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Syntheses of PVA/starch grafted hydrogels by irradiation

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Abstract

A series of excellent polyvinyl alcohol (PVA)/starch blend hydrogels were prepared by gamma and electron beam radiation at room temperature. The influence of dose, the content of starch in blend systems on the properties of the prepared hydrogels was investigated. The gel strength was improved obviously after adding starch into PVA hydrogels, but the swelling properties decreased slightly due to poor hydrophilicity of starch. In order to elucidate the effect of component of starch on the properties of PVA/starch hydrogels as well as the formation mechanism of PVA/starch blend hydrogels under irradiation, the two components of starch, amylose and amylopectin, were chosen to blend with PVA to prepare the hydrogels, respectively. The results indicated that the amylose of starch was a key component that influenced the properties of PVA/starch blend hydrogels. The further analyses of FTIR, DSC and TGA spectra of the prepared gels after extracting sol manifested that there was a grafting reaction between PVA and starch molecules besides the crosslinking of PVA molecules under irradiation, and the amylose of starch was a key reactive component.

Keywords: Starch; Amylose; Amylopectin; PVA; Hydrogels; Radiation; Crosslinking; Grafting

1. Introduction

Hydrogels are three-dimensional hydrophilic polymer networks capable of imbibing large amounts of water, which have been used widely in the field of biomedicine and pharmacy (Peppas, 1986; Rosiak & Ulanski, 1999), such as soft contact lenses, wound dressing, super-absorbents, drug delivery systems, etc. Synthetic polymers such as polyvinyl alcohol (PVA), poly-*N*-vinyl pyrrolidone (PVP), polyethylene oxide (PEO) hydrogels have been studied widespread but their properties need to be improved further for special applications (Huglin & Zakaria, 1986; Yoshii, Zhanshan, Isobe, Shinozaki, & Makuuchi, 1999). Hydrogels of natural polymers, especially polysaccharides, also have been used recently because of their unique advantages. Polysaccharides are, in general, non-toxic, biocompatible, biodegradable, and abundant (Cascone et al., 2001; Chen, Jo, & Park, 1995). However, as polysaccharides dissolve easily in water, cannot form stable hydrogel, an effective method is to make them into a synthesized polymer gel networks to form natural and synthesized polymer blend hydrogels, which is becoming a subject of academic as well as of industrial interest. Entrapping crosslinking of polysaccharides with synthetic polymers has been reported (Kaetsu, 1996; Rosiak, Rucinka-Rybus, & Pekala, 1989). Recently, kappa-carrageenan (KC) was found to enhance the properties of the hydrogels by incorporating KC into water-soluble polymer systems such as PEO (Tranquilan-Aranilla, Yoshii, Dela-Rosa, & Makuuchi, 1999) and PVP (Zhai, Ha, Yoshii, & Makuuchi, 2000).

Starch is one of the most abundant and cheap polysaccharides. Usually starch includes about 30% amylose and 70% amylopectin. Chemically modified starches with improved properties are becoming more and more important in industry application not only because they are low in cost, but mainly because the polysaccharide portion of the product is biodegradable. Chemical modification of starch via graft copolymerization of vinyl monomers onto it has been studied widely in recent years (Athawale & Lele, 1998; Kiatkamjornwong, Chomsaksakul, & Sonsuk, 2000). But only a few studies on starch/synthesized polymer blend hydrogels have been reported (Hashim, Dahlan, & Noordin, 2000). In this work, a series of excellent PVA/starch blend hydrogels will be prepared by irradiation technique, and in the meantime the formation mechanism and characteristics of the prepared hydrogels will be studied in detail.

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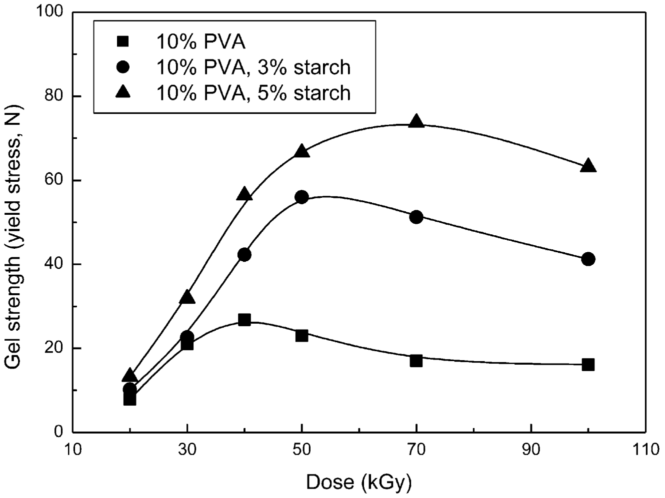

Fig. 1. Gel strength (yield stress) of PVA/starch blend hydrogels prepared by gamma irradiation.

