

Newly Developed Superior Flame Retardant All Water-Blown Polyisocyanurate Foams

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ABSTRACT

Recently hydrofluorocarbons (HFCs), hydrocarbons (HCs) and water have been used as blowing agents in a rigid polyurethane foam field. Taking into consideration of earth environmental protection, safety working conditions and cost, all water-blown system is the most superior one. Water reacts with isocyanate and produces carbon dioxide (CO₂) which is an inert gas with a lower global warming potential than HFCs. Different from HCs, CO₂ is a nonflammable gas and is not a Volatile Organic Compound. In addition, all water-blown systems do not require investment cost for safety operation such as a fire preventive equipment.

Rigid polyisocyanurate (PIR) foams show high flame resistance and thermal stability. However, all water-blown PIR foams have some problems compared with HFCs and HCs, such as poor dimensional stability, poor adhesion to substrates, flammability, insufficient storage stability of polyol premix and so on. In order to solve these problems, especially to improve flame retardancy, we have examined all water-blown PIR foams. The relationship between some components of PIR foams and combustibility behavior of foams was examined by using limited oxygen index (LOI), and cone calorimeter test. As a result, the PIR foam showed over 30 of LOI value at high index. Furthermore a new isocyanate was developed to improve flame retardancy.

Thus, we have developed new superior flame retardant all water-blown PIR foams. The newly developed system will be accepted for construction, especially for metal-faced sandwich panels and sidings which require high-level flame retardancy.

INTRODUCTION

Rigid polyurethane foams have been widely used as insulation materials in the construction industry. In Japan, the production of HCFC-141b for the blowing use has been terminated by the 31st December 2003. Nowadays, Hydrofluorocarbons (HFC-245fa, HFC-365mfc), hydrocarbon (cyclopentane) and water (CO₂) have been largely used as blowing agents.

These blowing agents have their disadvantages respectively. For example HFCs have high global warming potential (GWP) and are expensive. Because cyclopentane (CP) is a flammable and volatile organic compound, the fire preventive equipment is needed for its safety operation. CO₂ has high thermal conductivity and faster diffusion rate than air though CO₂ is an environmental friendly gas (lower GWP) [1,2]. However as a result of many investigations and improvements, all water-blown foams have been used in various applications including building materials where high-level thermal insulation performance is not required. In Japan, the market size of rigid polyurethane and polyisocyanurate foams that used water as blowing agent is about 30 percent of the total production in 2006.

Rigid PIR foams show high flame resistance and thermal stability. As one of the approaches to promote the application of environmentally friendly PIR system, the further development of high fire-resistant all water-blown PIR system is expected. However the improvement of flame retardant property of high index all water-blown PIR system is difficult from the following reasons. The system requires larger amounts of isocyanate than HFC and HC system under the same index because water reacts with isocyanate. The use of excess amount of isocyanate leads to poor cure, high friability, poor adhesion to facer materials, and a steep rise profile around gelling time.

Aromatic polyester polyols are primarily used in PIR systems to improve fire resistance performance. However polyester polyol is easily hydrolyzed in the coexistence of a certain amount of water and catalyst, especially high pH amine

based catalyst. The hydrolysis causes poor storage stability of polyol premix, delay of reaction, and deterioration of physical properties. Several investigations have been studied on preventing the hydrolysis [3-5]. As the case may be, a multi-component mixing head is needed in order to handle these components separately. Therefore, the system without aromatic polyester polyols was basically examined in this report. Tris β -chloropropyl phosphate (TCPP) was used as a flame retardant. The high index all water-blown PIR foams show good dimensional stability because of its high crosslink density even when more than 10wt% TCPP is used. The use of halogen-free flame retardant to all water-blown PIR system remains to be solved. Silicate was also investigated as a supporting flame retardant. It is considered that the silicone compounds form stable char layer containing Si-O, Si-C bond and aromatic ring structure during burning process.

In Japan, typical test method of evaluating flammability is an exothermic test using cone calorimeter. This flammability test based on ISO-5660 is arranged to match with Japanese regulation of building and construction materials. The Japanese classification is shown in Table 1. Total heat release (THR) and Peak heat release rate (Peak HRR) are calculated by oxygen consumption [6].

