

Effects of Liquid-Type Silane Additives and Organoclay on the Morphology and Thermal Conductivity of Rigid Polyisocyanurate-Polyurethane Foams

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ABSTRACT: This article investigates the effects of liquid-type silane additives and organoclay as a solid-type additive on the morphological, mechanical and thermal insulating properties of polyisocyanurate-polyurethane (PIR-PUR) foams. The organoclay likely acted as nucleating agents during the formation of PIR-PUR foams. When the liquid silane additives and organoclay were added, the cell size and thermal conductivity of the PIR-PUR foams appeared to be decreased. However, organoclay did not contribute to reduce the cell size distribution of the foam. PIR-PUR foams synthesized with tetramethylsilane as a liquid-type additive showed a smaller average cell size and lower thermal conductivity than that of PIR-PUR foams synthesized with the other silane additives or with

organoclay as a solid-type additive. For the PIR-PUR foam with organoclay/TEMS (1.5/1.5 php) mixture, cell size and thermal conductivity of the foam showed similar to the foam with TEMS. These results suggest that smaller cell size appears to be one of the major factors in the improvement of thermal insulation properties of the PIR-PUR foams. Silane additives did not seem to have a strong effect on the flammability of the PIR-PUR foams. However, heat resistance was more dominant for the foam with the organoclay at the higher temperature. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 3117–3123, 2012

Key words: rigid polyisocyanurate-polyurethane foam; thermal conductivity; morphology; mechanical property

INTRODUCTION

Rigid polyisocyanurate-polyurethane (PIR-PUR) foam and rigid polyurethane (PUR) foam have been widely used for insulation in construction and industrial applications due to their superior mechanical properties and low thermal conductivity.^{1–7} However, PUR foams have had limited use at high temperatures due to the low thermal stability of the urethane groups. The trimerization of isocyanate, forming isocyanurates, creates excellent high temperature-resistant cellular structural units. PIR-PUR foams in which some urethane groups were substituted by isocyanurate rings show high mechanical properties and improved flame retardant properties, but the foam tends to be more brittle due to the in-

crement of ring structures and the degree of cross-linking.^{8–17}

To overcome the problems mentioned above, researchers have attempted to develop techniques to decrease friability values by lowering the ratio of isocyanurate to urethane functional groups in PIR-PUR polymer chains.^{12–14} There have also been some attempts to blend PIR-PUR with other flexible polymers, as well as other composite preparation methods.^{15–18} These techniques to decrease the isocyanurate content to improve flexibility, however, may deteriorate the flame retardant characteristics of PIR-PUR foams.

In our early reports,^{5,19,20} studies were undertaken to develop environmentally friendly PUR foams that have high thermal insulation properties. The research thus far has elucidated the effect of clay as an additive on the cell size and thermal insulation of PUR foams. Also, previous work has studied methods to obtain small and uniform cells in PUR foams by adding surfactants²¹ or nucleating agents and liquid silane additive²² and also reported that lower cell size improved thermal insulation. The foams studied in our previous work were polyurethane foams which did not contain cyclotrimerization of isocyanate, forming isocyanurates by potassium 2-ethylhexanoate catalyst and excess isocyanate group.

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TABLE I
Chemical Compositions Used in the Preparation of PIR-PUR Foams

Chemicals	Content (php)					
	(a)	(b)	(c)	(d)	(e)	(f)
MDI (4, 4'-diphenylmethane diisocyanate)	160.0	160.0	160.0	160.0	160.0	160.0
Polyether polyol	40.0	40.0	40.0	40.0	40.0	40.0
Polyester polyol	60.0	60.0	60.0	60.0	60.0	60.0
Surfactant (polysiloxane ether)	2.0	2.0	2.0	2.0	2.0	2.0
Blowing agents (distilled water)	2.5	2.5	2.5	2.5	2.5	2.5
Catalyst (potassium 2-ethylhexanoate)	1.5	1.5	1.5	1.5	1.5	1.5
Flame retardant (tris(chloro 2-propyl) phosphate)	15.0	15.0	15.0	15.0	15.0	15.0
Organoclay	–	3.0	–	–	–	1.5
(3-Aminopropyl)triethoxysilane	–	–	3.0	–	–	–
Tetraethylorthosilicate	–	–	–	3.0	–	–
Tetramethylsilane	–	–	–	–	3.0	1.5

