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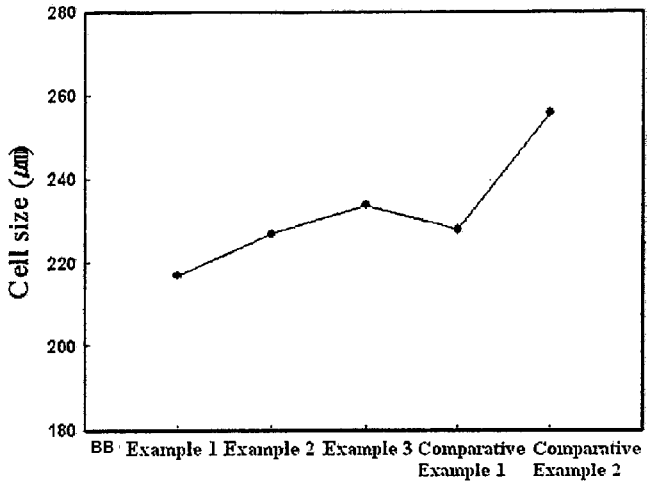
(54) Title: METHOD FOR PREPARING POLYISOCYANURATE FOAM BY USING LIQUID NUCLEATING AGENT AND POLYISOCYANURATE FOAM PREPARED BY THE SAME

[Fig. 6]



(57) Abstract: A method for preparing a polyisocyanurate foam is provided. According to the method, a polyisocyanurate foam is prepared by polymerizing a polyol compound with an isocyanate compound. A liquid silane compound is used as a nucleating agent for foam formation in the polymerization. Further provided is a polyisocyanurate foam prepared by the method. The polyisocyanurate foam has foamed cells whose size is relatively small compared to the size of foamed cells of conventional polyisocyanurate foams. In addition, the polyisocyanurate foam has excellent thermal and mechanical properties.

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Description

Title of Invention: METHOD FOR PREPARING POLYISOCYANURATE FOAM BY USING LIQUID NUCLEATING AGENT AND POLYISOCYANURATE FOAM PREPARED BY THE SAME

Technical Field

[1] The present invention relates to a method for preparing a polyisocyanurate foam by using a liquid nucleating agent and a polyisocyanurate foam prepared by the method. More specifically, the present invention relates to a method for preparing a polyisocyanurate foam by using a blowing agent causing no depletion of the ozone layer to obtain a small size of the foamed cells while achievinglow thermal conductivity and improved mechanical properties (e.g., high compressive strength), and a polyisocyanurate foam prepared by the method.

[2]

Background Art

[3] Heat insulating materials are used to block or reduce heat exchange between a space and the surrounding environment in order to increase the heating or cooling efficiency of the space. Heat insulating materials are widely used in a variety of applications, including construction panels, cold insulators for liquefied natural gas (LNG) ship, packaging materials for household electric appliances and interior materials for automobiles. Generally, the thermal conductivity of a heat insulating material is reduced due to the presence of gas filled in pores. Polyurethane foams are popular heat insulating materials at present because they have heat insulating performance and processability superior to those of other synthetic resins. Recent stringent regulations regarding the flame retardance of heat insulating materials have increased the demand for polyisocyanurate (PIR) foams with flame retardance superior to polyurethane foams. A typical polyisocyanurate foam contains isocyanurate moieties in which three isocyanate groups of a polyurethane foam are bonded together to form a ring structure. Due to the presence of such ring structures, polyisocyanurate foams have a thermal decomposition temperature as high as 300 ℃ and are more thermally stable than any other heat insulating material. In addition, polyisocyanurate foams exhibit excellent performance characteristics in terms of mechanical strength, such as compressive strength or flexural strength.

[4] Like a polyurethane foam, a polyisocyanurate foam can be prepared by reacting a mixture of a polyol, an isocyanate, a catalyst, a blowing agent, etc. Foaming gas is

produced during the reaction and makes the polyisocyanurate foam porous. The foaming gas is contained within the cell structure of the polyisocyanurate foam and is diffused toward the outside with the passage of time, and instead, air takes up the internal space of the cells. Generally, the thermal conductivity of the foam increases gradually over time because air is more thermally conductive than the foaming gas, leading to deteriorated heat insulating performance of the foam. Water is being investigated for its potential to replace hydrochlorofluorocarbon (HCFC), hydrofluorocarbon (HFC) and pentane blowing agents that are currently in use. Most foam manufacturers employ HCFC-141b as a blowing agent. The use of HCFC-141b, which has been found to cause the depletion of the ozone layer, will be completely banned from 2030. In recent years, considerable research efforts have been made in developing blowing agents posing no danger of depletion of the ozone layer. At the same time, research has been conducted on methods for preparing polyurethane foams or polyisocyanurate foams by using the clean blowing agents. Most blowing agents developed hitherto as replacements for conventional blowing agents are based on pentane or water. However, these replacements are known to have poor heat insulating performance due to their thermal conductivity higher than HCFC and HFC blowing agents, and are not suitable for use as heat insulating materials due to their poor mechanical properties in terms of compressive strength and flexural strength.

[5] A technology for replacing conventional blowing agents is associated with the use of solid additives to ensure the physical properties of heat insulating materials. In recent years, an attempt has been made in which a solid additive, such as clay or Aerosil (ultrafine silicic anhydride), is dispersed in a polyol or an isocyanate, the dispersion is intercalated between additive layers, and the solid additive is peeled off from the layered structure. The heat insulating performance and the mechanical strength of a polyurethane foam including clay or Aerosil as a solid additive incorporated therein are improved to some extent, but the interaction between the polyurethane and the solid additive surface is very insufficient to overcome the binding force between the solid additive layers. As a result, the solid additive tends to aggregate. A dispersion of the solid additive in a polyol or an isocyanate becomes unstable during storage, which makes it difficult to obtain a uniform cell size of the foam product. Thus, there is a strong need to develop a heat insulating material with improved physical properties without causing the depletion of the ozone layer.

