ELSEVIER

Polymer 43 (2002) 1203–1206

polymer

www.elsevier.com/locate/polymer

Elongation-induced phase separation of poly(vinyl alcohol)/poly(acrylic-acid) blends as studied by ^{13}C CP/MAS NMR and wide-angle X-ray diffraction

Qun Chen[a], Hiromichi Kurosu[b,*], Lin Ma[b], Masaru Matsuo[b]

[a]*Analytical Center and The Key Laboratory of Education Ministry for Optical and Magnetic Resonance Spectroscopy, East China Normal University, Shanghai 200062, People's Republic of China*

[b]*Department of Textile and Apparel Science, Faculty of Human Life and Environment, Nara Women's University, Nara 630-8506, Japan*

Received 13 September 2001; accepted 1 October 2001

Abstract

The membrane samples of poly(vinyl alcohol)/poly(acrylic-acid) (PVA/PAA) blend with different draw ratios were studied by both ^{13}C CP/MAS NMR and wide-angle X-ray diffraction (WAXD) measurements. Phase separation induced by elongation of the sample was observed and the change of the phase structure with draw ratio was found to be dependent on the composition of the blend samples.

Keywords: Poly(vinyl alcohol)/poly(acrylic-acid) blend; Elongation; ^{13}C CP/MAS NMR

1. Introduction

Inter-polymer hydrogen-bonding interaction is one of the driving forces that can make dissimilar polymer pair become miscible on molecular level. By selecting polymer pairs with inter-polymer hydrogen-bonding interactions and by varying the relative mass fractions of the pairs, it is possible to continuously tailor the mechanical properties of the blends. Thus the nature of inter-polymer hydrogen-bonding and the miscibility of the corresponding blends are of great research interests in the area of polymer blend studies [1]. Poly(vinyl alcohol)/poly(acrylic-acid) (PVA/PAA) is a typical blend system in which molecular level miscibility is achieved by inter-polymer hydrogen-bonding interactions. Previous solid-state high-resolution ^{13}C NMR studies [2] on the system has revealed that due to the strong inter-polymer hydrogen-bonding interactions between the hydroxyl group of PVA and the carboxyl group of PAA, the crystalline phase of PVA can be destroyed completely when the molar ratio of vinyl alcohol is equal to or less than that of acrylic-acid in the blend. What is interesting is that the phase structure and the miscibility of PVA/PAA blend can be understood directly from the relative intensities of the three methine carbon peaks in the ^{13}C CP/MAS NMR spectrum, which are closely related with the inter- and/or intra-polymer hydrogen bonds.

In this work, we disclose the first results of ^{13}C CP/MAS NMR and wide-angle X-ray diffraction (WAXD) measurements on PVA/PAA blend samples with different draw ratios. An interesting phenomenon, which can be termed as elongation-induced phase separation in bulk system, is observed with its cause discussed.

2. Experimental

PVA and PAA that were purchased from Wako Co. were separately dissolved in hot water at a concentration of 5 wt% and mixed with different compositions. Two blend samples with PAA contents in monomer molar of 0.27 and 0.53 were prepared and designated sample I and sample II, respectively. The solution was stirred for ca. 4 h at 50 °C and then poured onto glass plates and stored at room temperature for 2–3 days. The obtained membrane samples were drawn to different ratios at 180 °C and then dried under vacuum at 55 °C for 2 days before NMR and WAXD measurements. For comparison, pure PVA and PAA membrane samples and PVA membrane sample drawn to eight times of its original length were also prepared using the same procedures.

^{13}C CP/MAS NMR measurements were carried out on

---

* Corresponding author. Tel./fax: +81-742-203-461.
E-mail address: kurosu@cc.nara-wu.ac.jp (H. Kurosu).