2. Experimental

2.1. Materials

PVA-117 was supplied by Kuraray Co. Ltd, Japan. Starch (cornstarch), amylose and amylopectin were supplied by Gunei Chemical Industrial Co. Ltd, Japan. Dimethyl sulfoxide (DMSO) used was of an analytical grade and distilled water was used for the preparation of the hydrogels.

2.2. Irradiation preparation of the blend hydrogels

Starch, amylose or amylopectin powder was first dissolved in distilled water to form gel-like solution and then added to PVA solution, and continuously stirred to form homogeneous mixture after heating at 90 °C for 30 min. The gel-like solution was transferred into the glass tube of diameter 15 mm to irradiate by ^{60}Co gamma source at room temperature. The gel-like solution also was poured into a petri dish to irradiate using a beam current of 1 mA and acceleration energy of 2 MeV generated by the Cockroft Walton Electron Beam Accelerator.

2.3. Gel strength and elongation at break

The hydrogels prepared by gamma irradiation were cut into cylinders with a 15 mm diameter and 20 mm height. Gel strength (yield stress) was measured by 75% compressing and decompressing gel samples between parallel plates at strograph-R1 material tester (Toyoseiki Co. Ltd, Japan) with a crosshead speed of 50 mm/min. The hydrogels prepared by electron beam (EB) irradiation were cut into dumbbell (ASTM D-1822-L), and then tensile strength and elongation at break were measured by the above material tester.

2.4. Gel fraction

The hydrogel samples were put into stainless net of 200 mesh and then the sol was extracted in distilled water at 121 °C for 4 h in an autoclave. (The sol of gel sample was also extracted in DMSO at room temperature for 72 h, and then washed by distilled water for three times. The result was the same as that gained by the above method). The remained gel was dried to constant weight at 50 °C. Gel fraction was measured gravimetrically.

$$\text{Gel fraction (\%)} = W_g/W_0 \times 100 \tag{1}$$

where W_g is the weight of dry gel after extraction and W_0 is the initial weight of dry gel.

2.5. Swelling behavior

Hydrogel samples were immersed directly in distilled water at room temperature to the equilibrium (72 h), after that the swollen hydrogel was dried at 50 °C to constant weight. The equilibrium degree of swelling (EDS) of the gel was calculated as:

$$\text{EDS} = W_e/W_d \times 100 \tag{2}$$

where W_e is the weight of gel at the equilibrium and W_d is the weight of dried gel after swelling experiment.

2.6. FTIR analyses of gel portion

The gel samples after extracting sol and irradiated starch were freeze-dried and pulverized. (Irradiated starch was prepared by irradiating 5% gel-like starch solution at 20 kGy.) Infrared spectra with a resolution of 4 cm^{-1} of the samples as KBr pellets were recorded by Shimadzu FTIR-8100A spectrometer.

