

Bisphenol-A Polycarbonate/Polydimethylsiloxane Multiblock Copolymers. II. Effects of Siloxane Oligomer Structure on the Properties of Copolymers

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Received 19 August 1996; accepted 16 January 1997

ABSTRACT: Polycarbonate-polydimethylsiloxane (PDMS) copolymers were synthesized by interfacial phosgenation of 2,2-bis(4-hydroxyphenyl)propane (bisphenol-A) with different types of PDMS oligomers including α,ω -amino-organofunctional polydimethylsiloxane (AT-PDMS oligomer), α,ω -hydroxy-organofunctional polydimethylsiloxane (HT-PDMS oligomer), and α,ω -phenol-organofunctional polydimethylsiloxane (PT-PDMS oligomer). ¹H-NMR spectra indicated the conversion of AT-PDMS-PC copolymer was in the range between 85 and 95%, HT-PDMS-PC was 45–55%, and PT-PDMS-PC was 70–80%. It was found that the intrinsic viscosity of PDMS-PC copolymers decreased with increasing PT-PDMS oligomer content. The intrinsic viscosity, IV, also decreased with increasing cumylphenol content. The melt indices of PDMS-PC copolymers blended with neat PC increased with increasing PDMS-PC content and the copolymers showed good processability. Izod impact strength of PDMS-PC copolymer was improved while retaining tensile and flexural strengths of neat PC. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 67–75, 1997

Key words: polycarbonate; polydimethylsiloxane; copolymer; structure; properties; processability

INTRODUCTION

Polycarbonate is a tough, transparent, impact-resistant and widely used engineering thermoplastic resin. However, it has high melting viscosity and poor thermal stability, which cause poor processability. In previous studies,^{1–5} copolymerization with polydimethylsiloxane (PDMS) oligomer was used to improve the thermal stability,¹ flame-retardancy,² transparency,³ low-temperature im-

pact resistance,⁴ low oxygen permeability,⁵ and oxygen-to-nitrogen permselectivity.⁵ The first objective of this research was to define an effective synthetic method and try to scale it up 10-fold. The second objective was to investigate the mechanical properties⁶ of PT-PDMS-PC copolymer after extrusion and injection molding.

EXPERIMENTAL

Materials

The phosgene used was supplied by Matheson Gas Production, U.S.A. with a purity of 99.0%. The amino-terminated polydimethylsiloxane (AT-

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Contract grant sponsor: National Science Council of the Republic of China; contract grant number: NSC-CS 85-0210-D-007-022.

Journal of Applied Polymer Science, Vol. 66, 67–75 (1997)

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CCC 0021-8995/97/010067-09

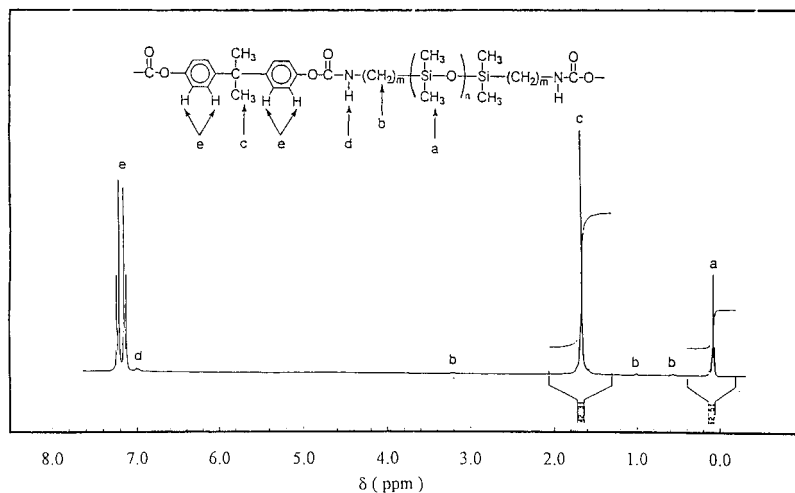


Figure 1 $^1\text{H-NMR}$ spectrum of AT-PDMS-PC copolymer.

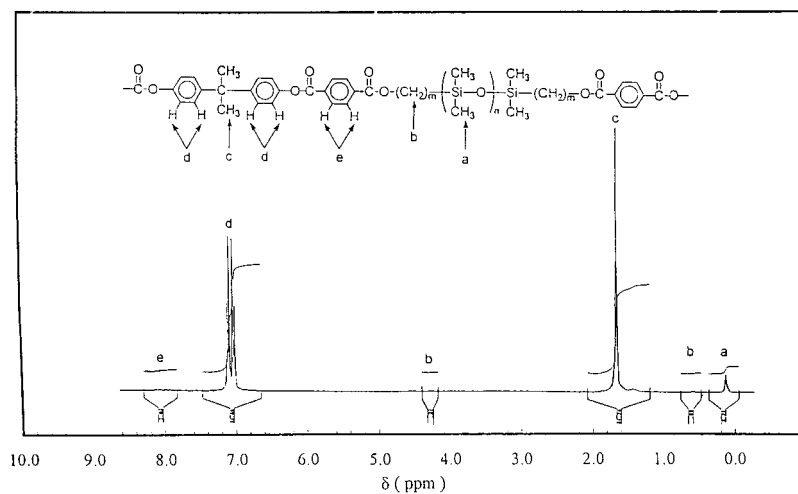


Figure 2 $^1\text{H-NMR}$ spectrum of HT-PDMS-PC copolymer.

