Synthesis and Swelling Characterization of Cross-linked PVP/PVA Hydrogels

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A B S T R A C T

Cross-linked poly(vinyl alcohol)/poly(vinyl pyrrolidone) (PVP/PVA) hydrogels were prepared in aqueous media using $K_2S_2O_8$. The gel fraction, degree of swelling in water, and mechanical properties, such as TGA, DSC, and tensile strength were measured. It was found that the gel fraction increases with increasing potassium peroxodisulphate concentration but never reach to 100%. The swelling behaviour of the gels were specified by a relatively fast rate of swelling at the beginning of the process and measured as gram of water per minute. The amount of absorbed water as immersion water uptake of greater than 1400% is obtained. Because of the neutrality of the hydrogels, the maximum of swelling was achieved at pH=7. Maximum extents of swelling were achieved at 25°C and the swelling of hydrogels was found to decrease at higher temperatures. The hydrogel could be considered as a good barrier against common microbes including *Sarcina lutea, Escherichia Coli,* and *Pesudomonase aeruginosa*. The thermal analysis shows that the gels are stable up to 350°C. According to the DMTA thermogram, the glass temperature of 44.8°C is observed for 50 % w/w of hydrogel sample. Tensile strength as high as 90.8-10.0 Kg/cm^2 and elongation-at-break about 60% were achieved using 1.1×10^{-5} M concentration of KPS.

Key Words:
hydrogels;
poly(vinyl alcohol);
poly(vinyl pyrrolidone);
gel fraction;
degree of swelling.

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INTRODUCTION

Development of hydrogels for temporary skin covers or as wound dressing is becoming a subject of great commercial interest. The first hydrogel dressing which was not far from ideal standard of wound dressing was produced by chemical polymerization and cross-linking of acrylamide and methylene bis-acrylamide in aqueous solution containing some additives [1]. The use of PVA based hydrogels as biomaterials has recently gained great importance in view of the low toxicity, non-car-

cinogenic, and high biocompatibility [2,3]. The main areas of hydrogels application include: topical applications as wound dressing; drug-delivery systems; transdermal systems; dental applications; injectable polymers; implants; soft contact lenses; superabsorbents; and stimuli-responsive systems [4]. Therefore, a number of methods have been reported for preparation of PVA hydrogels, including chemical methods using a covalent cross-linking agent, [5-12] physical methods using complexing agent, [13] and radiation methods using γ-radiation, [14-19] electron beams, or ultraviolet light [20]. One of the useful ways to make PVA hydrogels is low temperature gelation of PVA in aqueous solutions [21]. In spite of all these methods, the main disadvantage of PVP hydrogel is its weak mechanical strength. Recently, some effective routes have been reported to bring about the desired modification in sorption and mechanical properties of PVP hydrogels [7]. In this study cross-linked PVP/PVA hydrogels (Scheme I) is prepared in aqueous solution at 80°C in the absence of additives or cross-linker. In this work the water absorptivity and physical properties such as gel fraction and tensile strength using different ratio of PVA to PVP are investigated to evaluate the usefulness of hydrogels for wound dressing. The PVP/PVA hydrogels have good water absorptivity. Also, it is found that the PVP/PVA hydrogels prepared in this manner are good barriers to the penetration of microbes.

EXPERIMENTAL

Materials

Poly(vinyl alcohol) (PVA) with degree of polymerization 300, 1600, 2000 and molecular weight of 15000, 72000, 100000, and 49000, respectively, and degree of hydroxylation of 86-89 mol % were purchased from Fluka, Germany. Poly(vinyl pyrrolidone) (PVP) with

average molecular weight of 25000 was purchased from Merck. Both polymers were used without further purification. Buffers; pH = 2 (Citric acid/hydrochloric acid/sodium chloride), pH = 4 (citric acid/ sodium hydroxide solution/sodium chloride), pH = 6 (citric acid/ sodium hydroxide solution), pH = 7 (potassium dihydrogen phosphate/disodiuom hydrogen phosphate), pH = 8 (sodium tetraborate/hydrochloric acid), pH = 10 (sodium tetraborate/sodm hydroxide solution) and pH = 13 (glycine/sodium hydroxide/sodium chloride) were purchased from Fluka, redistilled water was used as a solvent. Potassium peroxodisulphate (KPS) extra pure was purchased from Merck.

