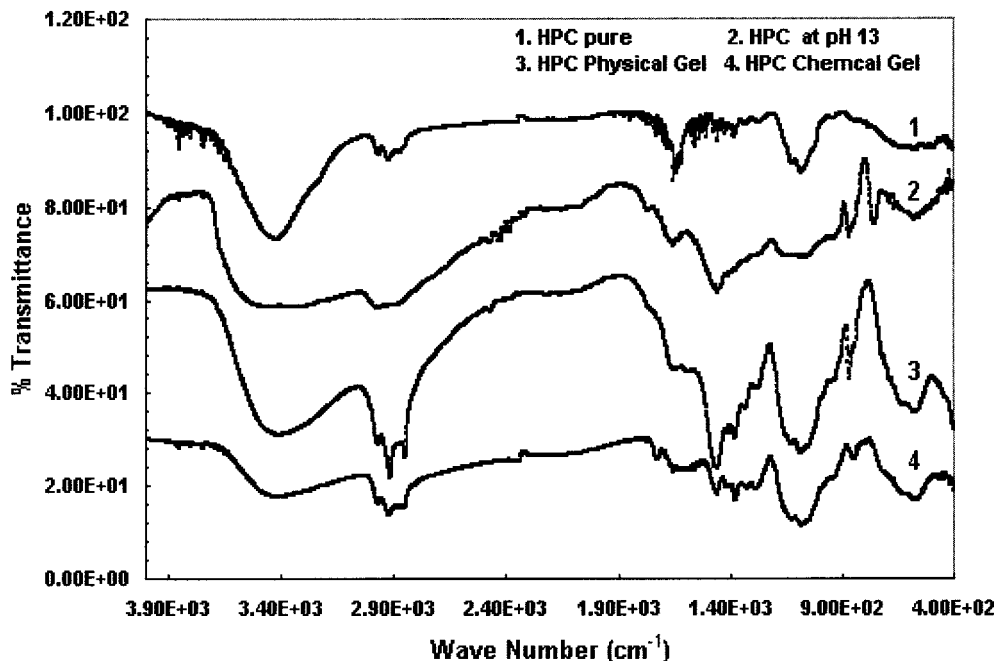


Figure 2 IR spectra for pure HPC gels formed under different conditions.

micrograph for the HPC dispersion formed by the reduction of pH from 13 to 9. To reconfirm the formation of the gel at pH 13, a pure solution of HPC was also tried without $\gamma\text{Fe}_2\text{O}_3$, and the formation of the HPC gel was observed at pH 13, which was converted to a HPC dispersion at pH 9. When crushed pellets of sodium hydroxide were added to this dispersion, it again transformed into a gel.

IR spectroscopy

IR spectroscopy (with a Nicolet Avatar Fourier transform infrared spectrophotometer) for both pure HPC and at pH 13 was performed. The results did not show a difference in the transmission band, except for some minor changes, which proved that there was no drastic structural changes in the compound formed at pH

