

Effect of Thermal Treatments on the Miscibility of Poly(vinyl cinnamate) Binary Blends

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ABSTRACT: Poly(vinyl cinnamate) (PVCN) could undergo thermal or photo crosslinking. PVCN was previously found to be miscible with poly(vinyl phenol) (PVPh) [also named poly(hydroxystyrene)]. In this article, the miscibility between PVCN with or without thermal crosslinking and poly(styrene-*co*-hydroxystyrene) (designated as MPS) was investigated. PVCN was determined to be miscible with MPS with 15% of hydroxystyrene (MPS-15) at two compositions but partially miscible or immiscible at PVCN/MPS-15(50/50) composition. For MPS with 5% of

hydroxystyrene (MPS-5), two T_g values were detected indicating mostly immiscibility. However, PVCN after thermal crosslinking was determined to be miscible with both MPS-5 and MPS-15. Immiscibility was found between thermally crosslinked PVCN and PVPh different from miscibility in the original PVCN/PVPh blends. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 900–903, 2008

Key words: poly(vinyl cinnamate); thermal treatments; miscibility

INTRODUCTION

In the past decades, polymer blends¹ have received much attention because they can offer a wide range of material properties. Since the physical properties of such blends are strongly influenced by the miscibility, a lot of experimental techniques such as thermal analysis, mechanical testing, light scattering, microscopy, and spectroscopy method^{2,3} were used to investigate blend or blend miscibility. In this laboratory, differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR) are often used to investigate the miscibility and the intermolecular interactions of polymer blends.^{4,5}

Poly(vinyl cinnamate) (PVCN) was produced by reacting poly(vinyl alcohol) with cinnamic acid. The reaction is often not complete; therefore, PVCN is actually a copolymer of vinyl cinnamate and alcohol. PVCN could undergo photo⁶ and thermal crosslinking by opening its double bonds. PVCN was determined to be miscible with poly(vinyl phenol) (PVPh).⁶ PVCN was likely to be immiscible with poly(styrene) because of no hydrogen bonding and difference in polarity. Is PVCN miscible with poly(styrene-*co*-hydroxystyrene)? In this investigation, poly(sty-

rene-*co*-hydroxystyrene) with 5 or 15 mol % of hydroxystyrene (designated as MPS-5 and MPS-15) were separately mixed with PVCN. Their miscibility behavior was determined mainly based on calorimetry data. Also, heat is often applied during polymer blend preparations. Therefore, PVCN mixed with MPS-5, MPS-15, and PVPh after thermal treatments were prepared. Effects of thermal treatments on PVCN and its miscibility with other polymers were discussed in this article.

EXPERIMENTAL

Materials

PVCN was obtained from Scientific Polymer Products (Ontario, NY) and had a M_w value of 200,000 g/mol. PVPh purchased from Polysciences, Warrington, PA, had M_w values of 20,000 g/mol and 30,000 g/mol. The poly(styrene-*co*-*p*-hydroxystyrene) (MPS) copolymer used for this study contained 5 or 15 mol of hydroxystyrene units (designated as MPS-5 and MPS-15) and was synthesized previously.⁷ The M_n and M_w/M_n values for MPS-5 and MPS-15 are 84,900 g/mol and 1.70, and 85,600 g/mol and 1.47, respectively. PVCN was mixed with MPS-5, MPS-15, and PVPh, respectively, to form blends in the weight ratios of about 1/3, 1/1, 3/1.

