

A METHOD TO ENABLE THE RECYCLING A STREAM OF POLYESTER WASTE MATERIAL AND A SYSTEM FOR APPLYING THE METHOD

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GENERAL FIELD OF THE INVENTION

10 The invention pertains to the field of recycling polyester waste material, in particular material comprising semi-crystalline polyester such as polyethylene terephthalate (PET), and to systems for applying such a recycling process.

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BACKGROUND OF THE INVENTION

Polyester, such as PET as commonly used for soda bottles and yarn materials for producing textiles, is commonly recycled. The post-consumer polyester recycling
20 industry started as a result of environmental pressure to improve waste management. The other aspect that acts as driving force for polyester recycling industry is that polyester products have a slow rate of natural decomposition. Many polyesters are non-degradable plastics in normal conditions since there is no known organism that can consume its relatively large molecules. Complicated and expensive procedures need to
25 be operated in order for polyester to degrade biologically.

The first recycling effort of polyester waste material (i.e. post-consumer polyester objects or material) in the world was in the 1970's but the development of adequate recycling processes evolved quickly. As an example, the total consumption of PET in
30 Australia for the year 2000 was 88,258 tons, in which 28,113 tons were recovered demonstrating a recovery rate of about 32%. Many researchers reported that in order to achieve successful PET recycling, PET flakes should meet certain minimum requirements. The major factor affecting the suitability of post-consumer PET flakes for recycling is the level and nature of contaminants present in the flakes. Minimising the
35 amount of these contaminants leads to better rPET (i.e. recycled PET) quality. PET is contaminated with many substances such as acid producing contaminants, water,

colouring contaminants, acetaldehyde and other contaminants such as detergents, fuel, pesticides, etc. due to the use of PET bottles for storing these substances.

5 Various distinct types of processes have been applied in order to recycle polyester waste materials, each having their pros and cons.

10 A first class of processes for recycling polyester waste material is so-called energetic recycling such as pyrolysis and carbonisation. Pyrolysis of polyester waste was first described in the early 1980's. It is an alternative to PET disposal in landfills. In general, polyester waste is pyrolysed without further purification of the plastic waste. The majority of pyrolyses are conducted to produce aliphatic and aromatic hydrocarbons as an alternative for fossil fuels or as a source for chemicals. Carbonisation is a second method of pyrolyzing polyester waste materials.

15 A second class of processes for recycling polyester waste material is the mere sorting of the polyester waste material, followed by use of the sorted materials as additive in stone mastic asphalt, cementitious materials, mortars or concrete composites. Since polyester waste may be supplied in mixtures with other polymers, the polyester material has to be separated from these polymers prior to re-processing. Therefore, several methods have
20 been developed including froth flotation, wet shaking table, swelling or thermo-mechanical procedures

Next to this, there is a class of processes that are based on (thermo-) mechanical methods to recycle polyester waste material. The simplest way of thermo-mechanical
25 recycling is re-melting the sorted polyester waste. This method is applied for example in bottle-to-bottle technologies, where sorted PET-bottles are re-melted in crushed shape and reprocessed to bottles as beverage packaging. Several studies have been conducted on thermal re-processing PET. During this process, the polymer is exposed to high temperatures, shear forces and pressures. Thus, thermal degradation of PET
30 occurs. As a consequence, reduced thermal and mechanical properties of the re-processed material typically occur. Hence, a repeated thermal re-processing of polyester waste leads to a downcycling of the material. The problem of unwanted colouration of the recycled polyester material is typically overcome by using additives. Since the collection of polyester waste entails generally a mixture of differently coloured
35 polyester materials, such thermally re-processed material leads to undesired colouration of recycled polyester. Therefore, the addition of complementary colours to

polyester waste has been applied to mask discolouration. Although being an approved procedure, this method severely limits the use of the recycled polyester, in particular as a food packaging material.

- 5 A fourth class of processes to recycle polyester waste are the so-called chemical recycling (chemolysis) processes, wherein recycling of polyester waste material is enabled by depolymerisation into monomers and/or oligomers. This class can be divided in numerous sub-classes depending on the type of reactant used for the chemolysis. With chemolysis a polyester can be broken down to its monomeric
10 components, which in theory means that the starting point for making new polyester polymer corresponds to that of when starting with virgin materials.

An example is the application of ionic liquids for de-polymerisation, first described around the year 2000. This method was developed to avoid the drawbacks of other
15 methods like alcoholysis (high pressure and temperature as well as a heterogeneous reaction product) or acidic and alkaline hydrolysis (pollution problems) to provide an eco-friendly degrading agent for polymers and to enable degradation under moderate reaction conditions. However, no application of the obtained reaction products has hitherto been described.

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As an alternative castor oil is applied for de-polymerisation. This method was developed to provide a renewable substitute of petrochemical agents (for example, glycols) for PET de-polymerisation. After de-polymerisation, the reaction products were aimed for the preparation of polyurethane systems. However, it appears to be very difficult to
25 determine characteristic molecular weights due to the excessive amount of applied castor oil. Also, even with precise control of the reaction temperature a heterogeneous mixture of reaction products is obtained.

The degradation of polyester polymers using enzymes was first described in the 1970's.
30 As the use of ionic liquids and castor oil, this bio-chemical method was developed to provide an eco-friendly procedure of polymer recycling in contrast to conventional chemical recycling methods. However, efficiency is rather low with respect to complete de-polymerisation of the polyester and hence quantitative recovery of homogeneous reaction products for re-use is not possible.

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Alcoholysis for de-polymerisation of PET was first described in the early 1990's. This

method was developed to avoid the drawbacks of the acidic and alkaline hydrolysis (pollution problems) to provide a renewable and more eco-friendly degrading agent for polymers. Generally, polyester is de-polymerised with an excess of an alcohol to yield corresponding esters of the corresponding acid and ethylene glycol.