[6]

Disclosure of Invention

Technical Problem

[7] In view of the foregoing and other problems of the prior art, a first object of the

present invention is to provide a method for preparing a polyisocyanurate foam by using a blowing agent having no influence on the depletion of the ozone layer to form uniform cells and to achieve excellent thermal properties and high mechanical strength while effectively preventing aggregation of additives.

[8] A second object of the present invention is to provide a polyisocyanurate foam prepared by the method.

[9]

Solution to Problem

[10] In order to accomplish the first object of the present invention, there is provided a method for preparing a polyisocyanurate foam by polymerizing a polyol compound with an isocyanate compound wherein a liquid silane compound is used as a nucleating agent for foam formation.

[11] In a preferred embodiment, the liquid silane compound is used in an amount of 0.5 to 10 parts by weight, based on 100 parts by weight of the polyol compound.

[12] In an embodiment, at least one hydrogen atom of the silane groups of the liquid silane compound may be substituted with a methyl group.

[13] In an embodiment, the liquid silane compound may be selected from the group consisting of hexamethyldisilazane, hexamethyldisiloxane, dimethoxydimethylsilane and mixtures thereof.

[14] In an embodiment, the isocyanate compound may be selected from the group consisting of polymeric methylene diphenyl diisocyanate, monomeric methylene diphenyl diisocyanate, polymeric toluene diisocyanate, monomeric toluene di-isocyanate, and mixtures thereof.

[15] In an embodiment, the polyol compound may be a polyester polyol or a polyether polyol.

[16] In an embodiment, the polyester polyol may be a polymerization product of phthalic anhydride or adipic anhydride with ethylene oxide, propylene oxide or a mixture thereof.

[17] In an embodiment, the polyether polyol may be a polymerization product of at least one alcohol selected from the group consisting of ethylene glycol, 1,2-propane glycol, butylene glycol, 1,6-hexanediol, 1,8-octanediol, neopentyl glycol, 2-methyl-1,3-propanediol, glycerol, trimethylolpropane, 1,2,3-hexanetriol, 1,2,4-butanetriol, trimethylol methane, pentaerythritol, diethylene glycol, triethylene glycol, polyethylene glycol, tripropylene glycol, polypropylene glycol, dibutylene glycol, polybutylene glycol, sorbitol, sucrose, hydroquinone, resorcinol, catechol and bisphenol with ethylene oxide, propylene oxide or a mixture thereof.

[18] In an embodiment, the polymerization of the polyol compound and the isocyanate

compound may be carried out in the presence of at least one catalyst selected from the group consisting of acetic acid, octanoic acid, 2,4,6-trisdimethylaminomethylphenol, 1,3,5-tris(3-dimethylaminopropyl)-s-hexahydrotriazine and potassium hexanoate.

[19] In an embodiment, the polymerization of the polyol compound and the isocyanate compound may be carried out in the presence of a surfactant to inhibit the growth of the foamed cells of the polyisocyanurate foam.

[20] In an embodiment, the polymerization of the polyol compound and the isocyanate compound may be carried out in the presence of at least one blowing agent selected from the group consisting of cyclopentane, isopentane, n-pentane and water.

[21] According to another aspect of the present invention, there is provided a method for preparing a polyisocyanurate foam, the method comprising (a) mixing a polyol compound and a liquid silane compound with stirring, (b) mixing the mixture obtained in step (a), a polymerization catalyst, a surfactant and a blowing agent with stirring, and (c) polymerizing the polyol compound of the mixture obtained in step (b) with an isocyanate compound with stirring to prepare a polyisocyanurate.

[22] In a preferred embodiment, steps (a) and (b) are carried out at a temperature between 20 and 40 ℃.

[23] In an embodiment, step (a) may be carried out by gradually increasing the stirring rate from 500 to 2,500 rpm.

[24] In a preferred embodiment, the stirring rate in step (c) is in the range of 2,500 to 5,000 rpm.

[25] In order to accomplish the second object of the present invention, there is provided a polyisocyanurate foam prepared by the method.

[26] In an embodiment, the polyisocyanurate foam may further comprise a flame retardant.

[27] In an embodiment, the polyisocyanurate foam may have foamed cells whose volume is 50 to 90% smaller than the volume of foamed cells of a polyisocyanurate foam prepared without using a liquid silane compound as a nucleating agent under the same polymerization conditions.

[28]

Advantageous Effects of Invention

[29] According to the method of the present invention, a blowing agent having no influence on the depletion of the ozone layer and a liquid nucleating agent are used to prepare a polyisocyanurate foam with low thermal conductivity and improved mechanical properties in terms of compressive strength and flexural strength. In addition, according to the method of the present invention, the foamed cells of the polyisocyanurate foam can be reduced in size. Furthermore, the polyisocyanurate foam has a

smaller cell size and a much lower thermal conductivity than polyisocyanurate/clay nanocomposites and polyurethane/clay nanocomposites of the prior art.

[30]

Brief Description of Drawings

[31] FIG. 1 is a scanning electron microscope (SEM) image of a polyisocyanurate foam prepared in Example 1.

[32] FIG. 2 is a SEM image of a polyisocyanurate foam prepared in Example 2.

[33] FIG. 3 is a SEM image of a polyisocyanurate foam prepared in Example 3.

[34] FIG. 4 is a SEM image of a polyisocyanurate nanocomposite prepared in Comparative Example 1.

[35] FIG. 5 is a SEM image of a polyisocyanurate foam prepared in ComparativeExample 2.

[36] FIG. 6 is a graph comparing the sizes of polyisocyanurate foams prepared in Examples 1 to 3 and Comparative Example 2 and a polyisocyanurate foam nanocomposite prepared in Comparative Example 1.

[37] FIG. 7 is a graph showing the thermal conductivities of polyisocyanurate foams prepared in Examples 1 to 3 and Comparative Example 2 and a polyisocyanurate foam nanocomposite prepared in Comparative Example 1.

