Effect of Molecular Structure of Polyarylates on the Compatibility in Polyarylate/Poly(vinyl chloride) Blends

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ABSTRACT: A homologous series of polyarylates were prepared by condensation polymerization of three different bisphenols, isophthaloyl, and terephthaloyl chlorides (their molar ratio = 2:1:1). The resulting polyarylates were tetramethyl bisphenol S-(TMBPS-), bisphenol S- (BPS-), and tetramethyl bisphenol A- (TMBPA-) polyarylates, and each have structural variants; (1) methyl or no substitution on the biphenyl rings of bisphenol, and/or (2) central group connecting the biphenyl rings with or without polarity. Only the polyarylate having both methyl substitution and polar connector, i.e., TMBPS-polyarylate, was found to be compatible with PVC. The sulfone groups of TMBPS-polyarylate and chlorides of PVC exerted a dipole-dipole interaction only when the tetramethyl substitution on the bisphenol rings was present. In the absence of tetramethyl groups (BPS-polyarylate), incompatibility with PVC was observed. The strength of polar interactions appeared to be influenced by the methyl substitution causing electronic rearrangement in bisphenol rings. However, due to the lack of polar connector groups, the inclusion of methyl substitution in TMBPA-polyarylate was found to have no effect on the specific interactions, and hence, the compatibility with PVC. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2173-2180, 1998

Key words: polyarylates; bisphenols; molecular structure; compatibility

INTRODUCTION

Polyarylates are a class of amorphous aromatic polyesters that are based on bisphenols and iso/ tere(50/50)phthaloyl chlorides.^{1,2} Due to the fact that they offer a high heat distortion temperature, an inherent UV stability, and excellent mechanical properties, and can exhibit transesterification upon mixing, ^{3,4} blends of polyarylates with other polymers have been studied for both industrial application and academic interest.

Most polymer blends consist of immiscible polymer pairs, which form discrete phases. However, from a practical view point, the blends seeking their actual end-use are neither completely homogeneous in the molecular scale nor completely heterogeneous; it is a matter of compatibility. The compatibility of polymer blends is primarily dependent on the molecular structures of their component polymers.^{5–7} Small changes in molecular structure of one or both components may enhance the interaction between the two polymers. If the interaction is an attraction sufficient enough to overcome the cohesive force of individual polymers, the resulting blend is par-

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tially miscible (i.e., compatible) or sometimes completely miscible. On the other hand, if minor structural changes cause very weak or repulsive interactions, the blends may be phase separated even in a macroscale and, hence, incompatible. For example, polycarbonate based on tetramethyl bisphenol-A is miscible with polystyrene (PS),⁸⁻¹⁰ while bisphenol-A polycarbonate (PC) is not.¹¹ This clearly indicates that substitution of four methyl groups on the bisphenol-A phenyl rings in PC increases the strength of the attractive interactions. Also, polycarbonate consisting of polar connector groups in the backbone rings is found to be more favorable with poly(methyl methacrylate) (PMMA) than that derived from nonpolar connector bisphenol.¹² Recently, Braun and Böhringer¹³ have reported that tetramethyl substituted polycarbonates showed an improved compatibility with poly(vinyl chloride) (PVC) compared to the unsubstituted ones. In addition, the polarity of the connector groups in polycarbonates played a significant role in rendering its blend with PVC compatible.

In this study, a homologous series of polyarylates were prepared by condensation polymerization from various bisphenols possessing structure variation. The bisphenols selected were tetramethyl bisphenol-S (TMBPS), bisphenol-S (BPS), and tetramethyl bisphenol-A (TMBPA). They differ in terms of the nature of (1) methyl or no substitution on the biphenyl rings, and/or (2) central group connecting the phenyl rings with or without polarity. Recognizing the structure variations of the polyarylates, it is conjectured that there exists polar attraction between the sulfone groups of TMBPS- and BPS-polyarylates and the chlorinated carbons of PVC. In addition, the tetramethyl substitution of TMBPS- and TMBPApolyarylates may or may not offer a closer balance of the dispersive forces of the blend components, thereby affecting compatibility. Therefore, the objectives of this study are to examine the compatibility of the three polyarylate/PVC blends and then to analyze the influence of the structural variations of the polyarylates on the compatibility with PVC. These are accomplished by differential scanning calorimetry (DSC) and Fourier-transform infrared (FTIR) spectroscopy.

