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Liquid nucleating additives for improving thermal insulating properties and mechanical strength of polyisocyanurate foams

Min Jung Kang · Youn Hee Kim · Gun Pyo Park · Mi Sun Han · Woo Nyon Kim · Sang Do Park

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Abstract The effects of liquid-type nucleating silane additives on the cell structure, mechanical strength, and thermal insulating properties of the polyisocyanurate (PIR) foams have been studied. The PIR foams synthesized with hexamethyldisilazane (HMDS) as a silane additive showed the smaller average cell size and lower thermal conductivity than those of the PIR foams prepared with the hexamethyldisiloxane, dimethoxydimethylsilane, and hexadecyltrimethoxysilane. When HMDS was added, average cell size of the PIR foam was becoming smaller due to lower surface tension of the polyol solution, thereby the nucleation rate and number of bubbles produced were increased and then the cell size becomes smaller. The additives likely act as nucleating agents during the formation of PIR foams. The smaller cell size appears to be one of the major reasons for the improvement of thermal insulation properties and mechanical properties of the PIR foams. From the results of cell size, thermal conductivity, and mechanical strength of the PIR foams, it is suggested that the HMDS may be the efficient liquid-type additive for the reduction of cell size and improvement of the thermal insulation property of the PIR foams.

Introduction

Rigid polyisocyanurate (PIR) foams have been used as insulation materials for construction and industrial applications since PIR foams produced by introduction of the cyclotrimerization of isocyanate groups in polyurethane (PUR) matrix show superior mechanical properties and thermal stability [1–7]. PIR foams having closed cell structures are produced by insertion of gas when forming a PIR polymer, which is the same process used for the production of PUR foams. Mechanical properties as well as insulation properties of the cell structured polymeric foams such as PUR and PIR are largely dependent upon size and uniformity of the cell. It has been shown that the cell size of the polymeric foam can be controlled during nucleation and growth step of the foaming process [8, 9]. There are also many researches trying to control the cell size using reaction catalysts, surfactants, and nucleating agents, which induce the formation of bubbles in the polymer matrix [10–13].

There were some attempts to reduce the cell size through increased nucleation rate by reduced surface tension using several types of polysiloxane surfactants or using organoclay as a nucleating agent [14–16]. In case of the solid nucleating agents, the results showed that the cell size was reduced and high mechanical strength could be obtained. However, when solid particles such as organoclay were used in the foam, the closed cell content was decreased with additive content due to uneven dispersion of the organoclay [15].

In case of tetramethylsilane (TEMS), which is a liquid-type nucleating agent, uniform dispersion of the agent in the solution was reported since the agent was miscible in the polyol solution and the cell size was also reduced [15]. There is, however, a disadvantage of the TEMS that it has a

M. J. Kang · Y. H. Kim · G. P. Park · M. S. Han · W. N. Kim (✉)
Department of Chemical and Biological Engineering, Korea University, Anam-dong, Seoul 136-713, Korea
e-mail: kimwn@korea.ac.kr

S. D. Park
Korea Institute of Energy Research, Yuseong-gu, Daejeon 305-343, Korea

high-vapor pressure and highly flammable. The volatile organic compounds induce the loss of low-boiling point organics during the polymerization of PUR or PIR since the reaction between isocyanate and polyol is highly exothermic. Therefore, it is desirable for the environments that the content of volatile organic compound should be as low as possible to protect from pollution.

Silane compound can be used as an emulsifying surfactant and also an efficient liquid-type nucleating agent. The purpose of this study is to find more efficient nucleating agent among silane compounds having high molecular weights, which means they have high boiling points. Effects of several liquid silane additives on the morphological, mechanical, and thermal insulation properties of the PIR foams have been investigated by scanning electron microscopy, thermal conductivity analyzer, and universal testing machine.

