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(54) **Title**: THERMALLY REGULATED SYSTEM

(57) **Abstract**: Disclosed herein are thermally regulated systems including, but not limited to, refrigerated truck, cold storage unit, transit packaging unit, cold chain insulated packaging system, for storage and transport temperature sensitive products that include fresh, frozen, warm and processed food, pharmaceutical, medical and clinical samples.

Thermally Regulated System

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of U.S. Provisional Application Nos. 61/973074 filed on March 31, 2014, 62/024669 filed on July 15, 2014, and 62/054471 filed on September 24, 2014, which are incorporated herein by reference in their entirety.

FIELD OF THE INVENTION

The present teachings relates to thermally regulated systems and in particular to the packaging systems comprising bio-based closed-cell insulation foams for storage and transport of temperature sensitive products.

BACKGROUND INFORMATION

Heat is the primary environmental hazard in the transportation of temperature sensitive products. A wide variety of thermally regulated packaging systems in several different configurations are disclosed in prior art for storage and/or shipping temperature sensitive products. These systems use different types of insulation and refrigeration to maintain a desired thermal environment within the container or package. The performance of an insulated packaging container to protect the products at the desired temperature for extended time depends on its total R-value which is measure of thermal resistance. The higher the R-value the higher is the resistance to heat.

Plastic foams are widely used as a protective packaging material mainly where shock absorption is the main concern. For this function, the foams must be open-cell and flexible. The closed-cell and rigid foams are generally used for insulation purpose to protect temperature sensitive products. Different types of plastic foam packaging that can be used are: expanded polystyrene, expanded polypropylene (EPS), polyurethane (PU), and expanded polyethylene. Some of the drawbacks with EPS are lower R value which reduces the shipping cycle shorter, thick liner and high density adds weight to package and thereby increases freight cost.

Polyurethane foams are derived from toxic isocyanates and when these foams burned can release high smoke containing toxic gasses dangerous to living beings. Furthermore, majority of these plastic foams are not environmentally friendly and are being manufactured from the chemicals derived from fossils fuel based feedstocks and are toxic. For example, phenolic foams use a phenol based monomer which is produced from a petroleum feedstock, a depleting non-renewable resource and formaldehyde as another monomer, which is classified as human carcinogenic. Current insulated materials do not have a good balance among high insulation performance, low material and logistic costs, low environmental impact, safety and health.

Hence, there is a need for sustainable thermally regulated systems with a packaging design having a good balance among high R-value, low material and logistic costs, low environmental impact, safety and health.

SUMMARY OF THE INVENTION

In an aspect, there is a thermally regulated system, comprising:

(a) an outer shell defining a retention chamber;

(b) at least one layer of bio-based closed-cell insulation foam lining the retention chamber so as to define an insulated retention chamber,

wherein the bio-based closed-cell insulation foam comprises a polymeric phase defining a plurality of open cells and a plurality of closed-cells,

wherein one or more blowing agents is disposed in at least a portion of the plurality of closed-cells,

wherein the bio-based closed-cell insulation foam is at least one of:

- a closed-cell condensed tannin-based foam derived from a foamable composition comprising a surface-active condensed tannin, a formaldehyde-free tannin-reactive monomer, a saturated or an unsaturated organic anhydride, a surfactant, a blowing agent, an acid catalyst, and an optional polyamine and/or plasticizer; or
- a closed-cell mixed tannin-phenolic foam derived from a composition comprising a volatile-free condensed tannin, a

formaldehyde-free tannin-reactive monomer, a phenolic-resole prepolymer, a polyamine, a surfactant, a blowing agent, an acid catalyst, and an optional saturated or unsaturated organic anhydride and/or plasticizer;

(c) a cold source or a hot source disposed within the insulated retention chamber to maintain the insulated retention chamber at a desired temperature during storage and/or transportation of a temperature sensitive product; and

(d) optionally a temperature monitoring device disposed inside the retention chamber,

wherein the bio-based closed-cell foam has an open-cell content of less than 15%, measured according to ASTM D6226-5, and an R-value per inch of at least 6.0 $hr \cdot ft^2 \cdot °F/Btu$.

In an aspect, the thermally regulated system further comprises a temperature monitoring device.

In an aspect, the thermally regulated system is a refrigeration unit.

In an aspect, the thermally regulated system is a refrigerated truck.

In an aspect, the thermally regulated system is a cold storage unit.

In an aspect, the thermally regulated system is a transit packaging unit.

In an aspect, the thermally regulated system is for a cold chain shipment of a temperature sensitive product.

In an aspect, there is a method for packaging a temperature-sensitive product for cold chain shipment comprising the step of:

a) providing an outer shell defining a retention chamber;

b) disposing at least one layer of bio-based closed-cell foam to line the retention chamber so as to define an insulated retention chamber, wherein the bio-based closed-cell insulation foam is at least one of:

- a closed-cell condensed tannin-based foam derived from a foamable composition comprising a surface-active condensed tannin, a formaldehyde-free tannin-reactive monomer, a saturated or an unsaturated organic anhydride, a surfactant, a blowing agent, an acid catalyst, and an optional polyamine and/or plasticizer; or
- a closed-cell mixed tannin-phenolic foam derived from a composition comprising a volatile-free condensed tannin, a formaldehyde-free tannin-reactive monomer, a phenolic-resole prepolymer, a polyamine, a surfactant, a blowing agent, an acid catalyst, and an optional saturated or unsaturated organic anhydride and/or plasticizer;

c) disposing a cold source within the insulated retention chamber to maintain the insulated retention chamber at a desired temperature during storage and/or transportation of a temperature sensitive product; and

d) disposing a temperature-sensitive product within the insulated retention chamber, wherein the thermal insulate the product during transportation.

In one aspect of the invention, the thermally regulated system further comprises a bio-based open-cell foam absorbed with a phase change material such as water or saline solution is used as a cold source.

In an aspect, the outer shell is wrapped up with a high density polyethylene film or a sheet.

The foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the disclosure, as defined in the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows the effect of maleic anhydride on moisture absorption by a closed-cell condensed tannin-based foam.

Figures 2A and 2B show GC-MS headspace spectra of commercial condensed tannin extracts from two different geographical regions: as-received Tannin-A and as-received Tannin-F respectively.

Figures 3A, 3B, and 3C show GC-MS headspace spectra of commercial condensed tannin extracts: as-received Tannin-F; volatile-free condensed tannin obtained by heating the as-received Tannin-F in air; and volatile-free condensed tannin obtained by heating the as-received Tannin-F in nitrogen respectively.

DETAILED DESCRIPTION

The disclosures of all patent and non-patent literature referenced herein are hereby incorporated in their entireties.

As used herein, the term “cold chain” refers to a temperature controlled supply chain, and consists of storage and distribution activities which maintain a product at a given temperature range for a specified amount of time. The cold chain is an unbroken process that originates at the point of product manufacture and terminates at the end consumer and thermal regulated systems are one of the tools being used in the process.

As used herein, the term “food” refers to fresh, frozen, warm and processed foods including, but not limited to vegetables, fruits, seafood, meat, beverage, and dairy products. As used herein, the term “chemicals” refers to cryogenic liquids, including but not limited to, liquefied natural gas. Cryogenic liquids *(also known as cryogens)* are gases at normal temperatures and pressures. However, at low temperatures, cryogenic liquids are in their liquid state. As used herein, the term “pharmaceutical products” refers to medications including, but not limited to, prescription medications, insulin, and vaccines. As used herein, the term “Medical products” refers to clinical and biological samples such as blood, tissue, organs, and cultured cells.

As used herein, the term “surface-active condensed tannin” is used interchangeably with “condensed tannin” and “tannin” and refers to bio-derived condensed tannins that when dissolved in 50 wt% of water has a

surface tension of less than 53.0 mN/m, wherein the amount in weight% is based on the total weight of the tannin and water.

As used herein, the term "volatile-free condensed tannin" refers to a surface-active condensed tannin composition, that is substantially free of one or more volatile compounds, wherein the one or more volatile compounds has a boiling point of greater than 277 °C, as analyzed by GC-MS headspace method disclosed *infra*. As used herein the phrase "condensed tannin composition substantially free of one or more volatile compounds" refers to tannin compositions wherein the amount of individual volatile component having boiling points greater than 277 °C, as measured by GC-MS headspace spectrum disclosed infra, and expressed as peak area is less than 1.0×10^{-5}, or less than 0.7×10^{-5}, or less than 0.5×10^{-5}. As used herein, the phrase "remove one or more volatile compounds" refers to significant reduction in the peak intensities of the one or more volatile compounds having a boiling point of greater than 277 °C, as measured by GC-MS headspace spectra due to evaporation and/or further reaction resulting in the formation of non-volatile compounds. Figures 3B and 3C shows GC-MS headspace spectra of volatile-free condensed tannin obtained by heating the as-received Tannin-F in air and in nitrogen respectively. As shown in Figures 3B and 3C, the volatile-free condensed tannin are substantially free of one or more volatile compounds having a boiling point of greater than 277 °C. For comparison, Figure 3A shows GC-MS headspace spectra of as-received commercial condensed tannin extract, Tannin-F comprising one or more volatile compounds having a boiling point of greater than 277 °C.

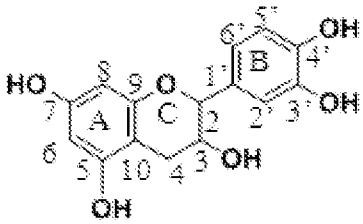
As used herein, the term "biologically-derived" is used interchangeably with "bio-derived" and refers to chemical compounds including monomers and polymers, that are obtained from plants and contain major amount of renewable carbon, and minor amount of fossil fuel-based or petroleum-based carbon, wherein the minor amounts are chemicals could be residuals from extraction process or additives added for stabilization or other purposes.

As used herein, the term "bio-based composition" refers to compositions that contains at least 25% renewable carbon, and less than 75% fossil fuel based or petroleum based carbon.

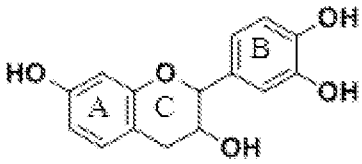
As used herein, bio-derived tannins are vegetable-based, extracted from leaf, bud, seed, root, bark, trunk, nut shells, skins of fruits, and stem tissues of plants and trees. As used herein, the term "mimosa tannin" refers to a tannin extracted from leaf, bud, seed, root, bark, trunk, or stem tissues of a mimosa tree. The condensed tannin may also be extracted from other plant resources, including, but not limited to bark such as wattle, mangrove, oak, eucalyptus, hemlock, pine, larch, and willow; woods such as quebracho, chestnut, oak and urunday, cutch and turkish; fruits such as myrobalans, valonia, divi-divi, tera, and algarrobilla; leaves such as sumac and gambier; and roots such as canaigre and palmetto. The main commercial sources of condensed tannins are from Quebracho (*Schinopsis balansae)* heartwood, Mimosa (*Acacia mearnsii, Acacia mollissima, Acacia mangium*) bark and pine (*Pinus radiate, Pinus pinaster*) bark, Spruce (*Picea abies)* bark Pecan *(Carya illinoensis)* bark and Catechu *(Acacia catechu)* wood and bark.

Condensed mimosa tannins are oligomers or polymers mostly composed of flavan-3-ols repeating units as shown in Scheme 1, linked 4-6 or 4-8 to each other, and smaller fractions of polysaccharides and simple sugars.

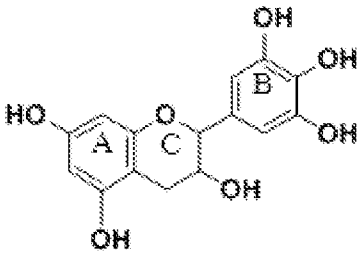
Catechin
A-ring: phloroglucinol
B-ring: catechol



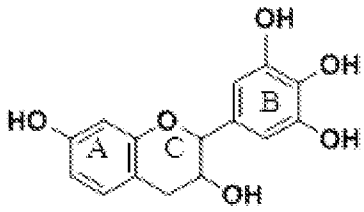
Fisetinidin
A-ring: resorcinol
B-ring: catechol



Gallocatechin
A-ring: phloroglucinol
B-ring: pyrogallol



Robinetidin
A-ring: resorcinol
B-ring: pyrogallol



Scheme 1

The commercial condensed tannins in general are extracted from the bark chips using a counter-current flow principle in pressurized autoclaves. The resulting liquid extract is then concentrated by evaporation and the hot viscous liquid is spray-dried to powder. The spray-dried tannins can absorb 6-8 wt% water from the atmosphere, due to hydrophilic nature of the tannins.

As used herein, the term “formaldehyde-free polymeric phase” means that the polymeric phase is formed without the use of formaldehyde as a monomer.

As used herein, the term “formaldehyde-free tannin-reactive monomer” is used interchangeably with the term “tannin-reactive monomer” and refers to those monomers that in the presence of an acid catalyst reacts with the A ring of the tannins at the free 5, 6 or 8 sites, as shown in Scheme 1. The tannin-reactive monomer as disclosed herein excludes formaldehyde.

As used herein, the term “phenolic-resole prepolymer” refers to a condensation product of phenol and phenol-reactive monomer, having reactive methylol groups and is generally prepared with a molar ratio of phenol-reactive monomer to phenol of ≥ 1 in the presence of a basic catalyst. The phenol used to prepare phenolic-resole prepolymer may be a substituted phenol or unsubstituted phenol. As used herein, the term "substituted phenol" refers to a molecule containing a phenolic reactive site and can contain another substituent group or moiety. Exemplary phenols include, but are not limited to, unsubstituted phenol, ethyl phenol, *p*-tertbutyl phenol; ortho, meta, and para cresol; resorcinol; catechol; xylenol; and the like.

As used herein, the term “phenol-reactive monomer” refers to any monomer that reacts with nucleophilic sites of the phenol. Exemplary phenol-reactive monomer include, but is not limited to formaldehyde, paraformaldehyde, furfuryl alcohol, furfural, glyoxal, acetaldehyde, glutaraldehyde, 5-hydroxymethylfurfural, levulinate esters, sugars, 2,5-furandicarboxylic aldehyde, difurfural (DFF) and sorbitol.

As used herein, the term “tannin-phenolic resole mixture” refers to a composition obtained by mixing a phenolic-resole prepolymer with a tannin solution comprising a condensed tannin dissolved in water and a tannin-reactive monomer.