The purpose of this study is to adopt these previously reported techniques that decrease foam cell size to prepare PIR-PUR foam with lower friability and higher mechanical and flame retardant properties. To obtain smaller cell sizes, the surface tension of the polymer solution has to be decreased, and generally, silane compounds are used for this purpose. In this study, the effects of solid organoclay and liquid silane additives on cell morphology, mechanical and thermal insulation properties of PIR foams blown by water alone were investigated by scanning electron microscopy (SEM), a universal testing machine (UTM) and thermal conductivity analysis, respectively.

EXPERIMENTAL

Materials

The materials used in this study were obtained from commercial sources. Polymeric 4, 4'-diphenylmethane diisocyanate (PMDI) was supplied by BASF Korea (Seoul, Korea). The average functionality of PMDI was 2.7 and the NCO content was 30–32 wt %. The polyols used in this study were polyether type and polyester type polyols. Pentaerythritol and glycerin-based polyether polyol (NaOH = 370 mg KOH/g, 2050 cps) were supplied by KPX Chemicals (Ulsan, Korea). Glycol-based polyester polyol (NaOH = 330 mg KOH/g, 2100 cps) was supplied by Aekyung Petrochemical (Seoul, Korea). Distilled water used as a chemical blowing agent was generated in our laboratory. The cyclotrimerization catalyst was potassium 2-ethylhexanoate from OMG Americas (OH). Polysiloxane ether (Tegostab B8462), used as a surfactant, was from Goldschmidt's (Essen, Germany). Flame retardant was tris(chloro 2-propyl) phosphate from Daihachi Chemical Industry (Tokyo, Japan). Amine-treated organoclay (30B clay, organic modifier: $N^+(\text{CH}_2\text{CH}_2\text{OH})_2\text{CH}_3\text{T}$, where T is tallow: C18/C16/C14 = 65/30/5, mean size: 14.9 μm)

was used as comparative solid-type additives, and was supplied by Southern Clay (TX). Three different kinds of silane liquid-type additives, (3-aminopropyl)triethoxysilane, tetraethylorthosilicate and tetramethylsilane (TEMS), were purchased from Sigma Aldrich Korea (Yongin, Korea). The polyols were dehydrated at 90°C for 24 hours in a vacuum oven before use, and the other chemicals were used as received. The chemical compositions of the materials used in the preparation of PIR-PUR foams are shown in Table I.

Preparation of PIR-PUR foam

First, polyols, catalyst, surfactant, flame retardant and silane liquid-type additive were put into a reactor and mixed for 30 seconds. Rotating speed started from 500 rpm and gradually increased up to 2500 rpm. Low speed at the initial stage of mixing is desirable for homogeneous mixing of highly viscous polyols and additives of low viscosity. Then, foaming agent was added and reactants were mixed again at 3000 rpm for 30 seconds. PMDI was next added into the reactants and all reactants were mixed for 15 seconds using a brushless type stirrer at 5000 rpm. Finally, the reactants were poured into the open mold (250 mm \times 250 mm \times 250 mm) to produce free-rise foams. They were cured for 1 day at room temperature to prevent deterioration of thermal conductivity and mechanical properties.

To prepare PIR-PUR foams with the organoclay, PMDI and the organoclay were premixed at 3000 rpm with a mechanical stirrer in an oil bath at 50°C for 2 hour. The organoclay content was fixed at 3 wt % based on PMDI. After premixing, ultrasound (40 kHz, BLT vibrator type) was applied to the mixture of organoclay and PMDI for 15 min. The PIR-PUR/organoclay foams were synthesized by reaction between the polyol and PMDI containing the modified clay with ultrasound. When distilled water alone was used as the blowing agent, the amount of

distilled water was 2.5 parts per hundred polyol by weight (php). The amount of blowing agent was controlled to set the density of all the PIR-PUR foam samples at 50 kg/m^3 .