This paper reports the flammability and the other physical properties of the newly developed superior flame retardant all water-blown PIR foams.

Class	Test condition	Requirements
Non-combustible materials	heat flux level 50 kW/m ² heating duration 20 minutes	THR < 8 MJ/m ² Peak HRR* < 200 kW/m ²
Quasi non-combustible materials	heat flux level 50 kW/m ² heating duration 10 minutes	No appearance deformation, melting, cracking, or other damage detrimental to the fire prevention
Fire-retardant materials	heat flux level 50 kW/m ² heating duration 5 minutes	

*Peak HRR is allowed to exceed 200 kW/m² provided the time interval where the heat release rate stayed above 200 kW/m² is less than ten seconds.

EXPERIMENTAL

Formulation and Raw Materials

Table 2 reports typical formulation presented in this paper. Mannich condensate-based polyether polyol was used as a solo polyol to enhance flame retardancy. The amount of TCPP was varied from 10% to 40% in the total formulation. The amount of silicone surfactant was fixed at 0.6%. Water content was varied from 0.9% to 1.5%. The isocyanate index was varied from 200 to 500. As shown in Figure 1, polyol wt% in the total formulation is decreased relatively when water content and isocyanate index are increased. Therefore it is theoretically impossible to increase index. Table 3 shows the relationship between water content in the total formulation and upper limit of the index. Polymeric MDI with its average functionality of 2.8 was used as standard isocyanate. In order to improve cure and adhesive strength, additives were used up to 0.5% according to need. Tertiary amine, quaternary ammonium salts, and organic acid potassium salts were used as catalysts. The amount of catalysts was adjusted to obtain the gelling time from 55 to 60 seconds.

Raw Material	Content (wt% in the total formulation)
Mannich condensate-based polyether polyol OHV=350	varied
TCPP	varied (standard level 20)
Silicone surfactant	0.6
Catalysts	GT=55-60
Water	varied (standard level 1.0)
Additives	varied (max 0.5)
Polymeric MDI	varied

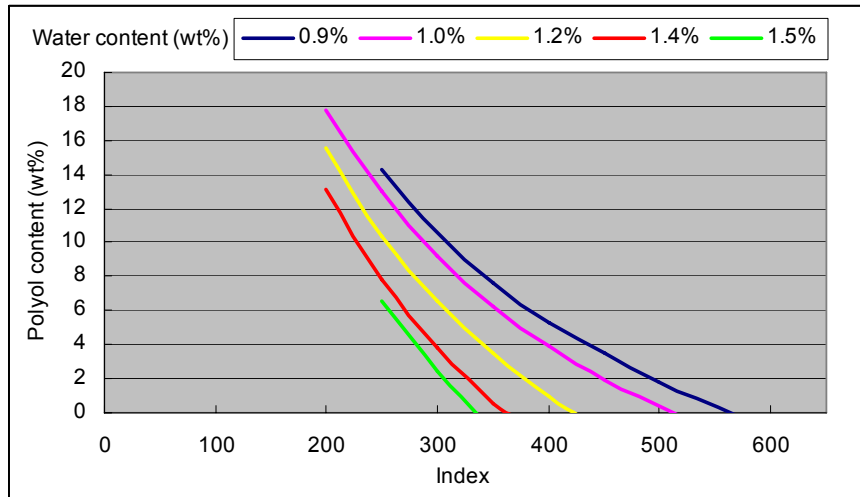


Figure 1. Relationship between index and polyol content

Water content in the total formulation (wt%)	0.9	1.0	1.2	1.4	1.5
Upper limit of Index	<600	<550	<450	<400	<350

Foam Preparations

All foam samples were prepared by using a standard hand mixing method as follows. Each temperature of polyol and isocyanate was kept at 20°C. For the measurement of reactivity and free rise density, the component of polyol and isocyanate was mixed at 6,000rpm for 4 seconds and poured into the aluminum open box of 250 (length) × 250 (width) × 250mm (height).

