

嘉南藥理學院教師專題研究計畫成果報告

計畫名稱：三相系統的相容性研究(兩個 PMA 和另一高分子)

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摘要

在以前的研究中發現，同排和亂排 PMMA 與 poly(vinylidene chloride-co-acrylonitrile)(Saran F)都相容，因為由這兩種混合物所製備的膜是透明的且呈現單一 T_g ，然而對排 PMMA 和 Saran F 卻不相容，因為大部份製備的膜是不透明的且偵測到兩個 T_g 。又根據文獻，亂排 PMMA 和對排 PMMA 是相容的。所以亂排 PMMA 和 Saran F 及對排 PMMA 兩者皆相容，但 Saran F 和對排 PMMA 卻不相容。由上述三者(亂排 PMMA, 對排 PMMA 和 Saran F)所形成的混合物是否相容，是一個有趣的課題。本研究就是針對此三相系統探討的報告。實驗中主要用到的儀器是微差掃描熱卡計(DSC)，由實驗結果是否呈現單一 T_g 來建立三相圖。結果顯示所有探討的成份都是相容的，而且大部份混合物的 T_g 符合 Fox equation。當三相混合物中對排 PMMA 和 Saran F 重量比例為 1:1 時，只要加入 12.5% 的亂排 PMMA 就足夠使三相混合物呈現相容性。

ABSTRACT: Previously, isotactic and atactic poly(methyl methacrylate)s (PMMAs) were found to be miscible with poly(vinylidene chloride-co-acrylonitrile) (Saran F) because all the prepared films were transparent and showed composition dependent glass transition temperatures (T_g 's). However, the syndiotactic PMMA/Saran F blends were immiscible because most of the cast films were translucent and had two glass transition temperatures. Atactic PMMA is known to be miscible with syndiotactic PMMA according to literature. So atactic PMMA is miscible with both Saran F and syndiotactic PMMA but Saran F and syndiotactic PMMA are immiscible. It will be interesting to study the miscibility of ternary blends of atactic and syndiotactic PMMAs and Saran F. Therefore an investigation based on this is reported in this article. Calorimetry was used as the principal tool to study miscibility. A blend composed of atactic and syndiotactic PMMAs was prepared previously and confirmed to be miscible. An approximate phase diagram of the ternary blends was established based on differential scanning calorimetry data. The results indicated that for all the studied compositions, the ternary blends were determined to be miscible. Most of the blend T_g values were fitted well by the Fox equation. For the syndiotactic PMMA/Saran F (wt ratio = 1) blend, adding of at least 12.5 wt% of atactic PMMA was sufficient to cause the immiscible blends to be miscible.

Ternary blends are gaining importance in the field of polymers through years. The first systematic study on ternary blends was reported by Kwei *et al.*¹ in 1977. In their study, the addition of (PVDF) to the immiscible pair PMMA/poly(ethyl methacrylate) (PEMA) was studied and found to be miscible. A list of ternaries investigated has been considerably enlarged since then.²⁻⁸ In nearly all these blends, a third component either a homopolymer or copolymer is added to homogenize an immiscible pair. Miscibility is often achieved in cases where this third component is miscible with other polymers.

Recently, Bicakci and Cakmak⁹ investigated the phase behavior of binary and ternary blends of poly(ethylene naphthalate) (PEN), poly(ether imide) (PEI) and poly(ether ether ketone) (PEEK) using differential scanning

calorimetry (DSC) and dynamic mechanical analysis (DMTA) techniques. PEN/PEI and PEI/PEEK binary blends exhibit single glass transition temperatures in full composition range and PEN and PEEK were found immiscible particularly at mid-concentrations.

When PEI is added to the immiscible PEN/PEEK system, first the blends form two separated PEN-rich and PEEK-rich phases below about 40% PEI concentration, and above this concentration, the three homopolymers form a miscible phase in the amorphous state exhibiting a single T_g . An approximate ternary phase diagram was established by them based on the DSC and DMTA results.