[38] FIG. 8 is a graph showing the compressive strengths of polyisocyanurate foams prepared in Examples 1 to 3 and Comparative Example 2 and a polyisocyanurate foam nanocomposite prepared in Comparative Example 1.

[39]

Best Mode for Carrying out the Invention

[40] Exemplary embodiments of the present invention will now be described in detail.

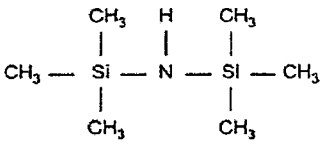
[41] The present invention provides a method for preparing a polyisocyanurate foam by polymerizing a polyol compound with an isocyanate compound. The method is characterized by the use of a liquid silane compound as a nucleating agent for foam formation.

[42] The polyisocyanurate foam is a material containing isocyanurate moieties in which three isocyanate groups of a polyurethane foam, which has been used as a heat insulating material, are bonded together to form a ring structure. The polyisocyanurate foam exhibits excellent performance characteristics in terms of thermal stability and mechanical strength due to the ring structures. According to the prior art, a solid additive, i.e. clay or Aerosil, is introduced into a polyol in the preparation of a polyurethane foam to reduce the size of the foamed cells. The size reduction of the foamed cells effectively improves the heat insulating performanceof the polyurethane foam. However, the introduction of the solid additive into the polyol causes problems

of poor dispersibility and storage stability. To solve these problems, the present invention presents a technique for forming closely packed and uniform foamed cells of a polyisocyanurate foam by introducing a liquid nucleating agent into a polyol. A heat insulating material exhibits superior heat insulating effects and high mechanical strength when foamed cells formed in the insulating material are small in size. Accordingly, the addition of a material which assists in the formation of nuclei in the initial stage of nucleation, together with a blowing agent, to polymerization reactants reduces the size of the foamed cells and increases the density of the foamed cells, thus achieving improved physical properties of the heat insulating material. The liquid nucleating agent refers to a material in the form of a liquid that is uniformly dispersed in the polymerization reactants to aid in nucleation. In the present invention, a liquid silane compound is used as the liquid nucleating agent.

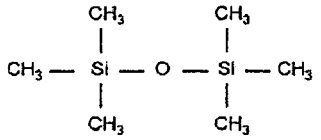
[43] Examples of liquid silane compounds that can be used in the present invention include hexamethyldisilazane (HMDS), hexamethyldisiloxane and dimethoxydimethylsilane, which are represented by Formulas 1, 2 and 3, respectively:

[44]



(1)

[45]



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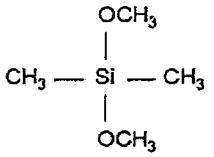
[46]



(3)

[47] In addition to the silane compounds of Formulas 1, 2 and 3, other silane compounds in the form of liquids are within the scope of the present invention.

[48] The liquid silane compound is preferably a silane compound in which at least one of the hydrogen atoms bonded to the silicon atom(s)is substituted with a methyl group. The silane compound can be advantageously used in the present invention because of its high stability in the polyol compound during stirring. It is preferred to usethe liquid silane compound in an amount of 0.5 to 10 parts by weight, based on 100 parts by weight of the polyol compound. The use of the liquid silane compound in an amount of

less than 0.5 parts by weight results in the formation of foamed cells at an excessively low density, which makes it impossible to ensure sufficient heat insulating performance and mechanical properties of the polyisocyanurate foam. Meanwhile, the liquid silane compound in an amount exceeding10 parts by weight is not readily uniformly dispersed.

[49] The polyol compound has two or more hydroxyl groups in one molecule. The polyol compound is polymerized with the isocyanate compound to form urethane bonds. The polyol compound may be a polyester or polyether polyol. The polyester polyol may be a polymerization product of phthalic anhydride or adipic anhydride with ethylene oxide, propylene oxide or a mixture thereof. The polyether polyol may be a polymerization product of at least one alcohol selected from the group consisting of ethylene glycol, 1,2-propane glycol, butylene glycol, 1,6-hexanediol, 1,8-octanediol, neopentyl glycol, 2-methyl-1,3-propanediol, glycerol, trimethylolpropane, 1,2,3-hexanetriol, 1,2,4-butanetriol, trimethylol methane, pentaerythritol, diethylene glycol, triethylene glycol, polyethylene glycol, tripropylene glycol, polypropylene glycol, dibutylene glycol, polybutylene glycol, sorbitol, sucrose, hydroquinone, resorcinol, catechol and bisphenol with ethylene oxide, propylene oxide or a mixture thereof.

[50] The isocyanate compound has one or more isocyanate groups in the molecular structure. The isocyanate groups of the isocyanate compound react with the hydroxyl groups of the polyol compound to form urethane bonds. In addition, the three isocyanate groups of the isocyanate compound react with each other (trimerization) to form an isocyanurate group. Generally, a material having a larger number of isocyanate groups than an isocyanate compound used in the preparation of a polyurethane is advantageously used for the formation of isocyanurate groups. In the method of the present invention, a diisocyanate compound having an NCO index as high as 250 is preferred as the isocyanate compound. As the isocyanate compound, there can be used at least one diisocyanate compound selected from the group consisting of polymeric methylene diphenyl diisocyanate, monomeric methylene diphenyl diisocyanate, polymeric toluene diisocyanate and monomeric toluene diisocyanate.

[51] In the method of the present invention, a polymerization catalyst, a surfactant, a blowing agent, a flame retardant, etc. may be mixed with the polymerization reactants of the polyisocyanurate foam.

[52] The polymerization catalyst serves to promote the trimerization of the isocyanate groups and to increase the rate of the reaction, thus helping to form isocyanurate groups. The polymerization catalyst may be selected from the group consisting of acetic acid, octanoic acid, 2,4,6-trisdimethylaminomethylphenol,

1,3,5-tris(3-dimethylaminopropyl)-s-hexahydrotriazine and potassium hexanoate.

