

Miscibility of poly(styrene-co-vinyl phenol) with poly(ϵ -caprolactone)

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Summary

Poly(styrene-co-vinyl phenol)(STVPh)/poly(ϵ -caprolactone)(PCL) blends showed enhanced miscibility over polystyrene/PCL blend, and showed single glass transition temperature when the contents of vinyl phenol(VPh) in copolymer were higher than 10 wt % (maximum content of VPh in STVPh used in this study was 20 wt%). STVPh 4, STVPh 7, STVPh 10 (4, 7, 10 were VPh wt%)/PCL blends showed cloud points on heating for miscible blend system, and this phase separation was reversible on cooling. From melting point depression of PCL, interaction parameter, B , for miscible STVPh 12/PCL blend system was evaluated.

Introduction

The enhancement of polymer-polymer miscibility through chemical modification by the functional groups capable of specific intermolecular interaction has been the subject of many investigations(1-3). It has been demonstrated in several cases that only a small amount of interacting groups are sufficient to get miscible blends, i.e., less than 5% of vinyl phenol(VPh) or hexafluoro-2-hydroxyisopropyl unit in polystyrene(PS) was required to form a miscible blend with poly(butyl methacrylate), with which PS itself is immiscible(4-6).

Poly(ϵ -caprolactone)(PCL) has been shown to be miscible with a number of other polymers, particularly when an opportunity exists for hydrogen bonding or other interactions with a second polymer(7-9). Enhanced miscibility of PCL with poly(styrene-co-vinyl phenol)(STVPh) over PS is anticipated, because OH group in

styrenic copolymer can form hydrogen bond with C=O group of ester linkage as in poly(styrene-co-allyl alcohol)/PCL or STVPh/poly(alkyl methacrylate) blends(10-12).

To the best knowledge of the present authors, no detailed contribution has become available so far for STVPh/aliphatic polyester blends. So, we report the phase behavior and the limit of miscibility in STVPh/PCL blends in this paper.

Experimental

Poly(styrene-co-4-acetoxy styrene) was prepared by the radical polymerization of purified and distilled styrene and 4-acetoxy styrene at 60°C for 2.5 hr using 2,2'-azobisisobutyronitrile as an initiator. STVPh was obtained after the hydrolysis of acetyl group in 9:1 (by volume) solution of dioxane and hyrazine hydrate(13). The absorption band of carbonyl group at 1753 cm⁻¹, which was present in parent polymer, disappeared completely after hydrolysis. Instead, absorption bands at 3532 and 3400 cm⁻¹, characteristic bands of free and self-associated hydroxyl groups, were observed. The ¹H-NMR spectrum exhibited resonance peaks at 1.5-1.8 (aliphatic backbone), 6.6-7.1 (aromatic), and 3.4 ppm (hydroxyl, broad in CDCl₃) instead of that at 2.3 ppm (methyl). Characteristics of STVPh's used in this study are shown in Table 1.

PCL(M_w=20,000, T_g=-65°C)(9,14) was purchased from Aldrich and used without further purification. PS (M_n=10,000, M_w=28,000, T_g=105°C) was synthesized by radical polymerization.

Blend films were cast from dried chloroform solution after the slow evaporation of solvent at room temperature for 1 day and dried in a vacuum oven for 3 day.

Table 1. Characteristics of poly(styrene-co-vinyl phenol)

Designation	Content of vinyl phenol ^a (wt%)	M _n ^b	M _w /M _n ^b	T _g (°C)
STVPh 2	2.1	60,000	3.1	107
STVPh 4	4.4	30,000	3.3	108
STVPh 7	6.5	20,000	2.6	111
STVPh 10	10.0	15,000	3.6	113
STVPh 12	12.2	16,000	2.7	116
STVPh 15	15.4	16,000	2.4	117
STVPh 20	20.4	11,000	2.1	119

^a determined by NMR

^b determined relative to PS standards by GPC

A differential scanning calorimeter(Mettler TA 3000) was used for the determination of glass transition temperature(T_g) and melting temperature(T_m). Each sample was annealed at 150°C for 3 min and quenched in liquid N_2 . It was reheated from -150°C to 170°C at a heating rate of 20°C/min to measure T_g and T_m . To get Hoffman-Weeks plot for determining equilibrium melting temperature of PCL(15,16), samples were heated at 20°C/min from 20°C to 100°C, where they were held for 5 min. The samples were then rapidly cooled to crystallization temperature(T_c) where they were held for 30 min prior to reheating at 20°C/min to measure T_m .

