

Synthesis and Characterization of Polycarbonate/Polydimethylsiloxane Multiblock Copolymer Prepared from Dimethylsiloxane and Various Aromatic Dihydroxyl Monomers

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ABSTRACT: This study utilizes different types of bisphenol monomers instead of bisphenol-A to synthesize phenol terminated polydimethylsiloxane-polycarbonate block copolymers. The copolymers were synthesized by interfacial phosgenation of α , ω -phenol-organofunctional polydimethylsiloxane oligomer with various aromatic dihydroxyl monomers. In addition, the thermal properties, flammability, and mechanical properties of the synthesized copolymers after extrusion and injection molding were investigated. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 545–552, 2000

Key words: polydimethylsiloxane; polycarbonate; multiblock copolymer; aromatic dihydroxyl monomers; interfacial phosgenation

INTRODUCTION

Polycarbonate (PC) is a high-performance amorphous engineering thermoplastic resin with an exceptionally high impact strength, clarity, heat resistance, and dimensional stability. However, high viscosity inhibits PC use when melting and poor thermal stability occurs. When used in injection molding, the melt viscosity is too high to fill in the thin wall of a mold, thereby limiting its applications. Therefore, in this study we attempted to reduce the melt viscosity of PC by a combination of cooperating flexible chains such as siloxane groups in the rigid molecules of PC.

Previous studies^{1–4} have used copolymerization with polydimethylsiloxane (PDMS) oligomer to improve the thermal stability, flame resistance, transparency, low temperature impact resistance, adhesion ability to metal, and good oxygen to nitrogen permselectivity. PDMS/PC copolymer is better than neat PC in melt viscosity and flame resistance. A related investigation⁵ in the 1960s confirmed the feasibility of synthesizing PDMS-PC block copolymers by reaction of bisphenol A with α , ω -chloro-terminated silicone followed by condensation with phosgene. More recent methods⁶ prepare the PDMSs with hydroxyaryloxy end groups, followed by phosgenation after adding other diphenols. In this study,^{7,8} PDMS oligomer is reacted with various aromatic dihydroxyl monomers to prepare the PC/PDMS multiblock copolymers. Also investigated herein are the thermal and mechanical properties and flammability of PDMS-PC block copolymers.

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EXPERIMENTAL

Materials

The phosgene used was supplied by Matheson Gas Production, with a purity of 99%. α , ω -phenol-organofunctional (PT)-PDMS oligomer with a weight average molecular weight of 3200 g/mL was supplied by the Shin Etsu Chemical Co., Ltd., Tokyo, Japan. The 1,1-bis-4-hydroxy-phenylcyclohexane (BPZ) and tetramethyl-bisphenol-A (TPA) were supplied by the Tokyo Chemical Industry Co., Tokyo, Japan. The neat PC (Lexan-121) was supplied by the G. E. Research & Development Center. Triethylamine (TEA) and 4-dimethylaminopyridine (4-DMP) were supplied by the Aldrich Chemical Co. All reactants and reagents were used as received.

Preparation of Two Types of PDMS-PC Copolymer

According to Figures 1 and 2, the bischloroformates of various aromatic dihydroxyl monomers (BPZ and TPA) and PDMS were prepared by interfacial phosgenation reaction. When the pH of the aqueous phase was less than 10.5, NaOH_(aq) (50 wt %) was added to adjust the pH into the

