

Impact Resistance of Fibrous Glass Reinforced Plastics Using Polycarbonate-Polydimethylsiloxane Block Copolymer

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ABSTRACT: By using reactive polydimethylsiloxanes that have phenolic hydroxyl groups at the ends of the chain, a polycarbonate-polydimethylsiloxane (PC-PDMS) block copolymer was prepared, and the properties of fibrous glass reinforced plastics (GF-PC) using this copolymer were examined. The Izod impact value of the PC-PDMS/GF composite increases with an increase in the degree of polymerization of reactive PDMS (n) between 40 and 160. When n is 40, the Izod impact value of the PC-PDMS/GF composite is equal to that of the PC/GF composite. The Izod impact

value is independent of the PDMS content of the copolymer when it is between 2 and 4 wt %. The PC-PDMS/GF composite is superior, in the balance between fluidity and impact resistance, to the PC/GF composite. From the results of SEM, adhesion between the polymer and GF of the PC-PDMS/GF composite is superior to that of the PC/GF composite. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 1123–1127, 2002

Key words: polycarbonate; polydimethylsiloxane; fibrous glass reinforced plastics; block copolymer; impact resistance

INTRODUCTION

Polycarbonates (PCs) are excellent engineering thermoplastics because of their good impact strength, thermal resistance, and transparency.^{1–2} They are used as base resins of fibrous glass reinforced plastics (GF-PCs) that are superior in rigidity and dimensional stability, but inferior in fluidity. When using PCs with low molecular weights, fluidity is increased, but impact resistance is decreased. Thus, the development of new GF-PCs with higher levels of fluidity and impact resistance than conventional GF-PCs is desired.

Among the latest studies on GF-PCs, some articles report their recycling by compression molding.^{3–4} Other articles report specific pigments that keep the toughness of GF-PCs.^{5–6} However, no article deals with improving the impact resistance of GF-PCs with PC copolymers.

This article describes the synthesis of a polycarbonate-polydimethylsiloxane (PC-PDMS) block copolymer that has the possibility of reforming adhesion between the polymer and GF, as well as properties of GF-PC using this copolymer.

EXPERIMENTAL

Material

Commercial bisphenol A (BPA), *p*-*tert*-butylphenol (PTBP), triethylamine (TEA), sodium hydroxide, di-

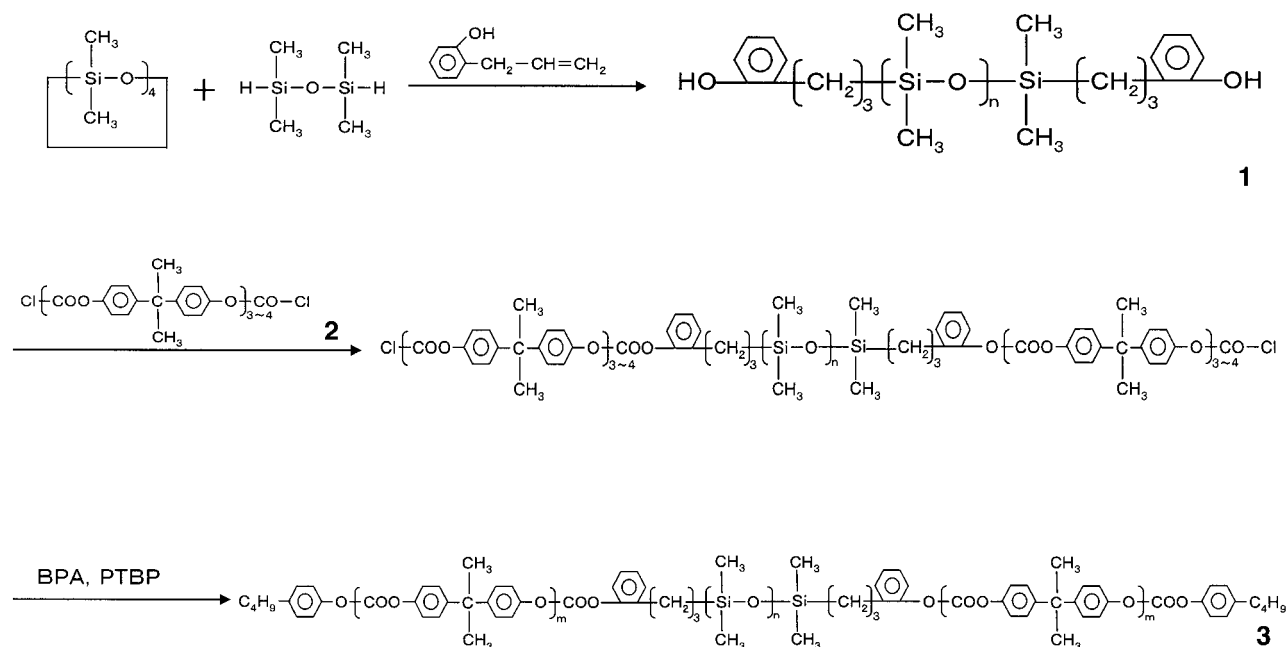
chloromethane, and sodium dithionite were used without further purification. Reactive PDMS was supplied by Dow Corning Toray Silicone Co., Ltd. (Tokyo, Japan). The GF used was MA-409C manufactured by Asahi Fiber Glass Co., Ltd. (Tokyo, Japan). The PCs used were Toughlon A1500 [average viscosity molecular weight (M_v) 15,000], A1700 (M_v : 17,500), and A2200 (M_v : 21,000) manufactured by Idemitsu Petrochemical Co., Ltd. (Tokyo, Japan).

