

The Effect of Oligomer Blending on the Flow Properties of Polycarbonate

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Abstract: We successfully prepared high-flow polycarbonate (PC) by blending commercial PC with a low molecular weight PC oligomer. The oligomer was synthesized by the addition of a large quantity of mono functional phenol groups, and the chain end group was reacted with *p*-tertiary butyl phenol (PTBP) to block the reactivity. The viscosity average molecular weight (M_v) for the oligomer was about 4,000-5,000 g/mol, compared to ~19,000 g/mol for the PC blend obtained by blending 10 wt% of the prepared oligomer with the commercial grade PC (M_v of 21,000 g/mol). The blended PC had a melt flow index of 45, which is 2.5 times higher, and a processing temperature that was 20 °C lower, than that of commercial grade PC having a similar M_v .

Keywords: PC, PC oligomer, blend, high flow, viscosity.

Introduction

Polycarbonate (PC) is an amorphous, clear polymer that exhibits three key characteristic properties: toughness, transparency, and heat resistance.¹⁻⁵ These desirable properties, combined with superior dimensional stability and good electrical resistance, have led to wide applications in automobile parts, electrical parts, optical materials, and steam sterilizable medical equipment. However, PC is not easily processed due to its high melt viscosity. In general, attempts to provide PC with better processability have had negative effects on the toughness and have impaired its value for engineering applications.

There have been many endeavors to overcome the processing problems. In general, additives are dissolved into the melt during processing to decrease the melt viscosity. There are several processing additives that improve processing at lower temperatures, but they may cause negative effects on the final product.⁶⁻⁸ Liu *et al.* reported that the blending of linear PCs and branched PCs having a molecu-

lar weight distribution (MWD) of 3.4~3.8 showed superior flow properties via a shear thinning effect at high shear rate.⁹ Furthermore, the properties of branched PC were changed by the type of branching agent and the degree of branching. The Korea Polymers Net Company and US Cyclics company reported that their commercial full name product (CBT) can be blended with PC to enhance the flow properties of PC by about 30~50%. Liang *et al.*¹⁰ also reported that the melt viscosity of PC could be decreased by adding a plasticizer, diallyl orthophthalate (DAOP), however, as a result, the transparency and glass transition temperature were compromised.

The objective of this study is to improve the processing conditions of PC while retaining its beneficial properties. In this experiment, we introduce a novel method of enhancing the processing conditions of PC by blending with low molecular weight PC oligomer. The chain end group of the oligomer was reacted with *p*-tert butyl phenol (PTBP) to produce a non-reactive component. The commercial grade PC was blended with PC oligomer and the effect of oligomer on the melt properties is discussed.

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Experimental

Materials and Characterization. Commercial grade PC and PC oligomer were provided by the Samyang Corporation and were used as received. *p*-tert Butylphenol (PTBP) was purchased from Aldrich and used without further purification.

The intrinsic viscosity of the oligomer was used for the calculation of the molecular weight of the polymers and was determined with a capillary Ubbelohde-type viscometer at 35 °C using a 0.5 g/mL polymer solution in methylene chloride. NMR spectra were acquired with a Bruker AVANCE DPX 400 NMR spectrometer at room temperature, using trifluoroacetic acid-d (TFA)/CD₂Cl₂ (1/5, v/v) mixed solvents. A pulse width of 11.8 μsec was chosen for the ¹H NMR measurement, using 256 scans. The molecular weight distribution of solution blended PC was determined with a Polymer Laboratories GPC (PL-GPC 200, UK). The melt viscosity was acquired from a Rheometric ARES rheometer using parallel plates (diameter 25 mm), while the melt index was measured by a melt indexer under a load of 2.16 kg at 300 °C during 10 min (ASTM D1238).

End Capping of PC-Oligomer. PC-oligomers usually have two types of reactive end groups,¹¹ chloroformate groups (~CF) and hydroxyl groups (~OH) and their composition is 63 to 27. The CF end group is capped with PTBP in order to prevent any side reaction during blend formation. The PTBP was added into the reaction solution with sodium hydroxide for 10 min, and the resulting PTBP-Na group reacts with the CF group to yield an unreactive terminal group. During this process, the terminal OH groups of the oligomer also reacted with CF groups to allow possible chain extension. In this treatment, the pre-oligomer with an average *M_v* of 1,000 g/mol showed an increase in the molecular weight to 4,000~5,000 g/mol. The shear viscosity of the oligomer is 1,000 poise with a shear rate 1/s at 220 °C.