In a previous study,¹⁰ isotactic, atactic and syndiotactic PMMAs (designated as i, a and sPMMAs) with ap-

proximately the same molecular weight were blended with poly(vinylidene chloride-co-acrylonitrile) (Saran F) (containing 20 wt% of acrylonitrile) in tetrahydrofuran to cast into films. The glass transition temperatures of the polymers were measured calorimetrically. iPMMA and aPMMA were found miscible with Saran F because all the prepared films were transparent and had a single composition dependent glass transition temperature (T_g). However, sPMMA is not miscible with Saran F because most of the cast films were translucent and had two T_g 's. Since sPMMA is miscible with aPMMA according to the literature¹⁰ but immiscible with Saran F and aPMMA is miscible with Saran F. Therefore an investigation of the miscibility of ternary blends composed of aPMMA, sPMMA and Saran F is worthwhile and was pursued in this laboratory. aPMMA is acting as a "cosolvent" between sPMMA and Saran F in this study.

In this article, the ternary blends of aPMMA, sPMMA and Saran F were prepared in several weight ratios. The glass transition temperatures of the ternary mixtures were determined calorimetrically. An approximate phase diagram of the ternary blends was established based on calorimetry data and a single T_g was used as the criterion for determining miscibility. The results indicated that the ternary blends were miscible for all the studied compositions.

EXPERIMENTAL

Materials

Atactic and syndiotactic PMMAs (designated as a and sPMMAs in this study) were purchased from Polysciences, Inc., Warrington, PA. According to supplier information, the molecular weights (M_w 's) of aPMMA and sPMMA are the same about 100000. The estimation of meso(m) and racemic (r) fractions was reported previously.¹¹ The calculated m and r fractions of aPMMA and sPMMA are 33.8% and 66.2% and 9.3% and 90.7%, respectively. The error is about 5 to 8%. The (vinylidene chloride-co-acrylonitrile) copolymer (Saran F) used for

this study contained 20 wt% AN units and was also obtained from Polysciences. The M_w value for Saran F is approximately 260000.

Film Preparation

Thin films of ternary blends of aPMMA, sPMMA and Saran F in different weight ratios were made by solution casting onto glass plates. The actual compositions of the ternary blends are shown in Table I. Tetrahydrofuran (THF) was used as solvent for all the blend compositions. THF is A.C.S. reagent purchased from Fisher Scientific, Fair Lawn, New Jersey. Because Saran F and its blends start to decompose at around 104–116°C, therefore the final drying step for all the films took place in a vacuum oven at 75°C for 15–23 h to avoid film degradation. Then the films were cooled to room temperature slowly by air to make as-cast samples. The as-cast samples were used for *d.s.c.* studies.

Differential Scanning Calorimetry (*d.s.c.*)

Glass transition temperatures (T_g 's) of the polymer blends were determined by a DuPont 2000 thermal analyzer. According to our experimental results, Saran F had a higher thermal stability in nitrogen environment than in vacuum. In repetitive test runs, we found that Saran F still maintained its thermal stability when the temperature was as high as 200°C. Therefore the experiments were performed in two consecutive scans from 30 to 200°C in the ambient environment of nitrogen gas at a flowing rate of 100–110 mL min⁻¹. At the end of the first thermal scan, the samples stayed at 200°C for one minute. The samples were then quenched to 0°C immediately using an ice-water bath and were scanned the second time. A heating rate of 20°C min⁻¹ was used in each scan. Based on the observation, the annealing time was enough for the determination of T_g . The samples were quenched quickly to prevent crystallization as detected by *d.s.c.* There was no trace of solvent in the films detectable by *d.s.c.* The inflection point of the specific heat jump of a thermal scan was taken as the glass transition temperature. The glass transition temperatures determined from the first and second thermal scans were designated as T_{gsc} and T_{gq} , respectively. Therefore, T_{gsc} is the T_g of the slowly cooled (as-cast) films and T_{gq}