Experimental

Materials

The materials used in this study were obtained from commercial sources. Polymeric 4, 4′-diphenylmethane diisocyanate (MDI) was supplied from BASF Korea Ltd. The average functionality of the MDI was 2.7 and NCO content was 30–32 wt%. Two types of polyols such as polyether polyol and polyester polyol were used in this study. Pentaerithritol and glycerin-based polyether polyol were supplied from KPX Chemicals Co. (Ulsan, Korea). Anhydride and glycol based polyester polyol were supplied from Aekyung Petrochemical Co. (Korea). Distilled water used as a chemical blowing agent was generated in our laboratory. Cyclopentane was used as a physical blowing agent. Cyclotrimerization catalyst was potassium 2-ethylhexanoate from OMG Americas, Inc. (Ohio, USA). Polysiloxane ether, used as a surfactant, was used from Goldschmidt's (Essen, Germany). Flame retardant was tris(chloro 2-propyl) phosphate from Daihachi Chemical Industry Co. (Tokyo, Japan). Four different kinds of liquid-type nucleating silane additives, which are hexamethyldisiloxane, hexamethyldisilazane (HMDS), dimethoxydimethylsilane, and hexadecyltrimethoxysilane, were used from Sigma-Aldrich Korea Co. (Yongin, Korea). The hexamethyldisiloxane is fairly innocuous like most siloxanes, and the HMDS is flammable. The dimethoxydimethylsilane has a low toxicity by inhalation, and the hexadecyltrimethoxysilane has an irritant property [17]. The polyols were dehydrated at 90 °C for 24 h in a vacuum oven before use and the other chemicals were used as received. The chemical compositions of the materials used for the preparation of PIR foams are shown in Table 1.

Preparation of PIR foams

First of all, polyols, catalyst, surfactant, flame retardant, and additives were put into an open-cup reactor with a size of 1.5 L and mixed for 30 s with a brushless-type stirrer, consisting of a ring-guard propeller for protecting the wall or sensors in the reactor, at ambient conditions. Rotating speed starts with 500 rpm and it was gradually increased up to 2,500 rpm. Low speed at the initial stage of mixing is desirable for homogeneous mixing of highly viscous polyols and additives having low viscosity. Then, foaming agent was added and reactants were mixed again at 3,000 rpm for 30 s. Then, MDI was put into the reactants and all the reactants were mixed for 15 s using brushless-type stirrer at 5,000 rpm. Finally, the reactants were poured into the open mold ($250 \times 250 \times 250$ mm^3) to produce free-rise foams. Then, they were cured for 1 day at room temperature to prevent deterioration of thermal conductivity and mechanical properties. When the distilled water was used as a blowing agent alone, the amount of distilled water was 2.5 parts per hundred polyol by weight (php). Also, when the mixed blowing agent was used, the amount of mixed blowing agent was 7.2 php that the ratio of cyclopentane and distilled water was 5.0/1.0 by weight. The amount of blowing agent was controlled to set the density of 50 kg/m^3 for all the PIR foam samples.

Surface tension measurements of polyol solutions

Surface tensions of the solutions containing the silane type additives (3.0 php) in polyol were measured at room temperature by Tensiometer K9 (KRUSS GmbH). The surface tension is calculated using Eq. 1:

$$\sigma = F/(L\cos\theta), \qquad (1)$$

where σ is the surface tension, F the force acting on the balance, L the wetted length, and θ the contact angle. The surface tension of five specimens per sample was measured and averaged.

Thermal conductivity measurements

Thermal conductivities of PIR foam with four different additives were measured using a thermal conductivity analyzer (model TCA Point2, Anacon), according to ASTM C518. PIR foam sample is placed in the test section between two plates, which are maintained at different temperatures during the test. Upon achieving thermal equilibrium and establishing a uniform temperature gradient throughout the sample, dimension of the specimen was $200 \times 200 \times 25$ mm^3 (width × length × thickness). The thermal conductivities of three specimens per sample were measured and averaged.

Table 1 Compositions used in the preparation of polyisocyanurate (PIR) foams

Chemicals	Description	Weight (g)
MDI	Polymeric 4, 4′-diphenylmethane diisocyanate	160.0
Polyol	Polyether/polyester polyol	100.0
Surfactant	Polysiloxane ether	2.0
Catalyst	Potassium 2-ethylhexanoate	1.5
Liquid-type silane additives	Hexamethyl disiloxane	3.0
	Hexamethyl disilazane	3.0
	Dimethoxy-dimethylsilane	3.0
	Hexadecyltrimethoxysilane	3.0

Surface morphology of PIR foams

Morphology of PIR foam was studied with a field emission scanning electron microscope (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.

Mechanical properties of PIR foams

Mechanical properties of PIR foam were measured under ambient condition using an Instron universal testing machine (Model 4467, Canton, Ohio). Compressive strength tests were conducted according to the ASTM D1621. The size of the specimen was 30 (*W*) × 30 (*L*) × 30 mm^3 (*T*) and the speed of crosshead movement was 3.0 mm/min. The strengths of 10 specimens per sample were measured and averaged for each mechanical test.

