

Compatibility of Poly(Butylene-Terephthalate) and Poly(Vinyl Chloride)

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Abstract: A poly(butylene terephthalate)-poly(vinyl chloride) blend made of the solution of the two polymers in N-methyl pyrrolidone has been studied on compatibility between the polymers as well as crystallization mechanism of poly(butylene terephthalate) in the blend. The blend shows a single glass transition temperature which was measured by means of differential scanning calorimeter and dynamic mechanical analyser for $\tan \delta$. The glass transition temperature of the blend satisfies the Fox equation in all the compositions. The poly(vinyl chloride) content less than 50% in the blend gives little change in the crystallinity of poly(butylene terephthalate) but the crystallization temperature of poly(butylene terephthalate) decreases with an increase of the poly(vinyl chloride) content in the blend. The poly(vinyl chloride) content more than 50% in the blend causes kinetic hinderance in the crystallization of poly(butylene terephthalate) in the blend.

1. INTRODUCTION

The study of polymer blends has received much attention lately as a result of the current emphasis on modifying existing synthetic polymers rather than manufacturing new ones. However, among polymers which are chemically dissimilar, there are only a few pairs of polymer blends in which compatibility is demonstrated over the whole range of compositions. Poly(vinyl chloride) (PVC) which shows the weakly proton-donating characteristic of the α -hydrogen has been shown to exhibit miscibility with some polymers containing carbonyl-group¹⁻³.

It is often observed that two polymers show good miscibility in melt but separation when one or both of the polymers crystallize. In this study, miscibility between PVC and crystallizable poly(butylene-terephthalate) (PBT) has been studied by various means. The glass transition temperature and melting and crystallization behavior of the mixture are characterized. The change of density of the mixture as well as the dynamic properties have been analysed with a view toward understanding the compatibility behavior of the two polymers. The effect of PVC on the crystallization of PBT has been studied with the polymer mixture prepared by a solution method.

2. EXPERIMENTAL

2-1. Materials

The PVC used are commercial products of the Lucky, Ltd. LS-080, LS-100 and LS-130, with $\bar{M}_n=50,000$, 62,500 and 81,250, respectively. The PBT used is a product of Poly-science with $\bar{M}_n=41,500$, which was determined from the intrinsic viscosity of the mixed solvent system of phenol-tetrachloroethane (60 to 40⁴ weight ratio). 1-methyl-2-pyrrolidone (NMP) used after purification was the solvent from Fisher Scientific Co.

PVC is degradable at the melting temperature of PBT (220°C) and not processible by a direct melt mixing technique. The polymer is stabilized by using BT-107 and TL-600 of Songwon Chemical Co., 3wt% and 0.4%, respectively. Both the stabilizers are liquid barium-tin organic complexes.

PVC was dissolved in NMP at 150°C to make 5% solution and PBT in the same solvent at 100°C to make 10% solution. The two solutions were mixed by vigorous stirring and the blend was precipitated in methyl alcohol and filtered followed by thorough wash with methyl alcohol to remove any residual NMP. The precipitated was then dried for 50hr in vacuum at 80°C to get powder.

2-2. DSC Experiments

DSC studies were carried out using a Perkin-Elmer DSC-4 with a microprocessor and procedure of the thermal treatment in DSC is shown in Figure 1. The powder blend of 5mg was heated to 230°C for 5min to erase completely the thermal history by melting and then quenched in liquid nitrogen.

While heating the quenched blend by 10°C/min, DSC thermogram might show the glass transition temperature, T_g and the crystallization peak temperature on heating, T_{ch} , and

the heat of crystallization, ΔH_{ch} was derived.

The polymer melt was recrystallized by cooling with a rate of 20°C/min starting at 230°C to obtain the crystallization peak temperature on cooling, T_{cc} and the heat of crystallization from melt, ΔH_{cc} , and then the crystallized blend was heated by 20°C/min starting at room temperature to obtain the melting temperature T_m and the heat of fusion, ΔH_f .

2-3. Rheovibron Viscoelastometer Experiments.

The sample specimens with thickness of 0.1 mm were obtained by pressing the blend powder with the stabilizers at 230°C and quenching in liquid nitrogen. The change in $\tan \delta$ of the specimen was measured by using a Rheovibron Viscoelastometer, Model DDV-II-C of Toyo-Baldwin Co.