Film preparation

Thin films of the aforementioned binary polymer blends were made by solution casting from tetrahy-

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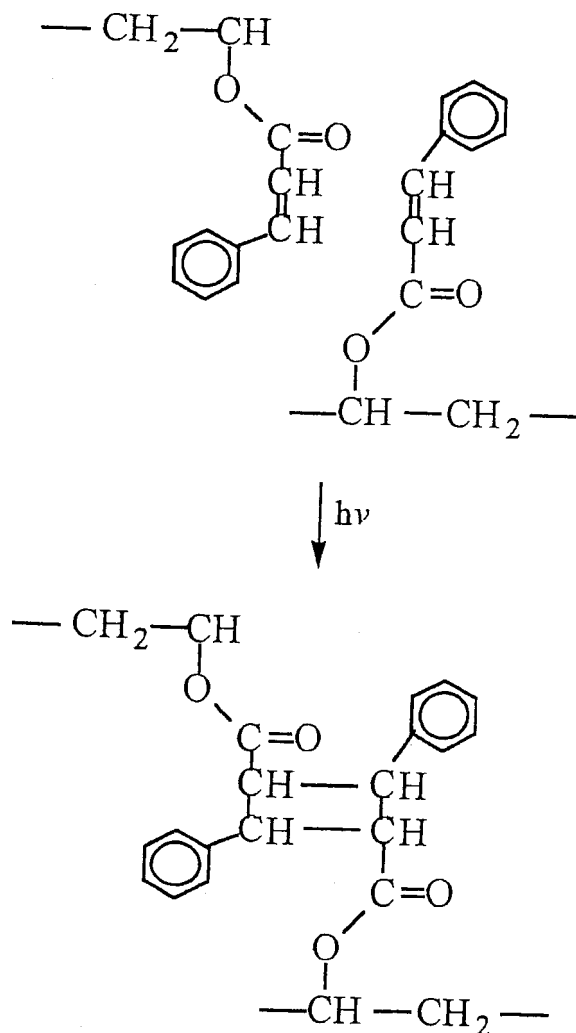


Figure 1 Thermal crosslinking of PVCN.

dofuran (THF) onto glass plates. THF is reagent grade purchased from Riedel-deHaën, Germany. The final drying step for all the films took place in a vacuum oven at 70°C for about 15–16 h. The temperature at 70°C was chosen to prevent PVCN from undergoing thermal cross-linking. The other set of films were vacuumed at 150°C for about 15–16 h to observe the effect of thermal crosslinking. Then all the films were cooled to room temperature slowly by air to make as-cast samples. The as-cast samples were later used for DSC studies.

Differential scanning calorimetry

Glass transition temperatures (T_g s) of the polymer blends were determined by a DuPont TA 2000 thermal analyzer. The scanning range for temperature was from 20 to 200°C and a heating rate of 20°C/min was used in every measurement. The experiments were often performed in two consecutive scans in the ambient environment of nitrogen gas at a flow rate of 90–110 mL/min. In the first thermal

scan, the samples stayed at 200°C for 1 min. Then the samples were cooled to 20°C using a cooling rate of 20°C/min. The inflection point of the specific heat jump of a second thermal scan was taken as the glass transition temperature. The cooling rate was proven to be fast enough to produce virtually the same results as quenching. ΔT_g is calculated as the difference between the onset and end points of the glass transition temperature region.

RESULTS AND DISCUSSION

PVCN could undergo a crosslinking reaction by addition between an excited cinnamoyl group of one polymer chain and an unexcited cinnamoyl group (ground state) of another, as schematically depicted in Figure 1.

PVCN binary blends

DSC thermograms of second thermal scans of PVCN with MPS-5, MPS-15, and PVPh ($M_w = 20,000$ g/mol) were presented in Figures 2–4, respectively. Table I lists the calculated glass transition temperatures (T_g s) of all the three binary blends. In Figure 2 and Table I, there were two T_g values observed in all the three studied PVCN/MPS-5 blend compositions. The results indicated immiscibility or partial miscibility. For PVCN/MPS-15 blends (shown in Fig. 3 and Table I), most blend compositions showed one T_g indicating miscibility except at one composition. For the PVCN/MPS-15(50/50) blend, partial miscibility or immiscibility was found on account of the observation of two T_g values. In Figure 4 and Table I, single composition dependent T_g was observed in the PVCN/PVPh blends. Therefore, PVCN formed miscible blends with PVPh in agreement with literature. ΔT_g values of all binary