Thermal conductivity measurements

Thermal conductivities of PIR-PUR foam with five different additives were measured using a thermal conductivity analyzer (model TCA Point2, Anacon) according to the ASTM C518 standard test method. The PIR-PUR foam sample was placed in the test section between two plates, which were maintained at different temperatures during the test. The temperatures of the upper and bottom plates were 37.7 and 10°C , respectively. To obtain steady state between the plates, the time required was about 20 min. Upon achieving thermal equilibrium and establishing a uniform temperature gradient throughout the sample, the thermal conductivity of the PIR-PUR foam was determined. The size of the specimen was $200 \times 200 \times 25 \text{ mm}^3$ (width \times length \times thickness). The thermal conductivities of three specimens per sample were measured and averaged.

Scanning electron microscopy (SEM)

Morphology of the PIR-PUR foam was studied with a field emission scanning electron microscope (FE-SEM) (Hitachi Model S-4300SE, Tokyo, Japan). The samples were cryogenically fractured and the surface was coated with gold before scanning. The accelerating voltage was 25 kV. We used image analysis software (ImageJ) to determine the cell size of the sample.

Mechanical properties

Mechanical properties of PIR-PUR foam samples were measured under ambient conditions using an Instron universal testing machine (Model 4467, Canton, OH). A compressive test was performed according to the ASTM D1621 test method. The size of each specimen was $30 \times 30 \times 30 \text{ mm}^3$ (width \times length \times thickness), and the speed of crosshead movement was 3.00 mm/min . The strengths of 10 specimens per sample were measured and averaged for each mechanical test. A flexural test was performed according to the ISO 1290 test method. The size of each specimen was $25 \times 120 \times 20 \text{ mm}^3$ (width \times length \times thickness). The span distance was 100 mm, and the crosshead speed was 10.00 mm/min .

Fire retardance test

The inflammability of the prepared PIR-PUR foams was measured according to ASTM D 635-98. The

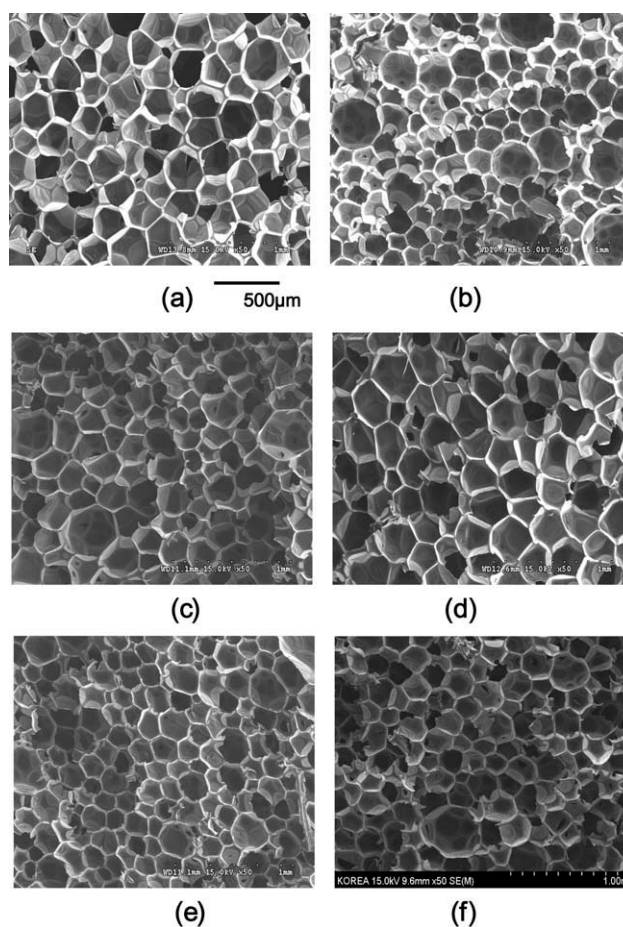


Figure 1 SEM of PIR-PUR foams blown by water with: (a) no additive, (b) organoclay, (c) (3-aminopropyl)triethoxysilane, (d) tetraethylorthosilicate, (e) tetramethylsilane, and organoclay/tetramethylsilane (1.5/1.5 php) mixture.

size of each specimen was $13 \times 130 \times 10 \text{ mm}^3$ (width \times length \times thickness). Test specimens were placed in the flame for 30 seconds. The ignition time of the burned length (75 mm) of the test piece was measured. The fire retardant properties of five specimens per sample were measured and averaged.

