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Computational modeling and experimental infrared spectroscopy of hydrogen bonding interactions in polyvinyl alcohol–starch blends

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ABSTRACT

This study aims to investigate the hydrogen bonding interactions in polyvinyl alcohol (PVOH)–starch blends. Semi-empirical AM1 (Austin Model 1) and PM3 (Parameterized Austin Model 3) methods were employed to model the blending. Binding energies, vibrational frequencies and solubility parameters results were used to analyze the compatibility and stability of the blends. Besides that, experimental infrared spectroscopy was also conducted to validate the modeling results. The computed negative binding energies justified the stability of the blending. On the other hand, the solubility parameters of PVOH and starch modeling complexes have been found close to each other. This confirms that PVOH and starch are compatible blends. In addition, vibrational frequency analysis of these molecular complexes has exhibited that the hydroxyl group shifts to lower wavenumbers due to formation of hydrogen bonds. Findings from the experimental infrared spectroscopy have shown agreement with computational vibrational frequency results. The wavenumbers of the specimens increase is dependent on the ratios of PVOH in the blends. Such increment indicates that PVOH and starch interact in a harmonize manner and the blending is compatible.

1. Introduction

Polyvinyl alcohol (PVOH) is produced through the hydrolysis of polyvinyl acetate. It is strong, durable and possesses high crystallinity structure [1]. For common applications, PVOH is dissolved in water as adhesives, sizing and coating agents as well as tissue scaffolding materials for biomedical applications [1,2]. It can also be injection moulded or blown film as plastic products for food wares and packaging applications [1]. In this study, starch is introduced because it is an abundant, cheap and natural material. Both PVOH and starch are biodegradable and readily consumed by microorganisms in the natural environment. Researchers have reported that blending of PVOH and starch is favorable [3–5] because both of them are polar substances which having hydroxyl groups (–OH) in their chemical structures [3,4,6]. These highly polar hydroxyl groups tend to form intermolecular and intramolecular hydrogen bonds which improve the integrity of PVOH–starch blends. Whereas blending of incompatible hydrophobic low density polyethylene (LDPE) and hydrophilic starch causes a deteriorated matrix structure of LDPE which lead to the loss of mechanical properties [7–10]. When a comparison was made between solution cast PVOH [6] and LDPE [8] with a starch content of 7.5 wt.% blending, the former PVOH–starch showed 0.74% reduction of tensile strength over neat PVOH whereas the tensile strength of LDPE–starch was 10.9% lower than neat LDPE. The formation of hydrogen bonds between hydroxyl groups of starch and PVOH tends to promote localised stability and subsequently improve the miscibility of starch and PVOH. Mao et al. [4] used PVOH as a reinforcing agent in thermoplastic starch to overcome the brittleness problem. By adding 10 wt.% PVOH to starch-glycerol compound, it would induce 2.2 MPa increment in tensile strength as well as an increase in percentage of elongation up to 37%. Exposures of starch granules blended with PVOH were not visible under Scanning Electron Microscope [4] thus indicating the compatibility of PVOH–starch blends.

This paper describes the hydrogen bonding effects in PVOH–starch that contribute towards enhancing the macroscopic stability of the blending. The presence of hydrogen bonds in hydroxyl groups is mainly due to large electronegativity differences between oxygen and hydrogen. Oxygen and hydrogen atoms of alcohol are partially negative and positive charged, respectively. The partially positive charged hydrogen atom induces weak interaction with the oxygen atom of immediate alcohol molecules to form hydrogen bond [11]. In this work, semi-empirical computational modeling and Fourier

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Transform Infrared (FT-IR) were used to reveal the vibrational frequency of these hydroxyl groups. The indication and diagnosis of the infrared absorption on the formation of hydrogen bonds can be found at range 3000–3400 cm^{-1} [11–13]. The variation of absorption within the range is affected by the number and strength of hydrogen bonds in the chemical environment of the substance. When there are more chemical environments, the hydrogen bond will absorb slightly different wavenumbers. Formation of hydrogen bond weakens the O–H bond which will cause bond elongation and lead to a lower O–H stretch/vibration frequencies as compared to non-interacting species. This phenomenon is known as “red shift” by He et al. [14] and it can cause a variation ranging from ten to hundreds of wavenumbers. This shift provides obvious as well as meaningful information about the formation of hydrogen bond within species [14].

