Polymer Bulletin 35, 329–336 (1995)

Polymer Bulletin

Blends of poly(2,6-dimethyl-1,4-phenylene oxide)/ poly(styrene-*co*-methacrylic acid)/ poly(ethyl methacrylate-*co*-4-vinylpyridine)

Zitouni Benabdelghani, Rachida Belkhiri, Said Djadoun *

Chemistry Institute, University of Sciences and Technology Houari Boumediene,
BP 32, El Alia, Algiers 16111, Algeria

Received: 30 March 1995/Accepted: 4 April 1995

SUMMARY

The miscibility of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) with poly(styrene-*co*-acrylic acid) (SAA) or poly(styrene-*co*-methacrylic acid) (SMA) containing respectively up to 22 mol % of acrylic or methacrylic acid was studied by Differential Scanning Calorimetry and viscosimetry. All PPO/SAA or PPO/SMA blends containing 60% or less by weight of PPO were miscible and showed only one glass transition temperature (Tg).Above 60 % of PPO, two Tg's were however observed for the blends in which the acid content in the SAA or SMA reaches 20% or 12 % by mole respectively ; the higher Tg is slightly lower than the one of pure PPO, while the lower one corresponds to a miscible blend of lower content of PPO.A DSC study showed that depending on the blend ratio , two or three glass transition temperatures were observed when a copolymer of ethyl methacrylate containing 8 mol % of 4-vinylpyridine (EM4VP-8) was added to miscible PPO/SMA-12 blends.The PPO dissolution in the SMA-12 copolymer was affected by the specific interactions that occurred between this latter copolymer and the EM4VP-8.

INTRODUCTION

It is well known that poly(2,6-dimethyl-1,4-phenylene oxide) is miscible in all proportions with polystyrene (1-4). Blends of these polymers have been extensively studied by several techniques (5-10). It is reported that Van der Walls interactions between the aromatic rings of PPO and those of polystyrene (PS) are responsible for the miscibility of these blends (11,12).A weak interaction parameter between these polymers was estimated by Kambour et al. (13).It has also been shown that blends of a homopolymer and a copolymer or of two copolymers may be miscible even in the absence of specific interactions, provided sufficient repulsions between the comonomers (14-19).Bazuin et al. (20) have reported in a very recent study , using dynamic mechanical thermal analysis , that blends of PPO and styrene-*co*-methacrylic acid are no longer miscible at 10 mol % of acid content.

In the present study , we have investigated the effect of incorporating carboxylic groups into polystyrene chains on the well known miscible PPO/PS blends.Styrene-*co*-acrylic acid or styrene-*co*-methacrylic acid of different compositions were prepared and blends of these copolymers with PPO were studied by DSC and viscosimetry.We have previously showed that as a result of specific interactions between the constituents of the blends , SAA or SMA copolymers were miscible in all proportions with poly(alkyl methacrylate-*co*-4-vinylpyridine).A study of ternary PPO/SMA-12/EM4VP-8 blends was then carried out by DSC to investigate the effect of adding EM4VP-8 to miscible SMA/PPO blends.

---

* Corresponding author

EXPERIMENTAL

PPO was supplied by Aldrich.Copolymers SAA or SMA of different compositions and EM4VP-8 copolymer were prepared by free radical polymerization at 60°C using azo-bis - isobutyronitrile as the initiator. The styrene and 4-vinylpyridine contents in these copolymers was determined by UV spectroscopy as previously described (21). Binary blends of PPO and styrene copolymers and ternary blends of PPO/SMA-12/EM4VP-8 used in the study by DSC were prepared from chloroform solution and coprecipitation in excess methanol. These blends were dried in a vacuum oven for 48 hours at 70°C. Glass transition temperatures of PPO, SAA, SMA and of the various binary or ternary blends were measured using a Perkin Elmer DSC-7 at a heating rate of 20 K/min under a nitrogen blanket. Chloroform solution of different concentrations of PPO or SMA-12 or of PPO/SMA-12 of various ratios were prepared.Viscosity measurements of these solutions were carried at 25 °C , using a manual capillary Ubbelohde viscosimeter.