RESULTS AND DISCUSSION

Cell morphology

The cell size and shape of the PIR-PUR foams are very important in determining the thermal conductivity and mechanical properties of rigid foams.^{23,24} Figure 1 shows scanning electron micrographs of cryogenically fractured cross-sectional surfaces of PIR-PUR foams blown by distilled water (2.5 php). Figure 1 also shows the effects of additives on the cell morphology of the PIR-PUR foams, with organoclay, (3-aminopropyl)triethoxysilane, tetraethylorthosilicate, tetramethylsilane (TEMS) and organoclay/TEMS (1.5/1.5 php) mixture shown in Figure 1(b–f), respectively.

TABLE II
Cell Size and Standard Deviation of PIR-PUR Foams with Additive

Additive	Without additive	Organoclay	3-(Aminopropyl) triethoxysilane	Tetraethyl-orthosilicate	Tetramethylsilane	Organoclay/tetramethylsilane (1.5/1.5 php)
Cell size (μm)	266	208	223	269	184	187
Standard deviation (μm)	35	43	43	40	32	36

In the PIR-PUR foam produced with the additive TEMS shows the smallest average cell size, about 184 μm in diameter, with a uniform distribution of cells, as observed in Figure 1(e). The average cell size of PIR-PUR foam with (3-aminopropyl) triethoxysilane [Fig. 1(c)] is smaller than that of the foam with tetraethylorthosilicate [Fig.1(d)], with approximate diameters of 223 and 269 μm , respectively. For the PIR-PUR foam with organoclay/TEMS (1.5/1.5 php) mixture, cell size of the foam shows similar to the foam with TEMS. These results are likely due to the lower surface tension of the asymmetric molecule (3-aminopropyl) triethoxysilane, which allows it to be emulsified more uniformly in the polymer solution, allowing a higher nucleation rate.²⁵ In the measurements of surface tension, the polyol solutions with TEMS, (3-aminopropyl) triethoxysilane and tetraethylorthosilicate added showed 41.6, 44.5, and 48.6 mN/m, respectively. Zhang et al.²⁵ have reported that as silane content and the silane backbone length are increased, the surface tension is decreased. In this work, TEMS has the highest silane content in its molecular structure, and it seems that its low surface tension prohibits the coalescence of bubbles and promotes the formation of small, dense cells. The cell size of each sample prepared and standard deviation of the PIR-PUR foams are shown in Table II.

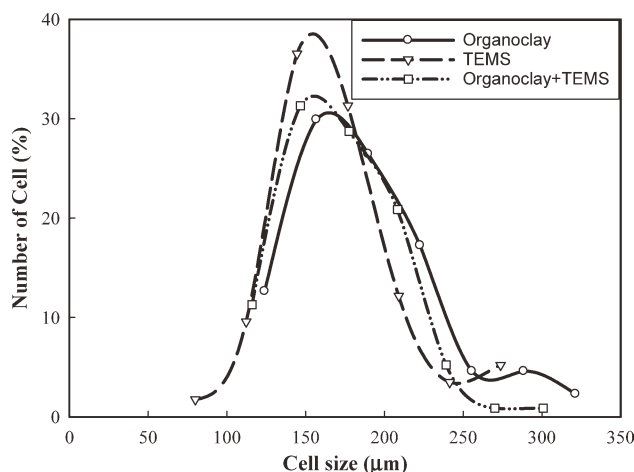


Figure 2 Cell size distribution of PIR-PUR foams with: (○) organoclay, (▽) tetramethylsilane, (□) tetramethylsilane/organoclay (1.5/1.5php) mixture.

Figure 2 shows cell size distribution of the PIR-PUR foams with organoclay, TEMS and organoclay/TEMS (1.5/1.5 php) mixture. From Figure 2, cell distribution is observed to be quite uniform for the PIR-PUR foams with TEMS compared the forms with organoclay and organoclay/TEMS mixture. From Table II, standard deviations for the PIR-PUR foam with organoclay, TEMS and organoclay/TEMS mixture are observed to be 43, 32, and 36 μm , respectively. From these results, it is suggested that organoclay may contribute to reduce cell size of the foams but not in reducing cell size distribution.