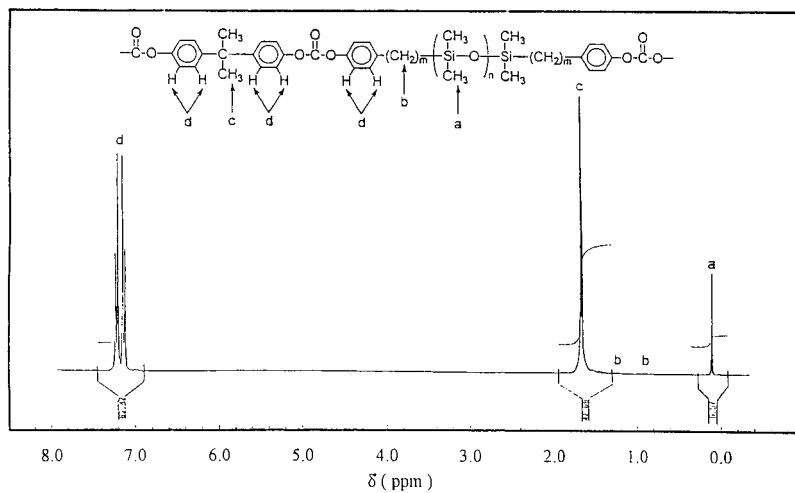


Figure 3 $^1\text{H-NMR}$ spectrum of PT-PDMS-PC copolymer.

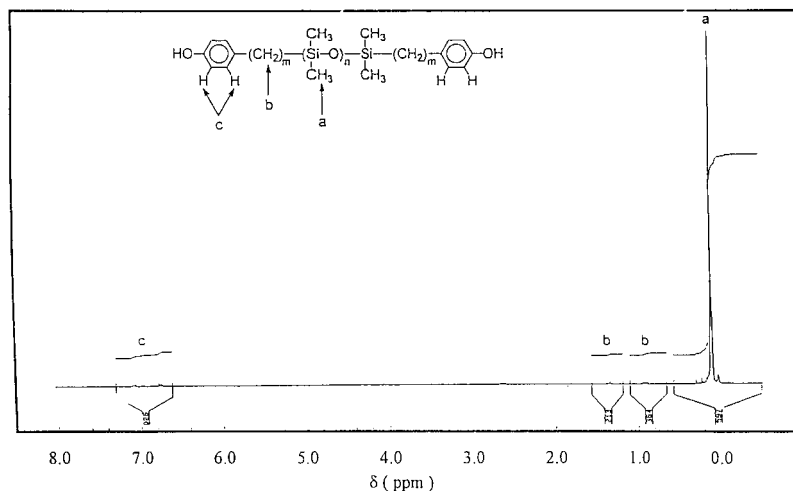


Figure 4 $^1\text{H-NMR}$ spectrum of PT-PDMS-PC oligomer (X-22-165B).

Table I The Conversion of Various Types of PDMS-PC Copolymers Calculated from $^1\text{H-NMR}$ Spectra

No.	PDMS Type	Wt %	Design ^a Mole Ratio	Integration Si—CH ₃	Integration C—CH ₃	Exact Mole Ratio	Conversion %
1	S-AT ^b	7	0.02342	7.94	39.53	0.02232	95.30
2	S-AT	10	0.03457	12.51	42.31	0.03285	95.03
3	B-HT ^c	3	0.00559	1.36	70.57	0.00241	43.11
4	B-HT	10	0.02327	3.71	44.74	0.01037	44.55
5	S-HT	1	0.00241	0.25	29.43	0.00106	44.08
6	S-HT	3	0.00647	1.94	69.93	0.00347	53.64
7	S-HT	7	0.01601	5.31	61.34	0.01082	67.59

^a Mole ratio of PDMS oligomer to bisphenol-A.

^b S-AT, S-HT : PDMS oligomers in the scale-up synthesis.

^c B-AT, B-HT : PDMS oligomers in the bench scale synthesis.

Table II The Conversion of Various Contents of PDMS Oligomer in PT-PDMS-PC Copolymers Calculated from $^1\text{H-NMR}$ Spectra

No.	PDMS Type	Wt %	Design ^a Mole Ratio	Integration Si—CH ₃	Integration C—CH ₃	Exact Mole Ratio	Conversion %
1	B-PT ^b	1	0.00079	1.14	45.66	0.00061	77.18
2	B-PT	3	0.00243	3.66	45.44	0.00197	81.13
3	B-PT	5	0.00413	5.57	47.69	0.00286	69.25
4	B-PT	7	0.00591	5.22	28.35	0.00452	76.47
5	B-PT	10	0.00872	14.05	57.95	0.00596	68.37
6	S-PT ^c	1	0.00079	0.96	40.02	0.00059	73.88
7	S-PT	3	0.00243	2.37	32.05	0.00180	74.35
8	S-PT	5	0.00413	3.20	24.25	0.00323	78.22
9	S-PT	7	0.00591	8.91	50.60	0.00432	73.15

^a Mole ratio of PT-PDMS oligomer to bisphenol-A.

