This invention relates to a foam, a foam-resin composite and a method of making foam-resin composites. The foam set forth in this invention comprises a urethane modified polyisocyanurate derived from an aromatic amino polyl and a polyether polyl. In addition to the polyisocyanurate foam, the composite of this invention further contains a resin layer, wherein the resin may be epoxy, bismaleimide, or phenolic resin. Such resins generally require cure or post-cure temperatures of at least 350° F.
FOAM, FOAM-RESIN COMPOSITE AND
METHOD OF MAKING A FOAM-RESIN
COMPOSITE

The invention described herein was made in the performance of work under NASA Contract No. NASA
36200 and is subject to the provisions of Section 305 of the
National Aeronautics and Space Act of 1958 (42

BACKGROUND OF THE INVENTION

1. Field of the Invention
This invention relates to foam, a foam-resin composite,
that is, a composite comprising a core or layer derived
from said foam and an integral resin layer, and a method
of making a foam-resin composite. More particularly,
this invention provides a formulation for a rigid, high
density urethane modified polysisocyanurate foam
which may be combined with a resin layer. The resin
is an epoxy resin, a bismaleimide resin, a phenolic resin,
or other resin which is cured or post-cured at a tempera-
ture of at least 350° F. The foam of this invention may
be used in a variety of situations where dimensional
stability at elevated temperatures, machinability, and
light weight are factors of concern. Also, this foam may
be used in a variety of manufacturing techniques to
make composite or resin finished products. The foam-
resin composite of this invention may be used in a vari-
fy of situations where high strength and light weight
are factors of concern.

2. Description of the Related Art
For a variety of reasons and in a variety of products,
it is often desired to combine a rigid foam with a layer
of a high strength material, such as a resin, to form a
composite having high strength yet low weight. A first
type of foam-resin application is the fabrication of foam
core panels or laminates for aerospace, aircraft, automo-
bile, boat, surfboard, ski, skateboard, etc. In this applica-
tion, the composite is used to form a strong, yet light-
weight, structure where the foam provides functions
such as structural reinforcement, or heat or noise insula-
tion.

A second application of foam-resin composites is the
construction of molds, models and prototypes. Here, a
foam-resin composite may be desired because a foam
may be shaped to the desired form and a resin may be
applied to a surface having significant curvature or
other non-uniformities.

While the combination of various foams and various
resins to form foam-resin composites is generally
known, foam-resin composites having a resin layer of
epoxy resin, a bismaleimide resin or phenolic resin
and having cure or post-cure temperatures of at least 350° F.
have uniformly been unsuccessful due to the high tem-
peratures and/or pressures required to cure these resins
and/or foam incompatibility with these resins. Known
foams are unsuitable when using these resins because of
dimensional instability at elevated temperatures, i.e., the
foam volume shrinks significantly or otherwise does not
hold the desired shape, lack of tensile strength, and low
compressive strength, i.e., the foam will not maintain
the desired shape in high temperature, high pressure
cure/post-cure conditions.

There exists a need for a foam-resin composite,
wherein the resin layer is formed of an epoxy resin, a
bismaleimide resin, a phenolic resin, or other resins
requiring cure or post-cure temperatures of at least 350°
F., and the foam is formulated so as to maintain dimen-
sional stability, provide suitable compressive and tensile
strength, and avoid thermal or chemical degradation
with these resins.

In addition, there exists a need to develop a foam which
does not contribute to ozone depletion. Many commer-
cial foams are made using chlorofluorocarbons as blowing
agents in the production of the foam. Chlorofluorocar-
bons, including hydrogenated chlorofluorocarbons,
are known to deplete the ozone in the earth's atmos-
phere. With these prior art foams, the chlorofluorocar-
bons are trapped within the closed cells when the rigid
foam is produced. Thus, the chlorofluorocarbons pro-
duce a detrimental environmental effect both when the
foam is produced and later, when it degrades and the
closed cells release the entrapped chlorofluorocarbons,
such as, for example in a landfill. Thus, there exists a
need to manufacture foam in such a fashion as to avoid
ozone depletion.