0032-3861/02/$ - see front matter © 2001 Elsevier Science Ltd. All rights reserved.
PII: S0032-3861(01)00690-5

JEOL JM-EX270 and Bruker DSX-300 spectrometers operating at 67.8 and 75.47 MHz, respectively. The MAS spinning rates were 4–6 KHz and the contact time for CP was 2 ms. The repetition time was 5 s and the ^{1}H decoupling field strength was about 55 KHz. The chemical shifts were determined relative to the higher field signal (29.5 ppm) of adamantane. 1 K fids were accumulated for each spectrum to obtain satisfactory signal to noise ratio. ^{1}H $T_{1\rho}$ was estimated by employing a CP pulse sequence modified by adding a variable spin-locking pulse immediately after the ^{1}H $\pi/2$ pulse [3]. It was found that small amount of residue water in the samples can lead to significant under-estimation of the ^{1}H $T_{1\rho}$ values of both PVA and PAA components. Therefore, sufficient drying of samples was found to be necessary to give comparable results of ^{1}H $T_{1\rho}$ measurement. The WAXD measurements were carried out at room temperature with a 12-KW rotating-anode X-ray generator (Rigaku RDA-rA) operating at 200 mA and 40 Kv. The detailed procedure of the measurement was described elsewhere [4].

3. Results and discussion

The room temperature ^{13}C CP/MAS spectra of PVA, sample I and sample II are depicted in Fig. 1. The peak at 180 ppm is due to the carbonyl carbon of PAA, while the peak resonated at 40–45 ppm is corresponding to the methylene carbon of PVA in Fig. 1a and the methylene carbon of PVA and methine and methylene carbons of PAA in Fig. 1b and c. Three overlapped peaks from 65 to 77 ppm are corresponding to the methine carbon of PVA and are designated peaks 1, 2 and 3, respectively, from low to high field. The nature of these three peaks has been investigated extensively [5–8]. Terao et al. [5] resorted to the intra-molecular hydrogen-bonding interactions to explain the splitting. Peaks 1, 2 and 3 are assigned to central methine carbons in triad sequences forming two, one, and no intra-molecular hydrogen bonds, respectively. On the other hand, Kobayashi et al. [8] suggested an alternative explanation for the splitting by considering both intra- and inter-molecular hydrogen-bonding interactions between hydroxyl groups. Peaks 1, 2 and 3 can then be simply assigned to triad sequences forming two, one and no hydrogen bonds. Apparently, no matter which assignment is correct, peak 1 and peak 2 can be considered to be closely associated with the hydrogen bonding interactions between hydroxyl groups. Zhang et al. [2] studied PVA/PAA blends and found that the relative intensities of peaks 1 and 2 decrease with the increase of PAA content, indicating the increase of the number of inter-polymer hydrogen bonds formed between hydroxyl and carbonyl groups at the expense of intra-polymer hydrogen bonds formed between hydroxyl groups. It is believed that the inter-polymer hydrogen bonds formed between hydroxyl and carbonyl groups, due to its relative longer bond length, do not lead to observable shift of the methine peak and the corresponding methine signal superposes with peak 3. With the support of the results in ^{1}H T_1 and $T_{1\rho}$ measurements, Zhang et al. revealed that the relative intensities of three methine peaks could serve as a sensitive measure of the miscibility of PVA/PAA blend. Similar result was also observed in Fig. 1. The relative intensities of peaks 1 and 2 are significantly weaker than that of PVA, demonstrating the molecular level miscibility of PVA and PAA in two blend samples.