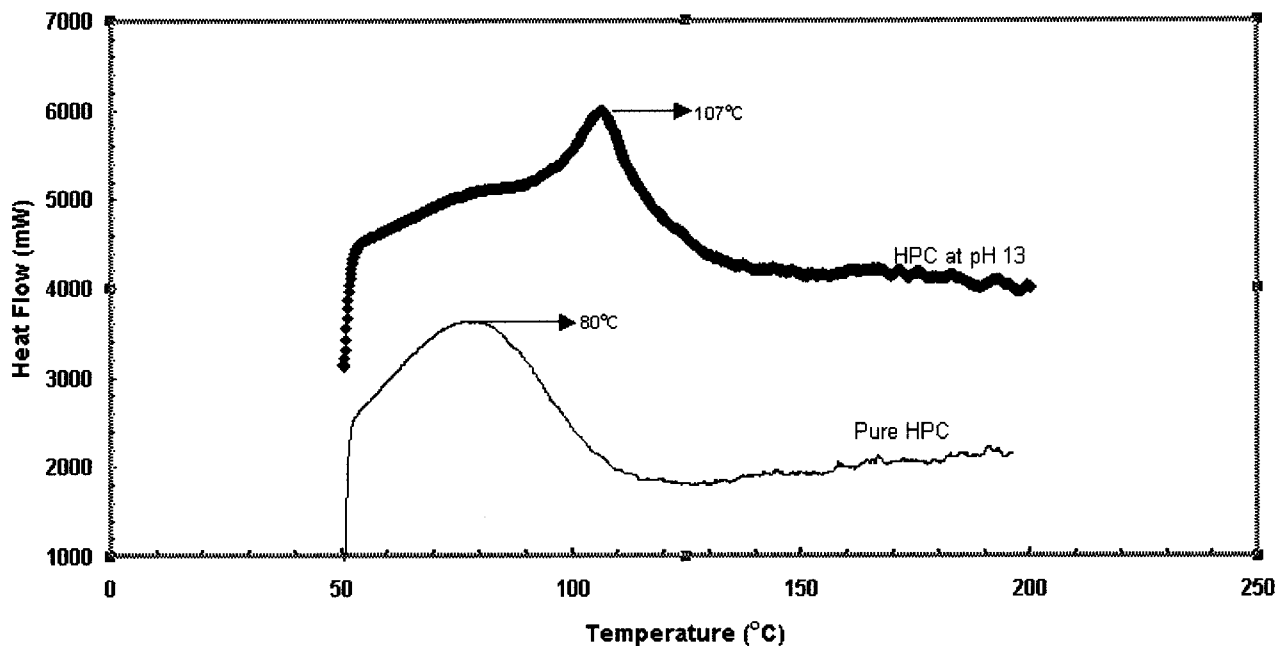
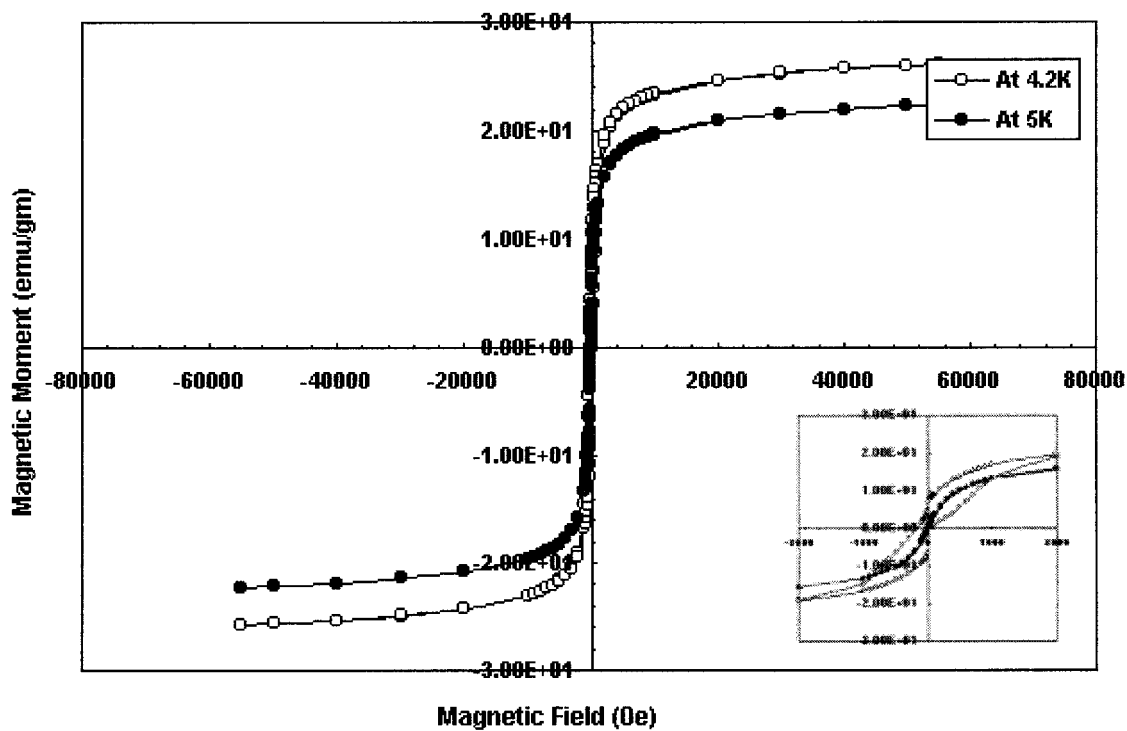
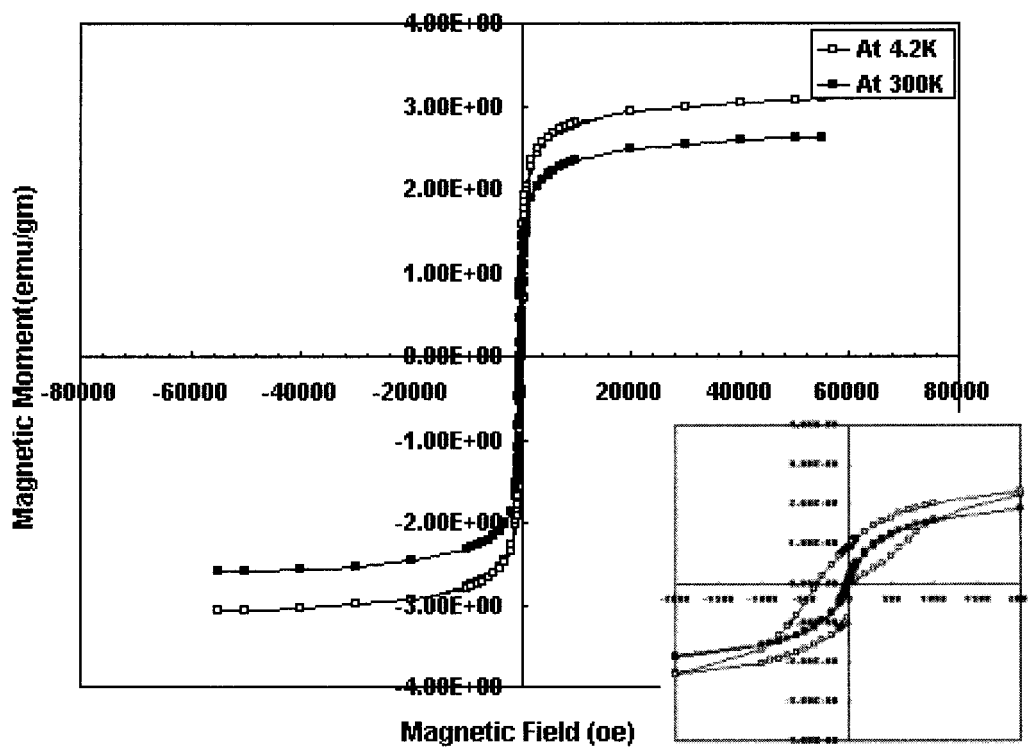