RESULTS AND DISCUSSION

The single glass transition temperature observed with all PPO/SAA-6.7 , PPO/SAA-20 and PPO/SMA-7.8 blends of different weight compositions can be considered as an evidence of the miscibility of these blends . Hydrogen bonding interactions are expected to occur between the carboxylic groups of the SAA-20 or SMA-7.8 and the ether oxygen of the PPO.The Tg's of these blends were plotted against the weight fraction of PPO. The negative deviation of the Tg values from the weight average of the glass transition of the pure components , observed with these blends, as shown in figures (1,2) is characteristic of weak interactions between PPO and these copolymers.

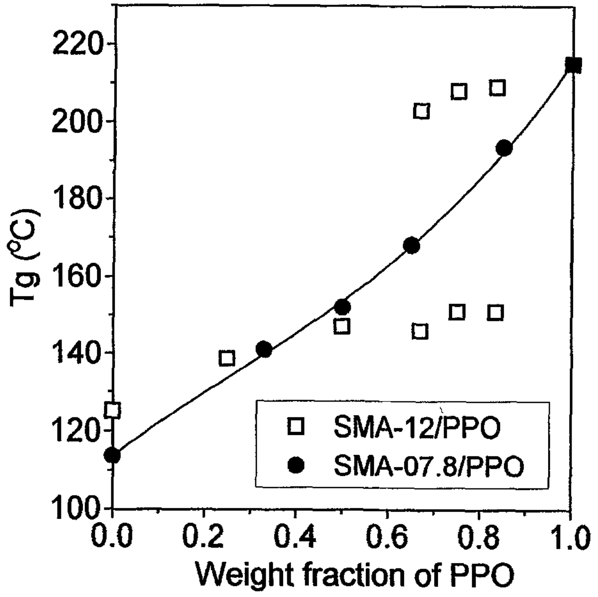

Figure 1: Glass transition temperature of PPO/SMA blends versus PPO weight fraction.

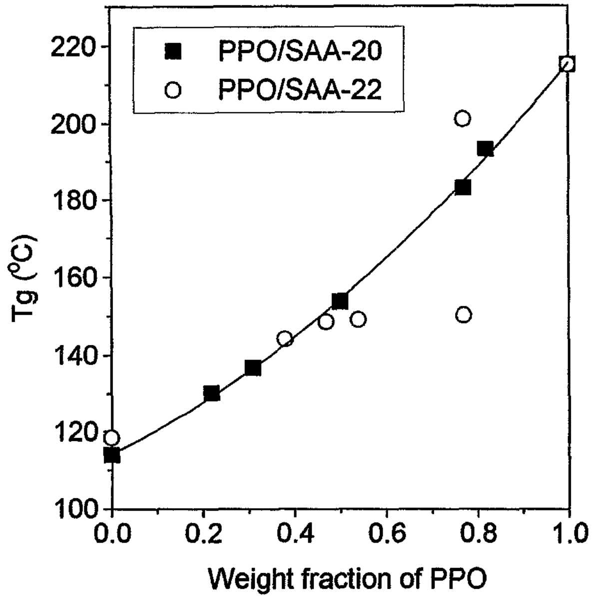

Figure 2: Glass transition temperature of PPO/SAA blends versus PPO weight fraction.

In all these cases, the Tg-composition can be described by the Gordon-Taylor equation :

$$T_g = (W_1T_{g1} + k\,T_{g2})/ (W_1 + kW_2) \qquad (1)$$

where W_1 ,W_2 and T_{g1} ,T_{g2} are the weight fractions and T_g's of components 1 and 2 respectively,with k values of 0.680 , 0.510 , 0.664 and 0.392 for miscible PPO/SAA-20, PPO/SAA-22, PPO/SMA-7.8 and SMA-12/PPO blends respectively .

It is observed from Figure (3) , in which the transition width of each blend composition is plotted against the PPO content in these miscible blend, that the Tg broadens and goes through a maximum located in the excess PPO region.