EXPERIMENTAL

Preparation of Polyarylates

Bisphenols used in this study were bis(4-hydroxy-3,5-dimethylphenyl) sulfone (i.e., tetramethyl bis-



Figure 1 Polymerization scheme for the preparation of polyarylate via condensation polymerization.

phenol-S, TMBPS), bis(4-hydroxyphenyl) sulfone (i.e., bisphenol-S, BPS), and 2,2-bis(4-hydroxy-3,5-dimethylphenyl) propane (i.e., tetramethyl bisphenol-A, TMBPA), all purchased from Tokyo Kasei Co. Ltd. Isophthaloyl chloride (IPC) and terephthaloyl chloride (TPC) were products of Aldrich Chemical Co. Ltd. Chloroform (Aldrich Chem. Co.) was used as a solvent and triethylamine (Junsei Chem. Co.) was used as an organic acid acceptor. Commercially available chloroform is usually stabilized by addition of up to 1% ethanol and contains a little water, and triethylamine also contains little water. Because these ethanol and water react with IPC (or TPC) in polymerization, they must be removed by an adequate purification method.¹⁴

To a three-necked round-bottomed flask fitted with a nitrogen sparger, pressure equilibrated addition funnel, and mechanical stirrer were added with 1/20 mol of bisphenol, 1/20 mol of iso/terephthaloyl chloride (50/50), and 130 mL of purified chloroform. During the reaction, triethylamine in the pressure equilibrated addition funnel was slowly added to remove HCl (byproduct). The reaction was completed after 4 h. Figure 1 shows the polymerization scheme of tetramethyl bisphenol S polyarylates (TMBPS-polyarylate).

Polyarylate	Molecular Structure of Repeat Unit		
Tetramethyl bisphenol-S Polyarylate (TMBPS-PAr)	$\begin{array}{c} H_3C & O \\ \hline H_3C & -S \\ H_3C & O \\ \hline H_3C & O \\ \hline$		
Bisphenol-S Polyarylate (BPS-PAr)	$- \underbrace{\bigcirc}_{0}^{0} \underbrace{\stackrel{0}{\underset{0}{}{}{}{}{}{}{\overset$		
Tetramethyl bisphenol-A Polyarylate (TMBPA-PAr)	$\begin{array}{c} H_{3}C \\ \hline \\ H_{3}C \\ \hline \\ H_{3}C \\ \hline \\ CH_{3} \\ \hline \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ $		

Table I Molecular Structures of Polyarylate

After the reaction was completed, the polymer solution was then poured slowly into a rapidly stirred methanol (nonsolvent) with 10 times its volume. The precipitated polymer was washed in a large amount of methanol and then by distilled water. And it was dried, purified by dissolving in N,N-dimethylacetamide (Aldrich Chem. Co.), and reprecipitated into distilled water. Finally, the polymer was dried in a vacuum oven until no further weight loss was observed. The molecular structures of the polyarylates, polymerized by the above procedure, are shown in Table I.

The relative viscosity of polyarylates used in this study was determined at a concentration of 0.5 g/100 mL in N,N-dimethylacetamide at 25°C and $\eta_{\rm rel}$ s of TMBPS–, BPS–, and TMBPA–polyarylate were 1.52, 1.17, and 1.62, respectively. Especially, the weight-average molecular weight (M_w) and the number-average molecular weight (M_n) of TMBPA–polyarylate were 32,000 and 20,000, respectively, which were determined by gel permeation chromatography (GPC) at room temperature.

Preparation of Blends

PVC used in this paper was LS-100 (LG Chem. Co.) with M_n 62,000. Polyarylate/PVC blends were precipitated by adding one part of N,N-dimethylacetamide (DMAc) solution (5 w/v %) of the polymers into seven parts of the methanol (nonsolvent). The precipitates were dried in a vacuum oven at room temperature until no further weight loss was observed.

Differential Scanning Calorimetry (DSC)

Glass transition temperatures of polyarylates, PVC, and their blends were measured using a Du Pont 2100 thermal analyzer at a heating rate of 20°C/min. Each blend sample was first heated from room temperature to 180°C followed by rapid quenching using liquid nitrogen. Then, a second run was made where the onset, the midpoint, and the end point of the heat capacity change in the glass transition region were recorded. The T_g is defined as the midpoint in the change in the heat capacity with temperature.

Fourier-Transform Infrared (FTIR) Spectroscopy

Thin films of the polyarylates/PVC blends were made KBr pellet form. All the films used in this study were sufficiently thin such that they were within absorbance range where the Beer-Lambert law is obeyed.¹⁵ Fourier transform infrared spectra were obtained on a MIDAC Prospect IR spectrometer. Sixty-four scans at a resolution of 4 cm⁻¹ were signal averaged, and the resultant digitized spectra were stored for further data manipulations. The "Absorbance subtraction method"¹⁶ was employed in this study.

RESULTS AND DISCUSSION

Figure 2 shows DSC thermograms for TMBPS– polyarylate, PVC, and their blends with various compositions. The glass transition temperatures



Figure 2 DSC thermograms of TMBPS-polyarylate/ PVC blends.

