Preparation and characterization of cationic poly vinyl alcohol with a low degree of substitution

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Abstract

The cationization of polymers has been regarded as an effective method to improve their performance for various applications. In this work, the cationization of poly vinyl alcohol (PVA) was investigated under different conditions, i.e., various glycidyl-trimethylammonium chloride (GTMAC) to PVA ratios, reaction temperatures, times, PVA and NaOH concentrations and solvent compositions. The results showed that the overall efficiency of the cationic modification was rather low, which was due to the hydrolysis of both GTMAC and cationic-modified PVA (CPVA) under the strong alkaline conditions employed. The results also showed that the optimum GTMAC/PVA ratio depended on the solvent composition. The cationization was confirmed by means of 1H NMR and FTIR analyses. The maximum efficiency in water was obtained under the conditions of 95 °C, 1 h, 0.5 (mol) GTMAC/PVA ratio, and 5% (mol) NaOH concentration, while that in the ethanol/DMSO mixture (1.25 v/v) was obtained under the conditions of 70 °C, 1 h, 0.5 (mol) GTMAC/PVA ratio, and 5% (mol) NaOH concentration. Additionally, the interaction of CPVAs with a silicon wafer (as a substrate) was determined by employing an atomic force microscope (AFM) in water and air.

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1. Introduction

Cationic polymers have been applied in various industries for different purposes. For example, they have been used as strength agents or retention aids in papermaking [1–4]. Copolymerization and grafting have been regarded as useful methods to induce tailored cationic polymers in the literature [1,5].

Although copolymerization is an efficient method to produce the cationic polymers, simultaneously controlling the molecular weight (MW) and charge density of the resulting cationic polymers may be a challenging task, as these properties are interrelated [5]. The copolymerization of vinyl acetate and diallyldimethyl ammonium chloride (DADMAC) was conducted in our previous work to produce cationic PVA (CPVA) [5]. The highest MW of the resulting CPVA was 80,000–90,000. On the other hand, the cationization of already produced polymers on the basis of grafting is a simpler process since the cationization degree can be controlled without any effect on the molecular weight of polymers. The modification of poly vinyl alcohol (PVA) using various chemical agents was reported in the literature [6–9].

In our previous work, the cationic-modified poly vinyl alcohol (CPVA) showed promising results in improving the pulp and paper strength [10,12–14], and the best results were obtained at employing PVA with the molecular weight of 142,000–186,000 [11]. Additionally, it was found that the optimum charge density of CPVA for various fiber systems may be different, varying between 0.3 and 0.72 meq/g, depending on the types of the fiber systems [10,12,13]. Therefore, it is important to understand the influence of parameters affecting the cationization of PVA with a tailored charge density.
In the literature, the cationization of starch and hemi-celluloses were conducted under various conditions, including wet or semi-dried environments [15–18]. The cationization reaction was also conducted in various solvents, e.g., water, ethanol or dimethyl sulfoxide (DMSO) [19,20]. In the cationization reaction, glycyltrimethylammonium chloride (GTMAC) has been commonly used as a cationic reagent [15–20].

An atomic force microscopy (AFM) has been employed as a powerful device to investigate the interactions between various materials [21–23]. This device can be used to determine how the charge of polymers influences their attraction/repulsion force with soft or hard surfaces. In this research, we aimed at understanding the factors influencing the cationization of high MW PVA to induce CPVA with a low charge density (<1 meq/g) under various conditions. The parameters evaluated were: GTMAC/PVA ratio, temperature, time, PVA concentration, solvent composition and NaOH concentration. The cationization of PVA was confirmed qualitatively via FTIR and quantitatively via $^1$H NMR analyses. Based on these results, the conditions that could induce the CPVA with a desired charge density and the maximum cationization efficiency were determined. Moreover, the interaction of CPVA (having a low charge density of 0.2 meq/g or a high charge density of 1.3 meq/g) with a silicon wafer (as a substrate) was determined via employing an AFM in either water and air.

