

# Compatibilization of Poly(2,6-dimethyl-1,4-phenylene oxide) and Poly(2,6-dichloro-1,4-phenylene oxide) with Sulfonated Polystyrene and its Na and Zn-neutralized Ionomers

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**Abstract:** Compatibility of acidic (H), Na, and Zn neutralized sulfonated polystyrene ionomer blends with Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and Poly(2,6-dichloro-1,4-phenylene oxide) (PDCIPO) was investigated by Dilute Solution Viscometry (DSV) and Differential Scanning Calorimetry (DSC). The intrinsic viscosities of the blends, are measured in suitable solvents. The degree of compatibility of the blends is characterized by  $\Delta b$  parameter. According to the results, PPO is completely miscible, except for Na-neutralized 1.7 mol% sulfonated polystyrene (Na1.7SPS) which is completely immiscible with PPO and PDCIPO. PDCIPO is completely miscible with Zn-neutralized sulfonated polystyrene (Zn4.8SPS) and partially miscible with acid sulfonated polystyrene (4.8SPS).

**Key words:** Poly(2,6-dimethyl-1,4-phenylene oxide), Poly(1,4-dichloro-2,6-phenylene oxide), sulfonated polystyrene ionomers, polymer blends, compatibility

## Introduction

In a continuation of our studies of the miscibility of 4.8SPS and its metal neutralized ionomers, Na1.7SPS, Zn4.8SPS with PPO and PDCIPO, we have systematically investigated the miscibility in six binary blend series with varying compositions. Polymer blends of Polystyrene (PS) and PPO are of unusual interest from both scientific and technological point of view [1-9].  $T_g$  of PS/PPO blends are extensively studied by several scientists [2-10] and concluded that no specific interactions between PS and PPO exist and only Van der Waals interactions between the aromatic rings of PS and PPO are primarily responsible for miscibility.

An area of continual interest is the examination of the miscibility of blends containing chemically modified components (one or both) of PS-PPO blends, such as Poly( $\alpha$ -methyl styrene) [11], halogenated PS [12], carboxylated PPO [13], sulfonylated PPO [6], and brominated PS [14].

In this study, we explore the phase behaviour of 4.8SPS and its Na and Zn neutralized ionomers blended with PPO and PDCIPO. Both miscibility and immiscibility are

observed depending on the specific polymer structure of each blend component and their respective composition. The method used in this study is mainly DSV which is partially supported by DSC [8, 15-20].

The compatibility of solutions has been characterised by a viscometry technique using the Krigbaum and Wall parameter,  $\Delta b$  which is expressed as;

$$\Delta b = b_{12} - b_{12}^*$$

$b_{12}$  is the interaction coefficient for the mixture of components 1 and 2. And  $b_{12}^*$  is the inter-specific interaction coefficient. Negative values of  $\Delta b$  are found for solutions of incompatible polymer systems while positive values of  $\Delta b$  refer to attractive interactions.

## Experimental

PPO was obtained from The Institute of Romanian Polymer Society and used without further purification.  $[\eta]$  of PPO is 0.495 dl/g at 30°C in chloroform. Na1.7SPS and PS were obtained from Exxon Chemical Company and Dow Chemicals Inc. with approximate molecular weights of 300.000 g/mole and 225.000 g/mole respectively. Lightly sulfonated PS is prepared by the sulfonation of PS according to Register et. al. [7]. PDCIPO is obtained through thermal decomposition of Bis(pyridine)bis(2,4,6-trichlorophenoxy) copper (II) complex in solution according to D. Kısakürek et. al. [21].

For the blend preparations, solution blending method is used for individual sets with various compositions. Six sets of blends 4.8SPS/PPO, Na1.7SPS/PPO, 4.8SPS/PDCIPO, Na1.7SPS/PDCIPO, Zn3.8SPS/PPO, Zn3.8SPS/PDCIPO are prepared. For the first and the second sets of blends chloroform, for the third and the fourth 1,4 dioxane, and for the fifth and the sixth tetrahydrofuran are used as solvents at blending and during viscosity measurement stages. Viscosity measurements are carried with an Ubbelohde viscometer in a constant temperature bath at 25°C. DSC Thermograms are obtained with TA instruments of DSC 910S using a heating rate of 10°C min<sup>-1</sup>. Blends are scanned from 25°C to 250°C. Two heating scans were applied to materials. The cooling rate is 20<sup>0</sup>/min. Second scans were used during all DSC analysis.  $T_g$  values are all mid-point  $T_g$  calculated by DSC instrument. Results are reproducible.

