# Flame Retardancy of Polycarbonate–Polydimethylsiloxane Block Copolymer/Silica Nanocomposites

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**ABSTRACT:** This report describes the flame retardancy and the thermal degradation behavior of polycarbonate–polydimethylsiloxane (PC–PDMS) block copolymer/silica nanocomposites. PC–PDMS block copolymer with dimethylsiloxane (DMS) block size 40 units increased the dispersibility of nanosized amorphous silica. Addition of the slight nanosized silica caused the increment of flame retardancy of PC–PDMS block copolymer, and the PC–PDMS block copolymer with 1.0 wt % PDMS had the highest limiting oxygen index value when the nanosized silica was added 0.5 wt %. The maximum rate temperature of the PC–PDMS block copolymer increased with the addition of silica and the maximum loss rate was the lowest when silica content is 0.5 wt %. The monodisperse nanosized silica had an effect that enhances the flame retardant mechanism of PDMS for PC. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3862–3868, 2006

**Key words:** polycarbonate; polydimethylsiloxane; silica; flame retardance; degradation

## INTRODUCTION

Polycarbonate (PC) has excellent mechanical properties and flame retardancy and is used for various applications. For electronic and electric applications, because high flame retardancy is required, flame-retardant technologies for PC have been developed.[1–8] 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 PC–polydimethylsiloxane (PC–PDMS) block copolymers with the moderate PDMS dispersion (domain size approximately 50 nm) had high flame retardancy.[14] Then, the flame retardancy is higher when the maximum loss rate is lower and the maximum rate temperature is higher. The thermal degradation causes the formation of many bubbles and the increment of char containing a lot of Si element (i.e. silica).[15] On the other hand, the flame retardant technologies of nanocompomsites have been developed recently.[16–20] Kashiwagi et al. reported that the addition of nanosilica (13% by mass) in poly(methylmethacrylate) reduced the peak heat release rate roughly 50% in Cone calorimeter, but the flame retardant effectiveness of nanosilica was not as good as that of silica gel that formed silica network to cover the entire sample surface.[19,20] However, flame-retardant PC/silica nanocomposite systems have been hardly reported in the literature.

This report describes the dispersibility of nanosized silica in PC and PC–PDMS block copolymer and the flame retardancy of PC–PDMS block copolymer/silica nanocomposites. Furthermore the relationship between the flame retardancy and the thermal degradation of PC–PDMS block copolymer/silica nanocomposite was studied.

## EXPERIMENTAL

### Materials

PC–PDMS block copolymer used in this study was the same as prepared in a previous article.[14,21,22] This PC–PDMS block copolymer has a viscosity-average molecular weight of 19,200 and melt flow index 20 g/10 min (conditions: 300°C, 1.2 kg), and contains the PDMS with DMS block size unit 40 at 3.0 wt % content. Polycarbonate used in this study was Toughlon FN1900A (trade name from Idemitsu Kosan Co.). This is bisphenol A-type polycarbonate having a viscosity-average molecular weight of 19,000 and melt flow index 20 g/10 min. The amount of PDMS was prepared by melt-kneading and extruding mixture of PC–PDMS block copolymer and PC (Toughlon FN1900A). Amorphous nanosized silica is Nyasil 6200 (Nayacol Nano Technology) with an average particle size of 50 nm. Colloidal silicas are Nyacol DP5820 and DP5480 (Nayacol Nano Technology) with ethylene glycol 30% silica sol and each average particle size is 20 and 50

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nm. Amorphous microsized silica used to compare is FB48 (Denki Kagaku Kougyo Kabushiki Kaisha) with an average particle size of 16 $\mu$m.

### 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.

### Haze

The haze was performed according to JIS K7205 method by using haze meter (Suga test instruments Co. HZ-1). The sample bars with 3 mm thickness were made by injection molding.

### Limited oxygen index

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 Seisaku-sho). 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 in open platinum pan under nitrogen (50 mL/min) 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.