As used herein, the term “blowing agent” is used interchangeably with the term “foam expansion agent”. In general, the blowing agent must be volatile and inert, and can be inorganic or organic.

As used herein, the term "azeotrope-like" is intended in its broad sense to include both compositions that are strictly azeotropic and compositions that behave like azeotropic mixtures. From fundamental principles, the thermodynamic state of a fluid is defined by pressure, temperature, liquid composition, and vapor composition. An azeotropic mixture is a system of two or more components in which the liquid composition and vapor composition are equal at the stated pressure and temperature. In practice, this means that the components of an azeotropic mixture are constant boiling and cannot be separated during a phase change.

The azeotrope-like compositions of the present disclosure may include additional components that do not form new azeotrope-like systems, or additional components that are not in the first distillation cut. The first distillation cut is the first cut taken after the distillation column displays steady state operation under total reflux conditions. One way to determine whether the addition of a component forms a new azeotrope-like system so as to be outside of the present disclosure is to distill a sample of the composition with the component under conditions that would be expected to separate a non-azeotropic mixture into its separate components. If the mixture containing the additional component is non-azeotrope-like, the additional component will fractionate from the azeotrope-like components. If the mixture is azeotrope-like, some finite amount of a first distillation cut will be obtained that contains all of the mixture components that is constant boiling or behaves as a single substance.

It follows from this that another characteristic of azeotrope-like compositions is that there is a range of compositions containing the same components in varying proportions that are azeotrope-like or constant boiling. All such compositions are intended to be covered by the terms "azeotrope-like" and "constant boiling". As an example, it is well known that at differing pressures, the composition of a given azeotrope will vary at least slightly, as does the boiling point of the composition. Thus, an azeotrope of A and B represents a unique type of relationship, but with a variable composition depending on temperature and/or pressure. It follows that, for azeotrope-like compositions, there is a range of compositions containing the same components in varying proportions that are azeotrope-like. All such compositions are intended to be covered by the term azeotrope-like as used herein.

As used herein, ozone depletion potential (ODP) of a chemical compound is the relative amount of degradation to the ozone layer it can cause, with trichlorofluoromethane (CFC-11) being fixed at an ODP of 1.0.

As used herein, the global-warming potential (GWP) used herein is a relative measure of how much heat a greenhouse gas traps in the atmosphere. It compares the amount of heat trapped by a certain mass of

the gas in question to the amount heat trapped by a similar mass of carbon dioxide, which is fixed at 1 for all time horizons (20 years, 100 years, and 500 years). For example, CFC-11 has GWP (100 years) of 4750. Hence, from the global warming perspective, a blowing agent should have zero ODP and as low GWP as possible.

As used herein, the term "polyamine" refers to an organic compound having two or more amino groups. Suitable examples of polyamine include, but are not limited to urea, melamine, and hexamine.

As used herein, the term "bio-based foam" is used interchangeably with "bio-based closed-cell insulation foam" and "bio-based open-cell for cold and/or hot source" and refers to foams that are derived from at least one monomer of the resin that is obtained from plants and the foam contains at least 25% renewable carbon, and less than 75% fossil fuel based or petroleum based carbon.

As used herein, the term "open-cell" refers to individual cells that are ruptured or open or interconnected producing a porous "sponge" foam, where the gas (air) phase can move around from cell to cell. As used herein, the term "closed-cell" refers to individual cells that are discrete, i.e. each closed-cell is enclosed by polymeric sidewalls that minimize the flow of a gas (blowing agent) phase from cell to cell. It should be noted that the gas phase may be dissolved in the polymer phase besides being trapped inside the closed-cell. Furthermore, the gas composition of the closed-cell foam at the moment of manufacture does not necessarily correspond to the equilibrium gas composition after aging or sustained use. Thus, the gas in a closed-cell foam frequently exhibits compositional changes as the foam ages leading to such known phenomenon as increase in thermal conductivity or loss of insulation value.

As used herein, the term "closed mold" means partially closed mold where some gas may escape, or completely closed mold, where the system is sealed.

Thermally Regulated Systems

Disclosed herein are thermally regulated systems comprising an outer shell defining a retention chamber, at least one layer of bio-based closed-cell insulation foam lining the retention chamber so as to define an

insulated retention chamber, and a cold or a hot source disposed within the insulated retention chamber to maintain the temperature of the insulated retention chamber during storage and/or transportation of a temperature sensitive product.

In an embodiment, the bio-based closed-cell insulation foam is at least one of a closed-cell condensed tannin-based foam or a closed-cell mixed tannin-phenolic foam, as disclosed herein below.

In an embodiment, the thermally regulated system further comprises a temperature monitoring device disposed inside the retention chamber.

In another embodiment, the thermally regulated system further comprises a temperature sensitive product disposed within the insulated retention chamber. The thermally regulated systems as disclosed herein can be used for insulated transportation to keep samples cold or hot at a certain temperature for extended periods of time, throughout the food, diary, pharmaceuticals, chemicals, biomedical, clinical sampling, and industrial manufacturing markets. Suitable temperature sensitive products include, but are not limited to food, flowers, chemicals, pharmaceuticals, and medical products.

In one embodiment, the thermally regulated system can be used for storing and shipping high perishable rating food items that include but not limited to asparagus, beans, broccoli, mushrooms, peas, sweet corn and berries.

In another embodiment, the thermally regulated system can be used for storing and shipping pharmaceutical products.

In an aspect, the thermally regulated system is a refrigeration unit.

In an aspect, the thermally regulated system is a refrigerated truck.

In an aspect, the thermally regulated system is a cold storage unit.

In an aspect, the thermally regulated system is a transit packaging unit. Transit packaging unit can be either single use for one way trip or reusable/returnable. While single trip packaging is mostly used for the dispatch of goods where return of the transit package is not feasible or economically viable, returnable transit packaging is more cost effective in the long run. In an embodiment, the transit packaging unit further

comprises one or more protective packaging materials. Suitable protective packaging materials include, but are not limited to, expanded polystyrene foam, corrugated fiber board boxes, packing peanuts, bubble wrap, wadding, absorbent materials, plastic bags, inflatable bags and others such as honeycomb, loose-fill, paper cushioning, etc, and mixtures thereof.

In an aspect, the thermally regulated system is for cold chain shipment of temperature sensitive product.

Cold chain packaging solutions are designed based on product fragility, method of transportation, destination and any special circumstances. A conventional cold chain packaging typically consists of an outer container, such as a corrugated carton, provided with a lining of insulation foam in the form of formed, molded or precut pads, and at least one pre-chilled gel pack, which is a sealed bag-like container of heavy plastic filled with a gel which freezes upon chilling and maintains a relatively low temperature in the container. Certain packaging systems also incorporate built-in temperature monitoring device and data monitoring systems.

The thermally regulated system, as disclosed herein comprises a bio-based closed-cell insulation foam having high insulation R-value, low density and low moisture absorption for storage and transport of temperature sensitive products, as part of a cold chain to protect the quality of the product while maintaining the inside temperature in the desired range for extended time.

The efficiency of a thermal regulated system depends on its resistance to heat flow and thereby on R-value of the system. The system R-value includes the size and shape of the container, the wall material and thickness and to some extent, the effect of the product. As such it is the property of the whole system, and the R-value of an insulating material is a significant contributor to the system's R-value.

The thermal resistance (R-value) is expressed as the thickness of the material normalized to the thermal conductivity, sometimes called a k-value or lambda-value (lowercase λ). The SI unit of R-value is $(m^2.K)/W$.

In an embodiment, the bio-based closed-cell insulation foam has an R value of at least 6.0 or 7.5 or 8.5 $hr \cdot ft^2 \cdot °F/Btu$ per inch at 23 °C.

In another embodiment, the thermally regulated system has an R value of at least 2 or 3 or 6.0 $hr \cdot ft^2 \cdot °F/Btu$ per inch at 23 °C.

Maintaining cold or hot temperatures, while shipping products, can been done using three basic methodologies: 1) employing a powered refrigeration or cold chain storage unit, 2) through contact with cold or hot source material, or 3) using the "coldness" or the “hotness” of the product itself. For example, while a refrigeration unit permits storage times of years, storage times using ice or dry-ice is commonly less than a week, and storage times of less than a day can be expected when employing the "coldness" of the product itself.

In a cold chain shipment, either active temperature controls such as use of refrigerated trucks or active refrigerated cold storage units or passive temperature controls such as use of insulation and phase-change materials are used to maintain the desired temperature in the course of transportation. Larger shipments particularly are often protected by a combination of temperature controls, plus insulation and gel packs to protect temperature sensitive products against hot or cold spots.

Referring back to the thermally regulated system, the outer shell defining a retention chamber can be selected from the group consisting of corrugated box, wooden pallet, plastic pallet, wooden crate and plastic crate. Crates and pallets (both wooden & plastic) are used in the thermally regulated systems such as, refrigeration unit and cold storage unit.

Containers such as six-sided corrugated boxes are widely utilized for the packaging and transport of temperature sensitive goods. The ubiquitous corrugated box, available in various sizes, has traditionally been the mainstay of single trip transit packaging all over the world. Its features in terms of ease of manufacture, handling, filling, closing and dispatch, combined with its cost economics and recyclability have made it one of the most enduring forms of packaging. The large corrugated boxes are wooden and plastic pallets or crates. Though the corrugated containers offer excellent bulk storage characteristics as well as space-efficient collapsibility, they do not exhibit significant insulation properties.

In addition, corrugated board is rigid and generally sturdy, does not greatly inhibit temperature transfer from the outside in or the reverse. Insulation materials are required for such a task.

In one embodiment the outer shell of the thermally regulated system, such as the corrugated container is wrapped up with a light weight nonwoven material such as high density polyethylene film or sheet (Tyvek® Air Cargo cover or Tyvek® ThermaWrap™ R5.0 are available from E. I. DuPont de Nemours & Company) to reflect solar radiation away from the container and to maintain stable R-value of the system.

The efficiency and efficacy of each storage method is most affected by the insulation characteristics of the container itself, or, in other words, the barrier that each container presents to external heating elements. Heating of a product occurs in three ways: conduction, convection, and through radiation. The successful insulation of a cold product inside a container is solely dependent on the ability of the container to inhibit these three heating factors. In general, when designing the container so as to meet the insulative standards desired, it is necessary to understand how each heating element can most effectively be countered.

Further, the container system also takes into account the size and weight of the final package and to this end, provides a relatively small and lightweight packaging for convenient, efficient and economical transport of the products. To maintain a narrow temperature range for an extended period of time, the amount of insulation and refrigerant required can be dramatic. The larger the temperature range allowed by the shelf life, the smaller and less insulation the package requires. These factors must be taken into account when identifying a carrier of the package, since commercial carriers charge by size and weight. If the package is going to be transported over ground, some variables to consider are whether the transportation is climate controlled, whether the package is being shipped in a shared cargo hold and, if not, whether the package will be given a direct route from the facility to the recipient.

In an embodiment, the thermally regulated system comprises an outer shell having an insulated retention chamber to provide an insulated shipping container configured for transporting temperature-sensitive

products therein. The shipping container can be, for example, a tannin based closed-cell foam cooler or, a corrugated cardboard box lined with an insulation material which has an R-value greater than 6.0 per inch. Preferably, the insulation material has an R-value greater than 7 per inch, and even more preferably an R- value greater than 7.5 per inch. The insulation material can be formed of a reactive product of renewably sourced polyphenol and polyphenol reactive component. Preferably, the polyphenol is a condensed tannin and polyphenol reactive component is furfuryl alcohol. This insulation material having a sufficiently high R-value provides adequate insulation and resists heat transfer. A liner formed of, for example, corrugated cardboard can surround the insulation material. Furthermore, the insulation foam materials are vapor impermeable- allowing only minute amounts of gases to pass through. Because of this characteristic, the insulation foam materials need not be sealed in a gas or fluid impermeable materials to remain effective.

Referring back to the thermally regulated system, any suitable cold or hot source maybe disposed within the insulated retention chamber to maintain the insulated retention chamber at a desired temperature during storage and/or transportation of a temperature sensitive product. If the product is hot, a heat source may or may not be necessary depending on the time of transportation or shipping. A heat source such as a hot brick may be used as the heat reservoir. If the product is cold, a cold source may be used, including, but not limited to ice, dry ice, gel packs, gel bricks, and phase change materials (PCM). The choice of cold source depends on many factors such as temperature to be maintained, outside temperature during transit and storage, transit and storage time. While a refrigeration unit is more appropriate for bulk shipments over long distances, use of a cold pack is more appropriate for an overnight shipment of a single product. A PCM in packaging is defined as an organic or inorganic substance that acts as payload's heating or cooling agent. As payload's temperature increases or decreases (depending on several factors, from ambient external temperature to the type of insulation use), the PCM works to maintain a stable, consistent temperature for the duration of its trip. Examples of phase change materials include water-

based gel packs, dry ice (frozen CO_2), vegetable oil-based PCMs such as fatty acids, petroleum-based PCMs such as paraffins, heavy water (deuterium oxide) and salts such as eutectic or hydrated salts. These packs can be shaped as refrigerant bricks. In one exemplary embodiment the refrigerant can include an arrangement of cold packs, preferably silicate gel packs. These silicate gel packs can be further classified as either refrigerated gel packs or frozen gel packs. The refrigerated gel pack should be of the type that can be refrigerated at a temperature range between -20 ^{o}C to 80 ^{o}C. The frozen gel pack should be of the type that can be frozen to about -20 ^{o}C. For example, the frozen gel pack can be of a type suitable for freezing. Preferably, each of these gel packs should be nontoxic and be made from a food grade formula (i.e., with ingredients included on the U.S. Food and Drug Administration's GRAS list as acceptable food additives).

In one embodiment, the thermally regulated system comprises a bio-based open-cell foam, as disclosed herein below, absorbed with a PCM material such as water or saline solution is used as a cold source.

Unlike closed-cell foams which absorb little amount of water, the low density open-cell foam can absorb water as high as 500% by weight. These foams can be used either in frozen form during summer to prevent against heat or in unfrozen form during winter to prevent against freezing. The benefit of these bio-based foams containing PCM is to minimize the water leakage in the package system. The open-cell content of these PCM foams is greater than 70%, preferably greater than 80% and most preferably greater than 90%. The density of the foams is less than 50 kg/m^3, preferably less than 40 kg/m^3 and most preferably less than 30 kg/m^3.

