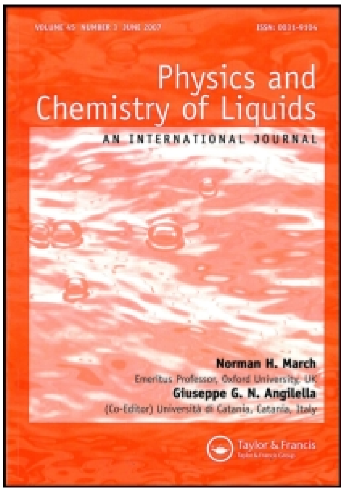

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STUDY ON THE MISCIBILITY OF CHLORINATED POLYPROPYLENE WITH ALKYD RESIN BY DILUTE SOLUTION VISCOMETRY

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The viscosity of dilute chlorinated polypropylene(CPP)–alkyd resin ($344^{\#}$ resin)–toluene solutions at different compositions was measured, and the criteria, α, Δk and β, were calculated from the experimental data. The results obtained indicate that the miscibility of the $344^{\#}$ resin–CPP blends can be predicted by the criterion α, and the blends are miscible when the weight percentage of $344^{\#}$ resin in the blend of CPP and $344^{\#}$ resin is less than 50% (w%), and immiscible when greater than 50% (w%), which is completely consistent with the result predicted by Δk and β. The results are proved by the stability of the $344^{\#}$ resin–CPP solutions and the glossiness of their films. Our work also gives a new blend system predicted by the dilute viscometry, which is miscible in some composition ranges and immiscible in other ranges. The experimental results are of significant value in preparing polypropylene coating.

Keywords: Chlorinated polypropylene; Alkyd resin; Miscibility; Viscometry

INTRODUCTION

In recent years, much attention has been paid to using the dilute solution viscosity method to predict the miscibility of polymer blends [1–6]. The key to the method is the miscibility criterion, which is calculated from the viscosity data of the dilute solution. There are mainly two criteria to predict polymer–polymer miscibility in present application. One is the thermodynamic factor α criterion proposed by Sun [1], the other is k_{12} criterion [3,4] proposed by Staszewska. Recently, after researching these criteria, Jiang and Han [5] found out their inner link and proposed a modified criterion β. But the references [1,5,6] only give some examples to describe the miscibility of polymer blends by the dilute viscometry which are all miscible or immiscible ones within the whole composition ranges of polymer blends. For example, the blend systems PVC–PMMA, PB(OH)–PBA and PB(OH)–PBMA are all miscible because they give positive values of α or β according to the viscometric data of the literatures. On the other hand, the blends PVC–PiBMA, PMMA–PiBMA, PMMA–PSt and PBA–PBMA

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are all immiscible because of their negative values of α or β in the literatures [1,5]. It is known that the miscibility of polymer blend is related to the ratio of two polymers, and the blend is often miscible in some composition ranges and immiscible in other ranges. Therefore, if a new blend example can be proved by the fact that miscibility of a polymer blend which change with the mixing ratio of two polymers can be predicted by the dilute viscometry, it will be important sense to the method of dilute viscometry. Our work will be developed under the purpose.

In this article, the criteria, α and β, were used to investigate the miscibility of alkyd resin ($344^{\#}$ resin)–CPP blends, and it was proved that the result predicted by the criterion α is consistent with the result predicted by β. Especially, the $344^{\#}$ alkyd resin–CPP system shows a new example, which gives not only positive values of α or β (miscible) when the weight percentage of $344^{\#}$ resin in the blend of CPP and $344^{\#}$ resin is less than 50% (w%), but also negative values of α or β (immiscible) when greater than 50% (w%). Since chlorinated polypropylene (CPP) is usually used as adhesion-promoting additives to polypropylene surface, the results in the article are of significant value in preparing polypropylene coating.

EXPERIMENTAL

Materials

CPP is a commercial product purchased from Jin Zhujiang Chemical Factory in Guangdong, which contains 30% chlorine by weight. Alkyd resin (commercial name is $344^{\#}$ resin) is an industrial product purchased from Zhengzhou Paint Family, which consists of 50% resin and 50% toluene by weight. Other solvents are of A.R. or C.P. grades.