Measurements of closed cell content of PIR foams

Closed cell content of was determined by an Automatic Pycnometer (Model UPY-20F, Quantachrome instruments). The specimens had dimensions of 25 (*W*) × 25 (*L*) × 25 mm^3 (*T*). For each data point, five samples were tested, and the average value was taken.

Results and discussion

Surface tension of polyol solutions

Lowering surface tension is one of the important factors to control the size of the cell; therefore, lower value of surface tension is desirable to reduce the cell size. Surface tension of polyol solutions with various additives are measured and given in Fig. 1. The effect of nucleating additives on the surface tension of polyol solutions has been studied. The polyol solution without nucleating additive has a surface tension of 50.5 mN/m. This value is further reduced by the addition of silane additives to the lowest value of about 41.7 mN/m when the HMDS is added. Zhang et al. [12] have reported that as the content of silane and the length of silane backbone in silicone molecules are increased, the surface tension is decreased. Thus, the polyol solution with the HMDS having the highest silane content in the molecular structure shows the lowest surface tension among the samples.

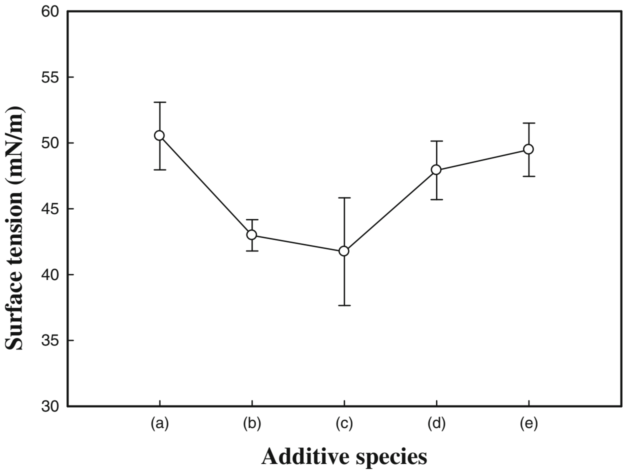

Fig. 1 Surface tension of polyol solutions with the different additives: **a** without additive, **b** hexamethyldisiloxane, **c** hexamethyldisilazane, **d** dimethoxydimethylsilane, **e** hexadecyltrimethoxysilane

It is also known that the methyl groups in organic compound have intrinsically low surface energy due to weak van der Waals attractive forces [18]. Therefore, when hexamethylsiloxane or HMDS having six methyl groups are added into the foaming system, the surface tension is decreased and uniform mixing can be obtained with the addition of them since it lowers the surface tension and the viscosity of the polyol solution.

Cell morphology of PIR foams

The shape and size of the cell of PIR foam are also important factors in the thermal conductivity of the PIR foam since the smaller cell size induces the lower thermal conductivity [19–21]. Figure 2a, b, c, d, and e shows the cryogenically fractured cross-sectional surfaces of the PIR foams blown by cyclopentane/distilled water (6.0/1.2 php) mixture, and the PIR foams contain the nucleating additives such as without additive, hexamethyldisiloxane, HMDS, dimethoxydimethylsilane, and hexadecyltrimethoxysilane, respectively. For Fig. 2c, when the HMDS is used as the nucleating additive, the smallest average cell size of about 217 μm in diameter is observed among the PIR foams observed in Fig. 2. This result is consistent with the result of surface tension of the polyol solution containing the HMDS, which has the highest silane content in the molecular structure among the nucleating additives used in this study.

Figure 3 shows the cell morphology of the PIR foam blown by water only (2.5 php) with the various nucleating additives. In Fig. 3, similar morphological results are observed compared the PIR foams blown by cyclopentane/distilled water (6.0/1.2 php) mixture. The foam produced with the HMDS shows the smallest average cell size of about 229 μm in diameter among the PIR foams in Fig. 3. When liquid-type additives are added, the cell size distribution of the PIR foam seems to be more uniform than that of the PIR foam without additive. In particular, HMDS has the highest silane content in its molecular structure and it seems that the low-surface tension prohibits the coalescence of bubbles and it promotes the formation of dense and small cells.

