Title: BIODEGRADABLE THERMALLY-STABLE FLAME RETARDANT COMPOSITE MATERIAL AND METHODS OF PREPARATION THEREOF

Abstract: The present invention provides a biodegradable flame retardant composite material having improved intumescent properties and thermal stability, and processes for its preparation. The present invention further relates to plastic materials comprising the flame retardant composite material of the invention and methods for a straight forward and facile preparation and compounding of such improved FR plastic materials.
BIODEGRADABLE THERMALLY-STABLE FLAME RETARDANT COMPOSITE MATERIAL AND METHODS OF PREPARATION THEREOF

FIELD OF THE INVENTION

The present invention relates to a biodegradable flame retardant composite material having improved intumescent properties and thermal stability and processes for its preparation. The present invention further relates to plastic materials comprising said flame retardant composite material and methods for their preparation.

BACKGROUND OF THE INVENTION

In the field of industrial applications such as automotive, consumer electronics and home appliances, all plastic components must be flame retardant (FR). Many of the well-known FR additives contain halogens (e.g. chlorinated and brominated substances), and therefore are potentially harmful to human health and to the environment.

Several alternative FR materials and halogen-free additives are known, such as the water releasing metal hydroxides additives. Metal hydroxides meet the environmental, health and cost requirements but the high concentration needed for an appropriate flame retardant effect restricts their use as an additive in many polymer types.

Phosphorus-containing FRs are of reduced ecological impact, and their range is wide and versatile due to the several potential oxidation states of phosphorus (P) atom. However, in some cases low molecular weight substances may be too mobile and leach out from the host polymeric matrix. Thus, a system containing such FRs should be well designed to prevent the migration of the phosphorous-based FR additive to the surface of the polymeric matrix.

The use and development of renewable resource derived materials have received increasing interest in recent years due to the raised awareness to environmentally friendly materials and processes. The use of renewable resources as FR green products such as lignin and chemically modified lignin was found to be beneficial. Lignin is one of the most abundant organic substances on earth and is increasingly available as a by-product of cellulose production. Lignin-containing materials demonstrate the ability to prevent the material from
dripping, forming a solid char upon exposure to high temperature and stays adhered to the exposed surface.

Physical barrier forming effect as described hereinabove is a known property of intumescent substances or systems comprising these substances. In such materials, an exposure to heat causes the material to swell, thus increasing the material's volume and decreasing its density. The swollen phase constitutes a new interface between the heat source, oxygen and other fire-enhancing gases, and the material itself and slows the flame's progress.

Ammonium polyphosphate (APP) based systems are efficient halogen-free flame retardants, mainly used in polyolefins, polyethylene and polypropylene (PE and PP respectively), thermostet resins such as epoxy resins, polyurethane, unsaturated polyester phenolic resins and others. APP is a non-toxic, environmentally friendly material and it does not generate additional quantities of smoke due to the unique mechanism of intumescence. However, stable intumescent systems are very often difficult to produce, demanding a complex and involved formulation and/or compounding processes.

Moreover, the onset temperature of APP decomposition is about 275°C whereas the processing temperature for engineering plastics such as nylon (PA6) is over 300°C. APP therefore cannot be used as an additive in such systems. Other materials can be used in such systems such as phosphinates and red phosphorous, but these are more expensive and have health and safety risks.


There remains an unmet need for, and it would be advantageous to have a halogen-free, solid intumescent FR system, which can be used as an additive to plastics, thereby enhancing their flame retardation properties at high temperatures, and can be manufactured in a facile and straight-forward process.

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SUMMARY OF THE INVENTION

The present invention provides a biodegradable composite material, comprising a flame retardant (FR) of renewable resource, namely, lignin-based material, an aldehyde, an amine-containing compound and ammonium polyphosphate (APP), coupled together to give a synergistic intumescent effect. The composite material of the invention is a solid material at room temperature and is characterized by low water solubility, a desired property in terms of environmental safety regulations. Furthermore, the composite material's distinct formulation gives rise to a chemically stable FR composite material, exhibiting high temperature resistivity.

The present invention is based in part on an unexpected finding that a chemically stable intumescent system can be formulated in a facile, convenient and cost-effective process. Thus, the present invention provides methods for the preparation of the FR composite material of the invention.

Furthermore, the FR composite material of the invention can be incorporated into commonly used plastic materials as an additive, and improve their FR properties, without jeopardizing their mechanical properties. Thus, the present invention further provides plastic materials comprising the FR composite material of the invention and processes for the incorporation of the FR composite material of the invention into plastic materials. According to some embodiments the plastic material is selected from bioplastics and synthetic thermoplastic and thermosetting materials.

According to one aspect, the present invention provides a biodegradable flame retardant (FR) composite material comprising a lignin-based compound, an aldehyde, an amine-containing compound, phosphoric acid and ammonium polyphosphate (APP), wherein said composite material is in solid form at room temperature. In some embodiments, the FR
composite material is a chemical adduct of a lignin-based compound, an aldehyde, an amine-containing compound, phosphoric acid and ammonium polyphosphate (APP).

In some currently preferred embodiments, the lignin-based FR is hgnosulfonate (LS). In some other embodiments, the amine-containing compound is selected from the group consisting of ammonia, an alkyl amine, a diamine, a triamine, a polyamine, an alkanolamine, a cyclic amine and an amino acid. In a specific embodiment, the diamine is ethylene diamine. In another embodiment, the triamine is melamine. In yet other embodiments, the aldehyde is selected from the group consisting of paraformaldehyde, formaldehyde, acetaldehyde, furfural, hydroxymethyl furfural, butyraldehyde, 4-hydroxy-3-methoxybenzaldehyde, 4-hydroxy-3,5-dimethoxybenzaldehyde, 4-hydroxybenzaldehyde and 2-hydroxybenzaldehyde. In a currently preferred embodiment, the aldehyde is paraformaldehyde.

In some embodiments, the composite material as described above is consisting of a lignin-based compound, an aldehyde, an amine containing compound, phosphoric acid and ammonium polyphosphate (APP). In some related embodiments, the composite material as described above is consisting of a LS, paraformaldehyde, ethylene diamine or melamine, phosphoric acid and APP.

According to another aspect, the present invention further provides a biodegradable FR composite material consisting essentially of a lignin-based compound, an aldehyde, an amine containing compound, phosphoric and ammonium polyphosphate (APP), wherein said composite material is in solid form at room temperature.

In some other embodiments, the composite material of the invention comprises: from about 35 to about 75 wt% APP; from about 15 to about 35 wt% LS; from about 10 to about 35 wt% phosphoric acid; from about 1 to about 15 wt% ethylene diamine or melamine; and from about 1 to about 15 wt% p-formaldehyde.

According to another aspect, the present invention further provides a plastic material comprising the FR composite material as described above. In some embodiments, the plastic material is of a natural origin. In some related embodiments, the plastic material is selected from the group consisting of polyhydroxyalkanoate (PHA), polyethylene glycol (PEG), polyester, polyamide, polylactic acid (PLA), polybutylene succinate (PBS), poly p-
phenylene (PPP), polytrimethylene terephthalate (PTT), polyethylene (PE), and combinations thereof, with each possibility represents a separate embodiment of the present invention. In a currently preferred embodiment, the plastic is polyhydroxyalkanoate (PHA). In a specific embodiment, the plastic is polyhydroxybutyrate (PHB).