TABLE I
Glass Transition Temperatures of PVCN Blends

	T_g (°C)	ΔT_g (°C)
PVCN/MPS-5		
100/0	74.1	7
74.8/25.2	80.4, 108.9	9, 4
50.0/50.0	81.2, 110.1	11, 6
25.0/75.0	92.6, 113.2	12, 7
0/100	108.6	8
PVCN/MPS-15		
100/0	74.1	7
74.9/25.1	84.8	9
50.2/49.8	85.9, 111.5	11, 9
25.0/75.0	114.6	9
0/100	120.9	10
PVCN/PVPh		
100/0	74.1	7
75.0/25.0	92.0	12
50.0/50.0	110.2	12
25.0/75.0	124.6	14
0/100	137.8	12

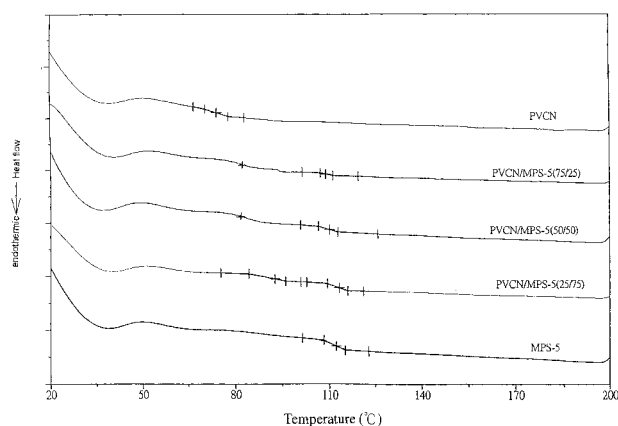


Figure 2 DSC thermograms of PVCN/MPS-5 blends.

blends are also tabulated in Table I for reference. PVCN was shown previously⁸ to form hydrogen bonds with PVPh on the basis of FTIR spectra. It is concluded that PVCN and PVPh are miscible because of sufficient intermolecular hydrogen bonding. The partial miscibility or immiscibility found between PVCN and MPS-5 was due to insufficient hydrogen bonding. For PVCN/MPS-15 blends, the miscibility was improved because of possible higher degree of hydrogen bonding than PVCN/MPS-5 blends. The miscibility behavior of PVCN after thermal crosslinking with MPS-5, MPS-15, and PVPh was changed markedly and presented in the next section.

PVCN binary blends after thermal treatments

DSC thermograms of the thermally treated PVCN binary blends were not presented for the sake of brevity. The calculated T_g values were demonstrated in Table II. A single composition dependent T_g was detected in both the PVCN/MPS-5 and PVCN/MPS-15 blends indicating miscibility. Higher T_g values of PVCN/MPS-15 blends above weight average indicated higher degree of hydrogen bonding than PVCN/MPS-5 blends. The results are obvious since MPS-15 contains

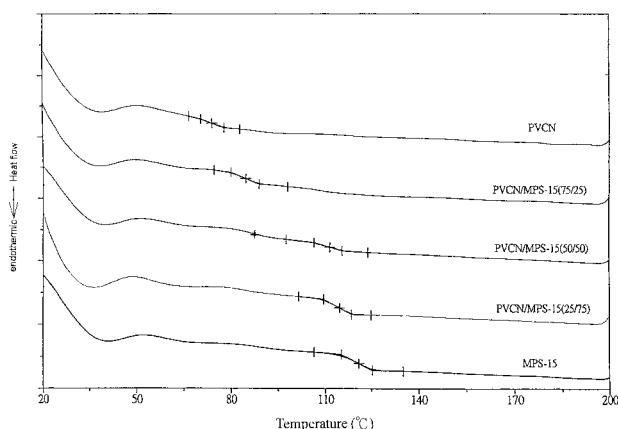


Figure 3 DSC thermograms of PVCN/MPS-15 blends.