Table I. Glass transition temperatures of ternary blends

Saran F/aPMMA/ sPMMA	$T_{gsc}/^{\circ}\text{C}$	$T_{gq}/^{\circ}\text{C}$	$T_g^*/^{\circ}\text{C}$	$\Delta T_{gq}/^{\circ}\text{C}$
1. (12.6/12.5/74.9)	101	110	110	20
2. (12.5/37.5/50.0)	96	106	106	18
3. (12.6/62.5/24.9)	---	99	101	15
4. (12.4/75.1/12.5)	91	102	99	18
5. (25.1/37.3/37.6)	101	97	98	22
6. (25.0/50.0/25.0)	102	96	95	17
7. (25.1/56.2/18.7)	88	96	94	19
8. (26.4/19.9/53.7)	74,94	101	100	22
9. (37.5/25.0/37.5)	81,123	93	92	22
10. (43.75/12.5/43.75)	---	111	90	8
11. (50.1/12.5/37.4) ^b	71,94	90	81	19
12. (49.9/25.2/24.9) ^b	67,92	90	84	27
13. (50.0/37.5/12.5) ^b	70,94	73	86	24
14. (75.0/12.5/12.5)	76	81	71	16

* Estimated from the Fox equation. ^b Taken from a previous publication.¹⁰

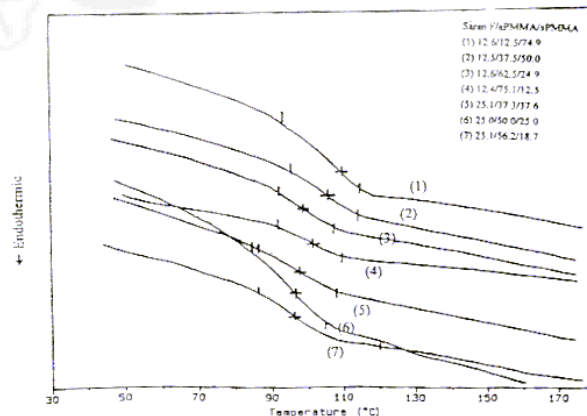


Figure 1. DSC thermograms of the ternary blends(#1-#7).

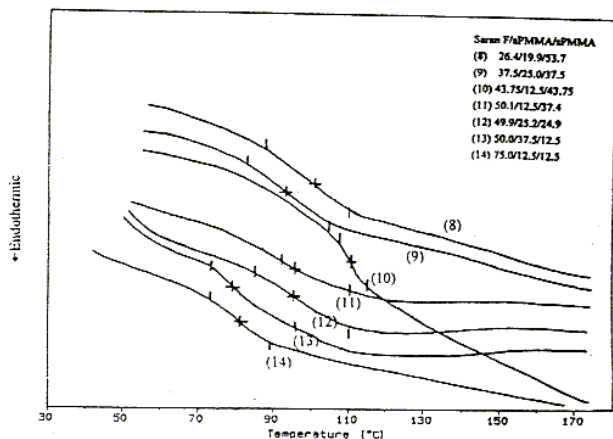


Figure 2. DSC thermograms of the ternary blends(#8—#14).

that of the quenched films.

RESULTS AND DISCUSSION

Glass Transition Temperatures

For representation, only the second thermal scans of the ternary blends are shown in Figures 1 and 2, respectively. Figure 1 presents thermal scans of the ternary blends containing *ca.* 12.5 or 25.0 wt% Saran F. Thermal scans of the ternary blends containing more than 25.0 wt% Saran F are given in Figure 2. Obviously all the studied ternary blends in Figures 1 and 2 showed one T_g . The estimated T_{gsc} and T_{gq} values of the ternary blends from the first (not shown) and second scans are listed in Table I. For several blend compositions especially those containing more than 25 wt% Saran F, there is difference between the T_{gsc} and T_{gq} values. Because the T_{gq} values are considered to be free of annealing or other thermal/solvent effects, the ternary blends are determined to be miscible based on a single T_{gq} value. Because slow-cooled #8 to #13 samples have two T_g s first, then after quenching all these samples show one T_g . Therefore thermodynamically speaking, they are miscible at 200°C but immiscible at room temperature. The glass transition temperature regions (ΔT_{gq}) (shown as the last column in Table I) were calculated as differences between the onset and end points of T_{gq} . ΔT_{gq} does show broadening in most of the compositions and this is quite common in the multi-component system.

