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(54) Title: PROCESS FOR PREPARING POLYFURFURYL ALCOHOL PRODUCTS

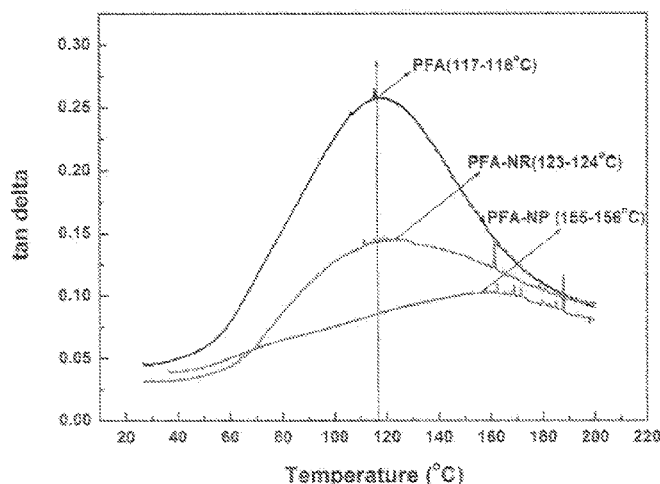


Figure 1 — tan delta curves for polyfurfuryl alcohol based bioplastics.

(57) **Abstract:** A process for producing a polyfurfuryl alcohol product includes mixing furfuryl alcohol (FA) and a catalyst component capable of catalyzing a condensation reaction of FA to polyfurfuryl alcohol (PFA). The mixing is effected at a temperature T_{mix} , where $T_{\text{mix}} < 30^{\circ}\text{C}$. The resultant polymerizable mixture is heated to T_1 , where $T_1 > T_{\text{mix}}$ and $50^{\circ}\text{C} < T < 60^{\circ}\text{C}$. The mixture is maintained at T_1 for a period of time t_1 , where t_1 is sufficiently long for polymerization to take place and for the polymerized product that is formed to set. The polymerized product is heated to T_2 , where $90^{\circ}\text{C} < T_2 < 110^{\circ}\text{C}$, and maintained 10 at T_2 for a period of time t_2 , where $0.5\text{h} < t_2 < 2\text{h}$, for curing of the polymerized product. The polymerized product is heated to T_3 , where $150^{\circ}\text{C} < T_3 < 180^{\circ}\text{C}$, and maintained at T_3 for a period of time t_3 , where $0.5\text{h} < t_3 < 2\text{h}$, for further curing of the polymerized product.



PROCESS FOR PREPARING POLYFURFURYL ALCOHOL PRODUCTS

THIS INVENTION relates to polyfurfuryl alcohol products. More particularly, it relates to products produced from controlled polymerization of furfuryl alcohol. Still more particularly, it relates to a process for producing a polyfurfuryl alcohol product.

Polyfurfuryl alcohol is a thermoset resin, and is usually synthesized by a condensation reaction of furfuryl alcohol in the presence of an acidic catalyst. However, once the catalyst has been mixed with the furfuryl alcohol, and polyfurfuryl alcohol starts forming, it is extremely difficult and in fact almost impossible to cure polyfurfuryl alcohol at low temperatures; on the other hand, at high curing temperatures the condensation reaction easily escalates out of control, which can result in an explosion occurring. This latter problem is exacerbated by the fact that, at above 80°C, an exothermic reaction (which is extremely difficult to control) sets in during the condensation polymerization of furfuryl alcohol. Hitherto, the problem of controlling the reaction kinetics has been insurmountable - once the exothermic reaction sets in, the viscosity of the polyfurfuryl alcohol increases dramatically, resulting in the resin achieving a non-workable state or consistency. Even if an explosion can be avoided, a polyfurfuryl alcohol product usually blisters or cracks once the exothermic reaction sets in.

It is hence an object of this invention to provide a process for preparing a polyfurfuryl alcohol product, whereby these drawbacks are avoided or at least reduced.