[53] The blowing agent serves to produce gas during polymerization to form foamed cells within the heat insulating material. The blowing agent remains inside the foamed cells after the preparation of the polyisocyanurate foam. Accordingly, a material having low thermal conductivity and high stability is advantageous as the blowing agent. The blowing agent may be selected from the group consisting of cyclopentane, chlorofluorocarbon, isopentane, n-pentane, hydrochlorofluorocarbon, hydrofluorocarbon and water. Particularly, cyclopentane, water or a mixture thereof, which is a chlorine-free blowing agent, is environmentally advantageous. The density of the polyisocyanurate foam can be controlled by varying the content of the blowing agent. In the method of the present invention, the density of the polyisocyanurate foam is adjusted to 50 kg/m^3, but is not limited to this value.

[54] The surfactant serves to control the surface tension of the foamed cells to inhibit excessive growth of the foamed cellsand stabilize the formation of the foamed cells. Various kinds of surfactants known in the art can be used in the present invention.

[55] The flame retardant is an additive to improve the flame retardance of the polyisocyanurate foam as the heat insulating material. Various kinds of flame retardants known in the art may be used in the present invention. For example, trischloropropylphosphate can be used as the flame retardant.

[56] Reaction conditions, such as stirring rate and reaction temperature, are important factors in the preparation of the polyisocyanurate foam. Hereinafter, individual steps of the method according to the present invention will be described in order to better explain preferable ranges of the stirring and reaction rates. First, the polyol compound is mixed with the liquid silane compound with stirring (step (a)). Subsequently, the mixture obtained in step (a) is mixed with the polymerization catalyst, the surfactant and the blowing agent with stirring (step (b)). Finally, the polyol compound of the mixture obtained in step (b) is polymerized with the isocyanate compound with stirring to prepare a polyisocyanurate (step (c)).

[57] In step (a), the polyol compound and the liquid silane compound are preferably stirred at a rate of 500 to 2,500 rpm. For uniform dispersion ofthe polyol compound and the liquid silane compound, step (a) is preferably carried out by stirring at a rate as low as about 500 rpm for about 15 sec in the initial stage, gradually increasing the stirring rate, and stirring at a rate as high as 2,500 rpm in the final stage. The liquid silane compound is not sufficiently dispersed at a rate lower than 500 rpm in the initial stage of the stirring because the polyol compound has a relatively high viscosity and the liquid silane compound has a relatively low viscosity. It is difficult to provide sufficient contact time for uniform dispersion of the polyol compound and the liquid silane compound at a rate higher than 2,500 rpm in the final stage of the stirring. Step

(a) is preferably carried out at a temperature of 20 to 40 ℃. Sufficient dispersion of the polyol compound and the liquid silane compound is substantially impossible at a temperature lower than 20 ℃. Meanwhile, the liquid silane compound having a low boiling point may be evaporated at a temperature higher than 40 ℃.

[58] In step (b), the stirring is preferably performed at a rate of 500 to 2,500 rpm, which is a set range for homogeneous mixing of the polymerization catalyst, the surfactant and the blowing agent. Out of this range, the respective additives are non-uniformly distributed, resulting in deteriorated physical properties of the polyisocyanurate foam. Step (b), the stirring is preferably performed at a temperature ranging from 20 to 40 ℃. The characteristics of the additives may be varied at a temperature exceeding 40 ℃. Particularly, the use of volatile cyclopentane as the blowing agent may vary the density of the polyisocyanurate foam, leading to a change in the physical properties of the polyisocyanurate foam.

[59] In step (c), the stirring is preferably performed at a rate of 2,500 to 5,000 rpm, which is a set range for the reaction betweenthe polyol compound and the isocyanate compound and the trimerization of the isocyanate groups of the isocyanate compound in a sufficiently short time. If the stirring is performed at a rate lower than 2,500 rpm, the mixing of the polyol compound and the isocyanate compound is not sufficient to allow the reactions to proceed smoothly. Meanwhile, if the stirring is performed at a rate higher than 5,000 rpm, the contact time between the polyol compound and the isocyanate compound is too short to complete the reactions. In step (c), the reaction temperature is preferably from 20 to 80 ℃. The condensation reaction between the polyol compound and the isocyanate compound and the trimerization reaction of the isocyanate groups of the isocyanate compound do not readily occur at a temperature lower than 20 ℃. Meanwhile, the reactions proceed excessively rapidly at a temperature higher than 80 ℃, impeding the stabilization of cells or causing evaporation of the reactants.

[60]

Mode for the Invention

[61] Hereinafter, the present invention will be explained in more detail with reference to preferred embodiments in the following examples. However, it will be appreciated by those skilled in the art that that these embodiments are given for illustrative purposes only and are not intended to limit the present invention.

[62]

[63] **EXAMPLES**

[64] Example 1

[65] Example 1-1 (Mixing of polyol compound and liquid silane compound)

[66] 3.0 g of hexamethyldisilazane (HMDS) as a liquid silane compound was added to 100 g of a mixture of a polyether polyol (KFT-200, Korea Polyol Co. (Korea)) and a polyester polyol (POL-1001, Aekyung Petrochemical Co. (Korea)) in a weight ratio of 4:6. The mixture was stirred at a rate of 500 rpm for 2 min in the initial stage (first stirring). This low stirring rate is to facilitate the intercalation of the liquid silane compound between the molecules of the polyol compound because the polyol mixture had a relatively high viscosity and the liquid silane compound had a relatively low viscosity. Thereafter, stirring was sequentially continued at 1,000 rpm for 2 min and at 2,500 rpm for 30 sec (second stirring). The overall stirring procedure was performed using a mechanical stirrer.

[67]

[68] Example 1-2

[69] Potassium hexanoate (H 977) as a catalyst, distilled water and a cyclopentane/water mixture (5:1 (w/w)) as a blowing agent were added to the mixture obtained in Example 1-1. Then, the resulting mixture was reacted with a diisocyanate compound(4,4'-diphenylmethane diisocyanate) to prepare a polyisocyanurate foam. The blowing agent was used in an amount to adjust the density of the polyisocyanuratefoam to about 50 kg/m^3. The polymerization between the polyol compound and the diisocyanate compound was carried out using amechanical stirrer at 5,000 rpm for 15 sec. The polymerization mixture was transferred to an open mold, where the polyisocyanurate foam was prepared.