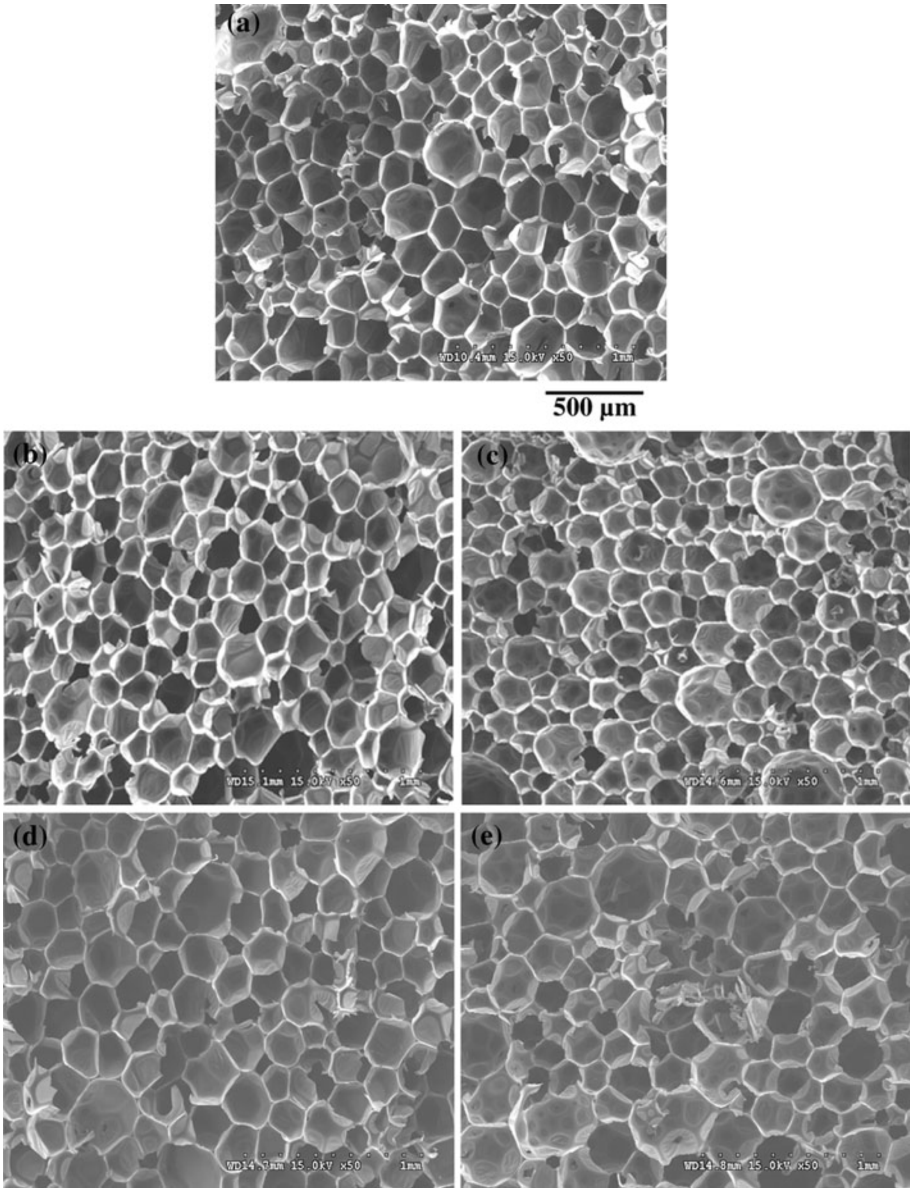

Fig. 2 Scanning electron micrographs of polyisocyanurate foams blown by cyclopentane/distilled water (6.0/1.2 php) mixture with the different additives: **a** without additive, **b** hexamethyldisiloxane, **c** hexamethyldisilazane, **d** dimethoxydimethylsilane, **e** hexadecyltrimethoxysilane

Figure 4 shows the effects of nucleating additives on average cell diameter of the PIR foams blown by cyclopentane/water (6.0/1.2 php) mixture and by water (2.5 php) only. When liquid additive, HMDS, is added to the system of the both PIR foams blown by cyclopentane/water mixture and water only, the lowest cell size is observed as previously shown in Figs. 1, 2, 3, the addition of HMDS seems to induce the low cell size of the PIR foams probably due to lower surface tension of the polyol solution resulting in high nucleation rate of the PIR foam.

Figure 4 also shows that the cell size of the PIR foams blown by cyclopentane/water mixture is smaller compared that of the foams blown by water only. The decrease in cell size of the foams blown by cyclopentane/water mixture can be explained such that exothermic reaction heat during polymerization of the PIR foam causes the increase of temperature of the reactants and at the vaporization point of the physical blowing agent (cyclopentane), the physical blowing agent evaporates extremely fast. In this case, the cell size of PIR foam becomes small compared to the foam blown by water only [6, 22].