Thus, according to the invention, there is provided a process for producing a polyfurfuryl alcohol product, the process including

mixing, in a mixing stage, furfuryl alcohol (FA) and a catalyst component capable of catalyzing a condensation reaction of FA to polyfurfuryl alcohol (PFA), with the mixing being effected at a temperature T_{mix} , where $T_{\text{mix}} < 30^{\circ}\text{C}$, to form a polymerizable mixture;

heating the polymerizable mixture to a first temperature T_1 , where $T_1 > T_{\text{mix}}$ and $50^{\circ}\text{C} < T_1 < 60^{\circ}\text{C}$, and maintaining the mixture at T_1 for a period of time t_1 , where t_1 is sufficiently long for polymerization to take place and for the polymerized product that is formed to set;

thereafter heating the polymerized product to a second temperature T_2 , where $90^{\circ}\text{C} < T_2 < 110^{\circ}\text{C}$, and maintaining it at the temperature T_2 for a period of time t_2 , where $0.5\text{h} < t_2 < 2\text{h}$, for curing of the polymerized product; and

then heating the polymerized product to a third temperature T_3 , where $150^{\circ}\text{C} < T_3 < 180^{\circ}\text{C}$, and maintaining it at the temperature T_3 for a period of time t_3 , where $0.5\text{h} < t_3 < 2\text{h}$, for further curing of the polymerized product.

While the catalyst component may comprise a catalyst as hereinafter described, it is preferably a catalyst solution comprising a catalyst as hereinafter described admixed with a minimum volume of distilled water, at room temperature. Thus, the concentration of catalyst in the catalyst solution may typically be in the range of 1gm catalyst / 10mL ('millilitres') distilled water to 1gm catalyst / 15mL distilled water.

The process may then include effecting the mixing of the catalyst solution with the FA in the mixing stage by adding the catalyst solution drop wise to the FA, preferably with slow / gentle mixing. By "slow / gentle mixing" is meant manual mixing or stirring using a rod or the like, during the drop wise addition of the catalyst solution to the FA. For larger volumes of FA, e.g. for commercial scale operation of the process of the invention, it is also advisable to use a rod or the like and to stir manually while the catalyst solution is added to the FA. Mechanical stirring or mixing of the FA during catalyst solution addition is to be avoided even for large scale production. The process of the invention is thus characterized thereby that no mechanical stirring or mixing is employed in the mixing stage.

The catalyst may, in particular, be an acidic catalyst, such as *p*-toluene sulphonic acid. The mass proportion of *p*-toluene sulphonic acid to FA used may be about 0.3:100. Other acidic catalysts such as pentyl sulphonic acid, hexadecyl sulphonic acid, tetradecyl sulphonic acid, decyl sulphonic acid and dodecyl sulphonic acid can instead be used; however, the amount of acidic catalyst used relative to the FA is critical in each case. Thus, for each acidic catalyst, the optimum mass proportion of acid catalyst to FA will need to be determined by routine experimentation, bearing in mind that even a small increase in the proportion of acidic catalyst used over and above the optimum proportion could lead to explosion and/or blistering.

T_{mix} is, preferably, room temperature, i.e. 20°C-25°C, or can be even lower depending upon the prevailing atmospheric conditions. However, it is advisable to cool down the FA to freeze point, and to maintain it at freezing overnight, if the room temperature of the place/environment is higher than 30°C, or if the volume of FA to which the catalyst solution is added is more than 1 to 1.5L ("litre").

The preparation of the acid catalysed FA solution could be a starting point of preparing the PFA resin when required to be used for preparing PFA based products using thermoset injection moulding/compression moulding methods. To use the resin for thermoset injection moulding/compression moulding methods it is advisable to keep the acid catalysed FA solution at a lower temperature (5-15°C) for 10-15 days. This will help in increasing the viscosity of the PFA resin slightly which ultimately will help in processing the material by abovementioned methods. It is also advisable not to keep acid catalysed FA solution for more than 1 month as there will be increase in viscosity leading to non-workable state of the PFA resin.

The mixing stage may comprise a vessel to which the catalyst solution is added drop wise to the FA at room temperature; the polymerization thereof and the curing of the polymerized product may be effected in a suitable mould, preferably a silicon rubber mould. A silicon mould is believed to be particularly suitable because of its stability at high temperature and its flexible

nature. Other types of mould with high thermal stability and flexible nature can also be used since PFA based products are hard and rigid, and a flexible mould is required to facilitate taking out the hard and rigid product after curing. The mould may have a relatively large surface area so that the product preferably has a large surface area to thickness ratio, e.g. may be in the form of sheets. The thickness of the PFA based product should not exceed 3cm with no limit to its surface area. Taking this fact into consideration, it may be possible to prepare large PFA based sheets in situ. Preferably, the polymerizable mixture is poured directly into the mould once all the catalyst solution has been added to, and mixed with, the FA. Furthermore, manual stirring of the polymerizable mixture with a glass rod should be ceased once all catalyst has been added to the FA.