## Result and Discussion

### 4.8SPS/PDBrPO System

Intrinsic viscosity ( $[\eta]$ ),  $\Delta b$  and  $T_g$  values obtained from viscosity measurements and DSC analysis are tabulated in Table 1 with their corresponding  $T_g$  values. Krigbaum and Wall parameter  $\Delta b$ , is positive for all and in good agreement with DSC results indicating miscibility of 4.8SPS/PPO system in all compositions.

**Table 1.** The viscometric and  $T_g$  data for 4.8SPS /PPO system in chloroform at 25°C

Wt % 4.8SPS	$[\eta]$ (dLg <sup>-1</sup> )	$\Delta b$	$T_g$ (°C)
00	0.875	-	211.00
20	0.569	2.926	180.71
40	0.515	2.235	155.78
60	0.667	2.571	134.79
80	0.504	3.464	118.45
100	0.585	-	102.69

Table 1 reflects that for a miscible blend, the expected single  $T_g$  is between the  $T_g$ s of the pure components. It is also observed that when the amount of 4.8SPS in the blend is increased, a decrease in glass transition temperatures is observed.

### *Na1.7SPS/PPO System*

**Table 2.** The viscometric and  $T_g$  data for Na1.7SPS /PPO system in chloroform at 25°C

Wt % Na1.7SPS	$[\eta]$ (dLg <sup>-1</sup> )	$\Delta b$	$T_g$ data (°C)
00	0.875	-	211.00
20	0.612	-6.384	135.75, 212.30
40	0.226	-0.500	135.11, 208.25
60	0.465	-2.823	137.44, 209.89
80	0.479	-4.234	120.01, 215.00
100	0.414	-	110.16

Table 2 represents the  $[\eta]$ ,  $\Delta b$  parameters and  $T_g$  values for Na1.7SPS/PPO system. As expected, the miscibility parameters ( $\Delta b$ ) in Table 2 are all negative and 2  $T_g$  values are expressing immiscibility. Neutralization of 1.7SPS with Na reduces the miscibility of blends. Since Na is an alkali metal, dispersing of Na<sup>+</sup> ionomers in the polymer matrix is unfavorable in terms of enthalpy which reduces miscibility [14], [22].

### *Zn4.8SPS/PPO System*

The calculated miscibility parameters for this system is tabulated in Table 3. Positive values for all miscibility parameters indicate miscibility in all compositions. Miscibility of an ionomer with another polymer is often very sensitive to the counter ion chosen for the ionomer.

**Table 3.** The viscometric and  $T_g$  data for Zn4.8SPS/PPO system in chloroform at 25°C

Wt % Zn4.8SPS	$[\eta]$ (dLg <sup>-1</sup> )	$\Delta b$	$T_g$ data (°C)
00	0.875	-	211.00
20	0.103	18.862	204.48
40	0.250	7.7470	143.08
60	0.253	69.083	125.63
80	1.254	62.420	116.18
100	0.205	-	109.78

In this study, Na1.7SPS proved to be immiscible with PPO while Zn4.8SPS showed miscibility. It is well known that Zn neutralization produces lower melt viscosity in the ionomers than does neutralization with alkali metals. Ionomers having elastomeric matrices also typically exhibit greater creep. These changes are not observed when the neutralizing cation is Na<sup>+</sup>. This is due to the more covalent bonding nature of Zn<sup>2+</sup> when compared with alkali metals, resulting in a lessened enthalpy of association between Zn<sup>2+</sup> salts. Consequently, the energy penalty involved in dispersing a Zn<sup>2+</sup> group in the matrix is less than the comparable penalty for a Na<sup>+</sup> group which accelerates the ion-hopping process by which ionomers flow [6].

#### 4.8SPS/PDCIPO System

Table 4 summarizes the  $\Delta b$  and  $T_g$  results for 8 different compositions for the blends of 4.8SPS/PDCIPO system. The  $\Delta b$  values reflect an immiscibility window for (30-60) weight percent 4.8SPS blends.