We have also used the third power equation (22) to analyze the eventual specific interactions that may occur between the constituents of these blends.Figure (4) displays plot of $(T_g\text{-}T_{g1}) / (T_{g2}\text{-}T_{g1})\, W_{2c}$ versus W_{2c} for PPO/SAA-6.7 , PPO/SAA-20 and PPO/SMA-7.8 blends where the corrected weight fraction of PPO (component of highest T_g) W_{2c} is given by :

$$W_{2c} = KW_2/(W_1+KW_2) \quad \text{and} \quad K = \rho_1T_{g1}/\rho_2T_{g2} \qquad (2)$$

where T_{g1} , T_{g2} , ρ_1 and ρ_2 are the glass transition temperatures and the densities of SAA or SMA and PPO in the blend .Weak interactions between the components of the blends as confirmed by very small positive deviation from volume additivity are observed.

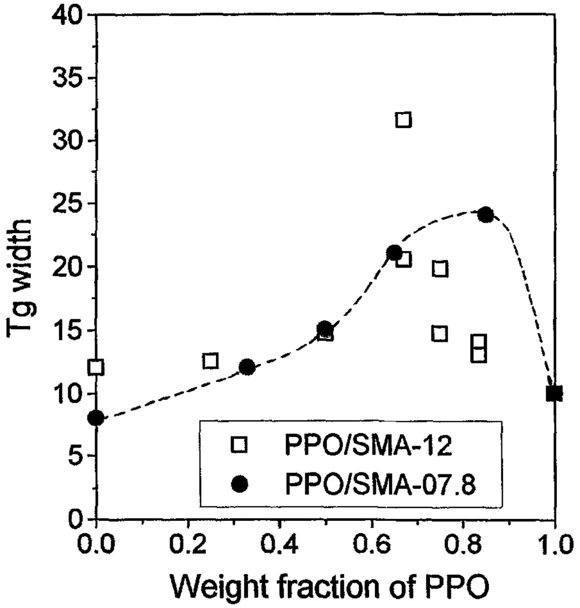

Figure 3: Glass transition temperature width of PPO/SMA versus PPO weight fraction.

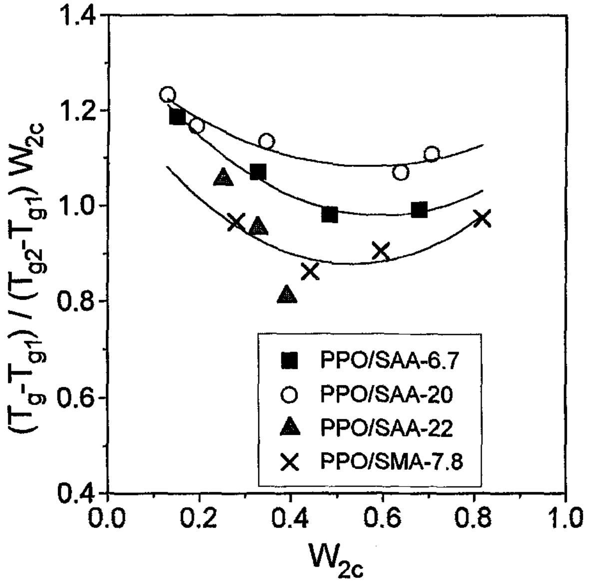

Figure 4: $(T_g-T_{g1})/(T_{g2}-T_{g1})W_{2c}$ versus W_{2c} for PPO/SAA and PPO/SMA blends.

Blends of PPO with SAA-22 or SMA-12 were also studied.A single T_g is observed with SMA-12/PPO or SAA-22/PPO blends containing respectively less than 67 or 77 weight % of PPO . A more negative deviation from linearity is observed for these blends. In a similar way as the blends above , the transition temperature range broadens with an increase of PPO in the blend.Two glass transition temperatures are however observed for blends containing high content of PPO. It is rather difficult to assess the immiscibility of these blends from the observation of the two glass transition temperatures only since transparent films were obtained for all compositions after solvant evaporation.The observed glass transition temperatures are not the same as those of the pure constituents of the blends.The width of each glass transition temperature of the two phases decreases at very high content of PPO. Even though the highest T_g of the PPO rich phases slightly lower, its value decreased by up to 12°C as compared to the one of pure PPO ; this indicates the presence of SAA-22 or SMA-12 in the PPO-rich phase.The lowest T_g is however higher by more than 25°C than the one of SAA-22 or SMA-12 , the other components of the PPO/SAA-22 or SMA-12/PPO blends ; this latter T_g seems to correspond to the one of the miscible SAA-22/PPO or SMA-12/PPO blends containing respectively 54 or 50 weight % of PPO.The obtained results show a better dissolution of PPO in the SAA copolymers. Similar observations were reported by Register et al. (23) for PPO/ Sodium sulfonated polystyrene ionomers. In a previous study of SAA-20 with polyethylene oxide blends (24), we have observed similar results whenever the ether polymer was in excess.

