The mechanical property and phase structures of wheat proteins/polyvinyl alcohol blends studied by high-resolution solid-state NMR

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Abstract

The phase structures of thermally processed wheat proteins (WP) and polyvinyl alcohol (PVOH) blends were studied by solid-state high-resolution NMR spectroscopy. The intermolecular interactions among the multi-component systems and the behavior of each component in the blends on scales of nanometers were examined. The mechanical properties of the blends were also measured and related to the phase structure studies. The results indicated that the polymer chains of WP could be homogeneously mobilized when thermally processed with glycerol and water as plasticisers, but the glycerol predominately associated with WP rather than PVOH in the blends. The intermolecular hydrogen bonding interactions between WP and PVOH caused some extent of miscibility in the system on scales of nanometers especially when the PVOH content was low. The tensile strength and modulus of the blends were improved as compared to WP. However, the intermolecular interactions were relatively weak and could not be further enhanced by increasing PVOH component in the blends. The particle miscible WP/PVOH blends contained plasticised WP and PVOH phases in conjunction with the miscible WP/PVOH phase. Increasing the PVOH content in the blends did not result in an increase of the percentage of the miscible phase and the blends tented to be immiscible while the elongation of the blends was reduced when increasing the PVOH content in the blends.
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1. Introduction

Material industries world-wide are undergoing a revolutionary shift from petro-chemical materials to environmentally sustainable materials due to increasing environmental concerns and diminishing petro-chemical resources. The development of biodegradable polymer materials is one of the ways to significantly reduce the amount of plastic waste in the environment and generate new materials. The main biodegradable polymers are divided into two groups: natural materials (starch, cellulose and protein) and synthetic polymers (mainly aliphatic polyesters) [1–3]. Synthetic biodegradable polymers with excellent properties have shown great potential to replace most of the plastics widely used in many applications; however, the cost is still too high in comparison to conventional polymers. In contrast, natural materials are relatively less expensive and they have been developed into various products for conventional applications. Currently, starch-based biodegradable products

have been used in many areas [4–9]. The main disadvantage for using starch-based materials is the water sensitivity that is difficult to overcome when water resistance is required in the application. Therefore, other technologies such as multi-layer extrusion (with protection layers on the starch films) are required with high cost materials (such as synthetic biodegradable polymers) as protection layers. The other main sources for natural biodegradable polymers are plant proteins [10–17]. Wheat or corn proteins have good water-resistance properties, strong tensile strength and excellent barrier properties. To develop biodegradable materials from wheat or corn proteins has become a challenge for material scientists.

Currently, wheat protein films are mainly manufactured by the solution casting method via dispersing wheat gluten in either alkaline or acidic medium consisting of ethanol and water. There have also been approaches to make wheat protein films via extrusion to make the process continuous and efficient [18–23]. It also overcomes the risks of working with large amounts of organic solvents. However, wheat proteins (WP) are relatively difficult to be thermally

processed since the materials are crosslinked in some extent with a low thermal decomposition temperature. Plasticisers are always required to reduce the strong intra/intermolecular interactions among wheat protein molecules, to increase the mobility of the protein chains, and therefore, to improve the flexibility and the extensibility of the materials. Without plasticisers, WP are difficult to be thermally processed. Water is the most ubiquitous plasticiser of WP because of its strong capability to modify the mobility of the molecules. Glycerol is the other common plasticising agent and the action of water and glycerol on WP have been extensively studied [18,24,25]. The use of a large amount of plasticisers in the process weakens the strength (especially the water resistant strength) and limits the application of the materials. Various reports have been published concentrating on the development of efficient plasticisers, polymer blending, and structure modifications of WP [24–30]. In many cases, these techniques are used simultaneously. PVOH is a semi-crystalline polymer with excellent strength and performance but also recognized as one of a very few polymers susceptible to ultimate biodegradation by suitably accli-mated micro-organisms [31]. Blending some extent of PVOH with WP could not only modify the mechanical property of WP, PVOH may also play a role as a plasticiser in the system to improve the processing property. After thermal extrusion of the materials, other curing techniques could be applied to the system to form chemical bonds between PVOH and WP matrix thus to improve the plasticiser retention and water resistant properties. A good understanding of the intermolecular interaction among various components in such a complicated system is the key to the development of a material with advanced properties. We have investigated WP and polyvinyl alcohol blends prepared via the solution casting method at a previous date in order to explore the intermolecular interactions in the system [30]. The results indicated that the hydrogen bonding interaction between the two polymers caused the blends to be partially miscible on nanometer scales. The study of thermal processed WP/PVOH blends is reported in this paper. The mechanical properties of the blends were measured. The glass transition behaviours of the blends were examined by dynamic mechanical analysis (DMA). Solid-state high-resolution ^{13}C and ^{1}H NMR spectroscopy was applied to examine the intermolecular interactions within the multi-component system, the mis-cibility of the system on scales of nanometers and the molecular motions of each component in the blends.

