Removal of Sodium Acetate in Poly(Vinyl Alcohol) and its Quantification by ^{1}H NMR Spectroscopy

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ABSTRACT: A major impurity in poly (vinyl alcohol) (PVA) is sodium acetate which remains after its preparation by a base catalyzed hydrolysis of poly(vinyl acetate), and the amount of sodium acetate in commercial PVA samples may reach several percentages. To establish an optimal condition for the removal of sodium acetate, several washing parameters such as washing period, solvent polarity, and temperature were investigated in this study. Nuclear magnetic resonance (NMR) spectroscopy was successfully applied to determine the residual amounts of sodium acetate in the purified poly(vinyl alcohol). The relative integral value for the methyl peak of sodium acetate in PVA was converted to a relative mass value and finally to the sodium acetate content contained in PVA. The results showed that over 95% of sodium acetate in PVA was removed by a washing of PVA with distilled water within 2 h. When methanol was used as a washing solvent, a higher temperature than room temperature was required for an effective removal of sodium acetate. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 3179–3183, 2008

Key words: NMR; poly(vinyl alcohol); sodium acetate; quantification

INTRODUCTION

PVA, a water soluble synthetic polymer contains many hydroxyl groups on the hydrocarbon polymer backbone. It has been widely used in a wide range of industrial, medical, and food applications. Since PVA is susceptible to a biodegradation by several microorganisms via an enzymatic process, its application for industrial and commercial purposes is currently increasing.[1] Recently, PVA has also been extensively studied for a wide variety of biomedical and pharmaceutical applications due to its low toxicity and easy formation of a hydrogel network.[2,3] For these bio-related applications, PVA should have low impurities and residual solvent levels to ensure its safety.

A major impurity in PVA is sodium acetate which remains after its preparation by a base catalyzed hydrolysis of poly(vinyl acetate) (Fig. 1). The amount of sodium acetate in commercial PVA samples may reach several percentages.[4] It is known that the presence of sodium acetate in PVA accelerates its thermal degradation during a heating period, which requires careful attention during the production of PVA fibers or blending materials at higher temperatures. This thermal degradation occurs through a dehydration of PVA and a subsequent polyene formation and oxidation process.[4] Generally, ash content (%) is marked on the commercial PVA bottles rather than the sodium acetate content. The ash content is calculated by measuring the ignition residue of PVA and the major component of the ash is sodium oxide (Na_2O) resulting from the oxidation of an ash precursor, sodium acetate.

Several purification procedures such as washing with solvents (generally, water),[5] ion-exchange resin treatments,[6] and recrystallizations[7] have been used to reduce impurities, more specifically sodium acetate content in PVA. Each method has its own advantages and disadvantages in terms of costs, effectiveness, and specific applications. Among these methods, washing with solvents could be the most convenient procedure to be applied in a laboratory. However, as far as we are aware, no systematic studies for an efficient PVA washing, along with suitable quantitative analysis techniques for the residual sodium acetate remaining in PVA have been reported in the literature.

NMR spectroscopy has been widely utilized to provide the structural information of chemically modified PVA polymers,[8,9] and the crystallinity and dynamic study of PVA in a gel state.[10,11] Because

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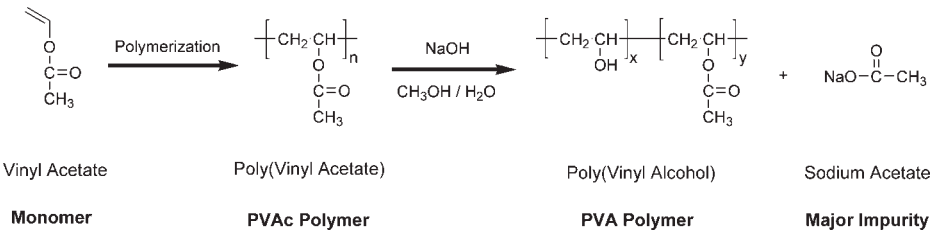

Figure 1 General procedure for the PVA preparation via base catalyzed hydrolysis.

^{1}H NMR spectroscopy requires a few milligrams of sample and a few minutes to provide reliable spectral data, it could be very useful in a quantification of sodium acetate content in a large number of PVA samples as long as the sodium acetate peak is not overlapped with other peaks. Such advantages over other analytical methods such as an infrared spectroscopy and titration motivated us to apply ^{1}H NMR spectroscopy to quantify the amounts of residual sodium acetate in PVA. In this article, several washing parameters such as washing period, solvent polarity, and temperature were varied in order to study the effects of these parameters and establish the optimal washing condition for a sodium acetate removal.