Solution Blend. The PTBP capped oligomer was added to commercial grade PC of *M_v*=21,000 during washing after polycondensation in the continuous interfacial polymerization process of PC.¹²⁻¹⁴ The oligomer dispersed PC was separated from the wash and the organic phase was further washed with 0.1 N HCl and distilled water several times. After washing, the organic phase was stored at a constant temperature of 75~78° and granulated with demetalized water. After the granulation, the granulated samples were dried at 110 °C and fabricated into pellets using an extruder. The shear viscosity of the solution blended PC is 2,000 poise with a shear rate 1/s at 260 °C.

Results and Discussion

The Characteristics of Solution Blended PCs. The chain end group of the oligomer was blocked with PTBP to prevent further side reaction during blending and processing.

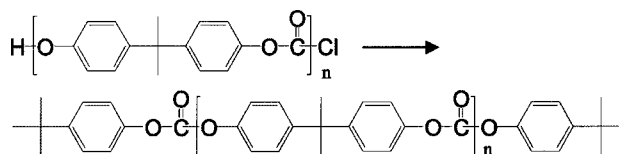


Figure 1. Structure of oligomer capped with PTBP.

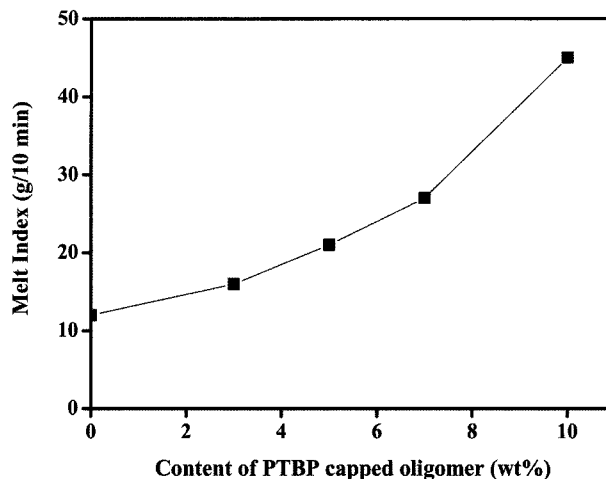


Figure 2. Melt-index of PC as a function of contents of oligomer.

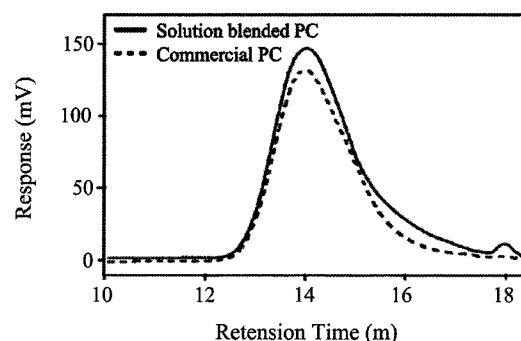


Figure 3. GPC-analysis of commercial PC and solution blended PC.

Figure 1 shows the chemical structure of the PTBP capped oligomer. The viscosity average molecular weights of the pre-oligomer and oligomer modified with end capping reaction were 1,000 and 4,500, respectively.¹⁴

High flow PC was prepared by the blending of commercial grade PC with end capped oligomer. The melt index of the blended PC increased with increasing oligomer contents as shown in Figure 2.¹⁵⁻¹⁷ Increases in melt index with increasing oligomer content may be related to the plasticization effect of the oligomer. The formation of blended PC was confirmed by GPC spectra, Figure 3. As shown, the blended PC with 10 wt% oligomer was compared with commercial grade PC. It is obvious that low molecular weight PC is present as indicated by the slightly increased response at a retention time of 15-17 min.

Although PTBP was used as an end capping agent in our experiment, it has also been used as a molecular weight

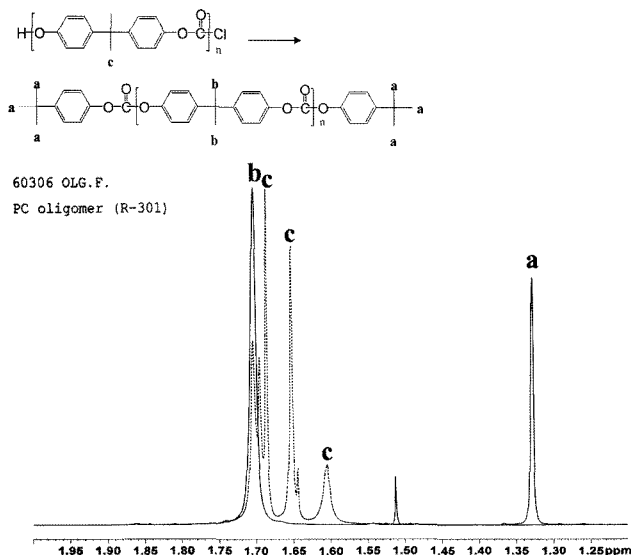


Figure 4. NMR spectra of commercial PC and solution blended PC.

