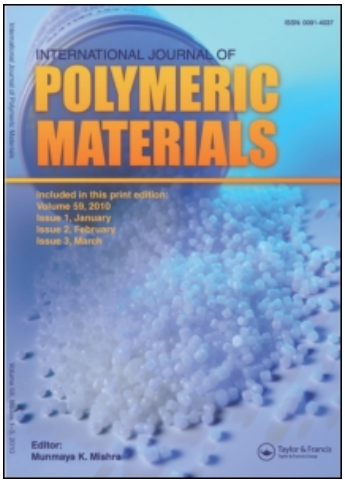

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Interpenetrating Polymer Network PVA/PAA Hydrogels

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Interpenetrating Polymer Network PVA/PAA Hydrogels

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A new type of interpenetrating polymer network (IPN) hydrogel based on polyvinyl alcohol (PVA) networking with difuctional monomer, acrylic acid (AA), and its polymer, polyacrylic acid (PAA), generated in situ, were prepared by a non-conventional emulsion method without any added crosslinker, using benzoyl peroxide as initiator and sodium chloride as additive. Structure and bonding in hydrogel due to interpenetrating network were confirmed by infrared spectroscopy. The networking was optimized by variation of reaction parameters such as concentrations of additive, monomer, time, and temperature. The response of the hydrogels with and without NaCl was observed by study of their swelling kinetics, and their apparent activation energies for diffusion (E_d) of water were calculated to be 29.28 and 35.97 J mol^{-1} K^{-1} with and without NaCl, respectively. The conductivity and pH were measured at different temperatures. The conductivity decreased largely with temperature whereas pH increased in presence of NaCl. The effect of swelling ratio was studied by variation of AA percentage and the optimal PVA/AA AA was determined. Biodegradability of the polymeric network was studied by culture media and the surface morphology investigated by scanning electron microscopy (SEM).

Keywords: IPN, hydrogel, swelling kinetics, biodegradability, SEM

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INTRODUCTION

Hydrogels are among the most promising types of polymers being used for new materials development [1]. The fundamental property of a hydrogel is its equilibrium water content, by which the permeation of oxygen through the hydrogel is substantially facilitated. They are polymeric networks that do not dissolve in water at a physiological temperature [2] and pH [3] but absorb and retain large amounts of water by considerable swelling in an aqueous medium [4–5]. In polymeric networks, there are hydrophilic groups that are hydrated in an aqueous environment, thereby creating a hydrogel structure. As the term network implies, crosslinks have to be present to avoid the dissolution of the hydrophilic polymer chains into the aqueous phase [6]. Hydrogels have been used in the medical device industry as contact lenses, artificial corneas, and dressings as coating for sutures, catheters, and electrode sensors. The hydrogel-type polyurethane foams were prepared from diisocyanate and polyol with hydrophilic moiety for wound dressing to protect from infection and to heal skin wounds [7]. Protein-based hydrogels are used for many applications, ranging from food and cosmetic thickeners to support matrices for drug delivery and tissue placement [8]. Microporous hydrogels find application as biocompatible implants in tissue, such as in the control nervous systems [9] or as substrates in cellular and tissue engineering [10]. Hydrogels, especially, have become excellent carriers for release of drugs and bioactive macromolecules either in their swollen equilibrium state or as dynamically swelling systems [11–13].

Porosity of hydrogels is usually achieved either by crosslinking polymerization in the presence of substances that are solvents for the monomers, but precipitants for the formed polymers [14–15] or crosslinking polymerization in the presence of soluble substances that are washed out from the hydrogel after polymerization [16–17] or by crosslinking polymerization in the presence of substance-liberating gases that remain in the resulting hydrogels [18] or by frost sublimation of the hydrogel swollen in water [19]. Interpenetrating polymer networks are defined as a combination of two or more interwinding crosslinked polymers where one of the network polymers is crosslinked in the presence of the other [20–21].

PVA is a water-soluble polyhydroxyl polymer employed in practical applications because of its easy preparation, and excellent desirable properties, such as non-toxicity, non-carcinogenicity, and biodegradability [22]. Chemically crosslinked PVA hydrogels have received increasing attention in biomedical and biochemical applications due to their permeability, biocompatibility, and biodegradability [23–24].

