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**Titre :** PROCÉDE DE DEPOLYMERISATION D’UN POLYESTER CONTENANT UN DICARBOXYLATE DE FURANE POLYESTER  
**Title:** PROCESS FOR THE DEPOLYMERIZATION OF A FURANDICARBOXYLATE-CONTAINING POLYESTER

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**Abrégé/Abstract:**  
A product comprising a furandicarboxylate compound and diol is obtained from a furandicarboxylate containing polyester in a process, which comprises reacting a polymer composition comprising furandicarboxylate containing polyester with water or an alcohol, such as an alkyl alcohol with from 1 to 12 carbon atoms, in the presence of a base, that is preferably selected from the group consisting of metal hydrides, metal alkoxides, metal carbonates, metal carboxylates, N-heterocyclic carbenes, amidines, guanidines, phosphazenes and mixtures thereof.
Abstract

A product comprising a furandicarboxylate compound and diol is obtained from a furandicarboxylate containing polyester in a process, which comprises reacting a polymer composition comprising furandicarboxylate containing polyester with water or an alcohol, such as an alkyl alcohol with from 1 to 12 carbon atoms, in the presence of a base, that is preferably selected from the group consisting of metal hydrides, metal alkoxides, metal carbonates, metal carboxylates, N-heterocyclic carbenes, amidines, guanidines, phosphazenes and mixtures thereof.
Process for the depolymerization of a furandicarboxylate-containing polyester

The present invention relates to a process for the depolymerization of a furandicarboxylate-containing polyester.

It is known to manufacture polyesters from furandicarboxylic acid or esters thereof and a diol. In this respect reference is made to GB 621971, wherein the preparation of polyesters has been described. In this preparation a glycol is reacted with dicarboxylic acids of which at least one contains a heterocyclic ring. As an example of such a dicarboxylic acid, 2,5-furandicarboxylic acid is mentioned.

EP 294863 describes aromatic polyesters that have liquid crystalline properties. The aromatic polyesters are characterised in that they contain heterocyclic units with two carbonyl groups. The heterocyclic unit may be derived from 2,5-furandicarboxylic acid, 2,4-furandicarboxylic acid, 2,3-furandicarboxylic acid or derivatives of these acids.

In US 2009/0124763 a polymer compound is provided that is the polymerisation product of a furandicarboxylic acid and a diol, and that has a polymerisation degree of 185 to 600. The polymer compound is stated to have excellent mechanical strength. The polymer compound that is exemplified contains 2,5-furandicarboxylate moieties and divalent hydrocarbon groups. Suitable hydrocarbon groups include alkylene groups with 2 to 5 carbon atoms. The polymer thus provided is used as structural material for ink tanks or toner containers or material for copiers, printers or cameras.

A process for the production of furandicarboxylic acids has been described in US 2007/0232815. According to this document furandicarboxylic acid can be prepared by the oxidation of a furan ring compound having two functional groups selected from a hydroxymethyl group, a formyl group and a carboxyl group with a metal permanganate in an alkaline environment. Alternative processes have been discussed in the opening paragraphs of this document. 5-Hydroxymethylfurfural appears to be a suitable starting compound for all processes. 2,5-Furandicarboxylic acid is stated to be a valuable intermediate for pharmaceuticals, agrochemicals, fragrances and so forth.

US 2009/0156841 teaches the production of 5-hydroxymethylfurfural by contacting a carbohydrate source with a solid phase catalyst. Agricultural raw material such as cellulose, starch, sucrose or inulin, can be used as starting material for the production of sugars such as hexoses and pentoses. These sugars are suitable carbohydrate sources for the production of 5-hydroxymethyl furfural. US 2009/0156841 further teaches that a mixture of hydroxymethylfurfural and one or more hydroxymethylfurfural esters may be oxidized to the
guide mechanism with respect to the main frame any forces exerted by the driving wheel may be easily absorbed by the transport unit.

According to a further embodiment there is provided a method for transporting a load along a rail comprising a strip, the method comprising:

engaging a drive wheel provided to a guide mechanism with the strip at an engagement point;

suspending a main frame from the guide mechanism with a bearing being positioned around, substantially equal and/or lower than the engagement point;

rotating the driving wheel so as to drive the guide mechanism along the rail; and,

allowing rotation of the guide mechanism with respect to the mainframe around the bearing.