control agent. Generally, the molecular weight of PC produced by interfacial polymerization is controlled by the addition of mono functional phenol group such as PTBP. The molecular weight of PC is thus decreased with increasing PTBP content. For example, the M_v of PC synthesized using 3.5 mol% and 4.5 mol% PTBP is 21,000 and 19,000 g/mol respectively. In ^1H NMR results presented in Figure 4, the PTBP was observed at a chemical shift of 7.43~7.45, which is related to the protons in the tert-butyl group. The peak intensity increased, going from 4.5 mol%/BPA (commercial grade PC) to 5.5 mol%/BPA (solution blended PC), when the oligomer was capped with PTBP by using 20 mol% BPA.

According to Figure 5, molecular weight of the solution blended PC was decreased from 21,000 to 19,100 g/mol as the content of the PTBP capped oligomer increases. In general, the MI of commercial grade PC with $M_v=19,000$ g/mol is 20 and the solution blended high flow PC is 45. In the case of the solution-blended PC using more than 10 wt% oligomer, thermal and mechanical degradation occurred during the extrusion process. The mechanical properties of solution blended PC were compared with commercial PC as shown in Table I. The MI value of blended PC is more than twice that of the unblended PC, however the glass transition temperature (T_g), impact strength and tensile strength are similar.

Rheological Behavior. The rheological properties were

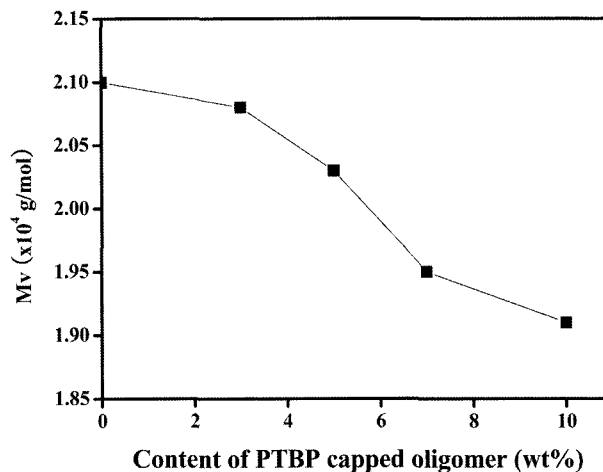


Figure 5. Molecular weight of PC as a function of contents of oligomer.

determined using an ARES rheometer using parallel plates at 280 °C, which is the general processing temperature of the PC.¹⁸ Figure 6 shows the shear viscosity of commercial grade PC and the solution blended PC. The shear viscosity was measured at 300 °C under 1.2 kg. At the same temperature, the solution blended PC has a lower melt viscosity than commercial grade PC. The melt viscosity of the blended solution measured at 260 °C has the same melt viscosity of as the conventional PC measured at 280 °C. The reason for this is the plasticizer effect of PTBP capped oligomer in the solution blended PC. This result indicates that

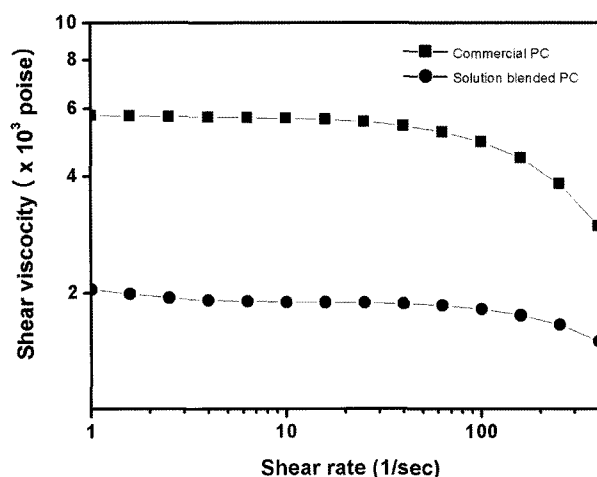


Figure 6. Shear viscosities of commercial PC and solution blended PC by ARES at 280 °C.