EXPERIMENTAL

Materials

PVA polymers were purchased from Aldrich Chemical Company (St. Louis, MO, USA, M_w 85,000–124,000, 99+% hydrolyzed, ash content maximum 1.2%). High graded solvents such as methanol (99.6%, 0.3% H_2O), absolute ethanol (99.5%, 0.1% H_2O), and acetone (99.5%, 0.3% H_2O) were obtained from commercial suppliers and used as washing solvents without any further purification.

PVA purification methods

For the removal of sodium acetate in PVA, 5.00 g of PVA resin was added to 25 mL of washing solvent in a vial and the mixture was stirred with a magnetic bar at a given temperature. At a selected time, the washing solvent in the mixture was exchanged to fresh solvent via two decantations and then one scoop of PVA slurry (ca. 300 mg) was saved for ^{1}H NMR analysis. The washing, solvent exchange, and sampling process were repeated until the given washing period. The collected PVA samples were placed in 60°C oven for at least 4 days to obtain dried PVA samples and utilized for ^{1}H NMR analysis.

For the recrystallization of PVA, 0.2 g of PVA was dissolved in 10 mL of distilled water at 100°C in an oven. The solution was cooled at room temperature and to 50 mL of acetone was added. The recrystallized PVA was dried at 60°C in an oven and then subjected to ^{1}H NMR spectroscopy. This recrystallization process was repeated one more time to obtain a 2nd purified PVA.

^{1}H NMR and IR spectroscopy

NMR spectroscopy (JEOL, 500 MHz for ^{1}H NMR) was used as a main tool for a quantitative analysis of the residual sodium acetate content in the washed PVA samples. About 7 mg of PVA sample was dissolved in 0.7 mL D_2O at 100°C oven for 2 h for NMR spectroscopy. During each ^{1}H NMR acquisition, relaxation time and the number of scans were fixed at 5 and 32 s, respectively. A typical PVA NMR spectrum shows a sharp single peak for sodium acetate (CH_3 at 1.75 ppm) and broad multiplets for PVA (CH_2 at 1.4–1.7 ppm, CH at 3.8–4.0 ppm). The relative integral value for the methyl peak of sodium acetate was obtained on the basis of the integral value for the methylene of PVA. Sodium acetate content (%) in PVA based on the ^{1}H NMR integral values was calculated by eq. (1). M_{NaOAc} and M_{PVA} represent the relative mass of sodium acetate and PVA repeating unit respectively and can be obtained by eqs. (2) and (3). I_{NaOAc} and I_{PVA} represent the integral value for the methyl peak of sodium acetate and the methylene peak of PVA respectively.

$$\text{Sodium acetate content (\%)} = (M_{\mathrm{NaOAc}}/M_{\mathrm{NaOAc}} + M_{\mathrm{PVA}}) \times 100 \quad (1)$$

$$M_{\mathrm{NaOAc}} = (I_{\mathrm{NaOAc}}/3) \times 82 \text{ g/mol} \quad (2)$$

$$M_{\mathrm{PVA}} = (I_{\mathrm{PVA}}/2) \times 44 \text{ g/mol} \quad (3)$$

IR spectra of PVA were obtained by using FTIR spectrometer Tensor-37 (Brucker, Germany). IR sample was prepared with KBr and the absorption band of the sodium acetate anion in PVA was observed at 1575 cm^{-1}.[4]

Titration with HCl

About 5.00 g of PVA was dissolved in 150 mL of distilled water by incubating the solution at 100°C in

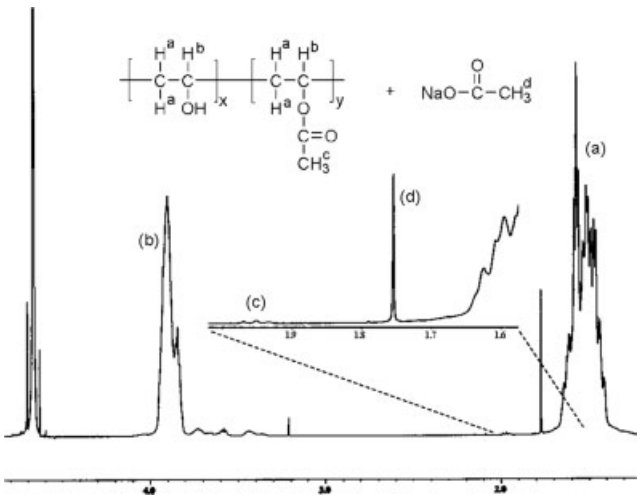

Figure 2 A typical ^{1}H NMR spectrum of PVA in D_2O.