In addition to experimental outcomes, theoretical methods such as lattice theory [15], lattice cluster theory [16], semi-empirical model potential [17] and molecular dynamics modeling [18] can also be employed to link between the experimental and theoretical investigations. Joshi and Mebel [19] employed semi-empirical method to study the hydrogen bonding interactions between polypropylene carbonate and starch species. Meanwhile, Tanaka and Goettler [20] and Toth et al. [21] used molecular dynamics method to predict the changes of binding energies of organoclay nanocomposite when interact with nylon 6.6 and polypropylene, respectively. Presently, there is a lack of theoretical study on the interactions of PVOH and starch. Thus, this study is very important to expand PVOH–starch use in biological applications since this compound has the potential to be widely adopted as a hydrogel and tissue scaffolding material in biomedical applications [2,10]. The objective of this study is to determine the extent of compatibility induced by hydrogen bonds in PVOH–starch and hence having an in-depth understanding of their molecular level. Both experimental FT-IR and semi-empirical theoretical outcomes were qualitatively compared to validate the interactions trend in the constituent of PVOH–starch blending.

2. Methodology

2.1. Samples preparation and FT-IR analysis

Fully hydrolysed PVOH grade BF-17H (viscosity 25–30 cps, hydrolysis 99.4–99.8 mole %, ash $< 0.7\%$) manufactured by Chang Chung Petrochemical Co., Ltd. was used in this study. Native *cassava* starch was purchased from Thailand – Cap Kapal ABC. PVOH, starch and distilled water were used as received. Different compositions of PVOH–starch blends were prepared with starch ranging from 20 to 50 wt.% as shown in Table 1. Specimens W28, W37, W46 and W55 were prepared by dissolving PVOH powder in distilled water and heating in water bath at 97 ± 2 °C for 30 min until PVOH particles were completely dissolved in the solution. After the PVOH was fully dissolved, starch was then added and the mixture was again heated at 97 ± 2 °C for 30 min. Meanwhile, specimens of neat PVOH (PV) and starch (ST) were heated respectively in 400 g of distilled water for 1 h. A motor driven stirrer (set at 800 rpm) was used to dissolve and gelatinize the mixtures. The different mixtures of equal weight were cast on *Petri* dishes and dried in a vacuum oven at 65 °C to constant weight. All the specimens were then immediately sealed in polyethylene bags. FT-IR analysis was conducted using Perkin Elmer Spectrum One. Since the specimens appeared as thin films, the films were cut into round shapes and fixed onto a stand for scanning. The scanning was done at 370–4000 cm^{-1}. The objective of this test is to determine the interactions of hydrogen bonds at 3000–3500 cm^{-1} for comparison with the computational modeling outcomes.

Table 1
Compositions of PVOH–starch in preparation of cast film.

Specimen	PVOH:Starch (wt.%)	PVOH (g)	Starch (g)
W28	20:80	2	8
W37	30:70	3	7
W46	40:60	4	6
W55	50:50	5	5
PV	100:0	10	0
ST	0:100	0	10

Table 2
Computational modeling of the Glu–mPVOH complexes.

Complex	Molecular weight Glu (g/mol)	Molecular weight mPVOH (g/mol)	Ratio molecular weight (Glu:PVOH)
1Glu–1mPVOH	180.16	46.07	80:20
1Glu–2mPVOH	180.16	90.12	70:30
1Glu–3mPVOH	180.16	134.18	60:40
1Glu–4mPVOH	180.16	178.23	50:50

ϕGlu or ϕmPVOH, $\phi =$ number of repeating unit.