Thermal conductivity of PIR foams

Effects of silane additives on the thermal conductivity of PIR foams are investigated and the results are given in Fig. 5. Thermal conductivity of the foam blown by

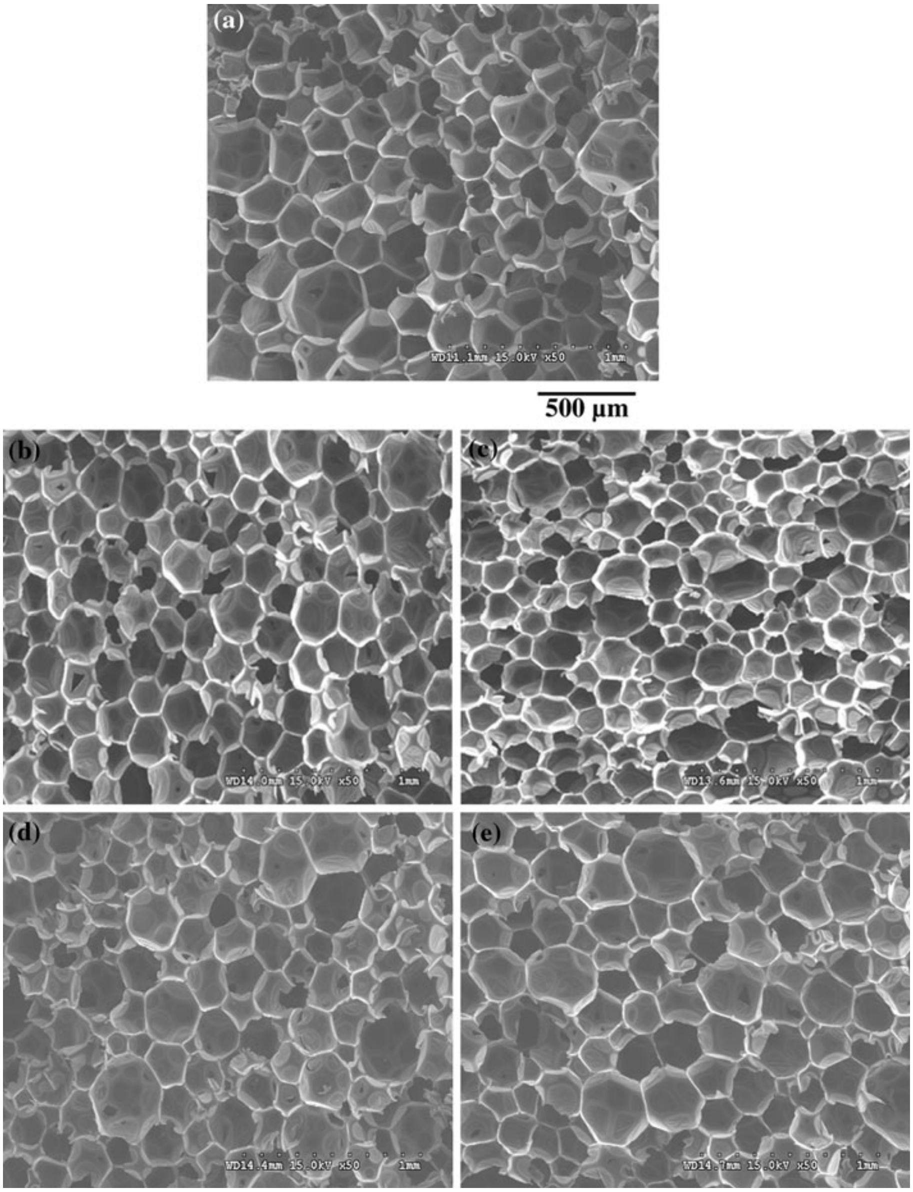

Fig. 3 Scanning electron micrographs of polyisocyanurate foams blown by distilled water only with the different additives: **a** without additive, **b** hexamethyldisiloxane, **c** hexamethyldisilazane, **d** dimethoxydimethylsilane, **e** hexadecyltrimethoxysilane

cyclopentane/water mixture shows lower value than that of the foams blown by water only, and the trend is the same as the results obtained from the cell size study. From Figs. 4 and 5, it is suggested that thermal conductivity increases with the increase of cell size of the PIR foams. In the studies of thermal conductivity of polystyrene foams as a function their cell size by Griffin and Skochdopole [23], they have shown similar results that thermal conductivity increases with cell size. Gibson and Ashby [10] have reported that this is partly because radiation is reflected less often in the foam with large cells and partly because, for cells of more than 10 mm or so in diameter, cell convection starts to contribute.