Preparation of the PC oligomer

Sodium dithionite (120 g, 0.69 mol) and BPA (60 kg, 263 mol) were dissolved in 5 wt % aqueous sodium hydroxide (400 L). This solution, dichloromethane, and phosgene were introduced through an orifice plate at 25°C with a flow rate of 138 L/h, 69 L/h, and 10.7 kg/h (108 mol/h), respectively, into a tubular reactor with an inner diameter of 10 mm and a length of 10 m. This procedure was continued for 3 h. Because phosgene is a toxic, irritating gas, it was dealt with only in an efficient fume hood. After allowing the reaction solution to stand for a certain time, the organic phase was separated to obtain a PC oligomer (PCO) solution with an oligomer concentration of 311 g/L and a chloroformate group (CF) concentration of 0.72 mol/L.

Preparation of the PC-PDMS block copolymer

A solution prepared by dissolving reactive PDMS (132 g) in dichloromethane (2 L), as well as 5.8 wt % aque-



Scheme 1 Synthesis of block copolymer.

ous sodium hydroxide (725 mL) and triethylamine (4.37 g, 43.2 mmol), was added to the PCO solution (10 L, CF: 7.2 mol). The mixed solution was stirred at 300 rpm at room temperature for 1 h. Sodium dithionite (1.2 g, 6.9 mmol), BPA (579 g, 2.53 mol), a solution prepared by dissolving sodium hydroxide (338 g, 8.45 mmol) in water (5 L), and a solution prepared by dissolving *p*-*tert*-butylphenol (236 g, 1.57 mol) in dichloromethane (10 L) were further added and stirred at 500 rpm for 2 h at a temperature of 23°C. After this, dichloromethane (5 L) was added, and the solution was washed successively with water (5 L), 0.01M aqueous sodium hydroxide (5 L), 0.1M aqueous hydrochloric acid (5 L), and water (5 L).

Then, the solvent was evaporated to obtain the PC-PDMS block copolymer in a flake form.

The resulting PC-PDMS block copolymer was dried for 12 h at 110°C and pelletized by an extruder at 260°C.

Preparation of the PC-PDMS block copolymer and GF composites

The PC-PDMS block copolymer and GF were pelletized at 300°C by a vented twin-screw extruder with a GF inlet downstream of the PC feeding hopper. The

TABLE I
Synthesis of PC-PDMS Block Copolymers

Run	Feed			Block copolymer	
	PDMS (<i>n</i>)	PDMS/PCO (weight ratio)	PTBP ^a (wt %)	<i>M_v</i>	PDMS content ^b (wt %)
1-1	36	0.042	2.9	14,700	2.9
1-2	77	0.042	2.9	14,600	3.1
1-3	104	0.042	2.9	14,600	3.2
1-4	158	0.042	2.9	14,800	3.3
1-5	347	0.042	2.9	15,100	3.0
1-6	104	0.028	2.9	14,600	2.2
1-7	158	0.028	2.9	14,800	2.0
1-8	347	0.028	2.9	14,800	1.9
1-9	104	0.057	2.9	14,700	4.1
1-10	104	0.021	2.9	14,800	1.0
1-11	158	0.042	2.3	17,900	3.0
1-12	158	0.042	2.2	19,800	2.9

^a Ratio of PTBP feedstock to the total amount of BPA, PCO, and PTBP feedstock.

^b Calculated by using ¹H-NMR.