It is known that polyacrylic acid has been considered as pH and electrically sensitive material due to ionic repulsion between anionic charged groups, and thus forms polymer complexes with polybases such as poly(vinyl pyrrolidone) or polyacrylamide [25–26].

The present work focuses on the development of a new hydrogel from PVA, copolymerized and crosslinked with a hydrophilic monomer, AA, and its homopolymer PAA that is formed in situ, in the presence of NaCl and in absence of an added crosslinker to highlight its two important potential properties like swelling and biodegradability. The capacity of this non-toxic hydrogel to absorb large amounts of water and its conductance are added significant advantages for its versatile use in different biomedical applications.

EXPERIMENTAL

Materials

PVA with an average molecular weight of 65,000–86,000 and NaCl were purchased from CDH India Ltd., AA and benzoyl peroxide (BPO) were from E. Merck. All other chemicals were reagent grade and used without further purification.

Copolymerization

Slurry of 10% (w/v) aqueous solution of PVA was prepared by dissolving in distilled water at 90°C for 24 h through stirring. A variation of 10, 20, 30, and 40% (v/v) of the difunctional monomer, AA, were prepared. A series of hydrogels were prepared using the following procedure. All the prepared solutions were added in a three-necked flask equipped with a mechanical stirrer, condenser, and N_2 line. The solution was stirred at 400–500 rpm for 15 m. Then the initiator, BPO [0.1–5.0% (w/v)], and NaCl [0.1–5.0% (w/v)] were added in a proper variation of concentrations and the temperature was maintained at 80°C with stirring. After 3 h of reaction, a gel was formed, washed with distilled water, and then dried in a vacuum oven at 60°C to get a constant weight of the hydrogel (PVA-co-PAA)/NaCl. A similar procedure was adopted to prepare PVA-co-PAA hydrogel without adding NaCl.

Measurement of Swelling Ratio and Conductance

One gram of the dried sample was immersed in distilled water with different time and temperature variations for getting better swellability

[27] ratio and simultaneously their conductance was measured in the solution by using an Ecoscan con5 (Singapore) instrument. The swelling ratio was measured by using the formula:

$$\text{Swelling ratio } (\%) = [(W_s - W_d)/W_d] \times 100,$$

where W_s is the weight at swollen state and W_d is the weight at dry state.

Biodegradation by Cultured Media and Quantitative Estimation of CO_2

A cultured medium was prepared by using a nutrient broth in which *E. coli* bacteria were inoculated. The pure cultures were maintained separately in the incubator. The nutrient broth so prepared was sterilized for 45 m at a pressure of 15 lb/in^2 at 80°C. Then, to 10 ml of sterilized broth, 0.1 g each of the samples, that is, PVA-co-PAA and (PVA-co-PAA)/NaCl were added aseptically in separate test tubes. Then, each tube of sample was separately supplemented with inoculome of different bacterial strains. Extent of biodegradation by *E. coli* was determined by both methods of weight loss and the amount of CO_2 evolved [28] during incubation periods of 8, 15, 21, and 28 days.

Quantitative Estimation of Free CO_2

The cultured sample ("X"ml) and blank tube were titrated against Na_2CO_3 (N/50) ("Y" ml) using phenolphthalein indicator until the pink color persists for at least 30 s. This was continued till a concordant reading was reached.

Calculation

The amount of free CO_2 released was determined by using the following reported formula [28]:

$$N_1V_1 = N_2V_2$$
$$(CO_2)\ (Na_2CO_3)$$
$$\Rightarrow N_1 \times X = (1/50) \times Y$$
$$\Rightarrow \text{Concentration} = (Y \times 22)/(50 \times X)$$
$$\Rightarrow \text{Free } CO_2 = [(Y \times 22 \times 1000)/(50 \times X)] \text{ mg/l}$$
$$\Rightarrow \text{Free } CO_2 = [(440 \times Y)/X] \text{ ppm.}$$

where $N_1 =$ Concentration of evolved CO_2 from the cultured sample, $V_1 =$ Volume of evolved CO_2 from the cultured sample,

N_2 = Concentration of the Na_2CO_3, V_2 = Volume of Na_2CO_3 consumed during titration by the sample (Y ml).