SUMMARY OF THE INVENTION

The invention relates to a foam, a foam-resin com-
posite and a method for making a foam-resin composite.
The foam of this invention comprises a rigid urethane
modified polysisocyanurate foam having a density of
about 5 to about 15 lb/ft³. The foam exhibits good di-
menional stability, good compressive strength, and
resistance to thermal and chemical degradation. The
foam may be used to produce composites when com-
pared with a resin. The resin may be selected from the
group consisting of epoxy resins, bismaleimide resins,
phenolic resins, or other resins requiring cure or post-
cure temperatures of at least 350° F.

DETAILED DESCRIPTION OF THE
PREFERRED EMBODIMENTS

The present invention relates to a foam, a foam-resin
composite and a method of making a foam-resin com-
posite. The high density rigid foam of this invention is a
two-component urethane modified polysisocyanurate.
The foam-resin composite is formed of two integral
parts, a foam section and a resin layer, which may be
fiber reinforced. The resin layer is formed of a resin
selected from the group of epoxy resin, bismaleimide
(BMI) resin, phenolic resin, or other resins requiring
cure or post-cure temperatures above 350° F., as dis-
cussed below. Generally, the foam section is first manu-
factured, either net shape molded or secondarily ma-
chined, either with a post cure or without a post cure
and then the resin layer or fiber reinforced resin layer is
applied to the foam section.

The foam is produced from a two-component foam
system, the components generally referred to as “A
component” and “B component”. The A component
contains isocyanate and the B component generally
contains a blend of polyols, surfactants, catalysts and
water. The A and B components may be combined by
hand mixing or foam making machines. The combina-
tion of the A and B components releases carbon dioxide
(CO₂) which is utilized as a blowing agent in the foam
manufacture. This mixture is then placed in a mold and
allowed to cure for about one hour at about 120° F. to
140° F. If desired, the foam may be post cured by fur-
ther heating the foam after the curing step.

The A component contains isocyanates having a
functionality of at least about 2.4, preferably between
about 2.4 and about 3.2, for example triisocyanates,
polysisocyanates, or mixtures thereof. The organic iso-
cyanoates may be derived from aliphatic, cycloaliphatic, aryl, aromatic or aromatic aliphatic isocyanates. Aromatic isocyanates are generally preferred.

Among the many isocyanates suitable for the practice of the subject invention are, for example, aliphatic isocyanates such as tetramethylene, hexamethylene, octamethylene and decamethylene diisocyanates and their alkyl substituted homologs; cycloaliphatic isocyanates such as 1,2-, 1,3- and 1,4-cyclohexane diisocyanates, 2,4- and 2,6-methylcyclohexane diisocyanates, 4,4' and 2,4'-dicycloyxylsdiisocyanates, 4,4' and 2,4'-dicyclohexylmethylene diisocyanates, 1,3,5-cyclohexane trisocyanate, and saturated (hydrogenated) polymethylene polyphenylene polyisocyanates; aliphatic isocyanates such as isocyanatomethylcyclohexane isocyanates, isocyanatoethylcyclohexane isocyanates, bis(isocyanatomethyl)cyclohexane diisocyanates, 4,4' and 2,4'-bis(isocyanatomethyl)cyclohexane, and isophorone diisocyanate; aromatic isocyanates such as 1,2-, 1,3- and 1,4-phenylene diisocyanate, 2,4- and 2,6-toluene diisocyanate, 2,4'-, 4,4', and 2,2'-biphenyl diisocyanates, 2,2', 2,4' and 4,4'-diphenylmethane diisocyanates, and polymethylene polyphenylene polyisocyanates (polymeric MDI); and aromatic aliphatic isocyanates such as 1,2-hexamethylene, 1,3- and 1,4-xylene diisocyanates.