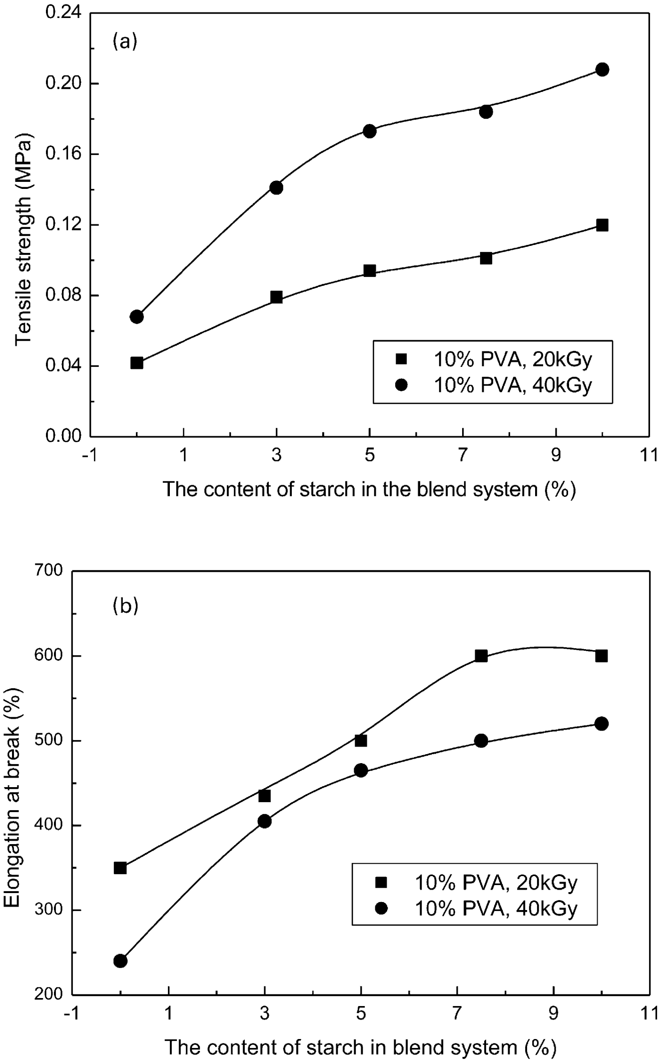

Fig. 2. (a) Tensile strength of PVA/starch blend hydrogels prepared by EB irradiation; (b) elongation at break of PVA/starch blend hydrogels prepared by EB irradiation.

2.7. Thermal analyses of gel portion

The melting points and melting enthalpies of the samples (8 mg) were studied using Perkin–Elmer Model DSC-7 differential scanning calorimetry (DSC) from 100 to 300 °C at a heating rate of 10 °C/min under nitrogen. Thermogravimetry (TG) of the samples (5 mg) were carried out in Shimadzu TGA-50 at a heating rate of 30 °C/min from room temperature to 150 °C and then at a heating rate of 5 °C/min from 150 to 495 °C under nitrogen.

3. Results and discussion

3.1. The characteristics of the PVA/starch blend hydrogels

3.1.1. Gel strength and elongation at break

The effect of the content of starch in PVA/starch blend systems and the dose on the gel strength (yield stress) was shown in Fig. 1. With the increase of starch% in the blend systems, the gel strength was improved largely. The gel strength also increased quickly with the increasing of the dose, but decreased slightly at high dose due to the degradation of the hydrogels.

The experiment showed that PVA/starch blend hydrogels had excellent elasticity and flexibility, so this kind of hydrogel can be used as wound dressing. PVA/starch blend hydrogel dressing was prepared by EB irradiation, its tensile strength and elongation at break was determined, and the results were shown in Fig. 2a and b. PVA/starch blend hydrogels had excellent tensile strength and elongation. Tensile strength increased with the increasing of the amount of starch in the blend systems or the dose, and elongation at break also increased with the amount of starch, but decreased with the increase of the dose.

3.1.2. Swelling behavior

The change of swelling behavior of PVA/starch blend

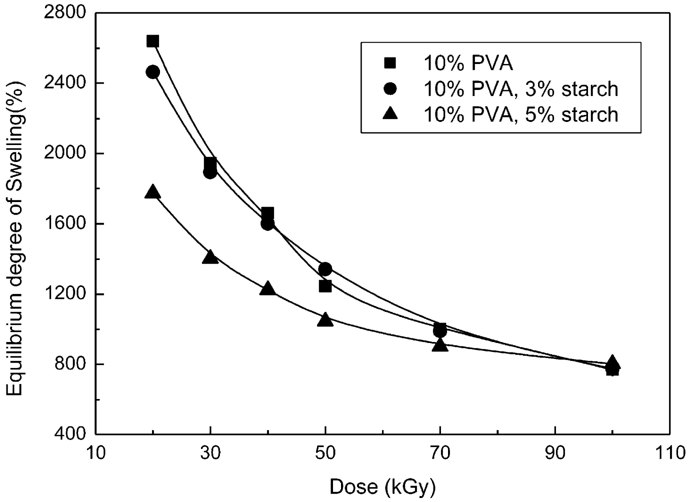

Fig. 3. EDS of PVA/starch blend hydrogels prepared by gamma irradiation.

hydrogels with the content of starch in PVA/starch blend systems and the dose was shown in Fig. 3. EDS of prepared hydrogels decreased with the dose reasonably, and also decreased slightly with the addition of starch due to poor hydrophilicity of starch.

3.1.3. Gel fraction

The changes of the gel fraction of PVA/starch blend hydrogels with the dose as well as the content of starch in PVA/starch blend systems were shown in Fig. 4. The gel fraction of PVA/starch blend hydrogels increased quickly and then leveled off around 20 kGy. But at high dose, gel fraction decreased slightly due to the degradation of the hydrogels.

