Thermomechanical, Tensile and Morphological Properties of Allylic Monomer as Reactive Plasticizer and Reinforcement in Polystyrene/Polyphenylene Oxide Blends

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Abstract. The use of diallyl phthalate (DAOP) monomer as both reactive plasticizer and reinforcement in polystyrene/polyphenylene oxide (PS/PPO) blends was investigated. The blends of a fixed amount of PS (80%) with different contents of PPO-DAOP were prepared using an internal mixer and glass transition temperature ($T_g$), tensile and morphological properties of the blends were studied. $T_g$ of the blends gradually reduced with the replacement of PPO with up to 4%DAOP might be due to the reduction of rigid component (PPO) but then plateau in the presence of 6%DAOP may be due to presence of higher content of cured DAOP. Tensile test conducted on the blends indicated that tensile strength and modulus increased with increasing DAOP content up to 4wt% and then slight reduced with further increased of DAOP with the value slightly higher than PS/PPO blend without DAOP suggesting that DAOP could act as reinforcement in PS/PPO blend. Morphological study of the blends showed single phase of 80PS/20PPO blend while blends with DAOP illustrated rough, two phase morphologies with DAOP particle size increased with increasing DAOP. However, in the presence of 6% DAOP, smoother surface was observed which translated into reduction of tensile strength and modulus of the blends.

1. Introduction

Engineering thermoplastics such as polyphenylene oxide (PPO), polyethersulfone and polyetherimide possess many desirable properties but difficult to be processed due to their rigid chain structure. They need to be processed at high temperature using special processing equipment in which they expose to degradation at that high temperature. One of the conventional methods to improve processibility of the thermoplastics is by blending with a more processable polymer. Commercially important application of the technique is blending of PPO with polystyrene (PS) producing segmentally miscible blend in all proportions due to favorable interaction between their aromatic rings with properties depending on the ratios of the components [1]. Addition of PS into PPO will ease processing by reducing glass transition temperature ($T_g$) (i.e. reduction of thermo-mechanical properties) with increasing proportion of PS [2].

Meanwhile, a few researchers reported the use of thermosetting monomers as reactive plasticizers in thermoplastics such as polyvinyl chloride [3], PPO [4] and polycarbonate [5]. In this application,
blending of small amount of crosslinkable monomers such as epoxies and allylic monomers reduce viscosity of the thermoplastic at the early stage of processing. Subsequently the monomer can be polymerized and will phase separated as dispersed particles in the thermoplastic matrix. The main advantage of this method is the improvement of processibility without or with a very slight reduction of thermo-mechanical properties throughout composition range [3,4]. In addition, there is possibility for the dispersed thermoset particles to act as toughener or reinforcement, depends on either the particles are rubbery or glassy. Most of the research conducted on improving processibility of thermoplastic in the presence of thermosets studied the effect of thermoset on viscosity and morphology of the blends. However, not much research has been done on the applicability of the thermoset as both reactive plasticizer and reinforcement/toughener in thermoplastic system. Therefore, this study aims to investigate the effect of different compositions of allylic monomers on the thermo-mechanical, tensile and morphological properties of PS/PPO blend.

2. Experimental

2.1 Materials

Two different thermoplastics were used in this research. Poly(2,5-dimethyl phenylene oxide) of polyphenylene oxide, PPO in powder form with a number and weight average molecular weights of 19,180 and 44,297 g/mol, respectively, was obtained from GE Plastics as C2000. Polystyrene (PS) in pellet form was obtained from Petrochemicals (Malaysia) Sdn. Bhd. Meanwhile, thermosetting monomer used was diallyl orthophthalate (DAOP) which was purchased from Sigma-Aldrich in the form of liquid. Dicumyl peroxide (DCP) or cumene peroxide, obtained from Sigma-Aldrich was used as an initiator to initiate chain growth polymerization of the allylic monomer. Both DAOP and DCP were used as received. The chemical structure of the thermoplastics, thermosetting monomer and initiator are shown in Table 1.