2. Experimental

2.1. Materials

Samples of WP were supplied by Manildra Group Australia. Raw WP (wheat gluten) normally contain about 80% proteins, 15% starch and 5% lipid and fibres. The

wheat protein sample studied in this paper (referred as WP) has been purified and contains over 90% of protein with a small amount of residual starch (< 5%) and other impuri-ties. De-amidation was also conducted on the WP under mild conditions resulting in 30–35% of amide bonds (mainly in the side chains) being broken leaving –COOH as end groups. The moisture content of the samples was around 8%. Polyvinyl alcohol (PVOH, Elvanol® 71-30, fully hydrolysed) was purchased from DuPont and used as received.

The sheet samples of WP, PVOH and WP/PVOH blends were prepared using glycerol and water as plasticisers with formulations listed in Table 1. The pH of the system was adjusted to 4.0 using acetic acid in all cases. Each sample with a designed formulation was mixed in a high-speed mixer for 1.5 min at a speed of 3000 rpm, left overnight, then thermally processed at 80 °C for 5 min in a Banbury mixer at a speed of 100 rpm, and finally thermally compression moulded at an optimum temperature of 130 °C for 5 min using a 200 kN heating press. The sample size was of 145 × 145 mm². The thickness of the sheet sample was 1.0 ± 0.1 mm. Tensile strength of the samples was measured after conditioning the tensile specimens at a relative humidity RH = 55% and room temperature (22–23 °C) for 4 days. The same samples were used for DMA and NMR studies.

2.2. Instrumentation

Mechanical properties (tensile strength, elongation at break and Young's modulus) of the samples were determined at an INSTRON 5566P and the data of each sample were obtained from an average of testing seven specimens. DMA experiments were operated at a Perkin–Elmer PYRIS™ Diamond DMA in dual cantilevers bending mode at a frequency of 1 Hz. The temperature range was set at −100 to 170 °C and the heating rate was 2 °C/min. The storage modulus (E'), the loss modulus (E'') and tan $\delta (= E''/E')$ were recorded against temperature through the experiment.

High-resolution solid-state NMR experiments were conducted using a Varian Unity plus spectrometer at resonance frequencies of 75 MHz for ^{13}C and 300 MHz for ^{1}H. ^{13}C NMR spectra were observed under cross-polarization (CP), magic angle sample spinning (MAS) and

Table 1
The plasticisers used in the WP or WP blends in weight parts

	WP-p35	PVOH-p35	WP/PVOH
WP or PVOH or the blends	100	100	100
Glycerol	20	20	20
Na$_2$SO$_3$	0.3	0.3	0.3
Water	10	10	10
Acetic acid	4.6	4.6	4.6
Total plasticisers	34.9	34.9	34.9

high power decoupling (DD) conditions or using a single 90° pulse excitation (SPE) method with high power decoupling on protons. The 90° pulse was of 4.5 μs for protons and C-13 while the spinning rate of MAS was set at a value in the range of 8–10 kHz. A contact time of 1.2 ms was used for measuring CP/MAS spectra. The relaxation delay time used for detecting SPE spectra was as short as 2 s. The chemical shift of ^{13}C CP/MAS spectra was determined by taking the carbonyl carbon of solid glycine (176.03 ppm) as an external reference standard. High-resolution solid-state ^{1}H NMR spectra were obtained under MAS conditions with a spinning rate at a value of 8–10 kHz using TMS as external reference. All the NMR experiments were conducted at room temperature.

3. Results and discussion

Wheat protein (WP) is a viscoelastic mass comprising a complex polymorphic mixture of over 50 varieties of polypeptides broadly divided into gliadins (aggregated by non-covalent interactions) and glutenins (crosslinked by disulphide bonds among polypeptides). The materials show good mechanical properties when processed under suitable conditions. When blending PVOH with WP, the tensile strength and modulus of the materials were significantly improved as compared to those of WP-p35 (shown in Table 2). Note that 21, or 27, or 54% enhancement in tensile strength was obtained when 10, or 18, or 25% of PVOH was used in the blends while the Young's modulus of the blends was also improved by 15–33%. However, the elongation of the materials was reduced when the PVOH component increases in the blends.