The gel fraction decreased with the increasing of the content of starch in PVA/starch blend systems, but the results also showed that the part of starch could not be removed by extraction, i.e. there were two kinds of starch in PVA gel (PG) after irradiation, one was entrapped in PG, which could be removed easily by extraction, the other could not be removed, was the latter grafted starch in PVA hydrogel?

Polysaccharide and synthesized polymer blend hydrogels have been prepared and studied widely, and many researchers thought maybe that there was chemical reaction between polysaccharide and synthesized polymer molecules because saccharide groups contain two reactive groups at C-2 and C-6 positions, but up to now no related research was reported (Kaetsu, 1996; Rosiak et al., 1989; Tranquilan-Aranilla et al., 1999; Zhai et al., 2000). Starch is a kind of polysaccharide. Is there any grafted starch in PVA/starch blend hydrogels prepared by irradiation? In addition, as starch consists mainly of amylose and amylopectin, before discussion on grafting reaction between PVA and starch molecules, it is essential to elucidate the influence of component of starch on the properties of PVA/starch blend hydrogels.

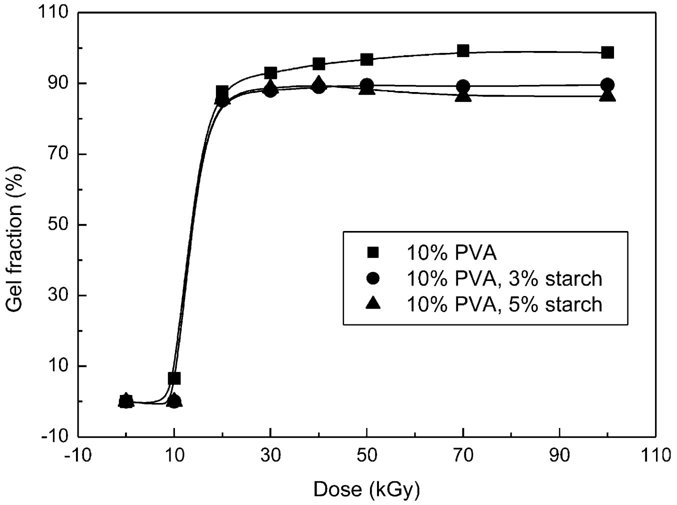

Fig. 4. Gel fraction of PVA/starch blend hydrogels prepared by gamma irradiation.