2.2. Computational modeling strategy

The computational modeling of PVOH–starch was carried out using Hyperchem® Professional 8.0 (Hyperchem) and ChemSW® Molecular Modeling Pro (ChemSW). Hyperchem was used to generate binding energy and vibrational frequency analysis to produce infrared absorption of the complexes. Meanwhile, the ChemSW was used to generate solubility parameters of the molecules. The computational modeling procedure is as follows:

1. For modeling purposes and to keep the models computationally manageable [19], the numbers of PVOH repeating unit interacting with starch monomer repeating unit D-glucose were kept to the minimum. Table 2 shows four pairs of molecular complexes of D-glucose (Glu) modeled with increasing PVOH repeating units (mPVOH). The combinations were used to represent the blending ratios of PVOH–starch so that the outcomes can be verified experimentally.
2. Each pair of the molecular complex was constructed on Hyperchem workplace. Initially, the distance of Glu and mPVOH was guessed. Then, semi-empirical quantum mechanics – AM1 (Austin Model 1) and PM3 (Parameterized AM1 Model 3) methods were selected for geometrical optimization by Polak-Ribiere algorithm. The distance and conformation of Glu and mPVOH changed by iterating until the total root-mean-square (RMS) gradient was less than 0.1 kcal/(mol Å). At this point, formation of hydrogen bonds would appear if present. Since the objective of molecular modeling of Glu–mPVOH complex was to determine the changes of binding energies and infrared absorptions through vibration frequency analysis, then, if no hydrogen bonds were formed in the first iteration, another distance and conformation of Glu–mPVOH would be guessed. Once hydrogen bonded Glu–mPVOH was obtained, the binding

Table 3
Binding energies, ΔE (kcal/mol) at AM1 and PM3 of the complexes.

Model	1Glu–1mPVOH	1Glu–2mPVOH	1Glu–3mPVOH	1Glu–4mPVOH	1Glu–4mPVOH
AM1	−4.05	−7.58	−5.12	−4.68	−3.94
PM3	−1.19	−5.35	−5.61	−6.50	−6.76
Hydrogen bond	Single	Single	Single	Single	Double

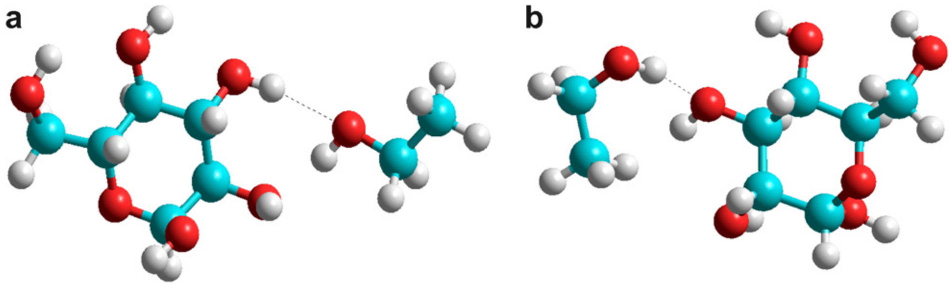

Fig. 1. Geometrically optimized structures of single hydrogen bond Glu–1mPVOH at (a) AM1 and (b) PM3.