an oven for 4 h. Methylene blue and methyl yellow (each 0.1% conc. in ethanol) solutions were mixed at a 1 : 1 ratio and the mixed indicator was added dropwise to the PVA solution until a light green color appeared. The 0.02*N* HCl was slowly added to the PVA solution until the light green color became reddish orange. For the blank test, 150 mL of distilled water with the mixed indicator was titrated with 0.02*N* HCl. Sodium acetate content (%) in PVA based on the titration was calculated by eq. (4). *A* represents the 0.02*N* HCl volume needed for the titration of PVA solution and *B* represents the 0.02*N* HCl volume needed for the blank test, respectively. *S* stands for the weight of the PVA added to the solution.

$$\text{Sodium acetate content (\%)} = [0.00164 \times (A - B)/S] \times 100 \quad (4)$$

RESULTS AND DISCUSSION

^{1}H NMR spectrum analysis of sodium acetate contained in PVA

A typical ^{1}H NMR spectrum of PVA in D_2O is illustrated in Figure 2. The two broad multiplets at 1.4–1.7 ppm and 3.8–4.0 ppm correspond to PVA polymer hydrocarbon backbone ($-CH_2-CH(OH)-)_n$. A hydroxyl peak of PVA was not shown in this spectrum because a deuterium exchange occurred to produce —OD in D_2O solvent. Instead, a peak resulting from HOD appeared at 4.7 ppm. Methyl peak of sodium acetate (CH_3CO_2Na) in PVA appeared at 1.75 ppm, as a sharp singlet. To verify the methyl peak of sodium acetate in the spectrum, additional sodium acetate was added to PVA sample and the resulting ^{1}H NMR spectrum showed an increase of the peak intensity. In the case where acetic acid was added to the PVA sample, a new methyl peak of acetic acid (CH_3COOH) appeared at 2.0 ppm, suggesting that no significant amount of acetic acid was present in PVA. Small triplet-like peak at 1.95 ppm was verified as a methyl peak of unhydrolyzed acetate on PVA polymer backbone by comparing it with the peak of an 80% hydrolyzed PVA sample.

Because the methyl peak of sodium acetate in PVA sample is isolated far enough apart from the other peaks, it can be easily used for a quantification of the sodium acetate content in PVA by comparing it with the hydrogen integral value of PVA repeating unit. The obtained relative integral value for the methyl peak of sodium acetate was then converted to a relative mass value and finally to sodium acetate content present in PVA as described in a previous experimental section. To obtain more reliable data, at least three ^{1}H NMR spectra per each PVA sample were taken and the averaged integral values of the peaks were used to obtain the sodium acetate content in the PVA. Another possible way to obtain reliable data is to use a large amount of PVA sample dissolved in a large volume of D_2O during NMR sampling process, but we excluded this process since the procedure is inefficient and generates large volume of waste.

Removal of sodium acetate in PVA

^{1}H NMR spectra in Figure 3 indicates that the methyl peaks of sodium acetate in PVA decrease as the washing time increases. The correlation graph for the washing time and sodium acetate content (%) obtained by ^{1}H NMR spectroscopy shows a very fast reduction of sodium acetate content within 1 h followed by a slow decrease over the remaining washing periods. In this experiment, over 95% of the

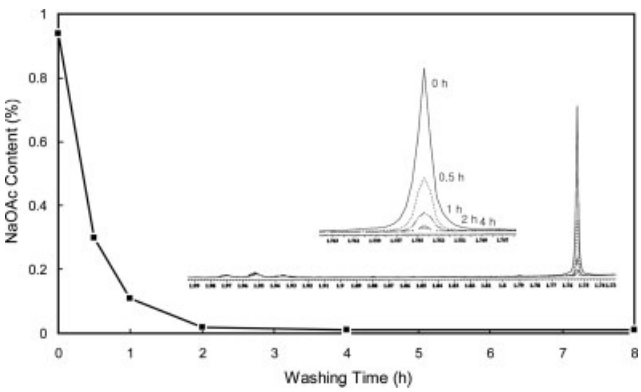

Figure 3 The sodium acetate ^{1}H NMR peak intensity and content (%) changes according to washing time with distilled water.

