ORIGINAL ARTICLE

Effect of ultrasound on the aqueous viscosity of several water-soluble polymers

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The effect of ultrasound (US) on the shear viscosity of water-soluble polymers, polyvinyl alcohol, polyethylene glycol and polyacrylic acid, was studied in aqueous solutions with US exposure of 23, 43, 96 and 141 kHz for an 8.5–9 W US. The US exposure significantly decreased the shear viscosity of the solutions in this order: 43 > 23 > 96 > 141 kHz. When US exposure was stopped, the shear viscosities of the aqueous polymer solutions reverted to their original values. US stimulation during the decrease in viscosity was supported by the ultrasonic power transmitted through the aqueous polymer solution. In addition, Fourier-transform infrared spectra obtained during US exposure showed that hydrogen bonds in the aqueous polymer solution could be broken, especially at 43 kHz. We concluded that US exposure influenced hydrogen-bond interactions between the OH groups of the polymer and water molecules in the aqueous medium. This finding was supported by US absorption of the aqueous polymer solution in the transmittance model, which shows the US absorptivity, ϵ_{US} , for each polymer system.

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INTRODUCTION

Ultrasound (US) has been widely applied in different fields, such as medicine, engineering and biology.¹ Because of the advantages of US, it is widely used in sono-chemical processes^{2,3} as well as in food engineering and separation processes.^{4,5} Smart materials responded when external stimuli, such as heat, light or magnetic fields, were applied.⁶ However, few studies of US have demonstrated the ability of external stimuli to change material properties. Recently, it was reported that US could be used as a new type of trigger in the drug delivery of polymeric composite materials. In these cases, a low US frequency was applied to encapsulate drugs, and the hydrophilicity and high permeability of the materials improved the penetration of water.^{7,8} In our previous works, copolymer microgels of *N*-isopropylacrylamide and acrylic acid using methylenebisacrylamide as a cross-linker demonstrated US-responsive behavior in spherical polymer microgels.^{9,10} In addition, a significant change in the shear viscosity was observed in Al₂O₃/polyacrylic acid (PAA) slurry,¹¹ and similar behavior was observed in *N*-isopropylacrylamide copolymers with PAA in aqueous media¹² and carrageenans.¹³ These variations were explained by the breaking of polymeric hydrogen bonds in the microenvironment when US exposure was performed in aqueous medium.

Regarding the changes in shear viscosity during US exposure, US absorption might induce polymer changes, particularly those related to hydrogen-bonded species in the aqueous polymers used. It was reported that ultrasonic adsorption to polymeric medium was

evaluated by absorption coefficients, sound velocities and viscosity, for different nonionic and ionic polymer solutions, such as polyethylene glycol (PEG), polyvinyl alcohol (PVA) and PAA, at high frequencies of 2–130 MHz.^{14–18} However, no results for US using lower frequencies have been reported.

Nevertheless, water-soluble polymers possessing different chemical structures for PEG, PVA and PAA are widely used in different industries. These polymers are generally used as stabilizers for aqueous colloidal suspensions, and their properties in aqueous media are strongly related to the viscosity of their aqueous media.^{19–24} Therefore, if the viscosity could be controlled by US, such a technology would possess quite an effective advantage. However, the effect of US in polymer systems has not been well characterized when lower US frequencies are used. The present study, therefore, investigated the shear viscosity properties of the aqueous polymers of PVA, PEG and PAA as a function of ultrasonication at various low frequencies: 23, 43, 96 and 141 kHz. In addition, the effects of US in aqueous solutions were studied using a US absorption model and were also observed using Fourier-transform infrared (FT-IR) spectroscopy in aqueous solutions. It was concluded that absorption of US altered hydrogen bonding in the aqueous solution.

EXPERIMENTAL PROCEDURE

Materials and preparation of sample solution

Water-soluble polymers, PEG, PVA and PAA, were purchased from Sigma Aldrich Co., St Louis, MO, USA. The molecular weight of PEG was

Scheme 1 US experimental setup for measuring the shear viscosity in polymer solutions.