^b B-PT : PT-PDMS in the bench scale synthesis.

^c S-PT : PT-PDMS in the scale-up synthesis.

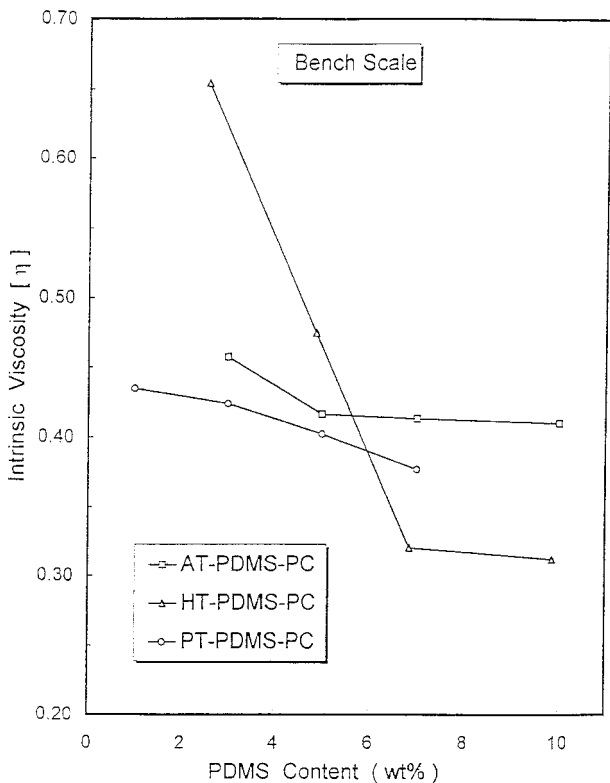


Figure 5 Effect of PDMS content and type of PDMS on the intrinsic viscosity of copolymer in the bench scale synthesis. (□) AT, (△) HT, (○) PT-PDMS-PC.

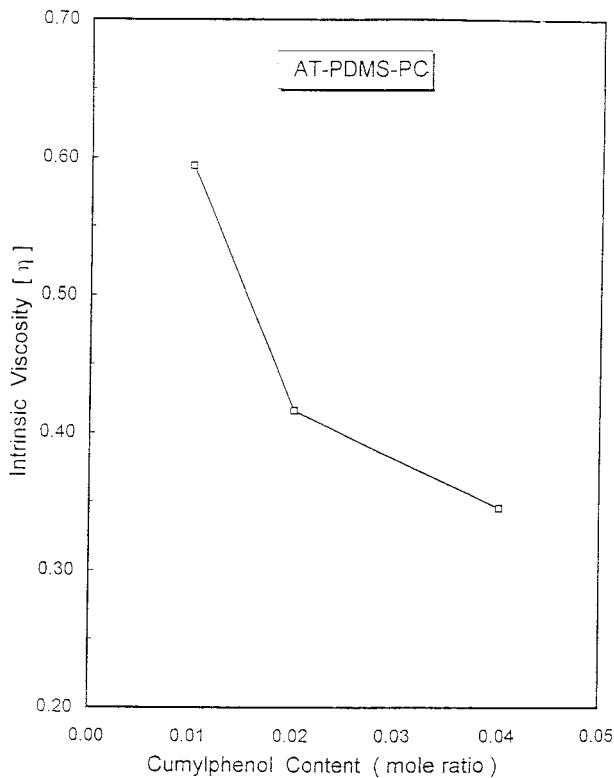


Figure 6 The intrinsic viscosity of AT-PDMS-PC copolymer with different contents of endgroup cumylphenol.