Most preferably, the A component contains 4,4'-diphenylmethane diisocyanate (MDI) prepolymer having a functionality of about 2.8 to 3.2, preferably with about 30-45% being in the monomer state, about 55-65% existing as higher polymers of MDI, with about 1-10% existing as 2,2 or 2,4 diphenylmethane diisocyanate. The preferred A component is marketed under the tradename "Mondur G 489", by Miles, Inc., Pittsburgh, Pa. This A component, as purchased, has a functionality (average number of reactive functional groups per molecule) of approximately 3.0, with a mol. wt. of approximately 415.

The B component contains about 60-90% of an aromatic amino polyol and about 5-35% of a polyether polyol, combined with trimerization catalyst(s), surfactant(s), and water.

The aromatic amino polyol may be any compound having the formula:

![Aromatic amino polyol formula]

where R is hydrogen or R', and R2 is hydrogen, R or the nonyl radical —C6H19. The preferred aromatic amino polyols have a functionality of about 3 to about 4. Most preferred are those set forth in U.S. Pat. Nos. 3,297,597 and 4,137,263, herein incorporated by reference. Such polyols include those marketed under the tradename "R350X" by Eastman Chemicals, Kingsport, Tenn. R350X has a hydroxyl number of 520-540 (mg KOH/g), a viscosity of about 15,000 cp @ 77°F, an equivalent weight of about 106, and a functionality of about 3. Most preferred, the aromatic amino polyol is about 60 to about 70 vol. % of the B component.

Suitable polyether prepolyols for use in this invention are polyalkylene polyether polyols such as the polymerization product of an alkylene oxide or of an alkylene oxide with a polyhydric alcohol. Any suitable polyhydric alcohol, including both aliphatic and aromatic, may be used such as glycerol, 1,1,1-trimethylo propane, 1,1,1-trimethylolhexane and hexane-1,2,6-triol. Also suitable are relatively high molecular weight polyoxyalkylene polyether prepolyols containing predominantly terminal oxypropylene oxide blocks (i.e., also containing predominantly terminal secondary OH-groups) which are produced by the usual methods. Such polyether prepolyols of this invention include polypropyleneether triols obtained by the chemical addition of propylene oxide to trihydroyxyl organic containing materials, such as glycerol; 1,2,6-hexanediol; 1,2,4-trihydroxy- 1,3,5-tetramethylene; 1,1,1-trimethylolpropane; 3-(2-hydroxyethoxy)-1,2-propanediol; 3-(2-hydroxypropoxy)-1,2-propanediol; 2,4-dimethyl-2-(2-hydroxyethoxy) methylpenetanediol-1,5; 1,1,1-tris-[2-(2-hydroxyethoxy) methyl]ethane; 1,1,1-tris[(2-hydroxypropoxy) methyl]-propane; and the like, as well as mixtures thereof. Preferably the polyether polyl is a triol polyl, i.e., having a functionality of about 3, which is produced by the propoxylation of glycerine to a mol. wt. of about 200 to about 700. The most preferred polyether polyl is marketed under the tradename "Voranol V2025" by Dow Chemical Company, Freeport, Tex. The polyl is present in an amount between about 5 to about 35 volume percent of the B component. Most preferred, the polyether polyl is about 25 to about 30 vol. % of the B component.