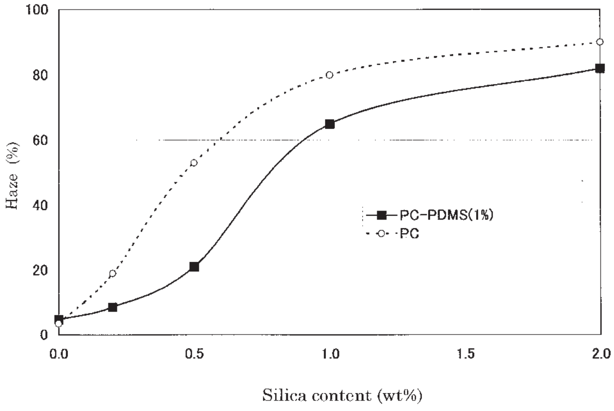
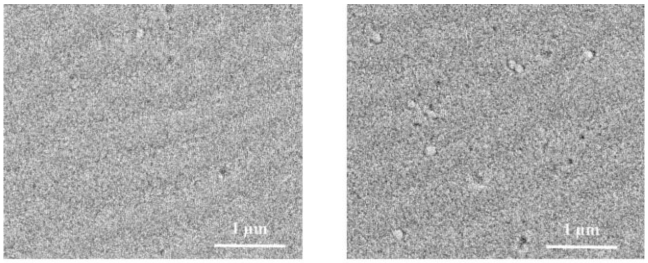


**Figure 1** Values of haze as a function of the nanosized silica content for PC–PDMS block copolymer with 1.0 wt % PDMS content and PC.



(A) PC-PDMS (B) PC

**Figure 2** Photographs of the nanosized silica dispersed in PC–PDMS block copolymer (a) and PC (b) by SEM.

### Scanning electron microscopy

PC–PDMS block copolymer containing the nanosized silica was observed by scanning electron microscopy (JEOL, JSM-6100) operating at acceleration voltage of 15 kV. The surface of samples was shaved by glass-cutter. The samples were coated with gold by using an ion sputter (JEOL, JEC-1100) to enhance conductivity.

## RESULTS AND DISCUSSION

### Dispersibility of nanosized silica in PC–PDMS block copolymer

First, the dispersibility of nanosized silica in the PC–PDMS block copolymer and PC was investigated. Figure 1 shows the values of haze as a function of nanosized silica content for the PC–PDMS block copolymer with 1.0 wt % PDMS and PC. When PDMS content in the PC–PDMS block copolymer with DMS block size unit 40 is 1.0 wt %, the flame retardancy is the highest. Large aggregations of silica particles increase the value of haze because PC and silica have a difference in index of refraction. Hazes of PC–PDMS block copolymer and PC increase as the nanosized silica content increases, but the haze of PC–PDMS block copolymer is lower than that of PC. So, the dispersibility of nanosized silica in PC–PDMS block copolymer is expected to be better than that in PC. Figure 2 shows the photographs of nanosized silica dispersed in PC–PDMS block copolymer and PC by SEM. The content of nanosized silica is 2.0 wt %. Silica aggregations (100–200 nm) in PC–PDMS block copolymer seem to be less than those in PC and it is thought that a lot of silica in PC–PDMS block copolymer exists as primary particles (50 nm) that can not be observed by the photographs of SEM. At least, it was found out that the aggregations of nanosized silica caused the increment of the haze.

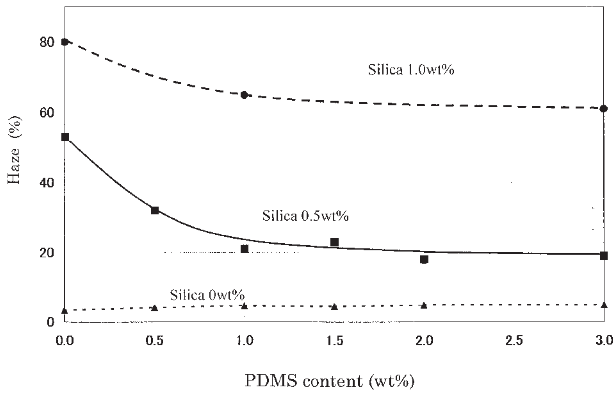


**Figure 3** Values of haze as a function of the PDMS content for PC–PDMS block copolymer with 0, 0.5, and 1.0 wt % silica.