The different types of cold sources provide different thermal properties that affect the overall function of the thermally regulated system, as disclosed herein. By varying the type of refrigerant source and its location relative to the temperature sensitive product, the desired temperature can be achieved within the packaging. The use of multiple temperature refrigerant sources creates convection within the package. The low temperature sources will act as heat sinks, and aid in buffering the

perishable product from the ambient temperature. The warmer refrigerant sources aid in buffering the perishable product from becoming too cold, and prevent the product from dropping below the temperature range of its shelf life. Further, all of the refrigerant sources add mass to the packaging and thereby dampens the effect of the ambient temperature on the temperature of the perishable product being transported.

The thermally regulated system of the present disclosure can be used for shipping a variety of different products that are sensitive to temperature. In particular, the thermally regulated system provides an environment that can maintain the insulated retention chamber at a desired temperature during storage and/or transportation of a temperature sensitive product. A cold source or a hot source disposed within the insulated retention chamber can be used to maintain the insulated retention chamber at a desired temperature during storage and/or transportation of a temperature sensitive product. The desired temperature can be in the range of -5 °C to 35 °C, more preferably at a range of -1 °C to 15 °C and even more preferably at a range of 2 °C to 8 °C. Preferably, the thermally regulated system can maintain the temperature of the product at the above specified ranges for a time period of at least 48 hours, more preferably 54 hours, even more preferably 60 hours, still more preferably 66 hours, even still more preferably 72 hours, and preferably still 96 hours, or even more preferably 120 hours or more. Such an environment would be suitable for products having shelf life requirements within those temperature ranges and which are intended for delivery over the course of up to between 2 to 4 days prior to reaching the intended recipient. The described temperature ranges can be achieved during the shipping process due to the combination of the insulation properties of the shipping container and the gel packs of frozen or refrigerated or a combination of both.

Bio-Based Closed-Cell Insulation Foams

The most important material utilized in thermal regulated systems is an insulated polymeric foam. Insulated foam can be different forms including but not limited to coolers, panels and liners. They can be made

from batch, semi-continuous and continuous, preferably by batch or semi-continuous.

Heat flows by means of three mechanisms: convection, conduction and radiation. In packaging applications, one or more of the above-mentioned modes of transmission usually plays a role. The wall thickness of shipping containers (conduction), the number of surfaces (convection) and the number of reflective surfaces such as aluminum foil (radiation) determines the insulating ability of a container. Any material that offers a high resistance to the transfer of heat by conduction, convection or radiation serves as a form of insulation. Most insulating materials utilize low thermal conductivity as a means of restricting the transfer of heat, although radiation and convection are also significant.

The ease with which heat flows through a material is measured by its thermal conductivity. The measurements are made under standard conditions and the values can be converted to a mean temperature of 10 ^{o}C. The higher the thermal conductivity, the easier the heat flow. A low thermal conductivity polymer, fabricated into low density foam consisting of a multitude of tiny closed-cells entrapped with foam expansion agents having low thermal conductivity, provides good thermal performance. The thermal conductivity of insulated foam depends on type of blowing agent and polymer matrix used, density, temperature, moisture and time of measurement. In addition, the thermal conductivity of the insulated foam also depends on the foamable composition, process conditions and foam cell morphology. Therefore, obtaining insulated foam with low thermal conductivity is not trivial.

The thermal conductivity in general decreases with decrease in temperature and therefore the foams are more effective insulators at lower temperatures as compared to room temperature. The insulation performance of the packaging container is mostly depends on the insulated materials and their thickness used to design the packaging container. For high performance packaging applications, the insulation foams must have very low thermal conductivity or high R-value per inch to be very effective. Increasing the thickness of an insulating layer increases the thermal resistance. For example, doubling the thickness of the

polyphenolic insulation foam will double its R-value, perhaps from 6.0 ft^2 F.h for 1 inch of thickness, to 13.0 ft^2 F.h for 2 inch of thickness. For efficient cold chain storage, insulation layers with high thickness and long term stability of thermal conductivity are desired. However, thicker foams in the package can increase the cost of shipping and therefore the shipping packaging containers must be designed to optimize the insulation R-value and weight of the foam to be cost effective.

The insulated containers can be made from molded plastic foams and sheets of foamed plastics. Often the containers are coated with reflective materials or metalized film to reflect away heat. Generally, insulated shipping containers are reusable and can be made available in a wide range of sizes. Special applications require actively controlled thermal shipping packaging, where the temperature is monitored electronically and cooling is provided by a battery powered heat pump, integral to the pack.

The bio-based closed-cell insulation foam of the present disclosure is at least one of a closed-cell condensed tannin-based foam or a closed cell mixed tannin-phenolic foam, as disclosed herein below.

Condensed Tannin-Based Foam

Disclosed are bio-based condensed tannin-based foams, either a closed-cell insulation foam and/or an open-cell foam for use as a cold source. A closed-cell insulation foam is formed by foaming and curing a foamable compositions at a temperature in the range of 50−100 °C, the foamable composition comprising a surface-active condensed tannin, a formaldehyde-free tannin-reactive monomer, water, a saturated or an unsaturated organic anhydride, a blowing agent, an acid catalyst, a surfactant, and an optional polyamine and/or plasticizer. The as-formed condensed tannin-based foam comprises a formaldehyde-free polymeric phase defining a plurality of open cells and a plurality of closed-cells. The as-formed condensed tannin-based foam also comprises one or more blowing agents disposed in at least a portion of the plurality of closed-cells, formed by the formaldehyde-free polymeric phase.

The polymeric phase of the closed-cell condensed tannin-based foam comprises an acid catalyzed tannin-based resin derived from a surface-active condensed tannin, a formaldehyde-free tannin-reactive monomer, a saturated or an unsaturated organic anhydride, an ethoxylated castor oil, and an optional polyamine, and/or plasticizer.

The polymeric phase of the open-cell condensed tannin-based foam comprises an acid catalyzed tannin-based resin derived from a surface-active condensed tannin, a formaldehyde-free tannin-reactive monomer, a silicone based surfactant, and an optional saturated or unsaturated organic anhydride, polyamine, and/or plasticizer.

The surface-active condensed tannin of the present disclosure refers to those bio-derived tannins that when dissolved in 50 weight% of water has a surface tension of less than 53.0 mN/m, wherein the amount in weight% is based on the total weight of the tannin and water. In an embodiment, the surface-active condensed tannin is extracted from at least one of a mimosa tree, a quebracho tree, or a pine tree. In an embodiment, the surface-active condensed tannin is a mimosa tannin extracted from plant *Acacia mearnsii*. In another embodiment, the surface-active condensed tannin is a volatile-free condensed tannin, as disclosed hereinabove.

Any suitable formaldehyde-free tannin-reactive monomer can be used, including, but not limited to furfuryl alcohol, furfural, glyoxal, acetaldehyde, glutaraldehyde, 5-hydroxymethylfurfural, acrolein, levulinate esters, sugars, 2,5-furandicarboxylic aldehyde, difurfural (DFF), glycerol, sorbitol, or mixtures thereof. In an embodiment, the formaldehyde-free tannin-reactive monomer is bio based furfuryl alcohol.

Any suitable saturated or unsaturated organic anhydride can be used including, but not limited to maleic anhydride, acetic anhydride, succinic anhydride, itaconic anhydride, phthalic anhydride and trimelletic anhydride. In an embodiment the saturated or the unsaturated organic anhydride comprises at least one of maleic anhydride, acetic anhydride, succinic anhydride, phthalic anhydride and trimelletic anhydride, and mixtures thereof. In another embodiment, the organic anhydride comprises maleic anhydride.

Any suitable polyamine can be used including, but not limited to urea, melamine, and hexamine. In an embodiment, the polyamine is urea and the organic anhydride is maleic anhydride

A class of suitable surfactants includes non-ionic organic surfactants such as the condensation products of alkylene oxides such as ethylene oxide, propylene oxide or mixtures thereof, and alkylphenols such as nonylphenol, dodecylphenol, and the like. Suitable non-ionic organic surfactants include, but are not limited to, ethoxylated castor oil available from Lambent Technologies; polysorbate (Tween®) surfactants available from Sigma-Aldrich Chemical Company; Pluronic® non-ionic surfactants available from BASF Corp., (Florham Park, NJ); Tergitol™; Brij® 98, Brij® 30, and Triton X 100, all available from Aldrich Chemical Company.

Another class of suitable surfactants includes siloxane-oxyalkylene copolymers such as those containing Si-O-C as well as Si-C linkages. The siloxane-oxyalkylene copolymers can be block copolymers or random copolymers. Typical siloxane-oxyalkylene copolymers contain a siloxane moiety composed of recurring dimethylsiloxy units endblocked with mononethylsiloxy and/or trimethylsiloxy units and at least one polyoxyalkylene chain composed of oxyethylene and/or oxypropylene units capped with an organic group such as an ethyl group. Suitable siloxane-oxyalkylene copolymeric surfactants include, but are not limited to, polyether-modified polysiloxanes, available as Tegostab B8406 from Evonik Goldschmidt Corporation (Hopewell, VA); (polyalkyleneoxide modified heptamethyltrisiloxane available as Silwet L-77 from OSi Specialties (Danbury CT).

The condensed tannin-based foam as disclosed hereinabove comprising a polymeric phase defining a plurality of cells (closed-cells and open cells) also comprises one or more blowing agent disposed in at least a portion of the plurality of closed-cells and wherein at least one of the one or more blowing agents is an azeotrope or an azeotrope-like mixture of isopentane and one other blowing agent selected from the group consisting of isopropyl chloride, 1,1,1,4,4,4-hexafluoro-2-butene and

1-chloro-3,3,3,-trifluoropropene. In an embodiment, the blowing agent is a mixture of isopentane and isopropyl chloride.

At least one or more blowing agents has an ozone depletion potential (ODP) of less than 2, or less than 1 or 0 and has a global warming potential (GWP) of less than 5000, or less than 1000, or less than 500. An exemplary blowing agent with zero ODP and a low GWP is a mixture of isopentane and isopropyl chloride (ODP of 0 and GWP of less than 20).

Suitable acid catalysts include, but are not limited to, benzenesulfonic acid, *para*-toluenesulfonic acid, xylenesulfonic acid, naphthalenesulfonic acid, ethylbenzenesulfonic acid, phenolsulfonic acid, sulfuric acid, phosphoric acid, boric acid, hydrochloric acid or mixtures thereof. In an embodiment, the acid catalyst is a mixture of two of more aromatic sulfonic acids selected from the group consisting of benzenesulfonic acid, *para*-toluenesulfonic acid, xylenesulfonic acid, naphthalenesulfonic acid, ethylbenzenesulfonic acid and phenolsulfonic acid.

The condensed tannin-based foam may also include at least one of a polyester polyol or a polyether polyol as an optional plasticizer. The polyester polyol can be formed by the reaction of a polybasic carboxylic acid with a polyhydridic alcohol selected from a dihydridic to a pentahydridic. Examples of the polybasic carboxylic acid include but are not limited to adipic acid, sebacic acid, naphthalene-2,6-dicarboxylic acid, cyclohexane-1,3-dicarboxylic acid, phthalic acid. Examples of the polyhydric alcohol include but are not limited to ethylene glycol, propylene diol, propylene glycol, 1,6-hexane diol, 1,4-butane diol and 1,5-pentane diol. In an embodiment, the plasticizer is an aromatic polyester polyol derived from phthalic anhydride and diethylene glycol. The average molecular weight of the polyester polyol is in the range of 100–5,000 g/mol, or 200–2,000 g/mol, or 200–1000 g/mol. Polyether polyols are made by reacting epoxides like ethylene oxide or propylene oxide with the multifunctional initiator in the presence of a catalyst, often a strong base such as potassium hydroxide or a double metal cyanide catalyst. Common polyether polyols are polyethylene glycol, polypropylene glycol,

and poly(tetramethylene ether) glycol. The average molecular weight of the polyester polyol is in the range of 100–5,000 g/mol, or 150–2,000 g/mol, or 200–1000 g/mol.

The polymeric phase of the condensed tannin-based foam of the present disclosure may also comprise one or more additives. Suitable additives include, but are not limited to, cellulose fiber, bacterial cellulose, sisal fiber, clays, Kaolin-type clay, mica, vermiculite, sepiolite, hydrotalcite and other inorganic platelet materials, glass fibers, polymeric fibers, alumina fibers, aluminosilicate fibers, carbon fibers, carbon nanofibers, poly-1,3-glucan, lyocel fibers, chitosan, boehmite (AlO.OH), zirconium oxide, or mixtures thereof.

In an embodiment, the closed-cell condensed tannin-based foam is derived from a foamable composition comprising a surface-active condensed tannin, a formaldehyde-free tannin-reactive monomer, a saturated or an unsaturated organic anhydride, an ethoxylated castor oil surfactant, a mixture of isopropyl chloride and isopentane, an aromatic sulfonic acid catalyst and an optional polyamine and/or plasticizer, wherein the closed-cell content is greater than 85%, or greater than 90% as measured according to ASTM D6226-5.

In an embodiment, the open-cell condensed tannin-based foam is derived from a foamable composition comprising a surface-active condensed tannin, a formaldehyde-free tannin-reactive monomer, a silicone based surfactant, a mixture of isopropyl chloride and isopentane, an aromatic sulfonic acid catalyst, a polyester polyol plasticizer and an optional saturated or unsaturated organic anhydride, polyamine and/or plasticizer, wherein the closed-cell content is greater than 70% or 80% or 90% as measured according to ASTM D626-5.

In an embodiment of the thermally regulated system, the bio-based closed-cell insulation foam is a condensed tannin-based foam derived from a surface-active tannin, furfuryl alcohol, maleic anhydride, ethoxylated castor oil, a mixture of isopropyl chloride and isopentane, an aromatic sulfonic acid catalyst, and optionally urea and/or a polyester polyol.

Process of Making a Condensed Tannin-Based Foam

In accordance with the present disclosure, there is provided a process of making a condensed tannin-based foam. The process comprises forming an agglomerate free solution comprising a surface-active condensed tannin, a tannin-reactive monomer, and water.