2. Experimental

2.1. Raw materials

Polyvinyl alcohol (PVA) with a molecular weight (MW) of 142,000–186,000 (99% hydrolyzed), glycyltrimethylammonium chloride (GTMAC, 75% in water), potassium bromide (KBr, analytical grade), and dimethyl sulfoxide (99.7%, sterile-filtered), were all obtained from Sigma–Aldrich. Cellulose fibers [21–23]. In this work, similar silicon wafers normally oxidized layer was used as a model substrate for cellulose fibers [21–23]. In this work, similar silicon wafers were first immersed in 98% H$_2$SO$_4$ for 6–8 h and rinsed with deionised and distilled water prior to the use [21–23]. To investigate the interaction of CPVA with the silicon wafers, an atomic force microscope (AFM) Nanoscope Illa, Veeco Instruments Inc., Santa Barbara, CA, was employed. The force analysis was conducted by using silica nitrate probes (NP-S20) with a spring constant of 0.32 N/m, and a resonance frequency of 273 kHz. This silica probes were coated with CPVAs according to the following procedure: at first, the probes were immersed in CPVA solutions (2% wt.) overnight; then, the CPVA-coated probes were washed with deionised and distilled water to remove unadsorbed CPVAs from the probes. The adhesion/repulsion force developed between the CPVA-coated probes and silicon wafers was measured in Picoforce mode with a vendor-supplied fluid cell at the temperature of 25 °C and the pH of 7 in water or in air. Each of 50 different spots was scanned 5 times on an area of $1 \times 1 \mu m^2$ at a constant tip velocity of 0.5 μm/s. The force-distance curves were obtained from cantilever deflection and displacement of the piezo.

2.3. CPVA characterization

To determine the charge density of CPVAs, their solutions (1% wt.) were titrated against a PVSK standard solution (0.5 mM) by using a Particle Charge Detector Müték PCD 03 (Herrsching, Germany). To quantify the degree of substitution of GTMAC with hydroxyl group on cationic-modified PVA (CPVA), CPVAs were dried at 105 °C overnight, and their $^1$H NMR spectrum was recorded in D$_2$O at 25 °C using an Oxford 300 MHz spectrometer operating at 300.13 MHz [8,9].

The unmodified PVA and CPVA with the charge density of 1.08 meq/g, which was prepared under the conditions of 11% (wt.) PVA, 0.5 (mol) GTMAC/PVA ratio, 5% (mol) NaOH concentration (based on PVA), 90 °C, 1 h, were characterized by using a Fourier transform infrared spectroscopy (FTIR) (Perkin Elmer Spectrum 100 FT-IR Spectrometer, USA). The oven-dried PVA or CPVA were embedded in KBr pellets in a mixture of about 1% (wt.) KBr. The spectra were recorded in a transmittance mode in the range 800–3800 cm$^{-1}$.

2.4. AFM analysis

In the literature, the AFM technique was employed to determine the interaction between CPVAs and a hard surface [21–23]. In fact, the silicon wafer with a 100 nm thermally oxidized layer was used as a model substrate for cellulose fibers [21–23]. In this work, similar silicon wafers were first immersed in 98% H$_2$SO$_4$ for 6–8 h and rinsed with deionised and distilled water prior to the use [21–23]. To investigate the interaction of CPVA with the silicon wafers, an atomic force microscope (AFM) Nanoscope Illa, Veeco Instruments Inc., Santa Barbara, CA, was employed. The force analysis was conducted by using silica nitrate probes (NP-S20) with a spring constant of 0.32 N/m, and a resonance frequency of 273 kHz. This silica probes were coated with CPVAs according to the following procedure: at first, the probes were immersed in CPVA solutions (2% wt.) overnight; then, the CPVA-coated probes were washed with deionised and distilled water to remove unadsorbed CPVAs from the probes. The adhesion/repulsion force developed between the CPVA-coated probes and silicon wafers was measured in Picoforce mode with a vendor-supplied fluid cell at the temperature of 25 °C and the pH of 7 in water or in air. Each of 50 different spots was scanned 5 times on an area of $1 \times 1 \mu m^2$ at a constant tip velocity of 0.5 μm/s. The force-distance curves were obtained from cantilever deflection and displacement of the piezo.

