

Relationship Between Thermal Degradation Behavior and Flame Retardancy on Polycarbonate–Polydimethylsiloxane Block Copolymer

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ABSTRACT: This article describes the thermal degradation behavior of polycarbonate–polydimethylsiloxane (PC–PDMS) block copolymer with dimethylsiloxane (DMS) block size 15 to 350 units, and the effects of the PDMS block size and the PDMS content on thermal degradation were studied. PC–PDMS block copolymer with DMS unit of 100 had the lowest value of maximum weight loss rate and the most residue containing silica in the other PC–PDMS block copolymers. The PDMS block size influenced

PDMS dispersibility in PC and the moderate PDMS dispersion (~ 50 nm) caused high flame retardancy for PC. The control of nanodispersion of PDMS caused the change of thermal degradation behavior and high flame retardancy in PC. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 1697–1705, 2006

Key words: polycarbonate; polydimethylsiloxane; block copolymer; flame retardance; degradation

INTRODUCTION

Polycarbonate (PC) is excellent in mechanical properties, and is used for various applications. However, for electronic and electrical applications, since high flame retardancy is required, the flame retardant technologies of PC have been developed.^{1–7} The PC flame-retardant technology by the organic metal salt is the control of the thermal decomposition of PC. This organic metal salt promotes the decomposition of PC and inhibits the combustion by generating incombustible carbon dioxide and forming a char layer at the burning surface.⁸ Alternatively, the PC flame-retardant technology by addition or copolymerization of silicone compound has been developed.^{9–13} In our previous article, it was reported that polycarbonate–polydimethylsiloxane (PC–PDMS) block copolymers with dimethylsiloxane (DMS) unit of 40–130 had high LOI value at 1.0 wt % PDMS and the moderate PDMS dispersion (domain size ~ 50 nm) caused high flame retardancy for PC.¹⁴ Then, it was indicated that PDMS block size and PDMS content in PC–PDMS affect the initial degradation temperature and the rate of weight loss. Grubbs and Kleppick¹⁵ reported the thermal analysis study of PC–PDMS, and it was found that PC–PDMS had

two degradation reactions (the first reaction: thermo-oxidative reaction of the methyl groups of DMS portion and the end groups of PC portion; the second reaction: depolymerization process). However, the effect of PDMS block size in small PDMS content on the thermal degradation was not discussed.

This report describes the effects of PDMS content and the block size on thermal degradation in PC–PDMS block copolymer, and the relationship between the flame retardancy and the thermal degradation of PC–PDMS block copolymer was studied.

EXPERIMENTAL

Materials

PC–PDMS block copolymers used in this study were the same as prepared in a previous article.^{14,16,17} Table I lists the characteristics of the resulting PC–PDMS block copolymers. Reactive PDMS compound with DMS block size 40 units was supplied by Dow Corning Toray Silicone. PC used in this study was Toughlon FN1900A (trade name from Idemitsu Kosan). This is bisphenol A-type PC having a viscosity-average molecular weight of 19,000 and melt flow index 20 g/10 min (conditions: 300°C, 1.2 kg). The amount of PDMS was prepared by melt-kneading and extruding mixture of PC–PDMS block copolymer and PC (Toughlon FN1900A). Furthermore, the PC and the PC–PDMS block copolymer blended simply with Reactive PDMS compound with DMS block

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TABLE I
Characteristics of PC-PDMS Block Copolymers

Kind	Block copolymer		
	DMS units (<i>n</i>)	M_v	PDMS content (wt %)
PC	0	19,000	0
PC-PDMS-15	15	19,300	2.8
PC-PDMS-40	40	19,200	3.0
PC-PDMS-100	100	19,300	3.0
PC-PDMS-150	150	19,500	2.8
PC-PDMS-350	350	18,900	2.6

size 40 units (PC/PDMS-40) were prepared by melt-kneading and extruding.

Molding

The resulting pellets were dried at 120°C for 5 h, and then injection-molded at an injection temperature of 280°C into test pieces for measurement of flame retardancy.

Limited oxygen index

LOI measurements were performed according to JIS K7201 method (ignition flame: 15–20 mm), using the candle type flammability tester (Toyo Seiki seisakusho). The sample bars with 3 mm thickness were made by injection molding, and conditioned for one week under 23°C and 50% relative humidity.

Thermogravimetric analysis

A Perkin-Elmer thermal analyzer TGA-7 was used to determine the weight loss during thermal degradation of the PC-PDMS block polymers. Experiments were carried out on 10 mg of sample under

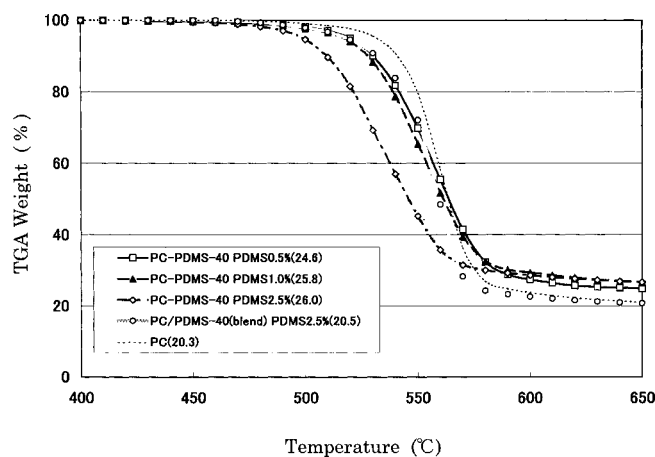


Figure 1 TGA curve and the amount of residue for PC-PDMS-40 with 0.5–2.5 wt % PDMS content, PC/PDMS-40 (blend), and PC and the number in parentheses shows the amount of residue.