Measurements were made at the heating rate of 1°C/min and the testing frequency of 110 Hz.

2-4. Density Measurement

A density gradient column of Techne Co., Model DC-1 with a set of solvents of n-heptane and carbon tetrachloride was used to measure the densities of the blend film at 20°C. The set of solvents was calibrated for density by using standard density floats

3. RESULTS AND DISCUSSION

3-1. Compatibility of PBT/PVC Blends

The results of DSC experiments are presented in Table 1 and Figure 1. It is generally believed that a compatible polymer blend shows one T_g over the whole range of composition and generalized behavior of T_g relationships for miscible polymer blends may be expressed as one of three curves, the linear relationship, the minimum or maximum deviation from linearity. Examples of a minimum variation from linearity are common and the data fit the Fox

Table 1: Thermal Analysis of PBT/PVC Blends with DSC

PBT/PVC	T _m (P1) °C	T _g (P2) °C	T _{ch} (P1) °C	T _{cc} (P1) °C	T _{cc} (P2) °C	H _f (P1) cal/g	H _{cc} (P1) cal/g	H _{cc} (P2) cal/g
100/0	38	224	—	188	183	11.3	32.9	32.9
90/10	—	222	—	—	195	10.8	—	10.6
75/25	—	218	—	190	192	8.9	8.5	8.4
65/35	45	—	69	188	—	—	7.0	—
50/50	51	—	75	176	181	2.3	4.7	5.0
35/65	54	—	94	—	—	—	—	—
25/75	—	210	—	128	130	—	1.8	1.8
0/100	73	—	—	—	—	—	—	—

* P1 : PVC with Mn=50000

* P2 : PVC with Mn=62500

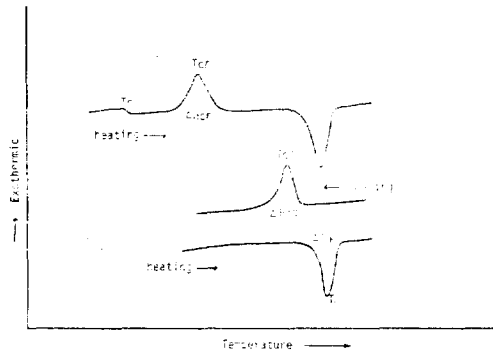


Fig. 1. Schematic diagram of DSC experimental
 T_g: glass transition temperature
 T_{ch}: crystallization temperature on heating
 T_{cc}: crystallization temperature on cooling
 T_m: melting point
 ΔH_{ch}: heat of crystallization on heating
 ΔH_{cc}: heat of crystallization on cooling
 ΔH_f: heat of fusion

equation⁵ :

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \dots\dots\dots(1)$$

where W_1 and W_2 represent the weight fractions of the polymers in the blend and T_{g1} and T_{g2} are the glass transition temperatures of the polymer components, respectively.

When the glass transitions are plotted against the PVC weight fractions as shown in Figure 2, the points deviate little from the Fox equation. Since the quenched specimens show

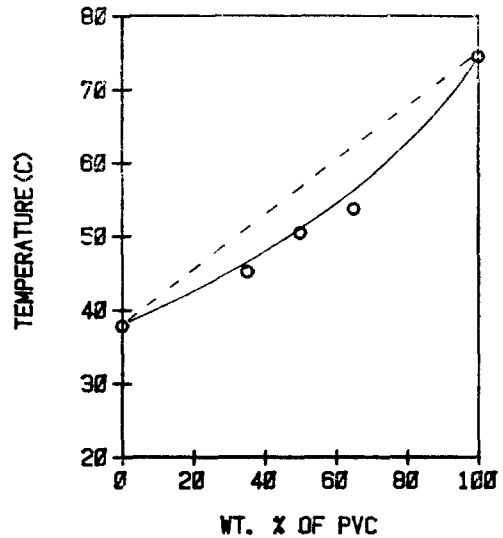


Fig. 2. Glass transition temp. of PBT/PVC blends
 ○ : PVC, Mn=50000
 ... : Weight average curve
 — : Fox-equation

only one T_g over the whole range of composition and the data fit the Fox equation reasonably well, the two polymers appear miscible and the quenched blends show the minimum deviation from linearity.