The DMA results of WP, PVOH and WP/PVOH blends are shown in Fig. 1. WP shows glass transition (T_g) behaviour as amorphous polymers with strong dependence of the content of plasticisers. The tan δ peak of WP-p35 corresponding to the glass transition appeared as a broad line with the maximum value appeared at 102 °C. This was consistent with the result reported previously [27]. The tan δ maximum value of the blends shifted to 109 or 113 °C when PVOH content was 10 or 18%, and further shifted to 120 °C when the PVOH content increased to 25%. Note that the moisture would start to evaporate out from the sample as temperature increased and losing plasticisers from the system should result in the T_g shifting to higher temperatures thus caused a broad tan δ peak for the samples. All WP and WP/PVOH blends showed a shoulder peak of tan δ at
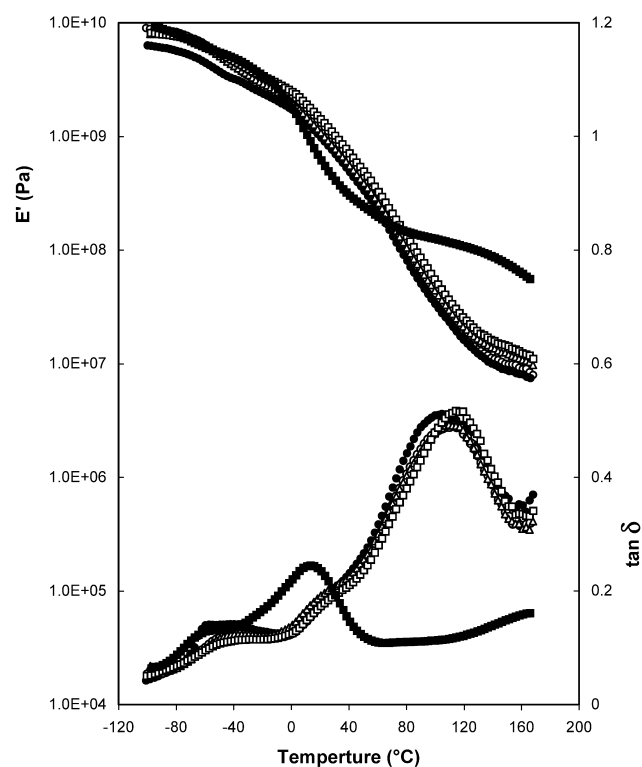

Fig. 1. The storage modulus (E') and tan δ of WP/PVOH blends from DMA. WP-p35 (●), PVOH-10% (○), PVOH-18% (△), PVOH-25% (□) and PVOH-p35 (■).

around 20–30 °C and these shoulder peaks could be corresponding to the T_g of the samples with designed formulations. PVOH-p35 presented a tan δ peak at around 10 °C but the peak disappeared in the blends or shifted to higher temperature that overlapped with the strong peaks corresponding to T_g transitions of the blends. Note that these maximum values of tan δ slightly varied in the blends but the peak broadness of the blends was similar to that of WP-p35 suggesting the multi-component blending systems were homogenously mixed. Both WP-p35 and PVOH-p35 presents a tan δ peak corresponding to β-transitions with the maximum at −60 °C, but the maximum of the peak shifted to −40 °C for the blends. This β-transition could be due to the glass transition of bound water and glycerol strongly associated with the polymer matrix through hydrogen bonding. The shift of the tan δ peak and the decrease in the peak intensity of the blends suggested the intermolecular interaction between WP and PVOH also modified the motions of plasticisers associated to the polymers.

These results indicate that WP/PVOH blends with

Table 2
Strength enhancement in WP/PVOH blends

	Tensile strength enhancement (%)	Elongation of the materials (%)	Young's modulus enhancement (%)
PVOH-10%	21.1	39.2	15.1
PVOH-18%	27.7	35.5	20.7
PVOH-25%	54.3	21.1	33.0

plasticisers are compatible multi-component systems with modified molecular motions and mechanical properties. However, the DMA study failed in providing detailed behaviours of each component in such a complicated system. The solid-state high-resolution NMR technique is particularly powerful to obtain information of structures and molecular motions of each component in a multi-component system and the interactions among these components in the system via examining the solid-state high-resolution NMR spectra in conjunction with various NMR relaxation parameters. These parameters can be measured at room temperatures ensuring the samples to retain the phase structures formed after thermal processing with designed material formulations.