Viscosity Measurement

Viscosity measurements were made with a suspended level Ubbelahda Viscometer which has a flow-time of 128.5 s for toluene at 298.15 K. The viscometer was calibrated at 298.15 K with water and toluene. Flow-time measurements were performed by using a Schott AVS 310 photoelectric time unit with a resolution of 0.01 s. For each solution, a 20-mL sample was loaded into the viscometer at 298.15 K, which is then placed into the thermostated Schott units which have a thermal stability of ± 0.005 K. Measurements were initiated after approximately 15-min equilibration time, and were continued until several elution time reading agreed to within 0.05 s. The capillary were selected so that kinetic viscosity corrections were minimal. The elution times (t) were determined from an average of several readings. The intrinsic viscosity of polymer, $[\eta]$, is obtained by plotting $\eta_{sp} \sim C$ curve, where $\eta_{sp} = t/t_0$, t and t_0 separately represent the flow-time of the solution and the solvent, and C is the polymer concentration of the solution (g/mL). In the process above, the density of the solvent (toluene) took the place of the density of the solution because of dilute solution.

Preparation of Mixed Solutions and Measurement of Films

Generally, if the molecules of polymer1 and polymer2 are attractive in dilute solution, specific interaction may occur in the bulk. Then the bulk solution can be stable and the blends can be miscible. Meanwhile, if the molecules are repulsive in dilute solution, the bulk solutions are laminated and the blends are certainly immiscible. Therefore, the miscibility of polymer blends can often be determined by the stability of the thick ternary solution in the coating industry. The procedure of the experiment is as follows: CPP, which was dissolved in toluene, and $344^{\#}$ resin were mixed in various proportions. Part of the mixture, which contained 30% (w%) resins in the solution was stirred uniformly, stewed for about 24 h and the stability of the solution was observed. Another part of the mixture was cast onto a glass sheet, the solvent was then completely removed at room temperature, and was prepared into the film.

Glossiness measurements were carried out by a KGZ-1B glossmeter. The relative glossiness was calculated by the following formula,

$$\text{Relative glossiness (\%)} = 100\% \times \text{glossiness of film/glossiness of glass sheet.}$$

CRITERIA OF MISCIBILITY

The relation of the viscosity and the concentration of binary polymer–solvent solutions at low concentrations may be expressed as

$$\frac{\eta_{sp}}{C} = [\eta] + bC = [\eta] + k[\eta]^2 C \tag{1}$$

where b is the interaction parameter between polymer and small molecule solvent, k is the Huggins coefficient whose values is commonly about $0.25 \sim 0.35$, but was ever reported greater than 0.7 in the reference [7], $[\eta]$ is the intrinsic viscosity, and C is the polymer concentration (g/mL). The viscosity of ternary solutions (polymer1–polymer2–solvent) at low concentrations may similarly be expressed as

$$\frac{\eta_{sp_m}}{C_m} = [\eta]_m + b_m C_m = [\eta]_m + k_m[\eta]_m^2 C \tag{2}$$

where $C_m = C_1 + C_2, C_1$ and C_2 separately represent the concentrations of the polymer1 and polymer2, and the suffix m represents the mixed polymers solution.

The criterion α of miscibility of the polymer1–polymer2 blends can be written as

$$\alpha = k_m - \frac{(\sqrt{k_1}[\eta]_1 x_1 + \sqrt{k_2}[\eta]_2 x_2)^2}{([\eta]_1 x_1 + [\eta]_2 x_2)^2} \tag{3}$$

where $x_1 + x_2 = 1$, x_1 and x_2 are separately the weight fraction of the polymer1 and polymer2 in the blends. The blends are miscible in their solvent-free systems if the α value is greater than or equal to zero, which indicates mutual attraction between polymer molecules in the solution. The blends are immiscible in their solvent-free systems if the parameter α is less than zero, which indicates mutual repellency between polymer molecules in the solution.

The criterion β of miscibility of the polymer1–polymer2 blends can be written as

$$\beta = \frac{2\Delta k[\eta]_1[\eta]_2 x_1 x_2}{([\eta]_1 x_1 + [\eta]_2 x_2)^2} \tag{4}$$

where Δk is defined as

$$\Delta k = k_{12} - (k_1 k_2)^{1/2} \tag{5}$$

$$k_{12} = \frac{b_m - k_1[\eta]_1^2 x_1^2 - k_2[\eta]_2^2 x_2^2}{2[\eta]_1[\eta]_2 x_1 x_2} \tag{6}$$

The reference [5] pointed out that the parameter, Δk, change with the compositions in a similar style with the criterion β and they can all be used as the criteria of polymer miscibility just like the α criterion.

RESULTS AND DISCUSSION

Viscosity of 344# Resin–CPP Dilute Solution

The intrinsic viscosity $[\eta]$ and Huggins coefficient k for CPP and alkyd resin in toluene can each be obtained by the intercept and the rate of slope of the plot of $\eta_{sp}/C \sim C$ according to Eq. (1). The ternary solution viscosities were plotted according to Eq. (2), and the apparent intrinsic viscosity $[\eta]_m$ and k_m were obtained in the same way and are given in Table I. Then the criteria α, Δk and β can be calculated by the equations above. The results are also given in Table I.