The trimerization catalyst may be any of a variety of known catalyst, including metal salts, alkali metal salts and tertiary amine trimerization catalysts which are well known to those skilled in the art. A great many catalysts are disclosed in the Journal of Cellular Plastics, December 1975, at page 329; and in U.S. Pat. Nos. 3,745,133, 3,896,052, 3,899,443, 3,903,016, 3,954,684 and 4,101,465, herein incorporated by reference. Suitable catalysts include, for example, strong bases such as quaternary ammonium hydroxides for example benzyltrimethylammonium hydroxide; alkali metal hydroxides such as sodium or potassium hydroxide; alkali metal alkoxides such as sodium methyate and potassium isopropylate; trialklyolphosphines such as triethylphosphine; dialkyldiminoalkylphenols such as 2,4,6-tris(dimethylaminomethyl)phenol; 3- and/or 4-substituted pyridines such as 3- or 4- methylpyridine, metal organic salts such as sodium tetrakis(hydroxymethyl)borate; Friedel-Crafts catalysts such as aluminum chloride, ferric chloride, boron trifluoride, zinc chloride and alkali metal salts of weak organic acids and nitrophenols and imides such as potassium octanoate, potassium 2-ethylhexanoate, potassium benzoate, sodium picate, and potassium phthalimide. Also used are the strongly basic N,N',N"-tris(dialkyldiminoalkyl)-s-hexahydrotriazines such as N,N',N"-tris(dimethylaminopropyl)-s-hexahydrotriazine, optionally combined with aliphatic, low molecular mono and/or dicarboxylic acids such as acetic acid and/or adipic acids, or aromatic carboxylic
acids such as benzoic acid. The trimerization catalyst is preferably a combination of a potassium salt trimerization catalyst and an amine trimerization catalyst. Preferably, the B component contains about 0.5-5% of a potassium salt trimerization catalyst. Particularly preferred are those sold under the tradename "T45" by Air Products Company, Lehigh Valley, Pa., which is a potassium alkyl hexoate/glycol blend. Most preferably, the tertiary amine trimerization catalyst is preferably present as the phenol salt, 2-ethylhexanoic acid salt and the like. The amine trimerization catalyst is preferably present as 0.5-5% of the B component and is preferably that marketed under the tradename "TMR4" by Air Products Company, Lehigh Valley, Pa., which is a tertiary amine/glycol blend. Most preferably, the tertiary amine trimerization catalyst is about 1.8 to about 3.2 vol. % of the B component.

Commonly used tertiary amine catalysts include N-methylmorphorine, N,N,N',N'-tetramethylpropylene diamine, 1,4-diazabicyclo [2,2,2] octane, (DABCO), 1,8-diazabicyclo[5,4,0] undecene-7 and its salts such as the phenol salt, 2-ethylhexanoic acid salt and the like. The amine trimerization catalyst is preferably present as about 0.5-5% of the B component and is preferably that marketed under the tradename "LM5420" by Union Carbide Chemicals and Plastics Company, Danbury, Conn., which is a polyalkyleneoxidemethylsiloxane copolymer. Most preferably, the surfactant is about 2.0 to about 5.0 vol. % of the B component. While the surfactant may be any of a variety of known surfactants, preferably, the surfactant is a silicone base surfactant, which are generally polyalkylene- polyoxyalkylene block copolymers which are either linear or pendant block copolymers. Representatives of this type of surfactant are those sold commercially by Dow Chemical under the name DC-193, DC-195 DC-198 and the like. Most preferably are the surfactants marketed under the tradename "LS420" by Union Carbide Chemicals and Plastics Company, Danbury, Conn., which is a polyalkyleneoxidesiloxane copolymer. Most preferably, the surfactant is about 2.0 to about 5.0 vol. % of the B component.

The B component also contains an amount of water sufficient to provide the required CO₂ as a blowing agent upon reaction with the MDI in the A component. Here, 100% of the blowing agent is CO₂ produced by the reaction of the A and B components; there is no need to use other physical blowing agents. This CO₂ is trapped in the closed cells of the rigid foam. Preferably, the B component contains about 0.5-1.5% water. This production and use of CO₂ as a blowing agent eliminates any concern relating to ozone depletion. Thus, the foam of the present invention is much more environmentally safe to produce and use than many other known foams, particularly those using chlorofluorocarbons.

