Flame-Retardant and Physical Properties of Poly(vinyl alcohol) Chemically Modified by Diethyl Chlorophosphate

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ABSTRACT: Phosphorylated poly(vinyl alcohol) (P-PVA) was prepared via the modification of the pendent hydroxyl groups of poly(vinyl alcohol) (PVA) in the presence of diethyl chlorophosphate (DECP). Chemical structures of the P-PVA were characterized by attenuated total reflection-Fourier transform infrared, ^{1}H NMR, and ^{31}PNMR spectra. The formed P-PVA showed good flame retardance, improved thermal stability, enhanced hydrophilicity, decreased tensile strength, and increased elongation at break compared with PVA. The crystallinity of P-PVA was much lower than that of PVA, and it decreased with the increase of phosphorus content. The reasons for the obvious differences between the aforementioned properties of PVA and P-PVA were investigated and discussed. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: poly(vinyl alcohol); flame retardance; mechanical properties; diethyl chlorophosphate; phosphorylated

INTRODUCTION

Poly(vinyl alcohol) (PVA) is one of the most important water-soluble vinyl polymers. It has been used in coatings, adhesive, fibers, films, hydrogels, polyelectrolytes, optics, and biomaterial etc. due to its excellent mechanical properties, good chemical resistance, easy processability, biodegradability, and water-solubility.[1–10] However, corresponding to its own intrinsic chemical composition and molecular structures, PVA is flammable, which greatly restricted its wide applications. Therefore, a flame-retardant PVA is urgently needed. As far as we know, most of the work related to the flame retardancy of PVA focuses on halogenated compounds. Generally, traditional halogen flame retardants show good flame retardancy in PVA,[11,12] but they also have some disadvantages, such as the release of some toxins during decomposition. Therefore, it is significant to develop halogen-free flame retardant.[13,14] Recently, our laboratory has successfully prepared a series of halogen-free flame-retardant PVA. A series of layered double hydroxide (LDH) are synthesized and applied in PVA matrix as synergistic agents so as to improve flame retardancy of ammonium polyphosphate (APP).[15] Metal chelates are also employed as synergist to improve the flame retardancy of PNOH and APP.[16]

For some special applications, chemical modifications of PVA are essential. PVA can be easily modified through its hydroxylic groups, and several methods have been published in the literatures. Multifunctional compounds capable of reacting with hydroxyl groups can be used. Mostly, the modification of PVA is concerned with ester formation via the reaction of hydroxyl groups with acyl chlorides or acid anhydrides.[17] PVA with high surface and interfacial activities have been prepared by incorporating hydrophobic urethane and alkyl groups onto PVA.[9] The introduction of phosphonic acid groups into PVA chains gives ionic conduction ability to PVA.[18] Transformation of some hydroxyl groups into carbonyl groups via oxidation process form poly(vinyl ketone). 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide is used as a nucleophile to incorporate onto the repeating unit of poly(vinyl ketone). The phosphorylation of PVA results in improvement in the flame retardance of PVA.[19–22] Arranz et al.[23] have presented some results available on the structural aspects and the kinetic characteristics of phosphorylated PVA. However, the influence of the molecular structure on the comprehensive properties of the modified polymer has not been reported. In this study, the effect of the molecular

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structure of phosphorylated poly(vinyl alcohol) (P-PVA) on its flame retardancy, mechanical property, and moisture absorption of P-PVA are studied systematically by limiting oxygen index (LOI), UL-94, thermogravimatric analysis (TG), FTIR, X-ray diffraction (XRD), and gravimetric method.

EXPERIMENTAL

Materials

Poly(vinyl alcohol) having a polymerization degree of 1700 and a saponification degree of >99% was provided by Sichuan Weinilun Industry Corporation (Chongqing, China). It was dried under vacuum in the presence of phosphorus pentoxide to constant weight before use. N-methyl-2-pyrrolidone (NMP, from Kelong Chemical Reagent Corporation, Chengdu, China) and pyridine (Py, from Kelong Chemical Reagent Corporation, Chengdu, China) were purified by distillation under reduced pressure in the presence of calcium hydride and 4Å molecular sieve. Diethyl chlorophosphate (DECP) was purchased from Jiacheng Chemical Industries Reagent Co. (Shanghai, China), and it was purified by distillation under reduced pressure immediately before use.