Thermal conductivity of PIR-PUR foam

Thermal conductivities of rigid PIR-PUR foams synthesized with five different additives were investigated, and the effects of these additives on thermal conductivity are shown in Figure 3. From Figure 3, the thermal conductivity of the foam with TEMS added is 0.0277 W/mK, also lower than that of the neat PIR-PUR foam, 0.0293 W/mK. The results can be explained by differences in the cell size of the foam. When the TEMS is used, the cell size of the PIR-PUR foam is decreased and consequently, the thermal conductivity is decreased. From the results presented in Figures 1 and 3, the cell size and

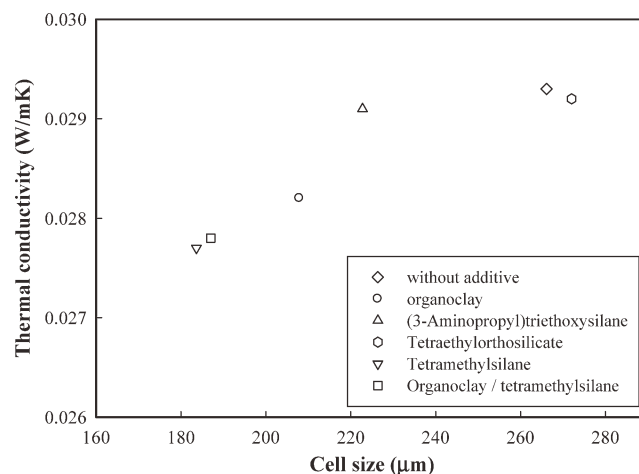


Figure 3 Relationship between thermal conductivity and cell size of PIR-PUR foams with: (◇) no additive, (○) organoclay, (△) (3-aminopropyl)triethoxysilane, (○) tetraethylorthosilicate, (▽) tetramethylsilane, and (□) organoclay/tetramethylsilane (1.5/1.5 php) mixture.

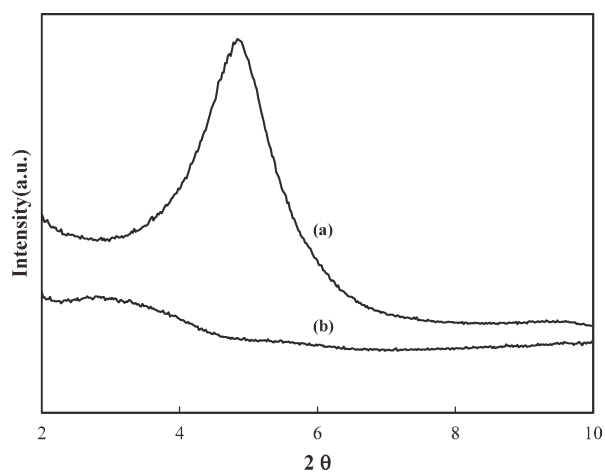


Figure 4 Wide-angle X-ray diffraction patterns of clay and PIR-PUR foams: (a) pure organoclay, (b) PIR-PUR foam filled with organoclay.

thermal conductivity of the PIR-PUR foam formed with organoclay are also decreased compared to PIR-PUR foam formed without additives. For the PIR-PUR foam with organoclay/TEMS (1.5/1.5 php) mixture, thermal conductivity of the foam shows similar to the foam with TEMS.

Figure 4(a,b) shows the wide-angle X-ray diffraction (WAXD) patterns of the pure organoclay and the PIR-PUR foam filled with clay, respectively. Generally, as the d-spacing of the clay layer increased, the 2θ peak of the clay layer decreased. Also, when the clay layer is intercalated or exfoliated, the intensity of the peak is decreased. As shown in Figure 4(b), ultrasound appears to assist clay modification to effectively break up clay agglomerates and facilitate intercalation of the sili-