These and other aspects, features and advantages will become apparent to those of ordinary skill in the art from reading the following detailed description and the appended claims. For the avoidance of doubt, any feature of one aspect of the present invention may be utilised in any other aspect of the invention. It is noted that the examples given in the description below are intended to clarify the invention and are not intended to limit the invention to those examples per se. Numerical ranges expressed in the format "from x to y" are understood to include x and y. When for a specific feature multiple preferred ranges are described in the format "from x to y", it is understood that all ranges combining the different endpoints are also contemplated.

Brief description of the figures

Embodiments of the invention will be described, by way of example only, with reference to the accompanying schematic drawings in which corresponding reference symbols indicate corresponding parts, and in which:

Figure 1a and 1b disclose a transport unit according to an embodiment of the invention;

Figure 2a discloses a stair lift with the transport unit of figure 1 and a chair mounted against it in a vertical bend of a rail;

Figure 2b discloses a stair lift with the transport unit 1 of figure 1 in a horizontal bend of a rail;

Figure 3 discloses a further embodiment according to the invention;

Figure 4a discloses a top view, figure 4b a front side view, figure 4c a bottom view, figure 4d a side view and figure 4e a back side view on a further embodiment according to the invention; and,
furandicarboxylate and mixtures thereof. However, mechanical strength has been shown to be a significant property of the polymers that have 2,5-furandicarboxylate moieties. Accordingly, the polymer composition of the present invention preferably comprises 2,5-furandicarboxylate containing polyester.

In addition to furandicarboxylate moieties, the polyester may comprise one or more other diacid or alpha/omega hydroxy carboxylic acid residues. Examples of other diacids include phthalic, isophthalic, terephthalic acid and alpha/omega alkylene-dicarboxylic acids, having from 2 to 10 carbon atoms. Examples of hydroxycarboxylic acids include lactic acid, citric acid, 3-hydroxypropionic acid, 3-hydroxy-2-methylpropionic acid, 3-hydroxybutanoic acid, 3-hydroxy-2-methylbutanoic acid, 3-hydroxy-2-methylpentanoic acid, 3-hydroxy-3-methylbutanoic acid, 2,3-dimethyl-3-hydroxybutanoic acid and 3-hydroxy-3-phenylpropionic acid.

The furandicarboxylate containing polyesters comprise moieties that result in a diol after depolymerisation. The furandicarboxylate polyesters may further comprise other moieties with at least two functional groups. The functional groups are suitably selected from amino, thiol and hydroxyl groups. Suitably these functional groups form part of monomers that also comprise alkylene groups. Preferably, the polyester is constituted by furandicarboxylate units and residues of diols. These diols may comprise di- or trialkylene glycol groups such as diethylene glycol, triethylene glycol, dipropylene glycol or tripolyethylene glycol. The preferred diols are alkylene diols. As has been described in the prior art, the alkylene group in the furandicarboxylate containing polyester may be selected from a variety of alkylene groups. So, preferably, the polyester comprises poly(alkylene 2,5-furandicarboxylate). Suitably, the alkylene groups, in particular those in the poly(alkylene 2,5-furandicarboxylate), comprise from 2 to 6 carbon atoms. Such groups include linear moieties such as hexamethylene, pentamethylene, tetramethylene, trimethylene and ethylene. Also branched alkylene groups may be used, such as 1,2-propylene, iso-butylene, s-butylene, isopentylene and neopentylene. Advantageously, the alkylene group is selected from linear hydrocarbyl groups having 2 to 4 carbon atoms.

The molecular weight of furandicarboxylate containing polyester that can be subjected to depolymerisation of the present invention is not critical. The polymer may be selected from oligomers to high molecular weight polyesters. US 2009/0124763 discloses poly(alkylene furan dicarboxylate) having a polymerisation degree of 185 to 600, corresponding to number average molecular weights that theoretically may vary from about 33,000 to 135,000. Such polyesters can suitably be depolymerised in the present process.