TABLE II
Preparation and Properties of GF-PC

Run	Polymer		GF	Flow value ^a ($\times 10^{-2}$ ml/s)	HDT ^b (°C)	Flexural modulus ^c (Mpa)	Izod impact value ^d (KJ/m ²)
	Kind	Amount (wt %)	Amount (wt %)				
2-1	Run 1-1	70	30	16	140	8300	8.2
2-2	Run 1-2	70	30	15	140	8200	12.3
2-3	Run 1-3	70	30	15	141	8700	13.6
2-4	Run 1-4	70	30	15	144	8500	14.5
2-5	Run 1-5	70	30	17	142	8200	14.2
2-6	Run 1-6	70	30	17	141	8600	12.6
2-7	Run 1-7	70	30	14	144	8500	14.2
2-8	Run 1-8	70	30	18	142	8500	13.6
2-9	Run 1-9	70	30	17	141	8400	13.2
2-10	Run 1-10	70	30	16	142	8500	10.5
2-11	Run 1-11	70	30	6.7	142	8200	17.1
2-12	Run 1-12	70	30	3.5	144	8200	18.2
2-13	A1500 ^e	70	30	16	142	8400	9.4
2-14	A1700	70	30	7.5	144	8200	10.5
2-15	A2200	70	30	3.5	147	7900	14.4

^a Measured in conformity to JIC K 7210.
^b Measured in conformity to JIC K 7191.
^c Measured in conformity to JIC K 7171.
^d Measured in conformity to JIC K 7110.
^e Manufactured by Idemitsu Petrochemical Co., Ltd.

pellets obtained were dried for 24 h at 120°C and subjected to flow value measurement.

Molding

The resulting pellets were injection molded to produce test pieces using IS-100-EN manufactured by Toshiba Machine Co., Ltd. The conditions were as follows: cylinder temperature, 290°C; mold temperature, 80°C; injection pressure, 100 MPa; injection rate, 30 mL/s; dwelling time, 12 s. The test pieces were subject to measurement of the heat distortion temperature

(HDT), flexural modulus, and the Izod impact test after leaving for 48 h at 23°C.

Measurement

The M_v of the PC-PDMS block copolymer was obtained by measuring the viscosity of the polymer-dichloromethane solution with different concentrations at 20°C by using an Ubbelohde viscometer and then by deriving intrinsic viscosity $[\eta]$ by extrapolation and substituting it in the following equation¹:

$$[\eta] = 1.23 \times 10^{-5} M_v^{0.83}$$

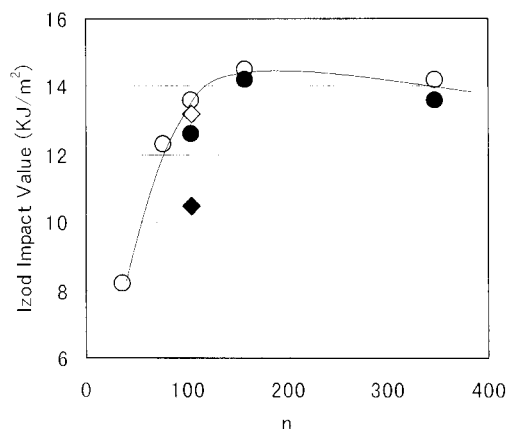


Figure 1 Relationship between the degree of polymerization of reactive PDMS (n) and the Izod impact value: (◆) PDMS: 1 wt %; (●) PDMS: 2 wt %; (○) PDMS: 3 wt %; (◇) PDMS: 4 wt %.

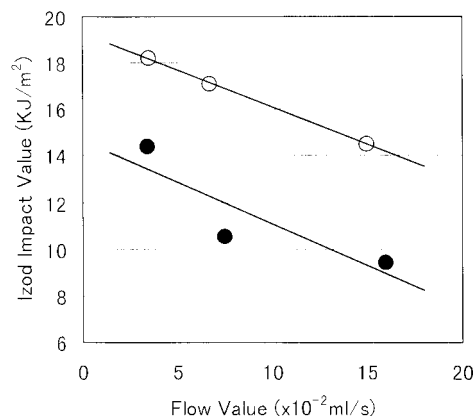


Figure 2 Relationship between the flow value and the Izod impact value: (○) PC-PDMS/GF composite; (●) PC/GF composite.