In some other embodiments, the plastic material is of a synthetic origin. In some related embodiments, the plastic material is selected from the group consisting of a thermoplastic material, a thermosetting material and an engineering plastic. In some embodiments, the thermoplastic material is polypropylene. In some other embodiments, the thermosetting material is selected from the group consisting of polyurethane, epoxy resin and unsaturated polyester. In some other embodiments, the engineering plastic is selected from the group consisting polyamide (PA) and polyethylene terephthalate (PBT).

According to other aspects, the present invention further provides methods for the preparation of a biodegradable composite material as described above. In one embodiment, the method for the preparation of the biodegradable composite material comprises the steps of: (i) mixing, with optional heating, lignin-based compound with amine-containing compound and an aldehyde; (ii) adding phosphoric acid; (iii) drying and optionally grinding the material obtained in step (ii); (iv) mixing with optional heating, of the material obtained in step (iii) with APP; and (v) optionally grinding the material obtained in step (iv) to obtain a solid, water-insoluble FR composite material.

In one embodiment, the heating in step (i) is carried at a temperature of between about 70 to about 150 °C. In another embodiment, the drying in step (iii) is carried at a temperature of between about 80 to about 150 °C. In an additional embodiment, the heating in step (iv) is carried at a temperature of between about 200 to about 300 °C. In yet another embodiment, the APP and the material obtained in step (ii) were mixed together in step (iv) in a 1:1 weight ratio. According to some embodiments, the lignin-based compound is lignosulfonate (LS). In some other embodiments, the amine-containing compound is selected from the group consisting of ammonia, an alkyl amine, a diamine, a triamine, a polyamine, an alkanolamine, a cyclic amine and an amino acid. In a specific embodiment, the diamine is ethylene diamine. In another embodiment, the triamine is melamine. In yet other embodiments, the aldehyde is selected from the group consisting of paraformaldehyde,
formaldehyde, acetaldehyde, furfural, hydroxymethyl furfural, butyraldehyde, 4-hydroxy-3-methoxybenzaldehyde, 4-hydroxy-3,5-dimethoxybenzaldehyde, 4-hydroxybenzaldehyde and 2-hydroxybenzaldehyde. In a currently preferred embodiment, the aldehyde is paraformaldehyde.

In another embodiment, the method for the preparation of a biodegradable FR composite material comprises the steps of: (i) mixing, with optional heating, sulfite spent liquor (SSL) with an amine-containing compound, sulfuric acid and an aldehyde; (ii) separating the solid phase obtained in step (i); (iii) adding, with optional heating, phosphoric acid to the solid material obtained in step (ii); (iv) optionally drying and/or grinding the material obtained in step (iii); (v) mixing, with optional heating, of the material obtained in step (iii) with APP; and (vi) optionally grinding the material obtained in step (iv) to obtain a solid, water-insoluble FR composite material.

In one embodiment, the heating in step (i) is carried at a temperature of between about 70 to about 150 °C. In another embodiment, the heating in step (v) is carried at a temperature of between about 200 to about 300 °C. In yet another embodiment, the APP and the material obtained in step (iv) were mixed together in step (v) in a 1:1 weight ratio. According to some embodiments, the lignin-based compound is lignosulfonate (LS). In some other embodiments, the amine-containing compound is selected from the group consisting of ammonia, an alkyl amine, a diamine, a triamine, a polyamine, an alkanolamine, a cyclic amine and an amino acid. In a specific embodiment, the diamine is ethylene diamine. In another embodiment, the triamine is melamine. In yet other embodiments, the aldehyde is selected from the group consisting of paraformaldehyde, formaldehyde, acetaldehyde, furfural, hydroxymethyl furfural, butyraldehyde, 4-hydroxy-3-methoxybenzaldehyde, 4-hydroxy-3,5-dimethoxybenzaldehyde, 4-hydroxybenzaldehyde and 2-hydroxybenzaldehyde. In a currently preferred embodiment, the aldehyde is paraformaldehyde.
BRIEF DESCRIPTION OF THE FIGURES

Figure 1 illustrates a Thermogravimetric analysis (TGA) profile of neat FR materials, demonstrating the decomposition onset of samples comprising ammonium polyphosphate (APP) and/or modified lignosulfonate.

5 Figure 2 illustrates a Thermogravimetric analysis (TGA) profile of bioplastics comprising FR materials, demonstrating the decomposition onset of samples comprising ammonium polyphosphate (APP) and/or modified lignosulfonate.

Figure 3 illustrates a Thermogravimetric analysis (TGA) profile of neat FR materials demonstrating the decomposition onset of samples comprising ammonium polyphosphate (APP) and/or modified lignosulfonate originated from spent sulfite liquor (SSL).

Figure 4 illustrates a Thermogravimetric analysis (TGA) profile of bioplastics comprising FR materials, demonstrating the decomposition onset of samples comprising ammonium polyphosphate (APP) and/or modified lignosulfonate originated from spent sulfite liquor (SSL).

10 Figure 5 depicts the enhanced intumescent effect demonstrated in a bioplastic comprising the composite material of the invention. The black arrow points at the swollen black material resulted from heating the plastic in a TGA apparatus.

Figure 6 illustrates a Thermogravimetric analysis (TGA) profile of neat modified LS FR originated from spent sulfite liquor (SSL). The bottom graph depicts the neat material before thermal treatment and the top graph depicts the material after treatment.

15 Figure 7 illustrates a Thermogravimetric analysis (TGA) profile of neat modified LS FR originated from spent sulfite liquor (SSL) compared to a commercially available APP-based FR. The top graph depicts the material after thermal treatment and the bottom depicts the APP-based FR.

20 Figure 8 depicts a Fourier transform infrared spectroscopy (FTIR) analysis of neat modified LS FR originated from spent sulfite liquor (SSL). The bottom graph depicts the neat material before thermal treatment and the top graph depicts the material after treatment.
Figure 9 illustrates a Thermogravimetric analysis (TGA) profile of composite materials comprising different ratios of modified LS FR originated from spent sulfite liquor (SSL) and APP-based FR.

Figure 10 illustrates a Thermogravimetric analysis (TGA) profile of composite materials comprising different ratios of modified LS FR originated from spent sulfite liquor (SSL) and water soluble APP.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to a biodegradable composite material, which is based on a natural flame retardant (FR) of renewable resource, namely, lignin-based FR, thereby promoting the use of discarded biomass products. The composite material of the invention comprises a distinct combination of said renewable resource FR material, an aldehyde, an amine-containing compound and ammonium polyphosphate (APP), which give rise to enhanced intumescent properties of the resulted composite material. The composite material of the invention is a solid material at room temperature, with low water solubility, thereby presents facile handling and environmentally friendly non-leaching characteristics.

Furthermore, it has been surprisingly found that the composite material's distinct formulation and preparation conditions promote the formation of a chemically stable FR composite material, exhibiting an enhance stability at high temperatures.

Biodegradable composite material

The biodegradable composite material of the invention demonstrate a unique combination between a biopolymer (lignin-based material), ammonium polyphosphate (APP), an aldehyde and amine-containing compound which yields a chemically stable material, characterized by a high concentration of hetero-atoms (non-carbon atoms) and therefore beneficial for use as a FR.

