行政院國家科學委員會補助專題研究計畫成果報告

※※※※※※※※※※※※※※※※※※※※※※※※※※
※ ※
※ 含 Saran F 等兩相及三相高分子混合物之相容性 ※
※ ※
※※※※※※※※※※※※※※※※※※※※※※※※※※

計畫類別：☑個別型計畫　　□整合型計畫

計畫編號：NSC 90－2216－E－041－001－

執行期間：90 年 8 月 1 日至 91 年 7 月 31 日

計畫主持人：徐文平

共同主持人：

計畫參與人員：

本成果報告包括以下應繳交之附件：

□赴國外出差或研習心得報告一份

□赴大陸地區出差或研習心得報告一份

□出席國際學術會議心得報告及發表之論文各一份

□國際合作研究計畫國外研究報告書一份

執行單位：嘉南藥理科技大學醫藥化學系

中　華　民　國　91 年 10 月 11 日

行政院國家科學委員會專題研究計畫成果報告

計畫名稱: 含 Saran F 等兩相及三相高分子混合物之相容性
計畫編號: NSC 90-2216-E-041-001
執行期限: 90 年 8 月 1 日至 91 年 7 月 31 日

主持人: 嘉南藥理科技大學醫藥化學系
徐文平

中文摘要:

Saran F, phenoxy, PSAN 及 PVPh 與 aPMMA 都是相容的, 但是 Saran F 與 Phenoxy (PSAN 或 PVPh) 是否一定相容? 是一個值得探討的問題. 由熱分析數據得知, Saran F 與 PVPh 不相容但兩者皆與 aPMMA 相容. Saran F, PVPh 及 aPMMA 的三相混合物的相容性與 Saran F/PVPh 之比例及 aPMMA 的含量之關係是本研究探討的另一課題.

ABSTRACT: Previously, poly (vinylidene chloride-co-acrylonitrile) (Saran F), poly (hydroxy ether of bisphenol A) (phenoxy), poly (styrene-co-acrylonitrile) (PSAN) and poly (vinyl phenol) (PVPh) were found to be miscible with poly (methyl methacrylate) (aPMMA), respectively. However, the miscibility of Saran F with the other polymer (phenoxy, PSAN or PVPh) is not guaranteed and is investigated in this article. Based on calorimetry study, Saran F was found to be only miscible with PSAN but not miscible with phenoxy and PVPh. Since Saran F and PVPh are not miscible, but these two are both miscible with aPMMA. What is the miscibility of a ternary blend consisting of Saran F, PVPh and aPMMA? Therefore the second part of this report is focused on the investigation of the miscibility of a ternary blend consisting of Saran F, PVPh and aPMMA. Factors affecting the miscibility including the ratio between Saran F and PVPh and the content of aPMMA were studied mainly based on calorimetry data. The established ternary phase diagram indicated that the ternary blends with low PVPh/Saran F weight ratio were found to be mostly immiscible.

A series of papers[1-4] has been published by this laboratory dealing with the influence of the tacticity of poly (methyl methacrylate) (PMMA) when it is blended with a chemically different polymer. For the PMMA/ poly (vinylidene chloride-co-acrylonitrile) (Saran F)[1] and PMMA/ poly (vinyl phenol) (PVPh) blends[4], isotactic and atactic PMMAs (denoted as iPMMA and aPMMA) were found to be miscible based on the transparency and/or a single glass transition temperature (T_g) of the films. However, syndiotactic PMMA (sPMMA) was immiscible with Saran F an PVPh because of the observations of two T_gs and opacity in most compositions of the blends. For the PMMA/ poly (styrene-co-acrylonitrile) (PSAN) blends[3] , aPMMA and sPMMA were found to be miscible with PSAN. However, the iPMMA/PSAN blends were determined to be not miscible: Poly (hydroxy ether of bisphenol A) (phenoxy)[2] was the only one in this series to be

miscible with iPMMA, aPMMA and sPMMA. As a summary, Saran F, phenony, PSAN and PVPh have a same characteristic, the miscibility with aPMMA.

Saran F has its application as a transparent film. Studies of blending of Saran F with another polymer are worthwhile. So the first part of this article is focused on the investigation of the miscibility of Saran F with phenoxy, PSAN and PVPh, respectively. The second part of this research is concentrated on using aPMMA as a cosolvent to homogenize Saran F/PVPh pairs. Factors influencing the miscibility of a ternary blend consisting of Saran F, PVPh and aPMMA such as the ratio between Saran F and PVPh and the amount of aPMMA were investigated through calorimetry data.