Preparation of PVP/PVA Cross-linked Hydrogels

In a three-necked round bottom flask equipped with a condenser and nitrogen gas inlet, a solution of PVA (6g) and PVP(6g) was prepared by using redistilled water (100 mL). The solution was kept under nitrogen atmosphere at room temperature for 1 h to remove air. Then potassium peroxodisulphate was added carefully and cross-linking reaction carried out at 80°C under vigorously mechanical stirring. The same procedure was preformed for different ratios of PVA to PVP. Nitrogen atmosphere was maintained during the reaction period. After 5 h the reaction mixture was poured in to a plastic mould and dried overnight at 50°C in vacuum oven.

Determination of Gel Fraction

The samples were extracted by water in a soxhlet apparatus for 24 h to remove sol content and then dried to a constant weight at 50°C in vacuum oven. The gel fraction was calculated gravimetrically by using the following formula:

$$G = W_g/W_0 \times 100 \tag{1}$$
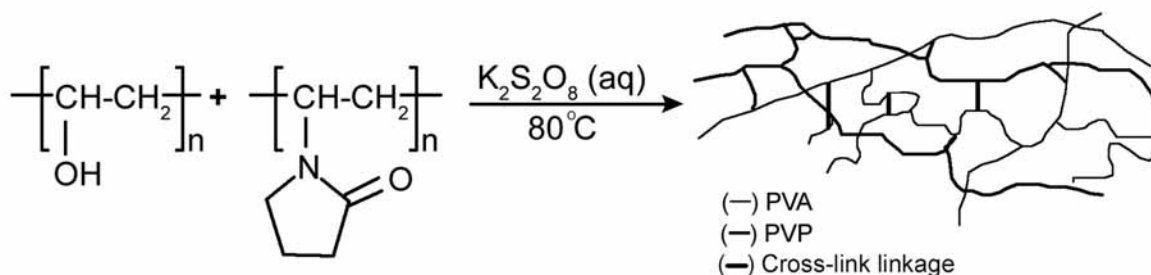
Scheme I. A simplified model of the structure of the synthesized cross-linked PVP/PVA hydrogels.

Where G, W_g, and W_0 are the gel fraction (%) and, the weights of sample after and before extractions, respectively.

Degree of Swelling

Degree of swelling could be described as water absorptivity (eqn 2) of the hydrogels. The preweighted samples were immersed in redistilled water for 24 h at room temperature until the gel reached the equilibrium state of swelling. Then, the water on the surface of the swollen gel was removed with tissue paper, and immediately weighted. The degree of swelling was defined as follows:

$$\text{Degree of swelling (\%)} = (W_s - W_d)/W_d \times 100 \qquad (2)$$

where W_s and W_d are the weight of the swollen gel and the weight of dried gel, respectively.

Swelling Rate Measurements

The capacity of equilibrium swelling was measured in distilled water and swelling rate (SR, g/g.min) defined as follows:

$$SR = S_t / t_{mr} \qquad (3)$$

In which S_t stands for swelling at the time related to minimum rate parameter, t_{mr}(min), obtained for the hydrogels from a set of similar experiments [22].

## Determination of Glass Transition Temperature (T_g)

A reasonable weight of samples was pressed in the sample cup for differential scanning calorimeter (DSC) measurement. The instrument was calibrated by using indium prior to the experiment. The glass transition temperature (T_g) was measured by using model (PL) and DMTA (PL-DMTAMIKII) at a heating rate of 10°C/min and the temperature range of 30-350°C and -150 to 150°C in nitrogen atmosphere, respectively.

Determination of Mechanical Properties

Tensile strength and elongation-at-break values were determined by using the dried hydrogels, specimens which were cut in to dumbbell shape according to ASTM D412, with a FRO30TH.A1K.001 (Zwick/Roell) and constant heating rate of 5mm/min at room temperature (25°C).