The good miscibility between PBT and PVC is due to the chemical structures of the two polymers. Since chlorine in PVC attracts electrons strongly, the acidity of hydrogen atoms

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ched to the carbon is enhanced to make a good hydrogen bonding to the carbonyl group in PBT. These phenomena have been well examined with the systems of PVC with polycaprolactone⁶, ethylene-vinyl acetate copolymer⁷ and poly(methyl methacrylate)⁸.

The good molecular interaction between PVC and PBT has also been proved by measurement of the blend densities as shown in Figure 3. Without any special interaction the density of a mixture may be expressed as equation (2) :

$$\frac{1}{g_B} = \frac{W_1}{g_1} + \frac{W_2}{g_2} \dots\dots\dots(2)$$

Where g_B , g_1 and g_2 represent the densities of a blend, component 1 and 2, respectively. W_1 and W_2 are weight fractions of component 1 and 2, respectively. The equation(2) draws a dotted line which is straight, as shown in Figure 3. The solid curve was obtained from the data points, which tells apparently that the blend of PVC and PBT experienced definite

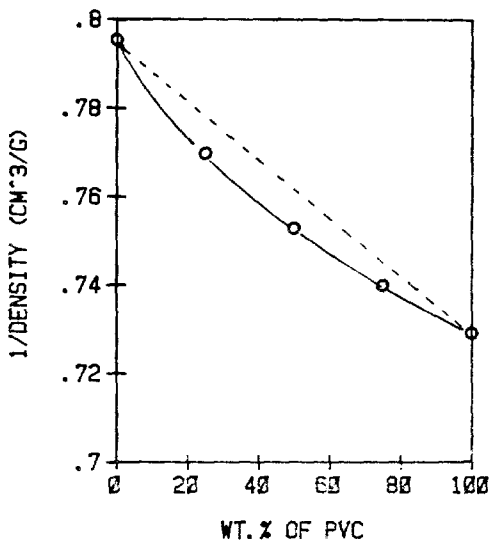


Fig. 3. Plots of density⁻¹ vs. composition of blends. (PVC, Mn=62, 500) Dotted line was calculated from eq. 2. Solid curve was obtained by density measurement.

interaction on molecular levels.

The transition behavior was also examined by a dynamic mechanical testing method using a Rheovibron. The $\tan \delta$ measured at the testing frequency of 110 Hz, while increasing the testing temperature by 1°C/min, has been plotted against temperature as shown in Figure 4. Only one peak was observed on all samples except a 50-50 blend, which shows a shoulder after the transition. The one-peak phenomenon is a further evidence of a miscible blend.

It is interesting to note that the shoulder appeared only on the 50-50 blend. DSC thermograms of quenched specimens show small crystallization peaks on heating except the 50-50

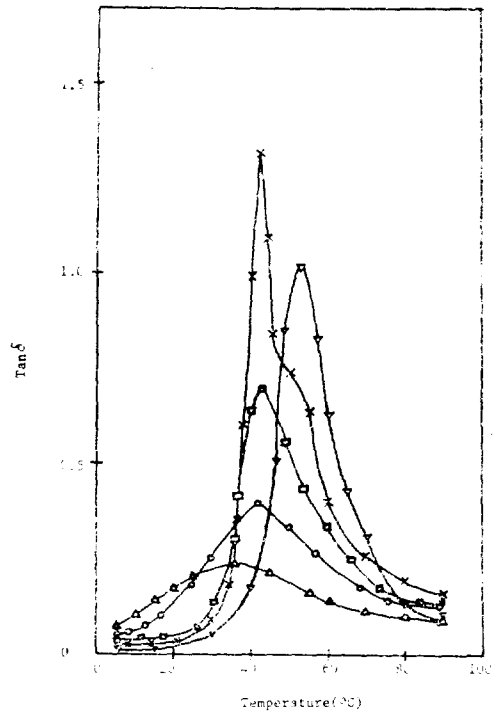


Fig. 4. Plots of $\tan \delta$ vs. temp. (PVC, Mn=32500)
 △ : PBT/PVC=100/0
 ○ : PBT/PVC=75/25
 × : PBT/PVC=50/50
 □ : PBT/PVC=25/75
 ▽ : PBT/PVC=0/100
 The frequency was 110 Hz.

blend. Since the quenched PBT showed no crystallization peak on heating, which means that possible crystallization has been finished while quenching, the quenched PBT-rich blend has also little component to be crystallized on heating. The quenched PBT-poor blend, however, has not enough component to be crystallized due to strong interaction between two components. In the 50-50 blend, a good amount of PBT was frozen on quenching but the blend allowed PBT to crystallize on heating because the effect of PVC on crystallization of PBT was not so great. The shoulder on the Rheovibron spectrum of the 50-50 blend might appear while PBT in the blend crystallized on heating of the quenched specimen. The PBT-rich or-poor blends show crystallization peaks but not big enough to be detected by the Rheovibron experiments.