3. Results and discussion

3.1. Preparation of cationic PVA

3.1.1. Effect of PVA concentration

Fig. 1 shows the charge density of the CPVA as a function of PVA concentration. As can be seen, by increasing the PVA concentration from 4% to 33% (wt.), the charge density of resulting CPVA increased from 0.22 meq/g to
1 meq/g. In the literature, by increasing the molar ratio of water/GTMAC from 2.8 to 100 (increasing the water content of the system), the cationization efficiency of starch was reduced from 80% to 27% [16]. Also, it was reported that the cationization efficiency of hemicelluloses using GTMAC was generally low, which was attributed to the hydrolysis of both GTMAC and resulting cationic hemicelluloses under strong alkaline conditions [17,24–27]. It was reported that the hydrolysis of GTMAC under an alkaline condition mainly resulted in forming N-(2,3-dihydroxy)propyl-N,N,N-trimethylammonium chloride, and dimer and trimer of GTMAC [15]. We propose that similar hydrolysbs probably occurred in the GTMAC/PVA reaction system, which impaired the cationization efficiency of PVA. The results in Fig. 1 imply that, at a low PVA concentration, the hydrolysis of GTMAC can be more pronounced, which is undesirable and reduces the efficiency of the cationization reaction.

To improve the cationization efficiency, the reaction of PVA with GTMAC was conducted under semi-dried conditions. This method has been utilized for the cationization of hemicelluloses in the past [17]. In one set of experiments, 1 g PVA granule (rather than PVA solutions) was mixed with GTMAC with 2.5 ml of ethanol or with ethanol/water mixture (2.5 v/v) at 65 °C for 1 h (GTMAC/PVA molar ratio of 0.5). The charge density of the resulting CPVAs were 0.23, 0.32 meq/g, respectively. As is well known, the high MW PVA does not dissolve in pure ethanol under the conditions specified above. However, it can dissolve in the ethanol/water mixture. Thus, the former system was heterogeneous, while the latter was homogeneous. It was reported that the efficiency of homogenous cationization reaction of starch (in water) was higher than the heterogeneous reaction (in ethanol) [20]. The higher solubility of starch in water, which favored the cationic reaction between starch and GTMAC, was the main reason for these results [20].

In another set of experiments, 1 g of PVA granule was dissolved in 2 ml DMSO at 65 °C, and then cooled down to room temperature. Subsequently, the PVA solution in DMSO was mixed with 2.5 ml of ethanol and the reaction was conducted at 65 °C for 1 h (GTMAC/PVA molar ratio of 0.5). The resulting CPVA had a charge density of 0.61 meq/g. Thus, compared with the ethanol and ethanol/water solutions, the ethanol/DMSO solution was more effective in producing CPVA with a high charge density. Others have found that the ethanol/DMSO system was more effective than the ethanol and ethanol/water systems when cationizing starch [19,20]. Therefore, the remaining experiments were conducted under the semi-dried condition in the ethanol/DMSO system (1.25 v/v).

3.1.2. Effect of GTMAC/PVA molar ratio

Fig. 2 shows the cationic modification of PVA as a function of GTMAC/PVA molar ratio in water or DMSO/ethanol. Clearly, the highest charge densities of 0.78 meq/g and 1.2 meq/g were obtained at GTMAC/PVA molar ratio of 0.5 in water and 1 in DMSO/ethanol solutions, respectively. In the cationic modification of starch, the GTMAC/PVA molar ratio of 3 was optimum, which was due to the fact that starch has three hydroxyl groups in its repeating unit, which can react with GTMAC [19].

By increasing the molar ratio of GTMAC to PVA, more GTMAC was available for the cationization reaction. However, its hydrolysis would also occur at the same time. These results showed that, by increasing the molar ratio of GTMAC/PVA more than 0.5 in water or 1 in the ethanol/DMSO mixture, more hydrolysis of GTMAC took place under the alkaline conditions studied, which reduced the efficiency of the cationization [17,24–26]. Furthermore, a higher charge density was obtained in the ethanol/DMSO mixture at 70 °C than in water at 80 °C, under otherwise the same conditions.

3.1.3. Effect of reaction temperature

Fig. 3 shows the charge density of the cationic-modified PVA as a function of the reaction temperature in water or in the DMSO/ethanol solution. Interestingly, by increasing the reaction temperature from 60 °C to 95 °C, the charge density of resulting CPVA was significantly increased in water, which implied that a higher temperature favored the cationization of PVA. However, a maximum charge density of 1.2 meq/g was achieved at 70 °C for the cationization in the ethanol/DMSO solution. Further increasing the temperature resulted in a decrease in the charge density of CPVA in the ethanol/DMSO mixture. This behavior is probably due to the evaporation of ethanol from the ethanol/DMSO solution. In the literature, the cationization efficiency of starch was lower in a pure DMSO solution than that in the ethanol/DMSO solution [20].