5 Among the alcoholysis methods, reaction with methanol has gained special importance because of the low price and the availability of methanol. Also ethylene glycol (a diol, the use of which is sometimes classed separately as "glycolysis", although it falls in the class of alcoholysis) is used mainly in reactive extrusion to produce low molecular weight oligomers. However, these oligomers have to be separated and purified for

10 further processing, since the crude reaction product consists of a heterogeneous mixture of monomer, oligomers and polymers. Various other alcohols are described to be useful such as pentaerythritol, 1-butanol, 1-pentanol and 1-hexanol and 2-ethyl-1-hexanol. Also other diols than ethylene glycol, like BHET, neopentyl glycol (NPG), tetraethylene glycol (TEEG), polyethyleneglycol, polytetramethylene oxide and

15 terpoly[poly(oxyethylene)-poly-(oxypropylene)-poly(oxyethylene)] are described in the art for depolymerising polyester by alcoholysis. However, in all cases mixtures of undefined low molecular weight oligomers are typically obtained. Another serious downside of alcoholysis is the need for a catalyst. The most important catalysts have been zinc acetate and manganese acetate. Further catalysts are cobalt and lead acetate. The

20 need of such catalysts hamper the wide application of alcoholysis for recycling polyester waste material.

Aminolysis and ammonolysis were developed for polyester recycling, since the reactivity of the amine-group is higher than the hydroxyl-group of alcohols used for

25 alcoholysis of polyester. However, as far alcoholysis, the need for a metal catalyst remains.

Lastly, an alternative chemical recycling of polyester is given by the controlled de-polymerisation of polyester using blocking chain scission with defined amounts

30 of the de-polymerisation agent (see Geyer et al. in *eXPRESS Polymer Letters* Vol.10, No.7 (2016) 559–586). This method produces polyester oligomers of well-defined molecular weights in a greater range than existing chemical methods like alcoholysis. However, this method requires sorted polyester material, which has to be free of

contaminants.

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While energetic and thermo-mechanical recycling entail downcycling of the material,

chemical recycling requires considerable amounts of chemicals, and chemical recycling has as main disadvantages being its high costs, the variability of the end product (which largely depends on the type of waste material), the need for using a (metal) catalyst and the difficulty of removing colourants. Therefore, a need exists for improved methods, systems and process to enable the recycling of polyester waste materials.

OBJECT OF THE INVENTION

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It is an object of the present invention to devise a process and system that allows in an economic and advantageous way the recycling of polyester waste materials, into to a high grade new polyester.

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SUMMARY OF THE INVENTION

In order to meet the object of the invention a process was developed to enable the recycling of a stream of polyester waste material by depolymerising the polyester present in the stream of polyester waste material into a reactive oligomeric ester, the process comprising providing the polyester in a liquid form in a reactor, and feeding an alcohol to the reactor to subject the polyester to the alcoholysis to depolymerise the polyester, while at the same time adding an amount of water and an amount of carboxylic acid (i.e. while depolymerising the polyester by the alcoholysis), to form the reactive oligomeric ester.

Surprisingly it was found that in the current alcoholysis process, even in the absence of a catalyst, when water and a carboxylic acid are co-fed while the depolymerisation induced by the alcohol takes place, an oligomer may be obtained with a high number of reactive groups (denoted as "reactive oligomeric ester", having groups that can react to form the ester linkages), even higher than expected based on the respective amounts of water and acid used. In other words, a synergy was found between the water and the carboxylic acid, which synergy led to the very advantageous process of arriving at an oligomer that can be reacted in a relatively short time and if desired, at a relatively low temperature, to a polyester. This way, apart from saving energy, unwanted thermal

degradation during the process of repolymerisation of the recycled polyester can be prevented or at least minimised. It appears that oligomers that are the result of a depolymerisation reaction are more prone to thermal degradation than oligomers made of virgin materials. The reason for this is unclear, but the result is that the known
5 alcoholysis and repolymerisation process may ultimately lead to a partly degraded polymer, which shows as a slight, yellowish discolouration, making the material less suitable, or even unsuitable for high end applications. This problem may be overcome by the current process.

10 Adding carboxylic acid while depolymerising a polyester seems counterintuitive for an economic depolymerisation process, but it was found that it actually stimulates the process of ending up with a highly reactive oligomer while not substantially negatively influencing the depolymerisation process. On the contrary, the synergy with water stimulates the provision of the highly desired reactive oligomers which can be used in a
15 fast repolymerisation process, this way minimising the unwanted thermal degradation that is typically seen when repolymerising pre-polyester products obtained from a polyester waste stream.

Also, the addition of water and the carboxylic acid provide the opportunity to fine tune
20 the relative amount of the reactive groups, which makes the material more suitable for use in a process wherein virgin compounds (alcohols, acids, oligomers, etc.) are copolymerised with recycled compounds.

The process of depolymerising a polyester by alcoholysis into oligomeric esters as such
25 is known from the prior art, such as e.g. from WO 2022/003084 (assigned to Cure Technology BV). Also, it is described that for repolymerisation of the oligomers, the mixture may be exposed in a so called condensation reactor to a low pressure. However, such condensation processes typically require long reaction times at relatively high temperatures and thus, may lead to thermal degradation processes. With the
30 present invention, repolymerisation can take place in considerably less time and a pre-condensation step may not even be necessary anymore.

It was found that the invention is effective for different types of polyesters, since the chemistry is basically the same. Correspondingly, the type of alcohol is not essential to
35 the depolymerisation process as such, and thus to obtain a reactive oligomeric ester for repolymerisation. Depending on the type of polyester, type and amount of alcohol,

one may arrive at different levels of de- and repolymerisation (when the other circumstances, such as residence time, are the same), or vary the circumstances to arrive at a predetermined level of de- or repolymerisation. This can be controlled i.a. by measuring the viscosity of the (partly depolymerised) polyester mixture, residence time
5 in the various reactors and other circumstances such as temperature and pressure. For any type of polyester at its various stages of de- and repolymerisation by a particular alcohol, a reference curve can be made beforehand that defines e.g. the relationship between viscosity and grade of polymerisation such that the required level of polymerisation can be obtained. Typically however, diols such as ethylene glycol, 1,3-
10 propanediol, butanediol, cyclohexane dimethanol and neopentyl glycol are used in the art, and advantageously also in the present invention.