100 000 Mw; the molecular weight of PVA was 146 000–186 000 Mw, with a degree of hydrolysis of approximately 86–88%; and the molecular weight of PAA was 450 000 Mw. An aqueous solution with a 10 wt% concentration for each polymer was prepared in distilled water and then purified using an ion exchange column. The polymer solutions were heated for 2 h to allow for full dissolution at 60 °C. The transparent solutions obtained were slowly cooled at room temperature and stored at that temperature for 1 day to allow for settling and to eliminate air bubbles.

Shear viscosity measurements of the water-soluble polymers

A sonoreactor device (HSR-305; Honda Electronics Co. Ltd., Toyohashi, Aichi, Japan) was used for the experiments (Scheme 1). The sonoreactor could be operated at four frequencies: 23, 43, 96 and 141 kHz. A calorimetric study was also performed to calculate the US power dissipated in the water bath.^{25,26} The power dissipated into the aqueous solution was between 8.5 and 9 W. The measurement setup, as shown in Scheme 1, includes a Brookfield rotating viscometer (Tokyo Keiki Inc., Ohta-Ku, Tokyo, Japan) to measure the shear viscosity of the aqueous solutions. The sonoreactor temperature was fixed at 25 °C for all experiments by flowing water through the sonoreactor. It was confirmed that no increase in temperature was detected during the experiments. The shear viscosity was measured both before and after US exposure. The viscosity was measured with a No. 2 rotor. The viscous solution was put into a cylindrical glass vessel with a diameter of 40 mm and height of 120 mm and was placed in the US sonoreactor. The sample solution was exposed to US for 5 min at each frequency. The shear viscosity was measured at 1-min intervals.

Measurements of the US effect on the FT-IR spectra of the aqueous solutions

FT-IR spectroscopy is a useful technique to examine the hydrogen bonding of polymeric materials. Accordingly, the US effect on chemical changes in water-soluble polymer solutions was analyzed by FT-IR spectroscopy, which was measured using an FT-IR 4100 series spectrometer (Jasco Corp., Hachioji Tokyo, Japan). Aqueous polymer solutions with a concentration of 10 wt% were lightly dropped onto a CaF₂ window (30 mm diameter, 2 mm thickness; Pier Optics Co. Ltd., Tatebayashi, Gunma, Japan). Another window was placed on top to cover the drop of solution, which formed a thin layer between the plates. To prevent penetration of water into the sample window, when being placed into the US water bath, the CaF₂ windows were sealed with parafilm. The windows had no effect on polymer adsorption and no influence on the resulting FT-IR spectra. All experiments were performed three times and were shown to have similar results within an experiment. The FT-IR spectra were measured immediately using absorbance mode following 1, 3 and 5 min of US exposure. For the FT-IR spectra, spectral analysis of the OH and CH stretching bands was deconvoluted using a method similar to that in our previous report, and these stretching bands ranged from 2400 to 3800 cm⁻¹ for PAA and from 3000 to 3800 cm⁻¹ for both PEG and PVA.¹³ When the centers of the fixed peaks of the original OH and CH stretching bands were determined in the spectral data, their bands were decomposed into Gaussian components with

peak centers, and the curve was then fitted using OriginPro 8.5.1 (LightStone Corporation, Tokyo, Japan).