Microbe Penetration Test

The hydrogel films with a thickness of 1-2 mm was
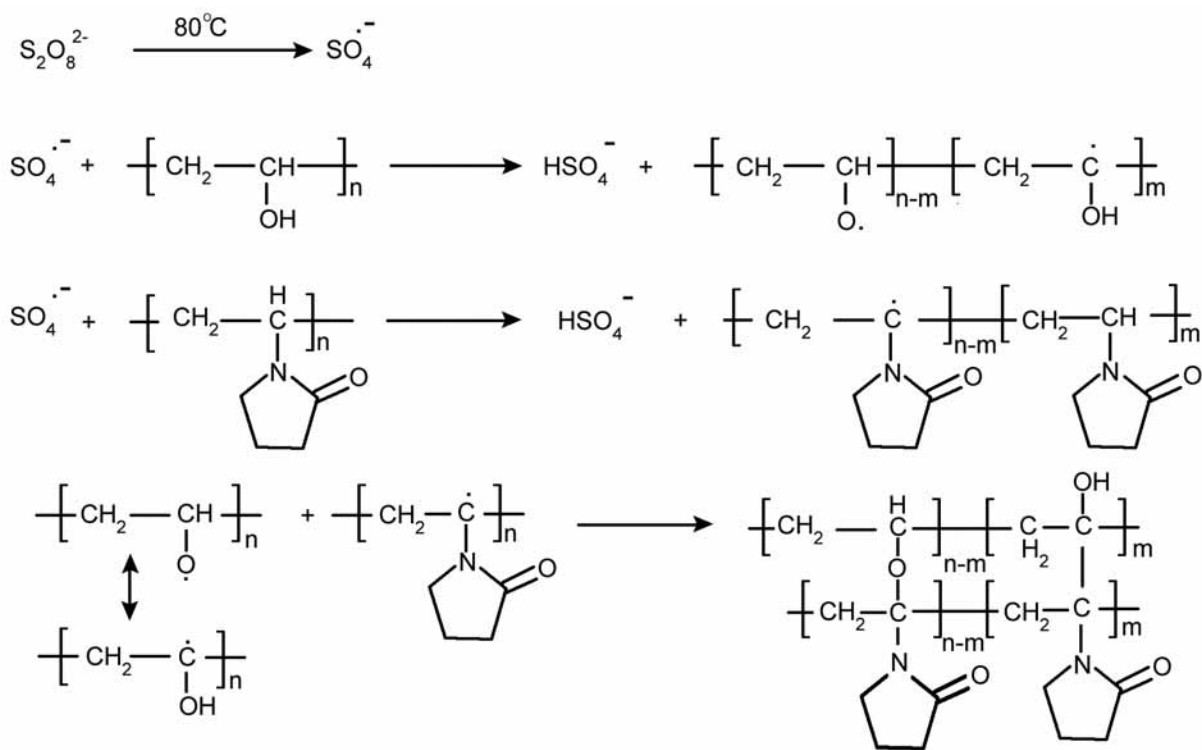
Scheme II.

sterilized by heating at 100ºC for 1 h and cut to the size of 2×2 cm and put on the Tryptose Soy Agar which had been incubated previously for 24 h at 30ºC. A suspension of bacteria (*Sarcina lutea, Escherichia coli, and Pesudomonase aeruginosa*) with concentration of 10^9/mL was sprayed on the films. Then the samples were incubated at 30ºC. The bacteria's penetration through the film was monitored after two weeks.

RESULTS AND DISCUSSION

On the basis of this observation, the mechanism of network formation may be proposed as shown in Scheme II. At first, radical formation by thermal cleavage of peroxydisufate generates some radical site on the hydroxyl group of PVA and/or in the backbone of the polymer chains. Finally, the full interpenetrating network (IPN) formation can be preformed upon recombination and coupling of these radicals.

Characterization of Cross-linked PVP/PVA Hydrogels

The FTIR (Bruker IFS 48) spectra of PVA, PVP, and PVP/PVA cross-linked hydrogels were assigned. The IR spectra of the end-hydrogels clearly mark the presence of hydroxyl group of PVA at 3442 cm^{-1} (O-H stretching) and vibrations of methylene at 1464, 1392, 1377, and 1292 cm^{-1}. The absorption pattern of cross-linked PVP/PVA hydrogels showed week absorption in 1725 cm^{-1} correspond to partial hydrolyzed acetate-C=O group which is changed to a sharp peak at 1651 cm^{-1} due to carbonyl stretching of amide linkage. The spectra also contain characteristic bands of C-O-C and stretching vibrations due to cross-linking of the chains. This suggests that a polymer comprising two or more networks which at least partially interlaced and can not be separated unless chemical bonds are broken.