The thermal conductivity of PIR foams blown by cyclopentane/water mixture with HMDS was shown to be 0.0208 kcal/mh °C and this is the lowest value among the PIR foams blown by cyclopentane/water mixture. The thermal conductivity of the foam with the HMDS blown by water only is 0.0222 kcal/mh °C and this is also the lowest value among the PIR foams blown by water only. The results of decreasing the thermal conductivity of the foam can be explained by the difference in cell size of the foam. When the HMDS is used as a nucleating additive, the cell size of the PIR foam is decreased and consequently, the thermal conductivity is decreased.

From Figs. 4 and 5, when the HMDS is used, the decrease in the cell size and thermal conductivity of the foam is found to be most significant compared those of the other silane additives are used. It seems that the HMDS acts efficiently on the PIR foaming system and it is probably because the HMDS, which has high silicone/molecular weight ratio and six methyl groups per molecule, affects on intrinsic van der Waals forces.

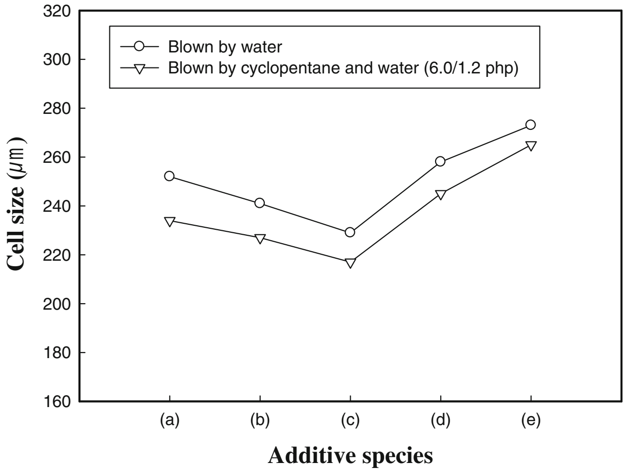

Fig. 4 Average cell size of polyisocyanurate foams with the different additives: **a** without additive, **b** hexamethyldisiloxane, **c** hexamethyldisilazane, **d** dimethoxydimethylsilane, **e** hexadecyltrimethoxysilane

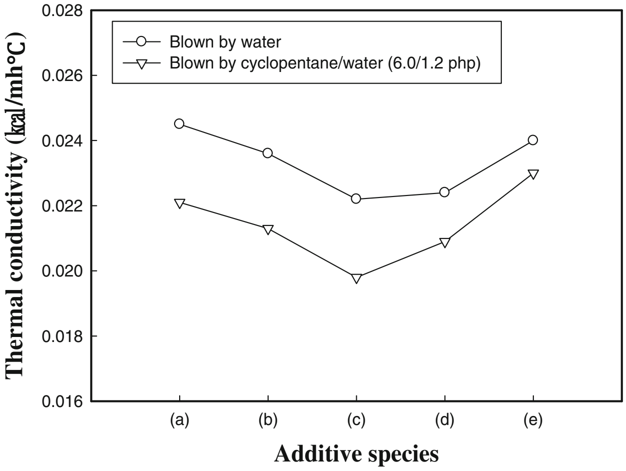

Fig. 5 Thermal conductivity of polyisocyanurate foams with the different additives: **a** without additive, **b** hexamethyldisiloxane, **c** hexamethyldisilazane, **d** dimethoxydimethylsilane, **e** hexadecyltrimethoxysilane

Mechanical properties of PIR foams

Compression and flexural strengths of the PIR foams with the various nucleating additives are shown in Figs. 6 and 7, respectively. The results indicate that the mechanical strengths of the PIR foam with the HMDS are higher than the foams with the other silane additives. From Figs. 4 and 6, it shows that the relationship between mechanical properties and cell size of the foams appears to be in inverse proportion. Also, it shows that the strengths of the foams blown by cyclopentane/water mixture are higher than those of the foams blown by water only. Especially, brittle fracture of the foam surface may be expected in case of water blown PIR foams and this brittleness has been a