Cloud points were measured with blend films on the heating apparatus with a magnifying lens at a heating rate of 5°C/min. The temperature at which the first faint opalescence appeared on heating was defined as a cloud point. Samples became completely opaque ca.10°C beyond this point.

Results and Discussion

The results from T_g measurement are shown in Table 2. PS/PCL blends show two separate T_g 's for the whole composition range. The shift in T_g is more evident in PCL blends with STVPh 4 and STVPh 7, i.e., when the contents of VPh in STVPh are larger, and single T_g 's are found at STVPh rich compositions. This shows the enhanced partial miscibility between two polymers(17). When the content of VPh in STVPh is more than 10 wt%, all STVPh/PCL blends show single T_g 's at whole compositions, indicating miscibility between two polymers. These results are summarized in Figure 1.

Table 2. T_g of STVPh/PCL blend

Composition (STVPh/PCL)	T_g (°C)							
	PS	STVPh 2	STVPh 4	PCL blends with				STVPh 20
				STVPh 7	STVPh 10	STVPh 12	STVPh 15	
100/0	105	107	108	111	113	116	117	119
90/10	-,105	-,105	75	77	78	83	85	87
70/30	-,105	-61,106	-	-	-	40	45	-
50/50	-61,105	-60,105	-60,-	-	-	-	-	-
30/70	-61,105	-60,105	-60,-	-60,-	-40	-35	-38	-33
10/90	-62,-	-62,-	-60,-	-60,-	-60	-57	-56	-57
0/100				-65				

- : not clearly observed

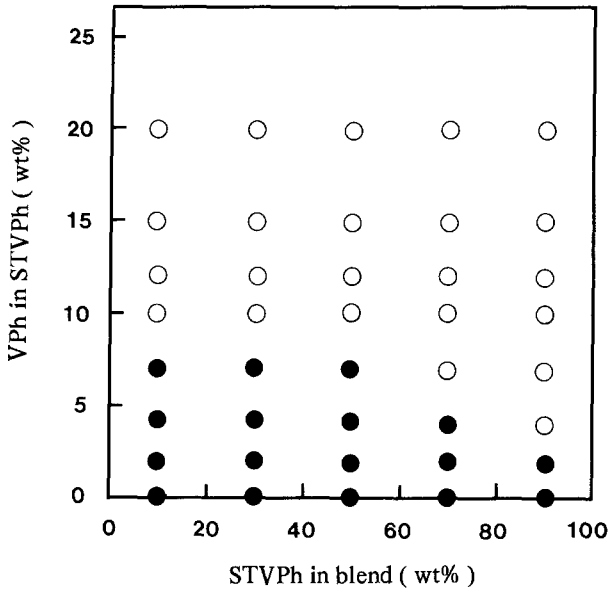


Fig.1. Miscibility in STVPh/PCL blends, (○); single Tg, (●); double Tg.

A melting point depression in polymer blends, when one component(component 2) is crystallizable, can be expressed by the following equation (1) when both components are of large molecular weights(18).

$$\Delta T_m = T_{m2}^0 - T_{m2b}^0 = - \frac{V_{2u}}{\Delta H_{2u}} B \phi_1^2 T_{m2}^0 \quad (1)$$

In this equation, T_{m2}^0 and T_{m2b}^0 is the equilibrium melting temperature of crystallizable component in pure state and in blend respectively, $\Delta H_{2u}/V_{2u}$ is its heat of fusion per unit volume for 100% crystallinity, ϕ_1 is the volume fraction of the other component in the amorphous phase, and B is binary interaction energy density. Therefore, with increasing miscibility, a smaller B and a larger effective ϕ_1 result, and this gives a larger ΔT_m . Data for T_m shown in Table 3 show that T_m decreases of PCL are more evident in blends with STVPh compared with those with PS, suggesting higher