Gel Fraction

Reaction of PVA and PVP with $K_2S_2O_8$ in aqueous solution leads to the formation of insoluble polymer network (gel). A typical dependence of gel fraction on the concentration of potassium peroxodisulphate is given in Figure 1. It can be seen that the gel fraction increases with increasing concentration of potassium peroxodisulphate and it seems never to reach 100 %. The reason for the observe increase in gel fraction is
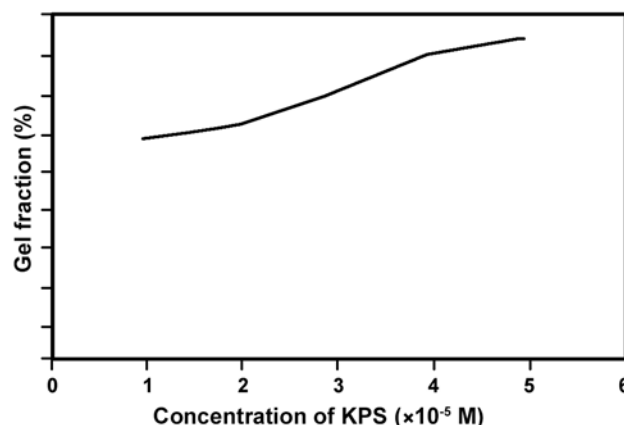

Figure 1. Gel fraction vs. concentration of $K_2S_2O_8$ (×10⁻⁵M) for PVP/PVA (50 w/w%) hydrogels.

quit expected as increasing KPS makes the IPN more and more interconnected, as a consequence the water permeation becomes increasingly difficult.

Degree of Swelling

As shown in Figure 2 and 3 it observed that water absorption of cross-linked PVP/PVA hydrogels tend to increase with increasing PVP ratio in copolymer, but decrease with increasing of potassium peroxodisulphate concentration. In fact, hydrogen bonding of PVA hydroxyl groups tends to crystallize the PVA chains through physical cross-linking. In the other hand, the
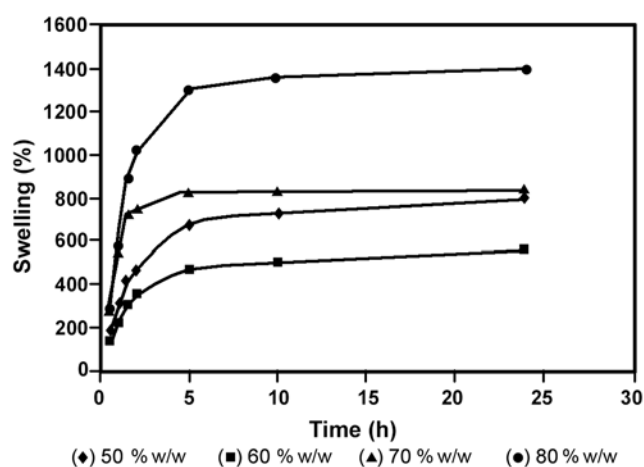

Figure 2. Degree of swelling vs. immersion time (h) for different composition of PVP/PVA hydrogels at 25ºC in $K_2S_2O_8$ 1.1×10⁻⁵ M.
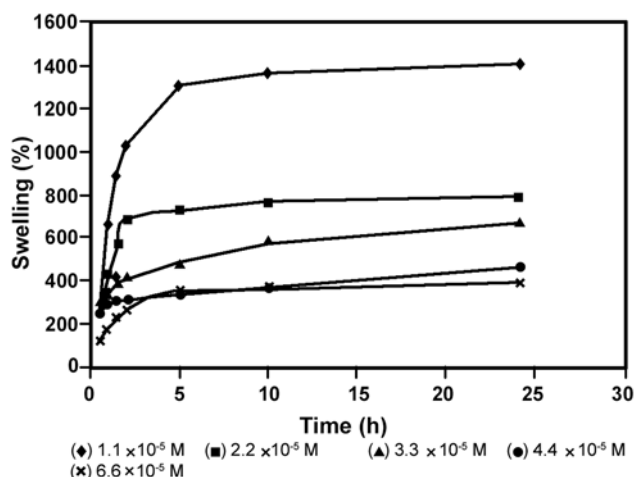
Figure 3. Degree of swelling vs. immersion time (h) for different concentration of $K_2S_2O_8$.

steric hindrance of the bulky pyrrolidon groups restricts the chains and decreases the crystallinity of PVA segments. Also, PVP is more hydrophilic than PVA, as it was observed when dissolving the polymer. The amorphous nature of PVP and its higher affinity for water makes network rich in PVP swell to a greater extent.