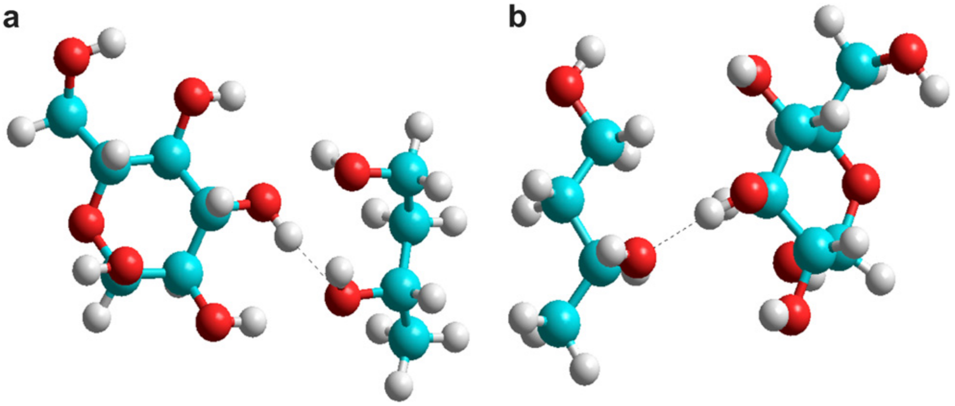

Fig. 2. Geometrically optimized structures of single hydrogen bond Glu–2mPVOH at (a) AM1 and (b) PM3.

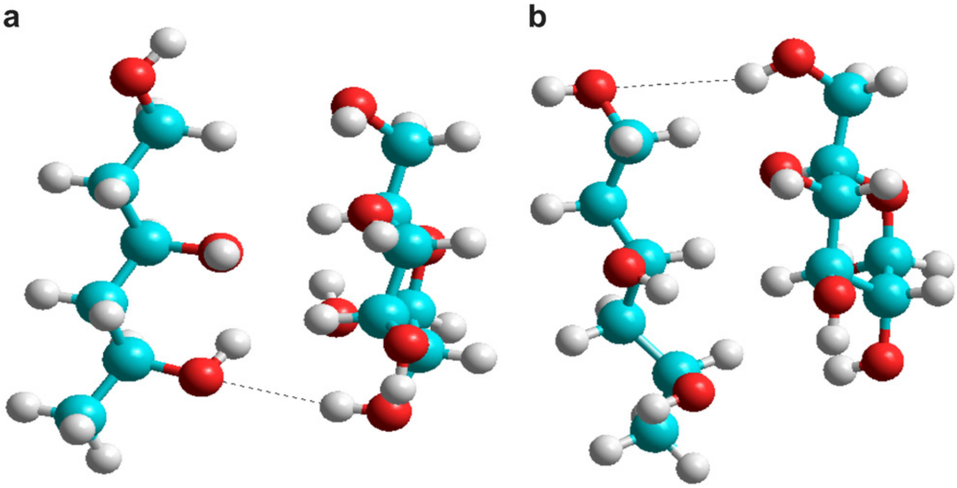

Fig. 3. Geometrically optimized structures of single hydrogen bond Glu–3mPVOH at (a) AM1 and (b) PM3.