The heating of the polymerizable mixture in the mould may be effected by placing the mould containing the mixture in an oven.

Preferably, T_1 is about 60°C. As indicated hereinbefore, t_1 is sufficiently long for polymerization to take place and for the polymerized product to set or harden. Thus, $90h > t_1 < 100h$; typically, t_1 is about 96h.

Preferably, T_2 may be about 100°C. Preferably, t_2 may be about 1h.

Preferably, T_3 may be about 170°C. Preferably, t_3 may be about 1h.

The polymerized product can thus be non-reinforced. However, if desired, the polymerized product can be a reinforced polymerized product. The process may thus include introducing a reinforcing material into the FA, into the polymerizable mixture and/or into the polymerized product before it is fully set. When the reinforcing material is introduced into the FA and/or into the polymerizable mixture, it may be in the form of loose fibres, such as cellulosic fibres; loose yarns; or loose particles, such as nanoparticles, e.g. clay particles. Such loose fibres, yarns or particles can thus easily be mixed with or into the FA and/or into the polymerizable product. When the reinforcing material is introduced into the polymerizable mixture and/or into the

polymerized product, this may be effected by locating the reinforcing material in the mould before, during and/or after introduction of the polymerizable mixture into the mould. The reinforcing material may then be in the form of one or more non-woven mats, e.g. non-woven mats of flax, hemp or kenaf fibres; or woven fabrics.

The process of the invention thus addresses the risks of explosion and blistering during condensation polymerization on the basis of improved chemical reaction kinetics. The reaction rate is dependent on, inter alia, temperature, stirring speed, and surface area. Temperature has been addressed by adopting the controlled ramped or stepped temperature profile as hereinbefore described. As discussed hereinbefore, mechanical stirring should be avoided in favour of slow/gentle mixing using a rod or the like, while adding the catalyst solution to the FA. Surface area has been addressed by specifying that the mould is such that products having a large surface area to thickness ratio can be produced.

The invention will now be described in more detail with reference to the specific examples set out hereunder and the accompanying drawings.

In the drawings,

FIGURE 1 shows tan delta curves for PFA based bioplastic products produced in Examples 1-3; and

FIGURE 2 shows thermogravimetric curves of PFA based bioplastic products produced in Examples 1-3.

In the Examples, tests are used to characterize the PFA based products. The tests used are as follows:

The tensile strength (σ), elongation at break, and the Young's modulus (E) of the samples were measured on an Instron 3369 tensile tester at a strain rate of $10\text{mm}\cdot\text{min}^{-1}$ according to ASTM D638-03. Flexural testing was carried out in accordance with ASTM D-790, at a crosshead speed of $5\text{mm}/\text{min}$ and a span length of 60mm . The sample dimension was $80\text{mm} \times 10\text{mm}$ for flexural

testing. An average value from five replicates of each sample was taken for each of the tests mentioned above.

Thermogravimetric analysis (TGA) of approximately 5mg dried PFA samples was carried out at a heating rate of $20^{\circ}\text{C min}^{-1}$ between room temperature and 700°C in nitrogen atmosphere on a thermogravimetric analyzer (Perkin Elmer, Buckinghamshire, UK).

Dynamic mechanical thermal analysis (DMTA) was performed on a dynamic mechanical analyzer (DMA8000, Perkin Elmer, Buckinghamshire, UK) with dual cantilever at a frequency of 1 Hz. The sheets tested were 50mm x 10mm (length x width) in dimension, and the test temperature ranged from 25 to 200°C , with a heating rate of $2^{\circ}\text{C per min}$. The α -relaxation temperature, α_r , was determined as the peak value of the loss angle tangent ($\tan \delta$).