As indicated above, the polymer composition that is used in the present process can be any composition that contains the furandicarboxylate containing polyester. Advantageously, the polymer composition has been obtained from polyester waste. The waste can be from any source, including the applications of electric and electronic
components and the like, as described in US 2009/0124763. Especially in the case of waste, the furandicarboxylate containing polyester may suitably be part of a polymer composition further comprising one or more polymers selected from the group consisting of polyethylene-
terephthalate, polyolefins, polyvinylchloride, polylactic acid, polyamides and mixtures thereof,

Dependent on the desired use of the product of the depolymerization, the skilled
person may select water or an alcohol. Suitably the alcohol is selected from those alcohols
that comprise from 1 to 12 carbon atoms. Since the depolymerization runs most smoothly
with the use of the lower alcohols, i.e. alcohols having from 1 to 4 carbon atoms, the more
preferred alkyl alcohols are methanol, ethanol, ethylene glycol, 1,3-propane diol, 1,4-butadiol
or mixtures thereof. In some instances it is advantageous to depolymerise the
furandicarboxylate containing polyester first in the presence of a diol, such as ethylene glycol,
and to transesterify the product thus obtained with a different alcohol, suitably a monoalcohol
such as methanol or ethanol.

The state of the art has disclosed a large number of depolymerisation catalysts. Such
catalysts include acidic catalysts, such as mineral acids, e.g. hydrochloric acid, sulphuric acid
and phosphoric acid. Other suitable acids include sulphinic acids, such as methane
sulphinic acid or p-toluene sulphinic acid, and carboxylic acids, e.g. those having from 2 to
20 carbon atoms. It is also possible to use various metal compounds as depolymerisation
catalyst. The metal of these compounds can be selected from a wide range, including the
alkaline earth metals, manganese, zinc, titanium and other transition metals. The anionic
moiety of the compounds is not critical and may include carboxylate, such as acetate, halide,
such as chloride, carbonate and sulphate. Preferably, the catalyst comprises a base.
Advantageously, the catalyst is homogeneous. The catalyst can be any homogeneous basic
catalyst known to those skilled in the art. Suitably, the homogeneous catalyst is selected from
the group consisting of metal alkoxides, metal hydroxides, metal carbonates, metal
carboxylates and mixtures thereof. The metal is such group is suitably selected from the alkali
metals, in particular sodium and potassium. When as product of the depolymerisation an
ester is envisaged and the depolymerisation takes place in an alcohol, the metal alkoxide is
preferably derived from the same alcohol as the alcohol in which the depolymerization takes
place. For example, if the reactant alcohol is methanol then the catalyst might be a metal
methoxide such as sodium or potassium methoxide.

Other suitable organic basic depolymerisation catalysts may be chosen from other
saponification or transesterification catalysts including N-heterocyclic carbenes, such as
triazol-5-ylidenes or 1,3-disubstituted imidazol-2-ylidene as disclosed in, e.g. J. Chem. Educ.,
87 (2010) 519-521 and Organic Lett., 4 (2002) 3587-3590, amidines, such as those
disclosed in EP 110 629, guanidines, such as di- or triphenylguanidine, guanidine carbonate
or tetramethylguanidine and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), and phosphazenes.
Phosphazenes are a class of chemical compounds in which a phosphorus atom is covalently
Figure 2b discloses a stair lift with the transport unit 1 of figure 1 in a horizontal bend of a rail 29 with a strip 31. The first and second intermediate frame 9 may be rotatable connected with the first and second guide frame 11 around axis 23 (see figure 1a). Visible is that in a horizontal bend of the rail both the first and second intermediate frame 9 may be rotated around the axis 23 so as that the guide frames 11 and the guide mechanisms 5 may follow the rail 29. The chair 27 may be connected to the transport unit 1 with a rotating axis driven by a motor 33 so as to keep the chair horizontal during driving over the rail.

Figure 3 discloses a further embodiment according to the invention. In this embodiment only one of the guide mechanisms 5 may be provided with a driving wheel 15. The other guide mechanism 35 is only provided with guides which may function to keep the transporting unit 1 in the right position on the rail. The driving axis of the driving wheel 15 may have a bearing in the guide frame 11 and in the guide mechanism 5 similar as the embodiment of figure 1a. In this way the driving axis functions to suspend the guide frame 11 from the guide mechanism 5. The transport unit may again comprises a protrusion below the guide frame 11 and which may be moveable in a slot (not shown) in the top of the guide mechanism 5. The protrusion in the slot may function as an end-stop for the rotation of the guide mechanism 5 and may provide a connection with the guide frame 11 above the engagement point of the driving wheel 15 so as to compensate for a torque of the guide mechanism 5 with respect to the guide frame 11 in a direction around the rail 29.