Figure 3 Temperature versus heat flow for pure HPC and HPC at pH 13.



(a)



(b)

Figure 4 Hysteresis plots for HPC magnetic gels formed by (a) chemical crosslinking and (b) physical gelation.

13, the pure HPC, or the compound formed at pH 9. The minor changes may have been due to some molecular aggregation that took place at higher pH values,

which was probably due to hydrogen bonding. With a decrease in pH (by the addition of water) and when the mix was shaken, the molecular aggregation weakened,

and gel transformed into a homogeneous solution. IR spectra for pure HPC, the HPC nonmagnetic gel, and the HPC magnetic gel formed by a change in the pH and by chemical crosslinking are given in Figure 2. A broad band was obtained for the gel formed at pH 13 (no. 2). The width of this band was about 250 cm^{-1} (3250 to 3500 cm^{-1}). The broadening of the IR band in the gel sample compared to that of the pure HPC (at 3440 cm^{-1}) indicated the presence of weak interactions due to intermolecular hydrogen bonding in the gel structure.¹ For the magnetic gels formed by HPC with $\gamma\text{Fe}_2\text{O}_3$, the band shifted from 3445 to 3401 – 3405 cm^{-1} . This occurred because of the complexation of HPC with $\gamma\text{Fe}_2\text{O}_3$. The IR spectra of HPC (at pH = 9) that was obtained by a decrease in the pH was similar to that of pure HPC.

Differential scanning calorimetry (DSC)

DSC (measured with a PerkinElmer DSC 7 with a 3700 data station) was performed for the pure HPC and that of the dried gel formed at pH 13. The melting point/softening point increased in the gel, as shown in Figure 3. Hydrogen bonding and agglomeration decreased the chain flexibility, which resulted in lower entropy of the chains, and the reduction of entropy change led to an increase in the melting temperature.¹⁸

Magnetic property studies

The magnetic property studies (done with a Quantum Design MPMS5 DC SQUID magnetometer) showed no significant difference in behavior between the crosslinked gel and the gel formed at a higher pH. The hysteresis plots for the crosslinked gel and the gel formed at pH 13 are shown in Figure 4(a,b) at 4.2 and 300 K . Both gels showed superparamagnetic behavior with no remnant magnetization at 300 K .¹⁹

CONCLUSIONS

In conclusion, pH-reversible magnetic and nonmagnetic gels were formed without a crosslinking agent. The large macromolecular structure of HPC loaded as much as 100% of its weight of iron oxide to form a complex structure, and a stable three-dimensional network was formed at a higher pH. So, a large value of magnetic moment was obtained from these gels. By this process of gelation with a magnetic material along with the cellulose polymer, heavy metals/metal oxides can be captured and separated with the help of an external magnet. This method could be useful in industries where separation and removal of heavy metals/metal oxides are necessary. These biodegradable gels can also be an efficient source of metallic iron for plants.

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