RESULTS AND DISCUSSION

Effect of USs on the shear viscosity of water-soluble polymers

The shear viscosity of the aqueous polymer solutions was measured after US exposure at 8.5–9 W for 5 min, after which time ultrasonication was stopped and the shear viscosity was measured at 1-min intervals. Figure 1 shows the change in shear viscosity as a function of time for each aqueous solution of (a) PEG, (b) PVA and (c) PAA at pH 3, (d) PAA at pH 5 and (e) PAA at pH 10. Here PAA solutions were prepared at three pH values, 3, 5 and 10, because the extent of dissociation of the –COOH group of PAA depends on the pH. The concentration of each polymer was fixed at 10 wt% for the viscosity measurements. As observed previously, the shear viscosity apparently decreased from the original values following US exposure in each case. When the viscosity returned to its original value, each sample was exposed to US a second time for 5 min. It was noted that the change in the shear viscosity during the second cycle appeared similar to that during the first cycle. Therefore, these results indicated that the US exposure could respond to the change in the shear viscosity. The results also indicated that the change in the shear viscosity was caused by the US stimulus, which was used as a trigger to induce a change in shear viscosity. Overall, the 43-kHz frequency was the most effective stimulus for the shear viscosity comparison with the other frequencies. The decrease in the shear viscosity occurred in increasing order of 43 > 23 > 96 > 141 kHz. It would be interesting to consider that the comparison of the chemical structures of each polymer is made based on the viscosity change due to US. For the 43-kHz sample, the PEG solution before US exposure was 543 cp and after US exposure changed to 474 cp. For the PVA solution, a change in viscosity was observed from 1690 to 1260 cp, following US exposure. For PAA, a change was observed from 785 to 725 cp at pH 3 and from 1740 to 1550 cp at pH 5. When the shear viscosity was measured at pH 10 for the PAA solution, a value of 2320 cp indicated that no change occurred in the shear viscosity upon US exposure. The polymer condition at pH 10 could be explained by the presence of electrostatic repulsions between the COO⁻ groups of PAA, thus leading to a higher viscosity than the other samples at pH 3 and 5. Therefore, the PAA polymer chains were considered to be more extended and to have fewer hydrogen bonds at pH 10.

Effect of US absorption on the aqueous polymer medium

Because these changes in the shear viscosity due to US were observed in aqueous solutions of polymers with different chemical structures, the US intensity was monitored both before and after transmittance of the US through the sample solution to analyze US absorption by the aqueous polymer solutions. Here the transmittance of US through the aqueous solution was investigated using a US detector to measure US intensity. Thus, the US intensity was attenuated from I_0 to I_{US} when the US passed through the sample medium in a glass cell having $L = 30$ mm, containing 60 ml total volume of the aqueous polymer solution at different polymer concentrations. The US intensity decreased from I_0 to I_{US} when the experiments were performed without and then with polymer in solution. The peak heights of the US profiles were measured by oscilloscope after the US intensity was received by the probe. Then, I_0 and I_{US} were observed both before and after US transduction at each aqueous polymer solution concentration. The transmittance $t = I_{US}/I_0$ (1) was calculated for different polymer solutions. Results show that the polymer solution exhibited a

Figure 1 Change in the shear viscosity for aqueous (a) PEG, (b) PVA, (c) PAA at pH 3, (d) PAA at pH 5 and (e) PAA at pH 10 with a 10 wt% concentration. The US power dissipated was 8.5–9 W.

Figure 2 US absorptivity ($A_{US} = \epsilon_{US}LC$) of for (a) PEG, (b) PVA, (c) PAA at pH 3, (d) PAA at pH 5, and (e) PAA at pH 10 with different concentrations. The US power dissipated was adjusted to 8.5–9 W.

Table 1 ϵ_{US} coefficient ($m^2 g^{-1}$) for aqueous polymer solutions at different frequencies

Frequency (kHz)	PEG at pH 3	PVA at pH 3	PAA at pH 3	PAA at pH 5	PAA at pH 10
43	5.3×10^{-5}	7.6×10^{-5}	6.3×10^{-5}	3.0×10^{-5}	3.0×10^{-6}
23	3.3×10^{-5}	5.0×10^{-5}	4.3×10^{-5}	2.6×10^{-5}	3.0×10^{-6}
96	2.3×10^{-5}	3.3×10^{-5}	3.0×10^{-5}	2.3×10^{-5}	3.0×10^{-6}
141	3.3×10^{-6}	3.0×10^{-6}	3.0×10^{-6}	3.0×10^{-6}	3.3×10^{-7}

Abbreviations: PAA, polyacrylic acid; PEG, polyethylene glycol; PVA, polyvinyl alcohol; US, ultrasound.