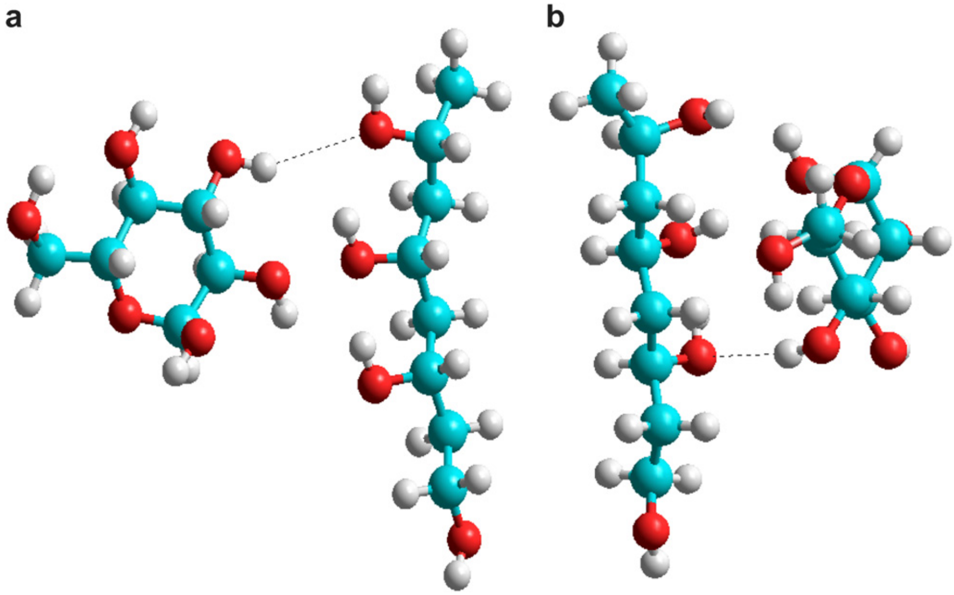

Fig. 4. Geometrically optimized structures of single hydrogen bond Glu–4mPVOH at (a) AM1 and (b) PM3.

energy was recorded. Based on the similar conformation of hydrogen bonded Glu–mPVOH, Glu molecule was deleted from the workplace and leaving mPVOH alone. mPVOH was then proceeded to single point calculation to determine the binding energy and infrared absorption. Similar to Glu, mPVOH was deleted from the workplace and leaving Glu for single point calculation. The change of binding energy, ΔE of each complex was calculated using the following formula:

$$\Delta E = E_{\text{complex}} - (E_{\text{Glu}} + E_{\text{mPVOH}}) \tag{2.1}$$

3. Vibrational frequency analysis was conducted using hydrogen bonded geometry optimized structure Glu–mPVOH complexes. There were various kinds of bonds in the Glu–mPVOH complex, but only the hydroxyl group (–OH) was considered because it was involved in the formation of hydrogen bonds.
4. The Glu and mPVOH after the single point calculation were exported to ChemSW to generate Hansen solubility parameters [22].

3. Results and discussion

3.1. Binding energies and solubility parameters analysis

Table 3 shows the binding energies of Glu–mPVOH complexes. ΔE with negative values indicate that the interactions of Glu and mPVOH are favorable towards lower energy hierarchy. This means that the interactions of PVOH and starch are considerably stable.

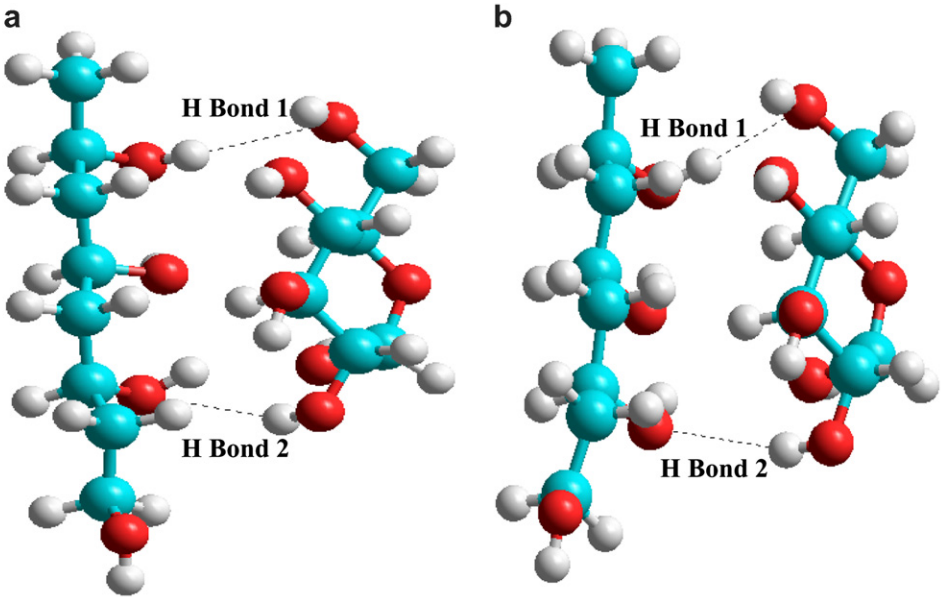

Fig. 5. Geometrically optimized structures of double hydrogen bonds Glu–4mPVOH at (a) AM1 and (b) PM3.

