

Tuning phase diagram of ternary polymer blends by tacticity

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Abstract

Previously, a ternary blend consisting of poly(vinyl phenol) (PVPh), poly(vinyl cinnamate) (PVCN) and poly(methyl methacrylate) (PMMA) was reported to exhibit a closed-loop behavior of immiscibility. In that study, PMMA was atactic PMMA and three binary pairs of PVPh, PVCN and PMMA were all miscible. In this article, isotactic and syndiotactic PMMAs (designated as iPMMA and sPMMA) were used to replace atactic PMMA to blend with PVPh and PVCN. For iPMMA ternary blends, the ternary phase diagram was found to demonstrate a closed-loop immiscibility behavior similar to the previous study. However, a completely miscible region was observed in sPMMA ternaries even though sPMMA and PVCN were found to be not miscible.

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1. Introduction

With the increasing application of multicomponent polymers [1,2], much interest has been directed toward ternary polymer blends recently. Since the early works of Scott and Tompa [3,4], most studies on the ternary polymer blends have been centered on the concept that polymer A, which is miscible with both polymers B and C, can compatibilize the immiscible binary pair B and C [5–8]. When all three binary pairs are miscible, a completely homogeneous ternary is possible [9]. However, differences in the interaction parameters of the binary system, the so-called “ $\Delta\chi$ effect”, can result in phase separation.

The phase relationships for ternary mixture where one component is solvent and the other two polymers have been described by Scott and Tompa [3,4] using the lattice theory of Flory and Huggins. Robard et al. [10] have demonstrated the existence of the $\Delta\chi$ effect in a ternary mixture of poly(styrene), poly(vinyl methyl ether) and chloroform. A distinguished feature in this ternary is the closed-loop region of immiscibility. The extension of the Flory–Huggins theory to ternary polymer blends has been conducted by Hsu and Prausnitz [11]. The effect of the asymmetry in the interaction parameters as well as the differ-

ence in molecular weight of the coexistence curves has been simulated. Su and Fried [12] also used the Flory–Huggins theory to compute spinodal curves and critical points for different interaction parameters, thus providing useful predictions in the phase diagrams of ternary systems.

In our previous study [13], a ternary polymer blend of poly(vinyl phenol) (PVPh), poly(vinyl cinnamate) (PVCN) and poly(methyl methacrylate) (i.e. atactic PMMA) was investigated calorimetrically. The binary pairs of this ternary all exhibited miscible behavior. However, a closed-loop behavior of immiscibility in the ternary phase diagram was observed. The reason for this observation is likely because of stronger PMMA/PVPh interaction than PMMA/PVCN interaction (the $\Delta\chi$ effect).

In this article, atactic PMMA (aPMMA) was replaced by isotactic or syndiotactic PMMA (iPMMA or sPMMA). A ternary blend of iPMMA(or sPMMA), PVPh and PVCN were prepared and measured by calorimetry. The results of iPMMA ternary were similar to previous aPMMA ternary study. All three binary pairs of iPMMA ternary were miscible. A closed-loop region of immiscibility was still observed but much smaller for iPMMA with approximately the same molecular weight as aPMMA. For iPMMA(1) with higher molecular weight and lower T_g (detail will be listed in Section 2), its ternary was found to exhibit larger immiscibility region than aPMMA ternary. However, for sPMMA ternary a completely miscible region of ternary phase diagram was detected even though sPMMA was not miscible with PVCN. The experimental results of

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calorimetry were presented in this article. Observation of phase diagram was expounded in terms of binary enthalpic interaction. The k value of the Gordon–Taylor equation was proven to be a good indicator of binary interaction. The results indicated tacticity of PMMA had a decisive effect on tuning its ternary phase diagram with PVPh and PVCN. To the best of our knowledge, these results of tacticity effect on ternary phase diagram were rare. In comparison with previous study of aPMMA ternaries [13], iPMMA or sPMMA with approximately the same molecular weight as aPMMA was shown mostly to demonstrate miscible behavior when blended with PVPh and PVCN.