The ^{13}C NMR spectra of WP powder and WP-p35 are shown in Fig. 2 observed using CP/MAS/DD (shown as A) and SPE (shown as B) methods, respectively. Usually the rigid polymer components with strong dipolar interactions are detected by CP/MAS method while mobile components are observed by the SPE method by using a short repetition time ca. 2 s. The CP/MAS spectrum of pure WP powders is quite consistent with the results reported previously [32–37] except that the residual starch signals are very weak. The major resonances at 173, 54, 30 and 26 ppm in the spectrum of WP powders are attributed to the carbonyl, C-α, C-β and C-γ carbons of the WP, respectively. Minor resonances in the spectrum at 157, 138, 129 and 116 ppm are due to Arg, Tyr and Phe [38]. Detailed analysis of the linewidth of the C=O resonance at 173 ppm suggested that the side chain C=O resonances could appear slightly downfield (near 180 ppm) as a shoulder [38]. The ^{13}C CP/MAS spectra of WP with a varied contact time are shown in Fig. 3 and the results confirmed the structure assignment of the WP sample. Only the C=O carbons without bonded hydrogen showed a weak cross-polarization capability that the intensity increased slowly with increasing cross-polarization contact time. The mobile components in WP as detected by SPE method shown in Fig. 2B are mainly due to the lipid (at 130 and 30 ppm) and some mobile protein
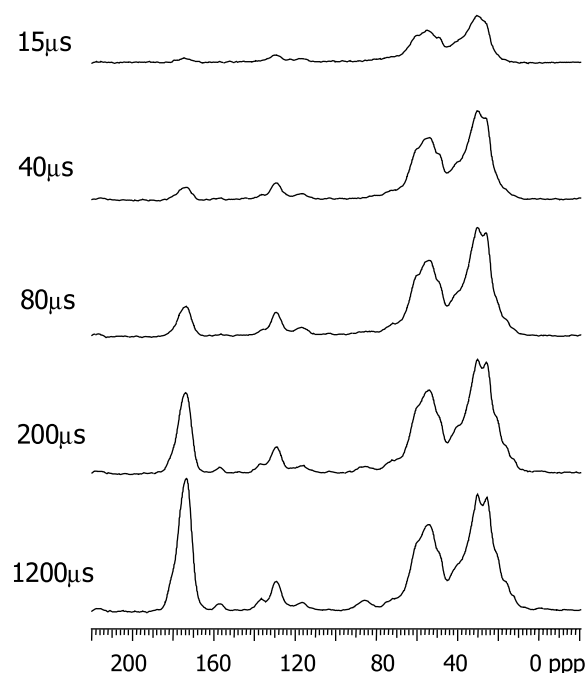
Contact time:

Fig. 3. ^{13}C CP/MAS spectra of WP powder sample observed at varied cross-polarization contact time.

chains such as side chains. The sharp peaks at 73 and 64 ppm of WP-p35 are due to the plasticiser glycerol as observed by both CP/MAS and SPE methods. Obviously, the glycerol resonances are greatly enhanced in the SPE spectrum.

The ^{1}H $T_{1\rho}$ values of the WP powder and the plasticised WP-p35 samples were measured via ^{13}C resonances through cross-polarization as reported in Table 3. The values obtained from all ^{13}C resonances are quite identical in each WP sample. The results indicate strong spin-diffusion interactions among each WP sample have averaged out the relaxation process of all protons so that the systems are homogeneous at the scales of the spin-diffusion path length within the $T_{1\rho}$ time, ca. 2–3 nm. The plasticiser effect is also
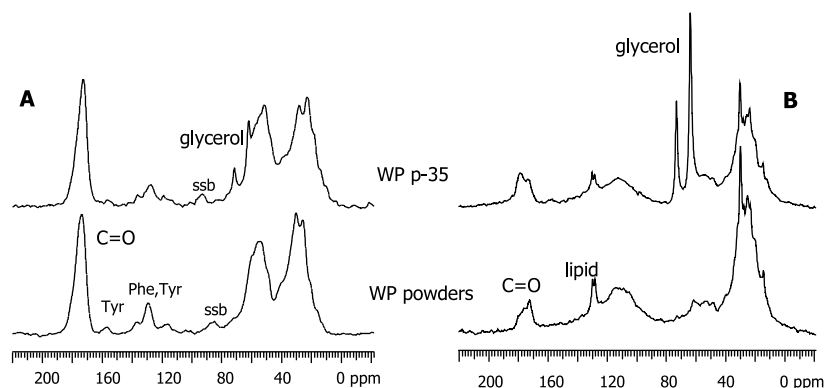

Fig. 2. ^{13}C CP/MAS spectra (A) and SPE spectra (B) of WP powder and WP-p35 sheet samples.