tendency to show that $I_0 > I_{US}$, meaning that the US transmittance decreased at each frequency as a function of US absorption. To examine the degree of US absorbed by the aqueous polymer solution, we defined US absorption as A_{US}

$$A_{US} = -\log_{10}(t) = \log_{10}(I_0/I_{US}) \quad (2)$$

The absorptivity of the US in the solution is expected to increase continuously with increasing polymer concentration. Notably, the experimental data showed a linear correlation in each polymer system. Therefore, the absorptivity of the US can be expressed as $A_{US} = \epsilon_{US}LC$, where L is the glass cell length (30 mm) and ϵ_{US} is the constant slope. The value ϵ_{US} represents the area of US absorptivity in the solution medium per unit weight at the transduced distance ($Lg^{-1} cm^{-1}$). Therefore, we were able to perform the following conversion of the absorptivity, ϵ_{US} , given in units of centimeters and

grams per liter: $Lg^{-1} cm^{-1} = 0.1 m^2 g^{-1}$. This unit constant indicates that the value of ϵ_{US} is the US absorption area for the unit weight of each polymer solution.

In Figure 2, the slope in the equation increased at a US of 43 kHz for PEG, PVA and PAA at pH 3. The resultant ϵ_{US} values are listed in Table 1. The trend increased in order of $43 > 23 > 96 > 141$ kHz for PEG, PVA and PAA at pH 3. For example, at 43 kHz, the values of ϵ_{US} were 7.6×10^{-5} , 6.3×10^{-5} and $5.3 \times 10^{-5} m^2 g^{-1}$ for PVA, PAA (at pH 3) and PEG, respectively. The value for PVA represented a higher absorptivity relative to the others, indicating that PVA solutions could adsorb more US. However, the PAA samples at pH 5 and 10 possessed different US absorptivities, even though the same polymer solution was used at different pHs.

Relative to the viscosity at pH 3, a high value for viscosity was observed at pH 10. This outcome was due to the extension of PAA chains because of the electrostatic effects of charged PAA. However, Figure 2 showed that the results for ϵ_{US} were very low at pH 10 for the PAA solution. This result seemed to suggest very low absorption of US in such a viscous solution as that of charged PAA. Therefore, very little US absorption occurred in the dissociated PAA without OH groups, although high viscosity was observed in the aqueous PAA solution at pH 10.

Effect of US on the change in the FT-IR spectra of aqueous polymers

To clarify the change in the shear viscosity and the level of US absorption in each aqueous polymer solution both before and after US exposure, FT-IR spectra were obtained for the aqueous polymer

Figure 3 FT-IR spectra before and after US exposure at different times for (a) PEG, (b) PVA, (c) PAA at pH 3, (d) PAA at pH 5 and (e) PAA at pH 10 at a 10 wt% concentration.

solutions. The experimental method was similar to previous reports for water-soluble polysaccharides¹³ and water-swelled hydrophilic microgels.¹⁰ In the present experiments, for PEG, PVA and PAA, a small amount of polymer solution was dropped onto the CaF_2 windows, and the sandwiched windows were then placed into the water bath of the sonoreactor to be exposed to US. FT-IR measurements were performed immediately after US exposure was terminated. It was confirmed that chemical adsorption of polymer to the CaF_2 windows did not occur after the FT-IR measurements were finished. This phenomenon was checked by washing the windows after US exposure.