Preparation of phosphorus-containing PVA

PVA was dissolved in NMP at 80–90°C under N_2. Prescribed amounts of pyridine and DECP were then added slowly to the aforementioned cold PVA solution while stirring. The homogeneous reaction was kept at 20°C for 24 h. The degree of phosphorylation of PVA was determined with the phosphorus content of the P-PVA. The product was precipitated in isopropyl alcohol. All polymers were purified by reprecipitation using tetrahydrofuran/water as solvents and isopropyl alcohol/diethyl ether as precipitants, and then dried *in vacuo* in the presence of phosphorous pentoxide.

Characterization of P-PVA

The structure of P-PVA was determined by attenuated total reflection-Fourier transform infrared (ATR-FTIR), ^{1}H NMR, and ^{31}P NMR spectra. ATR-FTIR spectroscopy spectra of PVA and P-PVA were recorded by a Nicolet FTIR 170SX infrared spectrophotometer. NMR spectra (^{1}H, 400 MHz; ^{31}P, 161.9 MHz) were obtained at room temperature using a Bruker AVANCE AV II-400 NMR instrument, with dimethyl sulfoxide-d_6 (DMSO-d_6) as the solvent, and with tetramethylsilane as the internal standard.

Determination of phosphorus content of P-PVA

The experimental phosphorus content of the P-PVA was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Iris Advantage, TJA solution).

Flame retardancy

The LOI measurements were performed on a HC-2C oxygen index meter (Jiangning, People's Republic of China) with a sheet dimension of $130 \times 6.5 \times 0.5$ mm^3 according to GB/T 2406-93. The Vertical burning tests were carried out on a CZF-2-type instrument (Jiangning, China) with a sheet dimension of $130 \times 13 \times 0.5$ mm^3 according to ASTM D3801. Thermogravimetric analysis (TGA) on PVA and P-PVA samples were performed on a TG 209 F1 instrument (NETZSCH, Germany) in flowing air (60 mL/min) at a heating rate of 10°C/min from 40 to 700°C. Residues obtained from P-PVA and PVA samples treated for 5 min at 500°C were characterized with KBr powder by using a Nicolet FTIR 170SX infrared spectrophotometer.

Mechanical properties

Tensile tests of the samples were carried out by the Universal Electricity Control Testing machine (Changchun, China) according to GB/T 1039-92. All the measurements were performed for five specimens and averaged. The XRD patterns of the samples were obtained with a Philips electronic instrument in steps of 0.03° using Cu-Ka radiation at 40 kV and 150 mA between 2 and 45° (2θ).

Water resistance

The films of pure PVA and P-PVA were dried at 70°C *in vacuo* until a constant weight was obtained, cooled to 25°C in a desiccator, and then accurately weighed immediately (M_0). The samples were conditioned in 50 and 100% relative humidity (RH) at 25 ± 1°C. Specimens were weighed at 1-day intervals until a constant weight was reached. The degree of water absorption was determined according to the following relationship:

$$\text{Water absorption}(\%)(M_t) = (M_1 - M_0)/M_0 \times 100 \tag{1}$$

where M_0 and M_1 are the weights of the samples before and after putting them into water at 25°C after 24 h of the test.

The gravimetric method was applied to determine the water resistance of the P-PVA samples. The films of pure PVA and P-PVA were dried in the same
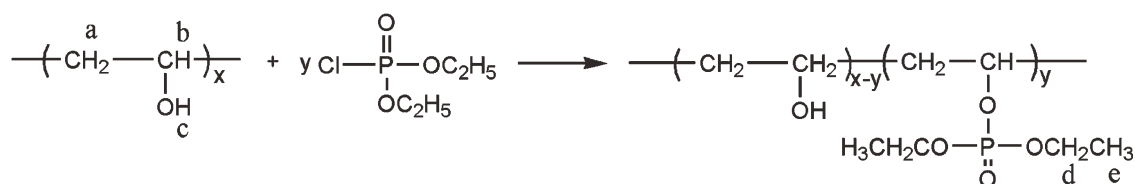
Scheme 1 Synthesis of P-PVA.

way for the water-absorption measurements. The samples were then accurately weighed and then immersed into distilled water. The degree of water absorption was calculated using eq. (1).