The step of forming an agglomerate free solution comprises mixing the surface-active condensed tannin with a formaldehyde-free tannin-reactive monomer, and water to form a mixture and providing a residence time to the mixture to effectively dissolve the tannin in the mixture. At the start of the residence time, the mixture may comprise agglomerates of tannin, wherein one may observe a two phase system with one phase being agglomerates of tannin and the other phase being liquid comprising dissolved tannin in a monomer, and water. As the agglomerates of tannin dissolves, the mixture becomes more viscous. At the end of the residence time, the mixture is a one phase system comprising dissolved tannin in a monomer, and water. The step of providing a residence time may involve keeping the mixture still for the residence time, or mixing the mixture for a certain amount of time, or mixing and keeping still for the rest of the residence time. The amount of residence time needed to obtain an agglomerate-free solution will depend on the temperature at which the tannin is mixed with the monomer and water and also on the composition and the extent of mixing. Any suitable method can be used to mix the surface-active condensed tannin with the tannin-reactive monomer, and water, to form an agglomerate-free solution, such as, for example, hand mixing, mechanical mixing using a Kitchen-aid® mixer, a twin screw extruder, a bra-blender, an overhead stirrer, a ball mill, an attrition mill, a Waring blender, or a combination thereof.

In an embodiment, the step of forming the agglomerate-free solution comprising a surface-active condensed tannin, a tannin-reactive monomer, and water can include first mixing the tannin with water and then adding the monomer to the mixture of tannin and water. In other embodiment, the step of forming an agglomerate-free solution comprising a surface-active condensed tannin, a tannin-reactive monomer, and water can include first mixing the tannin with the monomer and then adding

water to the mixture of tannin and monomer. In another embodiment, the step of forming an agglomerate-free solution comprising a surface-active condensed tannin, a tannin-reactive monomer, and water can include first mixing the monomer with water and then adding surface-active condensed tannin to the mixture of tannin-reactive monomer and water.

The amount of dried surface-active condensed tannin is in the range of 10–80%, or 20 –80%, or 50–80%, by weight, based on the total weight of the foamable composition. The amount of the formaldehyde-free tannin-reactive monomer present is in the range of 5–80%, or 10–50%, or 10–30%, by weight, based on the total weight of the composition. The amount of water present is in the range of 5-20%, by weight, based on the total weight of the foamable composition.

The process of making a condensed tannin-based foam also comprises adding a saturated or an unsaturated organic anhydride, and a blowing agent to the agglomerate free solution to form a pre-foam mixture. The process also comprises adding an acid catalyst to the pre-foam mixture to form a formaldehyde-free foamable composition.

The amount of organic anhydride is in the range of 0.5–20%, or 1–15%, or 1–10%, based on the total weight of the formaldehyde-free foamable composition. In an embodiment, the organic anhydride comprises maleic anhydride.

The process of making a condensed tannin-based foam may also comprise of 0.5–20% or 1–10% by weight of polyamine to the agglomerate free solution, such that the organic anhydride and the polyamine are present in a weight ratio of 1:0.1 to 1:1, wherein the polyamine comprises at least one of urea and melamine. In an embodiment, polyamine is urea.

The amount of blowing agent is in the range of 0.5–20%, or 1–15%, or 1–10%, by weight, based on the total weight of the formaldehyde-free foamable composition. In an embodiment, the blowing agent comprises an azeotrope or an azeotrope-like mixture of isopentane and one other blowing agent selected from the group consisting of isopropyl chloride, 1,1,1,4,4,4-hexafluoro-2-butene and 1-chloro-3,3,3,-trifluoropropene. In another embodiment, the blowing agent comprises a mixture of isopropyl

chloride and isopentane present in a weight ratio of 90:10 or 75:25 or 50:50 or 10:90.

The process of making a condensed tannin-based foam also comprises adding a surfactant to the agglomerate free solution. In another embodiment, a surfactant is added to the pre-foam mixture. The surfactant is first mixed with the blowing agent and then the mixture of blowing agent and surfactant is mixed with the agglomerate-free solution to form a pre-foam mixture. In another embodiment, a surfactant is mixed with the acid catalyst.

The surfactant is present in an effective amount to emulsify the formaldehyde-free foamable composition comprising surface-active condensed tannin, tannin-reactive monomer, the saturated or an unsaturated organic anhydride, the blowing agent, the catalyst and optional additives of the foamable composition. The surfactant is added to lower the surface tension and stabilize the foam cells during foaming and curing. In an embodiment, the surfactant is an ethoxylated castor oil, as disclosed hereinabove.

The type of the surfactant for a given foamable composition is critical and they may control the cell size and cell morphology (degree of open cell content) of tannin-based foams. Simply changing the ethoxylated castor oil surfactant that is optimized for a specific composition to silicone surfactant can completely change the foam morphology from closed-cell to open-cell (see Example 18). The amount of surfactant is in the range of 0.5–10%, or 2–8%, or 3–6%, by weight, based on the total weight of the foamable composition.

In an embodiment of the process of making a condensed tannin-based foam, the process comprises making an open-cell condensed tannin-based foam, wherein the step of adding a surfactant comprises adding 0.5–5% by weight of a silicone based surfactant to at least one of the agglomerate free solution or pre-foam mixture, wherein the amount is based on the total weight of the foamable composition.

In another embodiment of the process of making a condensed tannin-based foam, the process comprises making a closed-cell condensed tannin-based foam, wherein the step of adding a surfactant

comprises adding 0.5–5% by weight of an ethoxylated castor oil based surfactant to at least one of the agglomerate free solution or the pre-foam mixture, wherein the amount is based on the total weight of the foamable composition.

The process of making a condensed tannin-based foam further comprises adding an additive, disclosed hereinabove to at least one of the agglomerate-free solution or the pre-foam mixture. The amount of additive is in the range of 5–50%, or 10–45%, or 15–40%, by weight based on the total weight of the agglomerate-free solution. In an embodiment, the additive is a plasticizer comprising a polyester polyol or polyether polyol, as disclosed hereinabove.

The amount of acid catalyst disclosed hereinabove is in the range of 1–20% or 5–20% or 5–15%, by weight, based on the total weight of the formaldehyde-free foamable composition. In an embodiment, the acid catalyst comprises *para*-toluenesulfonic acid and xylenesulfonic acid in a weight ratio in the range of 0.67:1 to 9:1, or 2:1 to 7:1, or 3:1 to 5:1. Furthermore, the acid catalyst may be dissolved in a minimum amount of solvent, the solvent comprising ethylene glycol, 1,2-propylene glycol, triethylene glycol, butyrolactone, dimethyl sulfoxide, *N*-methyl-2-pyrrolidone, morpholines, 1,3-propanediol, or mixtures thereof. A catalyst is normally required to produce the foam but in some cases, a foam can be made without a catalyst but rather using thermal aging. A combination of thermal aging and a catalyst is commonly used. In some cases, the reaction is exothermic and hence little or no additional heat may be required.

The process of making a condensed tannin-based foam also comprises foaming and curing the formaldehyde-free foamable composition to form a foam comprising a polymeric phase defining a plurality of cells, and one or more blowing agents disposed in at least a portion of the plurality of cells. The step of processing the formaldehyde-free foamable composition comprises maintaining the formaldehyde-free foamable composition at an optimum temperature. In an embodiment, the optimum temperature is in the range of 50–100 °C, or 60–90 °C. In another embodiment, the step of processing the formaldehyde-free

foamable composition comprises foaming the formaldehyde-free foamable composition in a substantially closed mold or in a continuous foam line. In one embodiment, the formaldehyde-free foamable composition is first foamed at an optimum temperature in the range of 50–100 °C, or 60–90 °C in an open mold and then the mold is closed and kept at that temperature for a certain amount of time. In some cases, the foam is formed in a closed mold or under application of pressure to control the foam density. Pressures from atmospheric to up to 5000 kPa may be applied depending upon the desired foam density.

Mixed Tannin-Phenolic Foam

Disclosed are mixed tannin-phenolic foams, either a closed-cell insulation foams and/or an open-cell foams for use as a cold source

In an embodiment, the bio-based foam is an open-cell mixed tannin-phenolic foam derived from a foamable composition comprising a surface-active tannin, a formaldehyde-free tannin-reactive monomer, a phenolic-resole prepolymer, a surfactant, a blowing agent, an acid catalyst, and an optional saturated or unsaturated organic anhydride, polyamine and/or plasticizer.

In another embodiment, the bio-based foam is a closed-cell mixed tannin-phenolic foam derived from a foamable composition comprising a volatile-free condensed tannin, a formaldehyde-free tannin-reactive monomer, a phenolic-resole prepolymer, a polyamine, a surfactant, a blowing agent, an acid catalyst, and an optional saturated or unsaturated organic anhydride and/or plasticizer.

Since, the tannin-reactive monomer of the present teachings exclude formaldehyde, the overall amount of formaldehyde in the a mixed tannin-phenolic foam of the present teachings is lower than the phenolic-resole foam , thereby making the mixed tannin-phenolic foams of the present disclosure with improved benefits in terms of exposure and emission of formaldehyde.

In an embodiment, the phenolic-resole prepolymer is derived from a phenol and a phenol-reactive monomer and further comprises urea.

Suitable phenols include, but are not limited to, unsubstituted phenol, ethyl phenol, p-tertbutyl phenol; ortho, meta, and para cresol; resorcinol; catechol; xylenol; and the like.

Suitable phenol-reactive monomer include, but are not limited to, at least one of formaldehyde, paraformaldehyde, furfuryl alcohol, furfural, glyoxal, acetaldehyde, glutaraldehyde, 5-hydroxymethylfurfural, levulinate esters, sugars, 2,5-furandicarboxylic aldehyde, difurfural (DFF), sorbitol or mixture thereof.

In an embodiment, the phenolic-resole prepolymer is derived from an unsubstituted phenol, a phenol-reactive monomer and urea and has a number average molecular weight of less than 1500 or less than 1000 and has a viscosity less than 30,000 cPs or less than 15,000 cPs at 25 ^{o}C.

In an embodiment, the phenolic-resole prepolymer is derived from a phenol, formaldehyde, and urea.

In accordance with the present disclosure, there is provided a process of making a closed-cell mixed tannin-phenolic foam derived from tannin and a phenolic resole prepolymer, wherein the phenolic resole prepolymer further comprises urea. The process comprises first forming a volatile-free condensed tannin by heating a surface-active condensed tannin at a temperature in the range of 110−200 °C or 120−160 °C or 125−145 °C in air, oxygen or nitrogen for 1 hour to up to 6 days or 2 hours to 3 days or 6–48 hours or 12–24 hours to substantially remove one or more volatile compounds having a boiling point of greater than 277 °C. The process further comprises forming an agglomerate-free tannin solution, as disclosed hereinabove, except that the agglomerate-free tannin solution comprises a volatile-free condensed tannin, obtained by thermal treatment of a surface-active condensed tannin, dissolved in water and a tannin-reactive monomer. In an embodiment, the agglomerate-free tannin solution comprising volatile-free condensed tannin, furfuryl alcohol and water, has a viscosity in the range from 1000 to 150000 cP or 2000 to 100000 cP or 5000 to 50000 cP at 25 °C.

In an embodiment, the amount of the formaldehyde-free tannin-reactive monomer, disclosed hereinabove, is present in the agglomerate-free tannin solution in the range of 5–80%, or 10–50%, or 10–30%, by

weight, based on the total weight of the tannin solution comprising volatile-free condensed tannin, water and tannin-reactive monomer.

The process of making a closed-cell mixed tannin-phenolic foam further comprises adding 10–90% or 20−80% or 25−70%, by weight of a phenolic-resole prepolymer to the tannin solution to form a tannin-phenolic resole mixture.

The process further comprises adding at least one surfactant, one blowing agent and an aromatic sulfonic acid to the tannin-phenolic resole mixture, similar to that described for the process of making condensed tannin-based foam, with the difference being of adding blowing agent, acid catalyst, optional urea, plasticizer to the tannin-phenolic resole mixture, as opposed to the tannin.

The process further comprises adding 0.5-1.75%, or 0.75-1.50% of a surfactant, 0.5–20%, or 1–15%, or 1–10% of a saturated or an unsaturated organic anhydride, 0.5–20% by weight of polyamine to the tannin-phenolic resole mixture. The process further comprises adding 0.5–20% or 1–15%, or 1–10% by weight of a blowing agent to form a pre-foam tannin-phenolic resole mixture. The process also comprises adding 1–20% by weight of an acid catalyst to the pre-foam tannin-phenolic resole mixture to form a tannin-phenolic resole foamable composition, wherein the amount is based on the total weight of the mixed tannin-phenolic foam composition.

Any suitable blowing agent, as disclosed hereinabove may be used. In an embodiment, the blowing agent comprises a mixture of isopropyl chloride and isopentane present in a weight ratio of 90:10 or 75:25 or 50:50 or 10:90.

In an embodiment, the acid catalyst comprises *para*-toluenesulfonic acid and xylenesulfonic acid in a weight ratio in the range of 0.67:1 to 9:1, or 2:1 to 7:1, or 3:1 to 5:1. Furthermore, the aromatic sulfonic acid may be dissolved in a minimum amount of solvent, as disclosed hereinabove.

In an embodiment, the organic anhydride comprises maleic anhydride.

The process of making a mixed tannin-phenolic foam also comprises foaming and curing the tannin-phenolic resole foamable

composition at a temperature in the range of 50−100 °C or 60–90 °C to form a mixed tannin-phenolic foam comprising a polymeric phase defining a plurality of cells, and wherein one or more blowing agents is disposed in at least a portion of the plurality of cells. The step of processing the tannin-phenolic resole foamable composition comprises foaming the composition in a substantially closed mold or in a continuous foam line or in an open mold, similar to the process for making condensed tannin-based foams, as disclosed hereinabove.

In an embodiment, the closed-cell mixed tannin-phenolic foam is derived from a volatile-free condensed tannin, furfuryl alcohol, a phenolic resole prepolymer, a mixture of isopropyl chloride and isopentane, maleic anhydride, urea, an ethoxylated castor oil based surfactant, an aromatic sulfonic acid catalyst, and an optional plasticizer comprising at least one of a polyester polyol or a polyether polyol.

The bio-based foam of the present disclosure, as disclosed hereinabove is at least one of a condensed tannin-based foam or a mixed tannin-phenolic foam.

In one embodiment, the bio-based foam is a closed-cell insulation foam for use as thermal insulation having an open-cell content of less than 15% (or closed-cell content greater than 85%), or less than 12%, or less than 10%, or less than 8%, as measured according to ASTM D6226-5.