Next, the effect of PDMS content in PC–PDMS block copolymer on the dispersibility of nanosized silica was investigated. Figure 3 shows the values of haze as a function of PDMS content in PC–PDMS block copolymer for nanosized silica content 0, 0.5, and 1.0 wt %. The evaluated PC–PDMS block copolymer without nanosized silica is transparent until 3.0 wt % PDMS. The values of haze in PC–PDMS block copolymer with nanosized silica decrease greatly until 1.0 wt % PDMS, and especially the decrement is larger when nanosized silica content is 0.5 wt %. It is thought that such a behavior is because the nanosized silica is added with powder of an aggregated particle and cannot be distributed enough by only mechanical mixing.

## Flame retardancy and thermal degradation on PC–PDMS block copolymer with nanosized silica

The flame retardancy on PC–PDMS block copolymer with nanosized silica was investigated. The LOI values of PC–PDMS block copolymer and PC as a function of nanosized silica content are shown in Figure 4.

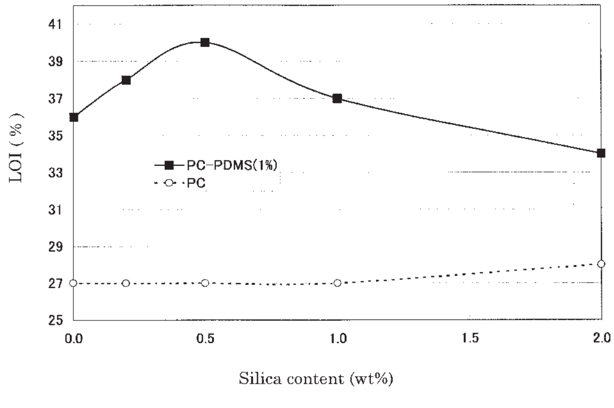


**Figure 4** LOI values as a function of the nanosized silica content for PC–PDMS block copolymer with 1.0 wt % PDMS and PC.

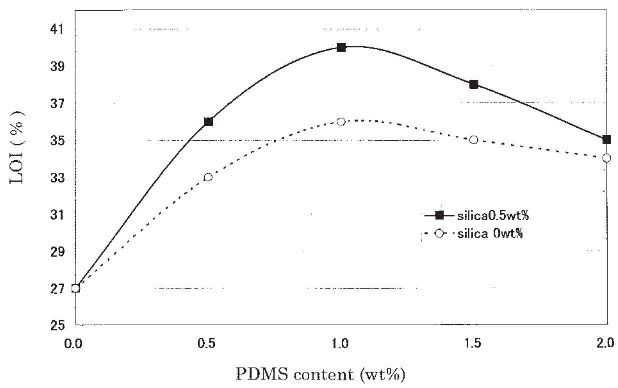


**Figure 5** LOI values as a function of the PDMS content for PC–PDMS block copolymer with 0.5 and 0 wt % silica.

The LOI values of PC–PDMS block copolymer increase with addition of the slight nanosized silica and the maximum LOI is 40 at 0.5 wt % silica. When the silica content increases more than 0.5 wt %, the LOI decreases to 34 at 2.0 wt % silica. The LOI value is lower than that of PC–PDMS block copolymer containing no silica. On the other hand, the LOI values of PC hardly change even though the nanosized silica is added and the slight nanosized silica has no effect of increment of LOI value.

Next, the flame retardancy of PC–PDMS block copolymer containing 0.5 wt % nanosized silica on the PDMS content was investigated. Figure 5 shows the result of LOI. This result was compared with PC–PDMS block copolymer containing no silica. The LOI values of PC–PDMS block copolymer containing 0.5 wt % nanosized silica are higher than those of PC–PDMS block copolymer containing no silica and get maximum at 1.0 wt % PDMS. The PC–PDMS block copolymers containing 0.5 wt % and no silica have similar LOI behavior with maximum value, but the maximum LOI with 0.5 wt % silica seems to shift to fewer PDMS content. Also in UL94 test, the PC–PDMS block copolymer containing 0.5 wt % nanosized silica had high flame retardancy and was ranked as V-0 at 1.0 mm thickness.