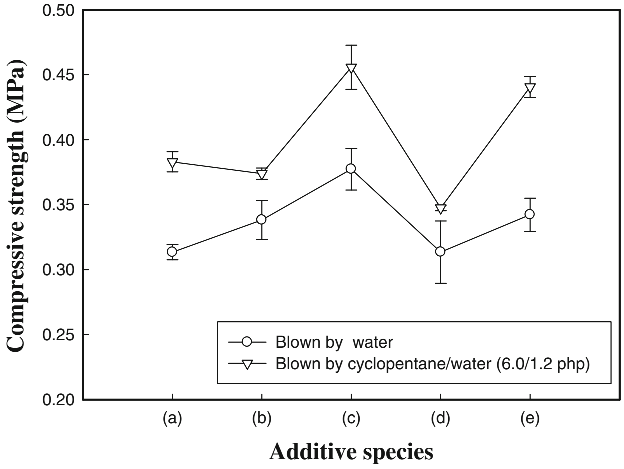

Fig. 6 Compressive strength of polyisocyanurate foams with the different additives: **a** without additive, **b** hexamethyldisiloxane, **c** hexamethyldisilazane, **d** dimethoxydimethylsilane, **e** hexadecyltrimethoxysilane

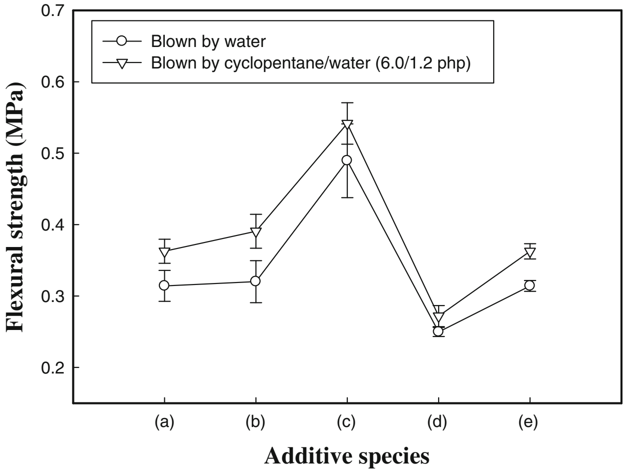

Fig. 7 Flexural strength of polyisocyanurate foams with the different additives: **a** without additive, **b** hexamethyldisiloxane, **c** hexamethyldisilazane, **d** dimethoxydimethylsilane, **e** hexadecyltrimethoxysilane

typical property of PIR foams blown by water due to high crosslinking density in the PUR polymer molecules.

From the results of Figs. 6 and 7, it is observed that the compressive and flexural strength of the PIR foams with HMDS blown by cyclopentane/water mixture show maximum values of about 0.46 and 0.54 MPa, respectively. The compressive and flexural strengths of the PIR foams blown by only water show similar behavior with the foams blown by cyclopentane/water mixture. Esmaeilnezhad et al. [24] have reported that there is a direct correlation between the microstructure and mechanical behavior of the foams. They report that the PUR/PIR foam with the smallest cell size and the narrowest cell size distribution has the highest mechanical properties. From the results of cell size and mechanical properties of the PIR foams, it is suggested that the increase of compressive and flexural strengths of the PIR foams with the HMDS can be explained by the smallest cell size of the foam.

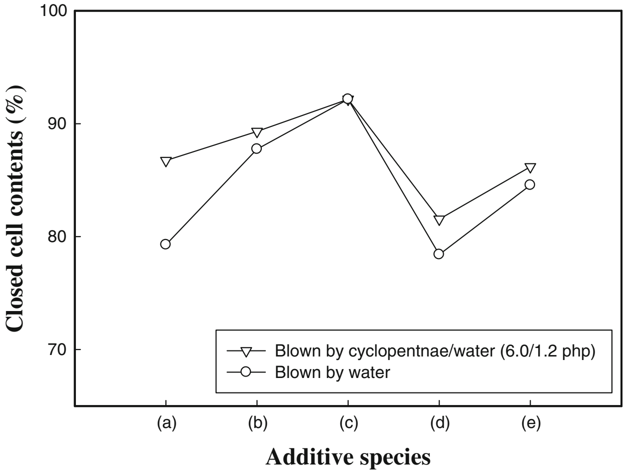

Fig. 8 Closed cell content of polyisocyanurate foams with the different additives: **a** without additive, **b** hexamethyldisiloxane, **c** hexamethyldisilazane, **d** dimethoxydimethylsilane, **e** hexadecyltrimethoxysilane

Closed cell content of PIR foams

Closed cell foams can be formed when the cells are initially filled with blowing gas having relatively lower thermal conductivity than air. The thermal conductivity of the PIR foams depends on the composition of the gas mixture in the cell. The gas in the cells diffuses out, and atmospheric gases diffuse in the cells. The higher value of closed cell content leads to prevent the diffusion of blowing gas out of the cells. Thus, the higher value of closed cell content equals better insulation.