A linear variation of the relative viscosity-weight fraction of PPO in the SMA-12/PPO blends , observed between 0 and 50 % of PPO, is characterisitic of miscible PPO/SAM-12 blends ; a change of slope , indicative of the existence of two phase systems , is however observed at higher PPO content in the blend .It can be sen from Figure (5) , that the plot of the experimental intrinsic viscosity of the blend as function of PPO weight fraction is of S-type : the negative deviation from the weight average of the pure components, observed with low PPO content is considered as an evidence of miscibility of these blends ,while the positive deviation is characteristic of their immiscibility at high PPO content .

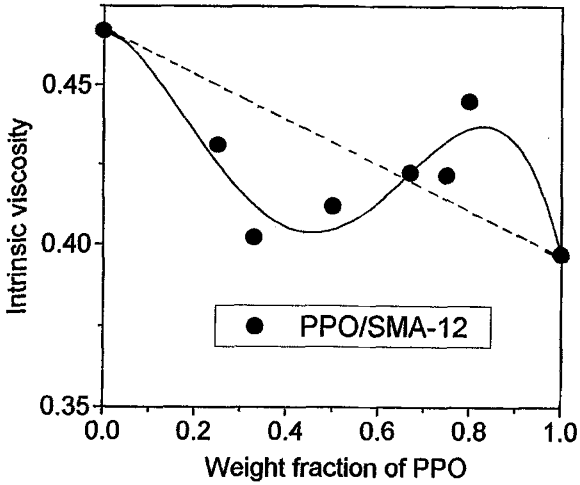

Figure 5 : Intrinsic viscosity of PPO/SMA-12 blends versus PPO weight fraction.

We have in addition, determined the experimental viscosimetric interaction parameter between the constituents of the blends of different ratios using chloroform as a solvent and the difference between the experimental and theoretical interaction parameters (Δb_{23}), using the approximative method of Krigbaum and Wall (25). Accordingly, the experimental viscosimetric interaction parameter b_{23} between the PPO and the SMA-12 is determined from the following equation :

$$b_{23} = [\, b_m - (x_2^2 b_{22} + x_3^2 b_{33})] \,/\, 2x_2.x_3 \qquad (3)$$

with b_m , the global interaction parameter between polymer species, x_2 ,x_3 b_{22} and b_{33} ,the weight fractions and interaction parameters of PPO and SMA-12 respectively. The theoretical interaction parameter was calculated from :

$$b_{23}^{the} = (b_{22}.b_{33})^{1/2} \qquad (4)$$

As shown in Figure (6) , slightly positive $\Delta\ b_{23}$, characteristic of miscible blends through weak interactions were obtained with blends containing up to 50 % of PPO.The formation of two phases at higher PPO content was confirmed by negative Δb_{23} values. This may be an evidence of absence of specific interactions between the carboxylic groups of SMA and the ether group of PPO.