Furthermore, the influence of silica size was tested. The tested samples are PC–PDMS block copolymers (1.0 wt % PDMS) containing 0.5 wt % silica, which have the highest flame retardancy. The amorphous

**TABLE I**
**LOI and Haze of Different Particle Size Silicas**

| Average particle size | LOI (%) | Haze (%) |
|---|---|---|
| Colloidal silica | | |
| 50 nm | 38 | 16 |
| 20 nm | 40 | 8.5 |
| Microsilica | | |
| 16 $\mu$m | 27 | 91 |

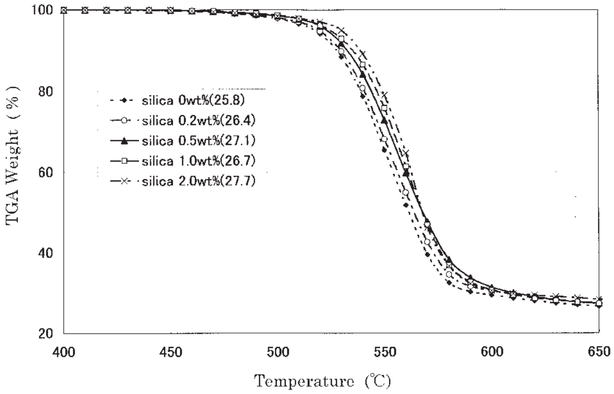


**Figure 6** TGA curve and the amount of residue for PC–PDMS block copolymer (1.0 wt % PDMS) with 0–2.0 wt % nanosized silica, the number in parenthesis shows the amount of residue.

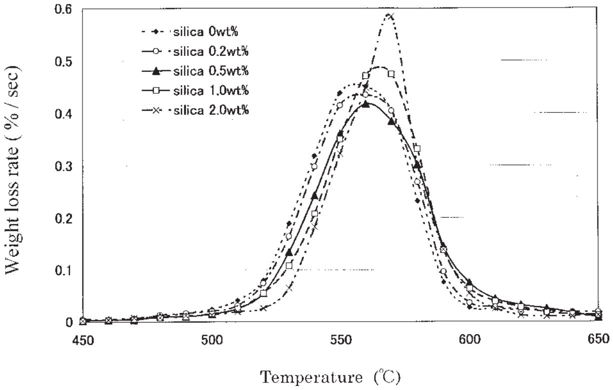


**Figure 8** Weight loss rate for PC–PDMS block copolymer (1.0 wt % PDMS) with 0–2.0 wt % nanosized silica on temperature by TGA.

microsized silica with an average particle size of 16 μm decreases largely the LOI of PC–PDMS block copolymer and the LOI value is almost the same as PC. The colloidal silica with an average particle size of 20 nm has higher flame retardancy as compared with the colloidal silica with an average particle size of 50 nm (Table I). It is thought that the colloidal silica has lower flame retardancy than the nanosized silica because the colloidal silica contains 70 wt % ethylene glycol, which has low flame retardancy.

The thermal degradation behavior of PC–PDMS block copolymer containing the nanosized silica was investigated to consider the increment of flame retardancy. The thermogravimetric analysis (TGA) curves of the evaluated samples with the different silica content are depicted in Figure 6. The value within parentheses shows the amount (%) of residue at 650°C. The TGA curves of PC containing the nanosized silica are shown in Figure 7, as compared with the curves of the PC–PDMS block copolymers. The initial degradation temperature of PC–PDMS block copolymer increases as the nanosized silica content increases, and then the residue tends to increase in consideration of the blended silica content. On the other hand, the TGA curves of PC are the almost same until 1.0 wt % silica and the thermal degradation temperature of PC with 2.0 wt % silica decreases contrary to the behavior of the PC–PDMS block copolymer. The increment of these residues by adding the silica is less than that of PC–PDMS block copolymer. Furthermore, Figures 8 and 9 show the weight loss rates of each PC–PDMS and PC sample on the temperatures in TGA to clear degradation behavior. The maximum weight loss rates of the PC–PDMS block copolymers decrease until 0.5 wt % silica, but on the contrary, the rates increase from 1.0 wt % silica. The maximum loss rate at 0.5 wt % silica is the lowest 0.42 wt %/s. Moreover, the maximum rate temperatures increase as the silica content increases. On the other hand, the maximum loss rates and the maximum rate temperatures of PC containing the nanosized silica decrease with the silica content.