 $(T_g s)$ of TMBPS-polyarylate and PVC are determined to be 264 and 83°C, respectively. For the blends, a single T_g is observable over the range of the corresponding compositions and shifts regularly to the intermediate value between $T_g s$ of TMBPS-polyarylate and PVC, indicating a compatibility of the two polymers. The compatibility is further ensured by examining the composition dependence of the blend T_g represented by the Gordon-Taylor expression,¹⁷

$$T_{gab} = \frac{W_a T_{ga} + k(1 - W_a) T_{gb}}{W_a + k(1 - W_a)}$$
(1)

where T_{gab} is the glass transition of the blend, T_{ga} and T_{gb} are the glass transitions of TMBPS-polyarylate and PVC, respectively, W_a is the weight fractions of TMBPS-polyarylate, and k(=3) is the ratio of the thermal expansion coefficients between the rubber and glass states of the component polymers, $\Delta \alpha_b / \Delta \alpha_a$. Figure 3 shows that the Goldon-Taylor equation fits the T_g data of TMBPS-polyarylate/PVC blend reasonably well. It is noted that, as seen in Figures 2 and 4, the glass transition regions of the blends become somewhat broader with the increase in TMBPSpolyarylate content. This observation suggests the presence of microscopic heterogeneity proba-



Figure 3 T_g of TMBPS-polyarylate/PVC blends.

bly ascribed to local concentration fluctuation¹⁸ and/or domains of the pure component(s).

The T_g s of BPS–, TMBPA–polyarylate, and their blends with PVC are summarized in Table II. All the blends clearly exhibit the presence of the T_g of the pure PVC fraction at ca. 84°C. However, the intermediate glass transition that lies between those of polyarylate and PVC does not appear, unlike the case of TMBPS–polyarylate/ PVC blend. These results indicate that BPS– and TMBPA–polyarylates are incompatible with PVC. It is noted that although the DSC measurements for the two blends were performed at the temperature ranging from 40 to 270°C, the T_g data were reliable only up to 170°C, beyond which the thermal degradation of PVC started.¹⁹ Thus, it was rather difficult to examine whether or not the T_g



Figure 4 The breadths of the glass transition regions for TMBPS-polyarylate/PVC blends.

Wt % of Polyarylate	T_{g} (°C)		
	TMBPS–Polyarylate/ PVC Blend	BPS–Polyarylate/ PVC Blend	TMBPA–Polyarylate/ PVC Blend
100	264.2	242.9	212
90	over 170	_	_
80		_	_
70	161.2	84	84
60	138.6	_	_
50	132.6	84	84
40	120.2	_	_
30	110.3	84	84
20	100.2	84	84
10	93	84	84
0 (PVC)	84	84	84

Table II T_{e} (°C) of Polyarylate/PVC Blends

of pure BPS- or TMBPS-polyarylate fraction in the blend existed.

From the DSC results it is explored that the variations of the chemical structure in polyarylates play a significant role in governing the compatibility of polyarylate/PVC blends. To acquire more precise information how the structural variants of polyarylates contribute to the compatibility with PVC, Fourier-transform infrared (FTIR) spectroscopy was employed. Figure 5 is the IR spectra for TMBPS-, BPS-, TMBPA-polyarylates, and PVC, respectively. In the TMBPS-polyarylate spectrum, the sharp peak at 1742 cm^{-1} is due to the carbonyl groups. The peaks at 1740, and $1100-1300 \text{ cm}^{-1}$ are assigned to carbonyl and sulfone groups, respectively. The peak at 1439 cm^{-1} arises from the tetramethyl groups substituted on biphenyl rings. In the BPS-polyarylate spectrum, there is no peak at 3000 cm^{-1} due to the absence of methyl groups substituted on the phenyl rings. The peaks at 1740, and $1100-1300 \text{ cm}^{-1}$ are assigned to carbonyl and sulfone groups, respectively. The TMBPA-polyarylate spectrum shows peaks at about 1740 cm⁻¹ arising from the carbonyl groups and at about 1440 cm⁻¹ from methyl groups on the phenyl rings, respectively. In the PVC spectrum, the peaks appearing at about 2900 cm^{-1} are due to stretching vibration of alkanes. The peaks at 1425, 1333, and 1256 cm^{-1} are due to bending vibration for methylene groups. The peaks arising from μ CCl are observed at 609, 632, and 694 cm^{-1} .

Figures 6–10 show IR analysis of the TMBPS– polyarylate/PVC blend. As seen in Figure 6, for PVC and the 50/50 blend, the absorbance peak at 956 cm^{-1} is shown. For TMBPS-polyarylate, however, the band at the same wavenumber is not observable. Thus, by subtracting the IR spectrum of PVC from that of the blend using an



Figure 5 IR spectra of TMBPS-, BPS-, TMBPA-polyarylate, and PVC.