EXAMPLE 1

0.3g of *p*-toluene sulphonic acid used as catalyst was dissolved in 5mL distilled water to obtain a catalyst solution. The catalyst solution was added drop wise to 100mL of furfuryl alcohol with gentle manual stirring using a glass rod at room temperature ($T_{\text{mix}} = 25^{\circ}\text{C}$) to form a polymerizable mixture. As soon as all the catalyst had been added to the furfuryl alcohol, the polymerizable mixture or solution was poured into a silicon rubber mould and heated to, and maintained at, 60°C (T_1) for 96h (t_1) in an oven. This was sufficiently long for the polymerizable mixture to polymerize into a polymerized product in the mould, and for the polymerized product to set or harden. Thereafter, the temperature was raised to 100°C (T_2) for 1h (t_2) and subsequently to 170°C (T_3) for 1h (t_3) to cure the polymerized product, which was thus in the form of a sheet of polyfurfuryl alcohol (PFA). The properties of the sheet were evaluated by determining mechanical properties as shown in Table 1 and thermal properties as in Figures 1 and 2.

EXAMPLE 2

Non-woven flax fibres (NR) in the form of web weighing 3.4g (150g/m^2) were used in this Example. 100 mL of furfuryl alcohol solution containing the same catalyst (and the same quantity thereof) as in Example 1, was poured (at

room temperature) on the NR web located in the mould, and heated to, and maintained at, 60°C (T_1) for 96h (t_1). Thereafter the temperature was raised to 100°C (T_2) for 1h (t_2) and subsequently to 170°C (T_3) for 1h (t_3) to obtain reinforced poly furfuryl alcohol (PFA-NR) in the form of a sheet (4000g/m²) after curing. The properties of the reinforced sheet were evaluated by determining mechanical properties as shown in Table 1 and thermal properties as in Figures 1 and 2. In this example, non-woven web from natural fibres such as flax, hemp, or kenaf can instead be used to prepare a natural fibre reinforced bioplastic product in accordance with the invention.

EXAMPLE 3

2.5% (wt%) nanoclay (NP) (laboratory grade from Sigma-Aldrich) in the form of powder was mixed, at room temperature) with furfuryl alcohol for 1 h under mechanical stirring at 50-60rpm. Thereafter, the required amount of catalyst (as described in Example 1) was added drop wise with gentle manual stirring using a glass rod, and still at room temperature, to the furfuryl alcohol and nanoclay mixture to obtain a polymerizable mixture. The mixture was poured into a silicon mould and cured in the same way as described in Example 1, to obtain reinforced poly furfuryl alcohol (PFA-NP) in the form of a sheet. The properties of the sheet were evaluated by determining mechanical properties as shown in Table 1 and thermal properties as in Figures 1 and 2.

The Examples demonstrate that the present invention, in its broadest aspects, establishes an approach for using naturally abundant FA from sugarcane bagasse. As discussed hereinbefore, conversion of FA into PFA involves an exothermic reaction which, if not controlled, often leads to explosion. For this reason, it has hitherto not been possible to fabricate PFA biopolymers or reinforced PFA composites on a commercial scale. In accordance with the present invention, kinetically controlled polymerisation of PFA is carried out by adding catalyst solution drop wise to furfuryl alcohol at room temperature under slow manual stirring using a glass rod or the like to obtain a polymerizable mixture of FA and catalyst. The polymerizable mixture is cast in silicon rubber mould and heated to 60°C for 96h or until the PFA which forms, has solidified. Thereafter, the temperature is increased to 100°C for 1h

for curing of the PFA product. Finally, the temperature was raised further to 170°C for 1h to ensure complete curing of the resin. Table 1 provides the important properties of the PFA products of Examples 1 to 3. In addition, Table 1 includes the properties of phenolics, epoxy and soy oil thermoset resins for further comparison.

Table 1 – Summarized results of mechanical properties of polyfurfuryl alcohol biopolymer product, fibre/nanoparticles reinforced polyfurfuryl alcohol products and their comparison with other commercial thermoset resins.