**Table 4.** The viscometric data for 4.8SPS/PDCIPO system in dioxane at 25°C

Wt % 4.8SPS	$[\eta]$ (dLg <sup>-1</sup> )	$\Delta b$	$T_g$ data (°C)
00	0.046	-	172.64
10	0.061	0.001	159.95
20	0.036	0.106	130.00
30	0.205	-0.140	96.00, 137.00
40	0.307	-4.140	101.39, 152.73
60	0.323	-0.160	100.10, 153.35
70	0.398	0.039	102.91
90	0.406	1.431	105.06
100	0.585	-	102.69

4.8SPS/PDCIPO system consisting of blends with non-neutralized ionomer is expected to show enhanced miscibility due to H-bonding interactions. However, dichloro-substituted phenyl rings adjacent to the ether groups certainly may reduce the access of the sulfonate group to the ether groups. Even if the acid group in principle has access to the ether oxygen, from steric point of view, local chain conformation may reduce the interactions between PS and PDCIPO segments, thereby rendering the acid-ether interactions unfavorable. Another factor may be that the ether oxygen

donates excess electron density to the neighbouring phenyl groups, thereby reducing the ability of the ether to interact with the proton acid [6].

### Na1.7SPS/PDCIPO System

In Table 5,  $\Delta b$  parameters and  $[\eta]$  for Na1.7SPS/PDCIPO system having various compositions are given. As seen from Table 5,  $\Delta b$  for all compositions are having negative values indicating phase separation in all the blends. The most interesting feature of this table is strongly influenced by the choice of neutralizing cation, which is  $\text{Na}^+$  ion. Since Na is an alkali metal,  $\text{Na}^+$  ion has small size and high strength for ionic association; the ion pairs tend to aggregate into groups of ion pairs via dipole-dipole interactions to form multiplets. These aggregates restrict the mobility of the nearest parts of the backbone chains to which they are covalently bonded. The existence of a sufficient number of multiplets that are close enough to one another gives rise to regions of reduced chain mobility; these regions are called clusters.

**Table 5.** The viscometric data for Na1.7SPS/PDCIPO system in dioxane at 25°C

Wt % Na1.7SPS	$[\eta]$ (dLg <sup>-1</sup> )	$\Delta b$
00.0	0.257	-
12.5	0.056	-0.224
25.0	0.142	-1.857
37.5	0.126	-0.482
50.0	0.136	-0.203
75.0	0.125	-0.804
87.5	0.237	-3.861
100.0	0.046	-

The experimental results show that ionic clusters do not accommodate a second phase in its matrix and no miscibility is detected by Na1.7SPS/PDCIPO system. Due to this phase separation, DSC thermograms showed several thermal transitions above and below the  $T_g$  values of the pure components.

### Zn4.8SPS/PDCIPO System

In Table 6, the miscibility parameters and  $T_g$  values for Zn4.8SPS/PDCIPO blends with varying compositions are tabulated. As seen from  $\Delta b$  values, blends with all compositions for this system are miscible. Single phase for Zn ionomer blend is expected by more covalent bonding nature of  $\text{Zn}^{2+}$  ion when compared to  $\text{Na}^+$  ion.

**Table 6.** The viscometric data for Zn4.8SPS/PDCIPO system in THF at 25°C

Wt % Zn4.8SPS	$[\eta]$ (dLg <sup>-1</sup> )	$\Delta b$	$T_g$ data (°C)
00	0.046	-	172.64
20	0.200	4.491	151.25
40	0.198	2.378	167.83
50	0.195	2.180	167.94
60	0.193	2.084	139.04
80	0.136	4.346	149.27
100	0.205	-	110.16

The miscibility of the Zn4.8SPS ionomer with PDCIPO can be partly attributed to the dissolution of some of the Zn sulfonate groups into the PS matrix; this reduces the amount of cluster material in the ionomer and hence allows increased interactions between PS segments and the PDCIPO chains. Ionomers having elastomeric matrices also exhibit greater creep when neutralized with  $Zn^{2+}$ . Finally  $Zn^{2+}$  ionomers exhibit a notable decrease in phase separation at elevated temperatures. Single  $T_g$  value is reproducible for any blend of the system.

## Conclusion

PPO is miscible with a wide range of styrene-based ionomers, provided the sulfonation level of PS or PPO content is low. PPO is completely miscible with 4.8SPS in all proportions. PDCIPO forms an immiscibility window with 4.8SPS. Both PPO and PDCIPO are not miscible with  $Na^+$  ionomer of 4.8SPS. However these polymers are miscible in all proportions with Zn4.8SPS.

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