Fig. 2a shows the room temperature ^{13}C CP/MAS spectra of sample I with different draw ratios. The relative intensities of three methine peaks were obtained by computer-fitting and plotted in Fig. 3 as a function of draw ratio. It can be clearly seen that when the draw ratio increases, the relative intensities of peak 1 and peak 2 increase while the intensity of peak 3 decreases. At the maximum draw ratio

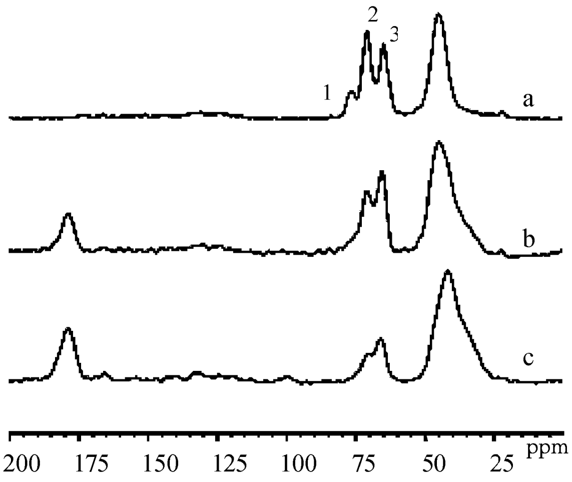


Fig. 1. ^{13}C CP/MAS spectra at room temperature: (a) PVA membrane sample; (b) sample I; (c) sample II.

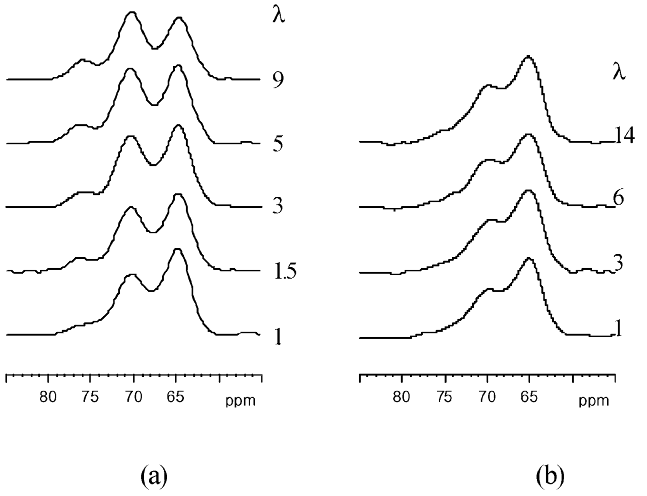


Fig. 2. ^{13}C CP/MAS spectra of the methine carbon of PVA: (a) sample I; (b) sample II with different draw ratios (λ).

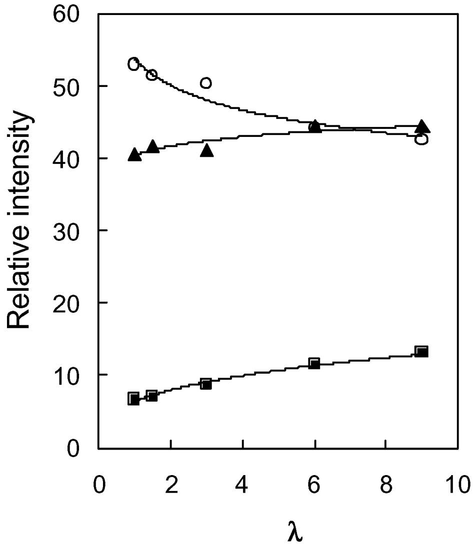
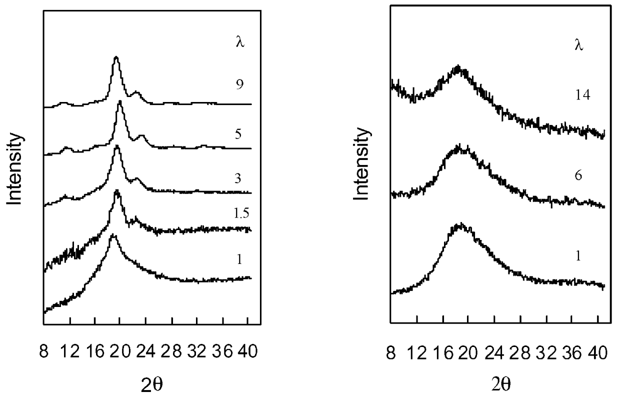


Fig. 3. Plots of the relative intensities of three methine peaks in the ^{13}C CP/MAS spectra of sample I against the draw ratio (λ), where (■), (▲) and (○) are corresponding to the data of peaks 1, 2 and 3, respectively.

