A process for impregnating wood or a wooden article comprises a process for forming a composite comprising wood or a wooden article and a polymeric material comprising the steps of: impregnating the wood or wooden article with a polymerisable composition comprising: (i) one or more wood compatible polymerisable monomers, or oligomers selected from the group consisting of furfuryl alcohol (FA), bishydroxymethyl furan (BHMF), trihydroxymethyl furan (THMF), oligomers of FA, BHMF and THMF condensation products of these compounds and mixtures thereof; (ii) a catalyst; (iii) a solvent selected from the group consisting of water, C4/C6 alcohols and mixtures thereof, wherein the one or more wood compatible polymers or monomers or oligomers has a boiling point not less than 50°C higher than the boiling point of the solvent and atmospheric pressure; and (iv) optionally one or more stabilisers or other ingredients; to produce impregnated wood or an impregnated wooden article; subjecting the impregnated wood or wooden article to a water removal process comprising maintaining the wood or wooden article in an atmosphere having a pressure of about 0.1 to about 0.5 bar, a temperature of about 50°C to about 90°C, for a duration sufficient to cause removal of water from the wood or wooden article; and maintaining the wood or wooden article at a higher temperature to cause polymerisation of the composition to form the polymeric material to produce polymer treated wood or wooden article.
— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))
PROCESS FOR POLYMER IMPREGNATING WOOD

This invention relates to a process for forming a composite composed of wood or wooden articles and a polymeric material particularly but not exclusively for formation of composites or composite articles comprising wooden or wooden articles impregnated or filled with a polymerisable composition particularly but not exclusively furfuryl alcohol, derivatives of furfuryl alcohol or oligomers of these compounds and subsequently polymerised.

Various processes have been used for polymer treatment of wood.


WO-A-2004/0 11216 discloses a process wherein wood is impregnated with an aqueous solution of furfuryl alcohol, an initiator such as an organic acid or anhydride, and a stabiliser. Impregnated wood is cured at a temperature from 25 to 140°C preferably 70 to 100°C to polymerise the furfuryl alcohol.

WO-A-2007/147804 discloses impregnation of wood with a di, tri and/or poly substituted furan compounds including bis hydroxymethyl furan, tris hydroxymethyl furan and hydroxymethyl difurymethane using a catalyst at a temperature of between 70 and 200°C.

Various methods have been used for impregnating wood with an aqueous monomer or oligomer composition including use of:

a) pressure alone, for example 1-10 atmospheres;

b) vacuum followed by pressure; or

c) atmospheric or low pressure followed by application of higher pressure and a final vacuum step.

Oscillating pressure methods have been used for woods e.g. spruce which are difficult to penetrate.

The concentration of furfuryl alcohol in the aqueous solution may be from about 0.5% to approaching saturation, usually about 10-50%. A co-solvent, for example ethanol or methanol may be used, for example, in an amount of 30-75%.
Drying of wood after polymerisation causes strain on a modified wood composite, leading to cracking and deformation. Such a strain during drying is generally undesirable for all woods. Drying of shaped wooden articles having a large thickness or other dimension is also prone to cause warping or cracking during drying as planks.

PCT/GB2010/000729 discloses a process for controlling treatment of wood or wooden articles, the disclosure of which is incorporated herein by reference for all purposes.

It is the object of the present invention to provide a process for polymer impregnation of wood or wooden articles which avoids cracking and deformation during drying, and which reduces the drying time in relation to a conventional wood kiln.