3.1.4. Effect of reaction time

Fig. 4 shows the charge density of the CPVA as a function of the reaction time. Clearly, the maximum charge density of 0.80 meq/g was obtained at 1 h in water. By extending the reaction time, the charge density of CPVA in water was reduced. A similar trend was reported for the cationization of hemicellulloses [17]. However, the maximum charge density of 0.9 meq/g was obtained in the ethanol/DMSO solution after 1 h, and the further prolonging of the reaction had a marginal effect on the cationization effi-
Fig. 2. Effect of GTMAC/PVA molar ratio on the charge density CPVA, [NaOH] = 5% (mol), 1 h, (in water: [PVA] = 11%, 80 °C; in ethanol/DMSO (1.25 (v/v)), 70 °C).

Fig. 3. Effect of reaction temperature on the charge density CPVA at [NaOH] = 5% (mol) for 1 h. (in water: [PVA] = 11%, GTMAC/PVA molar ratio = 0.5; in ethanol/DMSO (1.25 v/v): GTMAC/PVA molar ratio = 1).

Fig. 4. Effect of reaction time on the charge density of CPVA, GTMAC/PVA molar ratio = 0.5, and [NaOH] = 5% (mol) (in water: [PVA] = 11%, 80 °C; in ethanol/ DMSO (1.25 v/v), 70 °C).
ciency. It was reported that, by prolonging the reaction time, the hydrolysis of cationic hemicelluloses was enhanced, which reduced the efficiency of the reaction between GTMAC and hemicelluloses [17,23]. A similar phenomenon probably happened here by prolonging the reaction time for GTMAC and PVA system in water. However, the occurrence of side reactions was less in the ethanol/DMSO solution, as shown in Fig. 4.

3.1.5. Effect of NaOH

Fig. 5 shows the charge density of CPVA as a function of the NaOH concentration. As can be seen, the charge density was the maximum via adding NaOH up to 5% (mol), regardless of the solution media. A similar result was reported by Wang and Xie on the cationization of corn starch [19]. Additionally, it was reported that NaOH functioned as a catalyst for the cationization of hemicelluloses and the hydrolysis of GTMAC [15,19]. Thus, the concentration of NaOH in solutions should be sufficient to promote the main cationization reaction. However, excessive amount of NaOH would result in more extensive GTMAC and CPVA hydrolyses. The results in Fig. 5 show that the maximum of 5% (mol) was sufficient to obtain the maximum cationization efficiency, regardless of the cationization medium.

3.2. Characterization of CPVA

The reaction scheme of GTMAC with PVA was reported in our previous work [10]. Fig. 6 shows the ¹H NMR spectrum of CPVA. The peak at 3.2 ppm belongs to protons attached to the quaternary ammonium group of the PVA backbone, which confirmed the cationic modification of PVA [7]. The peak at 4 ppm is assigned to the CH₃ of the PVA backbone, while the peaks between 3.2 and 3.8 ppm are due to the CH₂ of the attached cationic group on the PVA backbone. Also, the peaks between 1.5–2 ppm belong to CH of the PVA backbone. The degree of substitution can be quantified by considering the areas under the peaks at 3.2 and 4 ppm and the number of protons associated with each peak, which is 4.9% (mol) for the CPVA studied in Fig. 6. The charge density of this CPVA can be theoretically calculated by considering the degree of substitution via the ¹H NMR analysis and assuming that each quaternary mol of ammonium groups attached to PVA backbone has a charge density of 1 eq. The charge density of the CPVA via this ¹H NMR analysis was 0.99 meq/g, which is in a good agreement with that of 1.08 meq/g obtained via the PCD analysis.

The efficiency of the cationic modification can be determined based on the degree of substitution analysis of ¹H NMR. In this respect, the efficiency is identified by considering the amount of GTMAC added to the system for the cationic reaction and the amount of GTMAC attached to the backbone of resulting CPVA. For the CPVA investigated in Fig. 6, the amount of GTMAC added was 0.5 mol (per mole of PVA) and the amount of GTMAC attached to PVA backbone was 0.049 mol (per mol of PVA), which implied that the efficiency was about 10%. A similar analysis was conducted on the other CPVAs produced, and the maximum efficiency obtained in water was about 12% under the conditions of 95 °C, 1 h, GTMAC/PVA molar ratio of 0.5 (mol), and the NaOH concentration of 5% (mol). The maximum efficiency in the ethanol/DMSO mixture was about 10% under the conditions of ethanol/DMSO (1.25 v/v), 70 °C, 1 h, GTMAC/PVA molar ratio of 0.5, and NaOH concentration of 5% (mol). The rather low efficiency is due to the occurrence of the side reactions, as discussed earlier. The cationic modification of PVA or hemicelluloses using other cationic agents was also reported to be less than 10% [7,24,27]. The results in Figs. 2 and 3 also shows that the maximum charge density of CPVA was approximately 1.2 meq/g, regardless of the solvent composition; while the reaction efficiency was higher in ethanol/DMSO system than in water system at any GTMAC/PVA molar ratio studied (Fig. 2).