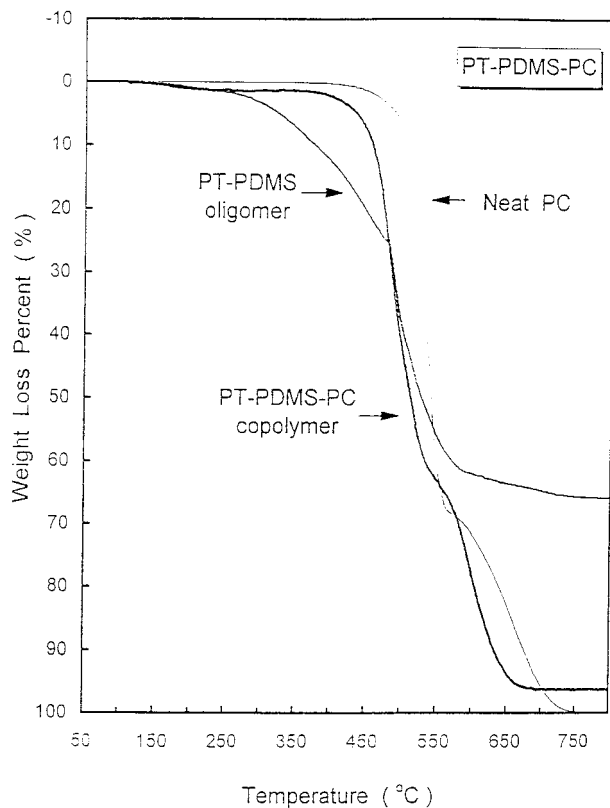


Figure 7 TGA curves of PT-PDMS-PC copolymer, PT-PDMS oligomer, and neat PC at a heating rate of 20°C/min in air.

PDMS) and hydroxy-terminated polydimethylsiloxane (HT-PDMS) oligomer with a weight average molecular weight of 800 g/mol were supplied by the Goldschmidt Pacific Ltd. Co., Germany. The phenol-terminated polydimethylsiloxane (PT-PDMS) oligomer with a weight average molecular weight of 3200 g/mol was supplied by the Shin-Etsu Chemical Co. Ltd., Japan. The 2,2-bis(4-hydroxyphenyl)propane (BPA), dichloromethane, acetone, and methanol were supplied by the Tokyo Chemical Industry Co., Japan. Triethylamine (TEA) was supplied by the Aldrich Chemical Co., U.S.A. Sodium hydroxide was supplied by the Janssen Chemical Co., Belgium. The neat PC (Lexan-121) was supplied by the G.E. Research & Development Center, U.S.A. All reactants and reagents were used as received.

Preparation of Three Types of Polydimethylsiloxane-Polycarbonate Copolymers

A freshly prepared solution of bisphenol-A (2500 g, 10.96 mol), NaOH (1000 g, 25.0 mol), and water (13500 mL) were added to a 40-L reactor. The

Table III The Degradation Temperatures and Residues of Various PDMS Oligomers, PDMS-PC Copolymers, and Neat PC by TGA Analysis

	$T_{5\%}^a$	$T_{10\%}^b$	% R_{800}^c
Neat PC (Lexan-121)	489.4	507.5	0
AT-PDMS	163.8	192.0	14.0
HT-PDMS	246.8	262.2	15.3
PT-PDMS	322.4	374.5	34.3
AT-PDMS-PC	340.5	408.5	2.1
HT-PDMS-PC	432.0	451.5	0.3
PT-PDMS-PC	434.0	456.9	3.8

^a Temperature (°C) for 5% weight loss.

^b Temperature (°C) for 10% weight loss.

^c TGA residue at 800°C.

reactor was equipped with a thermocouple, reflux condenser, phosgene inlet, anchor-type stirrer, and a water-cooling coil. When the solution was cooled to $\sim 30^\circ\text{C}$, dichloromethane (15600 mL)

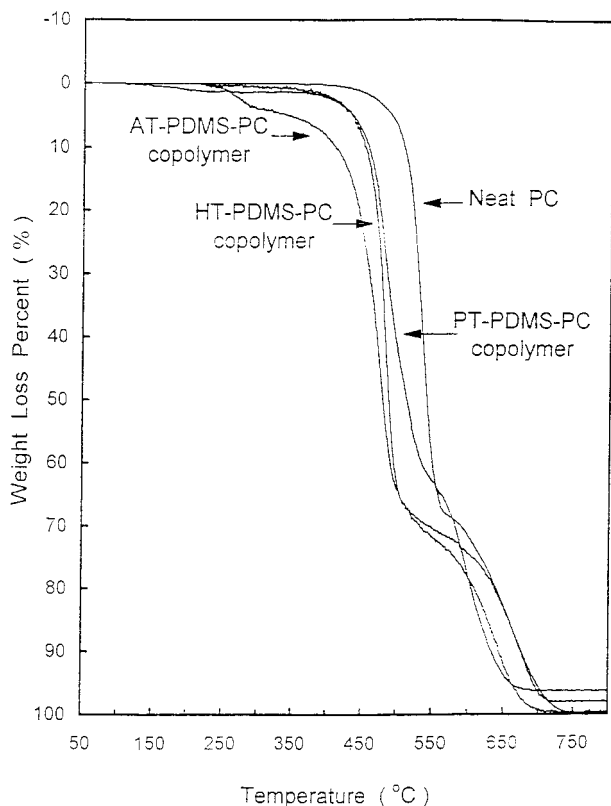


Figure 8 TGA curves of various PDMS-PC copolymers and neat PC at a heating rate of $20^\circ\text{C}/\text{min}$ in air