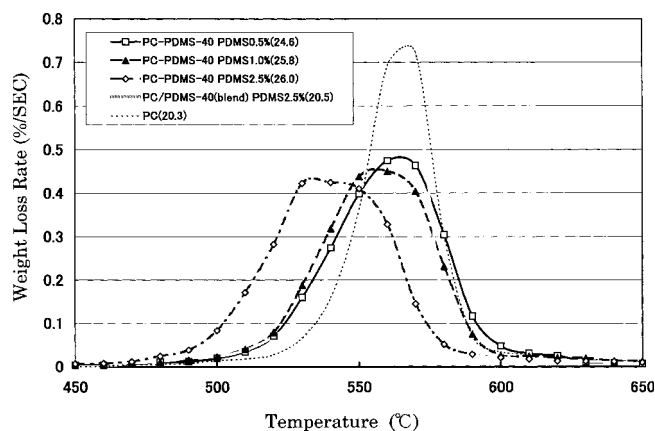


Figure 2 Weight loss rate and the amount of residue for PC-PDMS-40 with 0.5–2.5 wt % PDMS, PC/PDMS-40, and PC on temperature by TGA, and the number in parentheses shows the amount of residue.

nitrogen and furnace heating rate of 20°C/min up to 700°C. In combustion, oxygen is consumed in gas phase, and so degradation and char formation in solid phase would be generated under nonoxygen atmosphere.

Scanning electron microscopy

After LOI test, the morphology of char was observed by scanning electron microscopy (JEOL, JSM-6100) operating at acceleration voltage of 15 kV. The char sample was coated with gold by using an ion sputter (JEOL, JEC-1100) to enhance conductivity.

Elemental analysis

Each elemental content of PD-PDMS block copolymers was measured by elemental analyzer (DIA Instrument, AQF-100).

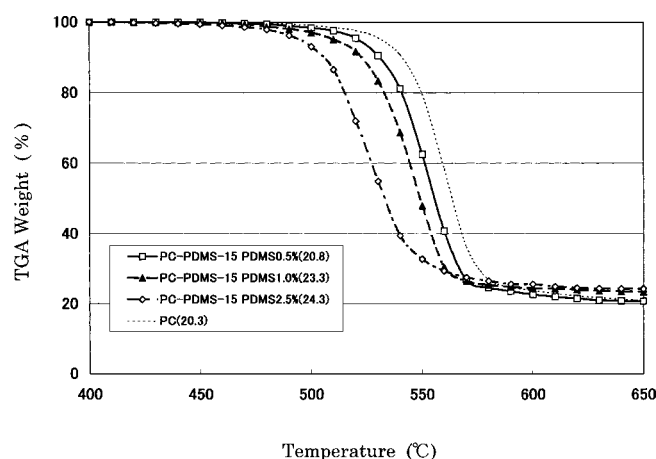


Figure 3 TGA curve and the amount of residue for PC-PDMS-15 with 0.5–2.5 wt % PDMS content and PC, and the number in parentheses shows the amount of residue.

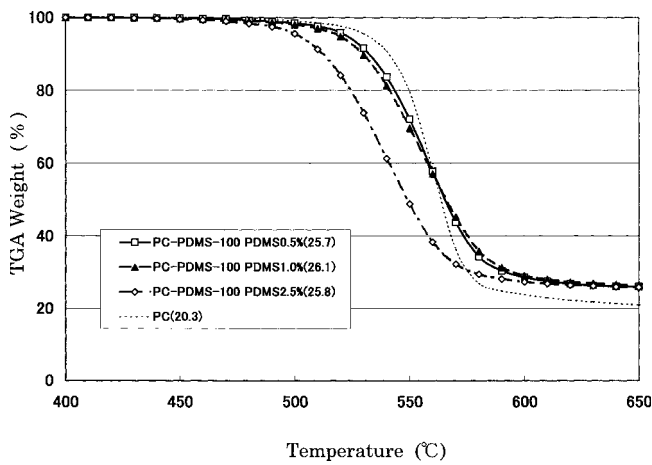


Figure 4 TGA curve and the amount of residue for PC-PDMS-100 with 0.5–2.5 wt % PDMS and PC, and the number in parentheses shows the amount of residue.

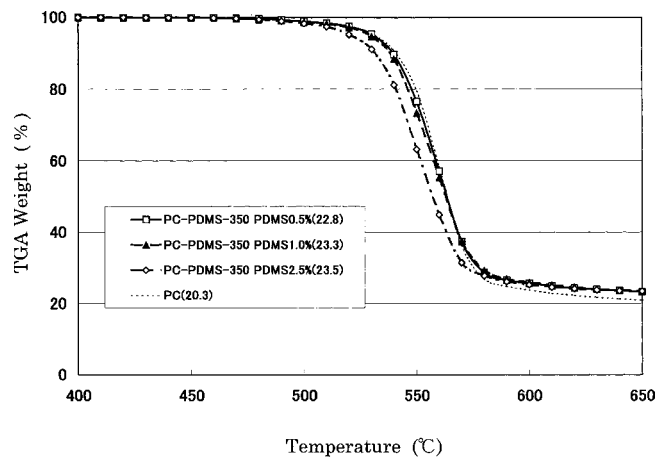


Figure 6 TGA curve and the amount of residue for PC-PDMS-350 with 0.5–2.5 wt % PDMS and PC, and the number in parenthesis shows the amount of residue.

RESULTS AND DISCUSSION

Thermal degradation behavior of PC-PDMS block copolymer

First, the thermal degradation behavior of PC-PDMS block copolymer having DMS unit of 40 (PC-PDMS-40) was tested. The PDMS copolymerization content (0–2.5 wt %) was prepared by the melt kneading and extrusion of a mixture of PC-PDMS-40 and PC. The PC blended simply with the same structural reactive PDMS compound (PC/PDMS-40) was measured for comparison. The thermogravimetric analysis (TGA) curves of all samples are depicted in Figure 1. The number of a parenthesis shows the amount (%) of residue at 650°C. The initial degradation temperature decreased and the amount of residue increased as the PDMS content increased except PC/PDMS-40 (blend). The initial degradation temperature of 3 wt % weight loss decreases from 526°C

to 491°C at 2.5 wt % PDMS. Figure 2 shows the rates of weight loss on the temperatures in TGA. The maximum rates of PC-PDMS-40 (copolymer) were lower than that of PC and PC/PDMS-40 (blend), and the temperatures of the maximum rates decreased as the PDMS content increased. On the other hand, the simple addition of the same structural PDMS to PC (PC/PDMS-40) did not cause a lot of change on degradation behavior, and so the change of degradation behavior in PC-PDMS-40 did not contribute to the PDMS itself.