According to a first aspect of the present invention a process for impregnating wood or a wooden article comprises a process for forming a composite comprising wood or a wooden article and a polymeric material comprising the steps of:

impregnating the wood or wooden article with a polymerisable composition comprising:

i. one or more wood compatible polymerisable monomers, or oligomers selected from the group consisting of furfuryl alcohol (FA), bishydroxymethyl furan (BHMF), trihydroxymethyl furan (THMF), oligomers of FA, BHMF and THMF condensation products of these compounds and mixtures thereof;

ii. a catalyst;

iii. a solvent selected from the group consisting of: water, CrC₄ alcohols and mixtures thereof, wherein the one or more wood compatible polymerises or monomers or oligomers has a boiling point not less than 50°C higher than the boiling point of the solvent and atmospheric pressure; and

iv. optionally one or more stabilisers or other ingredients;

subjecting the impregnated wood or wooden article to a water removal process comprising maintaining the wood or wooden article in an atmosphere having a pressure of about 0.1 to about 0.5 bar, a temperature of about 50 to about 90°C, for a duration sufficient to cause removal of water from the wood or wooden article; and
maintaining the wood or wooden article at a higher temperature to cause polymerisation of the composition to form the polymeric material to produce polymer treated wood or wooden article.

The preferred solvent is water, although methanol, ethanol, acetone or other volatile solvents may be employed.

A vacuum is preferably applied to the wood before drying or solvent removal and curing to remove air. This serves to reduce the risk of an explosion.

Preferred monomers are derived from biomass or are derived from renewable and sustainable resources and are capable of impregnating a wood or a wooden article. A single monomer may be most convenient for simplicity and ease of uniform impregnation. Use of furfuryl alcohol or bishydroxymethyl furan is preferred.

Further monomers or oligomers may include 2,5-furan dicarboxylic acid (FBCA) and succinic acid (SA).

The invention is particularly applicable to impregnation of woods which are sensitive to cracking or deformation during drying and curing at elevated temperatures. The invention is particularly suitable for treatment of hardwoods, especially beech, ash and maple. The invention is also applicable to impregnation of large dimension pieces of pine or other softwoods, for example, having a thickness greater than 30cm.

The process may be applied to a wide variety of wood species that can be impregnated, both softwoods and hardwoods, for example, Scots pine, southern yellow pine, beech, maple, birch, oak, aspen, poplar and alder.

The catalyst may be selected from the group consisting of: acids, for example, maleic anhydride, phthalic anhydride, maleic acid, malic acid, phthalic acid, benzoic acid, citric acid, zinc chloride, aluminium chloride, other cyclic organic anhydrides or latent catalysts such as ammonium salts organic anhydrides and mixtures thereof.
The stabilisers which preferably act as buffers may be selected from the group consisting of: sodium carbonate, sodium bicarbonate, sodium citrate, phosphates and calcium or ammonium salts of lignosulphonic acids.

Optional further compounds may include borates, for example borax, disodium tetraborate, and boric acid.

In a preferred process during the removal of water the relative humidity is maintained at about 80 to about 100%, more preferably at about 90%, for a period of 1 to 200 hours, usually 120 hours, followed by curing at a temperature preferably about 50 to about 180°C, more preferably about 90 to about 140°C, most preferably about 100 to about 130°C, especially about 120°C.

A heat exchanger or heat battery may be provided to allow direct heating of the atmosphere within the vessel.

Further heating may be preferably provided by injecting superheated steam into the vessel. Superheated steam is preferred in order to cause drying of the wood.

The relative humidity may be determined by the difference between the actual pressure at a given temperature as a percentage of the saturation pressure of steam at that temperature.

Relative humidity within the chamber generally decreases during the drying process as water is removed from the chamber.

Preferably the relative humidity is maintained above a minimum level during the heating up phase and at the end of the drying process in order to minimise deformation and cracking of the wood. The relative humidity by range from about 30% to about 100%. A preferred minimum relative humidity is about 35% more preferably about 40% dependent on the wood species and the dimension of the wooden pieces or articles being processed.

The relative humidity within the container may be controlled by regulation of pressure and temperature.
Following the drying step the wood or wooden articles are heated to a higher
temperature to cure the polymer. It is beneficial to remove water from the wood or wooden
articles before curing. This allows more rapid curing since thermal energy is not lost by
evaporation. A lower temperature may be used in comparison to a conventional process.
Also heating of the wood to the curing temperature may be achieved in less time and with
less energy due to the reduction of evaporative losses.

