

MISCIBILITY, THERMAL STABILITY AND RETENTION OF PVP FOR CROSSLINKED PVA/PVP BLENDS

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ABSTRACT

The thermal behavior, miscibility, crystallite conformation and thermal stability of crosslinked(CL-) PVA/PVP blends were studied by DSC and TG methods, respectively. DSC results showed that in the blend, the crystallinity, T_m and T_c of PVA were obviously lower than those of pure PVA; the crystal growth changed from three dimensional to two dimensional and only a single T_g was detected. These facts demonstrated that this crystalline and amorphous blend have good miscibility. TG curves showed that providing the quantity of $K_2S_2O_8$ added is more than 3 wt%, in the blends PVA will form a stable CL-network, whose thermal degradation temperature was near to that of PVP. But crosslinking reaction will not take place for PVP. The processes of thermal degradation of CL-blends are based on combining both the thermal degradation of PVP and that of PVA crosslinked with corresponding quantity of $K_2S_2O_8$ CL-agent, respectively.

The UV measurements showed that 75 wt% of PVP may be remained in CL-blend hydrogels crosslinked by adding (3–5 wt%) $K_2S_2O_8$.

This is mainly due to the stable CL-network formed and the good compatibility and proper entanglement between the composites in the CL-blends.

INTRODUCTION

Crosslinked (CL-) PVA hydrogel, having high strength, elasticity, durability and high absorbability of water, can be easily obtained by several treatment methods from PVA aqueous solutions. These gels are widely used as stationary phases in exchange and affinity chromatography and as support for some substances, such as enzymes, drugs or biomedical materials. Polyvinylpyrrolidone (PVP) exhibits a complexing capacity with numerous

compounds and polymers, due to its chemical structures having hydrophobic and hydrophilic functional groups. So PVP hydrogels are useful as flocculants, protectors for colloids and absorbents for wastes in pharmaceutical/cosmetic/food industry as well as for many technical applications. Nevertheless, it is well known that to prepare CL-PVP gel is not easy, so its mentioned applications are limited^[1,2].

In this study, we prepared CL-PVA/PVP blends to combine their excellent properties and characterized the blend properties. Research results show that the CL-blends have good miscibility, thermal stability, hydrogel properties and retention capacity for PVP, so this CL-blend gel could be used as separative and absorbent material.

EXPERIMENTAL

Material and procedures

The polymers used in this study were PVA and PVP, having $\bar{M}_w$ 1.28×10^5 and 8.8×10^4 , respectively. The saponification value of PVA was higher than 98.0 mol%. They were commercial products made in Japan.

The CL-blends films were prepared by mixing PVA aqueous solutions containing 1, 2, 3, 4 and 5wt% $K_2S_2O_8$, respectively, with PVP aqueous solution. The polymer weight ratio fraction (Φ_w) was 0.5. The mixed solutions were poured into the Perspex plates and dried at 50°C for 6 hrs. to finish crosslinking reaction, then the solid films were stored in a desiccator for use.

Measurements

The thermal properties of blends and homopolymers were measured by Perkin-Elmer DSC-2C in three scannings. The crystallization kinetic data can be got by Avrami equation in the cooling scanning simultaneously.

A special measurement for miscibility of blend consisted of the following procedures: heating the sample to above T_m (about 240°C), keeping it for 3 mins and then cooling to room temperature (RT) rapidly (at an apparent rate of $-320^\circ\text{C}/\text{min}$) to eliminate the crystallization of PVA, heating the blend sample again to a certain desired temperature, which was higher than T_g and lower than T_m , allowing it to anneal at this temperature for 10 mins and cooling it to RT at a cooling rate of 2.5, 5, 10, 20, and 40°C/min, respectively. Further heating it to measure T_g transition to determine blend miscibility.

Thermogravimetric Analysis (TG) for measurements of thermostability of PVA, PVP and their CL-blends were performed in the temperature ranging from 30 to 580°C at a rate of 10°C/min by using Perkin-Elmer TG-2 thermogravimetric Analyzer in air atmosphere.

The contents of PVP retained in CL-blend hydrogels were determined by using Backman DU-8B Ultra-Violet Photometer.