($\lambda = 9$), the relative intensities of three methine peaks are very close to that of the PVA membrane sample without elongation. According to the nature of three methine peaks, the above results indicate that upon elongation, the inter-polymer hydrogen bonds formed between the hydroxyl group of PVA and the carbonyl group of PAA gradually break and in the meantime more intra-polymer hydrogen bonds between hydroxyl groups are formed with the increase of draw ratio.

The X-ray diffraction intensity curves of sample I with different draw ratios I is depicted in Fig. 4a. Only one broad peak associated with the reflection of (110) and $(1\bar{1}0)$ planes of PVA crystals around 19.5° can be observed for the sample that was not drawn [4], demonstrating the low crystallinity of the sample as a consequence of blending. With the gradual increase of the draw ratio, more diffraction peaks appear and the main peak around 19.5° becomes sharper. For PVA samples with different draw ratio, similar changes in X-ray diffraction intensity curves, although less significant, can be observed. Such a change was related to the increase of crystallinity of PVA with increasing of draw ratio [4]. For sample I, we believe that the significant changes of X-ray diffractions intensity curves shown in Fig. 4a, not only reflect the increase of the degree of crystallinity of the PVA component with the increase of draw ratio, but also indicate that phase separation occurred during the elongation process. The reason is, for a miscible blend sample like sample I under elongation, the aggregation of the crystallizable component or in other words, phase separation is the necessary condition of crystallization. The conclusion that phase separation occurred during the elongation process is supported by the results of ^{13}C CP/MAS measurements as discussed earlier.



(a) (b)

Fig. 4. X-ray diffraction intensity curves normalized to the same total intensity: (a) sample I; (b) sample II with different draw ratios (λ).

Fig. 2b shows the room temperature ^{13}C CP/MAS spectra of sample II with different draw ratios. It is interesting to find that in contrast to the result of sample I, no obvious changes of the relative intensities of three methine peaks with increasing of draw ratio is observed. Meanwhile, the maximum draw ratio is found to be 14, apparently higher than that of sample I. Such a discrepancy can be ascribed to the difference in the compositions of two blend samples. For sample I, the PVA content in monomer molar is 0.73, which means PVA may be the matrix of the blend. Therefore, PVA chains may be subject to more influence of elongation compared with PAA chains. It is reasonable to imagine that during the drawing process, some PVA chains gradually slide from the blended structure accompanied by the breaking of inter-polymer hydrogen bonds with PAA, aggregate and then form crystalline structure. On the other hand, for sample II, the PVA content in monomer molar is 0.47, which is close to that of PAA. In such a case, both PVA and PAA chains may be almost equally affected by elongation, giving no obvious influence on the miscibility of the blend. Such a deduction is also supported by the result of X-ray diffraction experiments on sample II with different draw ratios shown in Fig. 4b. Contrary to the result of Fig. 4a, no increase in the crystallinity of the sample was observed with increasing of draw ratio, suggesting no PVA chain aggregation occurred during the drawing process. Furthermore, we believe the elongation-induced phase separation and subsequent crystallization of PVA chains is the main reason that sample I exhibits lower maximum draw ratio than sample II does.