Utilizing a naturally-based eco-friendly polymer such as lignin-based material promotes the use of renewable resources for versatile industrial applications, and allows beneficial FR properties originating from environmentally-safe materials. The composite material of the invention demonstrates synergistic FR characteristics and mechanical properties.
In some embodiments, the present invention provides a biodegradable flame retardant (FR) composite material comprising a lignin-based compound, an aldehyde, an amine-containing compound, phosphoric acid and ammonium polyphosphate (APP), wherein said composite material is in solid form at room temperature.

In some embodiments, the composite material of the present invention is the chemical reaction product of a lignin-based compound, an aldehyde, an amine containing compound, phosphoric acid and ammonium polyphosphate (APP). The chemical reaction product has distinctive chemical and physical properties, compared to the properties of the starting materials. Specifically, it has improved flame retardant properties.

In some related embodiments, the lignin-based FR, aldehyde, amine-containing compound, phosphoric acid and APP are covalently coupled. In some related embodiments, the FR composite material is a chemical adduct of lignin-based FR, aldehyde, amine-containing compound, phosphoric acid and APP. Without being bound to by theory or mechanism, it is contemplated that at least some of the components are covalently coupled in the composite material of the invention. In one embodiment, the amine-containing compound is covalently bound to the phenolic ring of the lignin-based material by a condensation reaction involving the aldehyde. In another embodiment, the APP is covalently bound to the lignin-based material through at least one of the lignin-based hydroxyl groups. Without being bound by mechanism it is contemplated that the phosphoric acid forming a salt with the amine-containing compound.

In some embodiments, the composite material as described above is consisting of a lignin-based compound, an aldehyde, an amine containing compound, phosphoric acid and ammonium polyphosphate (APP).

In some embodiments, the amine-containing compound used in the composite material as described above is selected from the group consisting of ammonia, an alkyl amine, a diamine, a triamine, a polyamine, an alkanolamine, a cyclic amine and an amino acid. In a specific embodiment, the diamine is ethylene diamine. In another embodiment, the triamine is melamine.

In other embodiments, the aldehyde used in the composite material as described above is selected from the group consisting of paraformaldehyde, formaldehyde, acetaldehyde,
furfural, hydroxymethyl furfural, butyraldehyde, 4-hydroxy-3-methoxybenzaldehyde, 4-hydroxy-3,5-dimethoxybenzaldehyde, 4-hydroxybenzaldehyde and 2-hydroxybenzaldehyde. In a currently preferred embodiment, the aldehyde is paraformaldehyde.

In some embodiments, the composite material of the invention comprises: from about 35 to about 75 wt% APP; from about 15 to about 35 wt% LS; from about 10 to about 35 wt% phosphoric acid; from about 1 to about 15 wt% ethylene diamine or melamine; and from about 1 to about 15 wt% p-formaldehyde. In a specific embodiment, the composite material as described above is consisting of a LS, paraformaldehyde, ethylene diamine or melamine and APP.

In some embodiments, the composite material of the invention comprises the reaction products formed by reacting: about 35 to about 75 wt% of APP; about 15 to about 35 wt% of LS; about 10 to about 35 wt% of phosphoric acid; about 1 to about 15 wt% of ethylene diamine or melamine; and about 1 to about 15 wt% of p-formaldehyde. In a specific embodiment, the composite material as described above is a product obtained by reacting the materials from the group consisting of a LS, paraformaldehyde, ethylene diamine or melamine and APP.

According to another aspect, the present invention further provides a flame retardant (FR) composite material prepared from combining a lignin-based compound, an aldehyde, an amine containing compound, phosphoric acid and ammonium polyphosphate (APP), wherein said composite material is in solid form at room temperature.

In some embodiments, the combination for preparing the flame retardant (FR) composite material comprises about 35 to about 75 wt% APP. In some embodiments, the combination comprises about 15 to about 35 wt% lignin-based compound. In some embodiments, the lignin-based compound is LS. In some embodiments, the combination comprises about 15 to about 35 wt% LS. In some embodiments, the combination comprises about 10 to about 35 wt% phosphoric acid. In some embodiments, the combination comprises about 1 to about 15 wt% amine containing compound. In some embodiments, the amine containing compound is ethylene diamine or melamine. In some embodiments, the combination comprises about 1 to about 15 wt% ethylene diamine or melamine. In some embodiments,
the combination comprises about 1 to about 15 wt% aldehyde. In some embodiments, the aldehyde is p-formaldehyde. In some embodiments, the combination comprises about 1 to about 15 wt% p-formaldehyde.

It is to be understood that the weight percentages above refer to the weight of the recited ingredient divided by the total weight of the combination. For example, for a FR material prepared from combining a lignin-based compound, an aldehyde, an amine containing compound, phosphoric acid and APP, the phrase the combination comprises about 1 to about 15 wt% aldehyde means that the total weight of aldehyde divided by the combined weights of the aldehyde, the amine, the phosphoric acid and the APP, is in the range of about 1% to about 15%.

The term about, as used herein refers to ±20% of a recited value. Preferably the term refers to ±10% of the value. For example, the phrase "the combination comprises about 1 to about 15 wt% p-formaldehyde" means that the weight of the p-formaldehyde is in the range of 0.8% to 18% based on the total weight of the combination used for preparing the FR material.

According to another aspect, the present invention further provides a biodegradable FR composite material consisting essentially of a lignin-based compound, an aldehyde, an amine containing compound, phosphoric acid and ammonium polyphosphate (APP), wherein said composite material is in solid form at room temperature.

Preparation of composite material

The present invention is based in part on an unexpected finding that a chemically stable intumescent system can be formulated in a facile, convenient and cost-effective process. Thus, the present invention provides methods for the preparation of the composite material of the invention.

According to the principles of the invention, the preparation of the composite FR material is carried by mixing of a lignin-based compound, an aldehyde, an amine containing compound, phosphoric acid and ammonium polyphosphate (APP) in the conditions appropriate to achieve said composite material, as described herein below.
The present invention utilizes an economically favored and abundant starting material, namely, lignin-based material, which is available as a by-product of large scale cellulose production processes. According to some embodiments, the lignin-based compound is a lignin derivative or a modified lignin molecule. According to some embodiments, the lignin-based compound is a molecule having lignin attached to said molecule's backbone chain as a side group. In further embodiments, said molecule's backbone chain comprise additional side groups or moieties. In some currently preferred embodiments, the lignin-based FR is lignosulfonate (LS). In some embodiments, the lignin-based compound is a component in a composition comprising the lignin-based compound. In some embodiments, the composition comprises technical lignins. In some embodiments, the composition is selected from Spent Sulfite Liquor (SSL), Black Liquor (BL) and a combination thereof. In some embodiments, the composition is SSL. In some embodiments, the composition is BL.

Two widespread processes for cellulose production are the Kraft process and sulfite processes. In accordance with the sulfite processes, wood chips or other lignocellulose are cooked under pressure in sulfite liquor so that lignins of the lignocellulose are solubilized and thereby separable from the insoluble cellulose, in a process generally known as pulping. The cellulose is then separated from the liquor, the liquor resulting from the separation is known as spent sulfite liquor (SSL). Such liquors include lignosulfonates and wood sugars (e.g. xylose, mannose, galactose, glucose). Typically SSL is composed of 55% total solids (about 35% lignosulfonates and 20% sugars w/w).