Specimens	Mechanical Properties		Water uptake (%)
	Tensile / Flexural Strength (MPa)	Tensile/Flexural Modulus (GPa)	
Polyfurfuryl alcohol (PFA) (Example 1)	15-17 / 60-72	2.0-2.6 / 3.2-3.7	0
Polyfurfuryl alcohol with nonwoven fibre mat (PFA-NR) (Example 2)	20-22 / 36-38	1.9-2.1 / 1.7-2.2	0.45
Polyfurfuryl alcohol with nanoclay (PFA-NP) (Example 3)	18-20 / 80-96	2.7-3.3 / 9.6-14	0.5
Phenolic resins ^{1a,b,c}	22-24 / 52-58	2.7-2.9 / 3.4-3.7	0
Epoxy resins ^{2a,b}	50-60 / 100-108	3.0-3.2 / 2.6-2.8	0
Soy oil based ³ thermoset	21-39 / 70-87	1.7-2.5 / 1.8-2.4	0

^{1a}Min Ho Choi, In Jae Chung, Mechanical and thermal properties of phenolic resin-layered silicate nanocomposites synthesized by melt intercalation, *Journal of Applied Polymer Science*, 90, 2316–2321 (2003).

^{1b}Cevdet Kaynak, Onur Cagatay, Rubber toughening of phenolic resin by using nitrile rubber and amino silane, *Polymer Testing*, 25, 296–305 (2006).

^{1c}www.hexion.com

^{2a}G. Sui, W.H. Zhong,, M.C. Liu, P.H.Wu, Enhancing mechanical properties of an epoxy resin using “liquid nano-reinforcements”, *Materials Science and Engineering A* 512, 139-142 (2009).

^{2b} Rosa Medina, Frank Hauptert, Alois K. Schlarb, Improvement of tensile properties and toughness of an epoxy resin by nanozirconium-dioxide reinforcement, *Journal of Material Science* 43, 3245–3252 (2008).

³ <http://www.dynacheminc.com/biobasedgreenresins.html>

Thus, in the Examples, a black coloured polyfurfuryl alcohol based bioplastic product was prepared (Example 1) from furfuryl alcohol solution with a catalyst, and was designated as PFA. PFA was further reinforced with nonwoven flax fibres to produce a natural fibre reinforced biocomposite product designated as PFA-NR (Example 2). The reinforcement of polyfurfuryl alcohol with nanoclay was also accomplished (Example 3) and the product was designated as PFA-NP.

The PFA based biopolymer showed tensile strength and tensile modulus of 15-17 MPa and 2.0-2.6 GPa respectively, with almost 100% water resistance. On reinforcement with natural fibre nonwoven, mechanical properties decreased except the tensile strength. On the other hand, incorporating reinforcement with nanoparticles, all the mechanical properties increased except the tensile strength. Interestingly, tensile and flexural moduli for nanoparticle-reinforced PFA increased to a large extent.

Figure 1 shows that the glass transition temperature of the PFA resin is 117°C-118°C. An increase in the glass transition temperature with reinforcement of the PFA emerges clearly from Figure 1. It also implies that the biopolymers can be effectively used under ambient conditions. This shows that there is an increase in the stiffness of the material upon reinforcement which may be the reason for high mechanical properties for PFA-NP (Table 1). Thermal stability of PFA bioplastics is very high, with 63% char yield at 700°C as shown in Figure 2. The maximum degradation temperature is 475°C. However, upon reinforcement with only fibre, the char yield decreased to 42% with a two step mass loss, whereas reinforcement

with nanoclay increased the char yield to 65% at 700°C. The thermal properties of the biopolymer prepared in accordance with the invention are similar or somewhat higher than those of phenolics. The polyfurfuryl alcohol based bioplastic products or biocomposites were subjected to mechanical tests and the results are given in Table 1. The mechanical properties of the materials prepared according to the invention are comparable with those of similar material obtained from phenolics or epoxy resins, as can be seen from Table 1. Overall, the thermal stability of PFA prepared by the process of the invention is high with comparable mechanical properties to phenolics and epoxy resins.