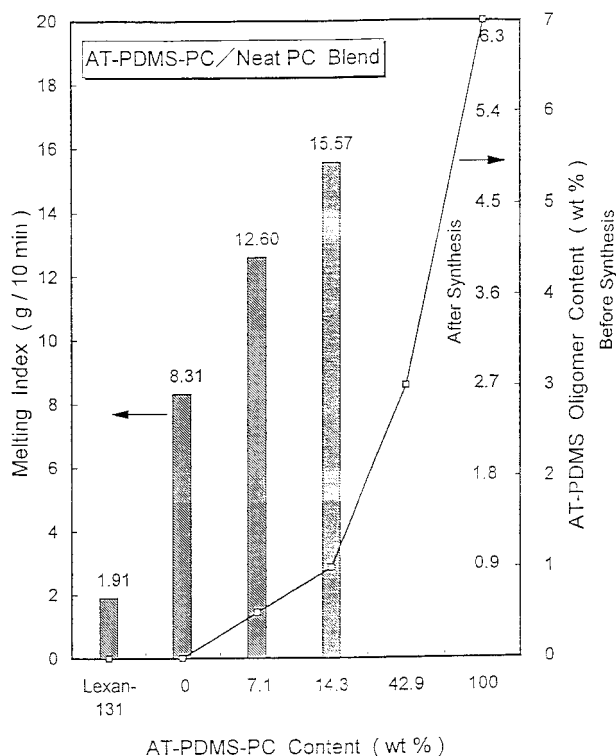


Figure 9 Effect of AT-PDMS-PC content on the melting index of AT-PDMS-PC copolymer blended with neat PC (Lexan-121).

and PDMS oligomer (211.28 g) were added to form a two-phase immiscible solution. The phosgene inlet was then turned on and the phosgene stream was adjusted to a flow rate of $20\text{ g}/\text{min}$ with vigorous stirring at 20°C . When the pH value of the aqueous phase was <11.0 , $\text{NaOH}_{(\text{aq})}$ (50 wt %) was added to adjust the pH value to the range of 11.5 to 12.0.⁷ When the addition of the phosgene was completed (1600 g, 16.18 mol), an excess of 50% caustic solution was charged into the reactor in order to adjust the pH value of the aqueous phase to 11.5–12.0, and triethylamine was added immediately to allow polymerization to proceed. After stirring for 60 min, a highly viscous, semi-transparent fluid was formed in the organic phase indicating that polymerization was complete. The organic phase was then washed with dilute $\text{NaOH}_{(\text{aq})}$ (6 wt %), then with dilute $\text{HCl}_{(\text{aq})}$ (6 wt %), and with distilled water three times. The polymer was coagulated in a mixed reagent of equal volume of acetone and finally dried in an oven at 80°C for 24 h. The yield of the dried copolymer was in the range between 2400 and 2500 g in most cases.

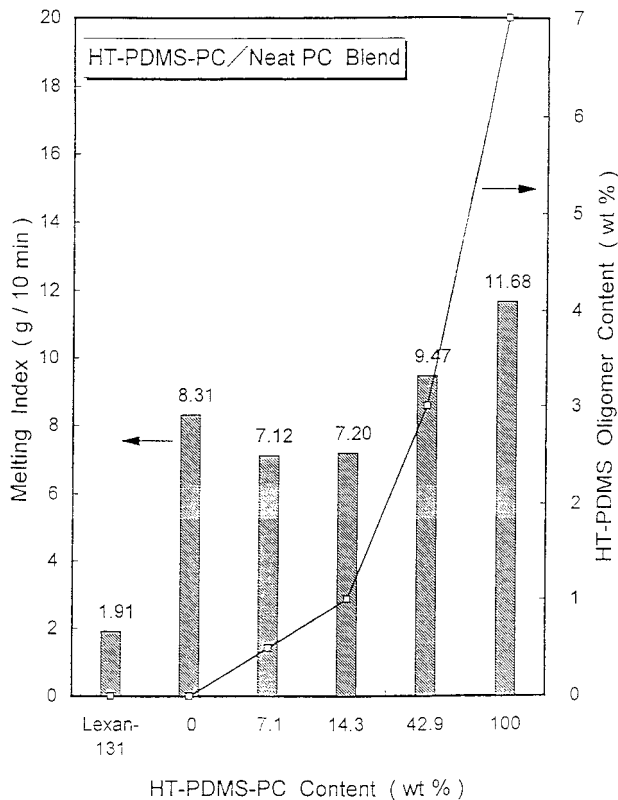


Figure 10 Effect of HT-PDMS-PC content on the melting index of HT-PDMS-PC copolymer blended with neat PC (Lexan-121).

Instruments

The $^1\text{H-NMR}$ spectra of the copolymers were recorded on an AM 300 MHz NMR spectrometer, Bruker, Germany. The intrinsic viscosity of the copolymer was measured with an Ubbelohde viscometer in dichloromethane at 25°C . The thermogravimetric analyzer (TGA) used was a Perkin-Elmer TGS-2. The extruder used was a Plasti-Corder, PL-2100, Brabender, Germany. The injection molding machine used was an IS55 EPN, Toshiba Machine Co. Ltd., Japan. The melt flow indices of homogeneous polycarbonates and PDMS-PC copolymers were measured under a load of 2.16 kg at 260°C by a melt-flow indexer. Mechanical properties of tensile strength and flexural strength were tested by using an Instron 4468 tester, Instron, U.S.A. The Izod impact tester used was manufactured by Testing Machines, TMI-43-1 Izod type, U.S.A.