[70]

[71] Example 2

[72] A polyisocyanurate foam was prepared in the same manner as in Example 1, except that hexamethyldisiloxane was used instead of hexamethyldisilazane (HMDS).

[73]

[74] Example 3

[75] A polyisocyanurate foam was prepared in the same manner as in Example 1, except that dimethoxydimethylsilane was used instead of hexamethyldisilazane (HMDS).

[76]

[77] Comparative Example 1

[78] Comparative Example 1-1 (Preparation of organoclay-containing polymeric MDI)

[79] An organoclay having hydroxyl groups (30B clay, Southern Clay Co.) as a solid nucleating agent was dried in a vacuum oven for 24 hr to remove moisture contained therein. Then, 160 parts by weight of polymeric 4,4-diphenylmethane diisocyanate ("polymeric MDI", M50, BASF) was added to 4.8 parts by weight of the solid nucleating agent. The polymeric MDI was homogeneously mixed and reacted smoothly with the solid nucleating agent using a mechanical stirrer at a rate of 3,000 rpm for 2 hr

in a thermostatic oil bath while maintaining the temperature at 60 ℃.

[80]

[81] Comparative Example 1-2 (Preparation of 30B clay-polyisocyanurate nanocomposite)

[82] 160 g of the organoclay-containing polymeric MDI prepared in Comparative Example 1-1, 100 g of the polyol mixture used in Example 1, a catalyst and a surfactant were allowed to react at room temperature to prepare a clay-polyisocyanurate nanocomposite. The organoclay-containing polymeric MDI was added in an amount 5 wt% larger than the stoichiometric ratio. The reaction was carried out using a mechanical stirrer at 5,000 rpm for 5 sec.

[83]

[84] Comparative Example 2

[85] A polyisocyanurate foam was prepared in the same manner as in Example 1 without the addition of the liquid nucleating agent or any solid nucleating agent.

[86]

[87] Experimental Example 1 (Comparison of morphologies of foamed cells with or without the addition of nucleating agent)

[88] The polyisocyanurate foams prepared in Examples 1-3 and Comparative Example 2 and the polyisocyanurate foam nanocomposite specimen prepared in Comparative Example 1 were cut into specimens, each of which had dimensions of 30 mm (w) 30 mm (l) 80 mm (h). Each of the specimens was put into liquid nitrogen and was cut into pieces. The cross-sectional morphology of the foamed cells of the specimen was observed using a scanning electron microscope (SEM). FIGS. 1 through 5 are cross-sectional SEM images of the specimens produced in Examples 1-3 and Comparative Examples 1-2, respectively. The average sizes of the foamed cells are compared in FIG. 6. Referring to FIGS. 1 through 6, the foamed cells of the specimens of Examples 1-3, each of which was prepared using the liquid nucleating agent, were smaller in size than the foamed cells of the specimens of Comparative Examples 1-2, which were prepared without using any liquid nucleating agent. Particularly, the foamed cells of the specimen of Example 1, which was prepared using hexamethyldisilazane as the liquid nucleating agent, were smallest. The molecular structure of hexamethyld-isilazane is believed to be responsible for the smallest foamed cells of the specimen of Example 1. That is, hexamethyldisilazane has larger numbers of silane and methyl groups than the other liquid nucleating agents. The larger the number of substituted methyl groupsin the silane compound, the weaker the van der Waals force, resulting in lower surface tension of the foamed cells. Therefore, it appears that the close packing of the smaller foamed cells is because bubbles are prevented from adhering and ag-gregating together.

[89]

[90] Experimental Example 2 (Thermal conductivity test depending on the addition of nucleating agent)

[91] The polyisocyanurate foams prepared in Examples 1-3 and Comparative Example 2 and the polyisocyanurate foam nanocomposite prepared in Comparative Example 1 were measured for thermal conductivity in accordance with the procedure of ASTM C518 in order to compare the heat insulating performance of the foam products. The results are shown in FIG. 7. Referring to FIG. 7, the foam products of Examples 1-3, each of which was prepared using the liquid nucleating agent, had lower thermal conductivities than the foam product of Comparative Example 2, which was prepared without using any liquid nucleating agent. The polyisocyanurate foam prepared in Example 1 had the lowest thermal conductivity. Like polyurethane foams, polyisocyanurate foams have a low thermal conductivity as the cell size decreases. These results lead to the conclusion that the addition of the liquid silane compound having more methyl groups increased the tendency to decrease the thermal conductivity of the polyisocyanurate foam.

[92]

[93] Experimental Example 3 (Compressive strength test depending on the addition of nucleating agent)

[94] The polyisocyanurate foams prepared in Examples 1-3 and Comparative Example 2 and the polyisocyanurate foam nanocomposite prepared in Comparative Example 1 were measured for compressive strength in accordance with the procedure of ASTM D 1621. The results are shown in FIG. 8. The polyisocyanurate foam of Example 3 had the highest compressive strength. The reason for the highest compressive strength is believed to be the ability of the polyisocyanurate foam having small-sized and closely packed cells to better withstand the applied force.

[95]

[96] From the experimental results in Examples 1-3 and Comparative Examples 1-2, it can be confirmed that the polyisocyanurate foams of Examples 1-3 had lower thermal conductivities than the polyisocyanurate foam of Comparative Example 2. The thermal conductivity of a polyisocyanurate foam as a heat insulating material is considered the most important physical property associated with the heat insulating performance of the polyisocyanurate foam. The experimental results demonstrate that the polyisocyanurate foams of Examples 1-3, each of which was prepared using the liquid silane compound as the nucleating agent, showed improved heat insulating performance. The polyisocyanurate foam of Comparative Example 1 showed physical properties similar to the polyisocyanurate foams of Examples 2 and 3 in terms of thermal conductivity, but it showed disadvantageous results in terms of storage stability, which is attributed

to the use of the solid additive. The compressive strength of a heat insulating material is considered attendant to the fundamental heat insulating performance of the heat insulating material. In conclusion, the polyisocyanurate foams of Examples 1-3 had physical properties suitable for use as heat insulating materials although the polyisocyanurate foams of Examples 2 and 3 had lower compressive strengths than the foam products of Comparative Examples 1 and 2.