The drying and curing steps may be carried out in the same container, that is without
a need for unloading from a drying oven and reloading into a separate curing oven.

During curing the pressure within the container may be maintained at about 1 bar
and a relative humidity of about 40 to about 100%, preferably about 50 to about 90%.
Alternatively, a pressure greater than 1 bar may be used, for example, about 1 to about 4 bar.

Pressures below 0.1 bar are not preferred for the drying or curing steps on account of
poor heat transfer within the container and the need for powerful vacuum pumps to remove
water released by the wood.

According to a second aspect of the preferred invention apparatus for polymer
impregnation of wood or a wooden article comprises a container adapted to receive a quantity
of wood or one or more wooden articles to be treated, the container having a pump for
applying reduced pressure to the container, a steam generator adapted to supply superheated
steam to the chamber and sensors adapted to monitor parameters selected from pressure,
temperature, humidity and concentration of volatile organic compounds within the container.

An inlet for superheated steam may be provided.

A heat exchanger within the vessel may be provided for direct heating.

The process in accordance with this invention may be applied to timber or shaped
wooden articles, for example floor boards, decking, cladding, roofing, poles, sleepers or other
partially or fully machined or worked components. Stock timber for subsequent machining
into constructional, engineering laminates and joinery components may be used. The
invention finds particular applicability to high performance wood or wooden articles with improved stability, increased hardness and prolonged durability for manufacture of products with precise dimensional and performance tolerances.

In this specification percentages and other amounts are by weight unless indicated otherwise. Percentages and other proportions are selected from any ranges quoted to total 100%.

The invention is further described by means of example but not in any limitative sense with reference to the accompanying drawings of which:

Figure 1 is a schematic view of a timber impregnation plant in accordance with this invention; and

Figure 2 illustrates the drying vessel of the plant.

Figure 1 is a schematic view of a timber impregnation plant. A supply of wood or wooden articles, for example planks (1), is organised into a separated stack (2) on a trolley or other carrier (not shown) using spacers so that each plank is separated from adjacent planks. The stack is then moved on the trolley into an impregnation autoclave (3).

The autoclave (3) is filled with an impregnating solution from buffer tanks (4,5) supplied from storage tanks (6,7,8) via a mixing and measuring tank (9).

After impregnation, the impregnated wood or wooden articles are transferred to one of four drying chambers (10). Each drying chamber is provided with a heat exchanger, or inlet for superheated steam and a condenser (14) connected to an outlet for recycling condensate collected from the condenser (14) to the storage tank (7). Gases from the condenser are routed through an air purifier (26).

The wood or wooden articles may be impregnated by any conventional technique including application of pressure up to 15 atmospheres, vacuum followed by pressure or by application of atmospheric or low pressure followed by higher pressure and a final vacuum step.
The impregnating solution may comprise one or more monomers selected from furfuryl alcohol, bis hydroxymethyl furan, tris hydroxymethyl furan or oligomers of these compounds.

Mixtures of monomers or of monomers and oligomers may be used, provided that they are sufficiently fluid to penetrate and impregnate the wood.

A general method which may be used includes the steps of securing the wood so that it will not float; closing the autoclave and applying a partial vacuum; filling the autoclave with the treating mixture while maintaining the vacuum to submerge the wood; pressurising the autoclave to a pressure in the range of 5-14 atmospheres dependent on the wood species, dimensions of the wood or wooden articles and desired rate of impregnation; reducing the pressure to 2 or 3 atmospheres and expelling the liquid using the remaining pressure within the autoclave. Finally, the pressure is released and the treated wood is removed.