The Kraft process is another process for conversion of wood into wood pulp. It entails treatment of wood chips with a hot mixture of water, sodium hydroxide, and sodium sulfide that breaks the bonds that link lignin, hemicellulose, and cellulose. In the process the wood chips are cooked in pressurized vessels. The solid pulp (about 50% by weight of the dry wood chips) is then collected and washed. At this point the pulp is known as brown stock because of its color. The separated combined liquids are waste known as black liquor (BL). They contain lignin fragments, carbohydrates from the breakdown of hemicellulose, sodium carbonate, sodium sulfate and other inorganic salts. Typically, the composition of BL concentrate (i.e. after water evaporation and skimming tall oil) is composed of 65%-85% total solids.
One of the advantages of the flame retardant and process disclosed herein is that crude natural lignin sources, such as BL and SSL may be used as is, without the necessity of extracting or purifying the lignin molecules from the bulk mixture. In some embodiments, the lignin-based composition comprises about 10% to about 60% lignosulfonates, or about 20% to about 50% lignosulfonates, or about 25% to about 40% lignosulfonates, or about 10% to about 40% lignosulfonates.

According to some embodiments, the preparation of a mixture comprising lignosulfonate (LS), amine containing compound and an aldehyde, which is referred to as modified lignosulfonate (mod-LS), can be carried utilizing neat lignosulfonate, by a direct extraction route from black liquor (BL), or by a direct extraction route from sulfite spent liquor (SSL). The mod-LS prepared from SSL biomass or from BL biomass may further comprise residual organic materials originated in said biomass, for example proteins, peptides, nucleic acid fragments and lipids, or residual inorganic salts. The modified-LS is further mixed with APP or APP-based composition to achieve the composite FR material of the invention. The term "APP-based composition" refers to a composition in which the main ingredient is APP, and it may further contain stabilizers such as alcohols, in particular alcohols containing a plurality of hydroxyl groups.

Thus, in some embodiments, the method for the preparation of the biodegradable FR composite material comprises the steps of: (i) mixing, with optional heating, lignin-based compound with an amine-containing compound and an aldehyde; (ii) adding phosphoric acid; (iii) drying and optionally grinding the material obtained in step (ii); (iv) mixing with optional heating, of the material obtained in step (iii) with APP; and (v) optionally grinding the material obtained in step (iv) to obtain a solid, water-insoluble FR composite material.

In some embodiments, the heating in step (i) is carried at a temperature of between about 70 to about 150 °C. In other embodiments, the drying in step (iii) is carried at a temperature of between about 80 to about 150 °C. In some additional embodiments, the heating in step (iv) is carried at a temperature of between about 200 to about 300 °C. In yet some other embodiments, the APP and the material obtained in step (ii) were mixed together in step (iv) in a 1:1 weight ratio.
In some related embodiments, the modified LS is prepared directly from SSL. Thus, the method for the preparation of modified LS comprises the steps of: (i) mixing, with optional heating, sulfite spent liquor (SSL) with ethylene diamine or melamine, sulfuric acid and paraformaldehyde; (ii) separating the solid phase obtained in step (i); (iii) adding, with optional heating, phosphoric acid to the solid material obtained in step (ii); and (iv) optionally drying and/or grinding the material obtained in step (iii). In some embodiments, the heating in step (i) is carried at a temperature of between about 70 to about 150 °C.

According to the principles of the present invention, the resultant modified LS is further mixed with APP or an APP-based composition to form the solid composite FR material of the invention. Thus, in some embodiments, the method for the preparation of a biodegradable FR composite material comprises the steps of: (i) mixing, with optional heating, sulfite spent liquor (SSL) with ethylene diamine or melamine, sulfuric acid and paraformaldehyde; (ii) separating the solid phase obtained in step (i); (iii) adding, with optional heating, phosphoric acid to the solid material obtained in step (ii); (iv) optionally drying and/or grinding the material obtained in step (iii); (v) mixing, with optional heating, of the material obtained in step (iii) with APP; and (vi) optionally grinding the material obtained in step (iv) to obtain a solid, water-insoluble FR composite material.

In some embodiments, the heating in step (i) is carried at a temperature of between about 70 to about 150 °C. In another embodiment, the heating in step (v) is carried at a temperature of between about 200 to about 300 °C. In yet another embodiment, the APP and the material obtained in step (iv) were mixed together in step (v) in a 1:1 weight ratio. According to some embodiments, the lignin-based compound used for the preparation of the FR composite material of the invention is lignosulfonate (LS). In some other embodiments, the amine-containing compound used for the preparation of the FR composite material of the invention is selected from the group consisting of ammonia, an alkyl amine, a diamine, a triamine, a polyamine, an alkanolamine, a cyclic amine and an amino acid. In a specific embodiment, the diamine is ethylene diamine. In another embodiment, the triamine is melamine. In yet other embodiments, the aldehyde used for the preparation of the FR composite material of the invention is selected from the group consisting of paraformaldehyde, formaldehyde, acetaldehyde, furfural, hydroxymethyl furfural, butyraldehyde, 4-hydroxy-3-methoxybenzaldehyde, 4-hydroxy-3,5-
dimethoxybenzaldehyde, 4-hydroxybenzaldehyde and 2-hydroxybenzaldehyde. In a currently preferred embodiment, the aldehyde is paraformaldehyde.

In another embodiment, the preparation of the composite material of the invention can be carried out using APP which is water soluble. Low molecular weight APP having a molecular weight of less than 10,000 g/mol, is often used in agriculture as a fertilizer and is highly water soluble and hygroscopic. According to some embodiments, the composite material of the invention comprises low molecular APP and modified LS. Upon thermal treatment of the resultant composite material, the later may present lower solubility of APP incorporated within the composite material and lower hygroscopic nature.

Plastic material comprising the composite material

The composite material of the invention can be incorporated into commonly used plastic materials as an additive in order to improve their FR properties without jeopardizing their mechanical properties. The beneficial thermal stability obtained by the unique composition of the composite material of the invention, allows the use of both bioplastics and engineering plastics for the generation of improved plastic materials in terms of FR properties. In one embodiment, the present invention provides a plastic material comprising the FR composite material as described above. In some embodiments, the plastic material is of a natural origin. In some related embodiments, the plastic material is selected from the group consisting of polyhydroxyalkanoate (PHA), polyethylene glycol (PEG), polyester, polyamide, polylactic acid (PLA), polybutylene succinate (PBS), poly p-phenylene (PPP), polytrimethylene terephthalate (PTT), polyethylene (PE), and combinations thereof, with each possibility representing a separate embodiment of the present invention. In a currently preferred embodiment, the plastic is polyhydroxyalkanoate (PHA). In a specific embodiment, the plastic is polyhydroxybutyrate (PHB).

It is understood that APP-based materials are not considered to be suitable as additives to engineering plastics as the processing temperatures of the latter very often exceed the decomposition temperature of APP-based materials. The stabilizing effect achieved by the composition of the composite material of the inventions allows the incorporation of APP-based material into such plastics. Thus, in some embodiments, the plastic material is of a synthetic origin. In some related embodiments, the plastic material is selected from the
group consisting of a thermoplastic material, a thermosetting material and an engineering plastic. In some embodiments, the thermoplastic material is polypropylene. In some other embodiments, the thermosetting material is selected from the group consisting of polyurethane, epoxy resin and unsaturated polyester. In some other embodiments, the engineering plastic is selected from the group consisting polyamide (PA) and polybutylene terephthalate (PBT).