Claims

[Claim 1] A method for preparing a polyisocyanurate foam by polymerizing a polyol compound with an isocyanate compound wherein a liquid silane compound is used as a nucleating agent for foam formation.

[Claim 2] The method of claim 1, wherein the liquid silane compound is used in an amount of 0.5 to 10 parts by weight, based on 100 parts by weight of the polyol compound.

[Claim 3] The method of claim 1, wherein at least one hydrogen atom of the silane groups of the liquid silane compound is substituted with a methyl group.

[Claim 4] The method of claim 1, wherein the liquid silane compound is selected from the group consisting of hexamethyldisilazane, hexamethyldisiloxane, dimethoxydimethylsilane, and mixtures thereof.

[Claim 5] The method of claim 1, wherein the isocyanate compound is selected from the group consisting of polymeric methylene diphenyl diisocyanate, monomeric methylene diphenyl diisocyanate, polymeric toluene diisocyanate, monomeric toluene diisocyanate, and mixtures thereof.

[Claim 6] The method of claim 1, wherein the polyol compound is a polyester polyol or a polyether polyol.

[Claim 7] The method of claim 6, wherein the polyester polyol is a polymerization product of phthalic anhydride or adipic anhydride with ethylene oxide, propylene oxide or a mixture thereof.

[Claim 8] The method of claim 6, wherein the polyether polyol is a polymerization product of at least one alcohol selected from the group consisting of ethylene glycol, 1,2-propane glycol, butylene glycol, 1,6-hexanediol, 1,8-octanediol, neopentyl glycol, 2-methyl-1,3-propanediol, glycerol, trimethylolpropane, 1,2,3-hexanetriol, 1,2,4-butanetriol, trimethylol methane, pentaerythritol, diethylene glycol, triethylene glycol, polyethylene glycol, tripropylene glycol, polypropylene glycol, dibutylene glycol, polybutylene glycol, sorbitol, sucrose, hydroquinone, resorcinol, catechol and bisphenol with ethylene oxide, propylene oxide or a mixture thereof.

[Claim 9] The method of claim 1, wherein the polymerization of the polyol compound and the isocyanate compound is carried out in the presence of at least one catalyst selected from the group consisting of acetic acid,

octanoic acid, 2,4,6-trisdimethylaminomethylphenol, 1,3,5-tris(3-dimethylaminopropyl)-s-hexahydrotriazine and potassium hexanoate.

[Claim 10] The method of claim 1, wherein the polymerization of the polyol compound and the isocyanate compound is carried out in the presence of a surfactant to inhibit the growth of the foamed cells of the polyisocyanurate foam.

[Claim 11] The method of claim 1, wherein the polymerization of the polyol compound and the isocyanate compound is carried out in the presence of at least one blowing agent selected from the group consisting of cyclopentane, isopentane, n-pentane and water.

[Claim 12] A method for preparing a polyisocyanurate foam, the method comprising:

(a) mixing a polyol compound and a liquid silane compound with stirring

(b) mixing the mixture obtained in step (a), a polymerization catalyst, a surfactant and a blowing agent with stirring and

(c) polymerizing the polyol compound of the mixture obtained in step (b) with an isocyanate compound with stirring to prepare a polyisocyanurate.

[Claim 13] The method of claim 12, wherein steps (a) and (b) are carried out at a temperature between 20 and 40 ℃.

[Claim 14] The method of claim 12, wherein step (a) is carried out by gradually increasing the stirring rate from 500 to 2,500 rpm.

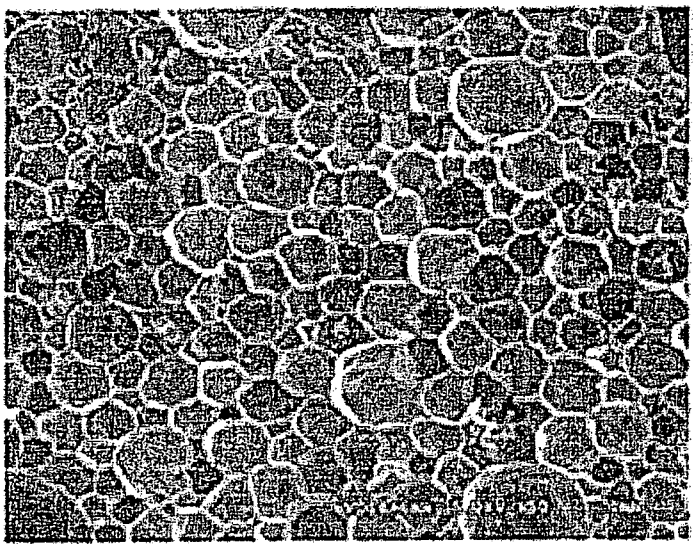
[Claim 15] The method of claim 12, wherein the stirring rate in step (c) is in the range of 2,500 to 5,000 rpm.

[Claim 16] A polyisocyanurate foam prepared by the method of any one of claims 1 to 15.