RESULTS AND DISCUSSION

Synthesis and characterizations of P-PVA

P-PVA was synthesized through the reaction of PVA and DECP according to Scheme 1. The structure of P-PVA was determined by ATR-FTIR, ^{1}H NMR, and ^{31}PNMR spectra. Table I showed the phosphorus content in P-PVA.

Figure 1 shows the ATR-FTIR spectra of PVA and P-PVA. The PVA shows absorption peaks at 3300–3400 cm^{-1} corresponding to the stretching vibration of hydroxyl (-OH) groups. It is observed that absorption peak intensity of P-PVA samples decreases with the increase of phosphorus content, indicating that the number of hydroxyl groups decreases after reacting with DECP. Meanwhile the ATR-FTIR spectrum of PVA shows some interesting changes when it reacts with DECP. After esterification, the stretching vibration of hydroxyl groups shifts towards higher frequencies owing to the cleavage of polymeric hydrogen bond.[24]

The peaks at 1022 cm^{-1} are assigned to P—O—C absorption and the peak at 1258 cm^{-1} is attributed to P=O absorption of P-PVA samples which does not appear in the spectrum of PVA. Meanwhile the absorption peak intensity increases with the increase of phosphorus content, which indicates that the reaction occurs between PVA and DECP, creating new covalent bonds and reducing hydrogen bonds between PVA chains.

Figure 2 shows the ^{1}H NMR spectra of PVA and P-PVA samples in DMSO-d_6. For the pure PVA, the

chemical shifts of methylene protons (Ha) appear at 1.30–1.50 ppm and the methane protons (Hb) attached to —OH appear at 3.82 ppm. The hydroxyl protons (Hc) of PVA are separated into triads at 4.22/4.47/4.67 ppm due to the hydrogen bonding between —OH groups of the polymer and DMSO.[25,26] In addition, the methyl resonance of vinyl acetate of PVA initial material can not be seen at 2 ppm in Figure 2. Comparing the spectra of PVA and P-PVA, we notice that, all the peaks, which appear in the PVA shown in Figure 2, also appear in the P-PVA with a very little change in the chemical shift values. However, extra peaks appear at 1.1 ppm and 4.0 ppm which are corresponding to the methyl and ethyl protons of the diethyl phosphate moieties, respectively. This clearly confirms the phosphorylation of PVA.

Furthermore, more direct evidence for phosphorylation comes from the ^{31}P NMR spectrum of P-PVA in Figure 3. Obviously, the peak at −2.2 ppm corresponds to the phosphorus containing unit [(—O—)$_2$P(=O)-O] in the P-PVA structure.

Based on the spectral results, it is reasonable to conclude that the P-PVA containing phosphorus in the side chain is synthesized successfully.

Flame retardancy

The LOI and the vertical burning test (UL-94) can be used as indicator to evaluate the flame retardancy of polymers. The LOI values and the UL-94 of PVA

TABLE I
Evaluation of Flame Retardancy of PVA and P-PVA

Samples	P^a wt %	LOI	UL-94
PVA	–	19.7	N.R
P-PVA1	0.33	21.3	V-2
P-PVA2	0.66	24.6	V-1
P-PVA3	1.28	26.7	V-1
P-PVA4	3.57	29.5	V-0

[a] Actual phosphorus content were tested by ICP.
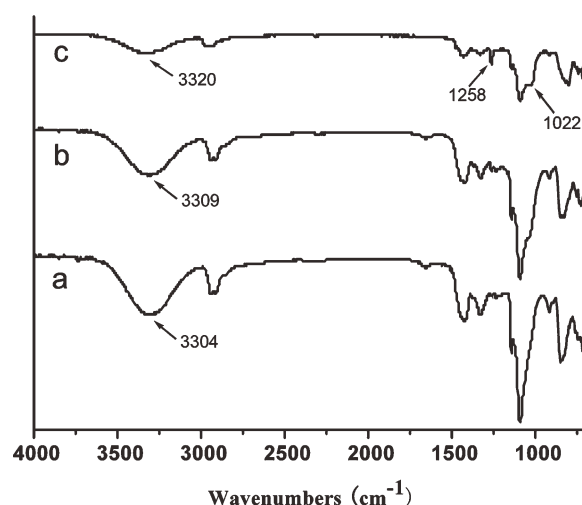
Figure 1 FTIR of PVA (a), P-PVA1 (b), and P-PVA3 (c).