It can be seen that the criteria, α, Δk and β change with the compositions in a similar style and there are the same plus–minus symbols from Table I, which is completely consistent with the results obtained in the reference [5]. The results obtained indicate that the miscibility of the 344# resin–CPP blends can be predicted by the thermodynamic criteria, α, Δk and β, and the blends are miscible when the weight percentage of 344# resin in the blend of CPP and 344# resin is less than 50% (w%), because the values of α, Δk and β are positive within the ranges, and the blends are immiscible when the values of α, Δk and β is negative within the range of greater than 50% (w%). In order to clearly distinguish the criteria of α and β, the data of α *vs.* x_1 and its fitting curve for the various polymer blends were plotted in Fig. 1. And the data of β *vs.* x_1 were also shown in the same figure by points. It is clear that the tendency of β *vs.* x_1 is in agreement with the fitting curve of the criterion α. Therefore, the miscibility

TABLE I The related parameters of dilute solution for different content mixtures of 344# alkyd resin/CPP at 298.15 K

344#/CPP	x_1*	$[\eta]$ (mL g^{-1})	k	α	Δk	β	*Miscibility*
0/1	0	79.52	0.374	–	–	–	–
1/5.78	0.146	69.90	0.383	0.0035	0.1822	0.0080	Miscible
1/1.9	0.345	54.31	0.594	0.2028	1.3971	0.1720	Miscible
1.06/1	0.515	43.08	0.466	0.0589	0.1735	0.0378	Miscible
2.08/1	0.675	33.27	0.192	−0.2422	−0.7017	−0.2393	Immiscible
4.25/1	0.810	25.34	0.254	−0.2225	−0.4064	−0.1879	Immiscible
4.4/1	0.815	23.77	0.248	−0.2312	−0.4792	−0.2236	Immiscible
10.64/1	0.914	17.29	4.399	−0.1474	−0.2342	−0.1136	Immiscible
1/0	1	10.66	0.687	–	–	–	–

*Weight fraction of 344# alkyd resin in the blend.

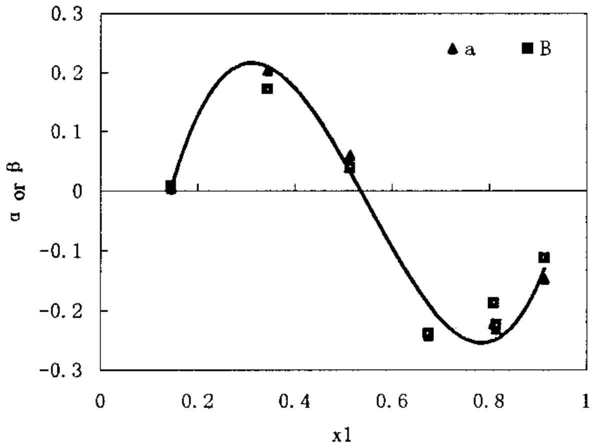

FIGURE 1 The relationship between interaction parameter α, β and content x_1 for dilute mixed solution of $344^{\#}$ resin and CPP.

TABLE II Miscibility and properties of films of $344^{\#}$ resin/CPP blends

No.	*$344^{\#}$/CPP*	*×1*	*Content of resin* (%)	*Solution state*	*Glossiness* (%)
CPP	0/1	0	30.0	not lamination	89.0
1	1/10	0.091	30.0	not lamination	87.7
2	1/5	0.167	30.0	not lamination	87.3
3	1/2	0.333	30.0	not lamination	84.7
4	1/1	0.50	30.0	lamination	82.5
5	2/1	0.667	30.0	lamination	48.4
6	4.4/1	0.815	30.0	lamination	37.5
7	10/1	0.909	30.0	lamination	64.4
$344^{\#}$	1/0	1	30.0	not lamination	–

predicted by the criterion α is completely consistent with the result predicted by the criterion β.

There are many examples to describe the miscibility of polymer blends by the dilute viscometry in the references [5,6], which are all miscible or immiscible ones within the whole composition ranges of polymer blends. But the $344^{\#}$ alkyd resin–CPP system gives a new example which is miscible in some ranges and immiscible in other ranges. In fact, the examples are common in the field of the polymer blends and composites.

Stability of the $344^{\#}$ Resin–CPP Solutions

According to the specified mixing ratios of CPP to $344^{\#}$ resin, seven experiments were carried out. Stabilities of the $344^{\#}$ resin–CPP mixtures, which contained 30% (w%) resins in the solution, were determined with the naked eye (Table II). The stabilities of the solutions are in agreement with the results of the criteria α, Δk and β.