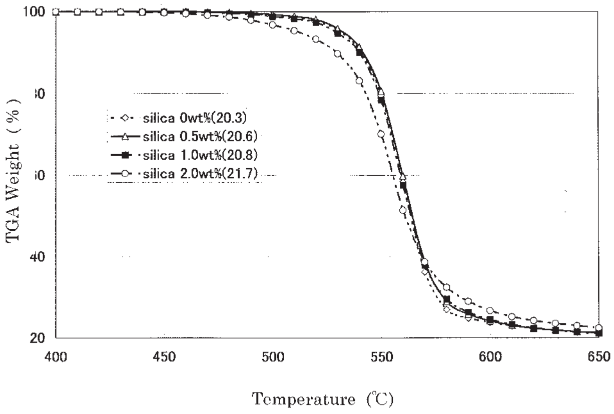


**Figure 7** TGA curve and the amount of residue for PC with 0–2.0 wt % nanosized silica, the number in parenthesis shows the amount of residue.

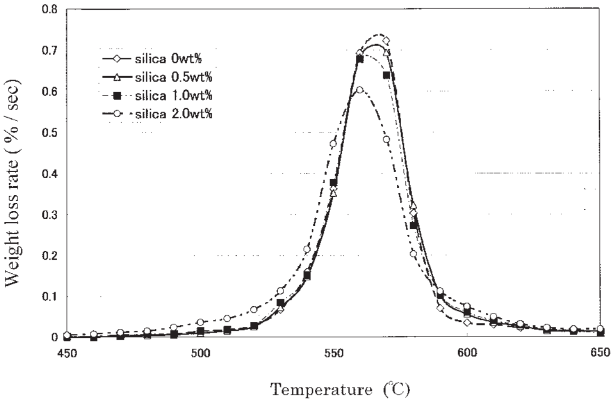


**Figure 9** Weight loss rate for PC with 0–2.0 wt % nanosized silica on temperature by TGA.

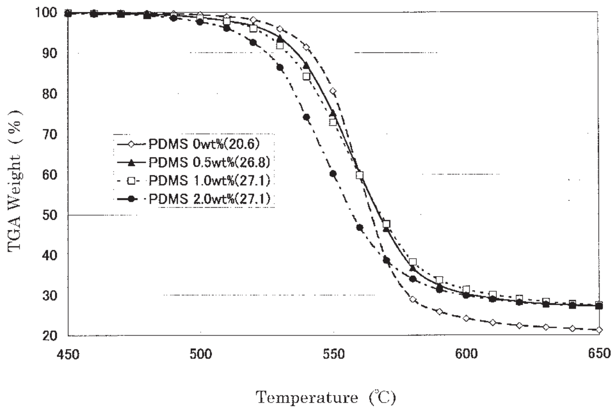


**Figure 10** TGA curve and the amount of residue for PC–PDMS containing 0.5 wt % nanosized silica with the different PDMS content, the number in parenthesis shows the amount of residue.

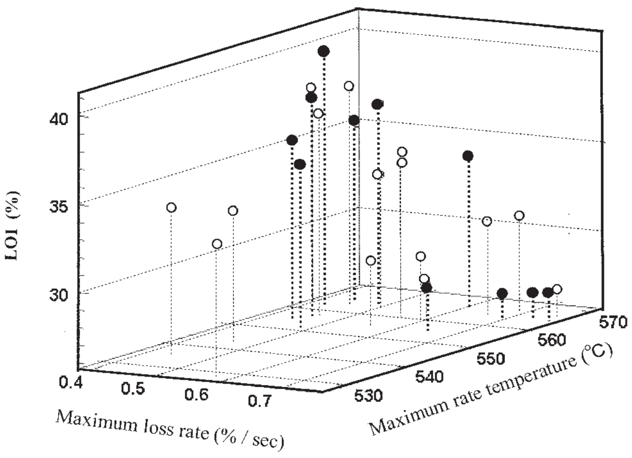


**Figure 12** LOI to the maximum loss rate and the maximum rate temperature, (●) indicates copolymer containing silica, (○) indicates copolymer containing no silica.