However, in the ratios lower than 28 molar percent of PVP, the water absorption increases smoothly due to local concentration increment of hydroxyl groups. However, the swelling character of this hydrogel did not differ significantly from the PVA rich hydrogel.

It can be seen in Figure 3,that the water absorption of the gel gradually diminished at higher potassium peroxodisulphate concentration. It is due to the cross-linking and gel fraction increases using higher amount of potassium peroxodisulphate in gelation process. The rate of water absorption will be significantly higher at the immersion times less than 5 h, whereas after it, the rate of absorption only slightly increases.

Swelling Rate Measurements

The degree of swelling was measured at different times for a set of experimental conditions. The results of the process and swelling rate measurements are summarized in Table 1. The swelling behaviour of the gels were specified by a relatively fast rate of swelling at the beginning of the process and measured as gram of water uptake per minute. The degree of swelling at equilibrium state is also determined as water uptake

Table 1. Swelling rate (g/g.min) of the synthesized cross-linked PVP/PVA hydrogels .

Gel No.	PVP/PVA ratio (% w/w)	$K_2S_2O_8$ concentration ($\times10^{-5}$ M)	PVA (M_w)	Temperature (°C)	Steady state swelling (% g/g)	p	r	SR (g/g.min)
G 1.1	50	1.1	15000	25	800	760.93	121.79	8.01
G 1.2	60	"	"	"	560	524.16	111.39	5.52
G 1.3	70	"	"	"	840	840	352.5	8.85
G 1.4	80	"	"	"	1400	1380.43	94.88	14.54
G 2.1	50	2.2	"	"	730	682.74	146.06	7.19
G 2.2	"	3.3	"	"	668	613.17	191.8	6.46
G 2.3	"	4.4	"	"	460	401.63	140.84	4.23
G 2.4	"	6.6	"	"	392	356.61	135.22	3.75
G 3.1	80	1.1	'	40	1140	1039.68	96.65	10.95
G 3.2	"	"	"	50	1100	1017.67	103.81	10.72
G 3.3	"	"	"	60	1030	960.37	110.9	10.12
G 4.1	"	"	49000	25	760	730.57	248.62	7.69
G 4.2	"	"	72000	"	730	706.96	229.58	7.45
G 4.3	"	"	100000	"	600	569.72	218.54	6.00

during the time to reach steady state. It is evident from Table 1, that the degree of swelling changes from 392 to 1400 % and the required time for equilibrium ranges from about 5 to 24 h.

In the first two sets of gelation process, G1 and G2 are different only in the extent of PVP segment and the concentration of KPS. Comparing entries G1.1 to G2.4 shows that increasing the concentration of KPS by factor of 6 decreased the steady state swelling to 40 %. The highest degree of swelling was obtained for PVP-rich hydrogel G1.4 using 1.1×10^{-5} mole of KPS at 25-40ºC.

The experimental swelling data follows Voigt model [23];

$$S_t = p \, (1 - e^{-t/r})$$

In which S_t, p, and r are the swelling at time t, equilibrium swelling (g/g), and the rate parameter of the hydrogels , respectively. The quantitative value of p can be estimated from the steady state value of each individual sample. The experimental data satisfactorily fitted for the entire cross-linked hydrogels base on this exponential expression.