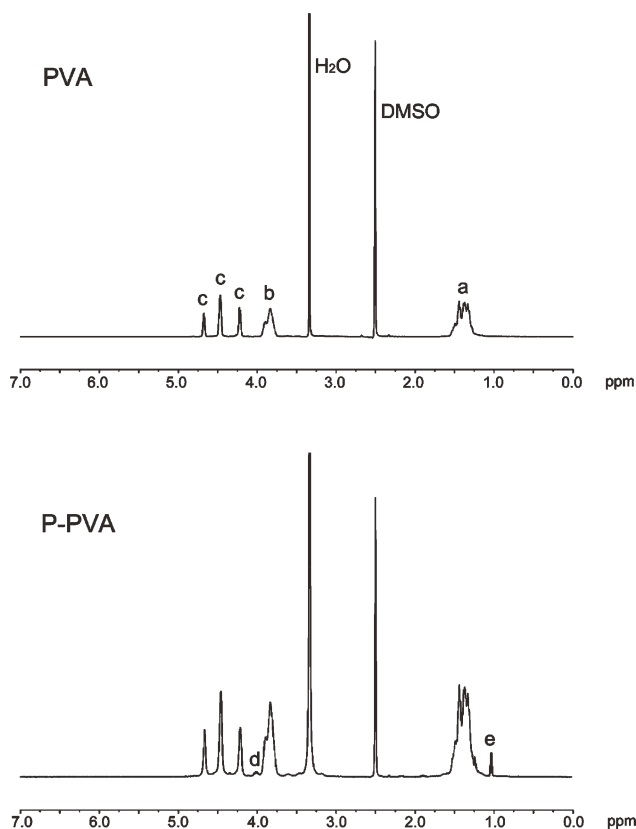**Figure 2** ^{1}H NMR of PVA and P-PVA4.

Figure 4 TGA curves of PVA and P-PVA in air.

and P-PVA are presented in Table I. It is clear that the flame retardance of PVA increases with increasing phosphorus content. When the incorporation of 3.57 wt % phosphorus into the PVA chains, the LOI values significantly increase from 19.7 to 29.5 and the UL-94 can achieve V-0 rating without melt dripping. This indicates that incorporating phosphorus-containing group can effectively improve the flame retardancy of PVA.

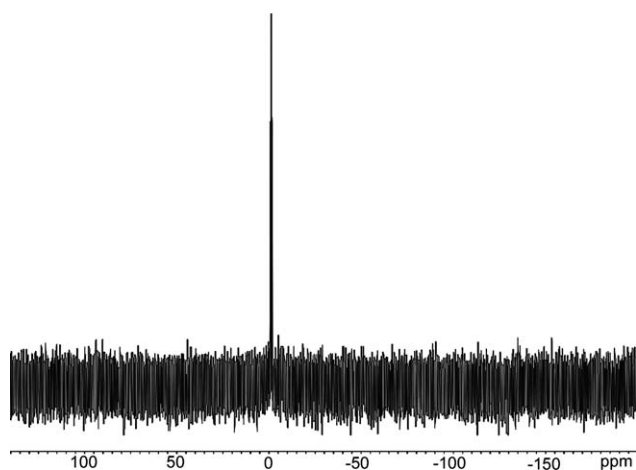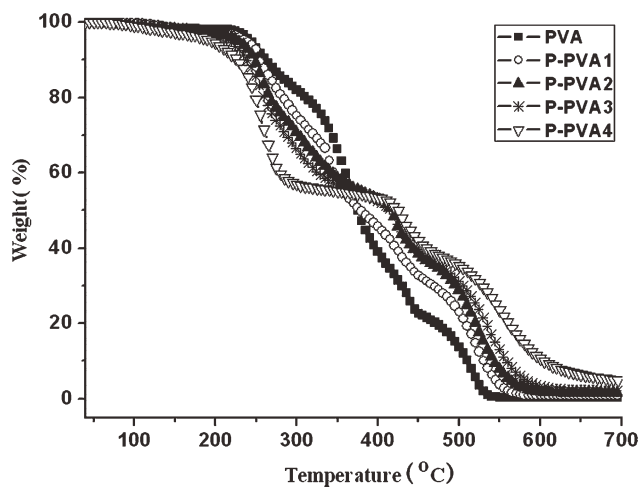TGA and the derivative thermogravimetric (DTG) curves of the PVA and P-PVA samples under air