In an embodiment, the open-cell mixed tannin-phenolic foam is derived from a surface active condensed tannin, furfuryl alcohol, a phenolic resole prepolymer, a mixture of isopropyl chloride and isopentane, maleic anhydride, urea, an ethoxylated castor oil based surfactant, an aromatic sulfonic acid catalyst, and an optional plasticizer comprising at least one of a polyester polyol or a polyether polyol.

In another embodiment, the bio-based foam is an open-cell foam with absorbed PCM having an open-cell content of greater than 70%, or greater than 80%, or greater than 90%.

In an embodiment, the tannin and furfuryl alcohol used in the foam are bio-derived. Furfuryl alcohol is obtained by catalytic reduction with hydrogen of furfural, which is obtained by acid hydrolysis of sugars and waste from agricultural processes.

In one embodiment, the bio-based foam has a density in the range of 10–50 kg/m^3 or 20–45 kg/m^3 or 30–40 kg/m^3.

In another embodiment, the bio-based closed-cell insulation foam has a thermal conductivity of less than 23 mW/m·K, measured at 25 °C. In an embodiment, the insulation foam has an aged thermal conductivity of less than 25 mW/m·K, measured at ambient temperature, 25 °C. The overall thermal conductivity of the foam is strongly determined by the thermal conductivity of the gas phase or the discontinuous phase, the open-cell content of the foam and size and strength of the foam cell. This is because the gas phase or the discontinuous phase disposed in at least a portion of the plurality of the closed-cells in a low-density foam (having a density in the range of 20–45 kg/m^3), usually makes up about 95% of the total foam volume. Hence, only those foams that are blown from low thermal conductivity blowing agents and result in closed-cell structures, with significant fraction of the blowing agent trapped within the closed-cells, can exhibit thermal conductivity lower than that of air.

In one embodiment, the bio-based foam is disposed between two similar or dissimilar non-foam materials, also called facers to form a sandwich panel structure. Any suitable material can be used for the facers. In one embodiment, the facers may be formed from a metal such as, but not limited to aluminum and stainless steel. In another embodiment, the facers may be formed from plywood, cardboard, composite board, oriented strand board, gypsum board, fiber glass board, and other building materials known to those skilled in the art. In another embodiment, the facers may be formed from nonwoven materials derived from glass fibers and/or polymeric fibers such as Tyvek® and Typar® available from E. I. DuPont de Nemours & Company. In another embodiment, the facers may be formed from woven materials such as canvas and other fabrics. Yet, in another embodiment, the facers may be formed of polymeric films or sheets. Exemplary polymers for the facer may include, but are not limited to, polyethylene, polypropylene, polyesters, and polyamides.

In an embodiment of the thermally regulated system, the bio-based closed-cell insulation foam is a closed-cell mixed tannin-phenolic foam

derived from a volatile-free condensed tannin, furfuryl alcohol, maleic anhydride, phenolic-resole prepolymer, ethoxylated castor oil, a mixture of isopropyl chloride and isopentane, an aromatic sulfonic acid catalyst, and optionally urea and/or a polyester polyol.

The bio-based closed-cell insulation foams, as disclosed hereinabove for use as thermal insulation for lining the retention chamber of a thermally regulated system has a high insulation R value, low water absorption of less than 10 wt%, or less than 8%, or less than 6.5%, generates less toxic gases upon incineration and is capable of maintaining the products at a desirable temperature range for a sufficient period of time while reducing environmental footprints.

The concepts disclosed herein will be further described in the following examples, which do not limit the scope of the disclosure described in the claims. From the above discussion and these examples, one skilled in the art can ascertain the essential characteristics of this invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various uses and conditions.

EXAMPLES

TEST METHODS

Surface Tension

Surface tension of the aqueous condensed tannin solutions and resins were measured using a platinum DuNouy ring in conjunction with a Cahn DCA-312 Force tensiometer.

GC-MS (gas chromatography-mass spectrometry) Headspace Analysis

Instrument: Agilent 7890A Gas chromatograph with 7697A headspace sampler and 5975C invert XL EI-MSD bench top mass spectrometer.

Sample preparation and procedure: 50 mg of sample in 20 mL headspace vials were evacuated and back flushed three times with

nitrogen in a vacuum oven at room temperature (22 °C), and were capped quickly and hand-tightened. Each vial was heated to 200 °C for one hour and then 1.0 mL of the headspace was injected via a heated sample loop into the GC/MS. Mass spectra were acquired at two per second. The total ion chromatograms were plotted, and the peak mass spectra were compared to NIST library spectra.

GC conditions: 30 °C for 1 min, then 15 °C/min to 280 °C for 15 min Run Time: 32.67 min; Column: Agilent HP-5, 30m X 0.25 mm, film 0.25 microns; Carrier: He, 0.7 mL/min

Mass Spec conditions: Detector; EI mode, Source : 230 °C MS Quad : 150 °C, EM Voltage : 1612, Low Mass : 14.0 High Mass : 600.0 Threshold : 150 Sample # : 2 sec(-1)

Density

Apparent density (ρ) of the foams was measured by a) cutting a foam into a regular shape such as a rectangular cube or cylinder, b) measuring the dimensions and the weight of the foam piece, c) evaluating the volume of the foam piece and then dividing the weight of the foam piece by the volume of the foam piece.

More specifically, three cylindrical pieces were cut from a test foam using a brass corer having an internal diameter of 1.651 mm (0.065") to calculate the average apparent density of the test foam. The diameter and the length of the cylindrical pieces were measured using Vernier calipers and then the volume (V) of the cylinder was calculated. The mass (m) of each cylindrical piece was measured and used to calculate the apparent density (ρ_a) of each foam piece.

$$\rho_a = \frac{m}{V}$$

Open-Cell Content

Open-cell content of foams was determined using ASTM standard D6226-5. All measurements were made at room temperature of 24 °C.

Pycnometer density (ρ) of each cylindrical piece was measured using a gas pycnometer, Model # Accupyc 1330 (Micromeritics Instrument Corporation, Georgia, U.S.A) at room temperature using nitrogen gas.

The AccuPyc works by measuring the amount of displaced gas. A cylindrical foam piece was placed in the pycnometer chamber and by measuring the pressures upon filling the chamber with a test gas and discharging it into a second empty chamber, volume (V_s) of the cylindrical foam piece that was not accessible to the test gas was calculated. This measurement was repeated five times for each foam cylindrical piece and the average value for V_s was calculated.

The volume fraction of open-cells (O_v) in a foam sample was calculated by the following formula:

$$O_v = \frac{(V - V_s)}{V}$$

Assuming the specific gravity of the solid tannin polymer to be 1 g/cm^3, the volume fraction of the cell walls (CW_v) was calculated from the following formula:

$$CW_v = \frac{m}{V}$$

Thus the volume fraction of closed-cells (C_v) was estimated by the following equation:

$C_v = 1 - O_v - CW_v$

Thermal conductivity

Hot Disk Model # PPS 2500S (Hot Disk AB, Gothenberg, Sweden) was used to measure thermal conductivities of the foams.

A foam whose thermal conductivity needed to be measured was cut into two rectangular or circular test pieces of same size. The lateral dimensions and the thickness of the foam pieces were required to be greater than four times the radius of the Hot Disk heater and sensor coil. The radius of the heater and sensor coil for all measurements was 6.4 mm

and hence the lateral dimensions and the thickness of the foam pieces were greater than 26 mm.

Before the start of a measurement protocol, the heater and sensor coil was sandwiched between two test pieces of foam and the entire assembly was clamped together to ensure intimate contact between the surfaces of the foam pieces and the heater and sensor coil.

At the start of a test, a known current and voltage was applied to the heater and sensor coil. As the heater and sensor coil heated up due to the passage of current through the coil, the energy was dissipated to the surrounding test pieces of foam. At regular time intervals during the experiment, the resistance of the heater and sensor coil was also measured using a precise wheat stone bridge built into the Hot Disk apparatus. The resistance was used to estimate the instantaneous temperature of the coil. The temperature history of the heater and sensor coil was then used to calculate the thermal conductivity of the foam using mathematical analysis presented in detail by Yi He in Thermochimica Acta 436, pp 122-129, 2005.

The thermal conductivity measurement on the test pieces at room temperature was repeated two more times. The thermal conductivity data was then used to calculate the average thermal conductivity of the foam.

Aged thermal conductivity

The foams were aged in oven at 70 °C for 4 days and then at 110 °C for 2 weeks and the aged thermal conductivity of the aged foam samples was measured at room temperature as described above.

Thermal resistance, R-value

The thermal resistance (R-value) is expressed as the thickness of the material normalized to the thermal conductivity, sometimes called a k-value or λ-value. The reported R-values are calculated from the thermal conductivity measured at room temperature (~23 ^{o}C) instead at 10 ^{o}C, an industry standard temperature. To get the R-value, the thickness of the insulation board is divided by the thermal conductivity. For example, a 2”

thick board with a TC of 0.021 W/m·K, the R-value in SI units would be (0.0508m)/(0.021 W/m·K) = 2.419 K·m^2/W. This value can be converted into US unit by multiplying the SI unit with 5.6783. The corresponding value in US unit would be 13.74 (h·ft^2·°F)/Btu. Since thermal conductivity decreases with decrease in temperature, and the R-values will be higher at 10 °C compared to reported values.

Moisture Absorption

Water vapor absorption capcity of Tannin-Foams was measured as described below: Foams having dimensions 3"x 2"x 1' (same as those used for thermal conductivity measurement) were dried at 70 °C for 16 h in a convection oven and sample weights were measured (W_{dry}). Then the foams were placed in a controlled room having constant humidity 52 % and temperature 22 °C for 24 h. After 24 h weight gain was measured ($W_{moisture}$) and moisture absorption was calculated as follows:

$$\text{Moisture absorption (\%)} = \frac{Wmoisture - Wdry * 35 * 100}{Wdry * Density}$$

Fire resistance properties

The fire resistance properties of the foams were tested using Cone Calorimeter according to ASTM E1354 and Limiting Oxygen Index method according to ASTM D-2863.

In the cone calorimeter test, a 100 mm x 100 mm x 13.5 foam sample is exposed to radiant heat at a heat flux of 50 kW/m^2 for a minimum of 300 seconds. The average values of three specimens for each sample were reported. The parameters tested include time to ignition (t_{ig}), peak heat release rate (HRR), average HRR after 180 seconds of burning, effective heat of combustion (EHC), total heat released (THR), average mass loss, average smoke production rate (SPR) and CO/CO_2 yield.

Starting Materials

All commercial materials were used as received unless otherwise indicated. Mimosa tannin extract (*Acacia mearnsii*) samples were received from two different sources and were used as received. Tannin-A was purchased from SilvaTeam (Italy) and Tannin-F was purchased from Tanac (Brazil). Furfuryl alcohol, maleic anhydride, and urea were from

Sigma-Aldrich (St. Louis, MO). Phenol-formaldehyde (PF-D) resole prepolymers which does not contain urea were obtained from DynaChem, Inc. (Westville, IL) and Phenol-formaldehyde (PF-M) resole prepolymers having urea were obtained from Momentive Specialty Chemicals (Mount Jewett, PA). Acid catalyst used was a mixture of 70/30 wt% *p*-toluene sulfonic acid and xylene sulfonic acid in ethylene glycol or triethylene glycol, and it was obtained from DynaChem Inc. Blowing agents used were isopentane and isopropyl chloride (2-chloropropane). Surfactants used were: LUMULSE CO-30Q and LUMULSE CO-40 are ethoxylated castor oils were purchased from Lambent Technologies (Gurnee, IL) and Tegostab® B8406, a silicone surfactant was purchased from Evonik Goldschmidt Corporation (Hopewell, VA). Stepanol PS-3152 is a commercial plasticizer purchased from Stepan.

Surface tension of resin solutions

Aqueous tannin solutions were prepared by dissolving tannin extracts obtained from two different sources (Tannin-A and Tannin-F) in 50 weight% of water, and the surface tension of these two different tannin extract solutions were measured by adding no surfactant. The surface tension data is reported in Table 1.

A tannin solution (Tannin-F/FA/H_2O) was prepared by dissolving Tannin-F in furfuryl alcohol and water. A 50/50 wt% Tannin-F/phenolic resole solution was prepared by mixing phenol-formaldehyde based resole and tannin solutions. The surface tension of this 50/50 Tannin-F/phenolic resole mix was measured with and without surfactant and compared with 100% resole (Table 1).

Table 1. Interaction of surfactant(s) with resole and resole/tannin mix

Tannin/Resole	Composition	Surfactant (wt%)	Surface Tension (mN/m)
Tannin-F	Tannin-F/H_2O (50/50)	None	42.7
Tannin-A	Tannin-A/H_2O (50/50)	None	53.5
Phenolic resole, PF-D	phenol-formaldehyde/water	None	61.4
Phenolic resole	phenol-formaldehyde/water	Tegostab® 8406 (2%)	37.5
Phenolic resole	phenol-formaldehyde/water	LUMULSE CO-30Q (2%)	39.7
Mixed Tannin-phenolic resole	50/50 Resole/Tannin-F/FA/H_2O (50/33/12))	None	54.1
Mixed Tannin-phenolic resole	50/50 Resole/Tannin-F/FA/H_2O (50/33/12)	Tegostab® 8406 (2%)	30.9
Mixed Phenol Tannin Resole	50/50 Resole/Tannin-F/FA/H_2O (50/33/12)	LUMULSE CO-30Q (2%)	37.8

As data from Table 1, the aqueous Tannin-F solution had lower surface tension (42.7 mN/m) than the Tannin-A solution (53.5 mN/m) suggesting that Tannin-F contains surface active components, and the composition of the two tannins is not identical. Furthermore, the surface tension of the neat phenol-based resole prepolymer (61.4 mN/m) was reduced from 61.4 to 54.1 mN/m when Tannin-F solution was added without a surfactant.

Preparation of agglomerate free stock solution of tannin, furfuryl alcohol and water (Tannin/FA/H_2O)

Furfuryl alcohol (320 g) and deionized water (108.9 g) were mixed in a kettle. Then Tannin-F (571.1 g, contains 7.2 wt % moisture) was added in increments with frequent stirring to form a solution. The total mass of the kettle was recorded. The kettle was heated in oil bath to 58-60 ^oC installed with the mixer with the oil bath and heater raised and the

solution was mixed for 4 hours at 300 rpm. Then the kettle was cooled and weighed to determine water loss, and additional water equivalent to that lost was added and the solution was mixed again until the solution is homogenized. The weight ratios of tannin, furfuryl alcohol and water in the solution were 53/32/10. The viscosity of this solution was measured at 25 ^{o}C and found to be 14,500 cP. This stock solution was used to prepare foamable compositions and foams.