Definitions

As used herein and in the claims the term "polymer" refers to a molecule composed primarily of a plurality of repeating units. It is to be understood that the names of the abovementioned polymers refer to the repeating units which make up the majority of the structure of the polymers, and are not meant to exclude the presence of additional functional groups in the polymer.

As used herein and in the claims the term "flame retardant" (FR) refers to a material which reduces the impact of fires. A flame retardant material is often added to or used in a coating treatment of flammable materials such as fabrics and plastics to prevent, delay, or limit the spread of fire and minimize fire damage. As used herein and in the claims the term "lignin-based FR" refers to a FR that is achieved by anchoring molecules bearing heteroatoms to lignin polymer groups. The anchoring can be carried by means of physical or chemical interactions or bonding.

As used herein, the term "biodegradable" refers to materials which are capable of degrading or decomposing upon interaction with the environment over a period of time. Biodegradable materials can undergo degradation from the action of naturally occurring microorganisms such as bacteria, fungi, and algae. Additional factors affecting the rate of the degradation include pH, temperature, pressure, water presence, etc. The degradation of biodegradable materials results in natural byproducts such as gases (CO₂, N₂), water, biomass, and inorganic salts. The approximated period of time for compounds to biodegrade can vary between about 1 to about 100 years. According to some embodiments, the composite material of the present invention undergoes biodegradation in about 1 to about 50 years. In further embodiments, said composite material undergoes biodegradation in about 1
to about 20 years, or from about 20 to about 50 years, or from about 50 to about 70 years, or from about 70 to about 100 years. In still further embodiments, said composite material undergoes biodegradation in about 1 to about 10 years.

The term "chemical reaction product", as used herein refers to a compound or a plurality of compounds, which is formed by a chemical reaction and includes atoms and/or chemical fragments derived from the starting components, which lead to its formation. The chemical reactions leading to the chemical reaction product may be, for example, a condensation(s), leading to a condensate(s), an acid-base netralization and/or addition (s), leading to an adduct(s).

As used herein the terms "modified-LS" and "mod-LS" are used interchangeably and refer to chemically modified lignosulfonate (LS). The chemical modification can be carried by anchoring molecules bearing heteroatoms to lignosulfonate polymer groups. The anchoring can be carried by means of physical or chemical interactions or bonding.

As used herein and in the claims the term "composite material" refers to a composition combining two or more materials from an organic and/or inorganic origin, which might differ in their chemical and/or physical properties, in a certain way to produce a new material with advantageous characteristics. The composite material can have a different set of properties from the individual components used for its formation.

As used herein and in the claims the terms "thermal treatment" and "annealing" are used interchangeably and refer to the optional heating of the composite material as a part of the preparation process. The heating may take place upon mixing modified LS and APP or after the two components are mixed together.

As used herein and in the claims the term "cyclic amine" refers to heterocycles comprising one or more secondary amine. For example, cyclic amines include but not limited to aziridine, pyrrolidine, piperidine and piperazine.

As used herein the term "hygroscopic" refers to the tendency of a material to absorb water from the atmosphere. For example, low weight APP is hygroscopic as it absorbs water molecules in an amount that can increase its initial mass in about 5%.
As used herein and in the claims the term "bioplastic" refers to a plastic material derived from a renewable biomass source.

As used herein and in the claims the term "plasticizer" refers to a material that improves the plasticity or fluidity of another material. The addition of such materials into plastic or bioplastic can increase the flexibility of the plastic and its durability. Examples of possible plasticizers are: citrate esters (e.g. CITROFOL™), bioplasticizers (e.g. LAPOL™), monoglycerides of hydrogenated castor oil (e.g. DANISCO™). As used herein and in the claims the term "nucleant" refers to a material promoting the crystallization of semi-crystalline polymers. Examples of possible nucleants are: saccharin, talc, boron nitride and ammonium chloride. As used herein and in the claims the terms "chain extender" and "cross-linking agents" refers to low molecular weight hydroxyl and/or amine terminated compounds that play an important role in polymer morphology. These materials can react through their hydroxyl and/or amine terminal groups with an existing polymer to enhance mechanical properties, increase viscosity and compatibility of plastic alloys. Examples of possible cross-linking agents are: isocyanates and aromatic carbodiimides (e.g. BIOADIMIDE™). As used herein and in the claims the term "lubricant" refers to a compound that can be inserted into a plastic and reduces the material's friction and wear, especially during processing, and increase the plastic's life. As used herein and in the claims the term "antioxidant" refers to a compound which helps to prevent the polymer reaction with oxygen. Oxidation can cause loss of impact strength, elongation, surface cracks and discoloration.

The term "thermoplastic materials" is understood in the art and used herein to denote compositions and materials that are generally capable of repeatedly softening when appropriately heated and hardening when subsequently cooled. Thermoplastic materials are generally in a solid or form stable state below the melting point or softening range, while generally being in a plastic or flowable state above the melting point or softening range. The term "thermoplastic material" as used herein further is understood to mean any thermoplastic polymer, including thermoplastic elastomers, and blends thereof.

As used herein, the term "thermosetting material" refers to a high polymer that solidifies or "sets" irreversibly when heated. This property is typically associated with a cross-linking
reaction of the molecular constituents induced by heat or irradiation. Phenolics, alkyds, amino resins, polyesters, epoxides, and silicones are usually considered to be thermosets.

The term "engineering plastics" as used herein refers to a group of plastic materials that have better mechanical and/or thermal properties than the more widely used commodity plastics. "Engineering plastics" usually refers to thermoplastic materials rather than thermosetting ones. Examples of engineering plastics include, but are not limited to, acrylonitrile-butadiene styrene (ABS), polycarbonates and polyamides (nylons).

The following non-limiting examples are presented in order to more fully illustrate certain embodiments of the invention. They should in no way, however, be construed as limiting the broad scope of the invention. One skilled in the art can readily devise many variations and modifications of the principles disclosed herein without departing from the scope of the invention.

EXAMPLES

Example 1 - composite material preparation

1) The preparation of modified hgnosulfonate (mod-LS) can be performed utilizing neat Hgnosulfonate or by a direct extraction route from sulfite spent liquor (SSL) a waste stream from the extraction of cellulose from wood pulp by the sulfite process. The different preparation methods are presented herein below:

A) 3500 g lignin sulfonate was solubilized in 3000 g water, and mixed with 450 g paraformaldehyde and 450 g ethylene diamine at elevated temperature ~ 80-1 10°C for three hours. 1770 g phosphoric acid was added to the mixture, which was kept at ~100°C for additional 2.5 hours. Then, the reaction mixture was dried in two stages: 1) under atmospheric pressure, at 110°C for 72 hours; and 2) under 20 mbar, at 100 °C for additional 16 hours. The dried material was milled using blade mill grinder to produce 5000-5500g of solid product.

B) 2.5 L of SSL was mixed with 828 g melamine, 195 g paraformaldehyde and 3360 g sulfuric acid 10%w/w. The mixture was heated to 90-110°C for four hours. During the reaction about 600 g of water was evaporated. The solid phase formed in the reaction was
collected using a filter press, and separated from the aqueous reaction phase. The reaction
gave rise to 2850 g of wet solid, which was mixed with 3100 g phosphoric acid 85% w/w.
The mixture was heated to 140°C for two hours. The resulted material was dried at elevated
temperatures: 48 hr at 130°C, 16 hr at 100°C under 20 mbar and finally 5 hr at 150°C. The
reaction yielded about 4500 g of dry product which was further milled using a blade
grinder.