A typical treatment solution may comprise:

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<tr>
<td>Furfuryl alcohol</td>
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<tr>
<td>Maleic anhydride</td>
<td>0.5%</td>
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<tr>
<td>Citric acid</td>
<td>1.0%</td>
</tr>
<tr>
<td>Ethanol</td>
<td>71.0%</td>
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<tr>
<td>Water</td>
<td>5.0%</td>
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</table>

A liquid uptake of 150% in relation to dry wood mass for pine sapwood may be achieved.

Alternative impregnating solutions are disclosed in WO2004/011216 and WO2004/011214 the disclosures of which are incorporated into this specification by reference for all purposes.

Figure 2 is a diagrammatic view of a drying chamber (10) shown in Figure 1. The chamber (10) includes nine fans (11) and an air inlet valve (12). An outlet (13) for evaporated water communicates with a condenser (14). A steam inlet (15) delivers superheated steam from a boiler (not shown) to an inlet (16) to supply heating and humidity to the chamber (10). Heat exchangers (17) circulate hot water from a heat exchanger (18) supplied by the steam inlet (15). In this way, dry heat is provided to the chamber as necessary.
A condensate tank (19) serves to collect condensate from the bottom of the tank (10). The condensate is separated in separator (27).

Condensate from the condenser (14) is delivered to measuring tanks (20) for measuring the amount of condensed water vapour. A pump tank (21) delivers the measured condensate to a pump (22) indicated with a water outlet and condensate storage tank (23). A gas water separator (24) separates gas from the condensed water. The condensed water is cooled by a heat exchanger (25).

In use of the dryer, steam may be supplied directly to the tank (10) through inlets (16) and dry heat may be supplied by the heat exchanger (17) so that the temperature and humidity within the tank can be independently controlled.

When the impregnated wood or wood articles have been placed within the drying chamber, a pre-vacuum is applied for a short period to remove any air from the chamber in order to prevent a risk of fire or explosion. The pressure during the pre-vacuum period may be up to 0.3 bar due to evaporation of water from the impregnated wood.

The container is then heated to a temperature of about 70°C over a period of 3-6 hours. During this heating up period the pressure may rise from the pre-vacuum pressure of less than 0.2 bar to between about 0.2 and about 0.4 bar, preferably about 0.3 bar.

The relative humidity may be about 90%.

The conditions within the container are maintained by control of pressure, injection of superheated steam and external heating.

The moisture content of the wood is determined by measurement of the amount of water collected from the container. The drying stage may be complete when the moisture content of the wood is about 15% or lower.

After the drying stage is complete the pressure is allowed to rise to about 1 bar and the temperature is increased to from about 100 to about 140°C preferably about 100°C with
the relative humidity increasing to about 60 to about 80% by addition of superheated steam to the container, in order to prevent cracking or deformation of the wood.

The curing conditions may be maintained for about 10 hours dependent on the nature of the polymer composition and the thickness of the wood or wooden articles.

When the curing is complete the polymer impregnated wood or wooden articles may be removed from the container for machining, package and distribution.
CLAIMS

1. A process for impregnating wood or a wooden article comprises a process for forming a composite comprising wood or a wooden article and a polymeric material comprising the steps of:

   impregnating the wood or wooden article with a polymerisable composition comprising:

   (i) one or more wood compatible polymerisable monomers, or oligomers selected from the group consisting of furfuryl alcohol (FA), bishydroxymethyl furan (BHMF), trihydroxymethyl furan (THMF), oligomers of FA, BHMF and THMF condensation products of these compounds and mixtures thereof;

   (ii) a catalyst and;

   (iii) a solvent selected from the group consisting of: water, C₁₋₄ alcohols and mixtures thereof, wherein the one or more wood compatible polymerises or monomers or oligomers has a boiling point not less than 50°C higher than the boiling point of the solvent and atmospheric pressure; and

   (iv) optionally one or more stabilisers or other ingredients;

   to produce impregnated wood or an impregnated wooden article;

   subjecting the impregnated wood or wooden article to a water removal process comprising maintaining the wood or wooden article in an atmosphere having a pressure of about 0.1 to about 0.5 bar, a temperature of about 50 to about 90°C, for a duration sufficient to cause removal of water from the wood or wooden article; and

   maintaining the wood or wooden article at a higher temperature to cause polymerisation of the composition to form the polymeric material to produce polymer treated wood or wooden article.