atmosphere containing different phosphorus content are shown in Figures 4 and 5, and the test data are summarized in Table II. The general degradation mechanisms of PVA are based on loss of side groups from the main chain. As PVA always contains a small quantity of free water (depending on RH), the first part of the TG curve of PVA (up to about 100°C) represents evaporation of this water. Growing weight loss from 160 to 280°C is related to the stage of degradation and elimination of volatile products (mainly water and acetic acid). Spontaneous degradation of PVA starts above 280°C. The thermal degradation pattern of P-PVA is changed after the incorporation of phosphate ester group compared with that of pure PVA. The onset degradation temperatures ($T_{initial}$) of the P-PVA samples are shifted to lower temperatures than that of pure PVA. Meanwhile, the $T_{initial}$ of the P-PVA samples decrease gradually with the increase of phosphorus content, which is attributed to the fact that the phosphate ester group in PVA acts as an initiator for the
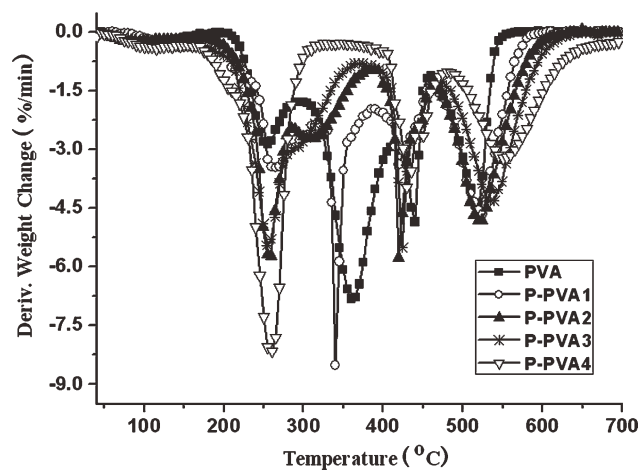

Figure 3 ^{31}P NMR of P-PVA4.

Figure 5 DTG curves of PVA and P-PVA in air.

TABLE II
Thermogravimetric Analysis Data of Various Samples

Sample	$T_{initial}$[a] (°C)	T_{max}[b] (°C)			Char residue (%)		
		T_{max1}	T_{max2}	T_{max3}	500°C	600°C	700°C
PVA	243	254	438	517	13.8	0.4	0.3
P-PVA1	229	263	419	524	23.1	0.9	0.9
P-PVA2	228	257	420	522	28.6	2.0	1.6
P-PVA3	214	256	423	539	31.1	3.3	2.2
P-PVA4	195	258	429	550	35.3	10.6	4.9

[a] $T_{initial}$ is the initial degradation temperature (temperature at 5% weight loss).
[b] T_{max} is the maximum-rate degradation temperature.

dehydration[27] and also reduces the number of intramolecular and intermolecular hydrogen bonds. However, P-PVA samples have a higher amount of residues at temperatures ranging from 370 to 700°C and the amount of the residue further increase with increasing phosphorus content. This behavior may be due to phosphate ester group that acts as an inhibitor for the degradation of the polymer.[27] As shown in Table II, the char yield of PVA is 0.3% at 700°C, while that of P-PVA4 which contains 3.57 wt % phosphorus increases to 4.9%. The char layer can play an important role in improving the flame retardancy of phosphorus-containing PVA. Furthermore, the char yields increase with the increase of phosphorus content, which is consistent with the flame retardancy of the samples characterized by LOI measurement and UL-94 test discussed above.