Bio-Based Closed-Cell Insulation Foams

Examples 1-3: Closed-Cell Condensed Tannin-Based Foams For Thermal Insulation

A typical preparation of foamable composition and foaming process to form a tannin-based closed-cell foam is described below. The actual amounts of various ingredients added and the calculated weight percentage of each ingredient, based on the total weight of the foamable composition are reported in Table 2.

A portion of the tannin/FA/water mix solution, plasticizer (Stepanol PS-3152) and ethoxylated castor oil surfactant (LUMULSE CO-30Q) were added in 100 mL beaker, mixed thoroughly and cooled in an ice bath. To the above solution, a mixture of isopropyl chloride/isopentane (IPC/IP) (3:1 weight ratio) was added to form a pre-foam mixture. The beaker containing the pre-foam mixture was weighed and additional amount of the 3:1 mixture of IPC/IP was added to compensate evaporated amount during the mixing. After cooling the pre-foam mixture again in ice bath, a 70/30 mixture of *p*-toluenesulfonic acid/xylenesulfonic acid (a 70% solution in ethylene glycol) which was precooled at -10 ^{o}C, was added and mixed thoroughly for 30 seconds to form a formaldehyde-free foamable composition.

About 16 g of the as formed formaldehyde-free foamable composition was transferred quickly from beaker into non-stick paper box mold (3"x 3"x 3") previously heated in oven at 70 ^{o}C. This paper box was inserted in a metal mold having the same dimensions of paper box mold and closed tightly. After 30 minutes, the condensed Tannin-based foam

was taken out from the metal mold and the paper box, was placed in another oven and post-cured the foam at 70 °C for overnight.

The properties of the cured condensed tannin-based foam are reported in Table 2.

Comparative Example A: Closed-Cell Condensed Tannin-Based Foam

Example 1 was repeated with the exception that no maleic anhydride was added. The composition and the properties of the as-prepared condensed Tannin-based foam are summarized in Table 2.

Table 2. Bio based foams made in closed mold 3"x3"x3"at 70 °C

	Comparative Example A	Example 1	Example 2	Example 3
Tannin mix solution (53/32/15), g (wt%)	29.41 (73.1)	29.44 (72.1)	29.40 (71.8)	29.40 (71.0)
Maleic anhydride, g (wt%)	0 (0)	0.40 (1.0)	0.60 (1.50)	1.01 (2.4)
IPC/IP (75/25), g (wt%)	2.90 (7.2)	2.98 (7.3)	2.94 (7.2)	2.92 (7.1)
Surfactant, LUMULSE CO-30Q , g (wt%)	0.82 (2.0)	0.81 (2.0)	0.80 (2.0)	0.80 (1.9)
Plasticizer, Stephanol PS 3152 g (wt%)	0.40 (1.0)	0.40 (1.0)	0.40 (1.0)	0.40 (1.0)
70% Acid catalyst solu, g (wt%)	6.71 (11.7)	6.79 (11.6)	6.81 (11.6)	6.91 (11.7)
Thermal conductivity, mW/m.K	22.0	22.2	21.4	21.6
R-value per inch, ft^2.hr. °F/Btu, at 10 °C	6.56	6.50	6.74	6.68
Open-cells, %	16.4	7.4	5.9	6.7
Apparent density, kg/m^3	36.4	36.3	35.7	40.5
Dimensional stability	Visibly shrink	No shrink	No shrink	No shrink
Water vapor absorption, Weight gain at 52%RH, %	6.68	6.12	6.06	6.36

It is clear from the data in Table 2, the cured tannin- based foams from the foamable compositions containing maleic anhydride had excellent insulation properties: the foams had density in the range of 35.7–40.5

kg/m³, low initial thermal conductivity and low open-cell content. The foams that had no maleic anhydride, i.e. Comparative Example A resulted in a poor quality foam with high open-cell content (16.4%) and high shrinkage as compared to foams that contained maleic anhydride (Examples 1-3).

In addition to excellent thermal insulation properties, the foams with increased amount of maleic anhydride had a surprising property of decreased affinity towards moisture present in air after normalizing for the density, as shown in Figure 1, which shows the effect of maleic anhydride on moisture absorption. The foams in general with low moisture absorption can have stable insulation performance.

Examples 4-7: Closed-Cell Condensed Tannin-Based Foams

Examples of 4-7 were the repeat of Example 2 with the exception that varied amounts of urea and maleic anhydride as shown in Table 3. The cured foam properties are reported in Table 3.

Comparative Example B: Closed-Cell Condensed Tannin-Based Foams

Example 2 was repeated with the exception that no maleic anhydride was added and the amount of urea was 1.5 wt%. The cured foam properties are reported in Table 3.

Table 3. The effect of maleic anhydride/urea on properties of foam made in 3"x3"x3" mold at 70 °C

	Comparative Example B	Example 4	Example 5	Example 6	Example 7
Tannin mix solution (53/32/15), g (wt%)	29.41 (71.8)	29.41 (70.8)	29.41 (70.4)	29.1 (68.6)	28.62 (67.4)
Maleic anhydride, g (wt%)	0 (0)	0.61 (1.5)	1.01 (2.4)	1.53 (3.6)	2.03 (4.8)
Urea, g (wt%)	0.60 (1.5)	0.36 (0.9)	0.36 (0.9)	0.72 (1.7)	0.72 (1.7)
IPC/IP (75/25), g (wt%)	2.95 (7.2)	3.10 (7.5)	2.98 (7.1)	3.00 (7.1)	3.00 (7.1)
Surfactant, g (wt%)	0.80 (2.0)	0.85 (2.0)	0.80 (1.9)	0.84 (2.0)	0.85 (2.0)
Plasticizer, g (wt%)	0.40 (1.0)	0.42 (1.0)	0.40 (1.0)	0.45 (1.1)	0.43 (1.0)
70% Acid catalyst solution, g (wt%)	6.80 (11.6)	6.80 (11.5)	6.81 (11.4)	6.80 (11.2)	6.80 (11.2)
Thermal conductivity, mW/m.K	Inferior foams	22.8	21.5	23.2	22.5
R-value per inch, ft^2.hr. °F/Btu, at 10°C		6.33	6.71	6.22	6.41
Open-cell, %		11.6	7.3	8.5	8.9
Apparent density, kg/m^3		42.0	36.2	37.2	36.1

It is clear from the data in Table 3, when urea was added to the foamable composition containing Tannin-F solution with no added maleic anhydride, the properties of the cured foam could not be measurable due to its inferior quality, as shown by Comparative Example B. However adjusting the amount of maleic anhydride with respect to urea amount, the foams with excellent insulation properties were obtained. For example, the foamable composition containing 0.9 wt% of urea, maleic anhydride gave better insulation properties when the amount was increased from 1.5 to 2.4 wt%, as shown by Examples 4 and 5. Similarly, the composition containing 1.7 wt% of urea, maleic anhydride gave lower thermal conductivity with 4.8% than 3.6 wt%, as shown by Examples 6 and 7. The data suggest that it is possible to optimize the foam insulation properties by adjusting the ratio maleic anhydride to urea.

Examples 8-9: Aged thermal conductivity Closed-Cell Condensed Tannin-Based Foams

Two condensed tannin-based foams were prepared as described in Example 2. These two foams were aged in oven at 70 °C for 4 days and then at 110 °C for 2 weeks, and the thermal conductivity was measured at room temperature and found to be 22.1 and 22.2 mW/m.K respectively.

Fire properties of Closed-Cell Condensed Tannin-Based Foam containing maleic anhydride

Example 10: A Tannin-based foam was prepared as described in Example 3 with the following ingredients: Tannin/FA/water mix solution, Stepanol PS-3152 (1.23%), LUMULSE CO-40 (2.16%), maleic anhydride (1.5%), a mixture of isopropyl chloride/isopentane (7.36%) and 70/30 mixture of *p*-toluenesulfonic acid/xylenesulfonic acid (12.68%) in 30 % ethylene glycol. About 67 g of the composition was poured in 6"X6"X2" mold. The foaming and curing temperatures were 60 and 70 ^{o}C respectively.

Comparative Example C: Identical foam sample was prepared as described above without using maleic anhydride.

The fire properties of these two foams without facer were tested by using cone colorimeter and the results are reported in Table 4.

The tannin-based foam that contained maleic anhydride self-extinguished in 34 seconds much faster than the foam that contained no maleic anhydride (51 seconds).

Table 4. Fire properties of the closed-cell condensed tannin-based foams

Property	Comparative Example C	Example 10
Ignition time, s	0.3	0.3
Flameout time, s	51	34
Mass loss, wt%	41	27
Heat release rate (peak), kW/m^2	91	93
Total heat release, MJ/m^2	2.5	1.9
Effective heat of combustion, MJ/kg	9.9	11.9
Smoke production rate, m^2/s	0.0015	0.0023
CO/CO_2 yield	0.08	0.01

Example 11: A tannin-based foam was prepared as described in Example 10 with the following ingredients: Tannin/FA/water mix solution, Stepanol PS-3152 (1.2%), LUMULSE CO-30Q (2.2%), maleic anhydride (0.75%), a mixture of isopropyl chloride/isopentane (7.3%) and 70/30 mixture of *p*-toluenesulfonic acid/xylenesulfonic acid (12.6%) in 30 % ethylene glycol. The composition was foamed and cured in a closed mold with dimensions 6"x6"x2" at 70 ^{o}C.

The Limiting Oxygen Index (LOI) method was used to measure the flammability of the foam according to ASTM D-2863 and the LOI value for the tannin based foam was found to be 31.

As it is clear from the above descriptions, the foamable compositions that contained maleic anhydride resulting foams with improved dimensional stability, low initial and aged thermal conductivities, high closed-cell content, less sensitive to moisture and good fire resistance.

Phenolic Resole

Phenol-formaldehyde (PF-M) resole prepolymer containing urea was used to prepared mixed Tannin-Phenolic foams. The resole prepolymer was characterized and had the following properties:

Number average molecular weight (Mn) = 408

Weight average molecular weight (Mw) = 905

Polydispersity (Mw/Mn) = 2.2

Water (from Karl Fischer) = 12.6%

Residual Formaldehyde = 3.94%

Residual Phenol = 3.72%

Viscosity @ 25 ^{o}C, cP = 7150-7700

Preparation of volatile-free condensed tannin by thermal pre-treatment of Tannin-F

250 g of Tannin-F as received was placed in rectangular container having 220 cm^2 surface area and dried at 130 ^{o}C for 4 days in an oven with combined nitrogen flow and vacuum to flush out moisture and volatile impurities. After drying the observed weight loss was found to be 10.92 %. The pre-heated Tannin-F was used to prepare T/FA/H_2O solution as described above.

Compositional Analysis of the heat treated Tannin-F

Surface tension of Tannin-Aqueous solutions: Table 5 reports the surface tension of 50 wt% aqueous solutions of commercial Tannin-A and Tannin-F as received, and thermally treated Tannin-F at 130 ^{o}C for 3 days in air.

Table 5. Surface Tension of Aq. Tannin solutions

50% Tannin in water	Surface tension (mN/m)
Tannin-A	54.8
Tannin-F	43.9
Tannin-F pre-heated at 130 ^{o}C for 3 days in air	45.2

The data in Table 5 suggest that the Tannin-F differs from Tannin-A by having surface active components and the pre-heat treatment did not remove the surface active components present in Tannin-F.

Headspace GC-MS analysis

Figures 2A and 2B shows GC-MS headspace spectra of commercial condensed tannin extracts from two different geographical regions: as-received Tannin-A and as-received Tannin-F respectively. It is surprising to see that the presence of high boiling volatile components (boiling points greater than 277 ^{o}C at which resorcinol boils off) in Tannin-F which were absent in Tannin-A. The volatile components present in Tannin-F were identified by matching mass spectra with spectra of reference compounds in NIST (National Institute of Standards and Technology) mass spectral library and their associated GC retention times in minutes are listed below. It is speculated that the presence of high boiling volatile components in Tannin-F may be due to the nature of plant source, extraction method or any added additives after the extraction. From the Figure 2B and the foam data in Table 6, it is concluded that the high boiling volatiles (boiling points greater than 277 ^{o}C) present in Tannin-F were interfering with urea present in resole and led to poor insulation performance of the foam.

It should be noted that the low boiling volatile components (boiling points lower than 277 ^{o}C) which are present in Tannin-F are also present in Tannin-A despite of the fact that the two tannins belong to different regions of the world and their extraction methods might not be identical. Since Tannin-A had no impact on thermal insulation performance of a bio-based foam derived from tannin/PF-M resole mixture in the presence of urea, it was assumed that the low boiling volatile components do not affect the insulation performance.

Figures 3A, 3B, and 3C show GC-MS headspace spectra of commercial condensed tannin extracts: as-received Tannin-F; pre-heated Tannin-F in air; and pre-heated Tannin-F in nitrogen respectively. The absence of high boiling volatile components (boiling points greater than 277 ^{o}C) is evident in pre-heated Tannin-F samples both in air and in nitrogen at 130 ^{o}C, and the volatile profile of the pre-heated Tannin-F

samples are closely matched with that of Tannin-A rather than Tannin-F. The peak areas for resorcinol were measured in spectra of untreated and pre-heated Tannin-F samples to estimate the amount of high volatile components reduced during thermal pre-treatment. The resorcinol peak area in untreated Tannin-F sample was found to be 3.77×10^{-5} and this peak area was decreased in heated Tannin-F samples to 0.68 and 0.38×10^{-5} in nitrogen and in air respectively, and accounts to 80-90% decrease. Therefore it is concluded that the high boiling volatile components were decreased by 80-90% in heated tannin samples. The thermal treatment of Tannin-F clearly suggests that the high boiling volatile components present in Tannin-F may be either boiled-off and/or reacted to form non-volatile components. As a result, the urea had no impact on pre-heated tannin and the foams obtained from pre-heated Tannin-F had excellent thermal insulation performance.