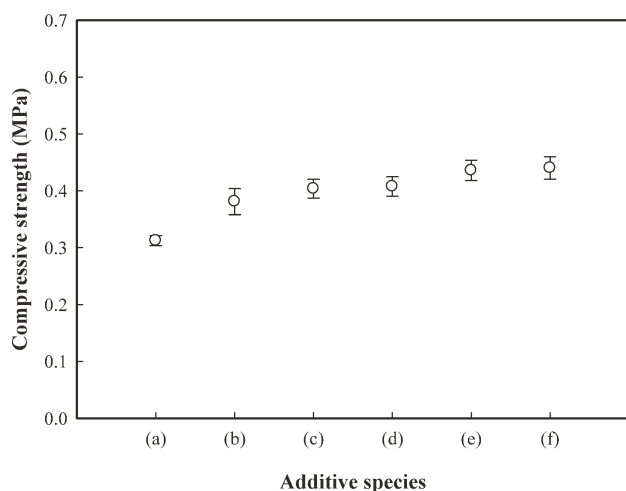


Figure 5 Compressive strength of PIR-PUR foams with: (a) no additive, (b) organoclay, (c) (3-aminopropyl)triethoxysilane, (d) tetraethylorthosilicate, (e) tetramethylsilane, and (f) organoclay/tetramethylsilane (1.5/1.5 php) mixture.

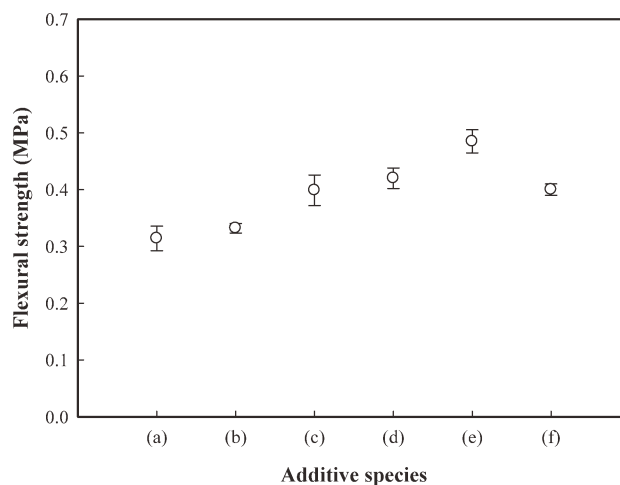


Figure 6 Flexural strength of PIR-PUR foams with: (a) no additive, (b) organoclay, (c) (3-aminopropyl)triethoxysilane, (d) tetraethylorthosilicate, (e) tetramethylsilane, and (f) organoclay/tetramethylsilane (1.5/1.5 php) mixture.

cate layers. Exfoliated organoclay layers are known to be a nucleation agent and serve as a site for bubble growth.^{26,27} If the organoclay is distributed uniformly, it can promote even nucleation and growth of PIR-PUR foam cells.

Mechanical properties of PIR-PUR foam

Compression and flexural strengths of PIR-PUR foams with various additives are shown in Figures 5 and 6, respectively. In particular, brittle fracturing of the PIR-PUR foam surface was observed in PIR-PUR foams blown by water, which is a property typically due to high crosslinking density in the polymer molecules. When liquid-type silane additives are added, mechanical properties of the foams are relatively

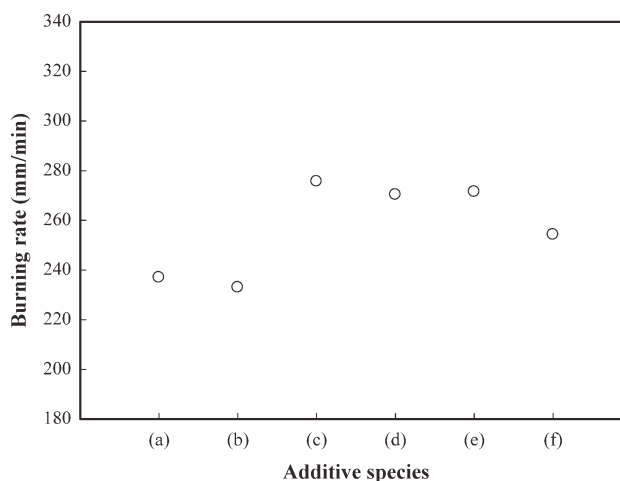


Figure 7 Flame retardant test of PIR-PUR foams with: (a) no additive, (b) organoclay, (c) (3-aminopropyl) triethoxysilane, (d) tetraethylorthosilicate, (e) tetramethylsilane, and (f) organoclay/tetramethylsilane (1.5/1.5 php) mixture.