2) Formulation conditions and preparation of FR composite material:

APP-based composition Exolit 766 (Clariant) and mod-LS powder prepared according to
either process A or B, were mixed in a weight ratio of 1:1.

The mixture was heated to 250°C for 3 hours (annealing) and the obtained solid mass was
ground to powder. A weight loss of -10-20% was observed during the annealing process.

The FR composite material as described above was shown to be insoluble in water.

Example 2 - High-temperature stability of neat composite material FR material
Thermo gravimetric analysis (TGA) was used in order to determine the onset decomposition

1) APP-based composition Exolit 766;

2) mod-LS (prepared as described in Example 1 process A);

3) mod-LS (prepared as described in Example 1 process A) after heating to 230°C for 1
hour; and

4) composite FR material prepared as described in Example 1 paragraph 2 (utilizing process
A).

The TGA analyses were obtained at a scan rate of 10°C per minute and the samples were
heated from 36°C to 400 °C under nitrogen.

The results demonstrate the significance of the annealing process to the thermal stability of
the material. A comparison between samples 2 and 3 shows a significant increase of the
thermal stability of mod-LS after the annealing process. Additionally, a stabilizing effect
can be observed by comparing samples 1 and 4. APP-based composition Exolit 766
degrades at a faster rate when heated by itself, losing about 10% weight at ~325°C
compared to the composite material FR comprising it, which appears to be more resistant and loses about 10% weight at an elevated temperature of about 345°C as demonstrated in Figure 1.

**Example 3 - incorporation of the composite material FR material into PHB**

The preparation process was carried out in two steps: Dry blending and Compounding. In the compounding step, the FR composite material as prepared in Example 1 (path A or B) was mixed with PHB and polybutylene succinate (PBS) to form a bioplastic material. The resulting material is then discharged and cut to form pellets which can be further molten and injected into the desired mold.

1) Dry blending - preparation of PHB formulation:

PHB powder and several commonly used additives such as plasticizer, nucleant, lubricant, antioxidant, chain extender, and a crosslink agent, were dry-blended in a turbomixer to obtain a homogeneous mixture of the PHB formulation. The turbomixer was also connected to a vacuum pump to remove any possible moisture during the mixing stage.

2) Compounding:

The composite material of as described above was mixed with the PHB and PBS. At the end of the extruder a vacuum pump was implemented in order to extract the volatiles produced during the compounding process.

**Example 4 - High-temperature stability of PHB comprising the composite FR material**

TGA was used in order to determine the onset decomposition temperature of different bioplastic materials comprising the composite FR material of the invention as follows:

1) neat PHB;

2) 1:1 mixture (by weight) of PHB and APP-based composition Exolit 766;

3) mixture of PHB, APP-based composition Exolit 766 and mod-LS in a weight ratio of 2:1:1, respectively; and

4) 1:1 mixture (by weight) of PHB + composite FR material prepared as described in Example 1 paragraph 2 (utilizing process A).

The TGA analysis obtained at a scan rate of 5°C per minute and the samples were heated from 40°C to 350°C under nitrogen.
The TGA results show that the addition of APP to PHB increases the overall thermal stability of the material compared to neat PHB. Moreover, it can be seen from Figure 2, that the PHB comprising the composite material of the invention maintains some of its structural integrity at elevated temperatures (>300 °C) whereas PHB comprising a similar composition of mod-LS and APP but with no annealing step, is less thermally stable and decomposes to a greater extent.

Example 5 - High-temperature stability of neat FR material, wherein the mod-LS is originated from spent sulfite liquor (SSL) TGA was used in order to determine the onset decomposition temperature of different FR materials. In the measured samples comprising mod-LS, the LS component was produced directly from sulfite spent liquor (SSL) biomass as described in Example 1 process B. The samples measured were as follows:

1) mod-LS;
2) mod-LS after heating to 230 °C for 1 hour;
3) APP-based composition Exolit 766 (Clariant);
4) composite FR material, prepared as a 1:1 mixture of mod-LS as described in Example 1 paragraph 2 (utilizing process B).

The TGA analysis obtained at a scan rate of 10°C per minute and was samples were heated from room temperature to 400 °C.

The TGA results demonstrate the improvement in thermal stability of neat mod-LS (obtained from SSL) achieved by a short heating of mod-LS. Additionally, the results show that the conjugation of mod-LS and APP is more stable than the neat mod-LS, but the composite material is not as stable as the neat APP system. An important and surprising finding can was detected at about 360°C, where a sharp change in the thermogram was observed for the composite material due to an enhanced intumescent effect (Figure 3). This effect was further investigated in a PHB formulation comprising such composite material, as presented in example 6.

Example 6 - High-temperature stability of PHB comprising composite material FR material TGA was used in order to determine the onset decomposition temperature of different bioplastic materials comprising the composite material FR material of the invention. In the
measured samples comprising mod-LS, the LS component was produced directly from sulfite spent liquor (SSL) biomass as described in Example 1 process B. The samples measured were as follows:

1) neat PHB;

2) 1:1 mixture (by weight) of PHB and APP-based composition Exolit 766;

3) PHB and mod-LS in a weight ratio of 1:1; and

4) 1:1 mixture (by weight) of PHB + composite FR material prepared as described in Example 1 paragraph 2 (utilizing process B).

The TGA analysis obtained at a scan rate of 5°C per minute and samples were heated from 36°C to 350°C.

The TGA results demonstrate an improvement in thermal stability of a PHB-based plastic material upon the insertion of APP intumescent system, compared with neat PHB (Figure 4). Furthermore, the stability of 1:1 PHB with mod-LS prepared from SSL has a higher onset decomposition temperature than both neat PHB and 1:1 PHB : APP systems (weight ratio). An additional effect can be detected in the beneficial combination of PHB and the composite FR material of the invention, demonstrating both high onset decomposition temperature and reduced decomposition level, which without being bound by any theory or mechanism is contemplated to be a result of the enhanced intumescent effect achieved by the unique composite material composition. A photograph of the resulted intumescent effect occurred in sample 4 comprising the composite FR material is presented in Figure 5.

Example 7 - Chemical and thermal effects of the annealing process
A modified LS was prepared as described in Example 1 paragraph 2 (utilizing process B) and analyzed using inductive couple plasma (ICP) and elemental analysis (Table 1).

Table 1 - composition of mod-LS:

<table>
<thead>
<tr>
<th>C</th>
<th>N</th>
<th>H</th>
<th>P</th>
<th>S</th>
<th>Ca</th>
<th>Na</th>
<th>Mg</th>
<th>Fe</th>
<th>O (calculated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13±3</td>
<td>10±1</td>
<td>4.0±0.5</td>
<td>17±2</td>
<td>2.3±1</td>
<td>2.3±0.5</td>
<td>0.02±0.01</td>
<td>0.2±0.1</td>
<td>1±0.1</td>
<td>45±5</td>
</tr>
</tbody>
</table>

The material was heated to 300°C for 1 hour and was analyzed chemically and thermally before and after the annealing process.
The TGA analysis obtained at a scan rate of 10°C per minute and the samples were heated from 35°C to 400 °C.

According to the TGA analysis, the annealed material demonstrated a significant thermal stability, where the decomposition of the material starts only around 300°C as demonstrated in Figure 6.