RESULTS AND DISCUSSIONS

1. DSC study on miscibility of PVA/PVP blend

Thermal characteristics and phase transition temperatures were summarized in Tab. 1. This demonstrated that certain crystallinity of PVA is retained in the existence of PVP ($\Phi_w = 0.5$) at lower reduced reticulation ($K_2S_2O_8 < 3\text{wt}\%$), but at higher reticulation ($K_2S_2O_8 > 3\text{wt}\%$), the crystallization of PVA and its segment movability have been lost and it is difficult to detect the T_m and T_c in DSC curves.

Table 1 Thermal characteristics and phase transition temperature of PVA, PVP and CL-PVA/PVP-blends

Sample PVA/PVP $K_2S_2O_8$ No. (w · w ⁻¹) ^a (%) ^b			First heating		Second heating			Cooling		
			T_m /°C	ΔH_f /J · g ⁻¹	T_g /°C	ΔC_p /J (g°C) ⁻¹	T_m /°C	ΔH_f /J · g ⁻¹	T_c /°C	ΔH_f /J · g ⁻¹
1	100/0	0	223.6	63.0	77.0	0.16	217.4	56.1	183.6	-57.2
2	100/0	1	220.7	61.8	79.8	0.17	220.1	53.4	194.9	-54.4
3	100/0	3	181.9	27.3	—	—	—	—	—	—
4	50/50	0	205.8	15.1	107.0	0.35	207.6	4.4	152.2	-5.4
5	50/50	2	202.2	13.6	112.2	0.24	199.3	2.0	147.3	-3.8
6	50/50	3	196.4	8.4	138.5	0.26	—	—	—	—
7	0/100	0			166.7	0.18				
8	0/100	1			171.6	0.22				
9	0/100	5			171.7	0.23				

a) Mixture of two polymer solutions based on weight fraction of polymers

b) Based on weight of PVA

Striking effects caused by blending PVA with PVP are the depressions of T_m , T_c and crystallinity of PVA. These suggest that some kinds of interaction between the two polymers are more prominent when near the T_m

of PVA. Such analogous depression phenomena have previously been observed in several polymeric blends exhibiting good miscibility.

In Table 2, Avrami exponent (n) obtained from crystallization kinetics decreased from 3 dimensions in the pure PVA to 2 dimensions in the blends. It is considered that the decrease of n means the depression of PVA crystallization ability and regularity, which are also favorable for enhancing the miscibility of blends.

Table 2 DSC crystallization kinetics of PVA and CL-PVA/PVP blends

sample No.	PVA/PVP /w • w ⁻¹ ^{a)}	K ₂ S ₂ O ₈ /% ^{b)}	PVA crystallization kinetics				
			n	$t_{1/2}$ /sec.	$\lg Z_c^{c)}$	$\lg Z_c^{d)}$	Z_c
1	100/0	0	3.90	27.2	-5.64	-0.56	0.27
2	100/0	1	3.38	40.0	-5.79	-0.58	0.26
3	100/0	3	—	—	—	—	—
4	50/50	0	2.09	183.4	-4.84	-0.48	0.33
5	50/50	2	2.08	168.7	-4.79	-0.48	0.33
6	50/50	3	—	—	—	—	—

c) Avrami rate constant d) Z_c divided by cooling rate

The special T_g measurements of blends, showed in Table 3 and Fig. 1,

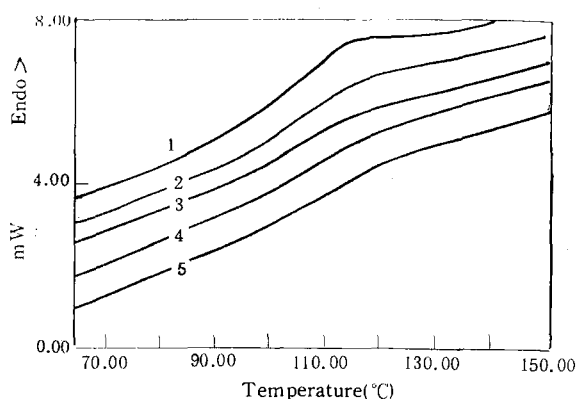


Fig. 1 Glass transition thermograms in second heating cycle for determining miscibility of PVA/PVP blend ($\Phi_w=0.5$) at different cooling thermal history
The cooling thermal history of the curves 1,2,3,4 and 5 are 2.5,5,10,20 and 40°C/min, respectively