Example 1 compares the foam of the present invention with a known commercial foam, which is generally a rigid polyisocyanurate foam having a density of 4-20 lb./ft.³ and which is marketed as a foam providing good dimensional stability at high temperatures. The A and B components were measured out such that the formulation for the foam tested was as follows:

<table>
<thead>
<tr>
<th>Overall Vol. %</th>
<th>% of A or B Component</th>
</tr>
</thead>
<tbody>
<tr>
<td>A Component</td>
<td></td>
</tr>
<tr>
<td>G 489</td>
<td>89.247</td>
</tr>
<tr>
<td>B Component</td>
<td></td>
</tr>
<tr>
<td>R300X</td>
<td>6.859</td>
</tr>
<tr>
<td>V2025</td>
<td>2.929</td>
</tr>
<tr>
<td>T45</td>
<td>0.281</td>
</tr>
<tr>
<td>TMR4</td>
<td>0.169</td>
</tr>
<tr>
<td>L5420</td>
<td>0.392</td>
</tr>
<tr>
<td>water</td>
<td>0.115</td>
</tr>
<tr>
<td>TOTAL</td>
<td>100.00</td>
</tr>
</tbody>
</table>

The foam may be produced either by known hand mix methods or via use of a high or low pressure foam making machine. The following are the typical parameters for hand mix, hand pour processing:

| A Component Temperature, °F. | 65 to 105 |
| B Component Temperature, °F. | 65 to 105 |
| Mix Time, sec                | 15 to 20  |
| Mold Temperature, °F.        | 120 to 140|
| Demold Time                  | One hour, if post cure not required |

In Mold Post Cure, hrs/°F.app.

A/FOAM W/POST CURE A/B Component Pressures, psi

| A Component Pressure          | 50 to 300 |
| Impeller Speed, RPM          | 4,000 to 9,000 |

The above mixing methods and formulation yielded the following reactivity profiles for the foam:

| Ratio A/B | 8.3/1.0 |
| Component Temp., °F. | 72 |
| A/B weight, g        | 410/49.4 |
| Mix Time, sec        | 15 |
| Start of Rise, sec   | 30 |
| Hard Gel, sec        | 110 |
| Tack Free, sec       | 140-155 |
| End of Rise, sec     | 140-200 |
| Cup Density, lbs/ft³ | 9-15 |

Where post cure is not desired, following the initial curing of the foam, the foam is generally allowed to sit at ambient conditions for one day to one week to further cure.
<table>
<thead>
<tr>
<th>TEST</th>
<th>FOAM W/O POST CURE</th>
<th>FOAM W/POST CURE</th>
<th>COMMERCIAL FOAM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>avg.</td>
<td>n</td>
<td>StD</td>
</tr>
<tr>
<td>(% volume change)</td>
<td>14.23</td>
<td>3</td>
<td>—</td>
</tr>
<tr>
<td>Density (lb/ft³)</td>
<td>765.4</td>
<td>5</td>
<td>25.0</td>
</tr>
<tr>
<td>@ Amb T (Amb P)</td>
<td>710.6</td>
<td>5</td>
<td>12.4</td>
</tr>
<tr>
<td>Compressive Strength</td>
<td>599.5</td>
<td>5</td>
<td>19.1</td>
</tr>
<tr>
<td>@ 250° F. (Amb P)</td>
<td>509.5</td>
<td>5</td>
<td>18.1</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>270.1</td>
<td>5</td>
<td>40.9</td>
</tr>
<tr>
<td>@ Amb T (Amb P)</td>
<td>289.2</td>
<td>5</td>
<td>27.6</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>217.2</td>
<td>5</td>
<td>11.6</td>
</tr>
<tr>
<td>@ 250° F. (Amb P)</td>
<td>No Test</td>
<td>5</td>
<td>—</td>
</tr>
</tbody>
</table>

As shown, a lower A/B ratio produced a foam with a lower density. A lower density may be desired when lower weight is a primary concern, e.g., flight related applications. Also, a lower density foam generally provides better insulation qualities than a higher density foam. As evidenced by Example 1, the foam of the present invention, the user has significant flexibility to tailor a foam to his specific needs.
conditions vary with the desired application. The purpose of the post cure step is to provide further cross-linking of the polymers in the foam to provide a more stabilized foam. The post cure conditions, depending on the application, may vary from a temperature of about 250° for 4 hours to a temperature of 350° for 18 hours. It is generally preferred to post cure the foam in the mold, rather than out of the mold, and at about 350° F. for about 3½ hours.