Figure 6 IR spectra of TMBPS–polyarylate, PVC, and TMBPS–polyarylate/PVC (50/50) blend.

appropriate weighting factor to eliminate the peak at 956 cm⁻¹, the IR spectrum of the TMBP-S-polyarylate fraction in the blend can be separately obtained. Conversely, separation of the IR spectrum of the PVC fraction in the blend is also possible by subtracting the spectrum of TMBPS-polyarylate from that of the blend. In Figure 7, the absorbance peak at ca. 1060 cm⁻¹, due to symmetric stretching vibration of sulfone groups,



Figure 8 IR absorbance spectra of —CCl (PVC) in PVC and TMBPS–polyarylate/PVC blends.

exists for TMBPS-polyarylate and all its blends. This peak gradually shifts to a higher frequency as PVC concentration in the blend increases. In Figures 8 and 9, two bands due to --CCl stretching (694 cm^{-1}) and —CH deformation vibration (1430 cm⁻¹) of PVC in its pure and blended states are shown, respectively. Comparing both figures, -CCl stretching band shifts to a higher frequency and the change in its band shape is more remarkable than that in -CH band. This indicates that in TMBPS-polyarylate/PVC blend, specific interaction between -SO₂- of TMBPSpolyarylate and --CCl of PVC is stronger than that between -SO₂- and -CH of PVC. In addition, the -SO2 groups exert dipole-dipole interaction with -- CCl in the blend rather than hydrogen bonding with —CH (α -hydrogen). Figure 10 represents absorbance bands at 1440 cm^{-1} for tetramethyl groups substituted on phenyl rings of TMBPS-polyarylate, in its pure and blended



Figure 7 IR absorbance spectra of —SO₂— (TMBPS– polyarylate) in TMBPS–polyarylate and TMBPS–polyarylate/PVC blends.



Figure 9 IR absorbance spectra of —CH— (PVC) in PVC and TMBPS—polyarylate/PVC blends.



Figure 10 IR absorbance spectra of —CH₃ (TMBPS–polyarylate) in TMBPS–polyarylate and TMBPS–polyarylate/PVC blends.

states, which are due to deformation vibration of $-CH_3$ groups. A gradual shift to a lower frequency as a function of PVC concentration is observed. It is explained by the fact that the methyl groups are an electron donor, whereas phenyl rings are an electron acceptor.²⁰

The significant effect of the tetramethyl substitution on compatibility is well demonstrated in Figure 11, where the symmetric stretching band for sulfone groups of BPS appears at 1060 cm⁻¹. As seen in the figure, the shift of the band as a function of PVC concentration is negligible. Recognizing that (1) the only structural difference in BPS-polyarylate relative to TMBPS-polyarylate is the absence of the tetramethyl groups, and (2) tetramethyl groups and phenyl rings have proton--donor and acceptor characteristics, respectively, the tetramethyl substitution brings about electronic rearrangement in phenyl rings, which en-



Figure 11 IR absorbance spectra of —SO₂— (BPS– polyarylate) in BPS–polyarylate and BPS–polyarylate/ PVC blends.



Figure 12 IR absorbance spectra of —CH₃ (TMBPA– polyarylate) in TMBPA–polyarylate and TMBPA–polyarylate/PVC blends.

hances the polarity of the connector $-SO_2$ -groups and, hence, the compatibility in the blend. Therefore, the sulfone groups alone cannot give interactions strong enough to bring about a compatibility with PVC.

The $-CH_3$ band shift in TMBPA-polyarylate and its blends is shown in Figure 12. Similar to the case of TMBPS-polyarylate, the band moves to a lower frequency with increasing PVC concentration. Although the tetramethyl groups donate their electrons onto the phenyl rings, it is inferred that the nonpolar connector groups of TMBPApolyarylate hinder the compatibility with PVC.

CONCLUSIONS

In this study, three different polyarylates with structural variations were condensation polymerized and blended with PVC. The combined results by DSC and FTIR analysis provided a clear insight into the effect of varying the molecular structure of polyarylates on compatibility with PVC. TMBPS-polyarylate/PVC blend showed a single glass transition that changes regularly with blend compositions. The fact that the T_g value was intermediate between those of component polymers confirmed that TMBPSpolyarylate is compatible with PVC. In BPSpolyarylate/PVC and TMBPA-polyarylate/PVC blends, the glass transitions pertinent to the component polymer were observed, indicating an incompatibility.

FTIR studies concluded that in the TMBPSpolyarylate/PVC blend, dipole-dipole interaction existed between the sulfone groups of TMBPSpolyarylate and chlorine atoms of PVC. It appeared that the tetramethyl substitution in TMBPS-polyarylate apparently increased the strength of interactions relative to those observed in BPS-polyarylate, where the sulfone groups alone had an opposite effect. The inclusion of methyl groups in TMBPA-polyarylate, however, was found to have no contribution to the compatibility with PVC what so ever due to the absence of the polar connector group.

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