Transparency and Glossiness of $344^{\#}$ Resin–CPP Films

In order to test the result of the compatibility of $344^{\#}$ resin–CPP blends, transparency of the films were also investigated. The transparency of the films, which were prepared with the mixtures, is given in Fig. 2.

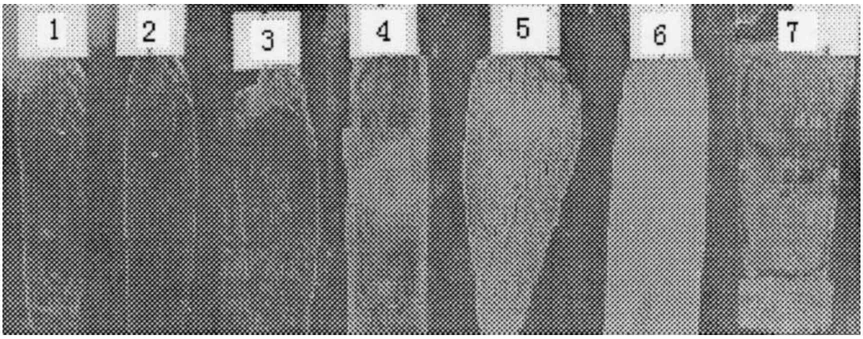

FIGURE 2 Clarity of the films at the different ratio of CPP to $344^{\#}$ resin.

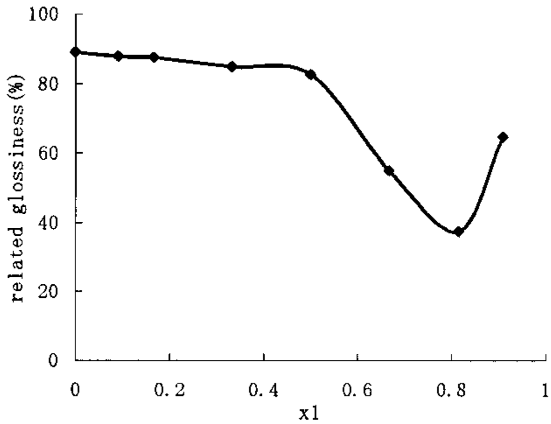

FIGURE 3 The relationship between glossiness of films and content x_1 for $344^{\#}$ resin/CPP blends.

The ground color of the films in the photograph in Fig. 2 is black. The transparent films reflect the black ground color, and the nontransparent films reflect the milky white in the photograph. From Fig. 2, it could be seen that the films are transparent when the weight percentage of $344^{\#}$ resin in the blend of CPP and $344^{\#}$ resin is less than 50% (w%), and the films are nontransparent when greater than 50% (w%).

In order to quantify the properties of the films, the glossiness were measured and the data were also given in Table II. The data of glossiness listed in Table II are consistent with clarity degree of films showed in Fig. 2. The results indicate that the compatibility of the blends is related to the mixing ratios of $344^{\#}$ resin to CPP. When the weight percentage of $344^{\#}$ resin in the blend of CPP and $344^{\#}$ resin is less than 50% (w%), CPP and $344^{\#}$ resin are fundamentally compatible. Table II also shows that the compatibility of the blends can be expressed by the glossiness of the films. Therefore, the data of the glossiness of the films *vs.* $344^{\#}$ resin composition (x_1) were plotted in Fig. 3 in order to compare the α criterion with the glossiness. When x_1 is less than 0.5, the $344^{\#}$–CPP blends are miscible and the related glossiness of the films are high, which is a horizontal line in Fig. 3. However, the shape of the glossiness curve is consistent with that of the curve of α and β when x_1 is greater than 0.5. It is clear that these phase behaviors for the various polymer blends are in good agreement with the results obtained by the criteria of α and β from Figs. 1 and 3.

From the discussion above, it was also seen that the weight percentage of 344# resin in the blend of CPP and 344# resin should be less than 50% (w%) in all the paint formula of CPP and 344# resin. This is also verified by our experimental results.

CONCLUSION

The miscibility of 344# resin/CPP blends at different compositions was investigated by the dilute solution viscometry, and the miscibility of their blends was predicted by the criteria α and β. The predicting results show that the 344# resin/CPP blends are miscible when the weight percentage of 344# resin in the blend of CPP and 344# resin is less than 50% (w%), and immiscible within the ranges of greater than 50% (w%), which is consistent with the results of the stability of the solutions, the transparency and the glossiness of their films. The results of the miscibility of 344# resin–CPP blends are of significant value in preparing polypropylene coating.

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