As noted, it is advantageous to post cure in some applications while post curing is not advantageous in others. This is illustrated by the following examples. In a filament winding application, a foam core, shaped to a predetermined shape, is wound with fibers impregnated with resin so as to form an exterior resin layer on the foam core. After filament winding, the resin is cured by heating. In this application, it is often advantageous that the foam is not post cured, as the heating to cure the resin causes the foam to expand somewhat, thereby exerting an “internal pressure” about the filament winding. This internal pressure aids in maintaining the desired shape of the resin layer. In these applications, often the foam core is removed, and this internal pressure helps to form a suitable internal surface of the resin layer. Post curing of the foam is generally preferred when the foam is used in a parasitic application, i.e., the foam is intended to remain as an integral part of the finished product wherein the foam section of the foam-resin composite is partially or completely removed. Often, it is desired to produce a product made from resin which has a hollow section. In this situation the hollow section may initially be filled with the inventive foam, and the resin applied about the foam. Then, after the resin is suitably cured, including post curing if desired, the foam is removed by water blasting or carbon dioxide blasting, resulting in a hollow, open space where the foam had existed.

The resin layer may be applied or adhered in a variety of known ways to the foam section of the foam-resin composite. Such methods of adhering the resin include spraying, filament winding, and hand or machine lay-up procedures. Generally, it is preferred that the resin layer contains reinforcing fibers or filament to strengthen the resin layer. These fibers or filaments may generally be any suitable fibers or filaments which are known in the art, e.g., graphite, glass, kevlar or other.

Epoxy, BMI and phenolic resins have the advantage of being able to withstand higher in-use temperatures than other resins. Generally, the higher the resin cure temperature, the higher the design temperature (in-use temperature) of the finished product. Thus, there is an incentive to cure at higher temperatures. However, prior to this invention, these resins could not be cured at the optimum, higher temperatures, as the higher temperatures (and pressures) required to optimally cure the resins has resulted in thermal degradation or breakdown of the known foams, thus resulting in failure of the known foam-resin combinations.

Generally, depending upon the application, epoxy resins may be cured at temperatures of 325°-350° F. or higher and at pressures of 5 psig or higher. BMI resin may generally be cured at temperatures of 375°-450° F. or higher with pressures ranging from 85 to 100 psig or higher. Phenolic resin may generally be cured at temperatures of 350°-375° F. or higher and at pressures of 25 psig or higher. As known foams are found to fail or lose dimensional stability particularly at temperatures above 350° F., it is generally more difficult to find a known foam which is suitable for use with a BMI resin than with epoxy resin and hence, though this invention relates to the use of epoxy resin, it is particularly applicable to BMI resin and phenolic resin which require higher cure temperatures. Also, many known foams fail as BMI and phenolic resins typically require even higher post cure temperatures to finish cross-linking of the resin. Post cure conditions are typically in the range of 20° to 75° above cure temperatures.

It is believed that the tri-functional polyols, the production of urea upon reaction of the MDI and water, and the subsequent reaction between the urea and MDI, combine to significantly increase cross-linkage and cross-linking of the foam, such that it is suitable for the high temperature and/or pressure curing requirements with epoxy, BMI, phenolic resins and other resins. What is claimed is:

1. A urethane modified polyisocyanurate rigid foam comprising the reaction product of:
   - an A component comprising polymeric isocyanate having a functionality of at least 2.4;
   - a B component comprising:
     - an aromatic amino polyol having the formula
The rigid foam of claim 1 wherein the polymeric isocyanate is polymeric 4,4'-diphenylmethane diisocyanate.