It was further shown that annealed mod-LS is thermally more stable than commercially available APP-based composition (Exolit 766) (Figure 7).

According to Fourier transform infrared spectroscopy (FTIR), a chemical change was observed upon the annealing process of mod-LS, as can be shown from the appearance of a strong peak at 1230 cm⁻¹, attributed to P=0 vibration upon annealing, and a change of peaks -800-1000 cm⁻¹, attributed to P-OH vibration, between the material before and after annealing (Figure 8).

Example 8 - Different possible formulations of FR composite material and their related thermal stability properties

The mod-LS as prepared and characterized herein above in Example 7, was further mixed with APP-based composition Exolit 766 in the ratios according to Table 2:

<table>
<thead>
<tr>
<th>Sample</th>
<th>mod-LS (%)</th>
<th>APP-based flame retardant</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Exolit 766 (Clariant)</td>
</tr>
<tr>
<td>1</td>
<td>87</td>
<td>13</td>
</tr>
<tr>
<td>2</td>
<td>72</td>
<td>28</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>4</td>
<td>30</td>
<td>70</td>
</tr>
</tbody>
</table>

The composite materials 1-4 were heated in the oven at 250 °C for 3 hours. During this time a slight release of ammonia was observed by wet pH paper (depicted pH~9). The resultant solids were ground to powders.
The TGA analysis obtained at a scan rate of 10°C per minute and the samples were heated from 36°C to 400 °C under nitrogen.

The thermal stability of the composite materials 1-4 was detected by TGA experiments. According to the results it appears that samples 2-4 have a similar decomposition profile and sample 1 has a higher thermal stability than the other samples (Figure 9). However, it was found that samples 2 and 3 were the only samples demonstrating the beneficial strong intumescent effect.

Example 9 - preparation of composite material utilizing agricultural grade ammonium polyphosphate

Agricultural grade ammonium polyphosphate is a water soluble, low molecular weight ammonium polyphosphate that is commonly used as a fertilizer.

A water solution of ammonium polyphosphate that contains 34% P2O5 was evaporated under vacuum yielding a white solid of ammonium polyphosphate. The dry form obtained was water soluble and hydroscopic, absorbed about 5% of water from the atmosphere.

Composite materials comprising the dry APP material and the mod-LS as described in Example 7 according to the ratios of Table 3(samples 1-3) and a control sample comprising only APP-based material (sample 4):

<table>
<thead>
<tr>
<th>Sample</th>
<th>mod-LS (%)</th>
<th>APP (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30</td>
<td>70</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>3</td>
<td>61</td>
<td>39</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>

The composite materials were annealed for 3 hours at 250 °C.

The TGA analysis obtained at a scan rate of 10°C per minute and the samples were heated from 35°C to 400 °C under nitrogen.

According to the thermal decomposition profile obtained by TGA, the obtained composite materials demonstrated an enhanced thermal stability, especially compared with the neat
APP-based material (sample 4). Additionally, a strong intumescent effect was detected upon heating the samples to 400 °C. The resulted composites were also less hydroscopic than the neat APP.

Example 10 - preparation of thermoplastic material comprising the composite material of the invention

1) Polypropylene (PP):

Modified-LS prepared according to Example 1A was dried in an oven in 100°C for 24h with moisture content < 1%. Initial moisture was about 5% and final moisture about 0.5%. APP and mod-LS were mixed to create the composite of the invention. The composite was further mixed with Triazine in order to increase the heteroatom content. The mixture was then further homogenized in a PLASMEC turbo-mixer for 5min at 1000rpm under vacuum before compounding.

Finally, the compounding process was carried out in a EURLAB PRISM twin screw extruder with 16mm of screw diameter. The polypropylene and coupling agent were premixed and fed together into the extruder together with the composite material and additional amine source triazine. A vacuum pump removed volatiles and residual moisture from the process. The compounding process was carried out using a reverse profile temperature from 210 to 190°C, at 200 rpm and 1.5kg/h. The molten strand was cooled in a water bath and cut into pellets with a strand pelletizer.

The obtained pellets were dried after drying for 4h at 80°C and bagged under vacuum to prevent moisture absorption.

The obtained formulations were injected in an ENGEL Victory 50 hydraulic injection molding machine with a 25mm screw diameter and camping force of 50 Ton. The samples were injected using a profile temperature of 180 to 210°C and mold temperature of 30°C at 800 - 900 bars of injection pressure.

2) Polyamide (PA6):

The composite material of the invention prepared according to the procedure in Example 1 path A) was added together with antioxidant and lubricant in a PLASMEC turbo-mixer for 5 min at 1000rpm under vacuum before compounding.

The compounding process was carried out in a COPERION ZSK26 twin screw extruder with 26mm of screw diameter, and equipped with two side feeders. Glass fiber was fed in
the second side feeder to avoid the breakage of the glass fibres. A vacuum pump removed volatiles and residual moisture from the process. The compounding process was carried out using a profile temperature from 220 to 270°C, at 200 rpm and 10kg/h. The molten strand was cooled in a water bath and cut into pellets with a strand pelletizer. The obtained pellets were dried after compounding for 4h at 80°C and bagged under vacuum to prevent moisture absorption.

The obtained formulations were injected in a KraussMaffei Ex 160-750 electric injection molding machine with a 50mm screw diameter and camping force of 160 Ton. The samples were injected using a profile temperature of 220 to 260°C and mold temperature of 80°C at 1300 - 800 bars of injection pressure. The formulations with LSmod showed lower injection molding pressures.

3) Polybutylene terephthalate (PBT):
The composite of the invention was prepared as described in Example 1 (path A) and was further mixed with antioxidant and chain extender. PBT was compounded with the composite mixture and glass fibers in the Coperion ZSK26 twin screw extruder. The compounding process was carried out using a profile temperature from 220 to 275°C, at 200 rpm and 10kg/h.

The obtained formulations were injected in a KraussMaffei Ex 160-750 electric injection molding machine with a 50mm screw diameter and camping force of 160 Ton. The samples were injected using a profile temperature of 210 to 250°C and mold temperature of 80°C at 1800 - 2000 bars of injection pressure.

The foregoing examples of specific embodiments will so fully reveal the general nature of the invention that others can, by applying current knowledge, readily modify and/or adapt for various applications such specific embodiments without undue experimentation and without departing from the generic concept, and, therefore, such adaptations and modifications should and are intended to be comprehended within the meaning and range of equivalents of the disclosed embodiments. It is to be understood that the phraseology or terminology employed herein is for the purpose of description and not of limitation. The means, materials, and steps for carrying out various disclosed functions may take a variety of alternative forms without departing from the invention.
The EU Commission (FP7 project BRIGIT, Contract nr 311935) is acknowledged for their financial support.
CLAIMS

1. A biodegradable flame retardant (FR) composite material prepared from combining a lignin-based compound, an aldehyde, an amine-containing compound, phosphoric acid and ammonium polyphosphate (APP), wherein said composite material is in solid form at room temperature.

2. The FR composite material of claim 1, wherein said composite is a chemical adduct of lignin-based compound, an aldehyde, an amine-containing compound, phosphoric acid and ammonium polyphosphate (APP).

3. The FR composite material according to any one of claims 1 and 2, wherein the lignin-based compound is lignosulfonate (LS).

4. The FR composite material according to any one of claims 1 to 3, wherein the amine-containing compound is selected from the group consisting of ammonia, an alkyl amine, a diamine, a triamine, a polyamine, an alkanolamine, a cyclic amine and an amino acid.