Table 3. T_m of PCL in STVPh/PCL blend

Composition (STVPh/PCL)	$T_m(^{\circ}\text{C})$							
	PS	PCL blends with						
		STVPh 2	STVPh 4	STVPh 7	STVPh 10	STVPh 12	STVPh 15	STVPh 20
100/0	-	-	-	-	-	-	-	-
90/10	62	60	-	-	-	-	-	-
70/30	62	62	62	-	-	-	-	-
50/50	63	60	61	60	58	-	-	-
30/70	64	63	63	60	59	60	62	60
10/90	65	62	63	63	62	62	63	61
0/100				65				

- ; not observable

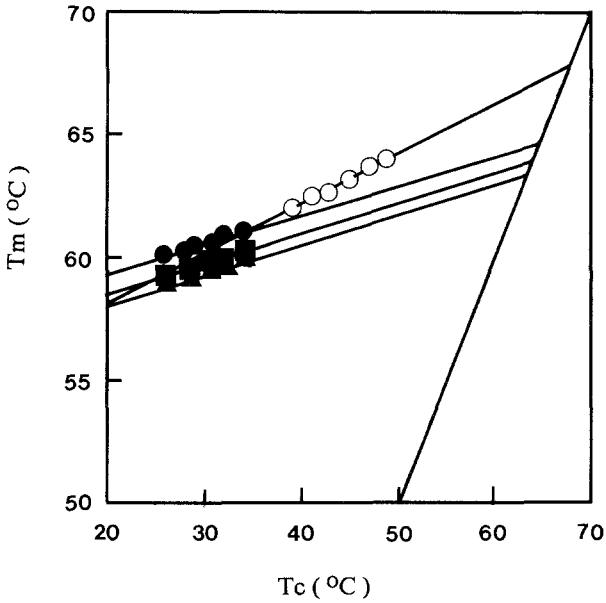


Fig.2. Hoffman-Weeks plot of STVPh 12/PCL blends with (○); 100, (●); 90, (■); 80, (▲); 70 wt% of PCL

interaction and enhanced miscibility. T_m of PCL is not clearly observed in blends with STVPh having higher content of VPh, especially at STVPh rich compositions, and this shows the hindered crystallization of PCL due to miscibility(19). The equilibrium melting temperature for the quantitative analysis by equation (1) can be determined by DSC from Hoffman-Weeks plots(15,16). Figure 2 represents the Hoffman-Weeks plot of STVPh 12/PCL blends. All the observed melting temperatures increase linearly with the crystallization temperature, and the experimental data are extrapolated to $T_m = T_c$ line by the least square analysis to obtain the equilibrium melting temperatures. If we assume roughly that B is independent of STVPh 12 content in blend, these results can be used to calculate B value of -1.8 cal/cm^3 from equation (1), where 35 cal/cm^3 is used for $\Delta H_{2u}/V_{2u}$ (20).

STVPh 4, STVPh 7, STVPh 10/PCL blends showed cloud points on heating for miscible blend system, which are shown in Figure 3. The reversibility of the phase separation was rapid in this system and the blends became clear again immediately upon cooling below the cloud points.

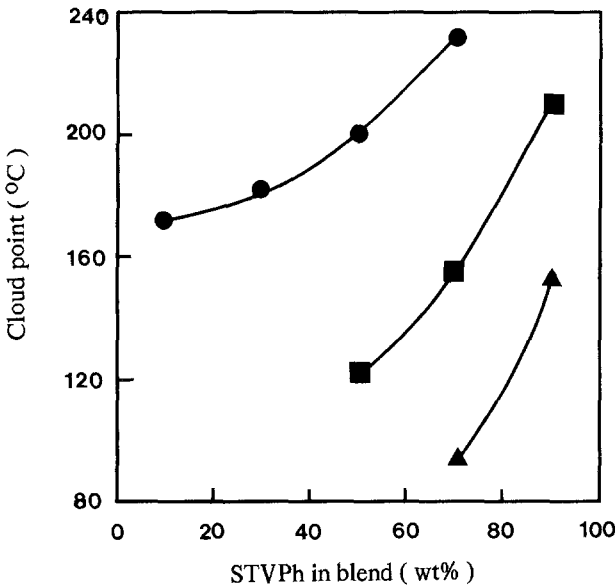


Fig.3. Cloud point curve of STVPh/PCL blends, (▲); STVPh 4, (■); STVPh 7, (●); STVPh 10.

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