Figure 3 shows the FT-IR spectra of the aqueous polymers for (a) PEG, (b) PVA, (c) PAA at pH 3, (d) PAA at pH 5 and (e) PAA at pH 10 both before and after various US exposures were performed for 1, 3 and 5 min. The FT-IR spectra exhibited characteristic bands for PEG and PVA at $3000\text{--}3800\text{ cm}^{-1}$.^{1,27–29} FT-IR peaks for PEG^{27,28} and PVA²⁹ in water were assigned at $3300\text{--}3500\text{ cm}^{-1}$ for OH stretching of the polymers and water molecules. For PAA, the OH stretching band was noted at $2500\text{--}3800\text{ cm}^{-1}$.³⁰ For the monomeric acid OH at $3500\text{--}3800\text{ cm}^{-1}$ and the hydrogen-bonded acid OH at $2500\text{--}3500\text{ cm}^{-1}$, a characteristic band for each polymer was observed in these regions.³¹ A non-hydrogen-bonded peak for the polymer chain and water molecules appeared in the $3400\text{--}3800\text{ cm}^{-1}$ region, and strong interactions between the polymer chain and water were observed in the $3000\text{--}3400\text{ cm}^{-1}$ region due to hydrogen bonding. In the $2500\text{--}2600\text{ cm}^{-1}$ region, Max *et al.*³² reported that the carboxylic

acid groups are hydrogen bonded to water, which is indicated by 'X' in the spectra in Figures 3c and d. Furthermore, carboxylic dimers display an OH stretching band in the region of $2500\text{--}3300\text{ cm}^{-1}$, which is generally centered near 3000 cm^{-1} .³³ Similar results for inter- and intra-hydrogen-bonded bands for PAA were reported.^{31–34} In addition, a band observed at $2800\text{--}3000\text{ cm}^{-1}$ was attributed to CH stretching from alkyl groups.^{28,31} The wavenumber region between 1500 and 1800 cm^{-1} corresponded to a C=O group, and the peak at 1640 cm^{-1} corresponded to OH bending. In PAA at pH 3, the carbonyl band was centered at 1710 cm^{-1} . When PAA was tested at pH 5, there were two peaks centered at 1710 and 1540 cm^{-1} for the carbonyl bands.^{35,36} This result indicated that the carboxylic acid group was partially dissociated: $\text{--COOH} \rightleftharpoons \text{--COO}^- + \text{H}^+$. For PAA at pH 10, it was interesting to note that the OH band shifted toward a lower wavenumber region of $3200\text{--}3400\text{ cm}^{-1}$ (Figure 4). Nevertheless, the spectral change caused by US exposure was less than that of the PAA solution at pH 3. For PAA solutions at pH 3 and 5, dimer formation of --COOH groups was observed in the $2400\text{--}2700\text{ cm}^{-1}$ region (Figure 5). However, for PAA at pH 10, no dimer formation was indicated, thereby indicating dissociation of $\text{--COOH} \rightarrow \text{--COO}^- + \text{H}^+$. In addition in Figure 5, the OH stretching band changed for (a) PEG, (b) PVA and (c) PAA at pH 3. For further analysis, the FT-IR spectra of these aqueous polymers were deconvoluted in the $2400\text{--}3800\text{ cm}^{-1}$ region to compare their peak positions.

For PEG and PVA, OH and CH bands were found in the resulting FT-IR spectra. Therefore, these spectra were deconvoluted to consider

Figure 4 Comparison of the deconvoluted OH stretching band of (a) PEG, (b) PVA and (c) PAA at pH 3, (d) PAA at pH 5 and (e) PAA at pH 10 without US exposure. Peak 1 was assigned to CH stretching at 2927–2939 cm⁻¹.

Figure 5 Comparison of the deconvoluted OH stretching band of (a) PEG, (b) PVA, (c) PAA at pH 3, (d) PAA at pH 5 and (e) PAA at pH 10 after 5 min of US exposure. Peak 1 was assigned to CH stretching at 2927–2939 cm⁻¹.

both stretching bands in the wavenumber region. The spectra were decomposed into Gaussian components by curve fitting.^{13,27} The peak center results are summarized in Table 2. Figure 4 displays the fixed curve of the OH stretching of aqueous polymer without US exposure for (a) PEG, (b) PVA and (c) PAA at pH 3. In addition, the fixed curve of CH stretching was included in the spectra. For the deconvoluted spectra, peak 1 was assigned to the CH stretching bands.^{28,31} Peak 2 was assigned to the strong hydrogen-bond interactions between water and the OH groups from the polymer chain.²⁷ Here, for PEG and PVA, peaks 3 and 4 were assigned to the strong hydrogen-bond interactions between the polymer and

water molecules and to the weak hydrogen-bond interactions between the polymer and water molecules, respectively.^{28,29} Peaks 5 and 6 were assigned to free OH groups from either the polymer or water molecules and to those from free water molecules, respectively.^{29,30,37}