Figure 4a discloses a top view, figure 4b a front side view, figure 4c a bottom view, figure 4d a side view and figure 4e a back side view on a further embodiment according to the invention. A transport unit 41 is provided with a main frame 42 and a guide mechanism 43. The guide mechanism 43 may be provided with at least two guides (not shown) to guide the transport unit along a rail and a drive mechanism provided with a drive wheel for driving the transport unit along the rail by engaging the strip at an engagement point, wherein the main frame 42 may be suspended from the guide mechanism 43 in a vertical position 45 around, substantially equal and/or lower than the engagement point. With around an engagement point a distance to the engagement point of less than 25 centimetres, preferably less than 10 centimetres and most preferably of less than 5 centimetres is meant. With substantially equal a distance to the engagement point of preferably less than 15 centimetres preferably less than 10 and most preferably less than 5 centimetres is meant. The guide mechanism 43 may be provided with a ball bearing 47 which may be provided in a space in the main frame 42 so as to suspend the weight of the mainframe 42 and any weight carried by it. Figure 4a discloses further a protrusion 49 provided to the drive mechanism 43. The protrusion fits in an opening 51 of the main frame 42. The opening 51 may be large enough to allow the protrusion 49 to move with respect to the main frame 42. In this way the main frame 42 comprises a connection with the guide mechanism 43 in a
from the product stream. The recovery of furandicarboxylate and diol may be easily effected by means of conventional separation techniques, such as precipitation and filtration or distillation. Optionally, the recovered products may be subjected to further purification. When water and a base are used, free dicarboxylic acid is suitably obtained after treatment of the recovered product with a Brønsted acid. Evidently, the selection of the Brønsted acid is not critical. The acid may be a mineral acid, such as hydrochloric, sulphuric or nitric acid, but it may also be an organic acid, such as a carboxylic acid, e.g. acetic acid or formic acid, or an alkane sulphonic acid, e.g., methane sulphonic acid, or an arene sulphonic acid, e.g., p-toluene sulphonic acid.

The furandicarboxylate that is recovered from the product stream may be used for various objectives, including for use as fuel or fuel additive. Since the alkyl esters of furandicarboxylic acid are excellently suited for use in the manufacture of furan dicarboxylate containing polyesters, at least part of the furan dicarboxylate that has been separated from the product stream is suitably used for the manufacture of furandicarboxylate containing polyesters. However, as already indicated above, the starting materials that have been recovered can be utilised for any purpose.

The invention will be further illustrated by means of the following examples.

EXAMPLE 1

Into a 10 mL vial equipped with a magnetic stir bar the following materials were placed: 0.50 g poly(butylene 2,5-furandicarboxylate) (PBF) (particle size 0.6-1.4 mm, number average molecular weight M[n]=17900), 5.0 mL methanol and 0.067 mL 25 wt% solution of sodium methoxide (c(final)=0.058 mol/L). The vial was placed to a 90 °C oil bath and stirring was started. The polymer dissolved completely within 30 minutes. The reaction mixture was left in the bath for another 90 minutes. The solution was transparent though slightly yellow. It was cooled down to ambient temperature and dimethyl 2,5-furandicarboxylate (DMF) crystallized out. The crystals were filtered and dried in a vacuum desiccator. The process yielded 265.6 mg dimethyl 2,5-furandicarboxylate (60.6%). When some methanol was evaporated from the solution, more DMF crystallised out. This indicates that the yield is determined by the solubility of DMF.

EXAMPLE 2

Into a 10 mL vial equipped with a magnetic stir bar 1.00 g poly(ethylene 2,5-furandicarboxylate) (PEF) (M[n]= 15,100, particle size of 0.6-1.4 mm) and 5 mL 2.5 M sodium hydroxide solution were placed. The vial was closed and heated at 100 °C for six hours under stirring. After that, the solution was cooled down to room temperature, filtered and diluted with 5 mL water. The diluted solution was then acidified under stirring with 2.5 M hydrochloric acid solution until pH 2. The precipitated white 2,5-furandicarboxylic acid was filtered, washed with water and dried in vacuum at ambient temperature overnight. The yield was 710.5 mg (82.9%).
EXAMPLE 3