Table 3
^{1}H $T_{1\rho}$ (ms) of WP/PVOH blends measured via ^{13}C resonances

	174 ppm	129 ppm	74 ppm	55 ppm	45 ppm	27 ppm
WP-native	4.9	4.9		4.9		4.8
WP-p35	2.5	2.4	2.4	2.4		2.5
PVOH-10%	2.6	2.5	2.9	2.5	3.1	2.5
PVOH-18%	2.6	2.5	4.4	2.6	4.3	2.7
PVOH-25%	2.6	2.5	4.3	2.5	4.4	2.6
PVOH-p35			5.0		4.9	
Pure PVOH			2.5 (38%)		2.3 (34%)	
			12.4 (62%)		12.8(66%)	

significant as the $T_{1\rho}$ values decreased in the WP-p35 sample. Note that the $T_{1\rho}$ value obtained from the intensity at 73 ppm (glycerol peak) of the WP sheet sample was also identical to the data observed from other resonances suggesting the signals detected by the CP/MAS method are the glycerol molecules strongly associated with WP chains via hydrogen bonding.

The ^{13}C high-resolution solid-state NMR spectra of semi-crystalline polymer PVOH detected via both CP/MAS and SPE methods are shown in Fig. 4. The three split peaks at 75.4, 70.8 and 64.7 ppm of the CH resonances in the CP/MAS spectrum of PVOH have been studied comprehensively and were assigned to the chain sequence and the formation of various intramolecular hydrogen bonds in the polymer [39–43]. When plasticisers were used (PVOH-p35), the relative intensity of the peak at 75.4 ppm decreased significantly while those at 70.8 and 64.7 ppm increased in the CP/MAS spectrum. This could be due to the formation of hydrogen bonding between the polymer and the plasticisers. Note that the glycerol signals were not detected in the CP/MAS spectrum indicating the hydrogen bonding between glycerol and PVOH was weak thus the glycerol was still mobile in the system with a weak cross-polarization capability. The hydrogen bonding between PVOH and water molecules was dominant in the system. This was quite different from the situation in WP-p35 where glycerol molecules were strongly associated with WP chains resulted in a strong cross-polarization capability.

The mobile amorphous PVOH component was observed by SPE method with a short repetition time of 2 s. Only one sharp peak at 71.3 ppm was observed in conjunction with a broad line for the CHOH resonance. The resonances should be attributed to the mobile amorphous PVOH component and those associated with water molecules. This peak slightly shifted to 70.3 ppm in the SPE spectrum of PVOH-p35. Glycerol signals were also detected in the SPE spectrum shown at 72.8 and 63.5 ppm.

The ^{13}C CP/MAS NMR spectra of WP, PVOH and their blends are shown in Fig. 5. The WP resonances at 173 ppm and 25–30 ppm do not overlap with those of either PVOH or glycerol so that the NMR characteristics obtained from the resonances such as the chemical shift, linewidth and relaxation behaviours should indicate the WP's behaviour in the blends while the CH_2 resonance of PVOH at 45 ppm should represent the phase structure of PVOH in the blends. The NMR parameters observed from the resonances at 55–74 ppm represent the mixed characters of WP, PVOH and glycerol in the WP/PVOH blends. If hydrogen bonding was formed between WP and PVOH in the blends, the carbonyl groups (C=O) of WP should be the hydrogen bonding acceptors while the nitrogen of the amide groups of WP and the hydroxyl group of PVOH could be both hydrogen bonding donators and acceptors. The chemical shift of the C=O resonance of the WP component shifted 0.2–0.4 ppm downfield in conjunction with a 10–20 Hz linewidth broadening in the WP/PVOH blends. These changes were
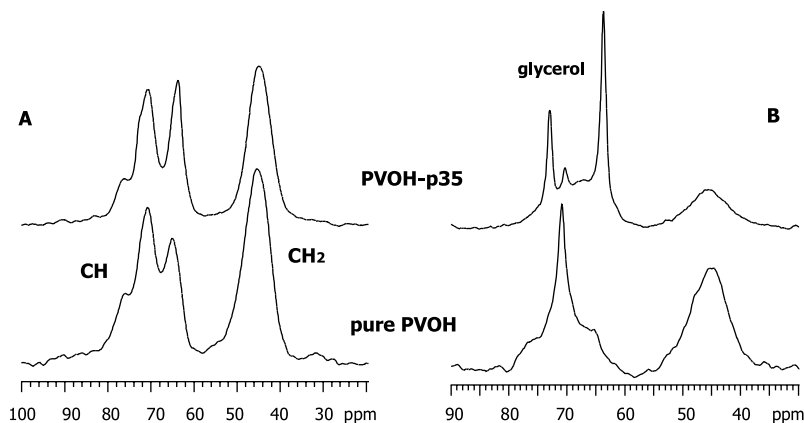