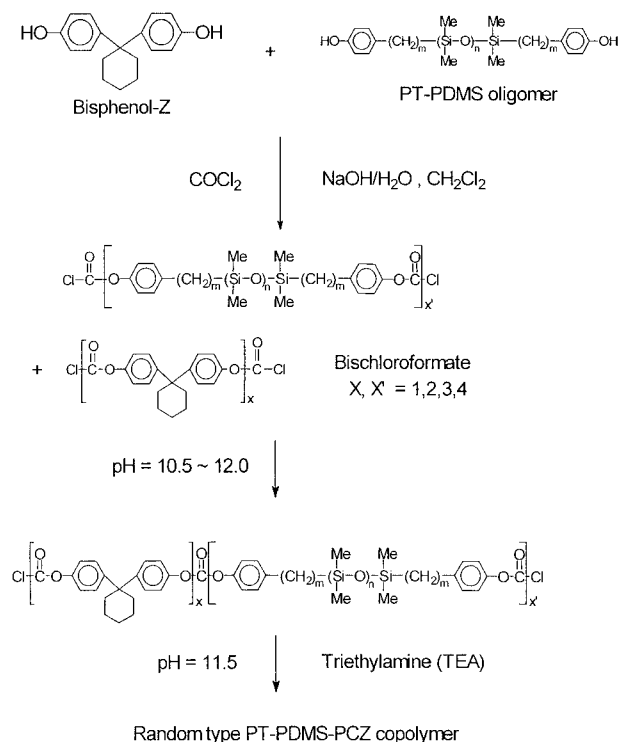


Figure 1 The mechanism of the synthesis method of BPZ-PDMS copolymer.

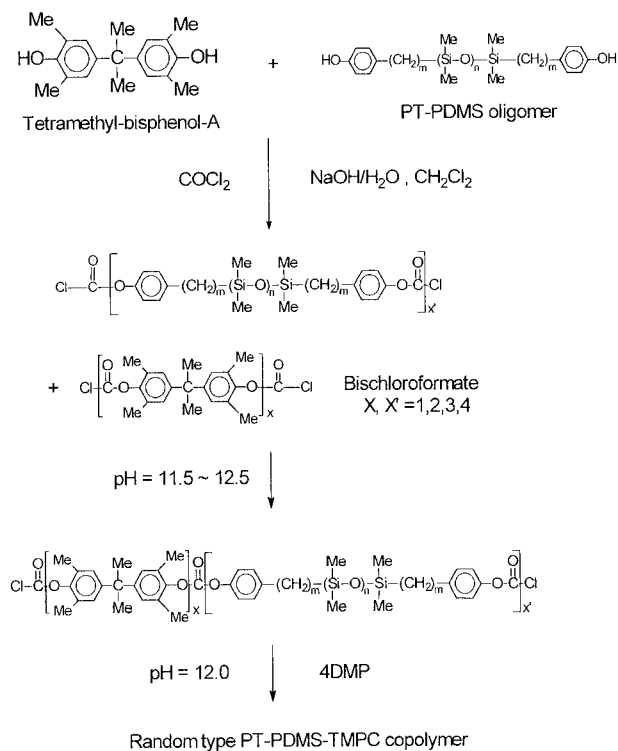


Figure 2 The mechanism of the synthesis method of TPA-PDMS copolymer.

range of 10.5 to 12.0. In addition, TEA was added as a catalyst when a desirable amount of phosgene was added and the pH of the aqueous phase was adjusted to the range of 11.0 to 11.5. As is generally known, TPA, a sterically hindered bisphenol, produces only low molecular weight polymers using the interfacial phosgenation process. Herein, the relative catalytic abilities of trialkylamine and pyridine derivatives (4-DMP) were determined in the homogeneous and interfacial systems to prepare TPA-PDMS. After stirring for 30–60 min, a copolymer of BPZ-PDMS and TPA-PDMS was formed in the organic phase which became a semitransparent, viscous fluid. The organic phase was washed with dilute NaOH_(aq) (6 wt %), then with dilute HCl_(aq) (6 wt %), and with distilled water three times. The copolymer of BPZ-PDMS and TPA-PDMS was coagulated with an equal volume of acetone and finally dried in an oven at 80°C for 24 h.