Table 1. Chemical structure of materials used

|         | PPO  | PS   | DAOP           | DCP  |
|---------|------|------|----------------|------|
| Structure| ![Image](structure_ppo.png) | ![Image](structure_ps.png) | ![Image](structure_daop.png) | ![Image](structure_dcp.png) |

2.2 Melt blending of PS/PPO or PS/PPO/DAOP blends

Blending of PS and PPO with composition of 80 wt% PS and 20 wt% PPO was used as control sample. Before blending, the PPO powder and PS pellets were pre dried at 120°C and 80°C, respectively for 12h. Then the PPO and PS were manually mixed and placed in an oven at 80°C for 2 hours to promote inter-diffusion of materials. After that, the sample was melt blended using Haake Polydrive Internal Mixer (Thermo Electron Corporation) at 220°C with 60 rpm mixing speed for a period of 15 minutes. The obtained blended sample was then compressed at 220°C with the pressure of 1000 psi for 5 minutes, using a compression moulding machine (Kao Tiew Go Tech Testing Machine) to obtain 1 mm thick plastic sheet.

Meanwhile, blends of 80 wt% PS with a total of 20 wt% of PPO and DAOP-DCP (formulation as shown in Table 2) were also prepared by melt blending. All the samples were melt blended using Haake Polydrive Internal Mixer at 200°C at 60 rpm and a total mixing time of 10 minutes. Before melt blending, a specified amount of PPO, DAOP and DCP were mixed at room temperature. The blending in internal
mixer was initiated by firstly melted PS for 5 minutes and subsequently added quantified PPO/DAO-DCP to the chamber. The mixing was then carried on for further 5 minutes. The obtained blended samples were then compressed at 200°C and with the pressure of 1000 psi for 5 minutes in a compression moulding machine to obtain 1 mm thick plastic sheet. The samples were further cured at 150°C for 3 hour.

Blends containing a reactive plasticizer and initiator are identified by the code wt%PS/wt%PPO/DAO-DCP so that 80PS/18PPO/2DAO-DCP represents the blend with 80 wt% PS and 18 wt% PPO and 2 wt% DAO-DCP (the concentration of DCP in DAO was fixed at 4 wt%). The compositions of PPO and DAO-DCP were chosen based on the findings that uncured blends of PPO and DAO were miscible at 70wt% and more of PPO content [4].

Table 2. Formulation of the blends

| Blends             | PS (wt%) | PPO (wt%) | DAO-DCP (wt%) |
|--------------------|----------|-----------|---------------|
| 80PS/20PPO        | 80       | 20        | 0             |
| 80PS/18PPO/2DAO-DCP | 80       | 18        | 2             |
| 80PS/16PPO/4DAO-DCP | 80       | 16        | 4             |
| 80PS/14PPO/6DAO-DCP | 80       | 14        | 6             |

2.3 Differential Scanning Calorimetry (DSC)

DSC studies were conducted using Mettler Toledo Star 1 DSC in order to determine the glass transition temperature $T_g$ of the blends. The samples were obtained from sheet formed after compression moulding and curing of the sample. Samples of approximately 10 mg for each composition were analyzed using DSC machine by placing the samples in the aluminum pans. All samples were heated from 30°C to 300°C at the heating rate of 10°C/min to flatten the samples and to remove thermal history of PPO/PS. Then the sample was cooled down from 300°C to 30°C at 10°C/min by using liquid nitrogen at the rate of 50ml/min. The heating process was repeated with the same heating rate and heating procedure to determine the $T_g$ of the blend.

2.4 Tensile test

Tensile tests for all samples were performed according to ASTM D882 using a testing machine (Instron Corporation, model 3366, USA) at 25°C and with the cross-head speed of 5 mm/min. Strip shaped specimens were cut from the sheets prepared from compression-moulding. At least five specimens of each sample were tested to determine the mean value of the results. Tensile strength, elongation at break and tensile modulus at 100% elongation were recorded.