The TGA curves of PC–PDMS block copolymers containing 0.5 wt % nanosized silica with the different PDMS content are depicted in Figure 10. The value within parentheses shows the amount (%) of residue at 650°C. The weight loss rates on the temperature are shown in Figure 11. The initial degradation temperature decreases as the PDMS content increases and the PC–PDMS block copolymers have a lot of residue, which seems not to depend on the PDMS content. The maximum weight loss rate is the lowest at 1.0 wt % PDMS and the maximum rate temperature decreases as the PDMS content increases. The behavior is similar to PC–PDMS block copolymer containing no silica,[14] but the thermal stability and the amount of residue for PC–PDMS block copolymer are slightly enhanced by adding the nanosized silica.

Figure 12 shows the change of the LOI to the maximum loss rate and the maximum rate temperature. The data are all evaluated samples containing the nanosized silica (black dots) and PC–PDMS block copolymer containing no silica (white dots).[14] When the maximum loss rate is low and the maximum rate temperature is high, the LOI tends to increase. The behavior is similar to PC–PDMS block copolymer containing no silica and the small amount (less than 1.0 wt %) of the nanosized silica is thought to enhance the flame retardancy of PC–PDMS block copolymer. The higher maximum rate temperature means the generation of flammable gases at higher temperature and so the ignition of the PC–PDMS block is more delayed. Moreover, when the maximum loss rate is lower, the degradation of the PC–PDMS block copolymer is more inhibited. Then the LOI value of PC–PDMS block copolymer containing the nanosized silica is higher. On the other hand, when the maximum rate temperature decreases, LOI values decrease because the flame spreads easily on the surface as we previously reported for PC containing organic metal salts.[8]

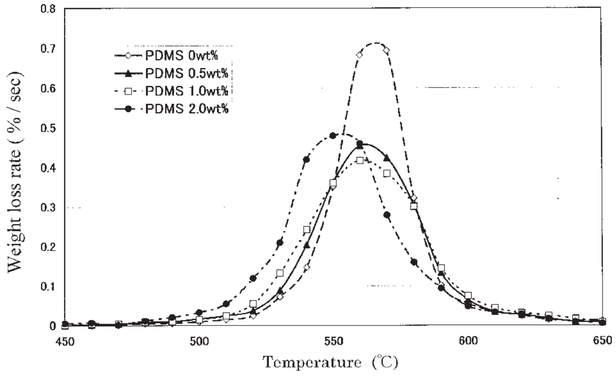


**Figure 11** Weight loss rate for PC–PDMS containing 0.5 wt % nanosized silica with the different PDMS content on temperature by TGA.

The enhancement of the flame retardancy of PC–PDMS block copolymer by adding the nanosized silica is considered. The PDMS of PC–PDMS block copolymer is mainly distributed on the surface of the nanosized silica by physical interaction of each Si—O bond.[22] Then it is thought that the thermal stability of PDMS increases and the surface activity of the silica decreases. Therefore, the reaction between the decomposing PC and the degrading PDMS occurs at higher temperature and so the maximum rate temperature would be higher (Fig. 8). On the other hand, when the nanosized silica is added to PC, the degradation of PC is promoted by the surface activity of the silica.

It is thought that the maximum loss rate decreases because nanosized silica particles increase in the residue and the residue having a good sealing efficiency forms.[14] The interaction between the silica and PDMS would be a factor that a lot of silica remains in the residue. When the size of silica is 20–50 nm, the sealing efficiency of residue would be higher. This size is