Figure 8 shows the effects of nucleating additives on the closed cell content of the PIR foams. When the HMDS is added in the PIR foam, the closed cell content of the PIR foams is increased as compared with the results of the neat PIR foam or the foams with the other silane additives. One of the reasons for the lower thermal conductivity of the PIR foams with HMDS is that the content of closed cell is higher and then, the blowing gas is contained in the closed cell.

Conclusions

Rigid PIR foams were synthesized with four different kinds of liquid-type nucleating silane additives, which are hexamethyldisiloxane, HMDS, dimethoxydimethylsilane, and hexadecyltrimethoxysilane. From the results of cell size, thermal conductivity, and mechanical strength of the PIR foams, it is suggested that the PIR foams prepared with the HMDS have smaller average cell size and lower thermal conductivity than the foams prepared with the other additives. The addition of HMDS seems to induce the low cell size of the PIR foams probably due to lower surface tension of the polyol solution resulting in high nucleation rate of the PIR foam. The PIR foams without adding additive showed higher thermal conductivity compared the PIR foams with the hexamethyldisiloxane, HMDS, or dimethoxydimethylsilane.

The smaller cell size appears to be one of the major reasons for the improvement of thermal insulation properties and mechanical properties of the PIR foams. From this result, it can be concluded the HMDS may be the efficient liquid-type additive for the reduction of cell size and improvement of the thermal insulation property of the PIR foams.

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References

1. Song B, Lu W-Y, Syn CJ, Chen W (2009) J Mater Sci 44:351. doi:10.1007/s10853-008-3105-0
2. You M, Zhang X, Wang J, Wang X (2009) J Mater Sci 44:3141. doi:10.1007/s10853-009-3418-7
3. Lim H, Kim SH, Kim BK (2008) J Appl Polym Sci 110:49
4. Campanella A, Bonnaillie LM, Wool RP (2009) J Appl Polym Sci 112:2567
5. Kim SH, Kim BK, Lim H (2008) Macromol Res 16:467
6. Oertel G (1993) Polyurethane handbook. Hanser Publishers, New York
7. Cotgreave TC, Shortall JB (1977) J Mater Sci 12:708. doi:10.1007/BF00548161
8. Seo WJ, Jung HC, Hyun JC, Kim WN, Lee YB, Choe KH, Kim SB (2003) J Appl Polym Sci 90:12
9. Baser SA, Khakhar DV (1994) Polym Eng Sci 34:642
10. Gibson LJ, Ashby MF (1997) Cellular solids. Cambridge University Press, Cambridge
11. Maris RV, Tamano Y, Yoshimura H, Gay KM (2005) J Cell Plast 41:305
12. Zhang XD, Macosko CW, Davis HT, Nikolov AD, Wasan DT (1999) J Colloid Interface Sci 215:270
13. Grimminger J, Muha K (1995) J Cell Plast 31:48
14. Han MS, Choi SJ, Kim JM, Kim YH, Kim WN, Lee HS, Sung JY (2009) Macromol Res 17:44
15. Kang JW, Kim JM, Kim YH, Kim WN, Jang W, Shin DS (2009) Macromol Res 17:856
16. Han MS, Kim YH, Han SJ, Choi SJ, Kim SB, Kim WN (2008) J Appl Polym Sci 110:376
17. Lewis RJ, Chichester S (2007) Hawley's condensed chemical dictionary, 15th edn. Wiley, New York
18. Russell KC (1980) Adv Colloid Interface Sci 13:205
19. Niyogi D, Kumar R, Gandhi KS (1999) Polym Eng Sci 39:199
20. Cunningham RL, Carr ME, Bagley EB (1992) J Appl Polym Sci 44:1477
21. Jung HC, Kang SJ, Kim WN, Lee YB, Choe KH, Hong SH, Kim SB (2000) J Appl Polym Sci 78:624
22. Choe KH, Lee DS, Seo WJ, Kim WN (2004) Polym J 36:368
23. Griffin JD, Skochdopole RE (1964) In: Baer E (ed) Engineering design for plastics. Van Nostrand Reinhold, London
24. Esmaeilnezhad E, Rezaei M, Razavi MK (2009) Iran Polym J 18:569