It is noted that in the art processes that partly use features of the present invention. For example, CZ 299244 (assigned to Sirek Milan) discloses a process of combined
15 alcoholysis and hydrolysis of waste PET based on the principle of two-stage decomposition to terephthalic acid salt and ethylene glycol. In the known process, in the first stage of the process the PET waste is degraded by simultaneously running extrusion hydrolysis and glycolysis, and wherein in the second stage a melt of the resulting oligomeric products of the PET reactive extrusion leaving the first stage, is
20 subjected in a continuous sequence and under continuous dosing of aqueous solution of alkali metal hydroxide and/or ammonium hydroxide to basic hydrolysis in the presence of a catalyst. The resulting product, e.g. pure terephthalic acid, is then used for repolymerisation.

25 WO2023281531 (assigned to C. Venkatesh) describes a process to synthesise hydroxyl and carboxyl functional oligomers from recycled PET and products thereof via depolymerisation of waste polyester in glycerin and/or triglyceride to yield OH-functional oligomers, which are thereafter reacted with anhydrides or polyfunctional acids to yield COOH-functional oligomers. However, there is no step of a combined
30 alcoholysis/hydrolysis in the presence of a carboxylic acid.

WO2023084378 (assigned to SHPP Global Technologies BV) describes a method for converting PET to TPA (terephthalic acid) via catalysed (using $\text{Zn}(\text{OAc})_2$) glycolysis at 150-230°C, followed by hydrolysis (using NaOH/water) at 35-100°C, and lastly
35 acidification (using HCl) to yield purified TPA. However, there is no step of a combined alcoholysis/hydrolysis in the presence of a carboxylic acid.

WO2023060768 (assigned to the NAT INDUSTRIAL INNOVATION CENTER OF POLYMER MATERIALS CO LTD) describes a method for preparing regenerated polyester by means of closed-loop recovery of waste polyester via microwave assisted glycolysis (in presence of e.g. NaCl, $(\text{Na})_2\text{CO}_3$, or AC). There is no step of a combined alcoholysis/hydrolysis in the presence of a carboxylic acid, although the polymerisation process is a microwave assisted polymerisation in presence of polyol, a chain extender and a catalyst in the presence of a dibasic acid.

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US 4620032 (assigned to Celanese Corporation) discloses a two-stage depolymerisation process, aiming at repolymerisation to a high grade polyester, based on hydrolysis. In particular, in the known process the polyester is intimately mixed with a depolymerising agent which is either one of the products resulting from the complete hydrolytic depolymerisation of the condensation polymer or water. The depolymerisation agent is mixed with the polyester for a time sufficient that the molecular weight of the polyester in a first stage is reduced by at least 50%. The treated condensation polymer of lower molecular weight is thereafter subjected in a second stage to neutral hydrolysis to effect complete hydrolytic depolymerisation to a monomeric material, which material that can be used for repolymerisation.

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WO9720886 (assigned to Eastman Chemical Company) discloses a one stage batch process wherein postconsumer or scrap polyester is reacted with glycol to produce a monomer or low molecular weight oligomer by depolymerisation of the polyester. The monomer or oligomer, as the case may be, is then purified using one or more of a number of steps including filtration, crystallisation, and optionally adsorbent treatment or evaporation to be able and used in a subsequent repolymerisation process to arrive at a polyester.

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The present invention also pertains to a system for recycling a stream of polyester waste material, the system comprising in consecutive order 1) an extruder, 2) a depolymerisation reactor and 3) a finishing polymerisation reactor, wherein the system is constituted such that polyester waste material is fed from the extruder to the depolymerisation reactor while at the same time alcohol, water and a carboxylic acid are independently fed to the depolymerisation reactor, wherein the extruder, the depolymerisation reactor and the finishing reactor are operatively coupled such that a

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stream of polyester waste material is able to flow from an entrance of the extruder to an outlet of the finishing polymerisation reactor in a continuous manner, while thus undergoing the subsequent processes of depolymerisation and repolymerisation.

- 5 The invention also pertains to a process for polymerising an oligomeric ester, comprising feeding a liquid mixture comprising the reactive oligomeric ester obtainable in a method as described here above in a continuous manner to a finishing polymerisation reactor. It was found that the reactive oligomeric ester is suitable for direct repolymerisation in a finisher reactor, not needing to use the common step of a
10 condensation reactor before the mixture is fed to the finisher.

The invention also pertains to a process for obtaining a polyester polymer (which could also simply be called "a polyester"), comprising mixing the reactive oligomeric ester obtained as described here above from a stream of polyester waste material, and a
15 virgin pre-polyester material (which can be one or more monomers and/or oligomers, as long as they have not been used before for producing a polymer), and reacting the oligomeric ester and the virgin pre-polyester to form the polyester polymer. The ratio between the amount of reactive oligomeric ester obtained by alcoholysis of a post-consumer polyester, and the virgin pre-polyester material is not critical and depends
20 mainly on the availability of various materials in the market as well as their price. Any ratio between these two materials between 1:100 and 100:1, in particular between 1:10 and 10:1 such as for example 1:1 respectively, is possible to obtain a high grade polyester.

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DEFINITIONS

A *polyester* is a polymer in which 100 monomer units or more are linked together by an
30 ester group. They are typically formed by polymerising a polyhydric alcohol with a polybasic acid, and used mainly in the manufacture of resins, plastics, and textile fibres. It is well known that polyesters may be prepared by a condensation polymerisation process in which monomers providing the "acid component" (including ester-forming derivatives thereof) are reacted with monomers providing a "hydroxyl component". If
35 desired the polyesters may also comprise other linking groups such as for example a proportion of carbonylamino linking groups -C(=O)-NH- (i.e. amide linking group) or -