For the preparation of foam samples for physical properties, the mixture of polyol and isocyanate was poured into the aluminum open mold of 500 (width) × 60 (breadth) × 500mm (height) which was adjusted to 60°C. The foam was demolded after 10 minutes and was conditioned more than 72 hours at room temperature.

Test Method

FOAM PHYSICAL PROPERTIES

Various physical properties were measured in accordance with the following standards.

Foam Density	ASTM D-1622
Compressive Strength	ASTM D-1621
Dimensional Stability	ASTM D-2126
Limited Oxygen Index	JIS K-7201
Cone Calorimeter Test	ISO-5660 (Quasi non-combustible test; test time 10min.; sample thickness 25mm)
Thermal Conductivity	ASTM C-518 (Auto lambda model HC-074)

ADHESION STRENGTH

The foam sample for the adhesion tests was prepared by using the aluminum open mold of 500 (length) × 250 (width) × 20mm (height). The mold temperature was kept at 75°C. The mixture (ca. 120g) of polyol and isocyanate was poured into the edge of the mold where an aluminum facer (thickness 0.07mm) was preset. Then the mold was closed with the upper aluminum plate where an aluminum facer was preset. The foam was demolded after 5 minutes. The sample was cut to the size of 100 × 100mm. Tensile tester (IMADA model DPS-50R) was used as a spring balance. The aluminum facer was pulled slowly from the edge of the sample. The maximum adhesion strength was measured immediately after demolding and after conditioning for 24h at room temperature, respectively.

FLOWABILITY

The foam sample for the flowability test was prepared by using the aluminum open mold of 500 (length) × 250 (width) × 20mm (height). The mold temperature was kept at 75°C. The mixture (ca. 120g) of polyol and isocyanate was poured into the edge of the mold, then the mold was closed with the upper aluminum plate. After demolding, the flowability was measured.

RESULTS AND DISCUSSION

Effect of Water content and Index

Figure 2 shows densities of test sample when water content and index are changed. In the case of the same water content, as index increases, a steep rise profile around gelling time makes the sample densities low. High functionality isocyanate was effective to prevent bubble destruction around cream time and coarse cells especially in the case of high index and high water content. The foam had very coarse cells under the conditions with water content 1.4% index 350, and water content 1.2% index 400, where polyol wt% in the total formulation became 1% or less. LOI under the conditions, except for these two points, is shown in Figure 3. LOI is proportional to the index. The LOI of low water content is more than that of high water content at the same index. αNCO is used as the weight fraction of isocyanate for the total formulation, i.e., $\alpha\text{NCO} = \text{weight of isocyanate} / \text{weight of (polyol + isocyanate)}$. In the each water content, the correlation coefficient of αNCO and LOI is higher than that of index and LOI. The results of THR and peak HRR are shown in Figures 4 and 5, respectively. As the isocyanate index is increased, the THR is tended to decrease. Peak HRR decreases as the isocyanate index increases and levels off at approximately 80 kW/m². Figure 6 shows the relationship between combustion time and THR. When the water content was 1.2% or more, the THR was above approximately 10MJ/m² and the combustion time was more than 100 seconds because the combustion flame spread to the back of the sample. When a crack occurred on the combustion surface, combustion time became longer and THR increased. THR was below approximately 10MJ/m² when the combustion time was less than 100 seconds. Quick formation of char layer on the combustion surface would lead to the decreasing combustion time. The quick formation of char layer in early combustion stage is the key point in order to reduce THR. In terms of fast and uniform char formation, fine-cell and voidless foam would be effective in order to reduce THR. Figure 7 shows a certain level of correlation between Peak HRR and LOI ($R^2=0.77$).