The main advantages of producing PFA products using the process of the invention are:

- 1) Furfuryl alcohol as monomer is readily available from waste of sugarcane bagasse. In this way, the waste can be used effectively with minimal negative impact on environment; however, furfuryl alcohol can also be obtained from fruit shells such as those of hazelnut, sunflower, walnut, and almond, as well as from agricultural wastes other than sugarcane bagasse.
- 2) By the novel approach of the process of the invention, the risk of explosion and blistering are easily eliminated while condensation polymerization of furfuryl alcohol takes place. Also, fibre or nanoparticles or filler reinforced polyfurfuryl alcohol based materials can be prepared as needed, in desired shapes.
- 3) Phenolics or epoxy resins have limited shelf life ($\pm$ 3 months) even though they are stored at a specific range of temperatures. The reason is that once initiator has been added during polymerization a condensation reaction starts even at room temperature. This is the reason why inhibitors are also added to these commercial resins. Despite this, after transportation of these resins to a desired location, the shelf life of these resins is limited to maximum 6 months even when stored at 5°C. In the process of the invention, there is no question of storing the resin, as the PFA product is synthesized when needed and the desired product produced immediately.

- 4) South Africa is the 12th biggest producer of sugar cane and furfuryl alcohol is available at a low price from China. The price of furfuryl alcohol can be significantly reduced further once the industrial production of PFA bioplastic products is contemplated. Bearing in mind the finite nature of synthetic plastics and government initiative to reduce carbon foot print, the process of the invention will provide an impetus for exploring innovative applications of PFA.
- 5) The PFA products produced in accordance with the invention have comparable mechanical/thermal properties with those of widely used phenolics.

The Applicant is also aware that injection moulding machines for thermoset resins are now available. In the process of the invention, the curing of the PFA product formed in the mould depends on the polymerization and curing temperatures as specified hereinbefore, and it will thus be possible to mould products from PFA for diverse uses such as mobile phones, computer keyboards and carparts, by using a specialized injection moulding machine.

Phenolics and epoxy resins derived from synthetic resources offer excellent high temperature resistant materials. What is needed today is a resin derived from renewable resources to reduce the carbon footprint and in view of the depleting fossil fuel resources. The resin (PFA) produced by the process of the invention, addresses these issues. The process of the invention can be used to produce large and small mouldable products. This invention thus relates to the synthesis of PFA at controlled rate for the production or fabrication of materials/product with or without reinforcements. The reinforcement of the biopolymer can be with materials in the form of fibres, yarns, nonwoven mats or as woven fabrics. Preference is given to cellulosic fibres, of any form, as the invention is based on the hydrophilic and hydrophobic properties of the FA and PFA, respectively. Particles/nanoparticles can also be added to modify polyfurfuryl alcohol. This invention also relates to the use of PFA as potential thermoset biopolymer resins derived from renewable resources. FA can be converted into black coloured solid PFA by controlled polymerization in accordance with the

invention. The controlled polymerisation process, therefore, can be exploited to develop a variety of products, from large panels to small parts for a wide range of applications in housing, automobiles, aerospace and also for mobile phone and computer accessories.

CLAIMS

1. A process for producing a polyfurfuryl alcohol product, the process including

mixing, in a mixing stage, furfuryl alcohol (FA) and a catalyst component capable of catalyzing a condensation reaction of FA to polyfurfuryl alcohol (PFA), with the mixing being effected at a temperature T_{mix} , where $T_{\text{mix}} < 30^{\circ}\text{C}$, to form a polymerizable mixture;

heating the polymerizable mixture to a first temperature T_1 , where $T_1 > T_{\text{mix}}$ and $50^{\circ}\text{C} < T_1 < 60^{\circ}\text{C}$, and maintaining the mixture at T_1 for a period of time t_1 , where t_1 is sufficiently long for polymerization to take place and for the polymerized product that is formed to set;

thereafter heating the polymerized product to a second temperature T_2 , where $90^{\circ}\text{C} < T_2 < 110^{\circ}\text{C}$, and maintaining it at the temperature T_2 for a period of time t_2 , where $0.5\text{h} < t_2 < 2\text{h}$, for curing of the polymerized product; and

then heating the polymerized product to a third temperature T_3 , where $150^{\circ}\text{C} < T_3 < 180^{\circ}\text{C}$, and maintaining it at the temperature T_3 for a period of time t_3 , where $0.5\text{h} < t_3 < 2\text{h}$, for further curing of the polymerized product.

2. A process according to Claim 1, wherein the catalyst component is in the form of a catalyst solution comprising a catalyst admixed with a minimum volume of distilled water, at room temperature.

3. A process according to Claim 2, wherein the catalyst solution has a catalyst concentration in the range of 1gm catalyst / 10mL distilled water to 1gm catalyst / 15mL distilled water.