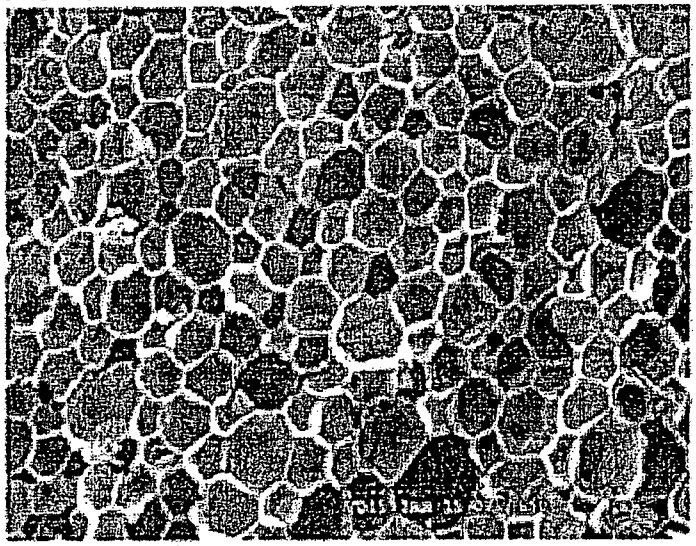
[Claim 17] The polyisocyanurate foam of claim 16, further comprising a flame retardant.

[Claim 18] A polyisocyanurate foam of claim 16, wherein the polyisocyanurate foam has foamed cells whose volume is 50 to 90% smaller than the volume of foamed cells of a polyisocyanurate foam prepared without using a liquid silane compound as a nucleating agent under the same polymerization conditions.

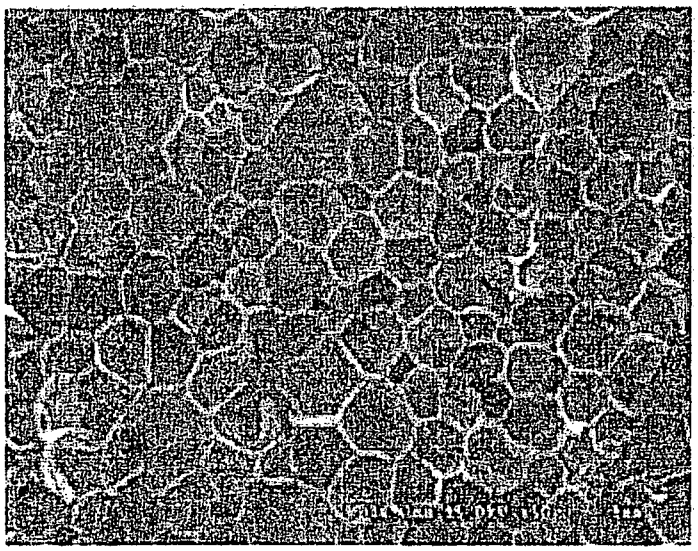
[Fig. 1]



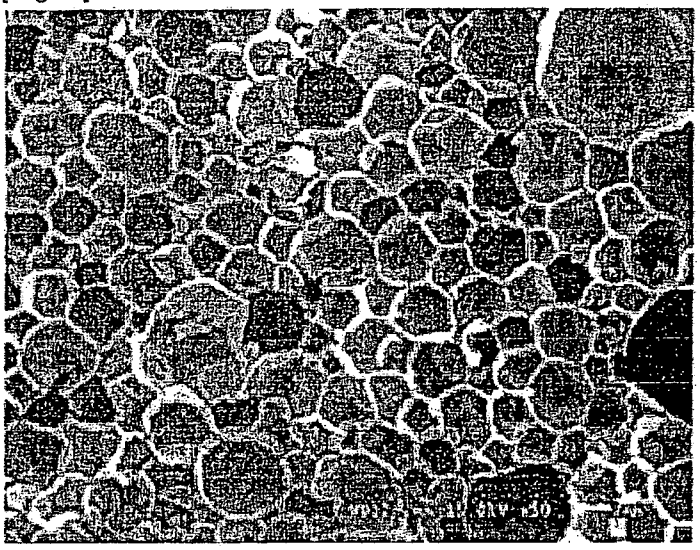
[Fig. 2]



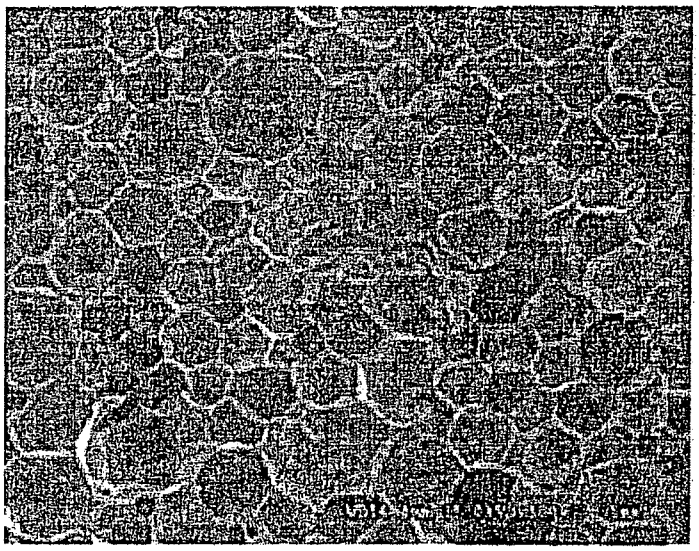
[Fig. 3]



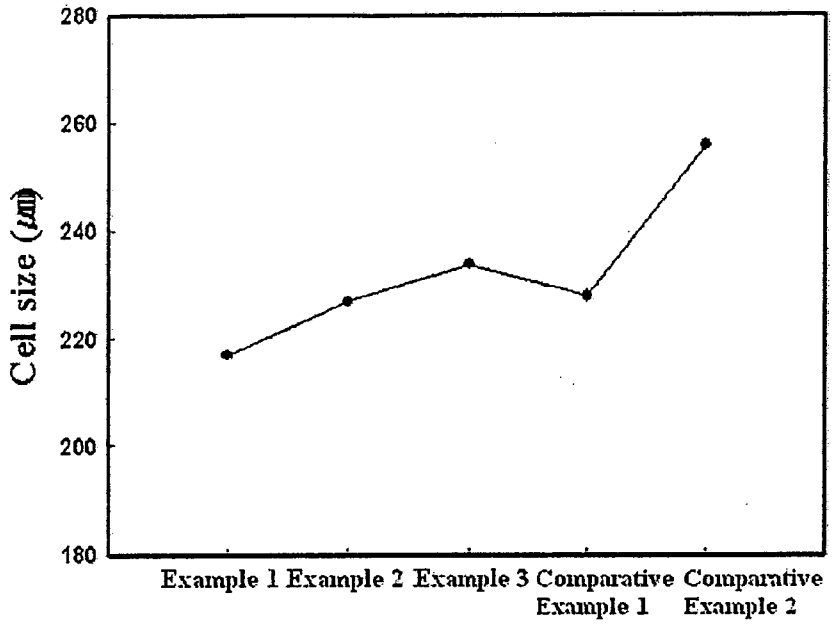
[Fig. 4]