CHARACTERIZATION

Infrared Spectra (IR)

For measuring the FT-IR spectra, KBr pellets of PVA, PAA, and (PVA-co-PAA)/NaCl were prepared by the following method [29]: The KBr (0.5 g) and the sample (0.01 g) were weighed and then ground in an agate mortar to obtain a mixed powder. The mixed powder (0.06 g) was compressed at a pressure of 10 Ton/cm^2 to prepare the pellet (diameter = 10 mm, thickness = 0.25 mm). Then the FT-IR spectra of the aforementioned samples were taken on a Perkin Elmer Paragon 500 FT-IR spectrophotometer in the range of 400–4000 cm^{-1}.

Scanning Electron Microscopy (SEM)

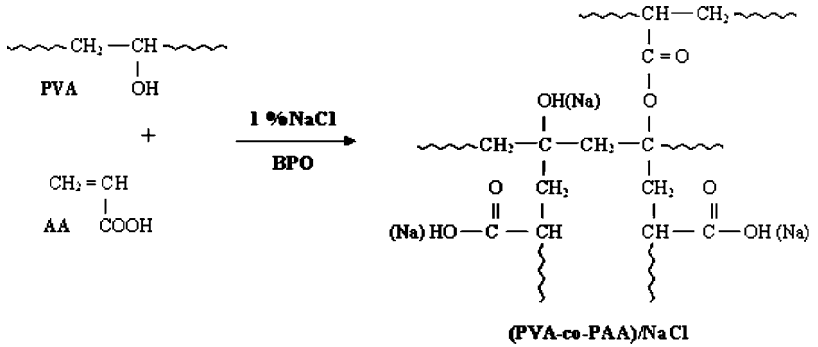
In addition to the study of the surface morphology of the hydrogels, the SEM micrographs of (PVA-co-PAA)/NaCl before and after biodegradation were recorded by Jeol Ltd, Japan, Model 5200 scanning electron microscopy with magnifications of ×1,000 and ×2,000.

Thermogravimetric Analysis (TGA)

Thermogravimetry is the study of the relationship between samples mass and its temperature to examine the thermal stability of samples. TGA of the samples were carried out using a Shimadzu DTG-50 Thermal Analyzer. The samples were heated in air to a temperature of 500°C at the rate of 10°C/m starting from room temperature (28 ± 2°C).

RESULTS AND DISCUSSION

AA was graftcopolymerized and crosslinked with PVA in absence and in presence of additive, NaCl, to form IPN hydrogels, PVA-co-PAA, and (PVA-co-PAA)/NaCl. The reaction mechanism of IPN formation between PVA and AA is proposed to occur in two ways: at first the AA is grafted onto the PVA backbone by radical copolymerization, secondly, the reaction between some of the hydroxyl groups of PVA and some of the carboxylic groups of PAA formed by homopolymerization of AA occurs to form an ester linkage resulting in the formation of a crosslinked IPN polymer (Scheme 1). The above mentioned mechanism

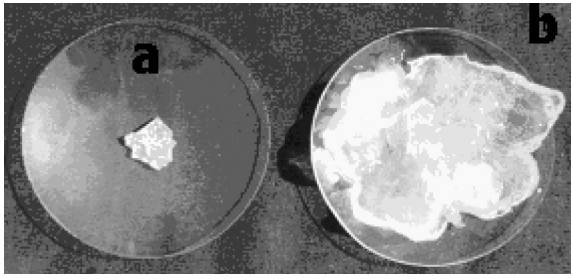


SCHEME 1 Formation and structure of (PVA-co-PAA)/NaCl IPN hydrogel.

is explained from the IR spectra, based on the identification of functional groups such as −OH, −COOH and ester groups in the IPN polymer. Addition of NaCl to the hydrogel increases the swelling and water absorption. Although the mechanism is not yet clear, most probably it is thought to be due to less crosslinking in presence of NaCl. The swelling of the hydrogel with NaCl is shown in Scheme 2.

Ionic Conductivity and Determination of Activation Energy for the Hydrogel

The plots of ionic conductances versus reciprocal temperatures for IPN hydrogels with and without NaCl were compared in Figure 1. The conductive environment of Na^+ ions in the IPN hydrogel is changed in the studied temperature region. It is evident that with increasing



SCHEME 2 Photograph of Volume of (PVA-co-PAA)/NaCl hydrogel before (a) and after (b) swelling, [PVA] = 20% (v/v), [AA] = 80% (v/v), [BPO] = 2.5% % (w/v), [NaCl] = 1% (w/v).