Into a 10 mL vial equipped with a magnetic stir bar the following materials were placed: 0.50 g PEF (d<0.2 mm, M_n=16,200), 5.0 mL methanol and 40.1 mg 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) (c(final)=0.058 mol/L). The vial was placed to a 90 °C oil bath and stirring was started. The polymer dissolved completely within 4 minutes. The reaction mixture was left in the bath for another 30 minutes. The solution was transparent though slightly yellow. It was cooled down to ambient temperature when dimethyl 2,5-furandicarboxylate (DMF) crystallized out. The crystals were filtered and dried in a vacuum desiccator. The process yielded 318.0 mg dimethyl 2,5-furandicarboxylate (63.1 %).

EXAMPLE 5

Comparison of methanolysis rate of PET and PEF.

Tensile bars were made from PET, poly(ethyleneterephthalate) (M_n 16,800), and PEF (M_n 16,200) with exactly the same dimension of 10x52x1 mm. The bars were placed separately into 13 mL methanol solution of sodium methoxide (c=0.044 mol/L) and the two vials were heated in the same oil bath at 90 °C.

After a given time, the vials were transferred into an ice bath, the bars dried and weighed. The results are shown in Table 1.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Weight (mg)</th>
<th>PET</th>
<th>PEF</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>768.1</td>
<td>787.6</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>765.1</td>
<td>607.9</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>758.9</td>
<td>474.8</td>
<td></td>
</tr>
<tr>
<td>75</td>
<td>755.1</td>
<td>419.7</td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>751.5</td>
<td>379.7</td>
<td></td>
</tr>
</tbody>
</table>

Table 1 shows that the PEF bar dissolves much faster than the PET bar, indicating that the methanolysis rate is much faster for PEF than for PET.
Claims

1. Process for the depolymerization of a furandicarboxylate containing polyester, which process comprises reacting the polyester with an alcohol or water in the presence of a depolymerisation catalyst to yield a product comprising a furandicarboxylate compound and diol.

2. Process according to claim 1, wherein the polyester comprises poly(alkylene 2,5-furandicarboxylate).

3. Process according to claim 2, wherein the alkylene moiety of the poly(alkylene 2,5-furandicarboxylate) comprises 2 to 6 carbon atoms.

4. Process according to any one of claims 1 to 3, wherein the depolymerisation catalyst comprises an acid catalyst, a metal compound or a base.

5. Process according to claim 4, wherein the depolymerisation catalyst comprises a base.

6. Process according to claim 5, wherein the base is selected from the group consisting of metal alkoxides, metal hydroxides, metal carbonates, metal carboxylates, N-heterocyclic carbenes, amidines, guanidines, phosphazenes and mixtures thereof.

7. Process according to any one of the preceding claims, which is preceded by dispersing at least part of the polyester in an alcohol or water to yield a polyester slurry.

8. Process according to any one of the preceding claims where, when water and a base are used, free dicarboxylic acid is obtained after treatment with a Brønsted acid.

9. Process according to any one of the preceding claims, wherein the furandicarboxylate containing polyester is part of a polymer composition further comprising one or more polymers selected from the group consisting of polyethyleneterephthalate, polyolefins, polyvinylchloride, polylactic acid, polyamides and mixtures thereof.
10. Process according to claim 9, wherein the polymer composition has been obtained from waste.

11. Process according to any one of the preceding claims, wherein the alcohol comprises from 1 to 12 carbon atoms, the alcohol preferably being methanol, ethanol, ethylene glycol, 1,3-propane diol, 1,4-butadiol or a mixture thereof.

12. Process according to any one of the preceding claims, wherein the reaction temperature ranges from room temperature to 350 °C.

13. Process according to any one of the preceding claims, wherein the process is performed in batch mode.

14. Process according to any one of claims 1 to 12, wherein a stream containing the polymer composition is continuously fed into a reactor and a product stream containing furandicarboxylate compound and diol is continuously withdrawn from the reactor.

15. Process according to claim 14, wherein the process is conducted in a continuous stirred tank reactor.

16. Process according to claim 14 or 15, wherein furandicarboxylate compound is separated from the product stream.

17. Process according to claim 16, wherein at least part of the furandicarboxylate compound that has been separated from the product stream is used for the manufacture of poly(alkylene furandicarboxylate).