indicate that: First, only a single T_g has been detected even at the lowest

cooling rate of $2.5^{\circ}\text{C}/\text{min}$, with which the sample was treated before T_g scanning. Second, T_g regions are almost the same whether with slower or faster cooling rate. These results demonstrate that phase separation has not occurred during the processes at different cooling rates and the blends have good miscibility. Because of a $40^{\circ}\text{C}/\text{min}$ cooling rate it should be rapid enough to prevent phase separation, whereas a slow cooling rate such as $2.5^{\circ}\text{C}/\text{min}$ would be favorable for phase separation and broadening the T_g transition regions^[3,4].

Table 3 Effect of cooling thermal history on miscibility of PVA/PVP blends ($\Phi_w=0.5$) by DSC measurements

Sample No.	$\text{K}_2\text{S}_2\text{O}_8$ /%	Cooling rate heating history ^{a)} / $^{\circ}\text{C} \cdot \text{min}^{-1}$	T_g transition at 2nd heating				
			$T_{g.b.}^{b)}$ / $^{\circ}\text{C}$	$T_{g.e.}^{b)}$ / $^{\circ}\text{C}$	$\Delta T^{c)}$ / $^{\circ}\text{C}$	T_g / $^{\circ}\text{C}$	$\Delta C_p \times 10^2$ / $\text{J}(\text{g}^{\circ}\text{C})^{-1}$
1	0	-2.5	80.0	118.5	38.5	103.7	37.9
2	0	-10	80.1	117.7	37.6	104.6	20.4
3	0	-40	83.1	120.0	36.9	107.8	16.7
4	1	-2.5	78.3	122.4	44.1	114.5	32.3
5	1	-10	80.0	123.2	43.2	111.1	33.6
6	1	-40	82.6	124.3	41.7	112.6	23.8

a) at which the sample was treated before T_g scanning

b) $T_{g.b.}, T_{g.e.}$ = beginning and end temperature of glass transition region, respectively

c) ΔT = the glass transition region

2. TG study on thermal stability of CL-blends

Results of TG, listed in Table 4, and TG curves, showed in Fig. 2 and Fig. 3, indicate that the thermal stability of PVP is higher than that of PVA and crosslinking reaction does not take place for PVP in this study. It is obvious to see whether PVP thermal degradation temperature does not improve in TG experiments or its T_g and ΔC_p value can not enhance in DSC measurements, even if the quantity of $\text{K}_2\text{S}_2\text{O}_8$ used as CL-agent amounted to 3–5 wt %.

Two district stages of thermal degradation of PVA, CL-PVA and CL-blends can be observed in the TG and DTG curves. Their degradation behavior was obviously affected by the amount of $\text{K}_2\text{S}_2\text{O}_8$ CL-agent used.

Table 4 Characteristic temperature and weight losses in the thermal degradation for PVA, CL-PVA, PVP and CL-blends