The volatile components identified in Tannin-F as received are: Methanol (2.252 min), water (1.8-2.8), acetone (3.009), furan (3.042), methyl acetate(3.387), formic acid (3.693), propanal, 2-methyl- (3.759), 2,3-butanedione (4.151), furan, 2-methylacetic (4.337), acetic acid (4.749), 2-propanone, 1-hydroxy (5.419), pyridine (6.495), 3(2H)-furanone,dihydro-2-methyl- (7.311), furfural (7.703), 2-propanone,1-(acetyloxy)-or a diester (8.015), 4-cyclopentene-1,3-dione (8.413), furan,2-ethyl-5-methyl- (8.752), butyrolactone (8.818), 1,2-cyclopentanedione (8.945), 2,5-furandione,dihydro-3-methylene- (9.124), 2-furancarcoxaldehyde,5-methyl- (9.423), 2,4-dihydroxy-2,5-dimethyl-3(2H)-furan-3-one (9.648), 1H-pyrrole-2-carboxaldehyde (10.02), 2,5-dimethyl-4-hydroxy-3(2H)-furanone (10.452), ethanone,1-(1H-pyrrol-2yl)- (10.657), 2-pyrrolidinone (10.737), phenol-2-methoxy- (11.009), an amine (11.507), 4H-pyran-4-one,2,3-dihydro-3,5-dohydroxy-6-methyl (11.707), 4H-pyran-4-one,3,5-dihydroxy-2-methyl (12.085), resorcinol (12.902), phenol,2,6-dimethoxy- (13.718), dodecane, 1-chloro- (14.741), C12 alcohol or similar (14.847), tetradecane, 1-chloro- (16454), C12 alkane or alcohol (16.825), 1-chloro-2-dodecyloxyethane or similar (16.925), tridecylbenzene isomer (17.967; 18.286), mixed overlapping complex products (18.5-25). It should be

noted that the retention times vary with the GC conditions such as carrier flow rate and temperature.

Example 12: Closed-Cell Mixed Tannin-Phenolic Foams

A portion of the tannin/FA/water solution that was prepared from preheated Tannin-F, PF-M resole, plasticizer (Stepanol PS-3152), and surfactant (LUMULSE CO-30Q) were added in 100 mL beaker, mixed thoroughly and cooled in an ice bath. To this solution, a mixture of isopropyl chloride/isopentane (IPC/IP) (3:1 weight ratio) was added incrementally and mixed the solution. The beaker containing the solution was weighed and additional amount of the IPC/IP mixture was added to compensate evaporated amount during the mixing. After cooling the mixture again in ice bath, a 70/30 mixture of *p*-toluenesulfonic acid/xylenesulfonic acid (a 70% solution in ethylene glycol) which was precooled at -10 ^{o}C was added and mixed thoroughly for 30 seconds.

About 16 g of the above solution was transferred quickly from beaker into non-stick paper box mold (3"x 3"x 3") previously heated in oven at 50 ^{o}C. This paper box was inserted in a metal mold having the same dimensions of paper box mold and closed tightly. After 30 minutes, the foam was taken out from the metal mold and the paper box, was placed in another oven and post-cured the foam at 70 ^{o}C for overnight. The cured foam properties are reported in Table 6.

Example 13: Closed-Cell Mixed Tannin-Phenolic Foams

Example 12 was repeated with the exception that the Tannin-F that was pre-heated in nitrogen atmosphere at 130 ^{o}C for 4 days was used, and the foam was molded in a 6'x6'x2' mold.

Example 14: Closed-Cell Mixed Tannin-Phenolic Foams

Example 13 was repeated with the exception that maleic anhydride was added with no plasticizer.

The composition, process conditions and foam properties are reported in Table 6.

Table 6. Closed-Cell Mixed Tannin-Phenolic Foams

	Example 13	Example 14	Example 15
Tannin-F pretreatment	130 °C in air for 3 days	130 °C in N_2 for 4 days	130 °C in N_2 for 4 days
Tannin/FA/H_2O (53/32/15) solution, g (wt%)	14.7 (37.1)	32.5 (36.7)	32.5 (37.4)
PF-M Resole, g (wt%)	14.7 (37.1)	32.5 (36.7)	32.5 (37.4)
Maleic anhydride, g (wt%)	0	0	1.28 (1.5)
Surfactant, g (wt%)	0.36 (0.91)	0.92 (1.0)	0.95 (1.1)
Plasticizer, g (wt%)	0.4 (1.0)	0.87 (1.0)	0
IPC/IP (75/25), g (wt%)	2.95 (7.4)	6.49 (7.3)	6.48 (7.45)
70% Acid in EG, g (wt%)	6.50 (11.5)	15.32 (12.1)	13.26 (12.2)
Foaming and curing temperature, °C	50/70	50/70	50/70
Thermal conductivity, mW/m.K	23.8	23.4	21.9
R-value per inch, ft^2.hr. °F/Btu, at 10 °C	6.06	6.16	6.59
Open-cells, %	6.8	6.1	6.1
Apparent density, kg/m^3	38.8	37.9	36.3

The data in Table 6 surprisingly shows that the foams, prepared from the commercial Tannin-F that was pretreated at 130 °C either in air or nitrogen atmosphere for 3-4 days, with excellent thermal insulation performance. The thermal conductivity of the foams was dropped significantly from about 31 (see Examples 19 in Table 8) to about 22-23 mW/mK when measured at room temperature and the open cell content of the foams was reduced to less than 10% (or closed-cell content was greater than 90%).

Since the TC value decreases with decrease in temperature, the TC values of the above foams will be lower at 10 °C, and these foams are useful as thermal insulation for cold chain applications.

Though the temperature and time to heat Tannin-F in pretreatment step were not optimized, the data clearly suggest that the volatile components present in Tannin-F might have reacted (condensed) or

evaporated during the pre-heat treatment at 130 °C. In addition to the pre-heat treatment of Tannin-F, it is also important to keep surfactant level around 1 wt% for the mixed tannin/resole formulation to obtain high percent closed-cells and thereby to obtain foams with low initial thermal conductivity.

Aged thermal conductivity of Closed-Cell Mixed Tannin-Phenolic Foams

Example 16: Closed-Cell Mixed Tannin-Phenolic Foams

A rigid bio based foam was prepared as described in Example 14 and aged in oven at 70 °C for 4 days and then at 110 °C for 2 weeks and the thermal conductivity was measured at room temperature and found to be 23.5 mW/mK.

Example 17: Closed-Cell Mixed Tannin-Phenolic Foams

A rigid bio based foam was prepared as described in Example 14 except no plasticizer was added to the formulation. The foam was aged in oven at 70 °C for 4 days and then 110 °C for 2 weeks and the thermal conductivity was measured at room temperature and found to be 22.8 mW/mK.

The low thermal conductivity of the aged foams (Examples 16 & 17) indicates their excellent insulation performance.

Bio Based Open-Cell Foam for Cold/Hot Source

Example 18: Open-Cell Condensed Tannin-Based Foam

A tannin-based foam was prepared as described in Examples 1-3 except that the ethoxylated castor oil surfactant was replaced with a silicone surfactant (Tegostab® B8406), and the composition was foamed and cured at 60 and 70 °C respectively in a 6"x6"x2" mold. The actual amounts of various ingredients added and the calculated weight percentage of each ingredient, based on the total weight of the foamable composition are reported in Table 7.

Table 7: Composition, process conditions and properties of bio based open- cell foam

	Example 18
Tannin mix solution (53/32/15), g (wt%)	64 (78.4)
Surfactant (Tegostab® B8406), g (wt%)	1.76 (2.16)
Plasticizer, g (wt%)	1.00 (1.2)
IPC/IP (75/25), g (wt%)	6.40 (7.3)
70% Acid catalyst, g (wt%)	14.84 (12.7)
Foaming and curing temp. ^{o}C	60/70
Thermal conductivity, mW/m.K	37.8
R-value per inch, ft^2.hr. ^{o}F/Btu	3.82
Open-cells, %	95.9
Apparent density, kg/m^3	30.5

Examples 19: Open-Cell Mixed Tannin-Phenolic Foam

An open-cell mixed tannin-phenolic foam was prepared as described in Example 12 except that the commercial Tannin-F was used to prepare tannin solution instead of preheated tannin, and the foaming and curing temperatures were 70 ^{o}C respectively. The actual amounts of various ingredients added and the calculated weight percentage of each ingredient to the total weight of the composition were reported in Table 8.

Table 8. Mixed Tannin-Phenolic Open-Cell Foam

	Example 19
Tannin	As-received Tannin-F
Tannin/FA/H_2O (53/32/15) solution, g (wt%)	14.5 (36.4)
PF-M Resole, g (wt%)	14.7 (35.9)
Surfactant, g (wt%)	0.83 (2.1)
Plasticizer, g (wt%)	0.41 (1.0)
IPC/IP (75/25), g (wt%)	2.96 (7.3)
70% Acid in EG, g (wt%)	6.80 (11.8)
Foaming and curing temperature, ^oC	70/70
Thermal conductivity, mW/mK	30.8
R-value per inch, $ft^2.hr.\ ^oF/Btu$	4.68
Open-cells, %	96.4
Apparent density, kg/m^3	32.5

The high thermal conductivity of these open-cell foams makes less attractive for use as thermal insulation, however these open-cell foams could be used as cold/hot source by incorporating phase change materials such water or salt solution.

CLAIMS

What is claimed is:

1. A thermally regulated system, comprising:

(a) an outer shell defining a retention chamber;

(b) at least one layer of bio-based closed-cell insulation foam lining the retention chamber so as to define an insulated retention chamber, wherein the bio-based closed-cell insulation foam comprises a polymeric phase defining a plurality of open cells and a plurality of closed-cells,

wherein one or more blowing agents is disposed in at least a portion of the plurality of closed-cells,

wherein the bio-based closed-cell insulation foam is at least one of:

- a closed-cell condensed tannin-based foam derived from a foamable composition comprising a surface-active condensed tannin, a formaldehyde-free tannin-reactive monomer, a saturated or an unsaturated organic anhydride, a surfactant, a blowing agent, an acid catalyst, and an optional polyamine and/or plasticizer; or
- a closed-cell mixed tannin-phenolic foam derived from a composition comprising a volatile-free condensed tannin, a formaldehyde-free tannin-reactive monomer, a phenolic-resole prepolymer, a polyamine, a surfactant, a blowing agent, an acid catalyst, and an optional saturated or unsaturated organic anhydride and/or plasticizer;

(c) a cold source or a hot source disposed within the insulated retention chamber to maintain the insulated retention chamber at a desired temperature during storage and/or transportation of a temperature sensitive product; and

(d) optionally a temperature monitoring device disposed inside the retention chamber,

wherein the bio-based closed-cell foam has an open-cell content of less than 15%, measured according to ASTM D6226-5, and an R-value per inch of at least 6.0 $hr \cdot ft^2 \cdot °F/Btu$.

2. The thermally regulated system of Claim 1, wherein the outer shell is selected from the group consisting of corrugated box, wooden pallet, plastic pallet, wooden crate and plastic crate.

3. The thermally regulated system of Claim 1, wherein the outer shell is wrapped with a high density polyethylene film or sheet.

4. The thermally regulated system of Claim 1, wherein the system is selected from the group consisting of a refrigeration unit, a refrigerated truck, and a cold storage unit.

5. The thermally regulated system of Claim 1, wherein the system is a transit packaging unit for transporting a temperature sensitive product.

6. The thermally regulated system of Claim 5, wherein the transit packaging unit optionally comprises one or more protective packaging materials surrounding the temperature sensitive product, and wherein the protective packaging material is selected from the group consisting of expanded polystyrene foam, corrugated fiber board boxes, packing peanuts, bubble wrap, wadding, absorbent materials, and plastic bags.

7. The thermally regulated system of Claim 1, wherein the cold source is selected from the group consisting of ice, dry ice, gel packs, gel bricks, and phase change materials.

8. The thermally regulated system of Claim 1, wherein the cold source comprises a bio-based open-cell foam absorbed with a phase change material.

9. The thermally regulated system of Claim 1 further comprising a temperature sensitive product disposed within the insulated retention chamber, wherein the temperature sensitive product is selected from the group consisting of food, flowers, chemicals, pharmaceuticals, and medical products.

10. The thermally regulated system of Claim 1, wherein the bio-based closed-cell foam further comprises a blowing agent, wherein the

blowing agent is an azeotrope or an azeotrope-like mixture of isopentane and one other blowing agent selected from the group consisting of isopropyl chloride; 1,1,1,4,4,4-hexafluoro-2-butene; and 1-chloro-3,3,3,-trifluoropropene.

11. The thermally regulated system of Claim 1, wherein the bio-based foam has a density in the range of 10-50 kg/m^3.

12. The thermally regulated system of Claim 1, wherein the saturated or the unsaturated organic anhydride comprises at least one of maleic anhydride, acetic anhydride, succinic anhydride, phthalic anhydride and trimelletic anhydride, and mixtures thereof.

13. The thermally regulated system of Claim 1, bio-based closed-cell insulation foam is a condensed tannin-based foam derived from a surface-active tannin, furfuryl alcohol, maleic anhydride, ethoxylated castor oil, a mixture of isopropyl chloride and isopentane, an aromatic sulfonic acid catalyst, and optionally urea and/or a polyester polyol.

14. The thermally regulated system of Claim 1, wherein bio-based closed-cell insulation foam is a closed-cell mixed tannin-phenolic foam derived from a volatile-free condensed tannin, furfuryl alcohol, maleic anhydride, phenolic-resole prepolymer, ethoxylated castor oil, a mixture of isopropyl chloride and isopentane, an aromatic sulfonic acid catalyst, and optionally urea and/or a polyester polyol.

15. A method for packaging a temperature-sensitive product for cold chain shipment comprising the step of:

a) providing an outer shell defining a retention chamber;

b) disposing at least one layer of bio-based closed-cell foam to line the retention chamber so as to define an insulated retention chamber, wherein the bio-based closed-cell insulation foam is at least one of:

- a closed-cell condensed tannin-based foam derived from a foamable composition comprising a surface-active condensed tannin, a formaldehyde-free tannin-reactive

monomer, a saturated or an unsaturated organic anhydride, a surfactant, a blowing agent, an acid catalyst, and an optional polyamine and/or plasticizer; or

- a closed-cell mixed tannin-phenolic foam derived from a composition comprising a volatile-free condensed tannin, a formaldehyde-free tannin-reactive monomer, a phenolic-resole prepolymer, a polyamine, a surfactant, a blowing agent, an acid catalyst, and an optional saturated or unsaturated organic anhydride and/or plasticizer;

c) disposing a cold source within the insulated retention chamber to maintain the insulated retention chamber at a desired temperature during storage and/or transportation of a temperature sensitive product; and

d) disposing a temperature-sensitive product within the insulated retention chamber, wherein the thermal insulate the product during transportation.