RESULTS AND DISCUSSION

$^1\text{H-NMR}$ Analysis and Intrinsic Viscosity of the PDMS-PC Copolymers

Figures 1–3 show the $^1\text{H-NMR}$ spectra of AT-PDMS-PC, HT-PDMS-PC, and PT-PDMS-PC co-

polymers. The peak at $\delta = 0.09$ is the proton absorption of the methyl group in PDMS. The peaks at $\delta = 0.6$ and $\delta = 1.0$ are the proton absorptions of the methylene group. The peak at $\delta = 1.68$ is the proton absorption of the methyl group of both ends of isopropyl group of the PC segment. Furthermore, the peaks around $\delta = 7.1$ – 7.3 are the benzene ring absorptions in the PC segment.

Figure 4 shows the $^1\text{H-NMR}$ spectrum of PT-PDMS-PC oligomer. The peak at $\delta = 0.09$ is the proton absorption of the methyl group in PDMS. The peaks at $\delta = 0.6$ and $\delta = 4.4$ are the proton absorptions of the methylene group. The peak of the proton absorption of the methyl group in the isopropyl group of the bisphenol-A segment is not found in PDMS oligomer. Furthermore, the peaks around $\delta = 7.1$ – 7.3 are the absorptions of the benzene ring both in the PC and PDMS segments.

The integration of the proton peak in the methyl group on silicone of the PDMS segment over the integration of the peak proton in the isopropyl group of the bisphenol-A segment could be used to estimate the mole ratio of PDMS to BPA

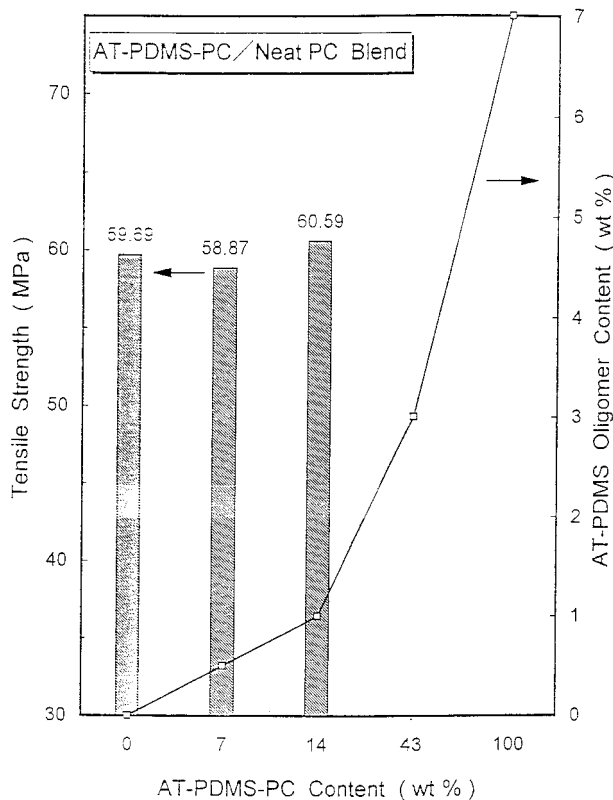


Figure 11 Effect of AT-PDMS-PC content on the tensile strength of AT-PDMS-PC copolymer blended with neat PC (Lexan-121).

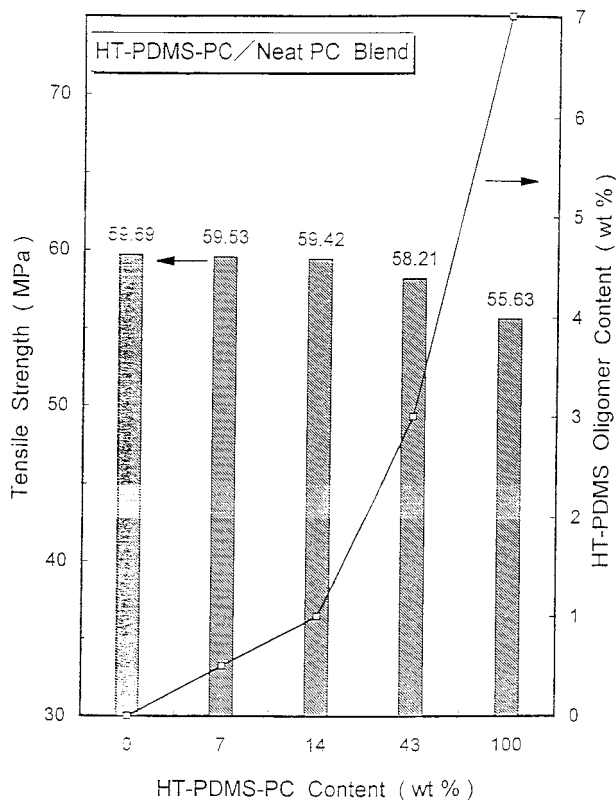


Figure 12 Effect of HT-PDMS-PC content on the tensile strength of HT-PDMS-PC copolymer blended with neat PC (Lexan-121).

in copolymer as summarized in Tables I and II. The $^1\text{H-NMR}$ spectrum indicates the conversion of AT-PDMS-PC copolymer was in the range between 85 and 95%, HT-PDMS-PC was 45–55%, and PT-PDMS-PC was 70–80%, estimated by the calculated mole ratio over the designed mole ratio. Results indicate this synthetic method was suitable to prepare the desired products.