Sample No.	PVA/PVP $K_2S_2O_8$ /w • w ⁻¹ /%	First stage of degradation				Second stage of degradation				T(W =50%)	
		$T_i^{a)}$ /°C	$T_m^{a)}$ /°C	$T_f^{a)}$ /°C	$\Delta W^{b)}$ /%	T_i /°C	T_m /°C	T_f /°C	ΔW /%	/°C	
1	100/0	0	230.1	292.6	397.0	69.5	397.0	439.7	488.9	11.3	342.6
2	100/0	1	233.8	372.0	427.8	65.4	427.8	445.5	500.0	18.1	376.4
3	100/0	3	160.2	236.7	287.4	27.1	412.4	447.6	502.0	38.6	424.1
4	100/0	5	160.3	206.6	287.5	27.1	417.6	444.8	513.9	37.4	431.6
5	0/100	0	371.3	448.5	497.8	82.0					443.4
6	0/100	1	371.2	449.2	498.9	79.0					444.0
7	0/100	3	368.4	447.8	496.3	74.5					444.1
8	0/100	5	353.6	447.0	499.9	71.5					444.0
9	50/50	0	236.7	358.0	399.1	41.5	399.1	452.1	507.0	43.5	409.4
10	50/50	1	250.0	378.6	415.4	44.3	416.1	450.7	493.3	40.3	413.9
11	50/50	2	274.2	371.3	404.4	27.2	405.1	452.2	498.5	55.1	438.9
12	50/50	3	241.1	278.6	318.3	13.2	409.5	452.1	505.8	68.4	442.6
13	50/50	4	221.3	265.4	301.4	13.7	408.7	450.6	510.9	66.3	441.8
14	50/50	5	172.0	244.8	290.4	17.0	413.2	458.8	516.1	63.6	447.7

a) T_i, T_m, T_f = initial, maximum and final temperature of DTG curves, respectivelyb) $\Delta W(\%)$ = weight loss

When the quantity of $K_2S_2O_8$ was less than 2wt% (with reference to A_0 , A_1 and M_0, M_1, M_2 curves showed in Fig. 2 and Fig. 4, respectively) the degradation temperatures of PVA and PVA crosslinked by $K_2S_2O_8$ were raised in the order with the increase of the $K_2S_2O_8$ content in the first main degradation stage (where the weight losses corresponded to degradation of olefin formed by dehydration of intermacromolecules and adjacent $-CH_2-CHOH-$ groups of PVA). This is due to CL-reaction occurs accompanying these degradation processes. In the second stage, the weight losses, which corresponded to the degradation of the network recombined by the olefinic fragments, were added together with the increase of the $K_2S_2O_8$ content. But as the quantity of CL-agent was small ($K_2S_2O_8 \leq 2\text{wt}\%$), enough to form a network with low reticulation, therefore the weight losses were

comparatively low in these cases^[5,6].

When $K_2S_2O_8$ quantity was added to as much as 3 – 5wt%, with reference to A_3 , A_5 and M_3 , M_4 , M_5 showed in Fig. 2 and Fig. 4, respectively, in the first stage, the degradation temperature of crosslinking products were sequentially decreased with the increase of $K_2S_2O_8$ quantity while degradation reactions occurred as early as on the 160 – 290°C range. This is because the more $K_2S_2O_8$ was added, the more PVA chain radicals was easily introduced. In the second degradation stage the weight losses distinctly increased because much more PVA chain radicals simultaneously recombined to form a stable CL-network in the decomposing processes of the first stage, comparing with that in the case of ≤ 2 wt% of $K_2S_2O_8$.

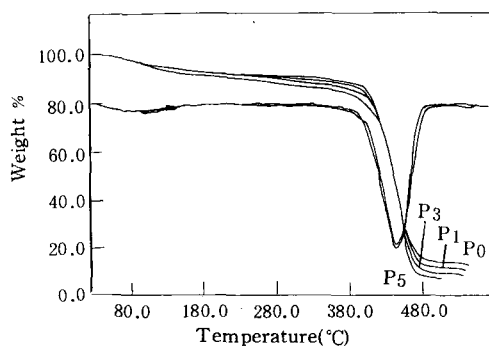


Fig. 3 TG and DTG thermograms of PVP and PVP with different content of $K_2S_2O_8$. $K_2S_2O_8$ added for PVP samples P_0 , P_1 , P_3 and P_5 are 0, 1, 3 and 5 wt%, respectively