C(=O)-N-R²- (tertiary amide linking group). Polyester as used in ever-day live can be aliphatic, semi-aromatic or aromatic. Typical examples are polyglycolic acid (PGA), polylactic acid (PLA), polycaprolactone (PCL), polyhydroxyalkanoate (PHA), polyhydroxybutyrate (PHB), polyethylene adipate (PEA), polybutylene succinate (PBS),
5 poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), polyethylene terephthalate (PET), polybutylene terephthalate (PBT), polytrimethylene terephthalate (PTT), polyethylene naphthalate (PEN), polyethylene furanoate (PEF) and Vectran, a polycondensation product of 4-hydroxybenzoic acid and 6-hydroxynaphthalene-2-carboxylic acid. Of these PET, also abbreviated as PETE, or the obsolete PETP or PET-P,
10 P, is the most common thermoplastic polymer resin of the polyester family and the virgin material is considered as one of the most important engineering polymers of the past decades. It is regarded an excellent material for many applications and is used in fibres for clothing, containers for liquids and foods, thermoforming for manufacturing, and in combination with glass fibre for engineering resins. It is also referred to by brand names
15 such as Terylene, Arnite, Eastapac, Mylar, Lavsan, Dacron etc. A polyester may contain up to 50% (w/w) of non-polyester polymer chains (e.g. 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 15, 20, 25, 30, 35, 40, 45, 50%) while still being referred to as a polyester material.

A *pre-polyester* is any compound that can be reacted, either alone or in combination
20 with one or more other compounds, to form a polyester. A pre-polyester includes for example monomeric alcohols and acids, and ester oligomers.

An *oligomer* is a short polymer having from 5 to 100 repeating monomeric units in its chain. For example, a PET oligomer having between 5 and 20 BHET units is any
25 oligomer from pentamer to eicosamer.

The *melting temperature* of a polyester is the temperature above which the polyester has the properties of a liquid. Since many polymers typically do not have a very sharp melting point, the melting temperature may be the highest temperature of a fairly broad
30 temperature range in which the polymer slowly becomes "leathery," then "tacky," and then finally liquid.

A *polyester waste material* is a post-consumer material at or after the end of its consumer life-time, i.e. the time during which it is used by a consumer for practical or
35 esthetical purposes., which in essence is composed of polyester and up to 10% (e.g. 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10) of additives like fillers (e.g. fibrous like material or particulate

matter), stabilisers, colourants etc.

A *virgin* material is a pre-consumer material that is made directly from unused raw material and thus has never been subjected to any processing other than for its
5 production.

Depolymerising means to lower molecular weight, by breaking down the original polyester molecules to shorter length molecules down to for example oligomers.

10 A *finishing polymerisation reactor*, often a so-called rotating disc reactor (see e.g. US 3,728,083 assigned to Allied Chemical Corporation) is a reactor wherein large vapor-liquid surface areas are provided, increasing the interface between the liquid mixture and the gaseous head space at least 5 times with respect to a horizontal cross section of the reactor, to be able and efficiently extract volatile materials such as alcohols.

15 A *continuous* process is a flow production process used to process materials without interruption. In such a process the materials, for example dry bulk or fluids are continuously in motion, undergoing chemical reactions and/or subject to mechanical or heat treatment. A continuous process is contrasted with a batch process.

20 An *alcohol* is a hydrocarbon substance or mixture of such substances formed when a hydroxyl group is substituted for a hydrogen atom in the hydrocarbon. The alcohol can be monovalent, divalent (i.e. a diol), etc.

25 *Intrinsic viscosity* is a measure of a solute's contribution to the viscosity η of a solution, see "*Progress in Biophysics and Molecular Biology*" (Harding 1997). The IV (or iv) can be measured according to DIN/ISO 1628. Typically, a concentration of 1% for the polymer is used and m-cresol as solvent, wherein the IV can be expressed in dL/g (often presented without the latter dimension). A practical method for the determination
30 of intrinsic viscosity is by using an Ubbelohde viscometer.

Two *consecutive* stages means that the respective first and second stage follow in a continuous manner, thus without interruption. This however does not exclude that one or more additional intermediate process steps takes place in between the two stages.

35 A *mixture* is a composition of two or more different substances combined or blend into

one mass. Mixing two compounds does not exclude that the compounds react while being mixed to form other compounds in the mixture.

The *interface between gas and liquid* is a surface dimension, thus a unit in m².

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The *cross section of reactor* is its footprint, thus its measures when projected on a horizontal surface.

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FURTHER EMBODIMENTS OF THE INVENTION

In a first further embodiment of the process according to the invention the amount of water and the amount of carboxylic acid are each independently chosen from an amount between 0.1 and 5% w/w with respect to the amount of polyester, such as an amount of 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.1, 2.2, 2.3, 2.4, 2.5, 2.6, 2.7, 2.8, 2.9, 3.0, 3.1, 3.2, 3.3, 3.4, 3.5, 3.6, 3.7, 3.8, 3.9, 4.0, 4.1, 4.2, 4.3, 4.4, 4.5, 4.6, 4.7, 4.8, 4.9 and 5.0% w/w. These amounts have been found to be advantageously useful in the present invention. Preferably, the amount of water is between 0.1 and 2% w/w, more preferably between 0.2 and 1% w/w, and the amount of carboxylic acid is between 0.2 and 3% w/w, preferably between 0.5 and 2% w/w.

In another embodiment wherein the polyester is based on a diol and a diacid, the carboxylic acid is a dicarboxylic acid. This way, the carboxylic acids matches the acid as used as a monomer for building the polyester. Typical di-carboxylic acids for use in the invention are adipic acid, succinic acid, terephthalic acid and naphthalic acid.

In yet another embodiment of the process according to the invention, the process comprises a first stage of feeding the polyester waste material into an extruder to melt the polyester and a consecutive second stage wherein the polyester is depolymerised into the reactive oligomeric ester. This two stage set-up was found to be advantageously suitable for applying the present process. This embodiment is restricted in that in the second stage the depolymerisation is completed. It is not excluded that also in the first stage the depolymerisation is initiated, e.g. by initiating the alcoholysis or any other depolymerisation process.

In a further embodiment of this process, the second stage is comprised of a first sub-stage wherein the molten polyester is subjected to alcoholysis, and a consecutive second sub-stage wherein the partly broken down polyester is further subjected to alcoholysis while at the same time adding the amount to water and the amount of carboxylic acid.