Next, the effect of the DMS block size in the PC-PDMS block copolymer on degradation behavior was investigated. The DMS units ranged from 15 to 350. The TGA curves of all PC-PDMS block copolymers are depicted in Figures 3–6. These PDMS contents were prepared into 0–2.5 wt % as well as PC-PDMS-40. The number of parenthesis shows the amount (%) of residue at 650°C. In all samples, the

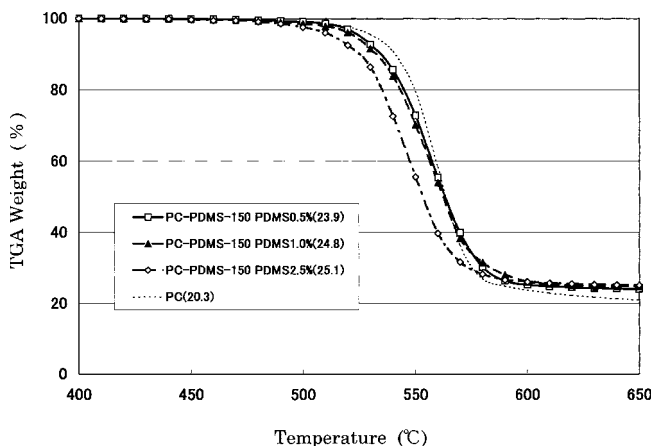


Figure 5 TGA curve and the amount of residue for PC-PDMS-150 with 0.5–2.5 wt % PDMS and PC, and the number in parentheses shows the amount of residue.

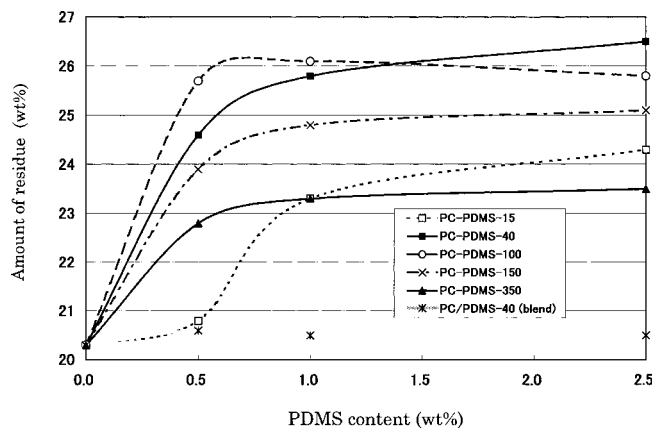


Figure 7 Amounts of residue as a function of PDMS content for PC-PDMS block copolymer with PDMS block size 15–350 and PC/PDMS-40 (blend).

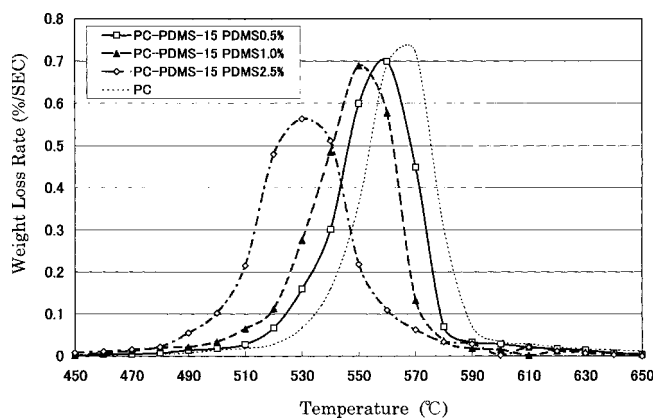


Figure 8 Weight loss rate for PC-PDMS-15 with 0.5–2.5 wt % PDMS and PC on temperature by TGA.

initial degradation temperature decreased as the PDMS content increased. Furthermore, when PDMS chain size was shorter, PC-PDMS block copolymers began to degrade at lower temperature. The initial degradation behavior of PC-PDMS-350 with 2.5 wt % PDMS became like PC/PDMS-40 (blend). The amounts of residue as a function of PDMS content for each PC-PDMS block copolymer are shown in Figure 7. The amounts of residue for each PC-PDMS block copolymer increased rapidly until about 1.0 wt % PDMS. The amounts of residue for PC-PDMS-100, PC-PDMS-150, and PC-PDMS-350 were almost saturated over 1.0 wt % PDMS and those for PC-PDMS-15 and PC-PDMS-40 increased slowly. PC-PDMS-100 increased the amount of residue at the small PDMS content. The amounts of residue for PC-PDMS-15 and PC-PDMS-350 were less than those for the other PC-PDMS block copolymers. On the other hand, the amount of residue for PC/PDMS-40 (blend) was almost the same as PC and did not change, although the PDMS content increased. Figures 8–11 show the rates of weight loss for each PDMS block copolymer on the temperatures in TGA. Furthermore, Figures

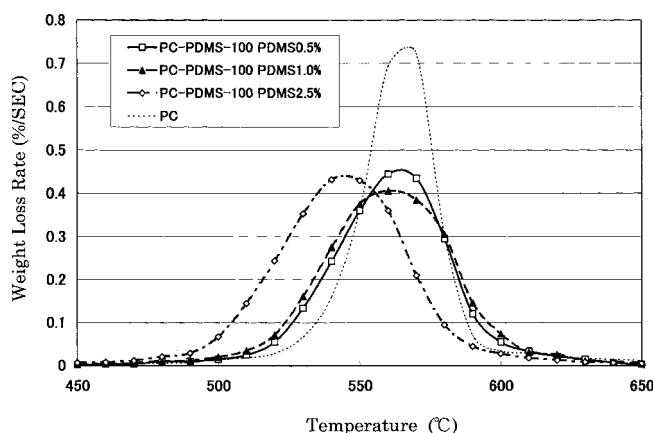


Figure 9 Weight loss rate for PC-PDMS-100 with 0.5–2.5 wt % PDMS and PC on temperature by TGA.