The PDMS oligomer content in copolymer and the cumylphenol content of chain endgroup affects the intrinsic viscosity $[\eta]$ of the PDMS-PC copolymer. Figure 5 shows that the intrinsic viscosity of the three types of PDMS-PC copolymers decreased as PDMS oligomer content increased. Figure 6 shows the intrinsic viscosity of AT-PDMS-PC copolymer also decreased as cumylphenol content increased. The intrinsic viscosities of PDMS-PC copolymer could be changed by adjusting the content of PDMS oligomer or cumylphenol.

Thermal Properties of PDMS-PC Copolymers

Figure 7 shows TGA curves of the PT-PDMS-PC copolymer, PT-PDMS oligomer, and neat PC

(Lexan-121) in air. The initial weight loss of the neat PC (Lexan-121) starting at 489°C was higher than for the PT-PDMS oligomer, which started at 322°C. The PT-PDMS-PC copolymer had its temperature for initial weight loss starting at 434°C which is between neat PC (Lexan-121) and PT-PDMS oligomer. Table III shows the amount of residue after heating to 800°C. The neat PC (Lexan 121) had no residue left after heating to 800°C. The PT-PDMS oligomer had 34.3% char and the PT-PDMS-PC copolymer had 3.8% char at 800°C. The thermal stability of PDMS-PC copolymer at high temperature was improved when the PT-PDMS oligomer was introduced into PDMS-PC copolymer. Figure 8 shows TGA curves of three types of PDMS-PC copolymer and neat PC (Lexan-121).

Figures 9 and 10 indicate that the melt flow indices (MFI) of AT-PDMS-PC and HT-PDMS-PC copolymer blended with neat PC (Lexan-121) increased with increasing PDMS-PC contents. The melt indices of AT-PDMS-PC and HT-PDMS-

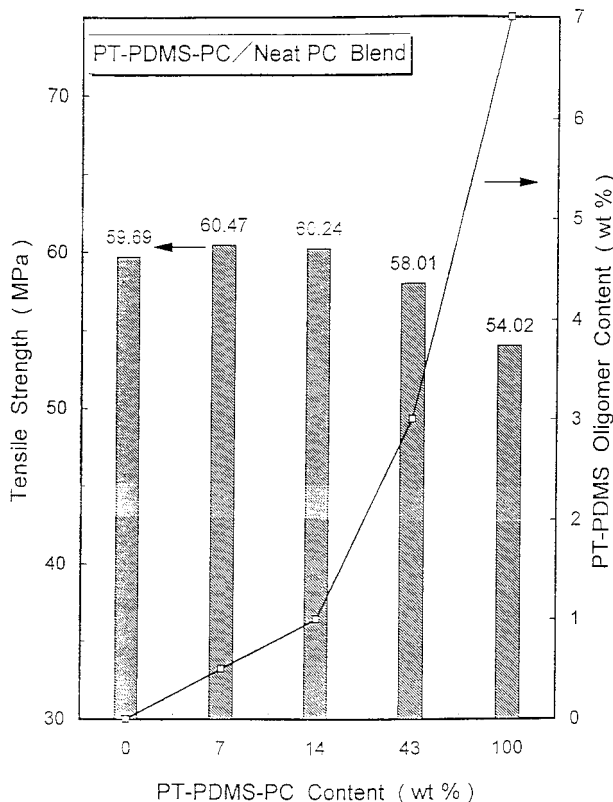


Figure 13 Effect of PT-PDMS-PC content on the tensile strength of PT-PDMS-PC copolymer blended with neat PC (Lexan-121).

PC copolymers increased from 8.3 to 15.6 and 11.6, respectively. The high melt indices of PDMS-PC copolymers indicated low melting viscosities, low processing temperatures, and good processability.

Mechanical Properties of PDMS-PC Copolymers

Figures 11, 12 and 13 illustrate the tensile strengths at break for various contents of the three types of PDMS-PC copolymer blended with neat PC (Lexan-121). The PDMS oligomer provides the PDMS-PC copolymer with a soft, flexible chain segment. Although the tensile strength decreased slightly with increasing PT-PDMS-PC content, the elongation increased, as shown in Figure 14. The flexural strength and toughness at yield for various contents of the three types of PDMS-PC blended with neat PC (Lexan-121) also decreased slightly with increasing PT-PDMS-PC content, but most of the tensile strengths of PDMS-PC copolymers were $\sim 90\%$ of neat PC.