pH - Responsive Swelling Studies

The role of pH on the extent of water sorption of polymeric gels is of great importance Since a change in pH of swelling media often causes a fluctuation i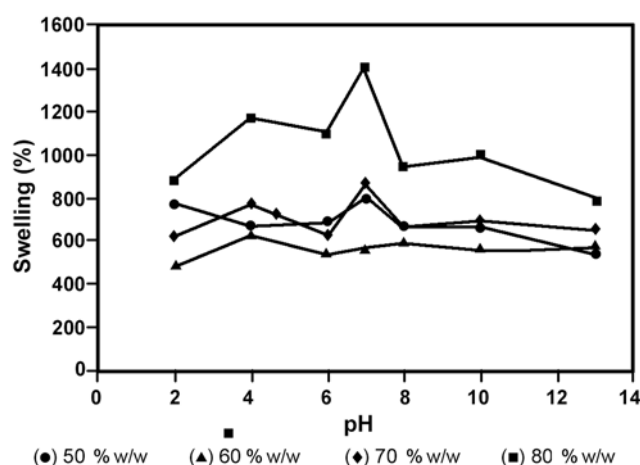n free volumes accessible to penetrating water molecules, it affects swelling properties of interpenetrating polymer. In the present work, equilibrium swelling behaviours of PVP/PVA cross-linked hydrogels were investigated as a function of pH in the range of 2.0-13 at 25ºC. Figure 4, illustrates swelling behaviour of different composition of PVP/PVA hydrogels at various pH. Swelling of hydrogels was found to increase with pH for all compositions of PVP/PVA hydrogels, and the maximum amount of it was at pH=7. It slowly decreases at pH grater than 7. Because of neutrality of hydrogel network the maximum of swelling will be obtained at pH=7.

Effect of Temperature on the Equilibrium Degree of Swelling

Figure 5 shows swelling behaviour of cross-linked PVP/PVA which was measured in redistiled water upon the various heating temperature. Swelling of hydrogels was found to decrease with increases in temperature, and maximum extents of swelling were achieved at 25ºC. In fact, the diffusion of water molecules in the copolymer network tend to increases as the heating temperature increased due to better swelling of copolymer molecules. But the absorbed water molecules as well, tends to migrate to solution to reach equilibrium. It was observed that 24 h elapse of time is enough to reach the equilibrium swelling. These results can be interpreted based on shrinkage of the polymer chains in terms of experimental temperature and extent of hydrogen bonding by hydroxyl group in PVA and amid group in PVP within the IPNs. At lower temperature, hydro-
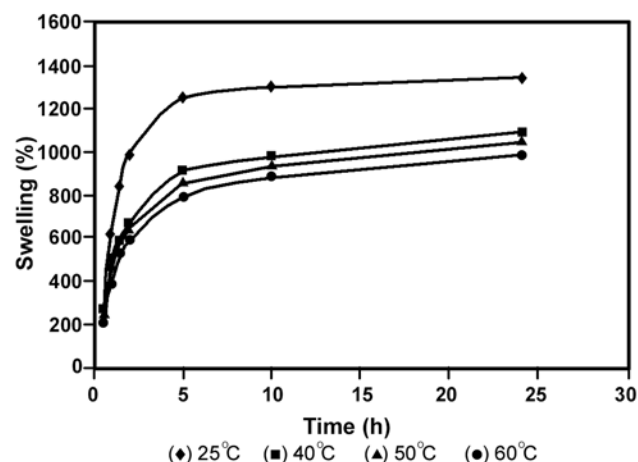

Figure 4. Effect of pH on the equilibrium degree of swelling values in different composition of PVP/PVA cross-linked hydrogels at 25ºC with immersion time of 24 h in $K_2S_2O_8$ 1.11×10^{-5} M.

Figure 5. Effect of temperature on the equilibrium degree of swelling of cross-linked PVP/PVA hydrogel 80 % w/w in $K_2S_2O_8$ 1.1×10^{-5} M:

gen bonding between hydrophilic groups of the cross-linked polymer chain and surrounding water molecule lead to the enhanced dissolution in water. The water molecules are in bound state at low temperature in the IPN hyrogels. However, hydrophobic interaction among hydrophobic groups become strengthened as the temperature increases because a water molecule will gain an enthalpy during the increase of temperature and the hydrophilic groups will be turned in to a intramolecular hydrogen bound [24]. Therefore, hydrogen bounding becomes weaker as temperature increases. These results may induce shrinking of the hyrogels due to interpolymer chain association through the hydrophobic interactions. All PVA/PVP hydrogels showed temperature responsive swelling behaviour base on the association/dissociation of hydrogen bonding.