4. A process according to Claim 2 or Claim 3, which includes effecting the mixing of the catalyst solution with the FA in the mixing stage by adding the catalyst solution drop wise to the FA, with slow / gentle mixing.

5. A process according to any one of Claims 2 to 4 inclusive, wherein the catalyst is an acidic catalyst selected from the group consisting in *p*-toluene sulphonic acid, pentyl sulphonic acid, hexadecyl sulphonic acid, tetradecyl sulphonic acid, decyl sulphonic acid and dodecyl sulphonic acid.
6. A process according to any one of Claims 2 to 5 inclusive, wherein T_{mix} is room temperature.
7. A process according to Claim 6, wherein, when the room temperature at which the mixing takes place is higher than 30°C, or if the volume of FA to which the catalyst solution is added is more than 1L, the FA is cooled down to freeze point, and maintained at the freeze point overnight.
8. A process according to any one of Claims 2 to 7 inclusive, wherein the mixing stage comprises a vessel to which the catalyst solution is added drop wise to the FA at room temperature, with the polymerization thereof and the curing of the polymerized product being effected in a mould.
9. A process according to Claim 8, wherein the mould is a silicon rubber mould.
10. A process according to Claim 8 or Claim 9, wherein the mould has a relatively large surface area so that the product preferably has a large surface area to thickness ratio, and wherein the thickness of the polymerized product does not exceed 3cm.
11. A process according to any one of Claims 8 to 10 inclusive, wherein the heating of the polymerizable mixture in the mould is effected by placing the mould containing the mixture in an oven.
12. A process according to any one of Claims 1 to 11 inclusive, wherein T_1 is about 60°C.

13. A process according to any one of Claims 1 to 12 inclusive, wherein $90h > t_1 < 100h$.
14. A process according to any one Claims 1 to 13 inclusive, wherein T_2 is about 100°C .
15. A process according to any one of Claims 1 to 14 inclusive, wherein t_2 is about 1h.
16. A process according to any one of Claims 1 to 15 inclusive, wherein T_3 is about 170°C .
17. A process according to any one of Claims 1 to 16 inclusive, wherein t_3 is about 1h.
18. A process according to any one of Claims 1 to 17 inclusive, which includes introducing a reinforced material into the FA, into the polymerizable mixture and/or into the polymerized product before it is fully set, so that the polymerized product is a reinforced polymerized product.

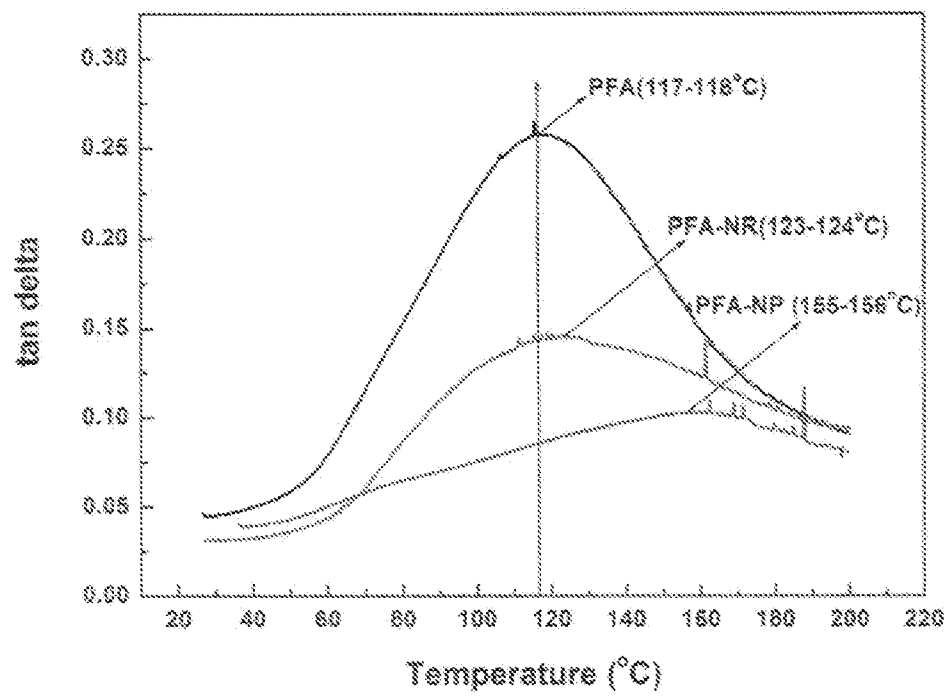


Figure 1 – $\tan \delta$ curves for polyfurfuryl alcohol based bioplastics.