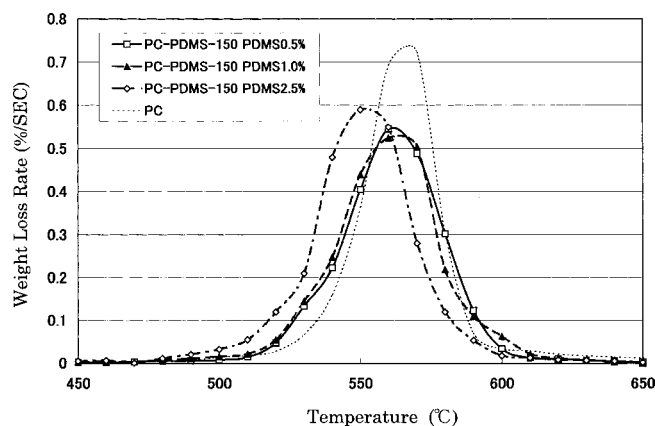


Figure 10 Weight loss rate for PC-PDMS-150 with 0.5–2.5 wt % PDMS and PC on temperature by TGA.

12–14 show the rates of weight loss for each PC-PDMS block copolymer with 0.5 wt % PDMS, 1.0 wt % PDMS, and 2.5 wt % PDMS on the temperatures in TGA. The maximum weight loss rates of PC-PDMS-40, PC-PDMS-100, and PC-PDMS-150 were lower than ones of PC and the other PC-PDMS block copolymer, and the maximum rate of PC-PDMS-100 decreased most from 0.73 wt %/s to 0.41 wt %/s at 1.0 wt % PDMS. The maximum rate of PC-PDMS-15 with a short PDMS chain hardly changed until 1.0 wt % PDMS, but the maximum rate of PC-PDMS-15 decreased at 2.5 wt % PDMS. The maximum rates of PC-PDMS-100 and PC-PDMS-150 were minimum at 1.0 wt % PDMS. On the other hand, the weight loss rate of PC-PDMS-350 on the temperature hardly changes compared with PC. So it is found out that the chemical bond between PC and PC-PDMS does not influence the thermal degradation because the amount of the chemical bond does not correlate with the change of the weight loss. The PDMS chain size in the PC-PDMS block copolymer affects the thermal degradation behavior at 0.5–2.5 wt % PDMS and the thermal

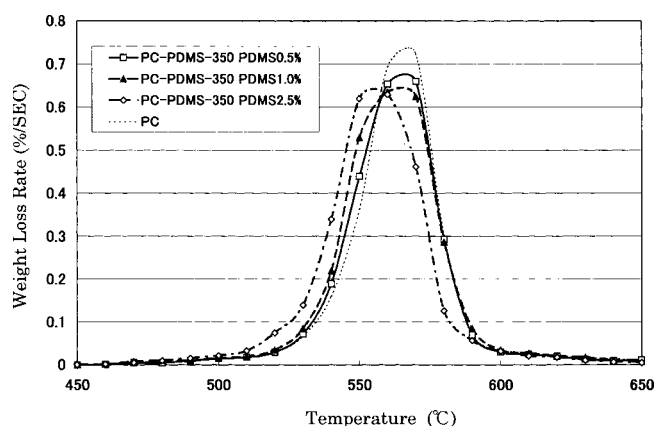


Figure 11 Weight loss rate for PC-PDMS-350 with 0.5–2.5 wt % PDMS and PC on temperature by TGA.

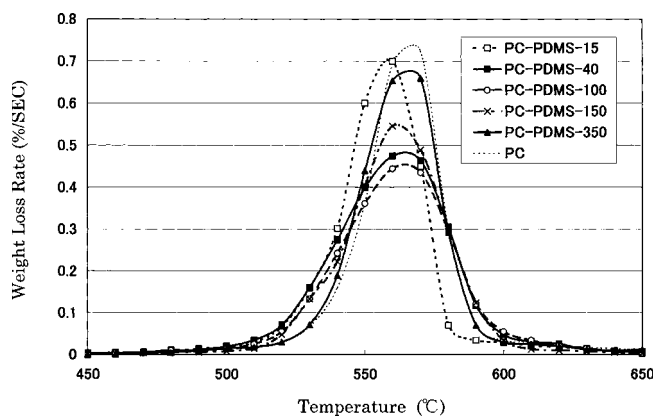


Figure 12 Weight loss rate for PC-PDMS block copolymer with 0.5 wt % PDMS and PC on temperature by TGA.

degradation is inhibited most effectively when PDMS chain size is 100.