Effect of Molecular Weight of PVA on the Equilibrium Degree of Swelling

Figure 6 shows swelling behaviour of cross-linked PVP/PVA 50 % w/w in terms of different molecular weight of PVA. Swelling of hydrogels was found to decrease with increasing of molecular weight of PVA in redistilled water at room temperature. In fact, interchain hydrogen bonding between hydroxyl groups on the long PVA chains and the carbonyl groups of the PVP can serve as a physical cross-linking which can limit the water absorption. Therefore, the gel fraction in the copolymer network tends to increase with increase
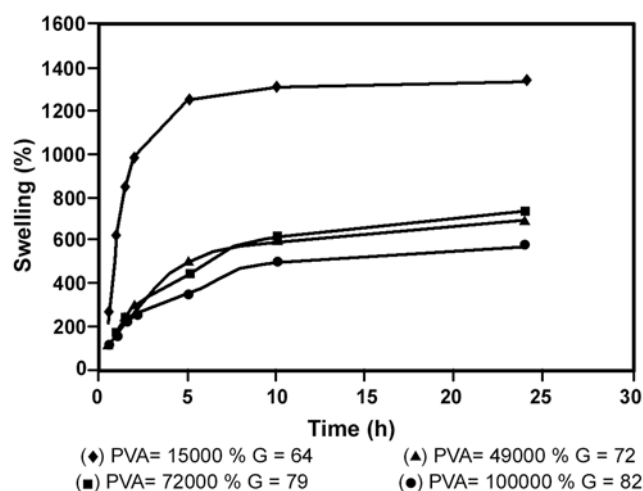

Figure 7. DSC thermogram of PVP/PVA cross-linked hydrogel 50 % w/w.

of molecular weight of PVA. It was observed that gel fraction of PVA with molecular weight of 15000-100000, changed between ranges of 64-82 %.

TGA, DSC, and DMTA Analysis

It is evident in Figure 7 that it is difficult to determine the accurate value of glass transition temperature (T_g), because the thermogram of DSC shows a broad and week peak with uncertainty about the proper base line. Roughly, the T_m about 220°C is estimated based on this thermogram which is related to the PVA chain. According to the DMTA thermogram in Figure 8, the glass temperature of 44.8°C is observed for 50 % w/w of hydrogel sample. The thermal stability of hydrogels is measured by TGA model of Perkin Elmer (Pyris 1) and thermograms are presented in Figure 9. It is shown that

Figure6. Effect of molecular weight of PVA on the equilibrium degree of swelling of cross-linked PVP/PVA hydrogels 80 % w/w in $K_2S_2O_8$ 1.1×10^{-5}M.
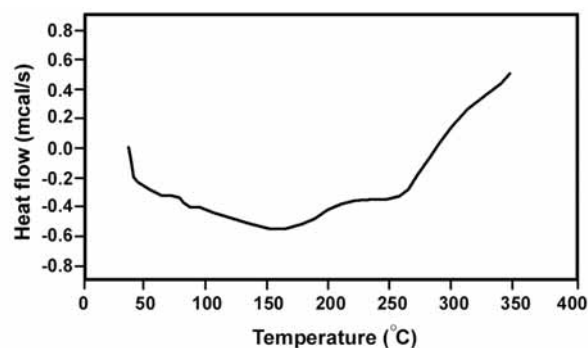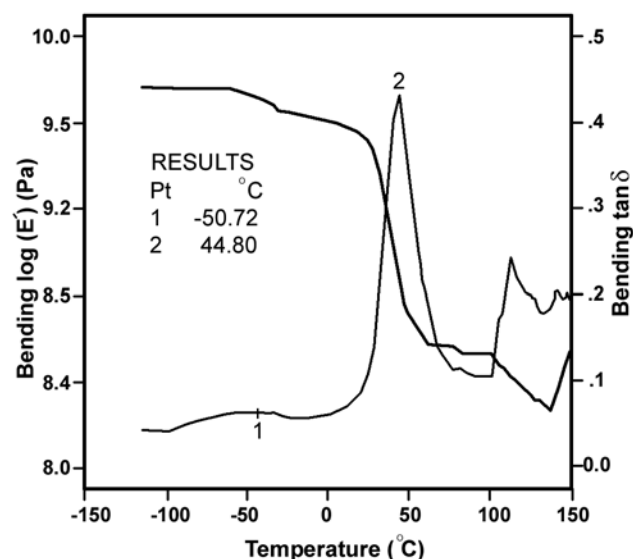