Fox and Other Equations

For polymer blends with weak or no interaction, the Fox equation¹² seems to predict the glass transition temperature quite well. The Fox equation extended for a ternary mixture is shown as below in eq 1

$$1/T_g = w_1/T_{g1} + w_2/T_{g2} + w_3/T_{g3} \quad (1)$$

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 ($i=1, 2, 3$). The T_g values of Saran F, aPMMA and sPMMA were obtained previously¹⁰ to be 59°C, 103°C, and 122°C, respectively. All these values were used in eq 1 to estimate the T_g values of the ternary blends (designated as T_g^* in Table I). For the ternary blends containing 37.5 wt% or less Saran F (#1 to #9 blends), the Fox equation seems to predict the experimental T_g quite well. The difference between the Fox equation predictions and experimental T_g values can be seen more clearly in Figure 3. Aside from #1 to #9 blends, the Fox equation seems to underestimate the T_g values of most of the rest of the ternary blends (from #10 to #14 except #13).

Attempts were made to fit T_g of #10 to #14 blends (#13 not included) using other equations. The methodology is briefly illustrated as follows: Since the aPMMA/sPMMA blends were observed previously¹⁰ to have a T_g elevation compared to the additivity rule. The simplified Kwei¹³ equation as in eq 2 was used to fit the T_g values of the aPMMA/sPMMA blends

$$T_g = w_1 T_{g1} + w_2 T_{g2} + q w_1 w_2 \quad (2)$$

where symbols have the same meanings as in eq 1 and q is a parameter related to the strength of interaction between two polymers. For the aPMMA/sPMMA blends, q was estimated to be 20. Then the ternary blends were assumed to be a pseudo-binary mixture of Saran F and aPMMA/sPMMA. The T_g values of these pseudo-binary blends were estimated by weight average:

$$T_g = w_i T_{gi} + w_j T_{gj} \quad (3)$$

For our special case, T_g , T_{gi} , and T_{gj} are the glass transition temperatures of a ternary blend, Saran F and aPMMA/sPMMA blend, respectively. w_i and w_j are the weight fractions of Saran F and aPMMA/sPMMA blend. The estimated T_g values (designated as T_g^a) from eq 3 are tabulated in Table II. The T_g values of the ternary blends containing *ca.* 50 wt% Saran F (#11 and #12) can be estimated by this method. Take #11 blend for example. The #11 blend has the composition of Saran F/aPMMA/sPMMA(50.1/12.5/37.4). So the blend is composed of 50.1% Saran F and 49.9% aPMMA/sPMMA. First, the T_g of aPMMA/sPMMA(12.5/37.4) converted to 25.1/74.9) was estimated from eq 2 to be 121°C. Then the T_g of blend #11 was calculated from eq 3 to be 90°C ($=0.501 \times 59 + 0.499 \times 121$). However for #10 and #14

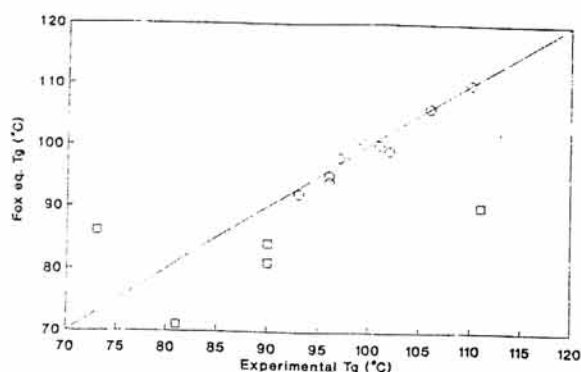


Figure 3. Glass transition temperatures of the ternary blends. ○: #1 to #9, □: #10 to #14.

Table II. Glass transition temperatures of certain ternary blends

Saran F/aPMMA/sPMMA	$T_{g,eq}/^{\circ}\text{C}$	$T_g^*/^{\circ}\text{C}$
10.(43.75/12.5/43.75)	111	94
11.(50.1/12.5/37.4)	90	90
12.(49.9/25.2/24.9)	90	88
14.(75.0/12.5/12.5)	81	74

* Estimated from the eq 3.

blends, the agreement between experimental and estimated T_g is not good. The T_g of the #10 blend is much higher than that estimated either by the Fox equation or eq 3. For blend #14, improvement in T_g estimation is seen in the prediction value by eq 3.