In yet again a further embodiment the first sub-stage is performed in an extruder and the second sub-stage is performed in a continuous stirred tank reactor (CSTR).

In another embodiment of the process as such, in which embodiment the polyester is polyethylene terephthalate (PET), the reactive oligomeric ester for over 50% w/w, preferably over 60, 70, 80 or even 90% w/w, comprises oligomers of 5 to 20 Bis(2-Hydroxyethyl) terephthalate (BHET) units (i.e. monomeric subunits), preferably 6 to 15 (BHET) units, most preferably, 8 to 10 BHET units.

In again another embodiment the reactive oligomeric ester is fed directly into a finishing polymerisation reactor (also denoted as "finisher" or "finishing reactor") for repolymerisation. As noted here above, the process of depolymerising a polyester by alcoholysis into a liquid mixture comprising oligomeric esters as such is known from the prior art, and also that it is described that for repolymerisation of the oligomers, the mixture may be exposed in a so-called condensation reactor to a low pressure. However, as indicated, a combination of two of these condensation reactors is typically needed. It was recognised by the present inventors that the known process has several disadvantages. Firstly, the process of repolymerisation in a condensation reactor takes a lot of time, typically around 8-10 hours or more. This means that the process, realising that the mixture has to be kept above its melting temperature, requires large amounts of energy and is thus relatively expensive to perform. However, it has always been believed that this is an inherent issue which cannot be avoided: high amounts of the alcohol monomer have to be removed in order to induce repolymerisation and that process simply takes time. Importantly however, the present invention recognised another major disadvantage, as indicated here above: It appears that oligomers that are the result of a depolymerisation reaction are more prone to thermal degradation than oligomers made of virgin materials. The reason for this is unclear, but the result is that the known process may lead to a partly degraded polymer, which shows as a slight, yellowish discolouration, making the material less suitable, or even unsuitable for high

end applications.

The inventors surprisingly found now, that despite the low intrinsic viscosity (iv) of oligomeric esters, typically having between 5 and 20 (sub-)units, viz. around 0.1 dL/g, such a mixture can be repolymerised by directly feeding it into a so-called finisher reactor. In traditional industrial polycondensation processes, a common feature is that multiple reaction stages are employed using several reactors in series, wherein the sequential reaction procedure includes (a) monomers, low molecular weight oligomers, and low molecular weight prepolymers being synthesised in regular condensation reactors, and (b) the prepolymers are then polymerised to higher molecular weight polymers in finishing polymerisation reactors (often rotating disc reactors; See e.g. US 3,728,083 assigned to Allied Chemical Corporation) where large vapor-liquid surface areas are provided (increasing the interface between the liquid mixture and the gaseous head space at least 5 times with respect to a horizontal cross section of the reactor) to extract the final alcohols. It is commonly known that the first stages are needed to increase the viscosity (lowering the amount of volatile monomers) to at least an iv of 0.3, since otherwise in the finisher the required low pressure cannot be obtained. The stepwise increase of the viscosity to at least 0.3 is deemed necessary for a stable and effective polymerisation process.

However, it was found now that the oligomeric product that results from an alcoholysis in line with the present invention, even when the polymerisation level is between 5 and 20 subunits, and thus the iv is very low (around 0.1) can be directly fed to such a finishing reactor. To an even greater surprise, the total amount of time needed to remove the volatiles can be kept below 120 minutes. This means that the novel process is far more economic, requiring substantially less energy, but also, since the time needed to expose the materials to the high melt temperatures (above 250°C) is considerably shorter and thus the thermal degradation of these materials is at a very low level if existent at all.

The reason that the low viscosity oligomeric esters can be fed directly into a finishing reactor and be able and (re-)polymerise the oligomers in a relatively short amount of time is not 100% understood. It is believed that one of the reasons is that the oligomer esters are the product of a de-polymerising alcoholysis, such as the one known from the '084 patent application identified here above. Another reason is believed to be the relatively high amount of reactive groups (high carboxylic end group number, i.e. the so

called CEG number), ensuring fast and adequate repolymerisation. Also, the degree of polymerisation of the oligomer, i.e. the number of subunits, may be important. Below 5 subunits the amount of volatiles is believed to be too high to be able and removed in a single stage process, let alone in a finisher with a high liquid-gas interface. Above 20
5 repolymerisation in a finisher would be possible as such, but the oligomer is then too viscous to allow a pre-polymerisation purification. This means that when such pre-polymerisation would be needed, necessary leaving this step may lead to a lower quality product. However, if no purification is needed, a mixture with a higher number of subunits, up to e.g. 100, may be used for direct repolymerisation in a finisher.

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In the finisher, an iv of up to 0.65 can be reached in a relatively short time frame, making the material ideally suitable for direct use, or as a starting material for even higher grade polyesters. The iv reached is a matter of time. Also, the design of a finisher (pump type and capacity, outlet diameter etc) allows a maximum iv which is still able to
15 be processed.

It is noted that instead of one large volume finisher, the finishers can be composed of two or more sub-finishers in line, as long as each of these sub-finishers have means to increase the interface between the liquid mixture and the gaseous head space at least 5
20 times with respect to a horizontal cross section of the reactor (i.e. the respective sub-finisher).

Preferably when repolymerising directly into a finisher, the reactive oligomeric ester comprises from 5 to 20 subunits, more preferably from 5 to 14 subunits, such as from 8
25 to 10 subunits. Also, it is preferred that the reactive oligomeric ester is repolymerised into a polyester having an intrinsic viscosity of at least 0.4 dL/g, preferably at least 0.5 or even 0.6 dL/g in less than 100 minutes, preferably less than 80 minutes, most preferably in less than 60 minutes.

30 Preferably, in the finisher reactor the pressure in the head space is kept below 20 mbar and preferably even below 10 mbar. This way the time needed for repolymerisation can be further decreased. Preferably the pressure in the head space is kept between 1 and 3 mbar, such as 2 mbar.

35 In yet another embodiment of the process according to the invention, the finisher reactor has means to increase the interface between the liquid mixture and the gaseous head

space at least 10 times with respect to the cross section of the reactor, preferably at least 20-100 times. An increased interface between the liquid mixture and the gaseous head space means that the repolymerisation can take place at a higher speed.