As is well known, ^{1}H $T_{1\rho}$ values of the individual components of blend samples can provide useful information about phase separation [2,3]. To further testify the aforementioned conclusions, ^{1}H $T_{1\rho}$s of the drawn and undrawn blend samples were estimated by measuring the ^{1}H $T_{1\rho}$ relaxation dependent ^{13}C CP/MAS spectra. For comparison, ^{1}H $T_{1\rho}$s of drawn PVA and undrawn PVA and PAA samples were also measured. It was found that for PVA and the blend samples,

Table 1
^{1}H $T_{1\rho}$s of PVA, PAA and the blend samples

Samples	Draw ratio (λ)	^{1}H $T_{1\rho}$ (ms)	
		CHOH (PVA)	C=O (PAA)
PVA	1	7.4	
PVA	8	8.3	
PAA	1		5.5
Sample I	1	6.0	5.6
Sample I	9	7.0	5.2
Sample II	1	6.3	5.9
Sample II	14	6.6	6.3

three methine peaks show almost same decay rate. Therefore, the total integral of three methine peaks was employed to calculate the ^{1}H $T_{1\rho}$ of PVA or PVA component in the blend samples. It is also found that for all the samples studied, each carbon peak appeared in the ^{13}C CP/MAS spectra exhibits single exponential ^{1}H $T_{1\rho}$ decay behavior. Such a result is in agreement with some of the previous studies, [9,10] but is different from that reported by Zhang et al. [2], in which PVA and PVA component in some blend samples were found to exhibit biexponential ^{1}H $T_{1\rho}$ decay behavior.

The obtained ^{1}H $T_{1\rho}$ values are listed in Table 1. From the table, the following analyses can be made: (1) elongation of PVA does not lead to a marked change of its ^{1}H $T_{1\rho}$ value; (2) the difference between the ^{1}H $T_{1\rho}$s of PVA and PAA at room-temperature is significant enough for phase separation analysis; (3) for sample I and sample II (undrawn), the PVA and PAA components exhibit close ^{1}H $T_{1\rho}$ values, suggesting that fast spin-diffusion among protons has equalized the ^{1}H $T_{1\rho}$s of the different components. This result indicates the good miscibility of these two blend samples; (4) for sample I with maximum draw ratio ($\lambda = 9$), the difference between the ^{1}H $T_{1\rho}$ of PVA component and that of PAA component is much bigger than that of the other blend samples. This result clearly indicates the phase separation of two components on a scale of 20–30 Å. While for sample II with maximum draw ratio ($\lambda = 14$), PVA and PAA component show very close ^{1}H $T_{1\rho}$ values, which suggests under such a high draw ratio, the PVA and PAA components are still miscible. Therefore, the results of ^{1}H $T_{1\rho}$ measurement directly support the aforementioned conclusion.

In conclusion, an elongation-induced phase separation of PVA/PAA blend is observed. The change of the phase structure with draw ratio is found to be dependent on the composition of the blend samples. The elongation-induced phase separation of polymer blend in the bulk state, to our knowledge, has not been reported before. Further works using above strategy on other PVA based blends are ongoing and will be reported in due course.

Acknowledgements

This work was supported by JSPS foundation and the foundation of Education Ministry of China.

References

[1] Miyoshi T, Takegoshi K, Terao T. Macromolecules 1999;32:8914 And references therein.

[2] Zhang X, Takegoshi K, Hikichi K. J Polym 1991;23:87.

[3] Dickinson LC, Yang H, Chu CW, Stein RS, Chien JCW. Macromolecules 1987;20:1757.

[4] Bin Y, Tanabe Y, Nakabashi C, Kurosu H, Matsuo M. Polymer 2001;42:1183.

[5] Terao T, Maeda S, Saika A. Macromolecules 1983;16:1535.

[6] Ketels H, de Haan J, Aerdts A, van de Velden G. Polymer 1990;31:1419.

[7] Horii F, Masuda K, Kaji H. Macromolecules 1997;30:2519 And references therein.

[8] Kobayashi M, Ando I, Ishii T, Amiya S. Macromolecules 1995;28:6677.

[9] VanderHart DL, Simmons S, Gilman JW. Macromolecules 1995;36:4223.

[10] Horii F, Hu S, Ito T, Odani H, Kitamaru R, Matsuzawa S, Yamaura K. Polymer 1992;33:2299.