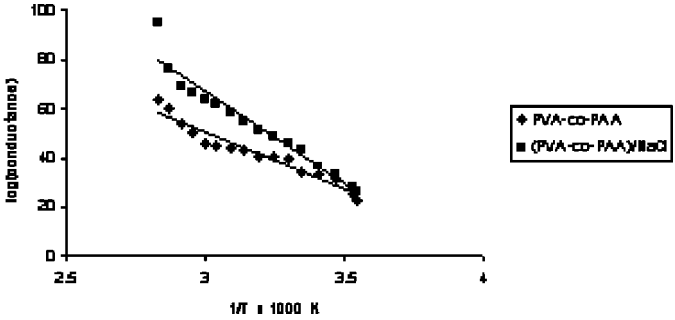


FIGURE 1 Temp. vs. conductance of PVA-co-PAA and (PVA-co-PAA)/NaCl for 2 h, [PVA] = 20% (v/v), [AA] = 80% (v/v), [BPO] = 2.5% (w/v), [NaCl] = 1% (w/v).

temperature from 281.5°K to 353°K, the ionic conductance of IPN hydrogel with NaCl increases from 26.3 μS to 94.6 μS whereas the pH value decreases from 4.05 to 2.95. But there is no significant change in the values of conductance and pH with increase in temperature of the IPN hydrogel in the absence of NaCl. The apparent activation energies for the diffusion process of water, (E_d), were determined for the IPN hydrogels by the Arrhenius equation:

$$\sigma = Ae^{-E_d/RT}$$

where σ, the ionic conductivity, R, the universal gas constant, T, the temperature in Kelvin (K) and A, a preexponential factor. The activation energy of (PVA-co-PAA)/NaCl hydrogel was found to be 29.28 J mol^{-1}K^{-1} and that for PVA-co-PAA was 35.97 J mol^{-1} K^{-1}. The σ value was higher in the presence of NaCl. It proved that water molecules diffused faster in presence of additive than in its absence. It is attributed to less crosslinking of IPN in presence of NaCl.

FTIR

Figure 2 shows comparative FTIR spectra of PVA, PAA, and (PVA-co-PAA)/NaCl. The characteristic peak of PVA is located at 3340 cm^{-1} for hydroxyl group and others are due to C−H stretching vibration. In PAA (Figure 2b), peak at 1715 cm^{-1} is due to −COOH acid group. In (PVA-co-PAA)/NaCl hydrogel (Figure 2c), in addition to the −COOH group peak at 1715 cm^{-1}, another peak at 1780 cm^{-1} appeared for ester group indicating a reaction between the −OH group of PVA with the −COOH group of PAA resulting in network formation.

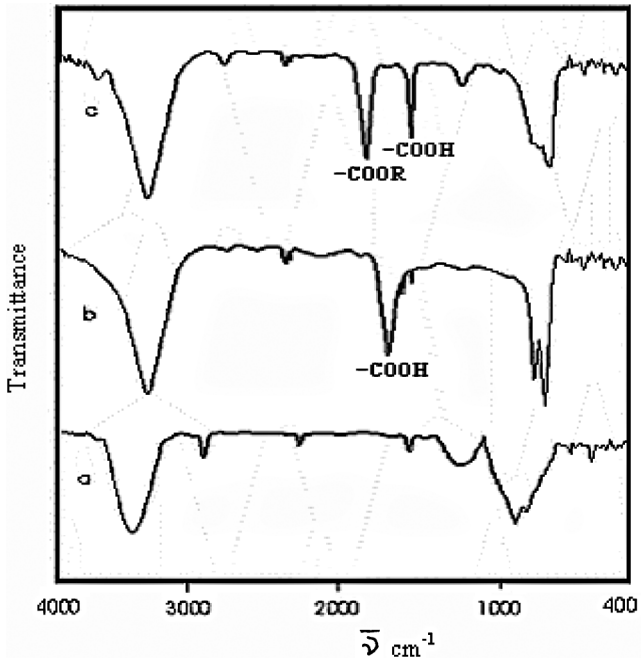


FIGURE 2 FTIR spectra of (a) PVA, (b) PAA, and (c) (PVA-co-PAA)/NaCl.