Figure 5 shows DTG curves of the samples which reflect the height of the peak in DTG curves corresponding to the major weight-loss stage. It is noticed that the first stage of decomposition occurs at a lower temperature and over a narrower range of temperature in P-PVA than in PVA. From the detailed discussion on TG and DTG curves, it appears that the introduction of phosphate ester group alters the course of the thermal degradation of PVA and improves the thermal stability of P-PVA at higher temperature, which is helpful for the flame retardancy.

To investigate the variations of the condensed phases, the FTIR spectra of the char residues of PVA and P-PVA after heating for 5 min in a muffle at 500°C in air were recorded (see Fig. 6). As can be seen, new peaks appear in Spectrum b, the peaks at 1001 cm^{-1} and 493 cm^{-1} are assigned to the stretching vibration and bending vibration of the P—O—C group,[28] which may be from DECP, or from the chemical interaction of DECP with PVA. The characteristic absorption peaks at 1154 cm^{-1} are attributed to P=O stretching. Moreover, the new band at 744 cm^{-1} related to the appearance of *cis* C=C group.[29] Compared with Figure 6(a,b), the intensities of peaks at 2920 cm^{-1}, 2851 cm^{-1} assigned to vibration of —CH$_3$ and —CH$_2$— obviously decrease. These results

indicate that the residues of P-PVA under 500°C can protect the material effectively under heating. The characteristic peaks of P=O and P—O—C appear, giving positive evidence of the phosphorus component in the condensed phases.

Mechanical properties

Mechanical properties are important criteria for many practical applications of materials. The mechanical properties of P-PVA samples are measured and compared with that of the pure PVA sample.

Table III shows the mechanical properties of PVA and P-PVA samples with different phosphorus contents at room temperature. Compared with the pure PVA, P-PVA shows a decrease in tensile strength and an increase in elongation at break significantly. Results show that the tensile strength of pure PVA is 39.2 MPa, while the tensile strength of the P-PVA1 with 0.33 wt % of phosphorus content decrease by 33.9% compared with that of the pure PVA. Moreover, the tensile strength of P-PVA gradually decreases as the phosphorus content increases from
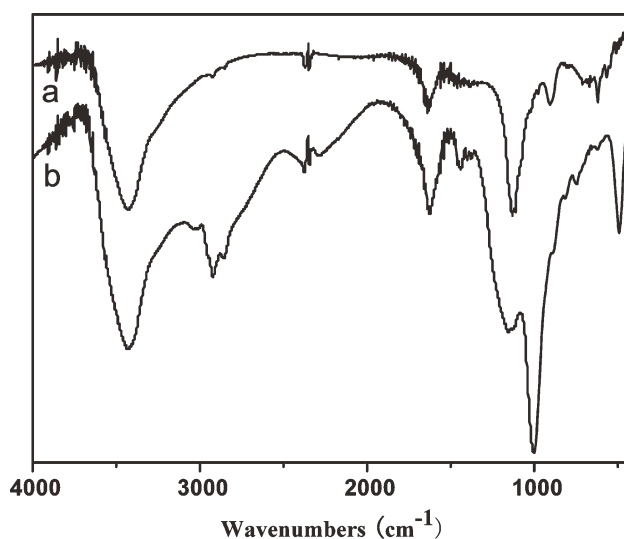

Figure 6 FTIR of residues of PVA (a) and P-PVA4 (b) at 500°C in a muffle for 5 min.