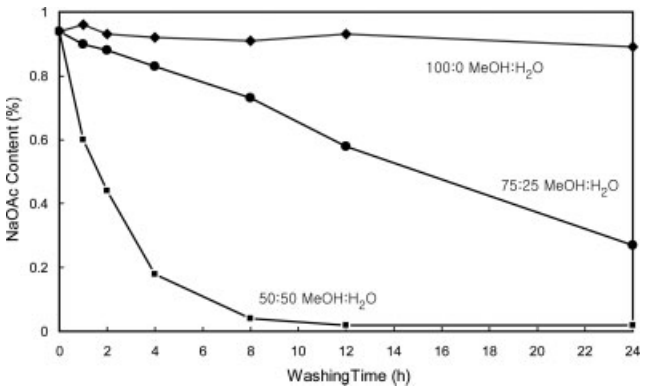

Figure 4 The sodium acetate content (%) changes according to washing time with methanol and methanol–water mixture.

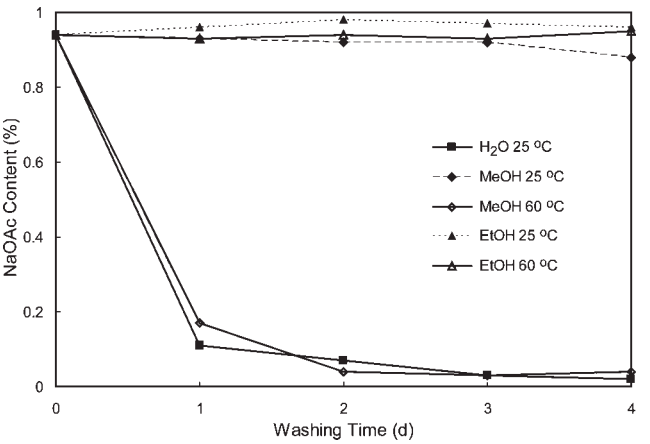

Figure 5 Temperature and washing solvent dependencies of sodium acetate content (%) in PVA.

sodium acetate in PVA was removed by washing it with distilled water within 2 h.

Figure 4 shows the degree of a sodium acetate removal when methanol and methanol–water mixtures are used for washing PVA at room temperature. No significant removal of sodium acetate was observed when pure methanol used as a washing solvent at room temperature. This figure also shows that the removal rate of sodium acetate becomes faster as the water content ratio increases. This behavior can be explained by two physical factors; higher solubility of sodium acetate and the swellability of PVA in a higher water content solvent. PVA used in this experiment has a relatively high molecular weight and over 99% degree of hydrolysis. Such PVA forms a relatively strong crystalline microstructure which retards dissolution of PVA in water. However, some of PVA with a loose crystal structure owing to a low molecular weight and/or low degree of hydrolysis can be more easily dissolved in water. To efficiently remove the sodium acetate in such a high water soluble PVA without a loss of PVA into the solvent, an increase of methanol content in washing solvent would be beneficial.

The degree of sodium acetate removal was also investigated with four different solvents (water, methanol, ethanol, and acetone) and at two temperatures (room temperature and 60°C) (Fig. 5). Large temperature dependency was observed when PVA was treated with methanol as shown in Figure 5. At room temperature sodium acetate content in PVA was not changed for 4 days when methanol used as a washing solvent. However, the washing experiment performed with methanol at 60°C shows a relatively fast reduction rate of sodium acetate content, which is somewhat similar to the reduction rate by a washing with water at room temperature. In the cases of ethanol and acetone, no significant sodium acetate removal was observed even at 60°C due to their lower polarities than methanol and water (acetone data is omitted in this figure for clarity). When the PVA was washed in water at 60°C, the solution became a very viscous gel within 20 min, therefore no more washing experiments with water were performed at this temperature.