5. The FR composite material according to claim 4, wherein the diamine is ethylene diamine.

6. The FR composite material according to claim 4, wherein the triamine is melamine.

7. The FR composite material according to any one of claims 1 to 6, wherein the aldehyde is selected from the group consisting of paraformaldehyde, formaldehyde, acetaldehyde, furfural, hydroxymethyl furfural, butyaldehyde, 4-hydroxy-3-methoxybenzaldehyde, 4-hydroxy-3,5-dimethoxybenzaldehyde, 4-hydroxybenzaldehyde and 2-hydroxybenzaldehyde.

8. The FR composite material according to claim 7, wherein the aldehyde is paraformaldehyde.

9. The FR composite material according to any one of claims 1 to 8, consisting of a lignin-based compound, an aldehyde, an amine-containing compound, phosphoric acid and ammonium polyphosphate (APP).

10. The FR composite material according to claim 9, consisting of a LS, paraformaldehyde, ethylene diamine or melamine, phosphoric acid and APP.

11. The composite material according to any one of claims 1 to 10, which comprises:
from about 35 to about 75 wt% APP;
from about 15 to about 35 wt% LS;
from about 10 to about 35 wt% phosphoric acid;
from about 1 to about 15 wt% ethylene diamine or melamine; and
from about 1 to about 15 wt% p-formaldehyde.

12. The FR composite material according to any one of claims 1 to 11, characterized in that it undergoes biodegradation in about 1 to about 100 years.

13. A biodegradable FR composite material consisting essentially of a lignin-based compound, an aldehyde, an amine-containing compound, phosphoric acid and ammonium polyphosphate (APP), wherein said composite material is in solid form at room temperature.

14. A plastic material comprising the FR composite material according to any of claims 1 to 11.

15. The plastic material according to claim 14, wherein the plastic component is of a natural origin.

16. The plastic material according to claim 15, wherein the plastic is selected from the group consisting of polyhydroxyalkanoate (PHA), polyethylene glycol (PEG), polyester, polyamide, polylactic acid (PLA), polybutylene succinate (PBS), poly p-phenylene (PPP), polytrimethylene terephthalate (PTT), polyethylene (PE), and combinations thereof.

17. The plastic material according to claim 16, wherein the plastic is polyhydroxyalkanoate (PHA).

18. The plastic material according to claim 17, wherein the plastic is polyhydroxybutyrate (PHB).

19. The plastic material according to claim 14, wherein the plastic is of a synthetic origin.

20. The plastic material according to claim 19, which is selected from the group consisting of a thermoplastic material, a thermosetting material and an engineering plastic.

21. The plastic material according to claim 20, wherein the thermoplastic material is polypropylene.

22. The plastic material according to claim 20, wherein the thermosetting material is selected from the group consisting of polyurethane, epoxy resin and unsaturated polyester.
23. The plastic material according to claim 20, wherein the engineering plastic is selected from the group consisting polyamide (PA) and polybutylene terephthalate (PBT).

24. A method for the preparation of a biodegradable FR composite material according to any one of claims 1 to 12, comprising the steps of:

(i) mixing, with optional heating, lignin-based material with amine-containing compound and an aldehyde;
(ii) adding phosphoric acid;
(iii) drying and optionally grinding the material obtained in step (ii);
(iv) mixing with optional heating, the material obtained in step (iii) with APP; and
(v) optionally grinding the material obtained in step (iv) to obtain a solid, water-insoluble FR composite material.

25. The method according to claim 24, wherein the heating in step (i) is carried at a temperature of between about 70 to about 150 °C.

26. The method according to claim 24 or 25, wherein the drying in step (iii) is carried at a temperature of between about 80 to about 150 °C.

27. The method according to any one of claims 24 to 26, wherein heating in step (iv) is carried at a temperature of between about 200 to about 300 °C.

28. The method according to any one of claims 24 to 27, wherein the APP and the material obtained in step (ii) were mixed together in step (iv) in a 1:1 weight ratio.

29. A method for the preparation of a biodegradable FR composite material according to any one of claims 1 to 12, comprising the steps of:

(i) mixing, with optional heating, spent sulfite liquor (SSL) with an amine containing compound, sulfuric acid and an aldehyde;
(ii) separating the solid phase obtained in step (i);
(iii) adding, with optional heating, phosphoric acid to the material obtained in step (ii);
(iv) optionally drying and/or grinding the material obtained in step (iii)
(v) mixing, with optional heating, of the material obtained in step (iii) with APP; and
(vi) optionally grinding the material obtained in step (iv) to obtain a solid, water-insoluble FR composite material.

30. The method according to claim 29, wherein the heating in step (i) is carried at a temperature of between about 70 to about 150 °C.
31. The method according to claim 29 or 30, wherein heating in step (v) is carried at a temperature of between about 200 to about 300 °C.

32. The method according to any one of claims 29 to 31, wherein the APP and the material obtained in step (iv) were mixed together in step (v) in a 1:1 weight ratio.

33. The method according to any one of claims 24 to 32, wherein the lignin-based material is lignosulfonate (LS).

34. The method according to any one of claims 24 to 33, wherein the amine-containing compound is selected from the group consisting of ammonia, an alkyl amine, a diamine, a triamine, a polyamine, an alkanolamine, a cyclic amine and an amino acid.

35. The method according to claims 34, wherein the diamine is ethylene diamine.

36. The method according to claim 34, wherein the triamine is melamine.

37. The method according to any one of claims 24 to 36, wherein the aldehyde is selected from the group consisting of paraformaldehyde, formaldehyde, acetaldehyde, furfural, hydroxymethyl furfural, butyraldehyde, 4-hydroxy-3-methoxybenzaldehyde, 4-hydroxy-3,5-dimethoxybenzaldehyde, 4-hydroxybenzaldehyde and 2-hydroxybenzaldehyde.

38. The method according to claim 37, wherein the aldehyde is paraformaldehyde.
A. CLASSIFICATION OF SUBJECT MATTER

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

IPC (2017.01) C09K 21/14

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols):

IPC (2017.01) C09K 21/14

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):

Databases consulted: PATENTSCOPE, Google Patents, Google Scholar

Search terms used: "flame retardant", "flame resistant", "fire resistant", "fireproof", intumescent*, "ammonium polyphosphate", lignin*, *aldehyde, *amine, urea, guanidine, phosphoric.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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Further documents are listed in the continuation of Box C. X See patent family annex.

* Special categories of cited documents:
  "A" document defining the general state of the art which is not considered to be of particular relevance
  "E" earlier application or patent but published on or after the international filing date
  "L" document which may throw doubts on priority claim(s) or which is considered relevant to patentability
  "O" document referring to an oral disclosure, use, exhibition or other means
  "P" document published prior to the international filing date but later than the priority date claimed
  "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
  "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
  "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
  "z" document member of the same patent family

Date of the actual completion of the international search: 02 Nov 2017
Date of mailing of the international search report: 05 Nov 2017

Name and mailing address of the ISA:
Israel Patent Office
Technology Park, Bldg.5, Malcha, Jerusalem, 9695101, Israel
Facsimile No. 972-2-5651616

Authorized officer
GARBER Nathan
Telephone No. 972-2-5651675

Form PCT/ISA/210 (second sheet) (January 2015)
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