For PAA, peaks 2 and X corresponded to the PAA dimer interactions, and an additional overtone of approximately 2650 and 2550 cm^{-1} (Silverstein *et al.*³⁵) indicated the presence of strong hydrogen-bond interactions between $-\text{COOH}$ groups. Peak Y was assigned to weak hydrogen-bond interactions.^{32,36,38} Figure 5 also contains the fixed curves of (a) PEG, (b) PVA, (c) PAA at pH 3, (d) PAA at pH 5 and (e) PAA at pH 10 for data regarding US exposure.

Comparison of (a) PEG with Figures 4a and 5a showed that peak 1 for the CH band and peak 2 for the hydrogen bonding of water–OH group underwent less change. However, the intensity of peak 5 decreased, whereas peak 4 became intense, after US exposure. The change in Figure 5a) meant that free OH groups of PEG could bind with water at the end of the polymer chain. For PVA having side OH groups, it was similarly observed that the intensity of peak 5 decreased, whereas peak 6 increased as a result of US exposure. This result could explain the US-enhanced breakage of the interactions between water molecules and the OH groups of PVA.

In the case of (c) PAA at pH 3, the band intensities of peaks 4 and 6 were intense following US exposure. However, hydrogen bonds due to the $-\text{COOH}$ group in the dimer at approximately 3000–3200 cm^{-1} were significantly changed. This result indicated that US was effective in breaking the $-\text{COOH}$ dimers and increased the population of free OH groups from $-\text{COOH}$ or water molecules. At pH 5 and 10, the population of each peak changed less before and after US exposure. The insignificant change at pH 10 could be due to the full dissociation

Table 2 Centered peak wavenumber determined by curve fitting for the OH stretching band

	PEG at pH 3		PVA at pH 3		PAA at pH 3		PAA at pH 5		PAA at pH 10	
US										
peak	0 min	5 min	0 min	5 min	0 min	5 min	0 min	5 min	0 min	5 min
X					2548	2555	2546	2546		
1	2921	2919	2948	2949	2927	2927	2939	2939	2941	2939
2	3071	3068	3061	3075	3092	3092	3048	3054	3080	3080
3	3243	3242	3221	3248	3249	3249	3228	3239	3226	3223
Y					3338	3338	3390	3387	3365	3368
4	3415	3430	3384	3395	3473	3453	3497	3473	3484	3461
5	3534	3537	3522	3499						
6	3617	3613	3623	3608	3615	3612	3633	3639	3630	3591

Abbreviations: PAA, polyacrylic acid; PEG, polyethylene glycol; PVA, polyvinyl alcohol; US, ultrasound.

Figure 6 Comparison of the deconvoluted C=O stretching bands of PVA, PAA at pH 3 and PAA at pH 5 before (a, c, e) and after 5 min of US treatment (b, d, f).

Scheme 2 Hydrogen-bond cross-linked structures of (a) PEG, (b) PVA and (c) PAA with water. A full color version of this figure is available at *Polymer Journal* online.

Table 3 Centered peak wavenumber determined by curve fitting for the C=O stretching band

US peak	PVA		PAA at pH 3		PAA at pH 5	
	0 min	5 min	0 min	5 min	0 min	5 min
a	1562	1561	1552	1552	1553	1552
b	1622	1623	1623	1626	1623	1626
c	1648	1648	1642	1643	1646	1647
d	1675	1676	1672	1671	1676	
e			1694	1692	1691	1696
f	1712	1714	1712	1710	1710	1710
g	1739	1738	1731	1728	1730	1728

Abbreviations: PAA, polyacrylic acid; PEG, polyethylene glycol; PVA, polyvinyl alcohol; US, ultrasound.