Properties Measurement of Two Types of PDMS-PC Polymers

The ¹H-nuclear magnetic resonance (NMR) spectra of the copolymers were detected by an AM 300

Table I The Conversion of BPZ-PDMS Copolymers Calculated from $^1\text{H-NMR}$ Spectrum

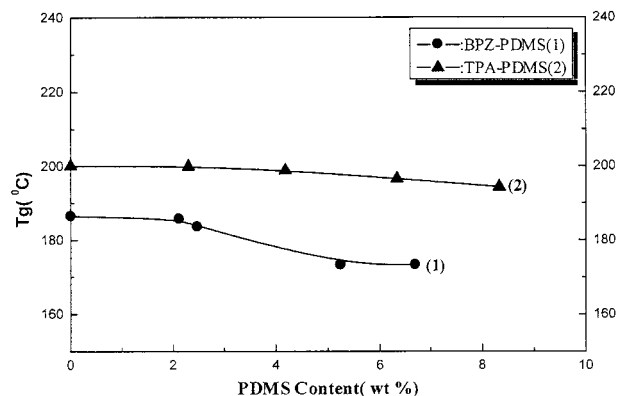
Designed PT-PDMS Content (wt %)	δ 0.06	δ 7.1 ~ 7.2	Real PT-PDMS Content (wt %)	Conversion
3	6.51	54.72	2.12	70.67%
5	7.48	53.75	2.47	49.40%
7	21.23	69.75	5.24	74.86%
10	20.54	52.01	6.70	67.00%

copolymers. According to these figures, the peak at $\delta = 0.06$ is the proton absorption of the methyl group in PDMS for the BPZ-PDMS copolymer. The peak at $\delta = 0.07 \sim 0.09$ is the proton absorption of the methyl group in PDMS for the TPA-PDMS copolymer. The peaks around $\delta = 0.6 \sim 1.4$ are the proton absorptions of the methylene group in the dimethylsiloxane segment. Notably, the $^1\text{H-NMR}$ spectra do not obviously indicate when the PDMS content in the copolymer is significantly lower. The peaks at $\delta = 1.5$ and $\delta = 2.2$ are the proton absorption of the methylene group of the cyclohexane group of the methylene group of the PC segment in Figure 3. The peak at $\delta = 1.6$ is the proton absorption of the methyl group of the isopropyl group and the peak at $\delta = 2.2$ is the proton absorption of the methyl group on benzene of the PC segment observed in Figure 4. Furthermore, the peaks around $\delta = 7.1 \sim 7.3$ are the absorptions of the benzene ring both in the PC and PDMS segments observed in Figure 3. Moreover, the peak at $\delta = 6.9$ is the absorption of the benzene ring both in the PC and PDMS segments observed in Figure 4.

The integration of proton in the methyl group on the silicone of PT-PDMS divided by the integration of proton in the benzene ring of BPZ and TPA can be used to estimate the mol and weight

Table II The Conversion of TPA-PDMS Copolymers Calculated from $^1\text{H-NMR}$ Spectrum

Designed PT-PDMS Content (wt %)	δ 0.07 ~ 0.09	δ 2.2	Real PT-PDMS Content (wt %)	Conversion
3	1.632	35.715	2.31	77.00%
5	3.245	38.433	4.18	83.60%
7	4.387	33.509	6.34	90.57%
10	6.717	38.238	8.33	83.30%

**Figure 5** Effect of PDMS content on T_g of synthesized BPZ-PDMS (1) and TPA-PDMS (2) copolymer.

ratio of PT-PDMS to BPZ and TPA in copolymers,⁸ as summarized in Tables I and II. The $^1\text{H-NMR}$ spectra indicate that the conversion of BPZ-PDMS copolymer ranged between 65 ~ 75% and the BPZ-PDMS copolymer was 75 ~ 90%, estimated by the calculated mol ratio over the designed mol ratio. Our results further indicate that this synthetic method is appropriate for preparing the desired products when the PT-PDMS oligomer content in copolymer is designed for 10 wt %.

Thermal and Flame Properties of PDMS-PC Copolymers

T_g was measured for the PDMS-PC copolymers prepared from various dihydric phenols. Figure 5 illustrates how the PT-PDMS content influences the T_g of BPZ-PDMS-PC and TPA-PDMS-PC copolymer. Some general inferences can be made from this figure. The added rigidity of these substituted, saturated rings and the accompanying restricted rotation of the aromatic rings tend to raise the T_g . In the pure PC cases, the amount of restricted rotation of the aromatic rings (producing stiffer polymer chains) is likely to be responsible for the observed variations. In addition, the content of PT-PDMS obviously influences the T_g of the corresponding PC. Figure 5 also reveals that the T_g is a linear function of the content of PT-PDMS linkages per unit chain length. Moreover, the PT-PDMS oligomer content increases with a decrease of T_g of BPZ-PDMS-PC and TPA-PDMS-PC copolymers. These phenomena are attributed to the fact that the PT-PDMS oligomer can provide the BPZ-PDMS-PC and TPA-PDMS-PC copolymer with the flexibility of the Si-O linkages.