Table 4
Hansen solubility parameters, δ_H of the modeled species.

	1Glu	1mPVOH	2mPVOH	3mPVOH	4mPVOH
δ_H (MPa$^{1/2}$)	28.3445	26.4947	27.5706	28.7126	28.7004
Difference with 1Glu	–	1.8498	0.7739	0.3681	0.3559

Figs. 1–5 show the geometrically optimized structures with the presence of hydrogen bonding between mPVOH and Glu. Hydrogen bonds are formed between mPVOH and Glu when the hydrogen-donor distance is less than 3.2 Å with the angle of the corresponding bonds to the donor and acceptor atoms being less than 120° [23]. As a result, it was found that 1Glu–4mPVOH has fulfilled the criteria with double hydrogen bonds (Fig. 5). The existence of extra hydrogen bonds further improves the molecular stability. PM3 binding energies show an increasing trend based on the ratios of mPVOH (refer Tables 2 and 3). However, a similar distinct tread is absent with the AM1 outcomes. Variations of AM1 and PM3 results are due to the different computational parameters. PM3 is re-parameterized of AM1 to include a wider variety of experimental versus computed molecular properties [24]. Overall, the interactions of starch and PVOH are preferable with higher binding energies which exhibit higher stability of the blending. When the ratio of mPVOH to Glu increases, the binding energies gets higher and this indicates that blending of 50 wt.% of PVOH with starch has greater intermolecular interactions as compared to 20 wt.% of PVOH. Moreover, higher ratios of PVOH to starch indicate that more hydrogen bonds will be formed. That would subsequently lead to improve molecular properties of the blending system.

In spite of that, the compatibility of PVOH and starch can be further justified through the comparisons of solubility parameters. Compatibility of the substances are met when the solubility parameters are very close to each other due to the energy of mixing released by the single component itself having in-balance conditions with the energy released by interactions with other substances [25]. When the solubility parameters of the components in polymer blends have huge differences (>10 MPa$^{1/2}$) [25], this will result in a phase separation or poorer adhesion and thus causing loss of properties [26]. Table 4 shows the Hansen solubility parameters of the modeled species. Since both PVOH and starch has huge numbers of hydroxyl group, thus, the solubility parameters of mPVOH are very close to Glu. This means that PVOH and starch are compatible. Among the mPVOH, 4mPVOH has the nearest solubility parameter to Glu. Higher ratio of PVOH is the driving force to form a stable and compatible system. In short, the addition of starch into PVOH can reduce the overall material cost without substantially affecting the physical properties. This result is in agreement with Mao et al. [4] who observed that exposures of starch granules were not visible under Scanning Electron Microscope after blending with PVOH.

Table 5
Vibrational frequencies of hydroxyl group at AM1 and PM3 of the 1Glu–1mPVOH, 1Glu–2mPVOH, 1Glu–3mPVOH, and 1Glu–4mPVOH complexes with single hydrogen bond and their corresponding decrease in frequencies.

Complexes	AM1		PM3	
	H Bond	V.F. (cm^{-1})	H Bond	V.F. (cm^{-1})
1Glu–1mPVOH	with	3448.78	with	3878.26
	without	3453.26	without	3888.65
Decrease		4.48		10.39
1Glu–2mPVOH	with	3440.92	with	3861.12
	without	3458.77	without	3920.35
Decrease		17.78		59.23
1Glu–3mPVOH	with	3430.20	with	3840.51
	without	3436.29	without	3880.73
Decrease		6.09		40.22
1Glu–4mPVOH	with	3456.20	with	3838.61
	without	3461.53	without	3875.58
Decrease		5.33		36.97

H Bond = Hydrogen bond; V.F. = Vibrational frequency.

Table 6
Vibrational frequencies of hydroxyl group at AM1 and PM3 of the 1Glu–4mPVOH complex with double hydrogen bonds and their corresponding decrease in frequencies.