In our previous article, it was reported that PC-PDMS block copolymer (PC-PDMS-40 : 3.0 wt % PDMS) inhibited the decomposition of the inside polymer by the outside char that contains more Si element.¹² Then, Si element analysis of the char in these PC-PDMS block copolymers treated at 400°C for 2 h under nitrogen atmosphere was carried out to clear the difference of thermal degradation on the PDMS chain size. PC and PDMS begin to degrade at 400°C.^{18,19} The changes of the elementary-composition ratio before and after the heat treatment are shown in Table II. The Si element in the upper char layer of treated PC-PDMS-100 and PC-PDMS-150 as well as PC-PDMS-40 increased, but that of PC-PDMS-15 and PC-PDMS-350 decreased reversely. The Si element of PC-PDMS-100 was the maximum. The amount of Si element in the upper char layer has relation to the thermal degradation behavior and the maximum rate of weight loss tends to decrease as the amount of remaining Si element increases. Then it is thought that the Si element can become

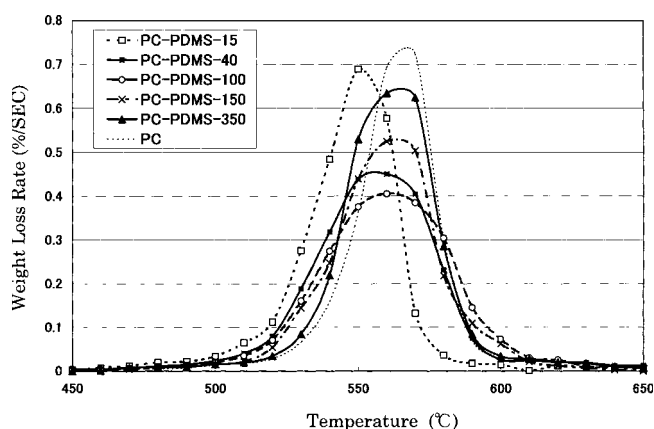


Figure 13 Weight loss rate for PC-PDMS block copolymer with 1.0 wt % PDMS and PC on temperature by TGA.

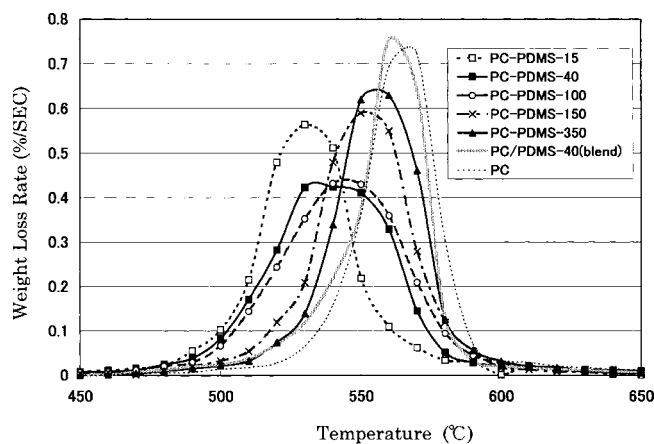


Figure 14 Weight loss rate for PC-PDMS block copolymer with 2.5 wt % PDMS and PC on temperature by TGA.

silica in the residue finally and the thermal stability of the residue increases.

To consider the difference of amount of remaining Si in the PDMS chain size, the thermal degradation behavior in PC-PDMS block copolymer is considered. The thermal decomposition of PDMS under nitrogen mainly occurs above 400°C (the temperature of 10 wt % weight loss is about 420°C).^{15,18} Then, the low molecular DMS and cyclic DMS are generated by the decomposition of rearrangement reaction and the methyl group as the side chain of PDMS removes. The decomposition of PC starts at 400°C by intermolecular-exchange reaction and many

TABLE II
Changes of the Elemental Composition Ratio on the Upper Layer of PC-PDMS Before and After Treated at 400°C for 2 h

	Elemental composition (wt %)			
	H	C	O	Si
PC	5.55	75.75	18.88	
Upper layer of PC treated at 400°C	4.99	75.58	19.43	
PC-PDMS-15 (PDMS 2.8 wt %)	5.58	74.44	19.02	0.96
Upper layer of PC-PDMS-15 treated at 400°C	5.06	75.06	19.26	0.62
PC-PDMS-40 (PDMS 3.0 wt %)	5.63	74.39	18.94	1.04
Upper layer of PC-PDMS-40 treated at 400°C	5.02	74.12	19.46	1.40
PC-PDMS-100 (PDMS 3.0 wt %)	5.6	74.34	18.98	1.08
Upper layer of PC-PDMS-100 treated at 400°C	4.93	74.01	19.55	1.51
PC-PDMS-150 (PDMS 2.8 wt %)	5.65	74.29	19.08	0.98
Upper layer of PC-PDMS-150 treated at 400°C	5.05	74.23	19.44	1.28
PC-PDMS-350 (PDMS 2.6 wt %)	5.5	74.74	18.91	0.85
Upper layer of PC-PDMS-350 treated at 400°C	5.12	75.16	19.26	0.46

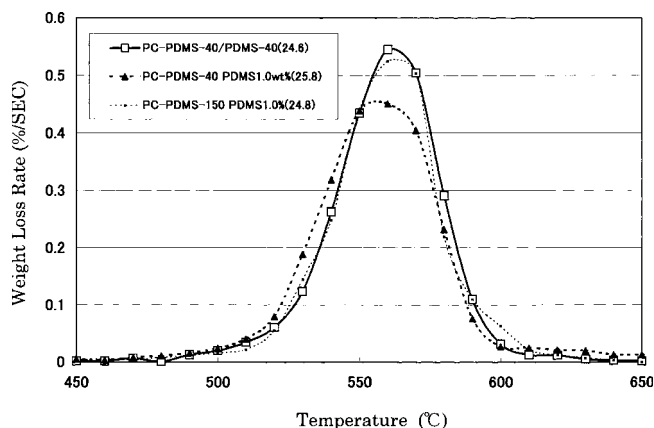
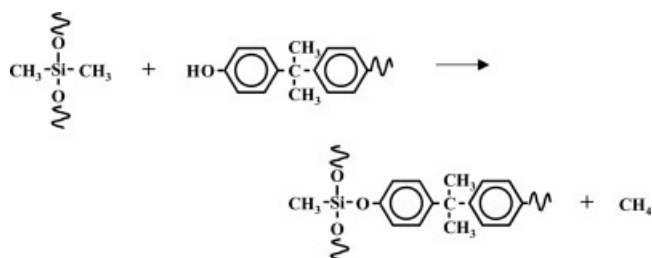


Figure 15 Weight loss rate for PC-PDMS-40 (0.5 wt % PDMS) blended with 0.5 wt % PDMS-40 on temperature by TGA.