Table III The Effect of PDMS Content on the UL-94 Flammability Test of BPZ-PDMS and TPA-PDMS Copolymers

Sample Name	PDMS Content	t_1	t_2	$t_1 + t_2$	Flaming Drops	Cotton Ignited	UL-94 Standard
Z-00	0.00	8	13.25	21.25	No	No	94 V-1
Z-03	2.12	3.5	12.5	16	No	No	94 V-1
Z-07	5.24	2	5.5	7.5	No	No	94 V-0
Z-10	6.70	0.5	3.5	4	No	No	94 V-0
TM-03	2.31	0.3	3.3	3.6	No	No	94 V-0
TM-05	4.18	0.7	2.3	3	No	No	94 V-0
TM-07	6.34	1	2	3	No	No	94 V-0
TM-10	8.33	0.5	2	2.5	No	No	94 V-0

Z, BPZ-PDMS; TM, TPA-PDMS.

When the PC copolymer containing PDMS is subjected to combustion, polysiloxane chain segments can be achieved forming carbonaceous char and inhibiting production of more heat, also proving to be a protective insulating layer at the solid material surface. Table III shows the effect of PDMS content on the UL-94 flammability test of BPZ-PDMS and TPA-PDMS copolymers. When the PT-PDMS segment content is more than 5.24%, the grade of flame resistance of the copolymer elevates from UL-94 V-1 to V-0 for BPZ-PDMS copolymer. According to Table III, the flaming time of the TPA-PDMS copolymer is

shortened with increasing PDMS content and, moreover, the grade of flame resistance of copolymer was UL 94 V-0.

Although inherent flammability of neat PC (General Electrical Co, Lexan) is classified as UL 94 V-2, BPZ-PDMS and TPA-PDMS can be divided into V-1 and V-0. As expected, the flame resistance of BPZ-PDMS/Lexan and TPA-PDMS/Lexan blends are higher than that of neat PC, with values of V-1 and V-0. Table IV summarizes the UL-94 test results of BPZ-PDMS/Lexan and TPA-PDMS/Lexan blends. According to Table IV, the copolymers blended with Lexan were UL 94

Table IV The UL-94 Test Result of BPZ-PDMS/Lexan Blend and TPA-PDMS/Lexan Blend

Sample Name	Lexan Content	t_1	t_2	$t_1 + t_2$	Flaming Drops	Cotton Ignited	UL-94 Standard
Z10-5	47.5	2.3	5.0	7.3	No	No	94 V-0
Z10-5	67.9	5.0	8.7	13.7	No	No	94 V-1
Z10-1	89.1	3.0	13.5	16.5	No	No	94 V-1
Z7-5	27.1	4.0	6.0	10.0	No	No	94 V-0
Z7-3	55.4	2.3	6.3	8.6	No	No	94 V-0
Z5-3	38.8	2.0	8.5	10.5	No	No	94 V-1
Z5-1	79.2	2.3	10.0	12.3	No	No	94 V-1
Z3-1	66.0	1.5	7.75	9.25	No	No	94 V-0
TM10-5	47.5	1.25	6.0	7.25	No	No	94 V-0
TM10-3	67.9	4.3	6.0	10.3	No	No	94 V-1
TM10-1	89.1	4.0	8.3	12.3	No	No	94 V-1
TM7-5	27.1	1.0	2.3	3.3	No	No	94 V-0
TM7-3	55.4	2.5	6.5	9.0	No	No	94 V-0
TM5-3	38.8	1.0	7.0	8.0	No	No	94 V-0
TM5-1	79.2	5.0	11.5	16.5	No	No	94 V-1
TM3-1	66.0	2.3	9.0	11.3	No	No	94 V-1

Z10-5: BPZ, 10 wt % PDMS in BPZ-PDMS, 5 wt % PDMS in blend, etc.; TM10-5: TPA, 10 wt % PDMS in TPA-PDMS, 5 wt % PDMS in blend, etc.