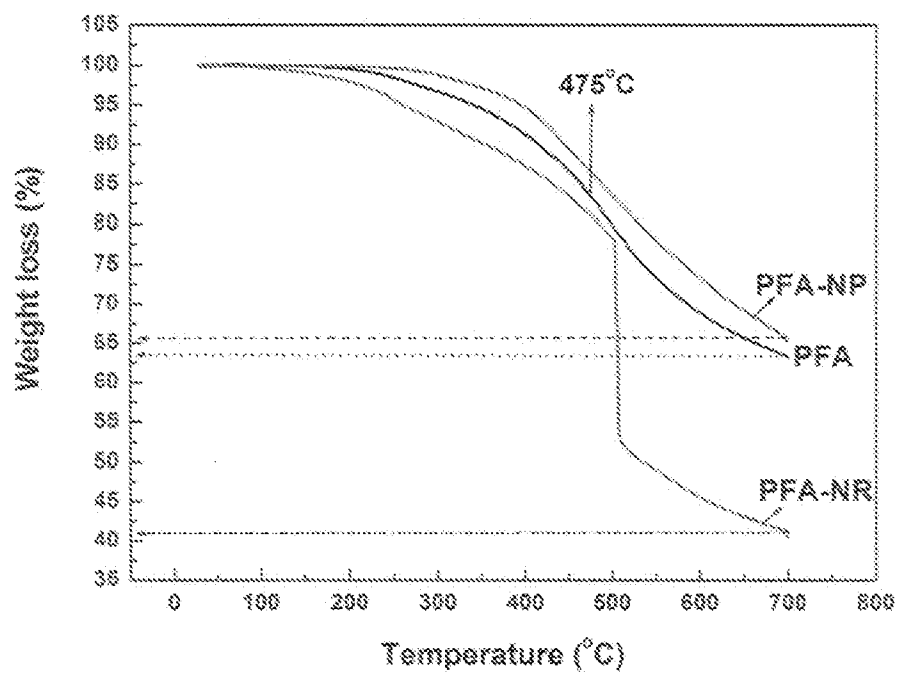


Figure 2 – Thermogravimetric curves of poly furfuryl alcohol based bioplastics.

INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G65/00
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)
C08G

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

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

EP0-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 271 421 A (ANWAR AKBAR MOHAMMED ET AL) 6 September 1966 (1966-09-06) examples 1-3	1-18
X	----- GB 595 208 A (HAVEG CORP) 28 November 1947 (1947-11-28) example 1	1-18
A	----- US 2 471 438 A (MCWHORTER JR PURNALL L) 31 May 1949 (1949-05-31) example I	1-18
A	----- US 3 158 592 A (NIELSEN ERIK R) 24 November 1964 (1964-11-24) example 1 ----- -/-	1-18

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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INTERNATIONAL SEARCH REPORT

International application No

PCT/IB2012/051201

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GONZALEZ R ET AL: "POLYMERIZATION OF FURFURYL ALCOHOL WITH TRIFLUOROACETIC ACID: THE INFLUENCE OF EXPERIMENTAL CONDITIONS", MAKROMOLEKULARE CHEMIE, HUTHIG UND WEPF VERLAG, BASEL, CH, vol. 193, no. 1, 1 February 1992 (1992-02-01), pages 1-09, XP000259409, ISSN: 0025-116X, DOI: 10.1002/MACP.1992.021930101 the whole document -----	1-18
A	CHOURA M ET AL: "THE ACID-CATALYZED POLYCONDENSATION OF FURFURYL ALCOHOL: OLD PUZZLES UNRAVELLED", MACROMOLECULAR SYMPOSIA, WILEY VCH VERLAG, WEINHEIM, DE, vol. 122, 1 August 1997 (1997-08-01), pages 263-268, XP000727275, ISSN: 1022-1360 the whole document -----	1-18

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2012/051201

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