SEM

A standard method for the observation of hydrogel morphology in aqueous medium is the scanning electron microscopy (SEM). Samples of the hydrogels with 10% (w/v) of PVA, 20% (v/v) of AA and the NaCl fraction 1% (w/v) were taken for SEM study. From Figure 3 it is clear that the pores were mostly interconnected with large amount of NaCl in the mixture, making the hydrogel more porous. Further, the SEM of the hydrogel before and after biodegradation clearly confirmed the extent of biodegradability, which is described later on.

Thermal Stability

The thermal behavior of PVA, PAA, and (PVA-co-PAA)/NaCl was examined by comparing their thermogram curves as shown in Figure 4. From the curves the temperatures of decomposition (T_D) were found to be 230°C for PVA, 170°C for PAA and 190°C for (PVA-co-PAA)/NaCl. The results obtained from the TGA graph indicated a decrease of

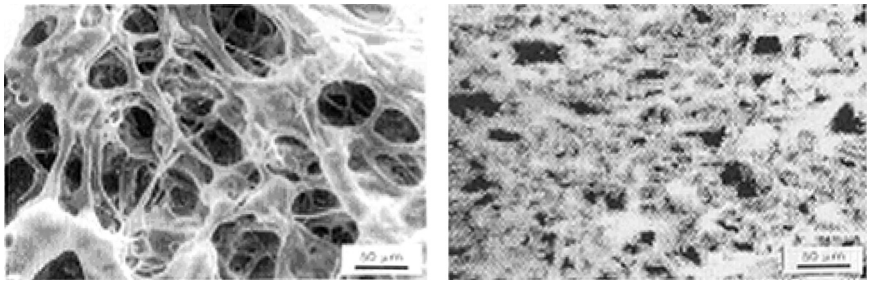


FIGURE 3 SEM of (PVA-co-PAA)/NaCl before (a) and after (b) biodegradation, [PVA] = 20% (v/v), [AA] = 80% (v/v), [BPO] = 2.5% (w/v), [NaCl] = 1% % (w/v).

thermal stability by copolymerization and crosslinking. This might be due to the increasing porosity of the hydrogel as evident from SEM.

Swelling Kinetics

Swelling kinetics of (PVA-co-PAA)/NaCl IPN hydrogels were compared with variation of different reaction parameters such as time, temperature, concentrations of NaCl, and monomer as shown in Figures 5–8 respectively.

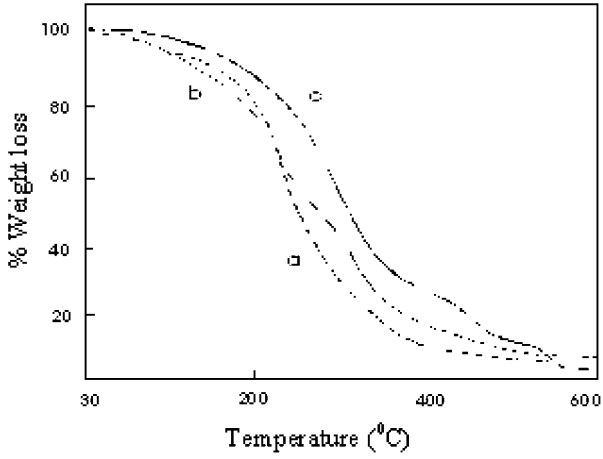


FIGURE 4 TGA thermograms of (a) PVA, (b) PAA, and (c) (PVA-co-PAA)/NaCl.

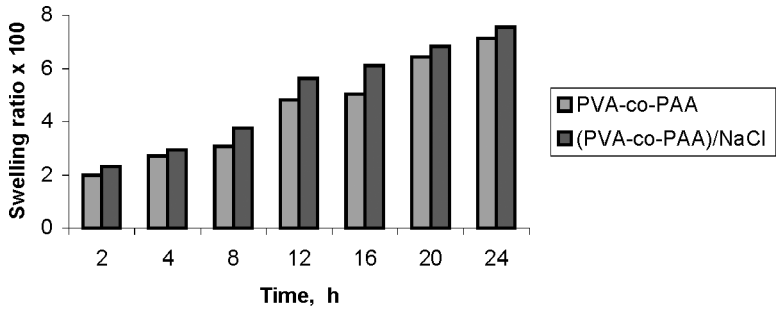


FIGURE 5 Effect of time on swelling ratio of PVA-co-PAA and (PVA-co-PAA)/NaCl at room temperature.

From the comparison plots, it was found that the swelling ratio increased with time (Figure 5) and with temperature (Figure 6) and it also explained the significant effect of the additive, NaCl, on the greater swelling ratio.