EXPERIMENTAL

Materials

The (vinylidene chloride-co-acrylonitrile) copolymer (Saran F) used for this study contained 20 wt% AN units was obtained from Polysciences, Inc., Warrington, PA. The M_w value for Saran F is approximately 260,000 g/mol. PVPh and aPMMA were also purchased from Polysciences. According to supplier information, the molecular weights (M_ws) of PVPh and aPMMA are 30,000 and 100,000 g/mol, respectively. The estimation of meso (m) and racemic (r) fractions was reported previously. The calculated m and r fractions of aPMMA are 33.8% and 66.2%. The error of calculation is estimated to be about 5 to 8%. The poly (hydroxy ether of bisphenol A) (phenoxy) was purchased from Scientific Polymer Products, Inc., Ontario, N. Y. The M_w value for phenoxy is 70,000 g/mol. The poly (styrene-co-acrylonitrile) (PSAN) copolymer containing 25 wt% of AN units was obtained from Aldrich Chemical Company, Inc., Milwaukee, WI. It has a M_w value of 165,000 g/mol.

Film Preparation

Thin films of binary blends of phenoxy, PSAN and PVPh with Saran F in different weight ratios were made by solution casting onto glass plates. The actual compositions of the binary blends are shown in Table I. 2-butanone was used as solvent for all the blend compositions. 2-butanone is A.C.S. reagent purchased from Aldrich Chemical Company. Thin films of ternary blends of Saran F, PVPh and aPMMA were made in several weight ratios. The weight ratios were designed in a way that the ratios between Saran F and PVPh were fixed at 3/1, 1/1 and 1/3, then the amount of aPMMA was added increasingly from 20 to 80% at a 20% interval. Because Saran F and its blends start to decompose at around 104-116℃, therefore the final drying step for all the films took place in a vacuum oven at 75℃ for 15-23 hrs 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 later used for d.s.c. study.

Differential Scanning Calorimetry (d.s.c.)

Glass transition temperatures (T_gs) of the polymer blends were determined by a DuPont 2000 thermal analyzer coupled with a mechanical cooling system. 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℃. Therefore the experiments were performed in two consecutive scans from 20 to 200℃ in the ambient environment of nitrogen gas at a flowing rate of 100-110 ml/min. At the end of the first thermal scan, the samples stayed at 200℃ for one minute. The samples were then cooled to 0 ℃ at a cooling rate of 20℃/min and were scanned the second time. A heating rate of 20 ℃/min was used in each scan. Based on the observation, the annealing time was enough for the determination of T_g. 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_{gfc}, respectively. Therefore, T_{gsc} is the T_g of the slowly cooled (as-cast) films and T_{gfc} that of the fast cooled films. The cooling rate was proven to be fast enough to produce virtually the same results as quenching. In the following section, the T_{gfc} values are used mainly for the discussion.

RESULTS AND DISCUSSION

For brevity, the thermal scans of the binary and ternary polymer blends are omitted in this presentation.

Binary Polymer Blends

Table I presents the T_{gfc} values of the phenoxy/Saran F and PVPh/Saran F blends. Fro phenoxy/Saran F blends, two of three blend compositions showed two T_gs indicating immiscibility. The phenoxy/Saran F (25.0/75.0) blend had a single T_g therefore is miscible. The high T_gs of the two immiscible blends are quite unusual to be even higher than phenoxy's T_g. Judging from the elevation of the low T_g of the two phase separated blends, it can be concluded that phenoxy and Saran F are partially miscible. For PVPh/Saran F blends, the blends showed similar behavior regardless of composition. In view of high T_g lower than PVPh's T_g and low T_g higher than Saran F's T_g, PVPh and Saran F are also partially miscible.

The results of the PSAN/Saran F blends are not shown. A single T_g was observed in all the studied blend compositions and therefore miscibility was detected in the PSAN/Saran F blends. An elevation of T_g above weight average is likely due to dipole-dipole interaction between acrylonitrile units existing both in PSAN and Saran F.

Several empirical equations have been proposed to describe the composition dependence of T_g of miscible blends that involve strong specific interactions. Since there are three blends data, the following two equations are chosen to describe the experimental data.

Firstly, the simplified Kwei equation[6]

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

Where w_1 and w_2 denote the weight fractions of components 1 and 2, respectively; T_g, T_{g1} and T_{g2} are the glass transition temperatures of a blend and polymers 1 and 2, respectively; and q is a parameter that depends on the net polymer-polymer interaction. A q value of 36.6

was obtained to describe the experimental data qualitatively.