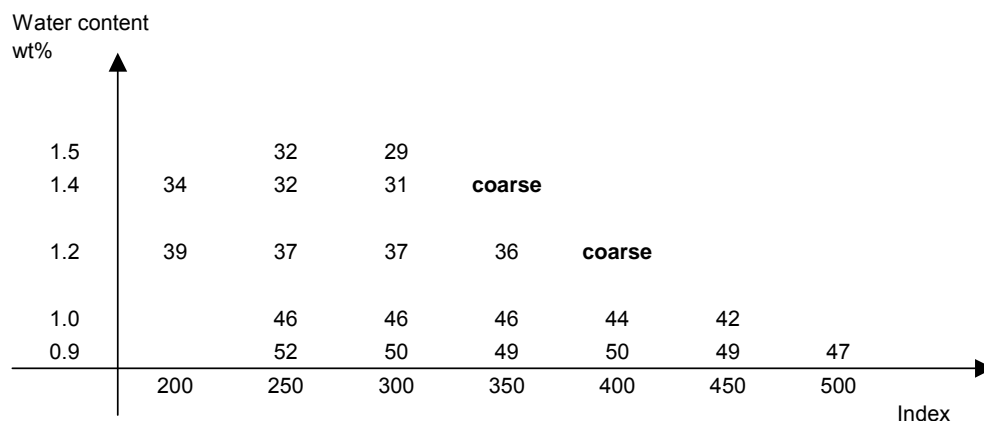


Figure 2. Relationship between Index and Test sample Density

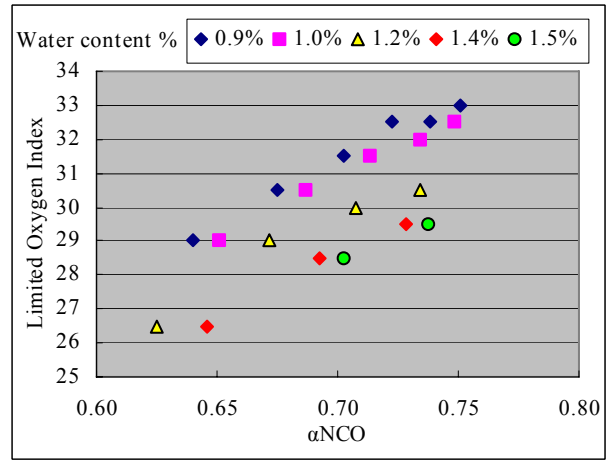
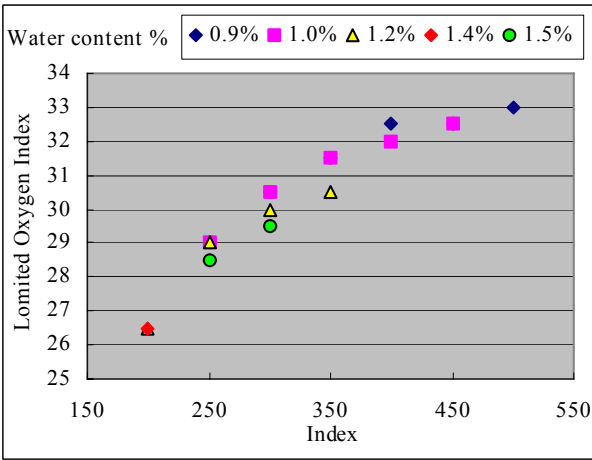


Figure 3. Relationship between Index (or α NCO) and LOI

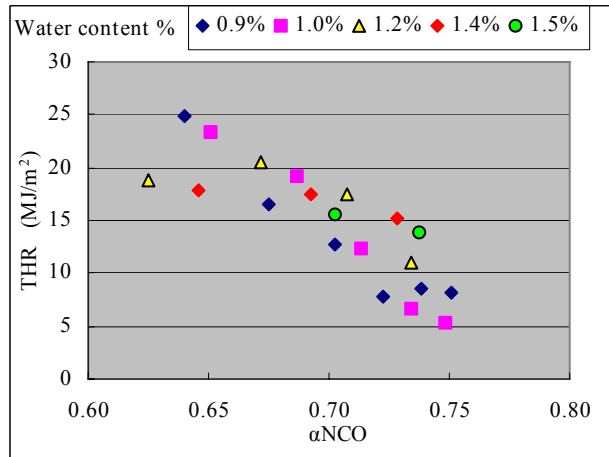
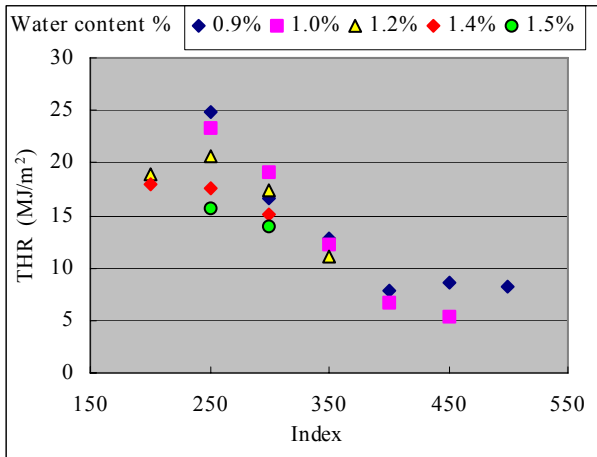