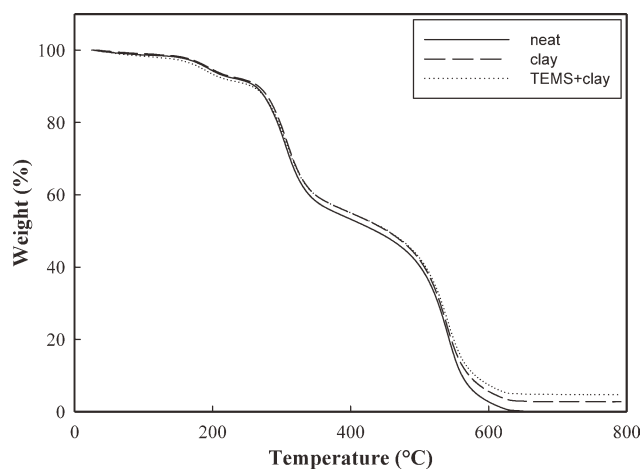


Figure 8 Thermogravimetric analysis of PIR-PUR foams with: (—) without additive, (---) organoclay, (····) organoclay/tetramethylsilane (1.5/1.5 php) mixture.

improved. Addition of organoclay and liquid silane additives seems to be desirable to improve the mechanical properties of PIR-PUR foams. The increase in mechanical strength is may be due to the decrease of the cell size of the PIR-PUR foams.

Inflammability of PIR-PUR foam

The flammability test results, measured by the procedure of ASTM D 635-98, are shown in Figure 7 for PIR-PUR foams blown by water alone. Liquid-type silane additives do not seem to have a strong effect on the flammability of PIR-PUR foams. However, flame retardance of PIR-PUR foams with organoclay added seems to be higher than the other foams, as can be seen from the burning rates shown in Figure 7.

In the thermal degradation studies of rigid PUR foams by many investigators,^{28–30} Pielichowski et al.^{29,30} have shown that there is a stabilization effect of additives such as sodium dihydrogenphosphate, trisodium pyrophosphate and sodium aluminumcarbonate in the initial stage of degradation, and the decomposition proceeded in two steps up to 600°C. Figure 8 shows thermogravimetric analysis of the PIR-PUR foams which contains tris(chloro 2-propyl) phosphate. From Figure 8, thermal degradation proceeds sharply at about 300°C, then the second weight loss proceeds sharply in between 500 and 600°C which is similar results by Pielichowski et al.^{29,30} From Figure 8, the weight loss is observed more significantly for the foam without adding organoclay compared the foams with organoclay. This is probably because that the organoclay inhibits heat transfer, therefore, heat resistance is more dominant for the foams with the organoclay at the higher temperature.

CONCLUSIONS

Rigid PIR-PUR foams were synthesized with liquid-type additives such as (3-aminopropyl)triethoxysilane, tetraethylorthosilicate and TEMS, and organoclay, a solid-type additive. Scanning electron microscopy and thermal conductivity measurements showed that PIR-PUR foams synthesized with TEMS have smaller average cell sizes and lower thermal conductivity than those synthesized with other additives. When TEMS was added, the average cell size of PIR-PUR foam became more uniform and finer due to lower surface tension of the polymer solution. The PIR-PUR foams with organoclay added, cell size and thermal conductivity of the foams were decreased. However, organoclay did not contribute to reduce the cell size distribution of the foam. For the PIR-PUR foam with organoclay/TEMS (1.5/1.5 php) mixture, cell size and thermal conductivity of the foam showed similar to the foam with TEMS. From the above results, smaller cell size appears to be one of the major reasons for the improvement of the thermal insulation properties of PIR-PUR foams.

PIR-PUR foams blown by water showed brittle fractures on the foam surface. Compression and flexural strengths of PIR-PUR foams with organoclay and silane additives showed slightly higher values than those of PIR-PUR foams without any additive. PIR-PUR foams produced by cyclotrimerization of isocyanate groups in the polyurethane matrix showed high flame retardance and thermal stability. Silane additives did not much affect flammability. However, the PIR-PUR foam with organoclay inhibited heat transfer, therefore, heat resistance was more dominant for the foam with the organoclay at the higher temperature.

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