3-2. Crystallization of Blends of PVC and PBT

A blend of a crystallizable polymer with an

uncrystallizable one shows interesting results when two polymers are miscible each other. The annealed blend of this system contains an amorphous region of a polymer liquid-liquid system as well as a crystalline region. Such a complex system is very interesting and a few work has been reported on this subject^{9,10}.

The blend system of amorphous PVC and crystallizable PBT proved to show only one T_g in this study. The blend was heated to melt at 230°C and then cooled by a rate of 20°C/min to get a phase separation due to crystallization of PBT. The peak temperature of crystallization of PBT in the blend was presented in Table 1 as T_{cc} and plotted against weight fraction of PVC as shown in Figure 5. The peak temperatures change little with PVC contents of less than 40% and it even shows the highest when PVC content is 10% in the blend. The peak temperature, however, drops quickly when the PVC content is more than 50% in the blend and there is no peak tem-

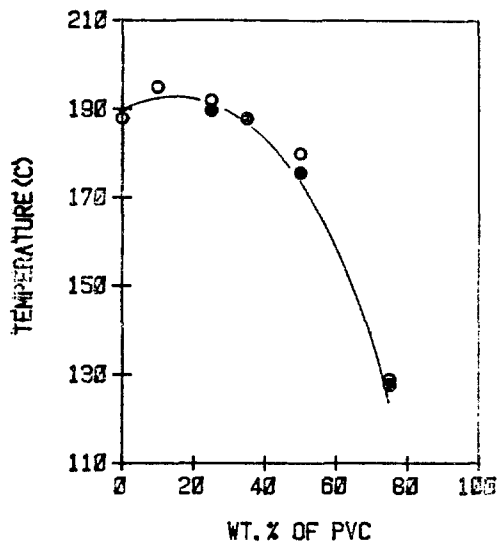


Fig. 5. Crystallization peak temp., T_{cc} from melt.
 ○ : PVC Mn=62500
 ● : PVC Mn=50000

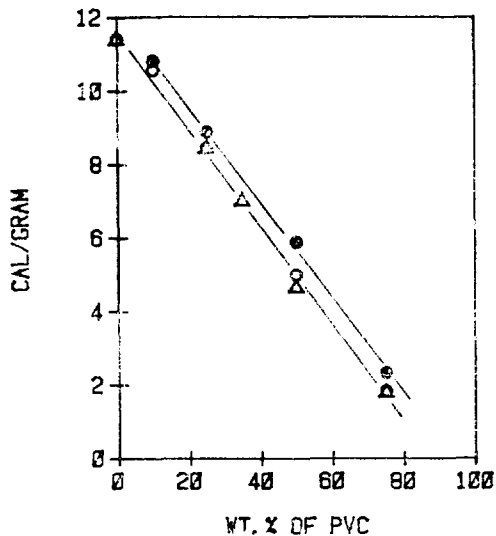


Fig. 6. Heat of crystallization and heat of fusion of PBT/PVC blends.
 ○ : PVC Mn=62500, from Hcc
 △ : PVC Mn=50000, from Hcc
 ● : PVC Mn=62500, from Hf

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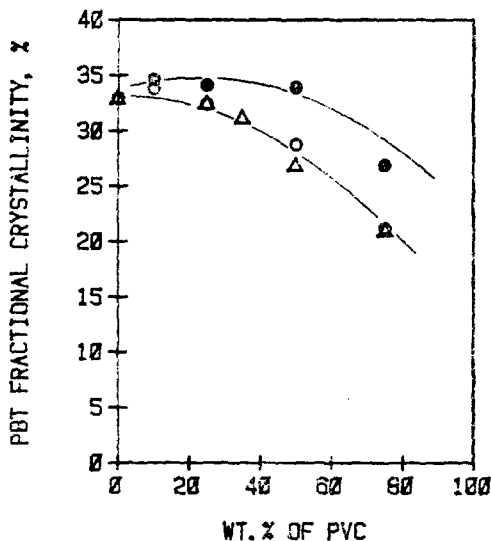