2. A process as claimed in claim 1 wherein the pressure is from about 0.2 to about 0.4 bar.

3. A process as claimed in claim 1 or 2 wherein the temperature is from about 60 to about 85°C.
4. A process as claimed in any preceding claim wherein the temperature is from about 60 to about 80°C.

5. A process as claimed in any preceding claim wherein the temperature is from about 70 to about 80°C.

6. A process as claimed in any preceding claim wherein the solvent is water.

7. A process as claimed in any preceding claim wherein the wood compatible polymerisable composition is selected from the group consisting of: furfuryl alcohol and bis hydroxymethyl furan.

8. A process as claimed in any preceding claim wherein the wood compatible polymerisable composition is derived from biomass.

9. A process as claimed in any preceding claim wherein the relative humidity is 80-100%.

10. A process as claimed in claim 9 wherein the relative humidity is about 90%.

11. A process as claimed in any preceding claim wherein the duration is from about 1 to about 200 hours.

12. A process as claimed in claim 11 wherein the duration is from about 37 to about 60 hours.

13. A process as claimed in any preceding claim wherein the curing of the polymeric material is carried out at a temperature of from about 50 to about 180°C; ambient pressure and a relative humidity of from about 40% to about 100%.

14. A process as claimed in claim 13 wherein the temperature is from about 90 to about 140°C.

15. A process as claimed in claim 14 wherein the temperature is about 100°C.

16. A process as claimed in any of claims 13-15 wherein the relative humidity is from about 50% to about 90%.
17. A process as claimed in any of claims 13-16 wherein the temperature and relative humidity during curing are controlled by addition of superheated steam to the container.

18. A process as claimed in any preceding claim wherein the wood or wooden article is derived from a species selected from the group consisting of Scots pine, southern yellow pine, beech, ash, maple, birch, alder, oak, aspen and poplar.

19. A process as claimed in any preceding claim wherein the wooden article is selected from the group consisting of: building components, marine components, outdoor furniture, decking, railings, stairways, walkways, boardwalks or playground equipment, bridge components, railway sleepers, cooling tower slats, utility poles, heavy timbers, fence posts, stakes, guard rail posts, guard rail plates, sign posts, light poles, flooring, tanks and buckets.

20. Apparatus for forming a composite compound of wood or a wooden article by a method as claimed in any preceding claim comprising:
   a container adapted to receive a quantity of impregnated wood or wooden articles;
   a pump for creating reduced pressure within the container;
   a steam generator adapted to supply superheated steam to the container;
   one or more sensors adapted to measure parameters selected from: pressure, temperature, humidity, concentration of volatile organic compounds.

21. Apparatus as claimed in claim 20 including means for measuring condensed water or other liquids removed from the container.
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**

**INV.** B27K3/15

**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:)

B27K

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

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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<tr>
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<td>5 February 2004 (2004-02-05) page 8, lines 7-34</td>
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<td>X, P</td>
<td>WO 2010/122156 A1 (KEBONY ASA [NO]; WESTIN MATS [SE]; LANDE STIG [NO]; BRYNI LDSEN PER [NO]) 28 October 2010 (2010-10-28) claims 15-18; figure 1</td>
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Further documents are listed in the continuation of Box C. X See patent family annex.

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"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**

28 September 2011

**Date of mailing of the international search report**

07/10/2011

**Name and mailing address of the ISA/IEP**

European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk

Tel. (+31-70) 340-2040, Fax (+31-70) 340-2016

**Authorized officer**

Bjola, Bogdan
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