Effect of swelling ratio with different percentage of NaCl (1 to 5 wt%) was studied in Figure 7. It was found that the swelling ratio increased and attained maximum at 1% [NaCl] and then decreased, thereby decreasing the hydrophilicity of the hydrogel [30]. According to Figure 7, at 1% [NaCl] in the reaction mixture, the density of pores was shown by the swelling volume of the hydrogel, that is, by the degree of its swelling (Scheme 2). Thus the hydrogel became macroporous, as evident from SEM about the open nature of pores.

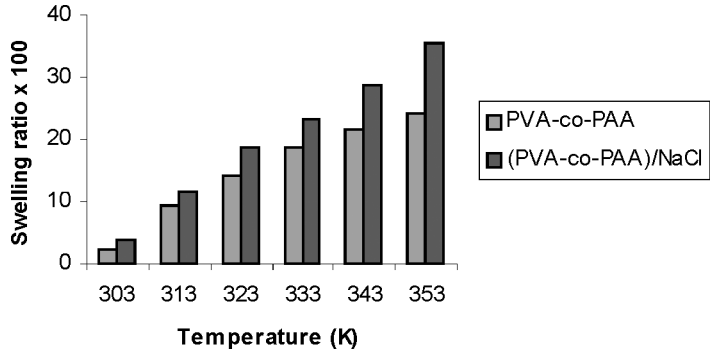


FIGURE 6 Effect of temperature (°K) on swelling ratio of both PVA-co-PAA and (PVA-co-PAA)/NaCl for 2 h.

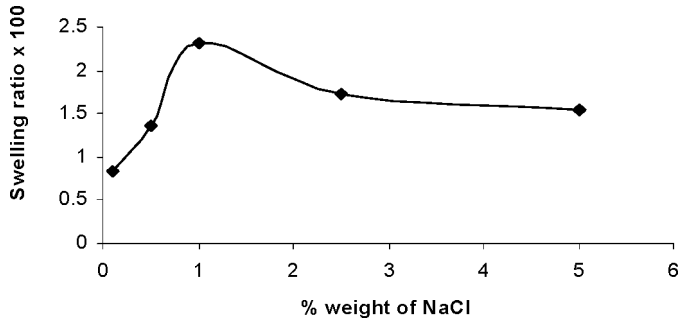


FIGURE 7 Effect of [NaCl] on swelling ratio of (PVA-co-PAA)/NaCl at room temperature for 2 h, [PVA] = 20% (v/v), [AA] = 80% (v/v), [BPO] = 2.5% (w/v).

The swelling ratio was found to increase with increased monomer concentration up to a maximum at 20% [AA], and then decreased as shown in Figure 8. This swelling variation was caused by the difference in both pore sizes and water absorbencies of component polymers.

Because water acted as a plasticizer, its molecules remained entrapped and strongly bonded to the polymer crosslinked structure [29] in the IPN hydrogels. Hence the samples exhibited some sponge-like characteristics by absorption of water. This new characteristic of the hydrogel was observed till 1% concentration of NaCl. On further increasing the concentration of NaCl, there was a decrease in swelling ratio, which might be ascribed to a more compact structure, thereby decreasing the swellability of the hydrogel [16].

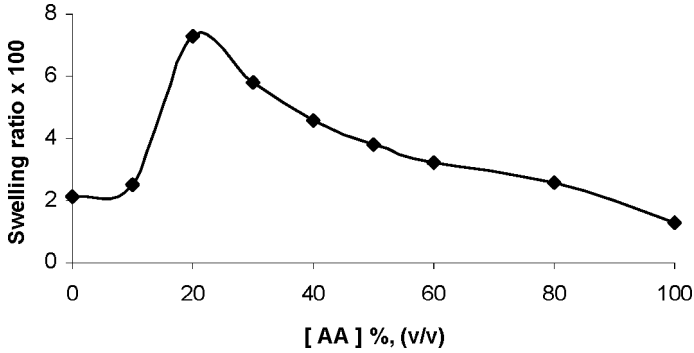


FIGURE 8 Effect of [AA] on swelling ratio of (PVA-co-PAA)/NaCl for 2 h, [PVA] = 20% (v/v), [BPO] = 2.5% (w/v), [NaCl] = 1% (w/v).