Figure 4. Relationship between Index (or α NCO) and THR

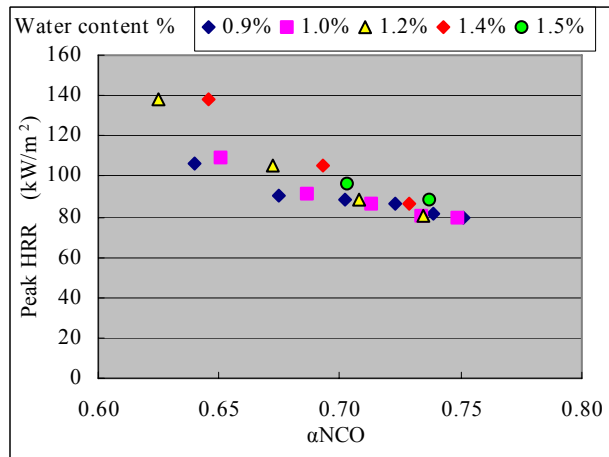
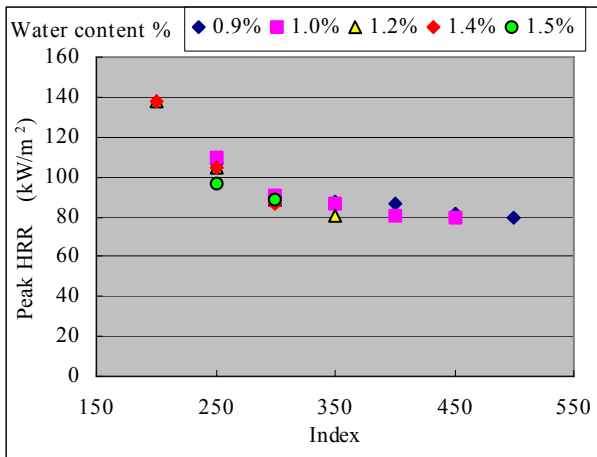