of carboxylic acid groups: $\text{COOH} \rightarrow \text{COO}^- + \text{H}^+$. Furthermore, the 1700 cm^{-1} band for C=O stretching contains useful information about the hydrogen-bonded and non-hydrogen-bonded carboxylic groups of PAA.³⁶ Therefore, analysis similar to that of the C=O band was performed with the OH band in Figures 4 and 5. Figure 6 shows the FT-IR spectra observed near the 1700 cm^{-1} region. In the C=O stretching region, the curve fitting spectra of the linear oligomer, cyclic dimer, side-on dimer and monomeric side-chain carboxylic groups were obtained for PAA at 1676, 1692, 1710 and 1730 cm^{-1} , respectively. The peaks at 1648 and 1622 cm^{-1} were assigned to water molecules interacting with PAA,^{39,40} and the peak at 1562 cm^{-1} corresponded to dissociation of carboxylic acid groups.³⁸ Table 3 also lists each band in the FT-IR spectra both without and with US exposure in the range of $1500\text{--}1800 \text{ cm}^{-1}$. By increasing the

Figure 7 Change in the ratio of I_{OH}/I_{CH} intensity as a function of time observed in the FT-IR spectra of (a) PEG (◆), (b) PVA (▲), (c) PAA at pH 3 (■), (d) PAA at pH 5 (●) and (e) PAA at pH 10 (*).

US exposure time from 1 to 5 min, the intensity of the 1690 cm^{-1} band increased. This result indicated that water molecules could associate with the $\text{C}=\text{O}$ group in PAA at pH 3 following US exposure. A similar tendency was observed in the spectrum at pH 5 for partial dissociation of COO^- in PAA, as shown in Figure 3b. A similar result was also observed in PVA at 1675 cm^{-1} for the $-\text{O}-\text{C}=\text{O}$ group, which remained intact without hydrolysis of the acyl acetate group. Altogether, these data indicated that US exposure enhanced water solvation to the $-\text{C}=\text{O}$ group in the polymer (Scheme 2). Figure 7 shows the change in the ratio of the I_{OH}/I_{CH} intensity as a function of time in the FT-IR spectra for (a) PEG, (b) PVA, (c) PAA at pH 3, (d) PAA at pH 5 and (e) PAA at pH 10. After US exposure ceased, the values of the peak ratios in the FT-IR spectra obtained at pH 3 and 5 increased. This outcome resulted from the attribution of the OH group to the free COOH group or water molecule, during US exposure. Notably, the values of I_{OH}/I_{CH} decreased gradually and returned to their original values within 60 min, when US exposure ceased. However, no change occurred at pH 10, even though US exposure occurred. Consequently, the hydrogen bonds were reformed, and the aqueous polymer solution became viscous again, as shown in Figure 1. It was reasonable to conclude that US exposure disrupted the hydrogen bonds of the aqueous polymer solutions of PEG, PVA and PAA at pH 3 and 5 due to US absorption and could enhance water solvation into the polymer.

As mentioned, the present paper could provide the first results of the effect of US on different chemical structures of water-soluble polymers, which exhibited similar amounts of US absorption to form free OH groups in water following US exposure, as shown in Scheme 2.

CONCLUSION

The present paper concluded that US, especially at 43 kHz, induced a change in the shear viscosity due to the disruption of hydrogen bonds by efficient US absorption by the aqueous medium, and due to the formation of free water with OH groups and of OH groups in the water-soluble polymers. We also evaluated the values of US absorptivity for ε_{US} , which were 5.3×10^{-5} , 7.6×10^{-5} , 6.3×10^{-5} , 3.0×10^{-5} and 3.0×10^{-6} for PEG, PVA, PAA at pH 3, PAA at pH 5 and PAA at pH 10, respectively, at a frequency of 43 kHz. US exposure disrupted the hydrogen bonds in the polymers, especially at

the OH groups, and also enhanced the solvation of water to each OH and $\text{C}=\text{O}$ group.

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