Secondly, the Gordon-Taylor equation[7]

$T_g = (w_1T_{g1} + kw_2T_{g2})/(w_1 + kw_2)$ (2)

All the symbols except k have the same meaning as in eq.(1). Here k is used as a fitting parameter. T_{g1} is designated as the low T_g one. A k value of 2.28 (represented as the dashed line) was found to represent the T_g data qualitatively. Based on the large q value and k bigger than 1, the interaction between PSAN and Saran F can be characterized as strong.

Ternary Polymer Blends

Table II presents the glass transition temperatures of the ternary blends. Five out of the twelve studied blends showed single T_g indicating miscibility.

For polymer blends with weak or no interaction, the Fox equation[8] seems to predict the glass transition temperature quite well. The Fox equation extended for a ternary mixture is shown as below in eq. (3)

$1/T_g = w_1/T_{g1} + w_2/T_{g2} + w_3/T_{g3}$ (3)

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, PVPh and aPMMA were used in eq. (3) to estimate the T_{gF} (Fox prediction) values of the miscible ternary blends. As shown in Table III, the T_{gF} values are always larger than experimental values. However, there seems to be a qualitative relation between T_{gfc} (experimental) and T_{gF} (Fox prediction) values since T_{gfc} increases with increasing T_{gF}. For compositions 1 and 2, the Fox prediction agrees quite well with experimental results.

CONCLUSIONS

Saran F was found to be miscible with PSAN likely because of dipole-dipole interaction between AN units exiting in both polymers. However, Saran F and Phenoxy are not miscible because two T_g values were observed. Saran F also formed partially miscible or immiscible mixtures with PVPh. Using aPMMA as a cosolvent to cosolubilize PVPh/Saran F pairs is successful when the PVPh content in ternary is lower than 25%. The reason for immiscibility observed in ternary phase diagram is because the interaction between aPMMA and PVPh is stronger than that between aPMMA and Saran F. Therefore when PVPh concentration is higher than (or equal to) 50%, aPMMA associates more with PVPh and less with Saran F. Phase separation was thus observed.

REFERENCES

1. W. P. Hsu and C. F. Yeh, *J. Appl. Polym. Sci.*, **75**, 1313 (2000).

2. W. P. Hsu and C. F. Yeh, *Polym. J.*, **32**, 127 (2000).

3. W. P. Hsu and C. F. Yeh, *J. Appl. Polym. Sci.*, **74**, 2894 (1999).

4. W. P. Hsu, *J. Appl. Polym. Sci.*, **83**, 1425 (2002).

5. W. P. Hsu and C. F. Yeh, *J. Appl. Polym. Sci.*, **73**, 431 (1999) and references therein.

6. T. K. Kwei, *J. Polym. Sci., Polym. Lett. Ed.*, **22**, 306 (1984).

7. M. Gordon and J. S. Taylor, *J. Appl. Chem.*, **2**,

493 (1952).

8. T. G. Fox, *J. Appl. Bull. Am. Phys. Soc.*, **1**, 123 (1956).

Table I Glass transition temperatures of phenoxy/Saran F and PVPh/Saran F blends

	T_{gfc} (℃)
(1) Phenoxy/Saran F	
(100/0)	99.5
(74.9/25.1)	86.0, 116.4
(49.7/50.3)	71.4, 115.0
(25.0/75.0)	87.9
(2) PVPh/Saran F	
(100/0)	155.6
(75.0/25.0)	85.5, 117.3
(50.0/50.0)	84.4, 116.6
(25.1/74.9)	85.0, 115.0
(0/100)	58.8

Table II Glass transition temperatures of ternary blends

	T_{gfc} (℃)
Saran F/PVPh/aPMMA	
1. (60.3/20.0/19.7)	81.9
2. (44.7/14.9/40.4)	85.4
3. (30.1/9.9/60.0)	84.7
4. (15.0/5.0/80.0)	89.3
5. (40.1/40.0/19.9)	81.0, 116.6
6. (29.7/29.7/40.6)	81.5, 117.8
7. (19.9/19.9/60.2)	83.5, 121.8
8. (10.1/10.0/79.9)	87.7
9. (19.9/59.5/20.6)	81.2, 149.2
10.(15.2/44.8/40.0)	84.2, 130.7
11.(9.9/30.0/60.1)	86.4, 108.4
12.(5.2/14.9/79.9)	85.6, 110.6

Table III. Glass transition temperatures of ternary blends by Fox eq. prediction

	T_{gfc} (℃)	T_g F(℃)
Saran F/PVPh/aPMMA		
1.(60.3/20.0/19.7)	81.9	83.1
2.(44.7/14.9/40.4)	85.4	88.0
3.(30.1/9.9/60.0)	84.7	92.6
4.(15.0/5.0/80.0)	89.3	97.6
8. (10.1/10.0/79.9)	87.7	102.3