Figure 5. Relationship between Index (or α NCO) and Peak HRR

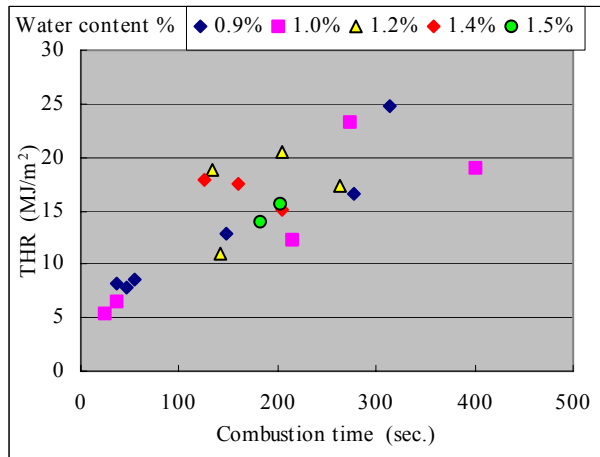


Figure 6. Combustion time and THR

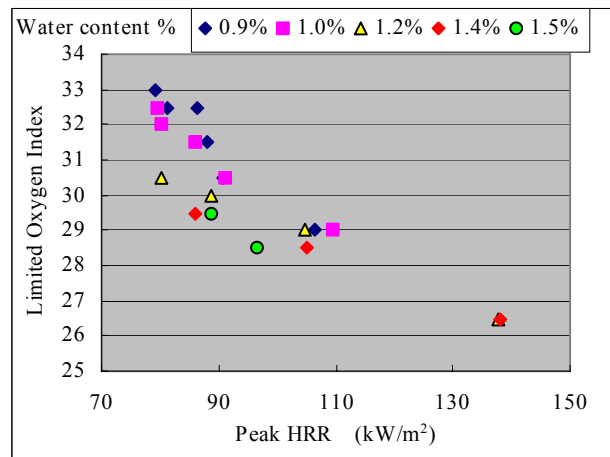


Figure 7. Peak HRR and LOI

Effect of Flame Retardant

The effect of flame retardant (TCPP) on foam physical properties is summarized in Table 4. TCPP wt% in the total formulation was varied from 10% to 40%. THR decreased as the amount of TCPP increased until it reached at 30%. TCPP at 40% showed a poorer result compared with TCPP at 30%. TCPP at 40% had a lot of small flames on the combustion surface. Judging from the combustion state and the combustion time, a char layer to cut off the flame would be insufficient because the foam contained excess amounts of plasticizer, TCPP. Volume change at 120°C deteriorated above 30%. Compressive strength decreased a lot, especially when TCPP quantity was 30% or more.

TCPP (wt%)	10	15	20	30	40
Index	350	350	350	350	350
Core foam density (kg/m ³)	43.5	42.8	44.4	44.5	44.4
Cone Calorimeter Test					
Peak heat release rate (kW/m ²)	95	86	87	89	92
Total heat release (MJ/m ²)	18.6	15.2	11.3	7.7	16.7
combustion time (sec.)	346	220	139	52	311
Weight retention (%)	25	28	28	27	23
Limited Oxygen Index	29.5	31.0	31.5	31.5	31.5
Dimensional stability (vol.%)					
120°C×48h	0.0	-1.2	-1.2	-4.5	-11.5
90°C×48h	0.3	-1.1	-0.6	-1.0	-2.5
70°C95%RH×48h	0.9	-0.1	-1.9	-0.9	0.0
-20°C×48h	-0.7	-0.9	-0.2	-0.3	1.3
Compressive Strength (MPa)					
Parallel	0.37	0.33	0.31	0.23	0.16
Perpendicular	0.17	0.17	0.18	0.14	0.11
Thickness	0.23	0.20	0.20	0.17	0.13

Effect of Isocyanate

The effect of isocyanate on flammability is summarized in Table 5. High functionality polymeric MDI showed lower Peak HHR, THR and higher weight retention than low functionality polymeric MDI. The foams that used higher functional isocyanate showed higher compressive strength and higher friability.

isocyanate functionality	2.7	2.8	2.9
Index	400	400	400
Core foam density (kg/m ³)	40.3	41.6	42.1
Cone Calorimeter Test			
Peak heat release rate (kW/m ²)	86	80	79
Total heat release (MJ/m ²)	7.1	6.7	6.6
combustion time (sec.)	45	41	34
Weight retention (%)	26	32	33
Limited Oxygen Index	32.5	32.5	32.5
Compressive Strength (MPa)			
Parallel	0.24	0.27	0.29
Perpendicular	0.13	0.14	0.17
Thickness	0.16	0.18	0.19

Effect of Isocyanate with Silicate

Silicate was added to a polymeric MDI with its average functionality of 2.9. The effect of isocyanate with silicate on flammability is summarized in Table 6. Silicon/Carbon mol% ratio of the sample surface after testing was higher than that of the sample bottom. It was assumed that the silicate contained in foam moved to the surface due to heat, some of the silicate decomposed and reacted with carbon to form glassy char layer. When the amount of silicate was increased from 0.2% to 0.7% in the total formulation, weight retention increased. On the other hand, weight retention decreased when the amount of silicate increased to more than 2.2%. It was assumed that an optimum amount of the silicate, which reacted with the carbon of the sample surface, was limited and an excessive amount of silicate deteriorated flammability because silicate itself was inflammable.