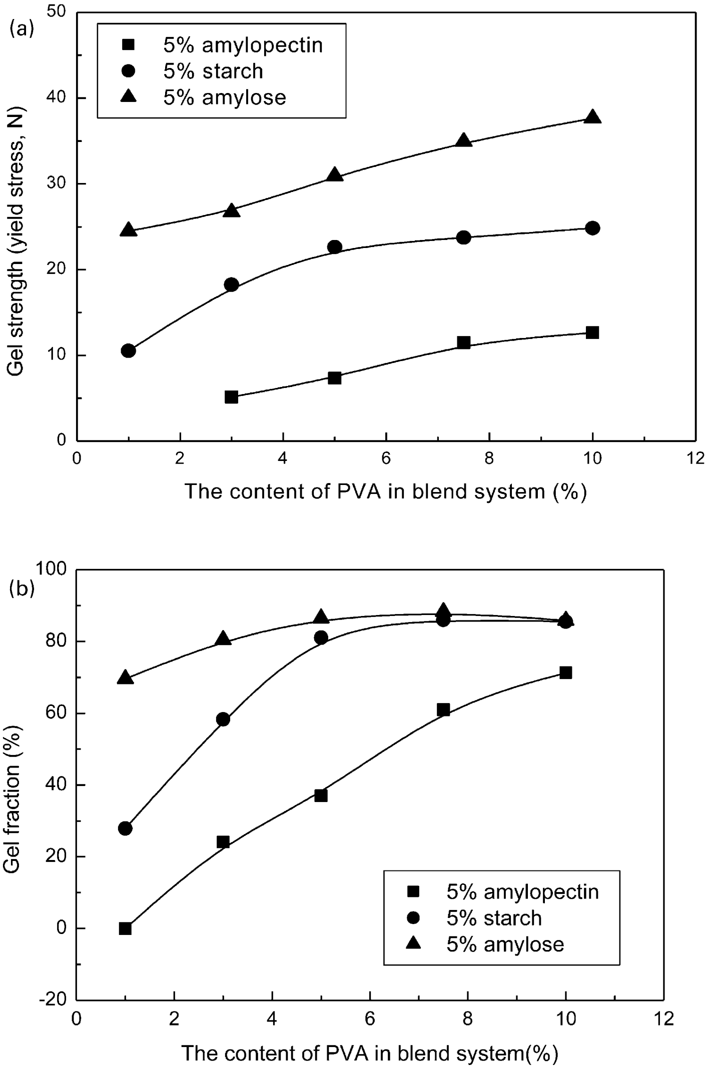

Fig. 5. (a) Gel strength (yield stress) of PVA/amylose, PVA/starch, PVA/amylopectin hydrogels prepared by gamma irradiation at 20 kGy; (b) gel fraction of PVA/amylose, PVA/starch, PVA/amylopectin hydrogels prepared by gamma irradiation at 20 kGy.

3.2. Effect of component of starch on the properties of PVA/starch blend hydrogels

In order to elucidate the effect of component of starch on the properties of PVA/starch blend hydrogels, amylose and amylopectin were chosen to blend with PVA to prepare the hydrogels, respectively. The change of gel strength (yield stress) and gel fraction of PVA/amylose, PVA/amylopectin and PVA/starch blend hydrogels with the content of PVA in the blend systems were shown in Fig. 5a and b, respectively. Compared with PVA/starch blend hydrogels, PVA/amylose blend hydrogels had higher gel fraction and mechanical strength. PVA/amylopectin blend hydrogels was over the left. It was very difficult to form homogeneous PVA/amylopectin mixture before irradiation due to bad intermiscibility of PVA and amylopectin molecules. After irradiation, the prepared PVA/amylopectin blend hydrogels was very weak, and the gel fraction was very low. When the content of PVA was 1% in the blend systems, an excellent PVA/amylose or PVA/starch blend hydrogel could be gained, and the gel strength of PVA/amylose blend hydrogel was higher than that of PVA/starch blend hydrogel, but the PVA/amylopectin blend hydrogel could not be prepared. It indicated that the possibility of reaction between PVA and amylopectin was very low, so the amylose of starch was a key component that influenced the properties of PVA/starch blend hydrogels. If there is a chemical reaction, i.e. grafting reaction between PVA and starch molecules besides crosslinking of PVA molecules under irradiation, the main reactive component of starch should be amylose. Cascone et al. (2001) prepared PVA/starch and PVA/amylose films by solution casting, and found that PVA/starch blends films were two-phase systems and PVA/amylose blend films were homogeneous one-phase structure. It also indicated that PVA could blend with amylose homogeneously, so there is the possibility of chemical reaction between PVA and amylose under irradiation.

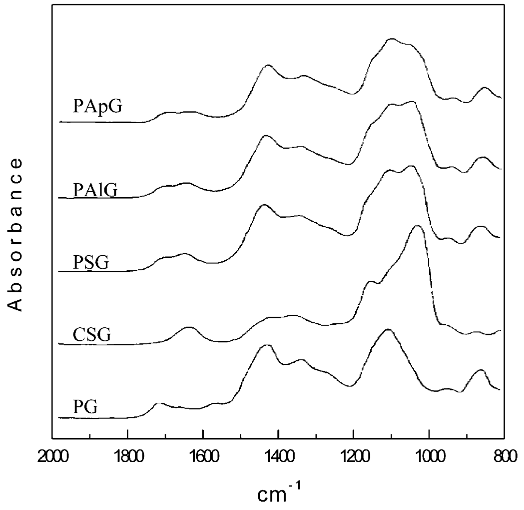

Fig. 6. FTIR spectra of gel portion of PVA, PVA/starch, PVA/amylose, PVA/amylopectin gels as well as starch prepared by gamma irradiation at 20 kGy. PG: 10% PVA gel, CSG: 5% irradiated starch; PSG: 10% PVA, 5% starch gel; PAlG: 10% PVA, 5% amylose gel; PApG: 10% PVA, 5% amylopectin gel.