Downside is that the reactor is typically of a more complicated construction and needs a higher pump capacity. This means the process becomes more expensive. Still, this may be compensated for by a higher quality of the end-product meaning that a higher price can be obtained.

The above does not exclude any variants from the process or additional process steps. For example, additional (pre-)purification/filtration steps can be added. Also, the invention is not restricted to particular types of filters, although screen changer type filters are believed to be ideally suitable for a continuous process as claimed since depending on the amount of particulate matter present in the polyester waste material, filters may need to be changed every few hours. Also, when applying a filter, this may very well be a cascade of two, three or more separate consecutive filters of descending mesh size in order to withstand pressure differences over the filters. Next to this, in order to be able and fully remove all colourants and dies, the melted material may advantageously be pumped through a bed filled with (activated) carbon granules, SiO₂ granules or powder, or any other small molecule absorbing material.

It is also foreseen to introduce copolymerisation in the repolymerisation process. For example, a slurry of a pure diacid and a pure diol can be prepared, and/or other monomer can be formed which can be added to the finisher to which the purified oligomeric mixture is added. When the diacid and/or diol differs from the monomers as present in the polyester waste material, a copolymer is being produced. Such monomers could for example be bio-based, to further reduce the CO₂ footprint or could be e.g. isophthalic acid, succinic acid, neo pentyl glycol, to obtain other product characteristics of the ultimate polyester to be produced, adapted to the intended application. Typically, the comonomer is pre-polymerised before it is fed to the finisher and mixed with the recycled oligomer.

Any of the above further embodiments can also embodied in the system of the invention. The invention will now be further illustrated using the following non-limiting figures and examples.

EXAMPLES

5

Figure 1 schematically depicts an overview of a process for de- and re-polymerising as known from the art.

Figure 2 schematically depicts a typical re-polymerisation configuration for industrial application.

10 Figure 3 schematically depicts a de- and repolymerisation configuration for a stream of polyester waste using prior art technology.

Figure 4 schematically depicts a de- and repolymerisation configuration according to the invention.

Example 1 describes a depolymerisation and repolymerisation experiment of post-
15 consumer PET flakes.

Example 2 describes solid state post-condensation experiments.

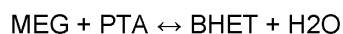
Example 3 gives various examples of feeding oligomer directly into a finisher. (not with material made according to the invention, but with even lower CEG value)

20

Figure 1

Figure 1 schematically depicts an overview of a process for de- and re-polymerising as known from WO 2022/003084, which process is as such useful for applying the method of the invention with some adaptations. In this example the polymer PET is
25 depolymerised and repolymerised in a continuous process through steps 1 - 8. Step 9 is an additional repolymerisation step including solid-state polymerisation, to arrive at a desired IV well above 0.6 for high end PET applications.

PET is formed by reacting monoethylene glycol and terephthalic acid according to the
30 following reaction (non stoichiometric formula):



BHET on its turn can be polymerised according to the following reaction, wherein MEG
35 is again formed:



The process of alcholysis is based on the fact that the above reaction is an equilibrium
5 reaction and can be shifted to either side depending on the reaction conditions. When
starting with PET, by adding MEG to the polyester melt, the equilibrium shifts to the left,
resulting in shorter polymer chains, ultimately oligomers (less than 100 repeating BHET
units, in particular less than 50, 40, 30, 20 or even 10 units) and decreasing viscosity.
By adding water to these oligomers, BHET will break down according to the top
10 reaction. However, this is not wanted for the present invention, which aims at arriving at
oligomers instead of the monomers.

For repolymerisation starting from BHET, by removing MEG, for example by using a
vacuum or nitrogen, the short chains react with each other to form a polyester again. By
15 controlling the depolymerisation rate, and thus the oligomer length, the viscosity of the
material is controlled. This chemistry is in principle the same for any industrial
polymerisation process for arriving at a polyester or a corresponding oligomer.

Now referring to figure 1, in step 1, a polyester waste material, in this embodiment
20 comprising pieces of (pure) PET carpet and flakes of PET bottles, is dried to a moisture
level of 50 ppm (0.005 w%). This is to make sure the total amount of water is controlled
to a known level, leading to a known CEG number for the reactive oligomer ester. Then,
in step 2 the dried stream of waste material is fed to a conical co-rotating twin screw
extruder. Due to the conical shape of the extruder the opening for feeding the material is
25 bigger than with a conventional twin-screw extruder so feeding is easier and it
generates less shear due to a more gentle natural compression giving less thermal
damage to the polymer. Thermal degradation generates undesirable side reactions and
formation of end groups giving an inferior end-product quality. The extruder is operated
at 280°C to melt the polyester completely. In this embodiment, adjacent the end of the
30 conical twin screw extruder (at 10% of its length) an injection point for dosing MEG
(indicated as arrow 50) is provided to obtain the first step in depolymerisation, thus
reducing the viscosity. For this, about 0.5% of MEG (w/w) is dosed. The reduction of the
IV also helps to minimise the pressure difference over the first filtration step 3 to make it
possible to filtrate with a mesh size of 80 micrometre. The filter also acts as a static
35 mixer to homogenise the mixture and distribute the added glycol with the molten
polymer to react completely with shorter polymer chains and a molecular weight

distribution at equilibrium (dispersion grade of about 2) as a result. Process parameters are chosen such that the MEG is (almost) fully reacted and no (hardly any) free MEG is present anymore.

5 The partly depolymerised and filtered material is fed to a single screw extruder in step 4. The design of the screw (see WO 2022/003084, figure 2) aims at maximising the percentage glycol which can be dosed (preventing the melt from becoming inhomogeneous). This maximum is increased by adjusting common process parameters like screw speed, pressure build up, etc. Typically, about 2-4% of MEG is dosed in this
10 extruder (indicated by arrow 50'). At the end of the extruder the viscosity of the melt is measured. The level of the viscosity is controlled by an automated control loop (not indicated in figure 1) controlling the level of MEG being dosed in the single screw extruder. This automated control loop results in a consistent viscosity, typically an IV between 0.1 and 0.2, independent of the IV of the starting material. Due to the inherent
15 transesterification reaction which takes place in the extruder, the polydispersity may remain low, preferably around 2-3, depending mainly on the residence time in the extruder (which may be adjusted in the process by controlling initial feed and extruder speed).