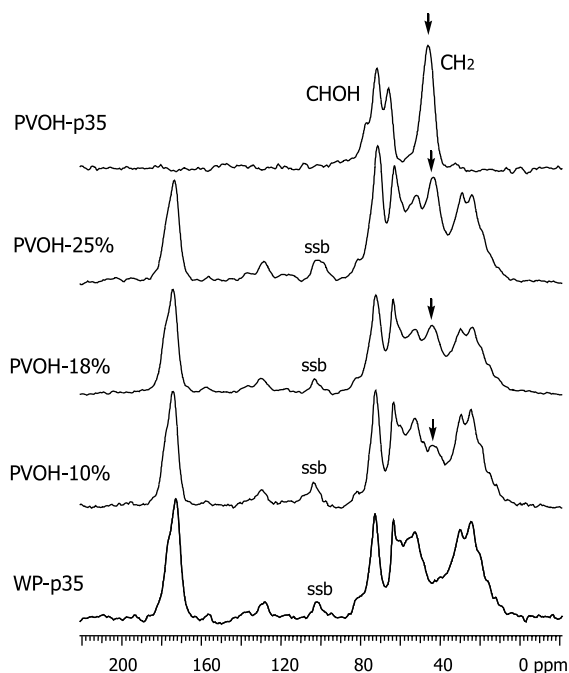Fig. 4. ^{13}C CP/MAS spectra (A) and SPE spectra (B) of PVOH powder and PVOH-p35 sheet samples.

Fig. 5. ^{13}C CP/MAS spectra of plasticised WP/PVOH blends.

not as pronounced as those observed in other miscible blends with strong hydrogen bonding among different polymer components [44–47] indicating the intermolecular interactions between WP and PVOH component were relatively weak in the blends as plasticisers were present in the system.

The miscibility of polymer blends can be studied via examining the change of NMR relaxation behaviours of each component in the blends [44–47]. The ^{1}H $T_{1\rho}$ values of the WP/PVOH blends measured via ^{13}C resonances through cross-polarization are listed in Table 3. Two ^{1}H $T_{1\rho}$ components were obtained for the pure crystalline polymer PVOH corresponding to the crystalline (long $T_{1\rho}$ component) and amorphous (short $T_{1\rho}$ component) phases, however, only one $T_{1\rho}$ component was detected for PVOH-p35 and the value (4.9–5.0 ms) was different from both of the components in pure PVOH. It suggested that the crystalline phase disappeared in PVOH-p35 after thermal processing. As mentioned before, WP-p35 showed a single ^{1}H $T_{1\rho}$ for all resonances and these values were very close to each other indicating a strong spin-diffusion interaction among the system has averaged out the relaxation difference within the materials including the immediate hydrogen bonded plasticiser glycerol. For the PVOH-10% blends, the ^{1}H $T_{1\rho}$ values obtained from the resonance at 45 ppm (the PVOH component) in the blends showed a single component with a value around 3.1 which was longer than those observed from WP resonances (2.5–2.6 ms) but shorter than that observed for PVOH-p35 (4.9–5.0 ms). The values of the WP component in the same blend also increased slightly as compared to those of WP-p35 but the change was not as significant as that for the PVOH component because the WP

was dominant in the blends. A $T_{1\rho}$ value of 2.9 ms was observed at 74 ppm representing a mixing behaviour of both PVOH and glycerol in the blend. The results suggested the presence of some extent of spin-diffusion interactions between WP and PVOH for forming miscible WP/PVOH phase in the blends. However, the interaction was not strong enough to average out the ^{1}H $T_{1\rho}$ relaxation behaviour in the whole system, the blends were partial miscible in a scale of 2–3 nm, the effective spin-diffusion length during the ^{1}H $T_{1\rho}$ times. In PVOH-18% and PVOH-25% blends, the $T_{1\rho}$ values observed from the PVOH components (at 45 ppm) decreased much less than that in PVOH-10% as compared to the value of PVOH-p35 while the values observed from the resonances of WP components (at 174, 129, 55 and 27 ppm) appeared similar to those in PVOH-10%. The result indicates that the interactions between the two components were not enhanced with increasing the amount of PVOH component in the blends.