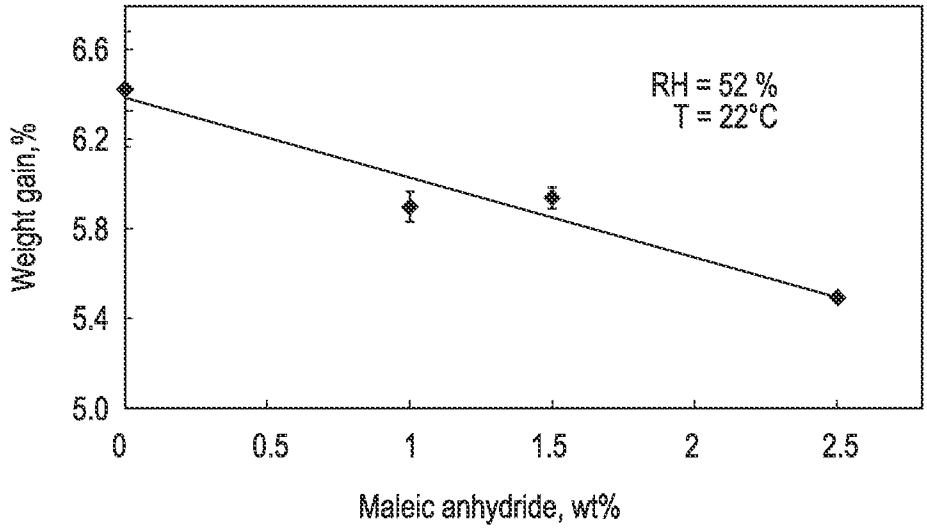

6.6
6.2
5.8
5.4
5.0
Weight gain,%
RH = 52 %
T = 22°C
0
0.5
1
1.5
2
2.5
Maleic anhydride, wt%

FIG. 1

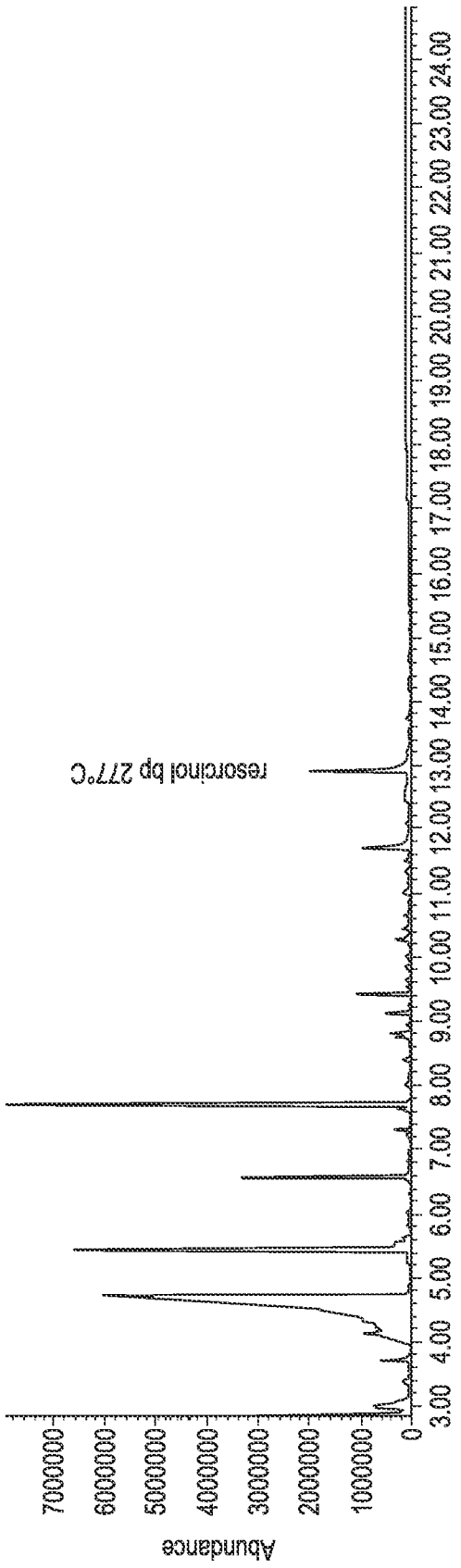

Abundance
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6000000
5000000
4000000
3000000
2000000
1000000
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3.00 4.00 5.00 6.00 7.00 8.00 9.00 10.00 11.00 12.00 13.00 14.00 15.00 16.00 17.00 18.00 19.00 20.00 21.00 22.00 23.00 24.00
Retention Time (minutes)
resorcinol bp 277°C

FIG. 2A

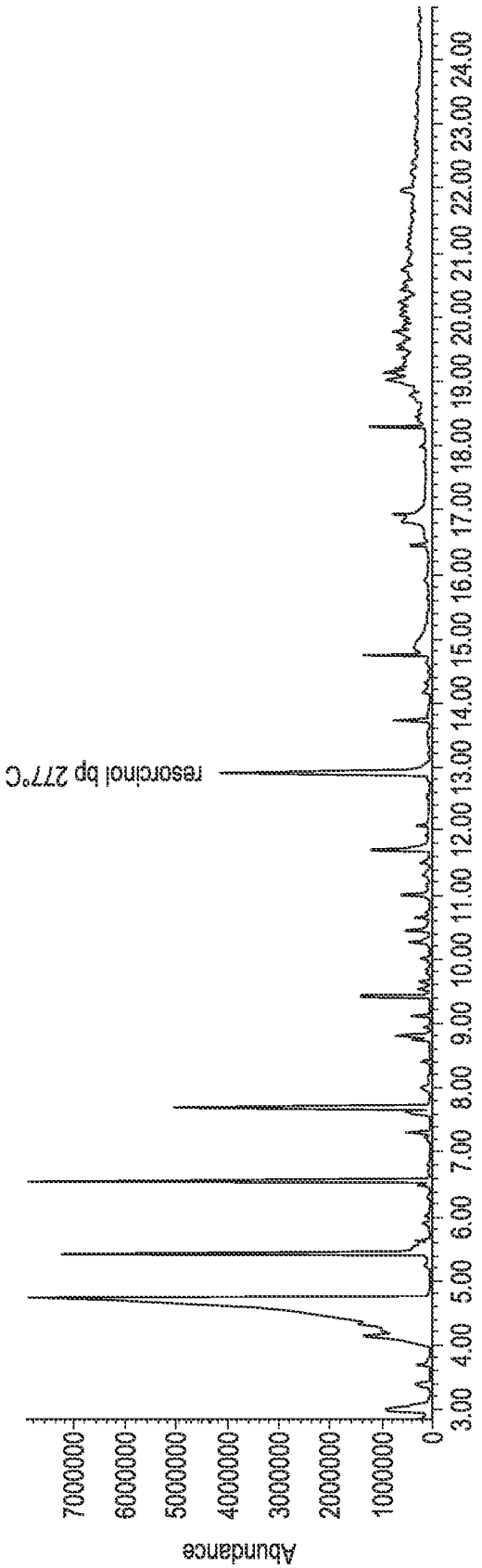

resorcinol bp 277°C
Abundance
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6000000
5000000
4000000
3000000
2000000
1000000
0
3.00 4.00 5.00 6.00 7.00 8.00 9.00 10.00 11.00 12.00 13.00 14.00 15.00 16.00 17.00 18.00 19.00 20.00 21.00 22.00 23.00 24.00
Retention Time (minutes)

FIG. 2B

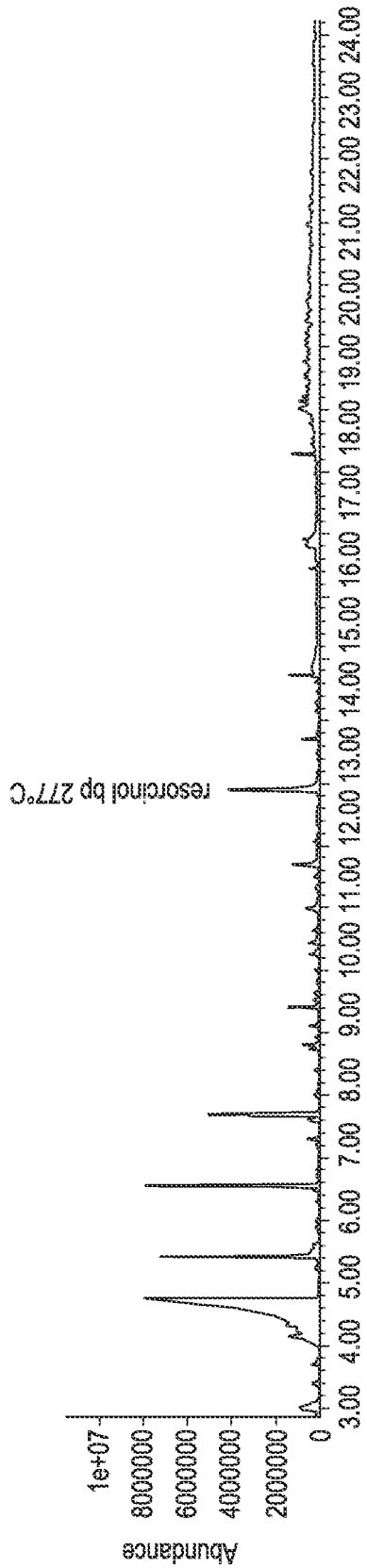

resorcinol bp 277°C
Abundance
1e+07
8000000
6000000
4000000
2000000
0
3.00 4.00 5.00 6.00 7.00 8.00 9.00 10.00 11.00 12.00 13.00 14.00 15.00 16.00 17.00 18.00 19.00 20.00 21.00 22.00 23.00 24.00
Retention Time (minutes)

FIG. 3A

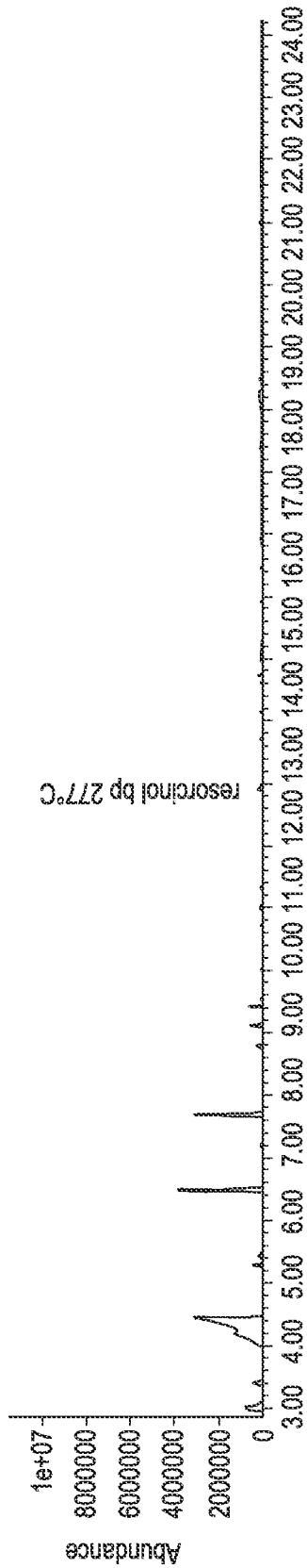

resorcinol bp 277°C
Abundance
1e+07
8000000
6000000
4000000
2000000
0
3.00 4.00 5.00 6.00 7.00 8.00 9.00 10.00 11.00 12.00 13.00 14.00 15.00 16.00 17.00 18.00 19.00 20.00 21.00 22.00 23.00 24.00
Retention Time (minutes)

FIG. 3B

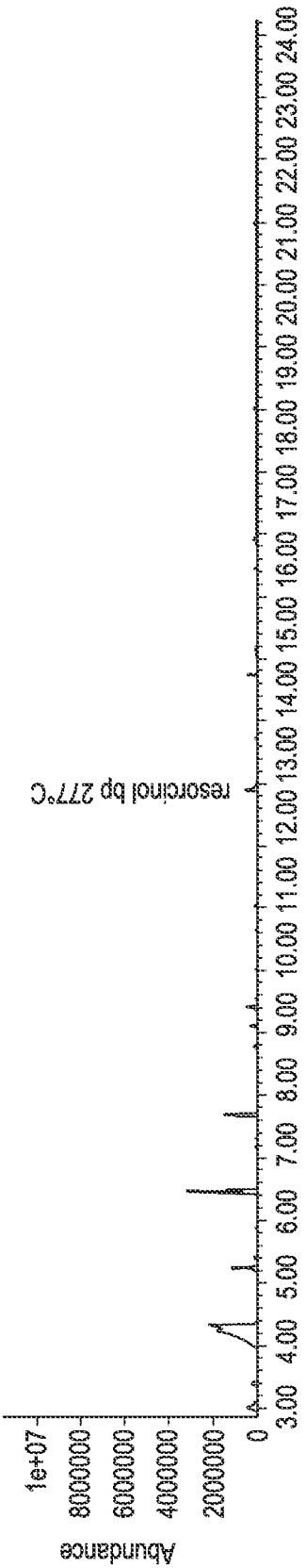

resorcinol bp 277°C
Abundance
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8000000
6000000
4000000
2000000
0
3.00 4.00 5.00 6.00 7.00 8.00 9.00 10.00 11.00 12.00 13.00 14.00 15.00 16.00 17.00 18.00 19.00 20.00 21.00 22.00 23.00 24.00
Retention Time (minutes)

FIG. 3C

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2015/023585

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08J9/14 C08J9/00 F25D3/00 B65D81/38
ADD.

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)
C08J F25D B65D

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)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 02/064672 A1 (STYROPHEN INTERNATIONAL PTY LTD [AU]) 22 August 2002 (2002-08-22) page 1, line 6 - line 18 page 2, line 14 - page 3, line 28	1-15
A	WO 2012/162645 A2 (DU PONT [US]) 29 November 2012 (2012-11-29) abstract; examples	1-15
A	WO 2012/162684 A2 (DU PONT [US]) 29 November 2012 (2012-11-29) abstract; examples	1-15
A	WO 2012/162649 A2 (DU PONT [US]) 29 November 2012 (2012-11-29) abstract; examples	1-15

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
8 June 2015	16/06/2015

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Lichau, Holger

1

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2015/023585

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2012/162681 A2 (DU PONT [US]) 29 November 2012 (2012-11-29) abstract; examples -----	1-15

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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