Complexes	AM1		PM3	
	H Bond	V.F. (cm^{-1})	H Bond	V.F. (cm^{-1})
1Glu–4mPVOH at H Bond 1	with	3453.19	with	3846.74
	without	3490.91	without	3869.21
Decrease		37.72		22.47
1Glu–4mPVOH at H Bond 2	with	3439.25	with	3845.39
	without	3455.81	without	3870.02
Decrease		16.56		24.63

H Bond = Hydrogen bond; V.F. = Vibrational frequency.

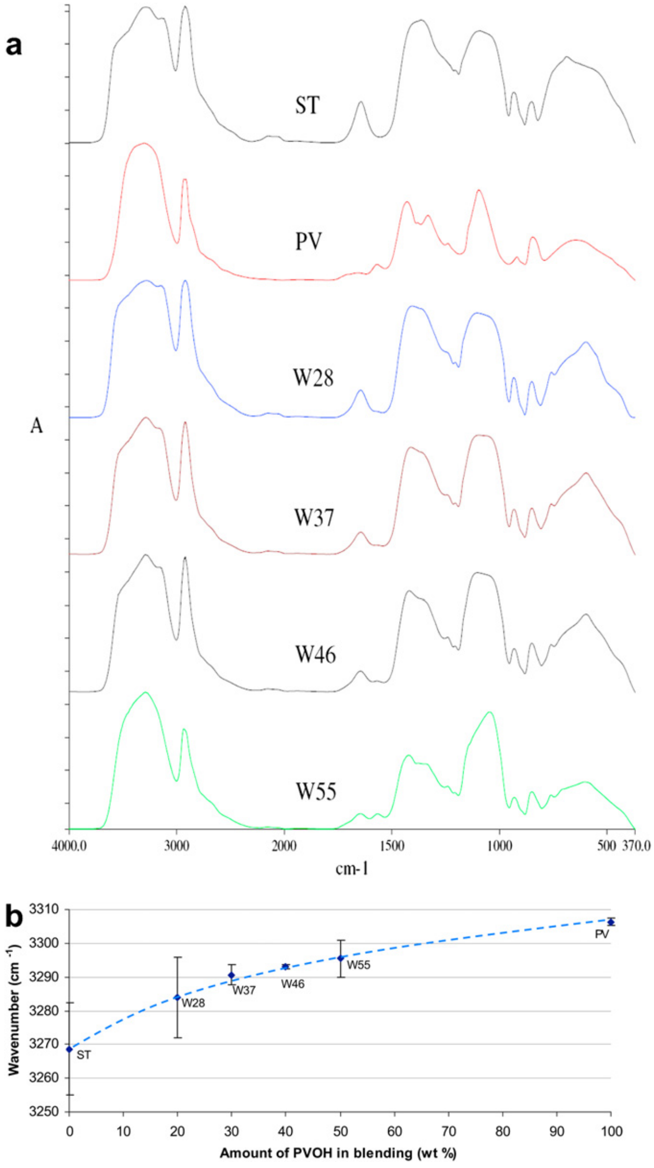

Fig. 6. (a) FT-IR spectra of film casting neat PVOH (PV), starch (ST) and PVOH–starch blends (W28, W37, W46 and W55), (b) Wavenumber shift of –OH peak in film casting neat PVOH (PV), starch (ST) and PVOH–starch blends (W28, W37, W46 and W55).

3.2. Vibrational frequency and experimental FT-IR analyses

In order to further investigate the intermolecular interactions of PVOH and starch, vibrational frequency analysis was also carried out to gain insight on the theoretical infrared absorption. The purpose of the vibrational frequency analysis is to discover the change of absorption due to formation of hydrogen bonding interactions of PVOH and starch. The vibrational frequency analysis was done using the readily built Glu–mPVOH structures in semi-empirical modeling to investigate O–H stretching frequency. Table 5 shows the frequencies of the hydroxyl groups in several complexes in the presence of a single hydrogen bond. Meanwhile, Table 6 shows the absorption of two separate hydrogen bonds found in Glu–4mPVOH. Although these two hydrogen bonds are present in Glu–4mPVOH but the absorption frequencies are different. This shows that different geometrical arrangements will cause changes in the hydrogen bonding strength.