TABLE III
Mechanical Properties of PVA and P-PVA

Sample	Tensile strength (MPa)	Elongation at break (%)
PVA	39.2 ± 1.6	231.2 ± 8.6
P-PVA1	25.9 ± 1.9	343.4 ± 10.4
P-PVA2	24.6 ± 2.5	354.2 ± 9.2
P-PVA3	21.2 ± 1.8	474.1 ± 4.6
P-PVA4	20.4 ± 2.4	496.7 ± 7.7

0.33 to 3.57 wt %. Compared with P-PVA1, P-PVA4 yields about 47.9% decrease of tensile strength. The dramatic effect of phosphorus content on the elongation at break could be observed. The P-PVA1 enhances 1.5 times of the elongation at break compared with the PVA, and the elongation at break continuously increases with the increase of phosphorus content. The elongation at break increases 2.1 times when 3.57 wt % of phosphorus is incorporated into the PVA chain. This phenomenon can be ascribed to the weakness of the hydrogen bonds among PVA molecules.

The above changes of mechanical properties are also related to the crystallinity of P-PVA. Figure 7 shows the XRD patterns of PVA and P-PVA samples. From Figure 7, we can see that there is an intense peak appeared at $2\theta = 19.6°$, corresponding to PVA characteristic crystalline peak.[24] Compared with that of PVA, the peaks intensity around $2\theta = 19.6°$ of P-PVA samples decrease. It is clear that the PVA sample exhibits greater tendency to crystallinity than the P-PVA samples. The decrease in peak intensity relates to an increase in phosphorus content of the P-PVA as shown in Figure 7, e.g., P-PVA4 sample shows lower peak intensity than P-PVA1 sample. These results indicate that conformation of the polymer is changed by the introduction of phosphate ester group onto PVA side-chain.
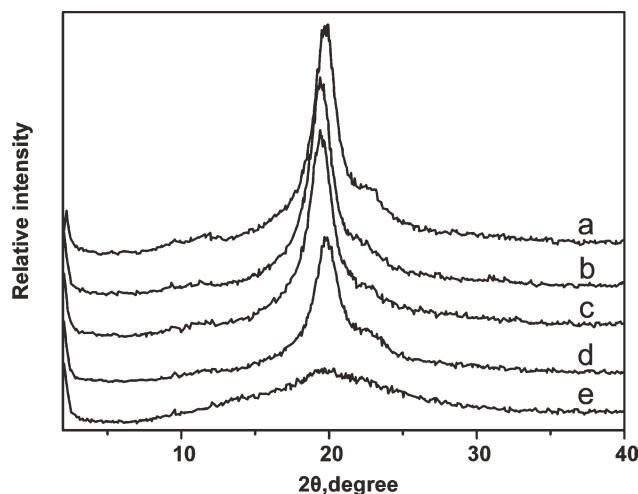

Figure 7 X-ray diffraction patterns of PVA (a), P-PVA1 (b), P-PVA2 (c), P-PVA3 (d), and P-PVA4 (e).
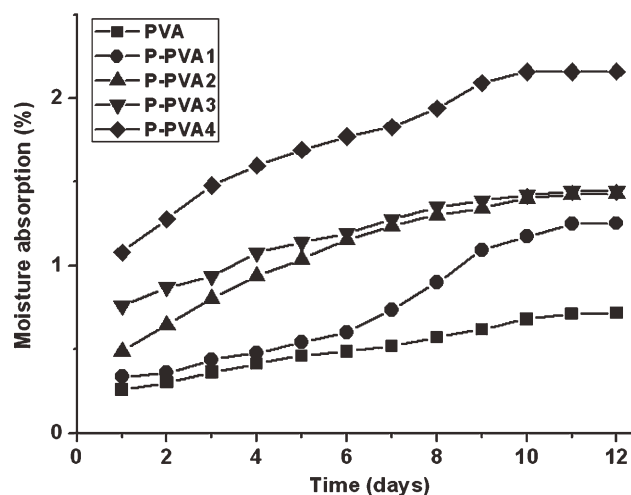
Figure 8 Moisture-absorption behavior of PVA and P-PVA in 50% relative humidity.

The phosphate ester group reduces the number of intramolecular and intermolecular hydrogen bonds, thus leading to a decrease in crystallinity.