2.5 Scanning Electron Microscopy (SEM)

The tensile fractured surface morphology of the blends was observed using Tabletop SEM Hitachi TM3000 with acceleration voltage of 5kV. The fractured samples were sputter coated with thin gold prior to examination using the SEM.

3. Results and discussion

3.1 DSC studies

The effect of incorporation of DAO-DCP on the $T_g$ of 80PS/20PPO was examined. Figure 1 shows the DSC curve of 80PS/20PPO blend and various blends of 80 wt% PS with a total of 20 wt% of PPO and DAO-DCP compounds while $T_g$ values are tabulated in Table 3.
For 80PS/20PPO blend, only single $T_g$ is observed suggesting miscibility of the blend. The $T_g$ observed was compared with $T_g$ calculated from Fox equation [7]. PPO is reported to has a $T_g$ of 250 [4] and 212 [6] which were obtained from Dynamic Mechanical Analyzer (DMA) and DSC, respectively while pure PS was observed to have a $T_g$ of 90°C. The $T_g$ obtained from DSC for the blends of 80PS/20PPO compares quite well with that calculated from Fox equation [7] which normally applicable for miscible blends and as well as for copolymers [8], assuming that no interaction occurs between PPO and PS. Meanwhile, in the presence of DAOP, single $T_g$ was also observed with $T_g$ slightly lower from the blends without DAOP. The presence of a single $T_g$ is unexpected since it is believed that the thermosetting monomer will phase separate after cured thus could produce two $T_g$. This observation might be due to the presence of only a small amount of DAOP thus the second $T_g$ could not be observed. On the other hand, the slight reduction of $T_g$ in the presence of cured DAOP might be due to the reduction of PPO content (high $T_g$ component) thus reducing the $T_g$ of the blends. With the presence of 6wt% DAOP, $T_g$ plateau at 94°C might be due to the presence of higher amount of cured DAOP which compensate the reduction of PPO.

Table 3. $T_g$ of 80PS/20PPO blend and blends of 80 wt% PS with different compositions of PPO/DAOP-DCP

| Compounds                  | $T_g$ obtained from DSC (°C) | $T_g$ predicted by Fox Equation (°C) |
|----------------------------|-----------------------------|--------------------------------------|
| 80PS/20PPO                 | 100                         | 109                                  |
| 80PS/18PPO/2DAOP-DCP       | 96                          | -                                    |
| 80PS/16PPO/4DAOP-DCP       | 94                          | -                                    |
| 80PS/14PPO/6DAOP-DCP       | 94                          | -                                    |

3.2 Tensile properties

The effects of various compositions of PPO/DAOP-DCP on tensile properties of 80PS/PPO/DAOP-DCP blends were studied. The tensile strength of 80PS/20PPO blend and blends of 80wt%PS with different amounts of reactive plasticizer (80PS/18PPO/2DAOP-DCP, 80PS/16PPO/4DAOP-DCP and 80PS/14PPO/6DAOP-DCP) are summarized in Figure 2. It can be observed that tensile strength of the blends increased with increasing amount of DAOP up to 4wt% DAOP but then slightly decreased with further increased of DAOP to 6wt%. In all compositions of PPO/DAOP-DCP blends, the value of tensile strength higher than 80PS/20PPO blend without reactive compatibilizer suggesting that DAOP could also act as reinforcement in 80PS/20PPO blends. It is believed that phase separated DAOP particles could cause higher force needed to break the blends thus improving tensile strength of the blends as normally found in polymer composite system [9]. However, in the presence of 6wt% DAOP, the tensile strength slightly reduced possibly because of high amount of DAOP could affect miscibility of PPO with PS or poor miscibility of PS and DAOP in the system with high DAOP content.
Figure 1. DSC curves of 80PS/20PPO and different compositions of reactive plasticized blends