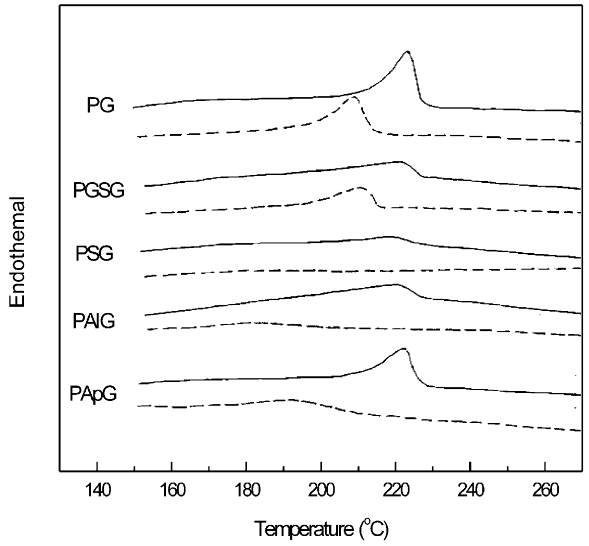

Fig. 7. DSC heating curves of gel portion of PVA, PVA/starch, PVA/amylose, and PVA/amylopectin gels as well as the mechanical mixture of PVA gel and starch prepared by gamma irradiation at 20 kGy. PGSG: PVA and starch mechanical mixture (70% PVA, 30% starch); others are the same as that in Fig. 6.

3.3. *Evidence for grafting reaction of starch to PVA gel*

When polymer aqueous solution was subjected to ionizing irradiation, hydroxyl radicals were the main reactive species responsible for reactivity transfer from water to polymer chains (Rosiak & Ulanski, 1999). After PVA/starch/water blend systems were irradiated, hydroxyl radicals could initiate PVA and starch radials. PVA radicals reacted easily with other PVA molecules to form crosslinked PVA networks (Huglin & Zakaria, 1986). Reaction probability between starch radials and other starch was very low, after irradiation, starch degraded obviously (Hashim et al., 2000). But starch radicals reacted with PVA to initiate graft reaction. Graft reaction between PVA and starch molecules depended on the probability of the combination of PVA and starch macroradicals. The following experiments will demonstrate further it.

Table 1
Melting point (T_m) and melting enthalpy (ΔH_m) of gel portion of PVA/starch blend gels

Composition (starch/PVA/water)	Dose (kGy)	Gel fraction (%)	T_m (°C)	ΔH_m (J/g)
0/10/90	0	0	222.73	56.30
0/10/90	20	87.70	221.78	51.85
0/10/90	30	92.93	220.40	49.38
0/10/90	40	95.53	219.29	44.96
0/10/90	50	96.73	218.54	43.62
0/10/90	70	99.19	217.47	40.30
0/10/90	100	98.72	213.98	39.82
3/10/87	0	0	222.72	57.90
3/10/87	20	85.20	221.58	39.52
3/10/87	30	87.94	220.24	37.46
3/10/87	40	88.97	218.93	36.13
3/10/87	50	89.51	218.80	36.38
3/10/87	70	89.13	217.05	36.23
3/10/87	100	89.54	213.23	26.14

3.3.1. *Infrared spectral analyses of gel portion*

The FTIR spectra of the prepared gels after extracting sol were shown in Fig. 6. To comparison, a FTIR spectrum of irradiated starch (CSG) was also appeared. Because the FTIR spectra of irradiated amylose and irradiated amylopectin were the same as that of irradiated starch, their spectra were not revealed. The irradiated PG showed absorption bands at 1452, 1336, 1238, 1095 and 843 cm^{-1}, which are attributed to the δ(CH–OH), δ(CH–OH), ω(CH), ν(C–O) and ν(C–C) resonance, respectively, in agreement with the literature data (Krimm, Liang, & Sutherland, 1956). The FTIR spectrum of irradiated starch (CSG) showed the characteristic absorption bands at 1646 and 1024 cm^{-1} for O–H and C–H bending, respectively, which is also the same as the reference data (Lutfor et al., 2001). The FTIR spectrum of PVA/starch (PSG) or PVA/amylose gel (PAlG) after extracting sol showed obviously characteristic absorption bands at 1646 and 1024 cm^{-1} for O–H and C–H bending of starch or amylose in addition to the absorption bands of PVA. But the FTIR spectrum of PVA/amylopectin gel (PApG) did not have obvious absorption bands for amylopectin molecules. The results suggested that there was obvious grafting reaction in amylose/PVA and PVA/starch blend systems, and the amylose of starch was main reactive component.