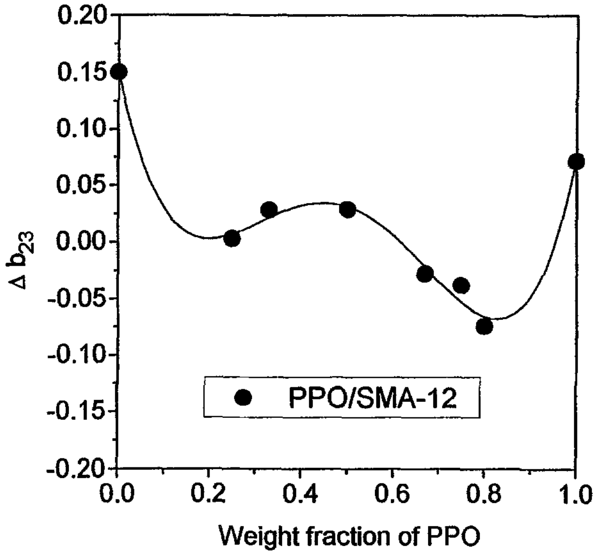

Figure 6 : Δb_{23} versus PPO weight fraction for PPO/SMA blends.

Based on the results above , we also have investigated by DSC some ternary PPO/SMA-12/EM4VP-8 blends containing an equal amount of PPO and SMA-12 or an excess of SMA-12 for which binary PPO/SAM-12 blends were miscible. Figure (7) exhibits the DSC traces of some of these blends which show, depending on the blend composition two or three Tg's.Blends of PPO/EM4VP-8 are expected to be immiscible.It can be seen that two glass transition temperatures are observed for the blend containing equal amount of the three constituents . The lowest T_{g1} (103.5 °C) is intermediate between those of EM4VP-8 (77.5°C) and SMA-12 (125°C), and seems to corresponds to the one of a miscible SMA-12 / EM4VP-8 blend whereas the highest one T_{g3} (205 °C) is characteristic of a phase containing mostly PPO and a small amount of SMA-12 (4%) as determined from the Gordon-Taylor equation.The dissolution of PPO in the SMA-12 decreased in the presence of EM4VP-8 as confirmed by the formation of such a high Tg phase, observed only with binary PPO/SMA-12 blends containg high fraction of PPO. The SMA-12 acts therefore as a preferential solvent. As the amount of EM4VP-8 in the blend decreases, another glass transition temperature T_{g2} is observed. T_{g1} and T_{g3} appeared in the same regions, whereas the third one, located between those of PPO and SMA-12 , remains practically constant (152 °C) ,characteristic of a miscible PPO/SMA-12 blends.In all cases of these ternary blends, specific interactions occurred preferentially between EM4VP-8 and SMA-12 and reduced the dissolution of PPO in such phase.The lowest Tg value, increasing as the amount of EM4VP-8 decreases, was found in all cases higher than the weight average Tg's of the pure EM4VP-8 and SMA-12 ,assuming that the SMA-12/EM4VP-8 phase contains the total amount of SMA-12.The observation of other phases at higher temperatures and containing a certain quantity of SMA-12 confirms that, due to hydrogen bonding between SMA-12 and EM4VP-8 copolymers , the lowest T_{g1} is even higher than the theoretical one.A study of binary PPO/SMA or ternary PPO/SMA/EM4VP blends containing higher densities of interacting species by DSC and inverse gas chromatography is in progress.

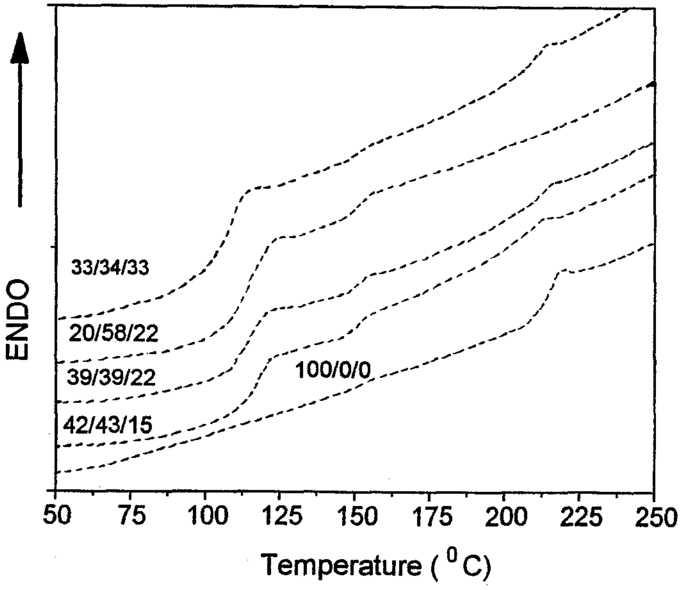

Figure 7 : DSC traces of PPO/SMA-12/EM4VP-8 blends.