3. The rigid foam of claim 1 wherein the trimerization catalyst is a combination of two catalysts.

4. The rigid foam of claim 3 wherein the trimerization catalyst consists of an amine catalyst and a potassium salt catalyst.

5. The rigid foam of claim 1 wherein the surfactant is a silicone based surfactant.

6. The rigid foam of claim 5 wherein the silicone based surfactant is polyalkyleneoximidylsiloxane copolymer.

7. The rigid foam of claim 1 wherein the A component is combined with the B component in a ratio of about 6 to about 10 parts of the A component to 1 part of the B component.

8. The rigid foam of claim 1 wherein the A component is combined with the B component in a ratio of about 3 to about 5 parts of the A component to 1 part of the B component.

9. The rigid foam of claim 1 wherein the aromatic amino polyol is about 60 to about 70 vol. % of the B component.

10. The rigid foam of claim 1 wherein the polyether polyol is about 25 to about 30 vol. % of the B component.

11. A method of making a foam-resin composite, comprising the steps of:

combining an A component with a B component to induce formation of a urethane modified polyisocyanurate rigid foam having a density of about 5 to about 15 lb./ft³;

the A component comprising a polymeric isocyanate having a functionality of at least 2.4;

the B component comprising:

an aromatic amino polyol having the formula

R₁ is hydrogen or R, and R₂ is hydrogen, R or the nonyl radical -CH₉H₁₉, said aromatic amino polyol being about 60 to about 90 vol. % of the B component;

a polyether polyol, said polyether polyol being about 5 to about 35 vol. % of the B component;

a trimerization catalyst;

an amount of water sufficient to provide, upon reaction of the A and B components, CO₂ as the sole blowing agent;

wherein the foam has a density of about 5 to about 15 lb./ft³.

2. The rigid foam of claim 1, wherein the polymeric isocyanate is polymeric 4,4'-diphenylmethane diisocyanate.

30. The method of claim 11 wherein the polyether polyol has a functionality of about 60 to about 90 vol. % of the B component;

a polyether polyol, said polyether polyol being about 5 to about 35 vol. % of the B component;

a trimerization catalyst;

a surfactant;

an amount of water sufficient to provide, upon reaction of the A and B components, CO₂ as the sole blowing agent;

curing the foam;

adhering to the foam a resin layer containing a resin selected from the group consisting of epoxy resin, bismaleimide resin and phenolic resin;

curing the resin layer at elevated temperature.

12. The method of claim 11 wherein the polymeric isocyanate is polymeric 4,4'-diphenylmethane diisocyanate.

13. The rigid foam of claim 11 wherein the polyether polyol has a functionality of about 60 to about 90 vol. % of the B component;

a polyether polyol, said polyether polyol being about 5 to about 35 vol. % of the B component;

a trimerization catalyst;

a surfactant;

an amount of water sufficient to provide, upon reaction of the A and B components, CO₂ as the sole blowing agent;

curing the foam; adhering to the foam a resin layer containing a resin selected from the group consisting of epoxy resin, bismaleimide resin and phenolic resin; curing the resin layer at elevated temperature.

14. The rigid foam of claim 11 wherein the aromatic amino polyol is about 25 to about 30 vol. % of the B component.

15. The method of claim 11 wherein the surfactant is a silicone based surfactant.

16. The method of claim 15 wherein the silicone based surfactant is polyalkyleneoximidylsiloxane copolymer.

17. The method of claim 11 wherein the A component is combined with the B component in a ratio of about 6 to about 10 parts of the A component to 1 part of the B component.

18. The method of claim 11 wherein the A component is combined with the B component in a ratio of about 3 to about 5 parts of the A component to 1 part of the B component.