PCs with the end group of BPA are generated.¹⁹ Moreover, it is known that PC with the end group of BPA and DMS react at high temperature as follows.^{20,21} Furthermore, this reaction was suggested in our previous article for PC-PDMS-40.¹²



It is thought that this reaction increases more above 400°C when the dispersion size of PDMS in PC is smaller. It is because the rearrangement reaction of PDMS hardly occurs without PDMS aggregation and the probability of the reaction between the decomposing PC and PDMS above 400°C increases. The copolymerization of PDMS to PC causes a good dispersion of PDMS and the dispersion size of PDMS is smaller as PDMS block size is shorter. The PDMS domain size of PC-PDMS-100 with 2.5 wt % PDMS is ~50 nm.¹⁴ The PC-PDMS block copolymers with small PDMS domains such as PC-PDMS-15, PC-PDMS-40, and PC-PDMS-100 can easily react between the decomposing PC and PDMS. (The PDMS domains of PC-PDMS-15 and PC-PDMS-40 were too small to observe; less than 10 nm is estimated.) This reaction causes the decrement of the initial degradation temperature and forms the residue containing a lot of silica without generating volatile cyclic DMS. A lot of bubbles of PC-PDMS-40 on the initial thermal degradation are attributed to this bridge formation reaction between the decomposing PC and PDMS that increases the melt tension. The bubble formation acts as the heat insulator and inhibits the decomposition of PC-PDMS block copoly-

mer in the early degradation process. Furthermore a lot of silica particles in the residue can remain by the reaction and the thermal stability of the residue increases. So it is thought that the bubble formation and the thermal stable residue cause the decrement of the maximum loss rate. However, the amount of the Si element in PC-PDMS-15 is low, even though the dispersion is the best of all. It is thought that the decomposition products are low molecular by the extreme reaction (containing the radical degradation reaction by the methyl radical from PDMS) and the silica particles generated from the short PDMS chain are extremely small. Then the silica particles tend to evaporate and so it will be hard to remain in the residue. On the other hand, when PDMS domain is larger and PDMS exists mostly on the surface such as PC/PDMS-40 (blend) (PDMS domain size more than 500 nm) and PC-PDMS-350 (PDMS domain size more than 200 nm), PDMS rearrangement reaction is thought to be promoted. The low molecular or cyclic DMSs by rearrangement reaction migrate easily and volatilize onto the surface and hardly remain in the residue as silica particles. As a result, the thermal degradation behavior in PC/PDMS-40 (blend) and PC-PDMS-350 is almost the same as in PC. The behavior of the maximum loss rate in the PC-PDMS block copolymer has relation to the dispersed PDMS domain size in PC. Therefore, the copolymerization of PDMS to PC and the copolymerized PDMS block size determine the PDMS domain size and influence the thermal degradation behavior of PC-PDMS in small PDMS content (less than 3 wt %). The PDMS domain size in PC causes the change of the thermal degradation process that affects the amount of silica particles in the residue. The TGA analysis for PC-PDMS block copolymer blended with PDMS compound was tested to prove this hypothesis. PDMS compound becomes smaller domain in PC-PDMS block copolymer than in PC because PC-PDMS block copolymer has the compatibility with PDMS com-

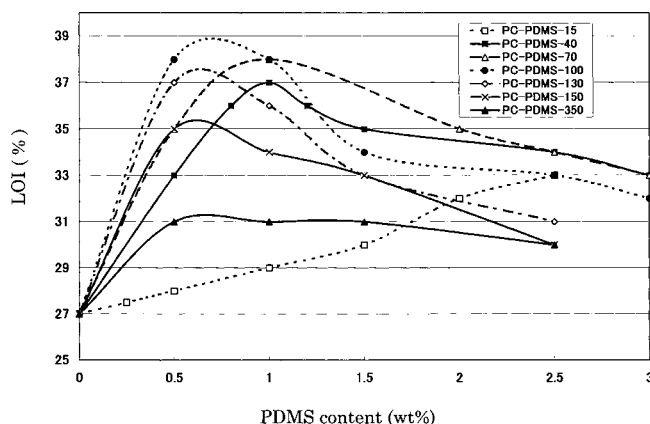


Figure 16 LOI values as a function of PDMS content for PC-PDMS block copolymers with PDMS block size 15–350.