Silicate (wt%)	0.0	0.2	0.4	0.7	2.2	3.6	
Index	400	400	400	400	400	400	
Core foam density (kg/m ³)	42.5	42.8	43.0	43.0	41.7	41.5	
Cone Calorimeter Test							
Peak heat release rate (kW/m ²)	78	75	75	80	92	98	
Total heat release (MJ/m ²)	6.8	5.8	5.4	8.3	19.9	18.2	
Combustion time (sec.)	36	24	35	71	299	257	
Weight retention (%)	33	36	38	37	22	21	
Limited Oxygen Index	32.5	32.5	32.5	32.5	32.0	31.5	
Element ratio of silicon and carbon (Si/C mol%)							
after testing	surface	1.29	1.31	3.77	6.73	8.25	9.44
	bottom	0.10	0.11	0.28	0.48	0.56	0.83
before testing		0.08	0.11	0.22	0.17	0.36	0.51

Properties of Newly Developed All Water-Blown PIR System

The properties of the newly developed all water-blown PIR system are summarized in Table 7. The properties of ortho phthalic acid based polyester polyol (PES), which has OHV=350, systems are also summarized for comparison. LOI of the new system was 32. The CP-blown system had longer combustion time and larger THR than the all water-blown system because of a crack which occurred on the combustion surface. Appearance of the test sample after the cone calorimeter test is shown in Figure 8. The new all water-blown system was superior in flammability to the CP-blown system. The superiority of the new all water-blown system in flammability would be influenced by the nonflammable gas and larger amount of isocyanate in the total formulation.

<i>Table 7. Physical properties of Newly Developed All Water-Blown PIR Systems</i>				
Polyol		Mannich	PES	PES
Blowing agent		water	water	CP
Water (wt%)		1.0	1.0	0.16
Index		400	400	400
α NCO		0.74	0.73	0.60
Free Foam Reactivity				
	Cream Time (sec.)	10	12	23
	Gel Time (sec.)	58	57	59
	Tack Free Time (sec.)	89	112	127
	Rise Time (sec.)	86	82	86
	Free Rise Density (kg/m ³)	41.1	38.2	38.5
Test Panel Foam				
	Core foam density (kg/m ³)	42.6	41.4	41.2
Cone Calorimeter Test	Peak heat release rate (kW/m ²)	74	73	96
	Total heat release (MJ/m ²)	5.9	5.4	14.1
	combustion time (sec.)	35	34	312
	Weight retention (%)	37	36	30
Limited Oxygen Index		32.0	32.0	30.0
Dimensional stability (vol.%)	120°C×48h	-1.4	-1.3	-1.2
	90°C×48h	-1.3	-1.2	-0.4
	70°C95%RH×48h	-1.4	-1.5	0.0
	-20°C×48h	-0.4	-0.7	0.3
Compressive Strength (MPa)	Parallel	0.29	0.28	0.28
	Perpendicular	0.17	0.16	0.12
	Thickness	0.18	0.16	0.12
Adhesion Strength (N/10cm)	Initial	10 / 7	11 / 10	14 / 15
upper side / under side	Aged for 24 hours	12 / 8	14 / 12	11 / 10
Thermal Conductivity (W/mK) at24°C	Initial	0.0246	0.0245	0.0211
Flowability (mm/120g)		409	424	462
Closed Cell Content (%)		91	90	91



Figure 8. Appearance of test sample after cone calorimeter test

CONCLUSIONS

A fundamental study about all water-blown PIR systems on the relationship between components of raw materials and foam combustibility was carried out. Char layer formation at the initial combustion stage is effective to reduce the THR in the cone calorimeter test. The new all water-blown PIR system has superior flame resistance compared to the CP-blown PIR system. The LOI value of the new system is 32. The newly developed system will be accepted for construction materials, especially for metal-faced sandwich panels and sidings which require high-level flame retardancy.

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BIOGRAPHIES

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