Table I. Mechanical and Thermal Properties of Commercial and Solution Blended PC

Type of PC	Molecular Weight [g/mol]	Melting Index [g/10 min]	T_g [°C]	Impact Strength [kgfcm/cm]	Tensile Strength [kgf/cm ²]
Commercial	19,000	20	144	12	650
Solution blended	19,000	45	143	10	660

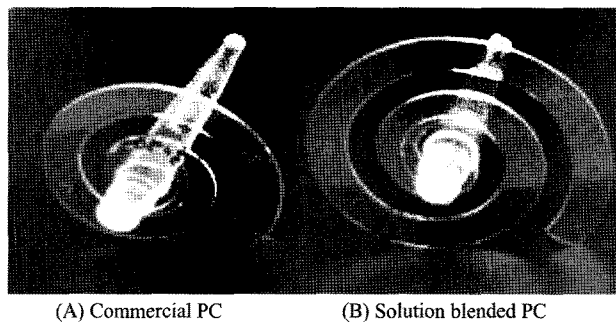


Figure 7. Photo of commercial PC and solution blended PC after spiral flow at 280 °C.

the PTBP capped oligomer is well dispersed in commercial grade PC by solution blending.

The Prediction of Injection Molding Properties. We examined the injection molding properties of solution blended PC using a spiral flow test. Figure 7 shows the results of the spiral flow test for the two PCs. Longer lengths of spiral flow indicate higher flow ability. The spiral flow length of solution blended PC is 18 cm compared to 12 cm of commercial grade PC, which implies that solution blended PC has better flow ability than commercial grade PC.

Conclusions

We prepared superior flow PCs by solution blending commercial PC with low molecular weight PC oligomer, which was treated by PTBP. The melt index increased as oligomer content increased. By way of comparison, the melt index of the solution blended PC with 10 wt% oligomer contents had a melt index of 45 g/10 min while the melt index of commercial grade PC was 20 g/10 min at the same molecular weight. The melt temperature of the solution blended PC for the same melt viscosity and same molecular weight as commercial grade PC was found to be lower by as much as 20 °C. Although 10 wt% of the low molecular weight oligomer was contained in the solution blended PC, thermal degradation did not negatively affect mechanical properties. Based on flow data, superior flow PC was successfully obtained by solution blending with PTBP capped oligomer.

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References

- (1) H. T. Pham, S. Munjal, and C. P. Bosnyak, in *Handbook of thermoplastics*, O. Olabisi, Ed., Marcel Dekker, New York, 1997.
- (2) T. M. Madkour, in *Polymer data handbook*, J. E. Mark, Ed., Oxford University Press, New York, 1999.
- (3) H. T. Pham, C. L. Weckle, and J. M. Ceraso, *Adv. Mater.*, **12**, 1881 (2000).
- (4) H. Schnell, in *Chemistry and physics of PC*, Interscience, New York, 1964.
- (5) C. Nguyen and J. Kim, *Macromol. Res.*, **16**, 620 (2008).
- (6) S. Li, P. K. Järvelä, and P. A. Järvelä, *J. Appl. Polym. Sci.*, **71**, 1649 (1999).
- (7) T. T. Hsieh, C. Tiu, K. H. Hsieh, and G. P. Simon, *J. Appl. Polym. Sci.*, **77**, 2319 (2000).
- (8) L. Jiang, Y. C. Lam, and J. Zhang, *J. Polym. Sci. Part B: Polym. Phys.*, **43**, 2683 (2005).
- (9) C. Liu, C. Li, P. Chen, J. He, and Q. Fan, *Polymer*, **45**, 2803 (2004).
- (10) G. G. Liang, W. D. Cook, H. J. Sautereau, and A. Tcharkhtchi, *Eur. Polym. J.*, **44**, 366 (2008).
- (11) J. Kroschwitz, in *Encyclopedia of polymer science and engineering*, Wiley, New York, 1985.
- (12) E. Yoshida and M. Nakamura, *Polym. J.*, **30**, 915 (1998).
- (13) E. Ranucci and P. Ferruti, *Macromolecules*, **24**, 3747 (1991).
- (14) V. Marousek, P. Svoboda, and J. Kralicek, *Angew Makromol. Chem.*, **178**, 85 (1990).
- (15) S. Munjai, *Polym. Eng. Sci.*, **34**, 93 (1994).
- (16) L. P. Fontana, K. F. Miller, A. A. Clasen, P. W. van Es, T. O. N. de Vroomen, C. B. Quinn, and R. W. Campbell, U. S. Pat. 5,321,114 (1994).
- (17) M. Okamoto, *Polymer*, **42**, 8355 (2001).
- (18) H. T. Pham, C. P. Bosnyak, J. W. Wilchester, and C. P. Christenson, *J. Appl. Polym. Sci.*, **48**, 1425 (1993).