CONCLUSIONS

This contribution shows that PPO is more miscible with SAA than with SMA copolymers.However weak interactions occurred between the constituents of these blends as confirmed by DSC and viscosimetry.Even though two glass transition temperatures and negative Δb_{23} were obtained with blend SAA-22/PPO or SMA-12/PPO containing an excess PPO , it is difficult to assess the immiscibility of these blends since transparent films were observed for all compositions after solvent evaporation.Due to preferential specific interactions between SMA-12 and EM4VP-8 , the dissolution of PPO in the SMA-12 phase is reduced .

REFERENCES

1 Shutlz A.R.and B.M.Beach B.M.(1974) , **Macromolecules** 7 : 902 .

2 MacKnightW.J. ,Karasz F.E. and Fried J.R. (1978) in " **Polymer Blends**" Paul D.R. and S.Newman ,eds., Academic Press ,New York ,vol **1** :185 .

3 Shultz A.R. and Gendron B.M. (1972), **J.Appl. Polym. Sci. 16** : 461 .

4 Stoelting J., Karasz F.E. and MacKnight W.J. (1970) , **Polym.Eng. Sci. 10** : 133 .

5 PrestW.M.J. and Porter R.S. (1973) , **J.Polym.Sci., Phys. Ed.**, **10** : 1639 .

6 Moconnachie A. ,Kambour R.P.,White D.M. ,Rostami S.and D.J.Walsh (1984) , **Macromolecules 17** : 2645 .

7 Su A.C. and Fried J.R. (1986) , **Adv. Chem.Ser. 211** : 59 .

8 Su A.C. and Fried J.R. (1989) **,American Chem. Society , Symp. Ser.**, vol. **391** : 155 .

9 Hseih D.T. and Peiffer D.G. (1992) , **Polymer** , **33** , **6** : 1210 .

10 Kambour R.P., Bopp R.C.,Moconnachie A.and MacKnight W.J.(1980) **,Polymer 21** :133

11 Wellinghoff S.T.,Koenig J.L.and Baer E.J.(1977)**,J.Polym.Sci.,Polym.Phys. Ed. 15** :1913

12 Mitchell G.R. and Windle A.H. (1985), **J.Polym. Sci., Polym.Phys. Ed. 23** : 1967 .

13 Kambour R.P. , J.T.Bendler J.T. and Bopp R.C. (1983), **Macromolecules 16** : 753 .

14 ten Brinke G. , Karasz F.E and MacKnight W.J.(1983), **Macromolecules 16** :1827.

15 Kressler J.,Kammer H.W. ,Klostermann K.(1986), **Polym. Bull. 15** :113 .

16 Lath D., Cowie J.M.G. and Lathova E.(1992) , **Polym. Bull. 28** : 361

17 Shiomi T.,Karasz F.E. and MacKnight W.J. (1986), **Macromolecules 19** : 2644 .

18 Goh S.H., Lee S.Y. and Leong C.L. (1992) , **J. Appl. Polym.Sci. 44** :199 .

19 Cowie J.M.G., Li G. ,Ferguson R.and McEwen I.J.(1992), **J.Polym.Sci., polym.Phys. Ed., 30 :** 1351 .

20 Bazuin C.G. ,Rancourt L. ,Villeneuve S. and Soldera A. (1993) **,J.Polym.Sci. Part B, Polym.Phys. 31 : 1431.**

21 Djadoun S., Karasz F.E. and Metref F.(1994), **Makromol.Chem. Macromol.Symp.78** : 155.

22 Brekner M.J., Schneider H.A. and Cantow H. (1988) , **J.Polymer 29** : 78 .

23 Tomita H. and Register R.A. (1993) , **Macromolecules , 26** : 2796 .

24 Cherrak D.E. and Djadoun S. (1991), **Polym.Bull.** , 27 : 289 .

25 Krigbaum W.R. and Wall F.W.(1950), **J.Polym.Sci., 5** : 505 .