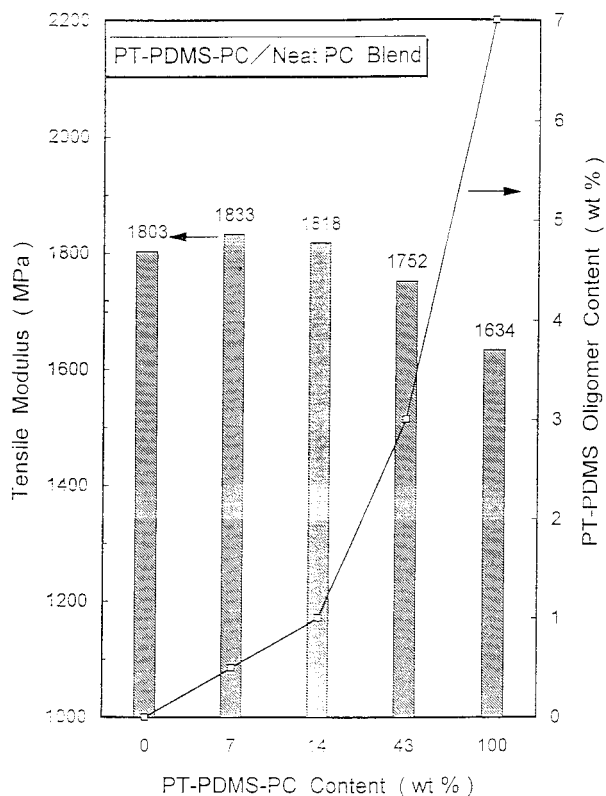


Figure 14 Effect of PT-PDMS-PC content on the tensile modulus of PT-PDMS-PC copolymer blended with neat PC (Lexan-121).

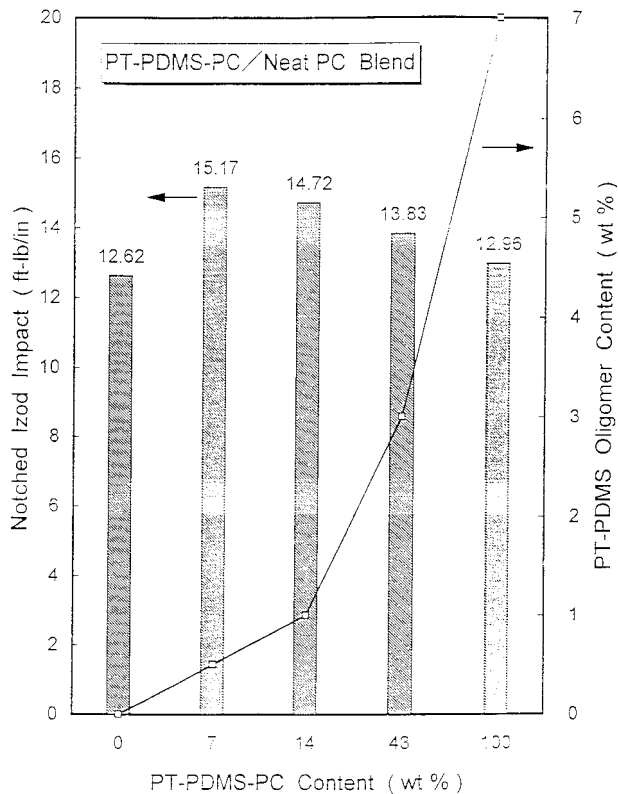


Figure 15 Effect of PT-PDMS-PC content on the notched Izod impact of PT-PDMS-PC copolymer blended with neat PC (Lexan-121).

Figure 15 shows the Izod impact strength of PT-PDMS-PC copolymer. Impact strength of PT-PDMS-PC was improved when the PT-PDMS oligomer was introduced into the PT-PDMS-PC copolymer. Impact strength of PT-PDMS-PC copolymer was improved from 12.6 ft-lb/in of neat PC to 13.0–15.2 ft-lb/in.

CONCLUSIONS

The $^1\text{H-NMR}$ spectrum indicated the conversion of AT-PDMS-PC copolymer was in the range between 85 and 95%, HT-PDMS-PC was 45–55%, and PT-PDMS-PC was 70–80%.

The processing temperature of neat PC was 265–275°C. The PDMS-PC copolymers showed low processing temperature (255–265°C) and good processability.

The melt flow indices of PDMS-PC copolymer blended with neat PC increased with increasing PDMS-PC content from 8.3 to 15.6 and 11.6 for AT-PDMS-PC and HT-PDMS-PC copolymers, respectively.

The mechanical properties of PDMS-PC copolymer blended with neat PC decreased slightly with increasing PDMS-PC content. The tensile and flexural strengths of PDMS-PC copolymer were $\sim 90\%$ of neat PC. Impact strength of PDMS-PC copolymer was improved from 12.6 ft-lb/in for neat PC to 13.0–15.2 ft-lb/in for copolymer.

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