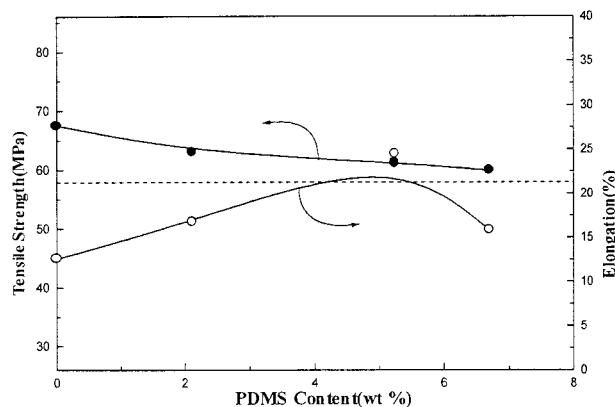


Figure 6 Effect of PDMS content on the tensile strength and tensile elongation of BPZ-PDMS copolymer (dashed line is Lexan-PC).

V-1 and V-0, depending on the Lexan content. In the BPZ-PDMS/Lexan blend system, even with neat PC content reaching 89.1%, the grade of flame resistance of the copolymer still maintained a V-1 rating. If neat PC content is lower than 60%, then, the grade of flame resistance of copolymer elevates from UL 94 V-1 to V-0. Consequently, BPZ-PDMS and TPA-PDMS copolymers blended with Lexan can be used to improve the thermal stability and flame resistance of blends.

Mechanical Properties of PDMS-PC Copolymers

The physical properties of PDMS-PC copolymers largely depend on the PC/PDMS ratio. Neat PCs show low elongation but high tensile strength. Incorporating PDMS units increases their elongation, but reduces their tensile strength. Figures 6 and 7 illustrate the tensile strength and tensile elongation for various PT-PDMS oligomer contents of BPZ-PDMS and TPA-PDMS copolymers. The PDMS provides BPZ-PDMS and TPA-PDMS copolymers with flexible chain segments. According to Figures 6 and 7, the elongation is raised by increasing the PT-PDMS oligomer content in the BPZ-PDMS copolymer. But the elongation is slightly decreased by increasing the PT-PDMS oligomer content in the TPA-PDMS copolymer. Although the tensile strength slightly decreases with increasing PT-PDMS oligomer content, the tensile strength is still better than Lexan, the neat PC. Figures 8 and 9 illustrate the tensile strength for various contents of BPZ-PDMS and TPA-PDMS copolymers blended with neat PC. The BPZ and TPA monomers provide the BPZ/Lexan and TPA/Lexan blends with rigid chain

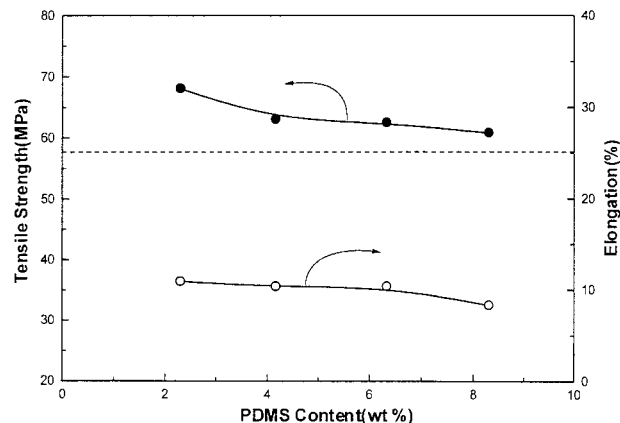


Figure 7 Effect of PDMS content on the tensile strength and tensile elongation of TPA-PDMS copolymer (dashed line is Lexan-PC).

segments, respectively. Moreover, the tensile strength increases with increasing BPZ and TPA monomer content. Our results further indicate that the tensile strengths of BPZ-PDMS and TPA-PDMS copolymers blended with neat PC are still better than the neat PC, even when adding to 50 ~ 90% content of Lexan.