Co-solvent Effect of aPMMA

For the purpose of illustrating co-solvent effect of aPMMA, the T_g values of the blends with sPMMA/Saran F wt ratio = 1 were plotted in Figure 4. Previous results¹⁰ of the aPMMA/Saran F and aPMMA/sPMMA blends were also presented for comparison. Since the T_g difference between aPMMA/Saran F and aPMMA/sPMMA blends with the same aPMMA composition is always greater than 20°C, the single T_g criterion for miscibility seems to be justified in our ternary system. The following comments can be drawn from Figure 4. Firstly, the ternary T_g values are located between those of the two binaries with the same aPMMA composition. Secondly, adding of at least 12.5 wt% aPMMA into the sPMMA/Saran F mixture is sufficient to cause miscibility. It is interesting that the addition of a small amount of aPMMA produces a single T_g of the ternary blends. The reason may be due to the immiscibility between Saran F and sPMMA is not very high. The unusual high T_g behaviour of the high T_g phase of sPMMA/Saran F(50/50) blend was explained previously¹⁰ to be likely due to a highly syndiotactic PMMA presence.

Phase Diagram and Binary Interaction Model

Using the single T_g as the criterion for the miscibility, the phase diagram of the ternary blends composed of Saran F, aPMMA, and sPMMA is shown in Figure 5. Because all the studied compositions of the ternary blends

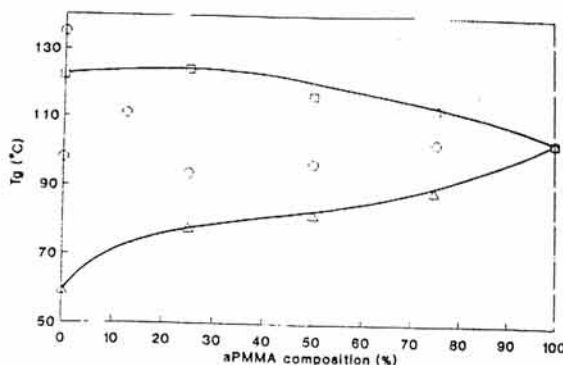


Figure 4. Change of T_g of the ternary blends with aPMMA composition (sPMMA/Saran F wt ratio = 1). ○: data point, △: T_g of aPMMA/Saran F blend (curve drawn for viewing), □: T_g of aPMMA/sPMMA blend (curve drawn for viewing).

are miscible, the only possible immiscible region is the area surrounding the two immiscible sPMMA/Saran F (75.0/25.0 and 50.0/50.0) blends. Therefore it can be concluded that the ternary blends containing sPMMA/Saran F wt ratio ≥ 1 and a very low concentration of aPMMA (definitely lower than 12.5% according to data) are likely to be immiscible.

A simple model without considering the effect of polymer molecular weight as the following was used to explain the immiscible region of the ternary blends. This model assumes mixing ΔH_m of a ternary system can be described in terms of binary interaction coefficients:

$$\Delta H_m = 2RT(\chi_{12}\Phi_1\Phi_2 + \chi_{13}\Phi_1\Phi_3 + \chi_{23}\Phi_2\Phi_3) \quad (4)$$

where R is the gas constant, T the temperature, χ_{ij} the thermodynamic interaction parameter between i and j (which determines the sign and magnitude of the best of mixing of i with j) and Φ_i is the volume fraction of component i in the mixture. Equation 4 assumes that the χ parameters are independent of concentration and symmetrical, i.e., $\chi_{ij} = \chi_{ji}$. For the purpose of the present discussion, eq 4 can be reduced, for measurements carried out at a constant temperature, to:

$$\chi \approx \chi_{12}\Phi_1\Phi_2 + \chi_{13}\Phi_1\Phi_3 + \chi_{23}\Phi_2\Phi_3 \quad (5)$$

where χ is the thermodynamic interaction parameter of the ternary blends.