20 The depolymerised material is filtered for a second time in step 5. Due to the IV of about 0.15 the filtration size can be reduced in comparison to the first filter, preferable being 40 micrometre, without a pressure difference over the filter being too high.

The material with an IV of about 0.15 (0.1-0.2) is continuously added to the CSTR in
25 step 6. In this CSTR also MEG is added (indicated by arrow 50'') to further depolymerise the material to the required viscosity/oligomer length. Due to the fact that the material already has a low (controlled) viscosity upon entry, the difference in viscosity with the added MEG is not so big that homogeneous mixing is critical. 4-6% of MEG can be homogeneously mixed easily, if needed. At the same time, water is fed into the CSTR
30 (indicated by arrow 61), as well as an amount of TPA (indicated by arrow 62) to make sure the CEG number obtained is at a high level (see Example 1 here below). Although the respective streams of water, MEG and TPA may be individual streams, it is also foreseen that the compounds are added as one or more mixtures. The residence time in the CSTR is long enough (typically 25-45 minutes) to depolymerise the material to the
35 required oligomer length, but also to have enough time for the transesterification reaction to obtain a polydispersity of 2. At the end of the reactor the viscosity is

measured and with an automated control loop controlling the addition of MEG in the reactor. This results in an extremely stable continuous process hardly dependent on the type (IV) of the starting material.

- 5 In the CSTR, further decolouration takes place by adding activated carbon, indicated by arrow 60. The activated carbon may be pre-selected for the best performance to absorb the colourants present in the polyester waste. After the CSTR, the low viscous oligomer/activated carbon mixture is pumped through a three-step micro filtration (20/10/5 micrometre) step 7 to remove the carbon particles loaded with colourant from
10 the oligomers. A parallel set of three filters is installed so that in case of a pressure difference over the filter that is too high, the melt can be pumped through the parallel set, while the first filter set can be cleaned.

- After the filtration while the melt having an IV of around 0.1 (the number of subunits in the reactive oligomeric mixite being on average about 10) is still at an elevated
15 temperature of about 250°C, the melt is pumped to a finisher reactor (step 30) which is operated under vacuum at 2 mbar, at a temperature of about 260°C, to remove the MEG, with the result that the equilibrium of the BHET/PET equilibrium shifts to the right forming the PET polymer in a short time frame. In the finisher a polyester with an IV
20 between 0.4 and 0.6 or higher can be obtained. The polymer is removed from the reactor and pumped through a die-plate provide with holes, thus generating polymer strands. These strands are cooled down and cut into amorphous granules.

- The amorphous granules may undergo an off-line crystallisation process by subjecting
25 the granules to a temperature of 130 – 180°C which leads to a crystallisation process. The partly crystallised granules are subjected to a solid-state polymerisation process wherein the polyester is heated to an elevated temperature below the melting temperature of this polyester while subjected to a vacuum or an inert gas. This way a solid state additional repolymerisation is induced, to arrive at an IV well above 0.6. The
30 obtained IV can be adjusted by processing parameters in a way that the IV matches the required IV for the intended application, having any value between 0.65 and 1.0 typically.

35 **Figure 2**

Figure 2 schematically depicts a typical re-polymerisation configuration for industrial

application as known from the prior art. This set-up is the so-called 2 reactor polycondensation technology, in which the polymerisation takes place in two consecutive polymerisation reactors. The first one, indicated with reference number 8 is a standard condensation reactor. The second one, indicated with reference number 30, is a so-called finisher, having the means to increase the liquid-gas interface in the reactor at least 5 times with respect to the footprint of the reactor.

The reactor 8 is the same as known from WO 2022/003084. For laboratory test purposes, the use of such a standard condensation reactor alone is often sufficient since time is not a principle issue. However, for industrial application, a standard condensation reactor is always followed by a finisher to allow faster repolymerisation. In this typical set-up, the oligomer mixture having a typical IV value of around 0.1 is fed (22) into the reactor 8 and forms a gas-liquid interface 23 halfway the reactor. The reactor is provided with a mixing means 21 that is driven by a motor 20. The alcohol is pumped away via means 24. This way, the oligomeric mixture can be polymerised to a higher grade (the number of units being 25 or higher) to an IV of at least 0.2 – 0.3, such as to be able and fed (25) into the finisher 30, forming a gas-liquid interface 230. In the example, the finisher is provided with a rotating disc mixer 210, driven by motor 200. Since the gas-liquid interface is established half-way the rotating discs, rotating of the discs and therewith elevating liquid film (on both sides of the discs) into the open gaseous space, will lead to a substantial increase of the gas-liquid interface, in this case about a factor 10 with respect to the footprint of finisher reactor 30. This way, the alcohol can be removed faster (240) leading to a stream of polyester 250 with in IV around 0.6 in a relatively short time frame.

This two-stage se-up is commonly used since it is known that a mixture with a low iv of around 0.1 cannot be directly fed into a finisher: the bulk of the alcohol has to removed before entering a finisher, otherwise a low pressure cannot be obtained in the finisher and thus polycondensation will hardly take place. In many cases even a three-stage set-up is used in the industry (adding an extra condensation reactor 8 before the finisher 30) for the stepwise reduction of the amount of alcohol and therewith stepwise increase in the IV until the mixture is suitable for feeding into the last stage finisher.

35 **Figure 3**

Figure 3 schematically depicts a de- and repolymerisation configuration for a stream of

polyester waste using prior art technology. In this set-up, the depolymerisation technology as known from WO 2022/003084 is used. In particular, as described in WO 2022/003084 in the examples section (which section is incorporated herein by reference), the waste stream is fed into a first extruder 2, then into a second extruder 4 and then into a CSTR 6. This corresponds to steps 1 through 6 in figure 1. Then the resulting oligomer mixture having an IV of around 0.1 is fed into condensation reactor 8. The remainder of the process is identical to what is depicted in figure 2.