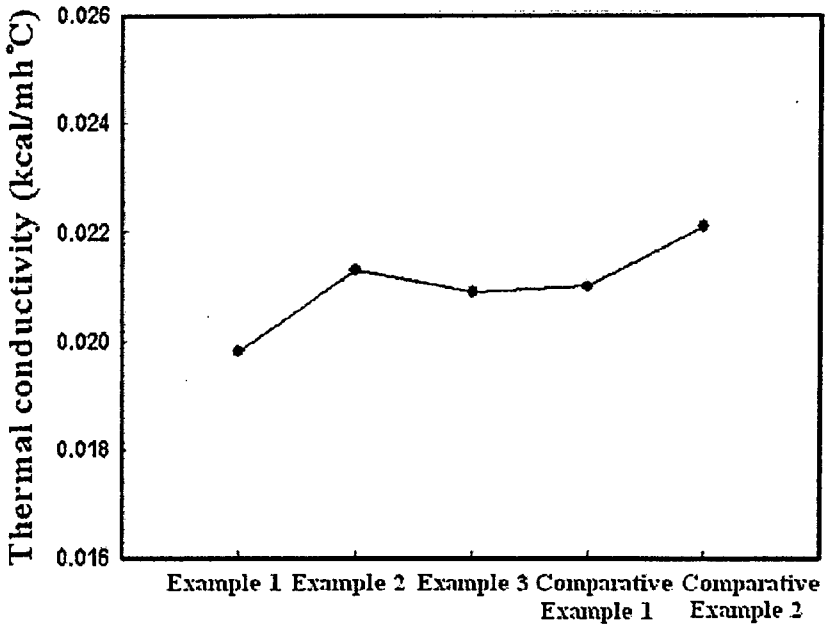
[Fig. 5]



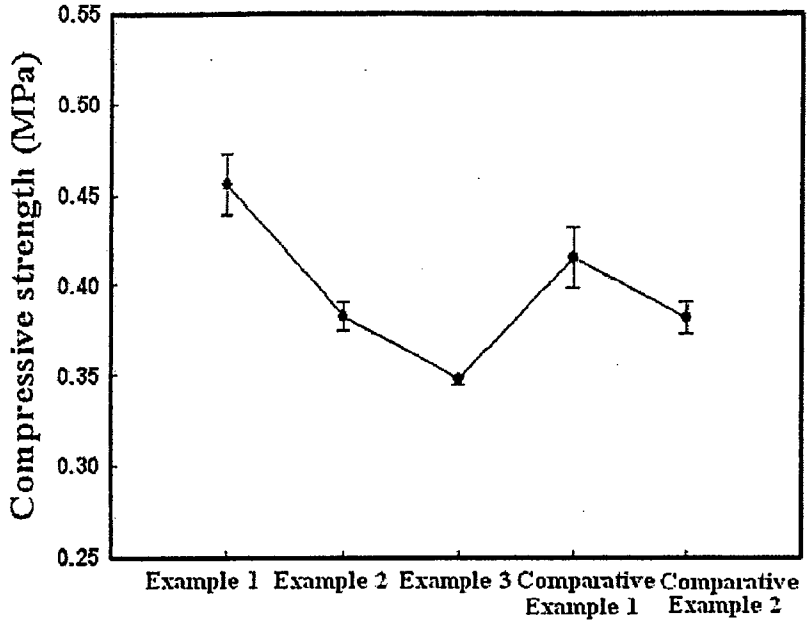
[Fig. 6]


280
260
240
220
200
180
Cell size (μm)
Example 1
Example 2
Example 3
Comparative Example 1
Comparative Example 2

[Fig. 7]


0.026
0.024
0.022
0.020
0.018
0.016
Thermal conductivity (kcal/mh°C)
Example 1
Example 2
Example 3
Comparative Example 1
Comparative Example 2

[Fig. 8]


Compressive strength (MPa)
0.55
0.50
0.45
0.40
0.35
0.30
0.25
Example 1
Example 2
Example 3
Comparative Example 1
Comparative Example 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2009/007486

A. CLASSIFICATION OF SUBJECT MATTER

C08J 9/30(2006.01)i, C08J 9/02(2006.01)i, C08G 18/82(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: C08J, C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal), Google Scholar & Keywords:polyisocyanurate foam, liquid silane, nucleating agent

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97/48757 A1 (IMPERIAL CHEMICAL INDUSTRIES PLC) 24 Dec. 1997 See abstract; page 2, lines 16-22; page 2, line 33-page 3, line 27; page 3, line 42-page 4, line 2; page 5, lines 25-28; page 5, line 34-page 6, line 25; claims.	1-18
A	US 5,854,296 A (WERNER, JOACHIM et al.) 29 Dec. 1998 See the whole documents.	1-18
A	US 6,121,336 A (OKOROAFOR, MICHAEL et al.) 19 Sep. 2000 See the whole documents.	1-18
A	US 2008/0188582 A1 (LEHMANN, PIT et al.) 07 Aug. 2008 See the whole documents.	1-18
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☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
11 AUGUST 2010 (11.08.2010)	**13 AUGUST 2010 (13.08.2010)**

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Facsimile No. 82-42-472-7140

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Telephone No. 82-42-481-8290

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR2009/007486

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		JP 2008-535989 A	04.09.2008
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