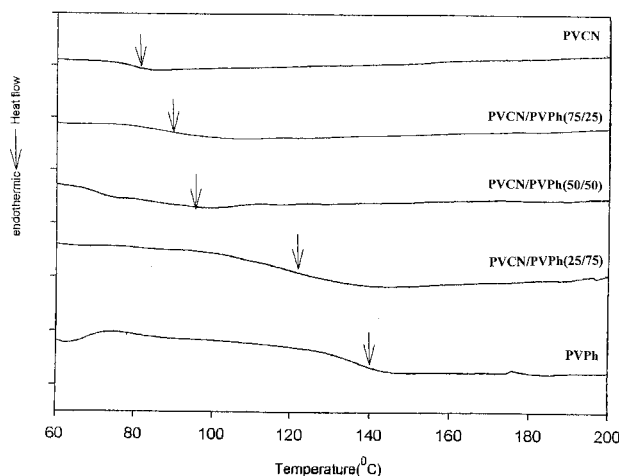


Figure 4 DSC thermograms of PVCN/PVPh blends.

higher fraction of hydroxystyrene than MPS-5 inducing more C=O—HO interaction with PVCN. However, ΔT_g values of PVCN/MPS-15 blends are larger than weight average demonstrating possible microheterogeneity. For PVCN/PVPh blends, thermal treatments caused the blends to change from miscible into partially miscible or immiscible behavior. Two T_g values were observed at the three studied PVCN/PVPh compositions. For PVCN/PVPh(50/50) blend, the blend phase separated into highly pure PVCN and PVPh phases. For the other two blends, the low T_g phase probably consists of PVCN and PVPh and the major component of high T_g phase is likely PVPh. Although PVPh ($M_w = 30,000$ g/mol) used in blending with PVCN annealed at 150°C had a slightly higher molecular weight than PVPh ($M_w = 20,000$ g/mol) annealed at 70°C , the results would likely be the same with the effect of thermal treatments.

TABLE II
Glass Transition Temperatures of Thermally Treated PVCN Blends

	T_g ($^\circ\text{C}$)	ΔT_g ($^\circ\text{C}$)
Treated PVCN/MPS-5		
100/0	86.4	15
75.3/24.7	108.2	4
50.1/49.9	104.1	6
25.6/74.4	108.7	5
0/100	108.6	8
Treated PVCN/MPS-15		
100/0	86.4	15
75.2/24.8	125.8	17
49.9/50.1	143.9	27
25.0/75.0	142.8	20
0/100	120.9	10
Treated PVCN/PVPh		
100/0	86.4	15
75.0/25.0	134.9, 171.9	14, 12
49.9/50.1	87.4, 176.4	14, 14
25.1/74.9	121.6, 174.5	13, 16
0/100	171.9	14

The effect of thermal treatments at 150°C was to alter the molecular structure of PVCN into more C—C crosslinked segments. It can be concluded from Tables I and II that thermal treatments are beneficial to the miscibility between PVCN and MPS-5 (or MPS-15). However, an adverse effect on miscibility was found between PVCN and PVPh after thermal treatments.