Sodium acetate quantification data obtained from ^{1}H NMR integral values were compared with the data from the acid–base titration in Figure 6. Large discrepancy between the two methods was observed, especially at a low sodium acetate content region (less than 0.3% sodium acetate based on ^{1}H NMR). In fact, it was difficult to determine the endpoint during titration since sharp color change couldn't be easily observed due to the low concentration of sodium acetate and the turbidity of PVA solution. We also prepared the blank solution without PVA on the basis of the assumption that the presence of PVA in sample solution does not alter the endpoint of a sodium acetate titration by interfering with a color change of the indicator during a titration. However, if PVA does affect the endpoint, it will produce inac-

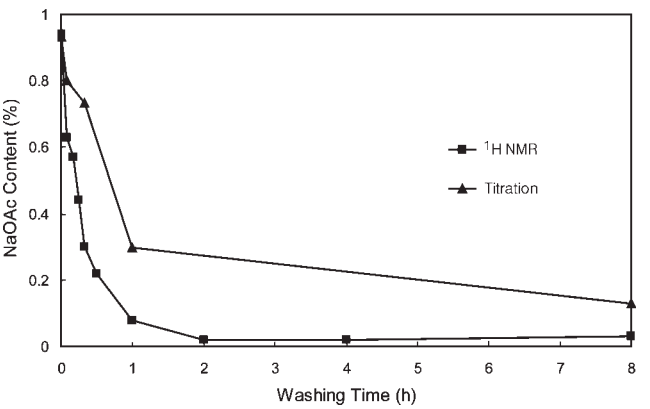

Figure 6 Comparison of sodium acetate content values (%) obtained from ^{1}H NMR integral values and acid–base titration.

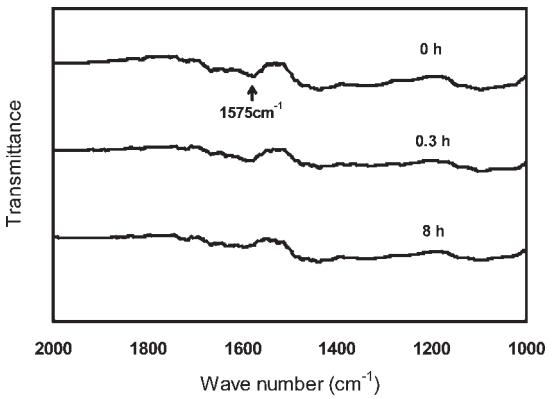

Figure 7 IR spectra of PVA containing different sodium acetate content.

curate results especially when a low level of sodium acetate is present. Therefore, the large discrepancy of sodium acetate content observed between 20 min and 8-h washing time is considered due to the blank solution prepared without PVA, and difficulties of determining endpoint during titration. We strongly believe that the quantification of sodium acetate in PVA utilizing ^{1}H NMR spectroscopy gives more accurate data especially when sodium acetate content in PVA is low as indicated in Figure 6.

IR spectra of raw and washed PVA with water are shown in Figure 7. Even raw PVA (0.94% sodium acetate) shows a fairly small absorption band of sodium acetate anion at 1575 cm^{-1}. Therefore, a decrease of the peak intensity according to a sodium acetate content reduction cannot be clearly observed with the IR spectra.

The purification of PVA via a recrystallization process was also conducted as described in the literature[7] and the residual sodium acetate content (%) in PVA was calculated by using ^{1}H NMR spectroscopy as described earlier. First recrystallization in water/acetone combination produced 0.10% sodium acetate content in PVA, which is equivalent with the residual sodium acetate content obtained after 1 h washing with water as shown in Figure 3. The subsequent second recrystallization produced 0.05% sodium acetate content; that is, less amount of sodium acetate remaining after 2 h washing process. These results from our experiments indicate that this washing process more effectively removes the residual sodium acetate in PVA than the recrystallization does. Furthermore, the recrystallized process generates organic wastes and also causes significant loss of PVA sample when compared with washing process (about 10 wt % of the recrystalized PVA was recovered after two rescrystallizations in this study while over 90 wt % of the washed PVA was recovered after 8-h washing with water at room temperature).

CONCLUSIONS

In this article, we demonstrated a reliable quantitative analysis method by utilizing ^{1}H NMR spectroscopy to measure the residual sodium acetate content in PVA. Sodium acetate removal efficiencies according to washing period, solvent polarity, and temperature were investigated. The results showed that over 95% of sodium acetate in PVA was removed by a washing of PVA with distilled water within 2 h. When methanol was used for a washing solvent, higher temperature than room temperature was required for an effective removal of sodium acetate. Quantitative analysis using ^{1}H NMR spectroscopy for sodium acetate content in PVA was proven to be more effective than other methods such as an IR spectroscopy and titration in this study.

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