Figure 10 shows the effect of PDMS content on the notched Izod impact ratio of BPZ-PDMS and TPA-PDMS copolymers to neat PC. Figure 10 indicates that the impact strengths of BPZ-PDMS and TPA-PDMS were lower than neat PC when the PT-PDMS oligomer was introduced into the PT-PDMS-PC copolymers. This behavior can be attributed to the fact that BPZ-PDMS and TPA-PDMS copolymers must generally be regarded as

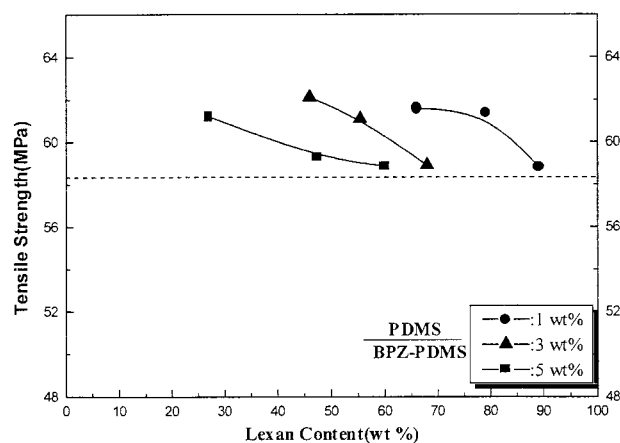


Figure 8 Effect of Lexan content on the tensile strength of BPZ-PDMS/Lexan blend (dashed line is Lexan-PC).

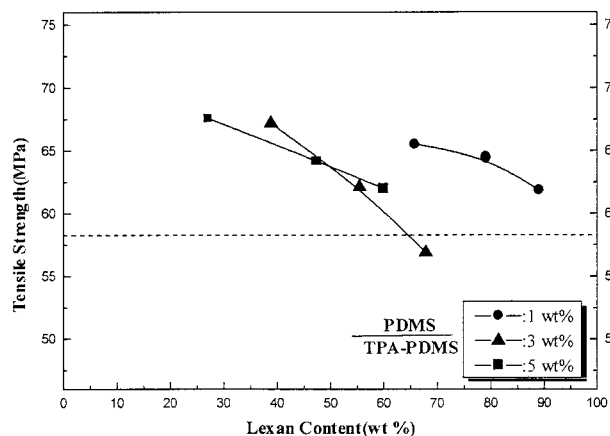


Figure 9 Effect of Lexan content on the tensile strength of TPA-PDMS/Lexan blend (dashed line is Lexan-PC).

brittle materials. Hence, in this study, the notched Izod impact strength of copolymers retained 60 ~ 80% of the strength of Lexan, the neat PC. Figure 11 shows the effect of Lexan content on the notched Izod impact ratio of BPZ-PDMS/Lexan blend to neat PC. Figure 12 shows the effect of Lexan content on the notched Izod impact ratio of TPA-PDMS/Lexan blend to neat PC. According to our results, the impact strengths of the blends were significantly greater than those of the BPZ-PDMS and TPA-PDMS copolymers. Furthermore, when PT-PDMS oligomer content remains constant, the notched Izod impact strength of blends increased with increasing Lexan content. This effect on impact strength appears to be attributed to the inherent toughness of the neat PC.