Figure 8. DMTA thermogram of cross-linked PVP/PVA hydrogel 50 % w/w.
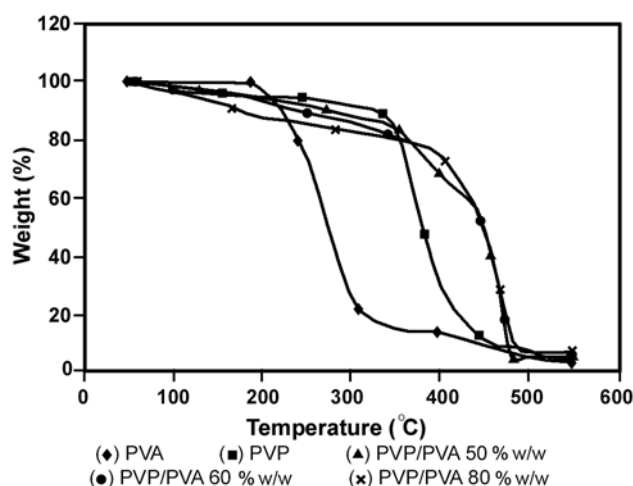
Figure 9. TGA thermogram of different composition of cross-linked PVP/ PVA hydrogels.

Figure 10. Stress vs. strain for cross-linked PVA/PVP hydrogel 50 % w/w in $K_2S_2O_8$ 1.1×10^{-5} M.

the decomposition temperature (T_d) of hydrogels is about 450ºC. The copolymer in which the ratio of PVP is higher than (80 %) decomposes slowly relative to PVA rich copolymer. In fact the PVA segment in the hydrogels easily undergoes dehydration followed by chain scission during the heat treatment.

Microbe Penetration Test

In this work some common bacteria such as *Escherichia coli, Pseudomonas aeruginosa,* and *Sarcina lutea,* were studied and practically no bacteria was found on the Agar media. So, the cross-linked PVP/PVA hydrogel prepared in this manner could be considered as a good barrier against these microbes. This property is very important for hydrogel dressing to protect wound from further infection.

Mechanical Properties

The tensile strength of cross-linked PVP/PVA hydrogels were measured. The results are summarized in Table 2. This shows an enhancement in strength of

Table 2. Tensile strength of PVP/PVA 50 % w/w dried hydrogels at different concentration of potassium peroxodisulphate.

Concentration of $K_2S_2O_8$ ($\times10^{-5}$ M)	1.1	2.2	3.3	4.44	6.66
Result (Kg/cm^2)	90.8	76.6	47.0	10.4	10.0

hydrogel films as the amount of potassium peroxodisulphate decreases in gelation process. As expected, the extra cross-linking took place by using higher concentration of potassium peroxodisulphate, and therefore copolymer became more brittle and showed low tensile strength. The molecular orientation of polymer chain is reflected in the observed changes of shape of the specimen (Figure 10) up to the yield stress, specimen deformation is essentially homogeneous. This means that it occurs uniformly over the entire length of the specimen. In comparison with previously reported methods of PVA/PVP hydrogel preparation by using γ-irradiation technique [15,17], the tensile strength as high as 90.8-10.0 Kg/cm^2 and elongation-at-break value about 60 % were achieved using 1.1×10^{-5} M concentration of KPS in aqueous condition. These values are enough to establish the mechanical properties required for wound dressing and pervaporation membranes.

CONCLUSION

The cross-linked hydrogel obtained from aqueous gelation by potassium peroxydisulphate in the absence of any cross-linker shows good thermal stability and mechanical strength together with relatively high water absorptivity at pH near 7. These hydrogels seem to improve mechanical strength with respect to the principle gels and even the γ-radiation induced gels. Gel strength for different PVP/PVA hydrogels before and after swelling exhibited significant differences due to the significant water absorptivity of hydrogel after swelling. The strength of nonswellen hydrogel is tend-

ed to increase with content of gel fraction decreasing. Therefore, radical coupling of PVA and PVP is an easy and suitable method for formation of cross-linked PVP/PVA hydrogels. This method showed advantages such as convenient preparation, possibility of hydrogel formation with a variety of linear hydrophilic polymers, and no necessity to add any cross-linkers which often are harmful and difficult to separate.

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