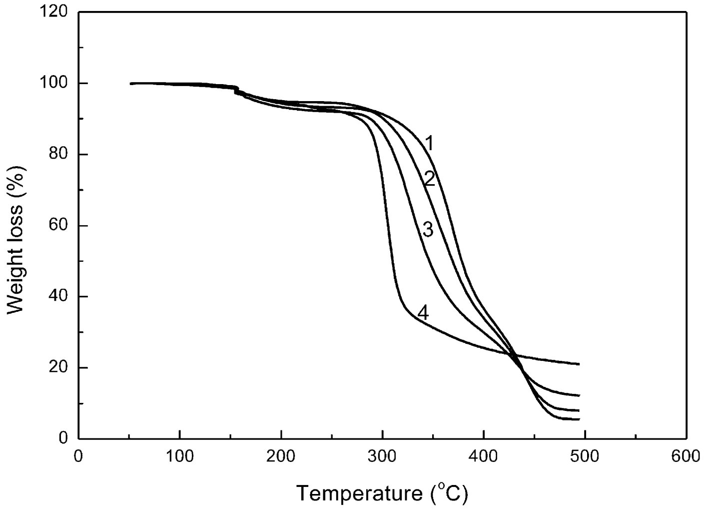

Fig. 8. TG thermograms of gel portion of PVA, PVA/starch gels as well as starch prepared by gamma irradiation at 20 kGy. Curve 1, 2, 3, 4 is 10% PVA gel, 10% PVA, 5% starch gel, 5% PVA, 5% starch gel and 5% irradiated starch, respectively.

3.3.2. Thermal analyses of gel portion

The results of DSC analyses of gel samples after extracting sol were shown in Table 1. The DSC results of unirradiated samples were also appeared as control. Before irradiation, the melting point of PVA did not change after adding starch in PVA, but its melting enthalpy increased. After irradiation, with increasing of dose, the melting points and melting enthalpies of both PG and PVA/starch blend gel decreased due to the crosslinking of PVA under irradiation, but at the same dose, the melting point and melting enthalpy of PVA/starch blend gel was lower than that of pure PG. Cascone et al. (2001) analyzed uncrosslinked PVA/starch blend films by DSC, and found that PVA melting temperature did not change by varying the starch content in the films while the PVA melting enthalpy increased by increasing the content of starch. It indicated that there was a different completely influence of starch on thermal behavior of PVA before and after irradiation. After irradiation, grafting reaction of starch into PGs influenced obviously thermal behavior of PVA.

DSC curves of gel samples after extracting sol and mechanical mixture of irradiated PVA and irradiated starch at the same dose were shown in Fig. 7. DSC curves of the second run of the prepared gel samples (dotted line) displayed that there still was a melting peak at pure PG, mechanical mixture of PVA and starch (PGSG) or PVA/amylopectin blend gel (PApG), but in PVA/ starch (PSG) or PVA/amylose blend gels (PAlG) melting peak almost disappeared with the addition of starch or amylose into PG, i.e. the incorporation of starch or amylose into PVA by irradiation prevented the recrystallization of PVA. It also showed further that the reactivity between PVA and amylose under irradiation was higher than that of PVA and amylopectin, and the amylose of starch was main reactive component.

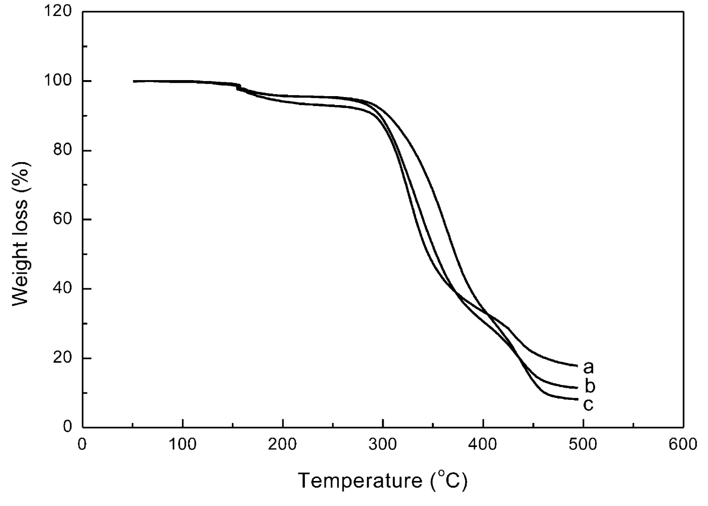

Fig. 9. TG thermograms of gel portion of PVA/amylose, PVA/starch, PVA/amylopectin gels prepared by gamma irradiation at 20 kGy. Curve a, b, c is 3% PVA, 5% amylose gel, 3% PVA, 5% starch gel, 3% PVA, 5% amylopectin gel, respectively.