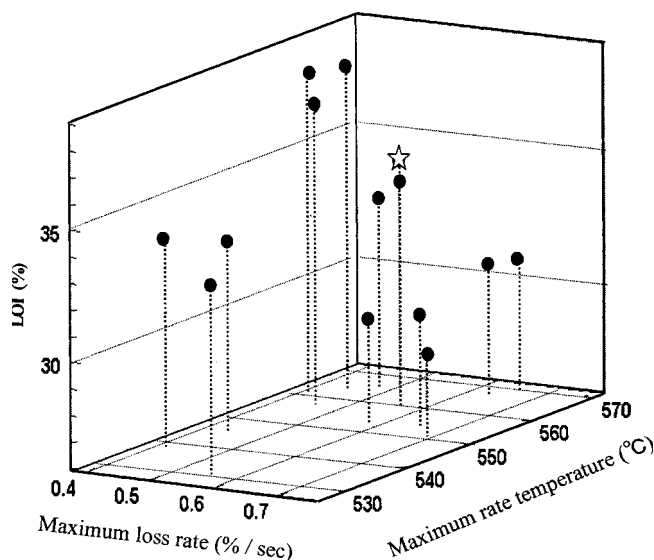


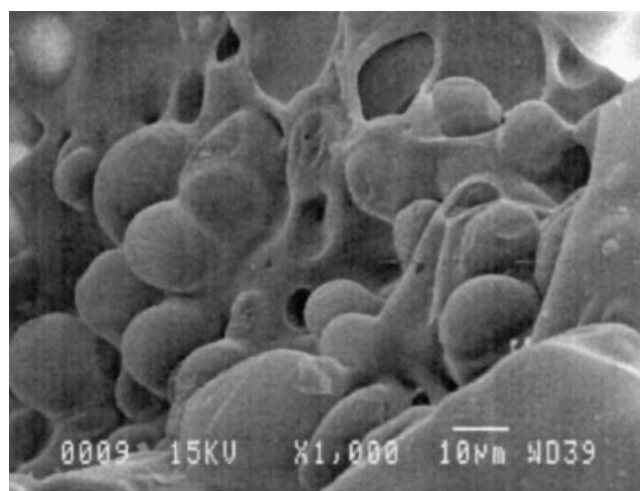
Figure 17 LOI to the maximum loss rate and the maximum rate temperature, Mark ☆: PC-PDMS-40 (0.5 wt % PDMS) blended with 0.5 wt % PDMS-40.

pound. And so the PDMS domain size can be somewhat controlled by amount of adding PDMS compound. The rate of weight loss for PC-PDMS-40 (0.5 wt % PDMS) blended with 0.5 wt % PDMS-40 is shown in Figure 15. The number of a parenthesis shows the amount (%) of residue at 650°C. The haze of the PC-PDMS-40 blended with PDMS-40 is 67% and that means that the blend has almost the same domain size as PC-PDMS-150 with 1.0 wt % PDMS (haze 63%). As compared with PC-PDMS-40 with 1.0 wt % PDMS, the maximum rate increased from 0.45 wt %/s to 0.55 wt %/s and the temperature of the maximum rate shifted to a little high temperature. That is, the thermal decomposition behavior is similar to that of PC-PDMS-150 with 1.0 wt % PDMS. This result is one reason that PDMS domain size affects the thermal degradation behavior. It is found out that the thermal degradation in the PC containing PDMS, which is copolymerized or added, is inhibited most when the PDMS domain size is ~ 50 nm. The control of nanodispersion of PDMS causes the change of the thermal degradation behavior in PC.

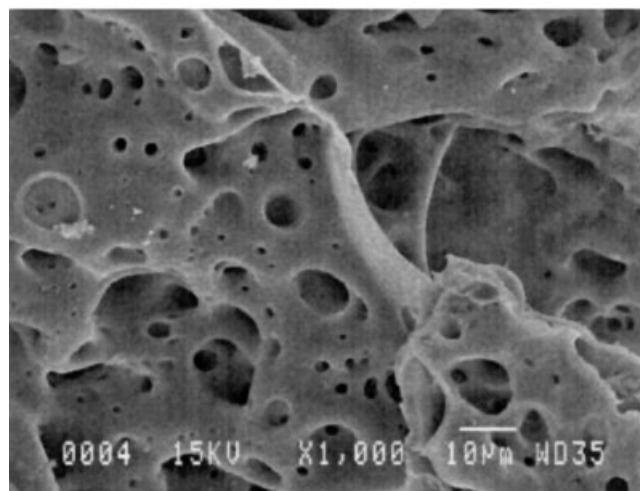
Relationship between thermal degradation and flame retardancy on PC-PDMS block copolymer

The thermal degradation behavior affects the flame retardancy for PC-PDMS block copolymer. So the efficient thermal degradation behavior for the flame retardancy on PC-PDMS block copolymer was considered. The LOI values as a function of PDMS content for each PC-PDMS block copolymer were reported in our previous article (Fig. 16).¹⁴ The PDMS content and PDMS block size influence the flame retardancy. Figure 17 shows the change of the LOI

to the maximum loss rate and the maximum rate temperature. The data are ones from the PC-PDMS block copolymers and PC-PDMS-40 (0.5 wt % PDMS) blended with 0.5 wt % PDMS-40. When the maximum loss rate is low and the maximum rate temperature is high, the LOI of PC-PDMS block copolymer tends to increase. The decrement of the maximum rate temperature means the generation of flammable gases at lower temperature and so LOI decreases because flame spreads easily on the surface. Then when the maximum loss rate is low, the degradation of polymer is inhibited and so LOI increases. The increment of LOI causes the formation of bubble in combustion and the properties of the char (morphology and thermal stability). The PC-PDMS block copolymers with high flame retardancy



PC-PDMS-40 (Copolymer)



PC/PDMS-40(Blend)

Figure 18 Morphologies of char by scanning electron microscopy: PC-PDMS-40 (copolymer, PDMS 1.0 wt %) and PC/PDMS-40 (blend, PDMS content 2.0 wt %).

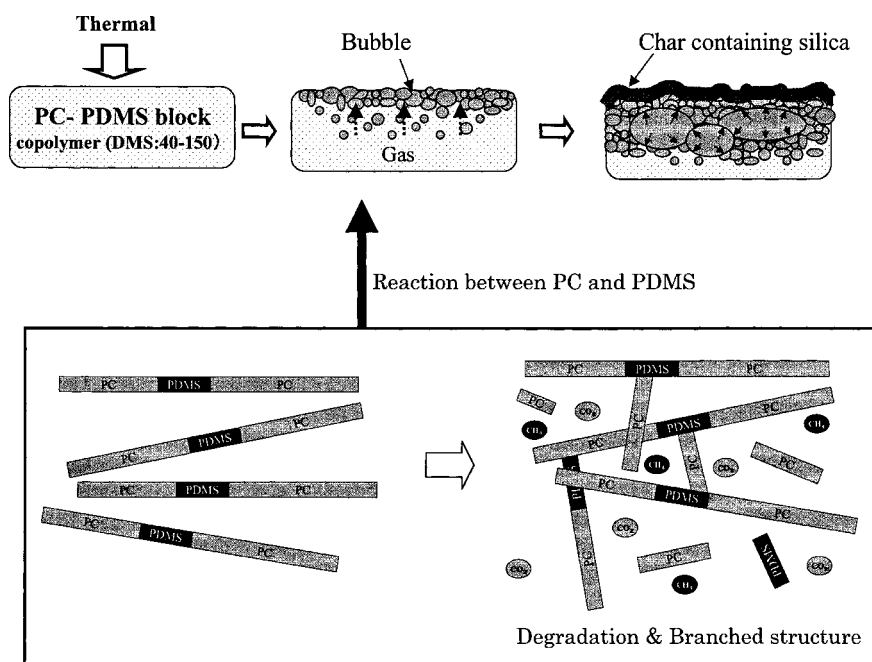


Figure 19 Schematic drawing of flame retardant behaviors in the PC-PDMS block copolymer.