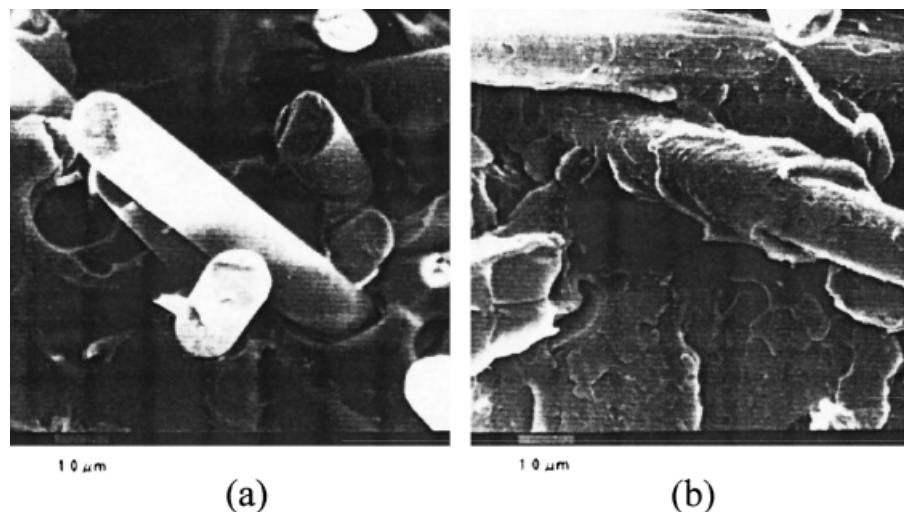


Figure 3 SEM photograph of fractured surface of GF-PC: (a) PC/GF composite (Run 2-13); (b) PC-PDMS/GF composite (Run 2-4).

The flow value, the HDT, the flexural modulus, and the Izod impact value were measured as indices for fluidity, thermal resistance, rigidity, and impact resistance in conformity to JIS K 7210, JIS K 7191, JIS K 7171, and JIS K 7110, respectively.

$^1\text{H-NMR}$ spectrum was recorded with a JEOL EX-400 NMR spectrometer operating at 400.15 MHz. The copolymer solution prepared had a concentration of 70 mg/ml in CDCl_3 .

The fractured surfaces after the Izod impact test were examined by SEM by using a JSM-6100 (JEOL) operating at an acceleration voltage of 15 kV. The fractured surfaces were sputtered coated with gold by using an Ion Sputter JEC-1100 (JEOL) to enhance conductivity.

RESULTS AND DISCUSSION

Preparation of the PC-PDMS block copolymer

The preparation of the PC-PDMS block copolymer was carried out according to Scheme 1. An insertion reaction of octamethylcyclotetrasiloxane (OMTS) into 1,1,3,3-tetramethyldi-siloxane (TMDS) and end capping by 2-allylphenol led to the production of reactive PDMS with phenolic hydroxyl groups at the ends of the chain (**1**). The degree of polymerization of **1** is controlled by the mixing ratio of OMTS to TMDS. In this article, the reactive PDMSs that were supplied by Dow Corning Toray Silicone Co., Ltd. were used. The degree of polymerization of **1** was calculated from the integral ratio of the methyl protons (0.1 ppm) to the trimethylene protons (0.6, 1.7, and 2.6 ppm) in $^1\text{H-NMR}$ spectroscopy.⁷

The synthesis of PC-PDMS block copolymer (**3**) was carried out as follows. The two-step method was used to prepare **3**. The first step was precondensation of **1**

and the PCO (**2**), giving the prepolymer with chloroformate groups at the ends of the chain. The second step was polycondensation of BPA and the prepolymer. The syntheses of **3** are summarized in Table I.

The structure of **3** was characterized by $^1\text{H-NMR}$ spectroscopy.⁷ The PDMS content of **3** was calculated from the integral ratio of the methyl protons (1.7 ppm) of the PC unit to the methyl protons of the PDMS unit (0.1 ppm).⁷

Properties of GF-PCs

Using the PC-PDMS block copolymer, the properties of GF-PCs were examined. The result is summarized in Table II. Figure 1 shows the relationship between the degree of polymerization of reactive PDMS (n) and the Izod impact value of the PC-PDMS/GF composite. The Izod impact value increases with an increase of the n value between 40 and 160. When n exceeds 160, the Izod impact value does not increase further. With an n value of 350, the Izod impact value shows a tendency to decrease slightly. When n is less than 40, the Izod impact value of the PC-PDMS/GF composite is equal to that of the PC/GF composite. Thus, it is considered that the adhesion between the polymer and the GF is improved when n is above 40. When the PDMS content of the copolymer is 1 wt %, the improvement of the Izod impact value is small but independent of the PDMS content between 2 and 4 wt %.

Using the PCs and PC-PDMS block copolymers of different molecular weights, the relationship between the flow value and the Izod impact value of GF-PC was examined. The PDMS content of the used copolymers was 3 wt %, and the n value was 158. The results are shown in Figure 2. With an increase in the

M_v of polymer, the Izod impact value increased while the flow value decreased. From the figure, it can be said that the PC-PDMS/GF composite is superior, in the balance between fluidity and impact resistance, to the PC/GF composite. Thermal resistance (HDT) and rigidity (flexural modulus) of the PC-PDMS composite were maintained at the same levels as the PC/GF composite.

Figure 3 shows SEM photographs of the fractured surface of GF-PC after the Izod impact test. By observation of the SEM results, adhesion between the polymer and GF of the PC-PDMS/GF composite is superior to that of the PC/GF composite.

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