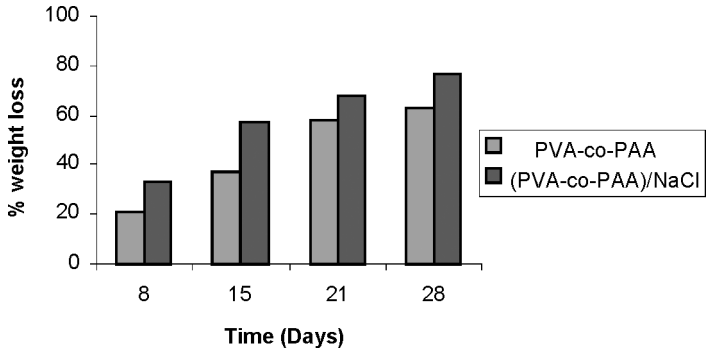


FIGURE 9 Biodegradation of PVA-co-PAA and (PVA-co-PAA)/NaCl by *E. coli* measured by weight loss, [PVA] = 20% (v/v), [AA] = 80% (v/v), [BPO] = 2.5% (w/v), [NaCl] = 1% (w/v).

Biodegradation

Biodegradation through *E. coli* was studied for PVA-co-PAA and (PVA-co-PAA)/NaCl hydrogels. At first, the degradation was calculated from the amount of weight loss after different periods of incubation, that is, 8, 15, 21, and 28 days. From Figure 9, it is clearly visible that (PVA-co-AA)/NaCl is more degradable than PVA-co-PAA, because the former hydrogel absorbs more water in its network and facilitated rapid bacterial growth, rapidly enhancing the biodegradation.

Furthermore, from Figure 10 it is confirmed that (PVA-co-PAA)/NaCl shows the highest rate of biodegradation, measured by calculating

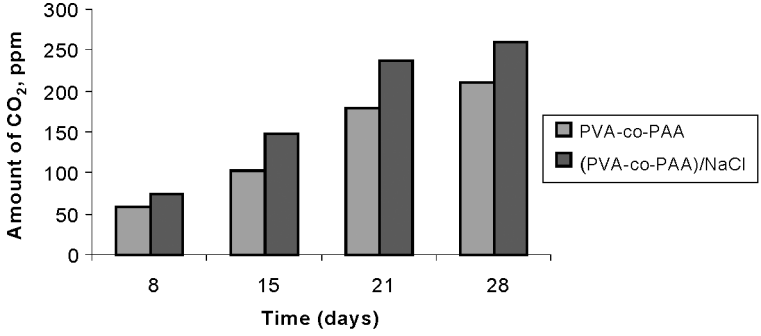


FIGURE 10 Biodegradation of PVA-co-PAA and (PVA-co-PAA)/NaCl by *E. coli* measured by evolved CO_2, [PVA] = 20% (v/v), [AA] = 80% (v/v), [BPO] = 2.5% (w/v), [NaCl] = 1% (w/v).

the amount of CO_2 evolved from the cultured medium at interval periods of time. Thus, the increased biodegradability of these nontoxic, hydrophilic IPN hydrogels reveals their potential application in the biomedical field.

CONCLUSIONS

The most significant result of the article is the development of a novel mechanistic path of preparing a new IPN macroporous hydrogel in a nonconventional way, in the absence of any added crosslinker. Swelling and biodegradation studies were investigated for PVA-co-PAA and (PVA-co-PAA)/NaCl IPN hydrogels prepared by emulsion copolymerization method using benzoyl peroxide as initiator and NaCl as additive. The swelling kinetics were significantly affected by variation of reaction parameters such as time, temperature, and monomer and additive concentrations. The swelling ratios were observed to be maximum at 1% w/v NaCl and 20% v/v monomer concentrations. The ionic conductivity was measured and the activation energy for diffusion of water was determined to be $29.28\,J\,mol^{-1}\,K^{-1}$, in the presence of NaCl. The IPN hydrogels showed moderate thermal stability and the surface morphology study by SEM revealed that the pores were mostly open in presence of NaCl, thus making the hydrogels macroporous. The nontoxic and highly hydrophilic nature of these IPNs made the authors study their biodegradability. A biodegradation study by *E. coli* showed that (PVA-co-PAA)/NaCl was more degradable than that without NaCl. Thus, the macroporous hydrogels may find some have potential use in biomedical applications.

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