form a lot of fine bubbles before the formation of char and the bubbles can inhibit the supply of flammable gases and heat transfer without the formation of char. So although the formation of char is late, the flame retardancy is possible. Moreover, the morphology of the char on PC-PDMS block copolymer differs from that of the PC-blended PDMS compound. Figure 18 shows the photographs of the chars by scanning electron microscopy. The char of PC-PDMS block copolymer (PC-PDMS-40) forms spherical closed cells that seem to cut off the gases efficiently, but the char of the PC blended PDMS compound has a lot of hole and sealing of the gases is not sufficient. The thermal stability of the char on PC-PDMS block copolymer is high because silica particles on the surface protect the heat. But the thermal stability of the char on the PC-blended PDMS compound is the same as ordinary PC when the LOI of char: oxygen index in which the char begins to glow).¹⁴ So the char generated from PC-PDMS block copolymer is excellent in flame retardancy and even the thin char layer could cut off the gases. The flame retardant behaviors of the PC-PDMS block copolymer is illustrated conceptually in Figure 19.

Considering this behavior, the flame retardancy of PC containing the silicone (e.g., PC-PDMS block copolymer) is higher when the maximum loss rate is lower and the maximum rate temperature is higher. To be such thermal behavior, it is necessary to control the reaction between PC and DMS by the dispersion and the content of PDMS. The optimum PDMS domain size is thought to be ~ 50 nm and on that

occasion the PDMS content is 0.5–1.0 wt %. The flame retardancy of PC-blended PDMS compound could increase if the size of PDMS domain were small adequately such as PDMS compound in PC-PDMS block copolymer. Furthermore, the thermal degradation could be controllable by the structure of silicone compound in addition to silicone domain size and so the maximum loss rate could decrease without lowering of maximum rate temperature, that is, the flame retardancy increases.

CONCLUSIONS

When the PDMS block size of PC-PDMS block copolymer is shorter than DMS unit of 150, the maximum rate temperature decreases with the PDMS content because the reaction between PC and PDMS increases. When DMS unit is 100, the amount of residue containing many silica particles increases and the maximum loss rate lowers most. The copolymerization PDMS to PC and the PDMS block size determine the PDMS domain size and influence the thermal degradation behavior, which depends on the PDMS domain size and the PDMS content. The thermal degradation in the PC containing PDMS is inhibited most when the PDMS domain size is ~ 50 nm. The control of nanodispersion of PDMS causes the change of the thermal degradation behavior in PC.

The PDMS block copolymer with DMS unit of 100 has highest flame retardancy at 1.0 wt % PDMS because this PDMS block copolymer has lowest maximum loss and higher maximum rate temperature. The optimum PDMS domain size for flame retard-

ancy is ~ 50 nm. The high flame retardant PC-PDMS block copolymers can form a lot of fine bubbles and the char with high thermal stability as the role of good thermal insulator by the reaction of PC and PDMS in combustion. The char has the preferable structure that prevents volatile fuel productions.

References

1. Nouvertne, W. U.S. Pat. 3,775,367 (1973).
2. Mark, V. U.S. Pat. 3,909,490 (1975).
3. Nodera, A. Jpn. Pat. 06-306268 (1994).
4. Nodera, A.; Umeda, H.; Hashimoto, K. U.S. Pat. 5,449,710 (1995).
5. Nodera, A. U.S. Pat. 6,127,465 (2000).
6. Nodera, A.; Chiba, J. Eur. Pat. EP 692522B1 (2002).
7. Wang, Y.; Yi, B.; Wu, B.; Yang, B.; Liu, Y. *J Appl Polym Sci* 2003, 89, 882.
8. Nodera, A.; Kanai, T. *J Appl Polym Sci* 2004, 94, 2131.
9. Kambour, R. P.; Klopfer, H. J.; Smith, S. A. *J Appl Polym Sci* 1981, 26, 847.
10. Nodera, A. In *Proceedings of FRCA 1999 International Conference*, New Orleans, LA, 1999; p 177.
11. Nodera, A. *J Mater Life Soc* 2003, 15, 61.
12. Nodera, A.; Uozumi, Y.; Hayashi, T. *J Mater Life Soc* 2004, 16, 95.
13. Iji, M.; Serizawa, I. *Polym Adv Technol* 1998, 9, 593.
14. Nodera, A.; Kanai, T. *J Appl Polym Sci* 2006, 100, 565.
15. Grubbs, G. R.; Kleppick, M. E. *J Appl Polym Sci* 1982, 27, 601.
16. Okamoto, M. *J Appl Polym Sci* 2002, 84, 514.
17. Okamoto, M. *J Appl Polym Sci* 2002, 86, 1123.
18. Funt, J. M.; Parekh, D.; Magill, J. H.; Shah, Y. T. *J Polym Sci Polym Chem Ed* 1975, 13, 218.
19. Noll, W. *Chemistry and Technology of Silicone*; Academic Press: New York, 1968; p 319.
20. Montaudo, G.; Puglisi, C.; Samperi, F. *Polym Degrad Stab* 1989, 26, 285.
21. Kambour, R. P. *J Appl Polym Sci* 1981, 26, 861.