It is noted that all the complexes exhibit a decrease in vibrational frequencies after the formation of hydrogen bonds. This is known as the "red shift" effect which has caused O–H bond elongation and subsequently lowered the energy required to stretch the O–H bond. It can be seen that PM3 method has overestimated the frequencies as compared to the AM1 method. AM1 method has shown more reasonable results within the range 3000–3500 cm^{-1} of experimental FT-IR used to study the existence of hydrogen bonds effects.

The current models used in this study simulate a simplified version of PVOH and starch. Thus, a quantitative comparison of absorption frequency with the experimental FT-IR may not be justified. However, a qualitative analysis of frequencies can provide preliminary evidence about the nature of interactions between starch and PVOH. Fig. 6(a) shows the FT-IR spectra of solution cast prepared specimens. In general, the spectra for all specimens seem to present in almost similar absorption manners except the peak at 1500–1700 cm^{-1} when it shows an absence in PV specimen which attributes to the vibrational of C–O–C functional group. This functional group is only present in starch compounds [27]. As the starch ratio in the blending increases, the absorption peak getting higher. A close inspection at 3000–3500 cm^{-1} shows that higher ratios of PVOH has caused a shifting of –OH absorption peak. A factor to be considered is that the strength of the hydrogen bond in species is not limited to the chemical environment within the molecules. Hydrogen bond may also be affected by other physical environments such as crystallinity and amorphous structures [14,27]. A crystal structure will cause a higher shifting of absorption spectra due to extra energy is required to overcome vibration/stretching in a constraint structure [27]. Fig. 6(b) shows that PV has the highest wavenumber among the specimens. PV possesses high crystallinity as compared to starch, thus higher energy is required to allow the hydroxyl group to stretch in the compact crystal structure [27]. In contrast, starch (ST) is a weaker substance and has a low energy (i.e. wavenumber) which is sufficient to stretch the hydroxyl group. The wavenumbers of the specimens increase in relation to the ratios of PVOH in the compounds. Such increment indicates that PVOH and starch interact in a harmonize manner whereby the compatibility of the PVOH–starch blends can be justified. In this study, the experimental FT-IR spectra in comparison with the molecular modeling outcomes have provided insights on the interactions of PVOH and starch. This illustrates favorable interactions between PVOH and starch with the actions of hydrogen bonding.

4. Conclusion

This study has illustrated the use of computational modeling and experimental FT-IR to investigate the nature of hydrogen bonding between PVOH and starch with the following findings:

1. The binding energies, ΔE of Glu–mPVOH with negative values indicate the interactions of Glu and mPVOH are favorable at the lower energy hierarchy. This exhibits that PVOH–starch is a stable compound.
2. The compatibility of PVOH and starch has been proven by Glu and mPVOH which possess solubility parameters very close to each other. 4mPVOH (i.e. 50 wt.% PVOH) has the closest solubility parameter to Glu and this indicates that a high ratio of PVOH is preferable to form a stable and compatible compound system.
3. Vibrational frequency analysis showed that the hydroxyl group of Glu–mPVOH complexes shifts to a lower wavenumber due to the formation of hydrogen bonds. Two hydrogen bonds with different absorption frequencies found to present in Glu–4mPVOH. This exhibits that different geometrical arrangements cause changes to the hydrogen bonding strength.
4. Results from the experimental FT-IR show agreement with the computational vibrational frequency analysis. The wavenumbers of the specimens increase in relation to the ratios of PVOH in the blends. Such increments indicate that PVOH and starch interact in a harmonize manner whereby compatibility of the blending can be justified.

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