Effect of thermal treatments on PVCN

It is very likely that not all the double bonds of PVCN were opened when the PVCN samples were thermally treated at 150°C. Therefore, PVCN after thermal treatments should still contain some small fraction of double bonded structure. FTIR spectra of PVCN annealed at 70 and 150°C were performed at room temperature with a Perkin-Elmer FTIR 2000. Sixty-four scans at a resolution of 4 cm⁻¹ were signal averaged. Spectra of the wavenumber from 1400–1900 cm⁻¹ were shown to observe the absorption peaks of C=C and C=O groups. As shown in Figure 5, the C=C peak at 1634–1636 cm⁻¹ was greatly reduced but still detectable after annealed at 150°C because of thermal crosslinking. There was another higher wavenumber shoulder observed slightly above 1710 cm⁻¹ after thermal treatments. The broadening of C=O absorption peak also indicated the forming of C—C crosslinks. The *T_g* value of PVCN after thermal treatments (as already shown in Table II) higher than PVCN in Table I also indicated crosslinking effect. The thermal stability of PVCN annealed at 70 and 150°C was investigated by a TGA2050 thermogravimetric analyzer. The experiments were performed from 50 to 700°C at a heating rate of 20°C/min in a nitrogen environment. The results were shown in Figure 6. The TGA curve of PVCN annealed at 70°C demonstrated a two-stage decomposition. However, PVCN annealed at 150°C

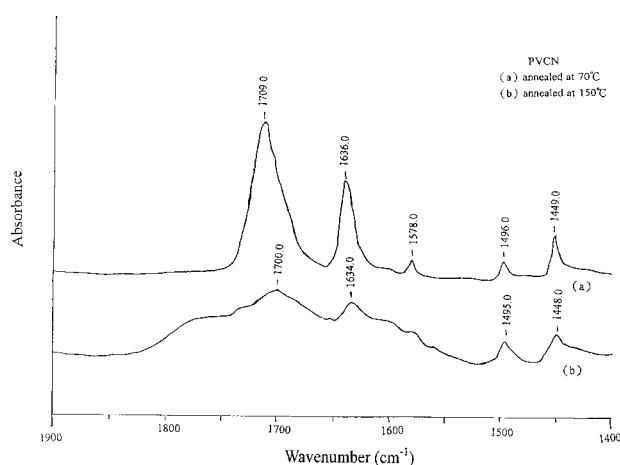


Figure 5 FTIR spectra of PVCN annealed at 70°C and annealed at 150°C.

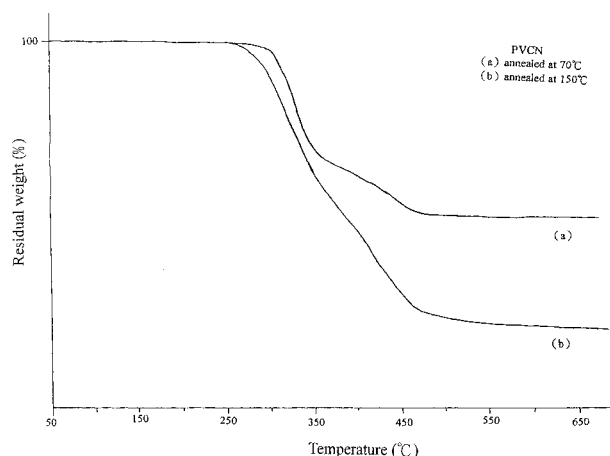


Figure 6 TGA curves of PVCN annealed at 70°C and annealed at 150°C.

showed a long one-stage decomposition. After two-stage decomposition, the residual amount at 700°C of PVCN annealed at 70°C was higher than of PVCN annealed at 150°C. This probably indicated thermally stabilized structure was formed after two-stage decomposition compared to one-stage decomposed PVCN.

In summary, the C—C crosslinked structure of PVCN is likely to be the reason for transforming the mixing behavior of its blend with MPS from partial miscibility or immiscibility into miscibility based on calorimetry data.

CONCLUSION

PVCN annealed at 150°C produces mostly cross-linked structure on the basis of FTIR spectra. The C—C crosslinked structure of PVCN probably transforms the mixing behavior of its blend with MPS from partial miscibility or immiscibility into miscibility based on calorimetry data. However, an adverse effect was found between PVCN and PVPh because of thermal crosslinking reaction. PVCN was miscible with PVPh when annealed at 70°C. Partial miscibility or immiscibility was found between PVCN (when the sample was annealed at 150°C) and PVPh.

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