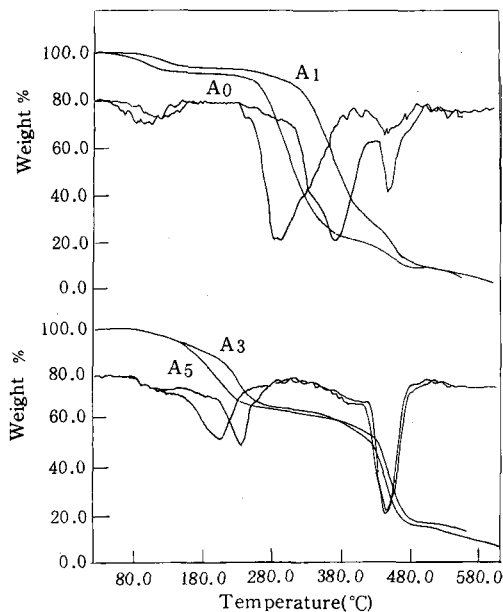


Fig. 2 Thermal gravimetry (TG) and derivative of weight loss (DTG) thermograms of PVA and CL-PVA. $K_2S_2O_8$ added for CL-PVA samples A_0 , A_1 , A_3 and A_5 are 0, 1, 3 and 5 wt%, respectively

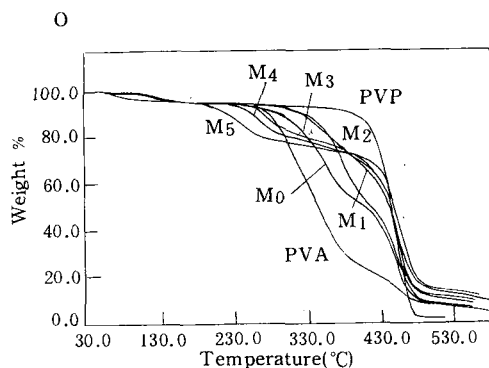


Fig. 4 TG thermograms of PVA, PVP and their CL-blends ($\Phi_w = 0.5$). $K_2S_2O_8$ added for blend and CL-blends samples M_0 , M_1 , M_2 , M_3 , M_4 and M_5 are 0, 1, 2, 3, 4 and 5 wt%, respectively

From the analyses and discussions mentioned above, it is not difficult to find out that the processes of thermal degradation of CL-blends are based on combining both the thermal degradation of PVP and that of PVA crosslinked with corresponding quantity of $K_2S_2O_8$ CL-agent, respectively.

3. Determination of PVP retention quantity in the CL-blend hydrogel by ultra-violet(UV) photometer

Full-range scanning of UV absorption spectrogram for PVP aqueous solutions demonstrated that the maximum absorption happened at 213nm wavelength while absorption intensity values were proportional with PVP concentration in the aqueous solution. Whereas there was not any absorption for PVA aqueous solution, therefore a standard work curve can be made. The remaining contents of PVP in CL-blend hydrogel network were measured by UV method for the solutions, where the CL-blend membranes were immersed and reached swollen equilibrium.

Table 5 Retention of PVP in CL-PVA/PVP ($\Phi=0.5$) hydrogel by UV method

Sample No.	$K_2S_2O_8$ /%	$T^{a)}$ / $^{\circ}C$	$t^{b)}$ /hr	$\Delta W_{PVP}^{c)}$ /%	$S^{d)}$ /%
1	0	50	4	100	
2	1	50	4	100	
3	1	80	7	100	
4	3	50	17	77	
			24	77	
5	3	80	7	24.7	632.7
			48	27.0	
6	5	50	17	63.6	
			24	64.0	
7	5	80	7	21.7	
			48	25.6	504.6

a) T =crosslinking temperature for CL-blend membranes;

b) t =a period of time immersed in water for CL-blend membranes;

c) ΔW_{PVP} =PVP quantity solubilized out from the CL-blend membranes after immersing and reaching swollen equilibrium in water;

d) S =swelling ratio

The experiment results, shown in Table 5, indicated that no PVP remained whether in blend or in CL-blend gel with lower reticulation degree

($\text{K}_2\text{S}_2\text{O}_8 < 2\text{wt}\%$), but 75wt% PVP may be entangled and remained in CL-blend hydrogels crosslinked by 3 – 5 wt% $\text{K}_2\text{S}_2\text{O}_8$, owing to the good miscibility and PVA stable network forming as mentioned above. The swollen ratio reached to 632.7%. These results quite well agreed with those obtained by DSC and TG methods.

Keywords:

Crosslinked PVA/PVP blends; Miscibility; Thermal stability; Hydrogel network

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