Water resistance

The dynamic moisture-absorption measurements of the samples are determined gravimetrically as a function of time. Figures 8 and 9 show the dynamic moisture-absorption measurements data of pure PVA and P-PVA. At both 50 and 100% RH, the moisture absorption (%) of all the samples increases gradually at first, and then level off after 11 days. It can be seen that all the P-PVA samples show higher moisture absorption at room temperature than pure PVA at both 50 and 100% RH, and the moisture absorption of PVA is 0.7% at 12 days and 86% at 11 days. After modification, the moisture absorption increases as the increase of phosphorus loading, i.e., the moisture absorption of P-PVA4 is 2.2 and 153%,
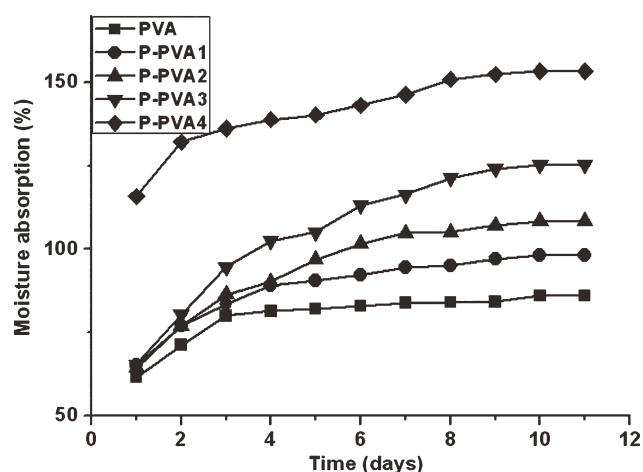

Figure 9 Moisture-absorption behavior of PVA and P-PVA in 100% relative humidity.
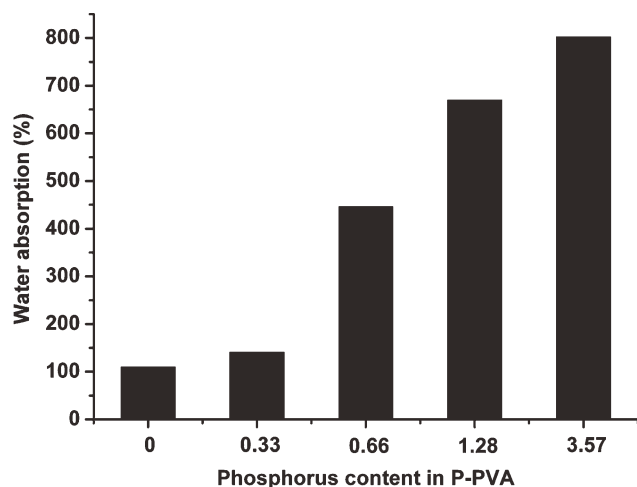
Figure 10 Water-absorption behavior of PVA and P-PVA.

respectively. Figure 10 shows the effects of phosphorus content in PVA matrix on the water absorption capacity of samples. It can be observed that the water absorption capacity of the P-PVA samples is higher than that of the unmodified one and the water absorption capacity of P-PVA samples increases significant with the increase of phosphorus content. As shown in Figure 10, the maximum water absorption of P-PVA4 reaches 803%. The relatively higher water absorption capacity of the P-PVA samples is closely related to those of the aggregation number of molecular chains. Very high degrees of hydrolysis, 98% or more, make the polymer highly crystalline and form strong inter and intra chain hydrogen bonding. The increase in number of hydrophobic groups (phosphate ester) after PVA modified with different contents of DECP, i.e., decrease of degree of hydrolysis, disrupts inter- and intra-chain hydrogen bonding. As a consequence, the water resistance of the P-PVA is much poorer than PVA due to the increase of the degree of hydrogen bonding between the P-PVA chains and water molecules.

CONCLUSIONS

PVA is successfully modified with different contents of DECP. The phosphorylated PVA shows improved thermal stability at high temperature and excellent flame retardance. The residual char of P-PVA containing polyphosphoric or phosphoric acid is formed during the combustion. The crystallinity of P-PVA decreases with increasing phosphorus content. The moisture absorption and mechanical properties of P-PVA are also affected by the phosphorus content. The P-PVA with higher phosphorus content significantly increases the surface hydrophilic character and reduces the water resistance. The P-PVA show a significantly decrease in tensile strength and an increase in elongation at break compared with PVA.

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