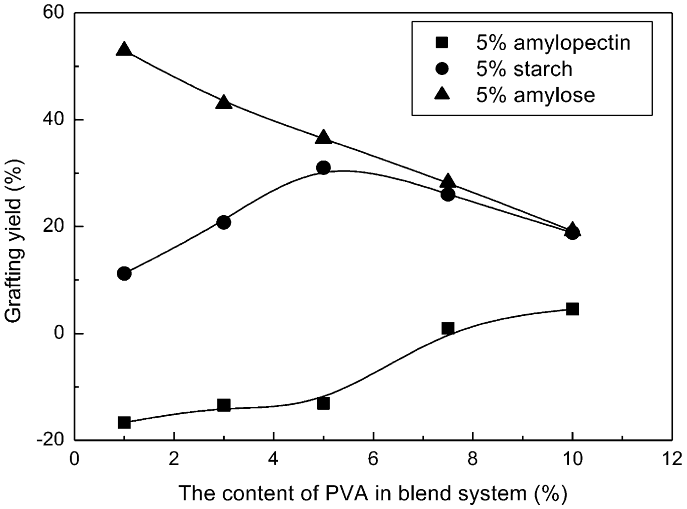

Fig. 10. Grafting yield of amylose, starch or amylopectin into PVA hydrogels prepared by gamma irradiation at 20 kGy.

Fig. 8 showed that TG thermograms of PVA/ starch blend gels after extracting sol prepared at the same dose with different composition. TG thermogram of irradiated starch (curve 4) was also appeared as control. Irradiated starch showed a characteristic three-step thermogram, wherein the major weight loss (69.95%) occurred from 291.5 to 321.9 °C. The thermogram of irradiated pure PG (curve1) was four-step thermogram, but its major decomposition temperature was from 335.5 to 408.3 °C and the major weight loss was 87.40%. In case of PVA/ starch blend gel, the onset temperature of decomposition and the major weight loss decreased with the increasing of the content of grafted starch in PGs (from curve 1 to curve 4).

TG thermogram of PVA/amylose (curve a), PVA/ amylopectin (curve c) in contrasting with PVA/starch blend gels (curve b) after extracting sol was showed in Fig. 9. The onset temperature of decomposition and main weight loss of PVA/starch was between that of PVA/amylose and PVA/ amylopectin. It also indicated that the reactivity between PVA and amylose under irradiation was higher than that of PVA and amylopectin. The conclusion was the same as the above analyses.

3.4. Grafting yield of starch, amylose or amylopectin to PVA gels

In the PVA/starch, PVA/amylose or PVA/ amylopectin blend system, if the starch, amylose or amylopectin that cannot be removed by extracting was defined as grafted starch, amylose or amylopectin into PGs, respectively. Supposed that PVA crosslinked completely under irradiation, then grafting yield can be calculated as follows:

$$\text{Grafting yield}\ (\%) = (W_g/W_0 - W_p/W_0) \times 100 \qquad (3)$$

where W_g is the weight of dry gel after extraction; W_0 is the initial weight of dry gel; W_p is the weight of PVA in the initial dry gel.

The results calculated from Fig. 5b were shown in Fig. 10. It can be found that there was completely different situation in three kinds of systems. In PVA/amylopectin blend systems, there was a minus grafting yield according to the above definition. With the increasing of the content of PVA, minus grafting yield changed into positive grafting yield. This is because incorporation amylopectin into PVA influenced seriously the crosslinking of PVA, with the increasing of the content of PVA, the influence of amylopectin on the crosslinking of PVA decreased. It also indicated that there was nearly no grafting reaction of amylopectin into PG. In PVA/amylose blend systems, a high grafting yield was gained, and with the increasing of the content of PVA, the grafting yield of amylose into PG decreased reasonably. In PVA/starch blend systems, when the ratio of starch to PVA was 1:1 (5%starch, 5%PVA), the grafting yield was up to maximum value. The result was just the combination of PVA/amylose and PVA/amylopectin blend systems. The analyses of grafting yield indicated further that there was a grafting reaction of starch into PGs besides the crosslinking of PVA under irradiation, and the amylose of starch was a key reactive component.

4. Conclusion

A series of excellent PVA/starch blend hydrogels could be prepared by changing the composition and the dose under gamma or EB irradiation.

There was a grafting reaction between PVA and starch molecules besides the crosslinking of PVA molecules under irradiation, and the amylose of starch was a key reactive component.

The amylose of starch was a key component to influence the properties of PVA/starch blend hydrogel too.

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