Fig. 7. Percent crystallinity of PBT normalized by weight fraction of PBT in each blend.
 ● : PVC Mn=62500, from Hf
 ○ : PVC Mn=62500, from Hcc
 △ : PVC Mn=50000, from Hcc

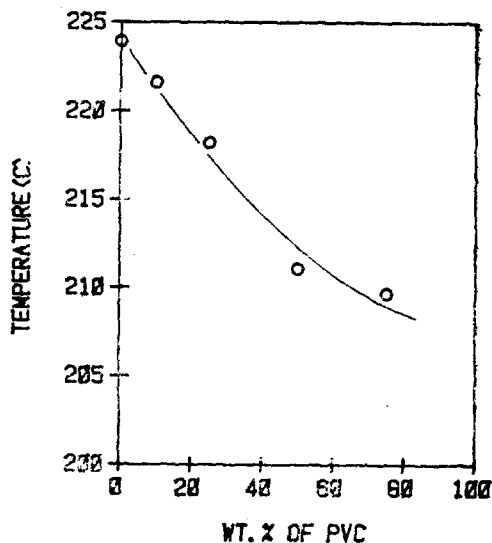


Fig. 8. Melting Point of PBT/PVC blends (PVC Mn=62500)

perature with the PVC content of more than 80% in the blend. There is no definite evidence of dependence on molecular weight of PVC to crystallization temperature of the blend. The highest peak temperature on crystallization of PBT in the blend with 10% PVC might be obtained by the role of PVC as nuclei.

In general, the increase of PVC content in the blend of PBT and PVC restrains crystallization of PBT. The heat of crystallization from the melt, ΔH_{cc} , has been plotted against the PVC content in the blend as shown in Figure 6. Figure 6 also shows the heat of fusion, ΔH_f . The values of ΔH_{cc} and ΔH_f decrease with an increase of PVC content in the blend, which means that the amount of crystallizable PBT in the blend decreases with an increase of PVC in the same blend. It is interesting to note that the values of ΔH_{cc} and ΔH_f decrease linearly with the increase of PVC in the blend and ΔH_f is slightly high-

er than ΔH_{cc} in all the compositions in the blend. The effect of molecular weight of PVC is negligible on ΔH_{cc} or ΔH_f as on T_{cc} .

It is not reliable to predict the degree of crystallization of PBT in the blend from either ΔH_{cc} or ΔH_f . In Figure 7, ΔH_{cc} and ΔH_f were normalized by the amount of PBT in the blend and plotted against PVC content. The normalized ΔH_{cc} to PBT in the blend, X_{cc} , changes little from that of pure PBT until the PBT content is more than 75% in the blend. X_{cc} decreases gradually with an increase of PVC content in the blend. The normalized ΔH_f to PBT in the blend, X_f , shows a slight increase with an increase of the PVC content up to 50-50 ratio and then decreases with a further increase of the PVC content.

X_f is larger than X_{cc} in all cases. PBT definitely crystallizes while heating to melt, although DSC thermogram shows no sign of crystallization except an indication of the baseline drift. PVC in the blend interferes crys-

tallization of PBT and the effect of PVC on crystallization of PBT becomes significant when the PVC content is more than 25% in the blend.

The existence of PVC in the blend lowers the melting temperature of PBT as shown in Figure 8. Although X_{cc} and X_f change little with the concentration of PVC of 25% or less in the blend, T_m of the blend drops markedly with the existence of PVC. The crystal lattice seems to develop poorly in the blend while crystallinity is not much different from that of the pure system of PBT.

4. CONCLUSION

The thermal history of quenched PBT-PVC blend by DSC shows only one T_g over the whole range of composition and dynamic mechanical analysis by Rheovibron produces only one peak for the blends, which suggests strongly an existence of good miscibility between PBT and PVC. The increase of density of the blend reveals that a strong interaction on a molecular level exists between the two polymers. There is a strong indication of a vital role of PVC on crystallization of PBT in the blend. PVC seems to act as a nucleus and enhance the crystallinity of PBT when the PVC content is less than 50%. However, the PVC content of more than 50% retards the crystallization rate and interferes development of crystal lattice in the blend.

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