19. The method of claim 11 wherein the aromatic amino polyol is about 60 to about 70 vol. % of the B component.

20. The method of claim 11 wherein the polyether polyol is about 25 to about 30 vol. % of the B component.

21. The method of claim 11 wherein the resin layer includes reinforcing fibers.
22. The method of claim 11, further comprising the step of forming the foam into a predetermined shape prior to adhering the resin layer.

23. A cured foam-resin composite, comprising:
(A) a urethane modified polyisocyanurate rigid foam produced by the process of reacting an A component with a B component;
the A component comprising a polymeric isocyanate having a functionality of at least 2.4;
the B component comprising:
an aromatic amino polyol having the formula

\[
\begin{align*}
\text{R}_1 & = \text{hydrogen or R}, \\
\text{R}_2 & = \text{hydrogen, R or the nonyl radical } \text{C}_9\text{H}_{19} \text{, said aromatic amino polyol being about 60 to about 90 vol.} \\
\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH} & = \text{CH}_3
\end{align*}
\]

where \( \text{R} \) is

\[
\begin{align*}
\text{CH}_3 & \text{CH}_2\text{OH} \\
\text{HC}-\text{OH} & \text{O} \\
\text{CH}_2 & \text{R}
\end{align*}
\]

24. The composite of claim 23, wherein the polymeric isocyanate is polymeric 4,4'-diphenylmethane diisocyanate.

25. The composite of claim 23 wherein the polyether polyol has a functionality of about 3.0 and a molecular weight of about 200 to about 700.

26. The composite of claim 23 wherein the trimerization catalyst consists of a tertiary amine catalyst and a potassium salt catalyst.

27. The composite of claim 23 wherein the surfactant is a silicone based surfactant.

28. The composite of claim 27 wherein the silicone based surfactant is polyalkyleneoximidethylsiloxane copolymer.

29. The composite of claim 23 wherein the A component is combined with the B component in a ratio of about 6 to about 10 parts of the A component to 1 part of the B component.

30. The composite of claim 23 wherein the A component is combined with the B component in a ratio of about 3 to about 5 parts of the A component to 1 part of the B component.

31. The composite of claim 23 wherein the aromatic amino polyol is about 60 to about 70 vol. % of the B component.

32. The composite of claim 23 wherein the polyether polyol is about 25 to about 30 vol. % of the B component.

33. The composite of claim 23 wherein the resin layer includes reinforcing fibers.

34. The rigid foam of claim 1 wherein the polyether polyol has a functionality of about 3.0 and a molecular weight of about 200 to about 700.

35. The rigid foam of claim 1 wherein the trimerization catalyst is a tertiary amine.

36. The rigid foam of claim 34 wherein the polyether polyol is alkoxylated glycercine.

37. The rigid foam of claim 4 wherein the potassium salt trimerization catalyst is potassium alkyl hexoate.

38. The rigid foam of claim 4 wherein the amine catalyst is a tertiary amine catalyst.

39. The rigid foam of claim 38 wherein the potassium salt catalyst is a blend of potassium alkyl hexoate and a glycol.

40. The rigid foam of claim 13 wherein the polyether polyol is alkoxylated glycercine.

41. The rigid foam of claim 11 wherein the trimerization catalyst is a combination of two catalysts.

42. The rigid foam of claim 41 wherein the trimerization catalyst consists of a tertiary amine catalyst and a potassium salt catalyst.

43. The method of claim 42 wherein the potassium salt trimerization catalyst is potassium alkyl hexoate.

44. The composite of claim 25 wherein the polyether polyol is alkoxylated glycercine.

45. The composite of claim 23 wherein the trimerization catalyst is a tertiary amine.

46. The composite of claim 23 wherein the trimerization catalyst is a combination of two catalysts.

47. The composite of claim 26 wherein the potassium salt trimerization catalyst is potassium alkyl hexoate.