The study of ^{1}H T_{1} relaxation behaviours of a blend can provide the miscibility information at a scale of ca. 20–30 nm, the effective spin-diffusion length during the T_{1} relaxation times [44–47]. The data of WP/PVOH blends observed via ^{13}C resonances through cross-polarization are shown in Table 4. The ^{1}H T_{1} data observed from each resonance of WP-p35 or PVOH-p35 were identical, respectively, suggesting each individual polymer system was homogenous as detected by the CP/MAS method. For the PVOH-10% blend, the ^{1}H T_{1} data of the WP component (observed at 173 and 27 ppm) increased to 0.41–0.43 s as compared to that of WP-p35 (0.35–0.37 s) while the ^{1}H T_{1} data of the PVOH component (observed at 45 ppm) decreased to 0.64 s as compared to that of PVOH-p35 (0.90 s). These results were consistent with those observed in ^{1}H $T_{1\rho}$ measurements, indicating the presence of miscible WP/PVOH phase with spin-diffusion interactions among the two polymer components and plasticisers. However, no further interaction enhancement was observed when increasing the amount of PVOH to 18 or 25% in the blends. The blends are still particle miscible even at ^{1}H T_{1} scales ca. 20–30 nm. It is interesting to note that the ^{1}H T_{1} data of the PVOH component in PVOH-25% (0.95 s observed at 45 ppm) were even longer than those of PVOH-p35 (0.90 s) suggesting that the phase structure of the PVOH component might be modified in the blend.

For these plasticised WP/PVOH blends, the mobility of the materials has made it possible to observe high-resolution

Table 4
^{1}H T_{1} (s) of WP/PVOH blends measured via ^{13}C resonances

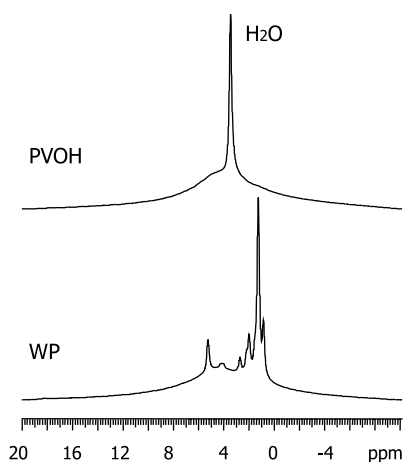|	174 ppm	129 ppm	74 ppm	55 ppm	45 ppm	27 ppm
WP-p35	0.39	0.37	0.35	0.35		0.35
PVOH-10%	0.43	0.43	0.54	0.42	0.64	0.41
PVOH-18%	0.43	0.43	0.80	0.41	0.84	0.42
PVOH-25%	0.44	0.45	1.1	0.45	0.95	0.44
PVOH-p35			0.90		0.90	

Fig. 6. ^{1}H MAS spectra of WP and PVOH powder samples.

solid-state ^{1}H NMR spectra by using the MAS technique. Fig. 6 shows the ^{1}H MAS NMR spectra of pure WP and PVOH powder samples, respectively, measured at a MAS speed of 10 kHz. The rigid parts of the polymers were missed in the spectra. The resonances of WP at 5.3 and 4.2 ppm should be assigned to amide hydrogen and H_2O, respectively, while the peaks at 2.7–2.0, 1.3 and 0.87 ppm are due to CH, CH_2 and CH_3 protons of lipid and mobile protein structure. The broad peak over a wide range in the ^{1}H spectrum of PVOH is assigned to the protons of the polymer while the sharp peak at 3.5 ppm is due to the

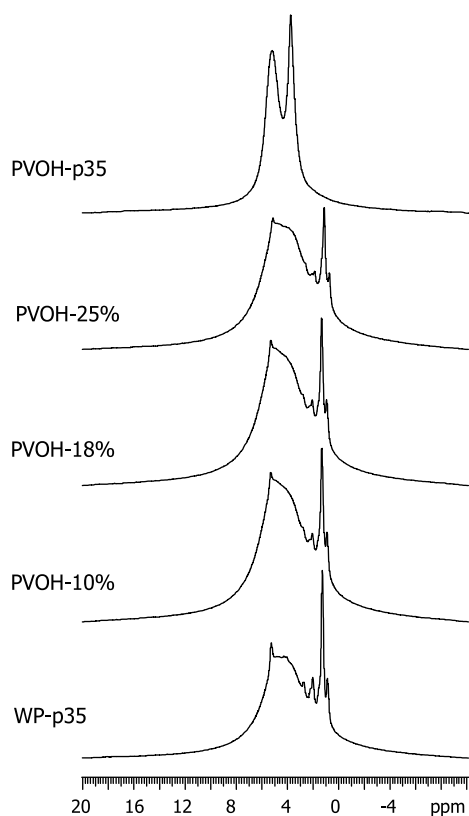
Fig. 7. ^{1}H MAS spectra of plasticised WP/PVOH blends.