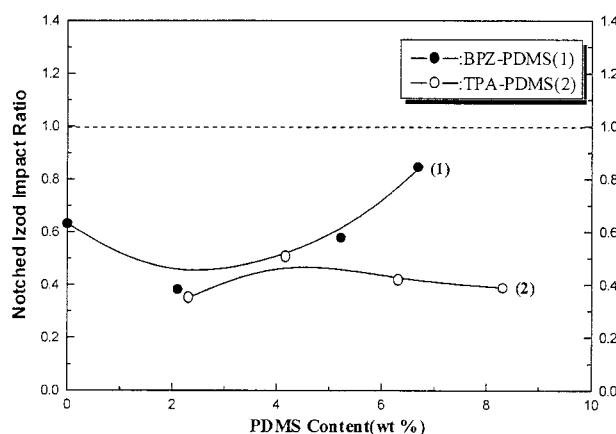


Figure 10 Effect of PDMS content on the notched Izod impact ratio of BPZ-PDMS (1) and TPA-PDMS (2) copolymers to neat PC.

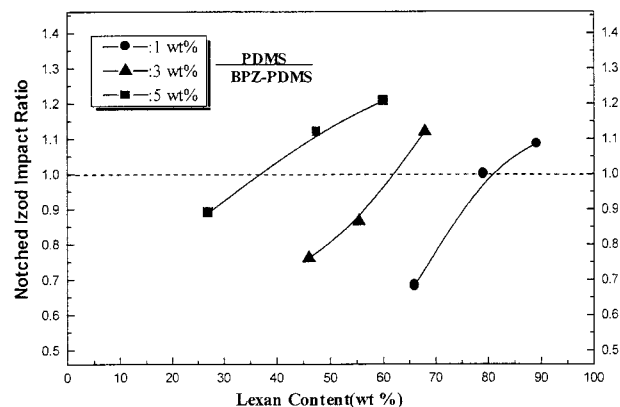


Figure 11 Effect of Lexan content on the notched Izod impact ratio of BPZ-PDMS/Lexan blend (dashed line is Lexan-PC).

CONCLUSIONS

This work describes synthesis of PDMS-PC block copolymers by interfacial phosgenation using various aromatic dihydroxy monomers (BPZ, TPA) and α , ω -phenol-organofunctional PDMS oligomer as raw materials. Based on the results presented herein, we can conclude the following:

1. The $^1\text{H-NMR}$ spectra indicate that the conversion of the BPZ-PDMS copolymer ranges from 65 ~ 75% and the TPA-PDMS copolymer ranges from 75 ~ 90%. This finding confirms the feasibility of using this synthetic method to prepare the desired products.
2. T_g s of BPZ-PDMS and TPA-PDMS copolymers decrease with an increase of PT-

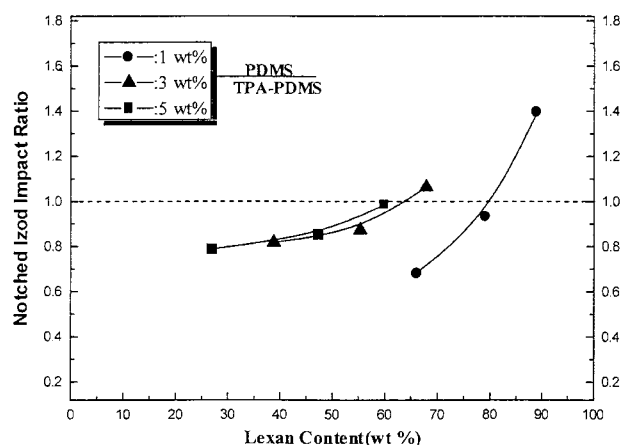


Figure 12 Effect of Lexan content on the notched Izod impact ratio of TPZ-PDMS/Lexan blend (dashed line is Lexan-PC).

- PDMS oligomer content. This occurrence is because the PT-PDMS oligomer can provide the BPZ-PDMS and TPA-PDMS copolymers with flexibility of the Si-O linkage.
3. When PT-PDMS segment content is more than 5.24%, the grade of flame resistance of BPZ-PDMS and TPA-PDMS copolymers will elevate from UL 94 V-1 to V-0. The flaming time is shortened with an increase of PDMS content.
 4. The mechanical properties of BPZ-PDMS and TPA-PDMS copolymers blended with neat PC slightly decreased with an increase of copolymer content. According to our results, the mechanical properties are a linear function of the content of BPZ (or TPA) monomer per unit chain length.

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