Equation 5 was then used to calculate miscibility/immiscibility boundary observed in Figure 5. For that purpose, immiscibility was associated with a positive χ value and miscibility with a negative χ value. χ is set equal to zero to calculate concentrations, assuming that a true ternary solution is present in the area where a single T_g is observed. In this calculation, aPMMA, sPMMA, and Saran F were designated as polymers 1, 2, and 3, respectively. Also the volume fraction was not used but the weight fraction was used tentatively. Since aPMMA(1) is both miscible with sPMMA(2) and Saran F(3), therefore their χ values were set to be negative. The value of χ_{13} , between aPMMA and Saran F, was selected being more negative than χ_{12} ; this is a nec-

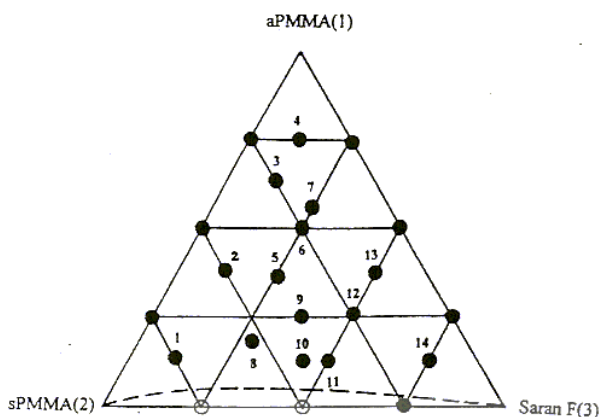


Figure 5. Phase diagram of the ternary blends. ●: miscible ○: immiscible,: estimated immiscible region, numbers in the figure indicate the same compositions in Table I.

essary requirement in order to induce an asymmetry to better corner the immiscible region. Finally, χ_{23} , between sPMMA and Saran F, was selected as being positive because of the immiscibility between these two polymers.

Although we don't have data of the absolute χ values of our ternary system, the following set of χ_{ij} (Scott-Tompa) values were used tentatively. $\chi_{12} = -0.003$, $\chi_{13} = -0.018$, and $\chi_{23} = 0.002$. The χ_{23} value was chosen to be 0.002 about twice χ_c of Saran F/sPMMA blend. χ_c was estimated to be about 0.001 based on the following relation¹⁴

$$\chi_c = (1/2) [(1/m_1)^{0.5} + (1/m_2)^{0.5}]^2 \quad (6)$$

where m_i is chain length of polymer i . As shown in Figure 5, agreement between model and data is not satisfactory but qualitative trend of the immiscible region can be described. Obviously, this model has some shortcomings. χ_{23} is concentration dependent based on experimental data.¹⁰ It was observed that at high concentration of Saran F binary blends of sPMMA and Saran F are miscible. At mid and sPMMA-rich concentrations, there are two distinct T_g values attributable to the blend components and characteristic of an immiscible blend. Therefore the assumption of concentration independence and symmetry is in error. The present approach, with its numerous assumptions and imperfect agreement with the experimental data, cannot be interpreted in a fully quantitative manner. Nevertheless, it certainly indicates favorable interactions in the aPMMA/sPMMA and aPMMA/Saran F blends, and some unfavorable interactions existing between sPMMA and Saran F. From the predictions of this simple model, it is implied that aPMMA/Saran F interaction is stronger than aPMMA/sPMMA interaction.

CONCLUSIONS

aPMMA is both miscible with sPMMA and Saran F. However, sPMMA and Saran F are immiscible. Addition of aPMMA into the sPMMA/Saran F mixture causes the

ternary blends of Saran F, aPMMA, and sPMMA to be miscible for all the studied compositions. For sPMMA/Saran F (wt ratio=1) blend, it is interesting to find out adding of a small amount of aPMMA (12.5 wt%) causes miscibility of the ternary blends. The possible immiscible phase regions are those ternaries containing a very low concentration of aPMMA and a high sPMMA/Saran F ratio. The simple interaction model suggests that favorable interactions exist in the aPMMA/sPMMA and aPMMA/Saran F blends and unfavorable interactions between sPMMA and Saran F. The model also implies that the aPMMA/Saran F interaction is very likely to be stronger than the aPMMA/sPMMA interaction.

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