2. Experimental

2.1. Materials

PMMA and PVPh were purchased from Polysciences, Inc., Warrington, PA. According to manufacturer information, the molecular weight of iPMMA (or sPMMA) was 100,000 g/mol about the same as aPMMA of previous study. iPMMA(1) with a M_w value of 300,000 g/mol was used to represent iPMMA with low T_g and obtained from Scientific Polymer Products, Inc. (Ontario, NY). The M_w values for PVPh were 9000–11,000 g/mol. PVCN also obtained from Scientific Polymer Products, Inc. had a M_w value of 100,000 g/mol.

2.2. Film preparation

Thin films of the following binary and ternary polymer blends were made by solution casting from tetrahydrofuran (THF) onto glass plates. The actual compositions of the binary and ternary blends are shown later in corresponding Tables and Figures. THF is reagent grade purchased from Riedel-deHaën, Germany. The final drying step for all the films took place in a vacuum oven at ca. 70 °C for about 24 h. The temperature at 70 °C was chosen to prevent PVCN from undergoing thermal cross-linking. Then 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.

2.3. Differential scanning calorimetry (DSC)

Glass transition temperatures (T_g s) of the polymer blends were determined by a DuPont TA 2100 thermal analyzer. The scanning range for temperature was from 30 to 220 °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 20 ml/min. In the first thermal scan, the samples stayed at 220 °C for 2 min. Then the samples were cooled to 30 °C using a cooling rate of 20 °C/min. The mid-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.

3. Results and discussion

Thermal scans of calorimetry were not shown for brevity. The calculated glass transition temperature data are presented in the following section.

3.1. PVPh/PMMA blends

Table 1 presents the glass transition temperatures (T_g s) of PVPh/PMMA blends. Single composition dependent T_g was detected in the blends indicating miscibility mostly in agreement with literature [14]. The only difference from literature is sPMMA was found to be miscible with PVPh in this article likely due to low PVPh molecular weight. Different T_g equations can be used to describe experimental results. In our case, the Gordon–Taylor equation [15] seemed to be applicable for different binary blends. The equation is as follows:

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} \quad (1)$$

where T_g is the glass transition temperature of a blend, T_{gi} and w_i are the glass transition temperature and the weight fraction of polymers i , respectively ($i = 1, 2$). k (originally a function of the cubic expansion coefficient and the specific volume) is commonly considered as an adjustable parameter. k values of 0.89, 1.93 and 0.22 were found to describe the T_g data in the order of PVPh/iPMMA(1), PVPh/iPMMA and PVPh/sPMMA blends approximately good. The T_{gG} values (estimated by putting T_g s of component polymers and corresponding k values into Eq. (1)) were listed in the middle column of Table 1. The k values can be used as an indicator of interaction. Therefore the strength of interaction can be arranged in the following order: PVPh/iPMMA > PVPh/iPMMA(1) > PVPh/sPMMA. The strength of interaction is qualitatively related to the Flory–Huggins interaction parameter. ΔT_g values of the afore-

Table 1
Glass transition temperatures of PVPh/PMMA blends

	T_g (°C)	T_{gG} (°C)	ΔT_g (°C)
PVPh/iPMMA(1)			
100/0	137.3	137.3	11
75.0/25.0	108.8	112.5	13
50.0/50.0	80.0	89.0	18
25.0/75.0	74.7	67.0	13
0/100	46.1	46.1	9
PVPh/iPMMA			
100/0	137.3	137.3	11
74.8/25.2	129.6	127.2	24
50.0/50.0	114.5	114.2	13
25.0/75.0	89.1	96.2	11
0/100	69.7	69.7	12
PVPh/sPMMA			
100/0	137.3	137.3	11
75.0/25.0	128.9	126.9	12
50.0/50.0	122.5	123.2	17
25.0/75.0	120.9	121.3	17
0/100	120.1	120.1	7

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