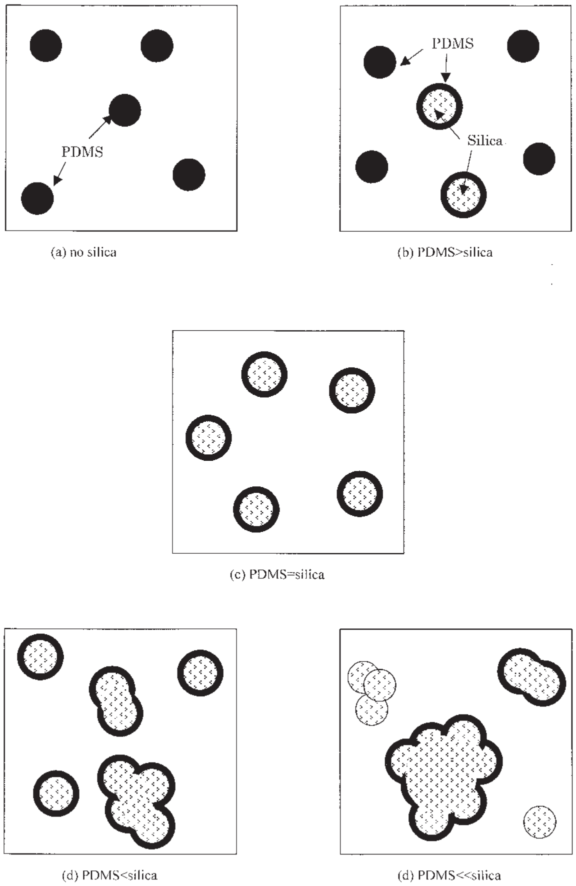


**Figure 13** Distributions of PDMS in the PC–PDMS block copolymers containing the nanosized silica.

the almost same as the size of PDMS domain effective in flame retardancy.

Microsized silica (or silica aggregated at more than 1.0 wt % silica in PC–PDMS block copolymer) has a little effect on the sealing efficiency of residue because microsized silica cannot cover enough on the surface of the residue. Furthermore, when the nanosized PDMS domains (~50 nm, which has high flame retardancy) move to surface of the microsized silica particles, the reaction between PC and PDMS decreases and so the flame retardancy of PC–PDMS block copolymer decreases. It is supposed that the PDMS on the surface of microsized silica takes a behavior similar to large PDMS domain ineffective in flame retardancy.[14] Therefore, LOI values of the PC–PDMS block copolymers with microsized silica or a lot of aggregated nanosized silica are lower.

Based on such results, the distributions of PDMS in the PC–PDMS block copolymers containing the nanosized silica are supposed. These conceptual models are shown in Figure 13. When the nanosized silica content is less than the PDMS content (Fig. 13(b)), mono dispersion of the silica is carried out and the silica surface is covered with the PDMS. The monodispersed silica is effective in the flame retardant enhancement of PC–PDMS block copolymer. As the nanosized silica content increases, a part of the silica particles aggregates and the aggregated silica surface is also covered with the PDMS (Fig. 13(d)). And as more increases, the aggregated silica particles and the silica particle that is not covered with the PDMS increase (Fig. 13(e)). Then, the flame retardancy of PDMS decreases. It is though that the change in the distributions of PDMS influences the thermal degradation behavior (i.e., flame retardancy) of PC–PDMS block copolymer. Furthermore, this result could clarify the flame retardant mechanism of PC–PDMS block copolymer by the moderate PDMS dispersion (domain size ~50 nm).[14]

The nanodispersion of silica (20–50 nm) in the PC–PDMS block copolymer is thought to increase the LOI. So, the higher flame retardancy of PC–PDMS block copolymer would be expected if the dispersibility of nanosized silica at high content gets excellent.

## CONCLUSIONS

The dispersibility of the nanosized silica in PC–PDMS block copolymer is more excellent than that in PC by physical interaction between silica and PDMS. The addition of a slight silica with average particle size of 20–50 nm causes the increment of flame retardancy in PC–PDMS block copolymer, and the PC–PDMS block copolymer with 1.0 wt % PDMS has the highest flame retardancy when the addition of the nanosized silica is 0.5 wt %. This is because the maximum rate temperature is higher than that of PC–PDMS block copolymer containing no silica and the maximum loss rate is the lowest. Then, it is thought that the PDMS is located on the surface of nanosized silica particle and so the PDMS has higher thermal stability and generates the high sealing residue covered with more nanosized silica particles in combustion. When PDMS content is not contained enough to the nanosized silica content, the silica particles aggregate. Then, the aggregated nanosized silica and the PDMS on the surface less remain as the nanosized silica particles in the residue and so the flame retardancy is lower. The monodisperse nanosized silica has an effect that enhances the flame retardant mechanism of PDMS in PC.

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