Fig. 7 shows the FTIR spectrum of unmodified PVA and the CPVA sample investigated in Fig. 6. A similar spectrum was reported for unmodified PVA in the litera-
The peak at 2850–3000 cm$^{-1}$ is assigned to C–H broad alkyl stretching band, 3600–3650 cm$^{-1}$ to –OH stretching band, and 3200–3570 cm$^{-1}$ to hydrogen bonding of the PVA molecule. The peak at 1090–1150 cm$^{-1}$ is assigned to C–O band [30]. An increase in the intensity of the absorbance at 1044 cm$^{-1}$ of CPVA (C–O–C bond) provides the evidence of the ether linkages between GTMAC and PVA [24]. Additionally, an increase was observed on the intensity of the absorption at 1462 cm$^{-1}$, which could be assigned to CH$_2$ bending and methyl groups of the GTMAC, which is now a part of the resulting CPVA [24,31].
3.3. Adhesion/repulsion force

Fig. 8 shows the adhesion force developed between the CPVA-coated AFM-probe and the silicon wafer in water. Interestingly, the adhesion force (−1.5 mN/m) developed for the CPVA having a charge density of 1.3 meq/g, was higher than that (−0.2 mN/m) for the CPVA having a charge density of 0.2 meq/g. A similar adhesion force (−1 mN/m) has been reported between the AFM-probe, coated with cationic starch having a charge density of 0.5 meq/g, and a silicon wafer \[32,33\]. In contrast, a marginal interaction between the uncoated AFM-probe and the wafer was observed either in water or air.

Fig. 9 shows the adhesion/repulsion force developed between the AFM-probes, coated with the same CPVAs, and the silicon wafer in air. The adhesion force for the CPVA with a charge density of 1.3 meq/g was strong (−70 mN/m), while the adhesion force for the CPVA having a charge density of 0.2 meq/g was weak (−15 mN/m). From the results of Figs. 8 and 9, it can be inferred that the interaction between the CPVAs and oppositely charged surfaces (silicon wafers) is more significant in air than that in water, which may be due to the fact that the water molecules can screen some of the charges of CPVAs in aqueous solutions \[34\].

In the above AFM force analysis, the approaching phase of the CPVA-coated AFM probe to the silicon wafer resembles the approaching of CPVA segment to a hard/soft surface for adsorption. Therefore, the attraction/repulsion force simulates the interaction of the CPVA with the surfaces \[12\]. The results show that the CPVA with a high charge density (1.3 meq/g) has a higher affinity for the
adsorption compared with the CPVA with a low charge density (0.2 meq/g).

4. Conclusions

In this work, the PVA cationization efficiency was determined as functions of a number of process parameters. The results showed that the overall efficiency of the cationization was rather low, which was due to the hydrolysis of GTMAC and CPVA under the strong alkaline environment. The optimum GTMAC/CPVA molar ratio was 0.5 in water and 1 in the ethanol/DMSO mixture (1.25 v/v). The maximum charge density was obtained after 1 h and a further extension of the reaction time reduced the charge density of CPVA. The maximum efficiency in water was obtained under the conditions of 95 °C, 1 h, GTMAC/CPVA molar ratio of 0.5, and 5% (mol) NaOH concentration; while that in the ethanol/DMSO mixture was obtained under the conditions of 70 °C, 1 h, GTMAC/CPVA molar ratio of 0.5, and 5% (mol) NaOH concentration. Additionally, the attraction force developed between a silicon wafer and the AFM-probe coated with CPVA having a charge density of 1.3 meq/g was larger than that developed between the silicon wafer and the AFM-probe coated with CPVA having a charge density of 0.2 meq/g. The attraction force was significantly higher in air than in water under otherwise the same conditions.

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