Figure 2. Tensile strength of 80PS/20PPO and various compositions of reactive plasticized blends

Figure 3 illustrates the modulus of 80PS/20PPO blend and different compositions of PPO/DAOP-DCP in 80PS/PPO/DAOP-DCP blends. It can be seen that tensile modulus slightly increased with increasing amount of DAOP up to 4wt% DAOP might be due to the presence of polyDAOP which disperses throughout the blends improves inter-chain friction thus decrease molecular mobility, as if the presence of filler in the blend [9]. However, in the presence of 6wt% DAOP, tensile modulus slightly reduced. The reason for that is less understood but possibly due to lesser miscibility among components.

Meanwhile, the presence of DAOP reduced the ability of the blends to elongate as shown by the significant reduction of elongation at break (Figure 4). The rigid DAOP might decrease deformability of the blends hence decrease the ability of the blends to elongate before rupture.

Figure 3. Modulus of 80PS/20PPO and various compositions of reactive plasticized blends

Figure 4. Elongation at break of 80PS/20PPO and various compositions of reactive plasticized blends

The tensile test results revealed that the optimum amount of DAOP that brought about improvement on the tensile strength and modulus is 4 wt%. These results show that DAOP can act as both reactive plasticizer and reinforcement in 80PS/PPO blend.

3.3 SEM

The tensile fractured surfaces of the blends were observed using SEM to evaluate the phase morphology of the blends. Evidence of phase separation and changes in the morphology with increasing DAOP
content in the cured 80PS/PPO/DAOP-DCP blends are illustrated in Figure 5. For 80PS/20PPO blend without DAOP-DCP, single phase morphology was observed due to miscibility of PPO and PS. The presence of intermolecular interactions (π-π electron transfer) are said to be responsible for the miscibility of the blend system [2]. Meanwhile, in the presence of 4 wt%DAOP, a rough surface was observed with some indication of the presence of small dispersed poly (DAOP) particles in PS matrix. With a further increase of reactive plasticizer content to 6 wt%, smoother surface than the blend of 80PS/16PPO/4DAOP-DCP blends could be observed. In addition, bigger size of dispersed particles than that present in 80PS/16PPO/4DAOP-DCP was observed might be due to the present of more poly (DAOP) content in the former. In addition, smoother surface was observed in the blend of 80PS/14PPO/6DAOP-DCP which is believed to be responsible for the slight reduction of tensile strength and modulus of the blends compared with 80PS/16PPO/4DAOP-DCP blend.

![Figure 5. SEM images of 80PS/20PPO and various compositions of reactive plasticized blends](image)

4. Conclusion

The replacement of PPO with DAOP in the blends of 80wt%PS slightly reduced the T_g of the blends. The presence of DAOP in 80PS/PPO blends improved the tensile strength and modulus up to 4wt% DAOP suggesting that DAOP could act as both reactive plasticizer and reinforcement in PS/PPO system. SEM micrograph indicated the presence of small particles in which DAOP phase separated in PS matrix.

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References

[1] Cizek EP and Arbor A., U.S.P. Office, Editor. 1968 General Electric Company: United States
[2] Stoelting J, Karasz FE, and Macknight WJ 1970 Polymer Engineering & Science 10 133
[3] Liang G G, Cook WD, Sautereau HJ, Tcharkhtchi A 2009 Polymer 50 2655
[4] Rusli A, Cook W and Liang GG 2011 European Polymer Journal 47 1775
[5] Liang G G, Cook WD, Sautereau HJ, Tcharkhtchi A 2008 European Polymer Journal 44 366.
[6] Rusli A, Cook WD and Saito K 2013 European Polymer Journal 49 4072
[7] Fox TG 1956 Bulletin American Physical Society 1 123
[8] Brostow W, Chiu R, Kalogeras IM, Vassilikou-Dova A 2008 Materials Letters 62 3152
[9] Manson JA and Sperling LH, 1976 Polymer blends and composites (New York: Springer Science + Business Media)