moisture in the polymer. When the plasticisers glycerol and water were used, the two strong peaks of PVOH-p35 observed (shown in Fig. 7) are due to glycerol and water while the mobile polymer resonances may also contribute to the signals in this range in a small proportion. The broad resonance of WP-p35 at 4.5–5.0 ppm is due to both glycerol and water and the broad signal is attributed to a chemical exchange process between the protons of glycerol and water in this case that is different from the situation in PVOH-p35. Note that only the sharp resonances at 1.0–2.0 ppm (CH_2 and CH_3 not directly bonded to O, N or C=O groups) should reflect the behaviour of the mobile WP component in the blends.

The ^{1}H T_1 relaxation times of the WP/PVOH blends measured via ^{1}H MAS spectra are listed in Table 5. The ^{1}H T_1 values observed for WP-p35 via ^{1}H MAS spectra are quite similar to those obtained via ^{13}C resonances reported in Table 4. The result suggests the mobility of WP-p35 detected via CP/MAS is similar to that observed in ^{1}H MAS spectra which further confirms the homogeneity of the plasticised WP materials. In contrast, the data of PVOH-p35 observed via ^{13}C resonances (Table 4) are relatively longer than those detected by ^{1}H MAS spectra suggesting PVOH-p35 is heterogeneous at ^{1}H T_1 scale ca. 20–30 nm. For WP/PVOH blends, the ^{1}H T_1 values of the WP component (detected at 2.0, 1.3 and 0.9 ppm) shown in Table 5 are always identical to those detected from the plasticiser peak (at 5.3 ppm) in each blend. The values became shorter when compared to those observed via ^{13}C resonances shown in Table 4 suggesting heterogeneity in the WP component in the blends at a scale of 20–30 nm. However, the ^{1}H T_1 of all components increased when the PVOH component increased in the blends indicating some extent of spin-diffusion interactions between the two polymer components. The intermolecular interactions between the WP and PVOH component resulted in some miscible interphase in the blends that caused an increase of tensile strength and modulus of the blends. However, increasing the amount of PVOH in the blends does not enhance the intermolecular interactions to generate a totally homogeneous system on scales of nanometers. Therefore the elongation at break of the partial miscible blends is reduced with increasing of the amount PVOH component in the blends.

Table 5
^{1}H T_1 of WP/PVOH blends measured via ^{1}H MAS spectra

	5.1–5.3 ppm	3.5 ppm	2.0 ppm	1.3 ppm	0.9 ppm
WP powder	0.48		0.45	0.43	0.46
WP-p35	0.32		0.31	0.33	0.34
PVOH-10%	0.37		0.36	0.36	0.38
PVOH-18%	0.37		0.36	0.36	0.37
PVOH-25%	0.41		0.40	0.39	0.40
PVOH-p35	0.75	0.73			
PVOH powder		1.54			

4. Conclusions

The high-resolution solid-state NMR study indicated that the molecular chains of WP could be homogeneously mobilized when thermally processed with glycerol and water as plasticisers. But the glycerol predominately associated with the WP component rather than PVOH in the WP/PVOH blends. DMA results suggested a homogenous mixing in the blends. The tensile strength and modulus of the blends were also improved as compared to WP. However, high-resolution solid-state NMR study provided detailed information of the behaviour of each component in the multi-component system and indicated that a phase heterogeneity was present in the blends. The intermolecular hydrogen-bonding interactions among WP, PVOH and the plasticisers resulted in some extent of spin-diffusion interactions in the system on scales of nanometers, but the interactions were not strong enough to average out the molecular motions of the whole system. The blends were particle miscible systems with different molecular motion characters in WP/PVOH miscible phase, plasticised WP and PVOH phases due to the different extent of interactions. Increasing the amount of PVOH in the blends did not enhance the intermolecular interactions between the two polymer components, thus the elongation of the blends reduced with increasing the content of PVOH in the blends.

Acknowledgements

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