10 **Figure 4**

Figure 4 schematically depicts a de- and repolymerisation configuration according to the invention. In principle, the set-up is the same as that of figure 3, albeit that the oligomer mixture that comes from CSTR 6 is fed directly into the finisher 30. The high number of reactive groups enables a very fast repolymerisation which is advantageous not only from an economical point of view but also to arrive at a high quality polyester.

Example 1

Example 1 describes a depolymerisation and repolymerisation experiment of post-consumer PET flakes. The experimental set up as depicted in Figure 1 comprised a lab-type finisher, which is able to process a liquid up to an IV of 0.3-0.35. In this example the influence of the addition of water, TPA, and a combination thereof on the final reactive properties of the depolymerised polyester is presented via depolymerisation-repolymerisation experiments using the experimental set-up as depicted in Figure 1. Melting and depolymerisation of the polyester material and subsequent repolymerisation of the liquid depolymerised polyester material were executed at a throughput of about 30 kg/h under conditions indicated here below. For each of the experiments basically the depolymerisation process as described in WO 2022/003084 was used, forming an intermediate liquid mixture of oligomeric esters with an average polymerisation degree of 15-20 (15-20 subunits of BHET per molecule) before repolymerisation in the finisher. In the first extruder the temperature was kept in each case between 270-280°C, no MEG was added. The amount of MEG (fibre grade, obtained from Vivochem) added to the second extruder was in each case 2.4% and the temperature was about 265-270°C. In the CSTR the amount of MEG added is indicated in below table. Both water (demineralised) and terephthalic acid (TPA, obtained from Indorama Ventures) were added to the CSTR as a mixture in ethylene glycol, respectively, and are calculated in

relation to the total amount of polyester material. The filling level in the CSTR was maintained at 40-50% ensuring an average residence of the partially depolymerised polyester of 30 minutes at a temperature between 260-270°C. The temperature in de finisher was kept at about 270°C. The PET flakes (light coloured MOPET A, obtained from Morssinkhof Plastics), were used as such, and, thus, were not dried and prepared beforehand. Some of the obtained polyester materials were post-condensed in an in-house labscale post-condensation set-up at 220°C under vacuum (<55 mbar) overnight (about 16 hours) to assess the effect of the carboxylic end groups on the post-condensation rate expressed in (Δ dL/g)/h (see Example 2).

The experiments are indicated in the below table 1 (percentages are weight percentages with respect to the amount of polyester; iV is in dL/g and CEG is in meq/kg; n.d. = not determined). Experiment 1 is a comparison experiment in which no water and TPA are added to the partially depolymerised PET flakes. The carboxylic end group number is about 20-25 meq/kg. Small amounts of water (see experiments 2 and 3) do not essentially alter the CEG number, which are still in the range of 20 to 25 meq/kg.

Table 1 Depolymerisation and repolymerisation of post-consumer PET flakes

Exp.	CSTR		Finisher residence time h	Obtained polymer		
	MEG %	Water/TPA %		iV	CEG	L*a*b
1	3.3	0/0	1.0	0.29	20-25	n.d.
2	3.3	0.2/0	1.0	0.27	24	n.d
3	3.3	0.2/0	2.0	0.29	22	50/0.5/11
4	1.7	0.5/0	1.0	0.30	46	n.d.
5	1.7	0.5/0	1.0	0.32	45	57/3/10
6	3.3	0/2.0	1.25	0.31	42	n.d.
7	3.3	0/2.0	1.5	0.31	52	62/4/10
8	3.3	0.4/1.7	1.25	0.32	70	51/2/5
9	3.3	0.4/1.7	1.25	0.31	67	51/2/5

When adding 0.5 w% of water the carboxylic end groups of the obtained polymer increase to over 40 meq/kg (experiments 4 and 5). Adding 2.0 w% TPA leads to a

comparable rise in CEG number, see experiments 6 and 7. Based on these results it was estimated that when combining 0.4 w% of water and 1.7 w% of TPA, about the same level of CEG would be obtained, thus around 45 meq/kg. However, surprisingly it was found that in this case of using post-consumer PET flakes, the CEG number
5 obtained was considerably higher, namely about 65-70 meq/kg, while sustaining solution viscosities of ca. 0.30 dL/g (experiments 8 and 9). Also the L*a*b values appeared to be on the low end, indicating very low thermal degradation.

10

Example 2

Example 2 describes solid state post-condensation experiments. In this example the effect of the carboxylic end groups of some of the polyester materials in their solid state as obtained from virgin PET granules and PET flakes on the post-condensation rate
15 (SSP rate) is assessed.

When using virgin PET, without adding water to the depolymerisation process, the CEG number obtained was 23 meq/kg. The solid state polymerisation rate (SSP) was 0.020 (Δ dL/g)/h. By adding 0.75% of water, the CEG number increased to 68, which higher
20 value led to a significantly increased SSP rate of 0.036 (Δ dL/g)/h. This shows that an increased CEG number has a positive effect on the SSP rate.

The same was found for post-consumer PET. Here the addition of TPA alone (2.0 w%) led to a CEG number of 52 meq/kg, in line with what is shown here above in Example 1,
25 leading to a SSP rate of 0.027 (Δ dL/g)/h vs. 0.020 (Δ dL/g)/h for the control.

The experiments show that the carboxylic end groups can be tuned by adding water, TPA, or a combination thereof to the (partially) depolymerised polyester material while yielding polymeric materials with comparable solution viscosities. The increase in
30 carboxylic end groups further shows a substantial effect on the repolymerisation process, such as the post-condensate rate to arrive at desired solution viscosities.

35 **Example 3**

Example 3 gives various examples of feeding PET oligomer directly into a finisher. The

reactive oligomer as used in this example was not made using the hybrid water and TPA addition according to the invention and thus the reactive oligomer is believed to have had a lower CEG number than what is shown here above in experiments 8 and 9 of Example 1. This example therefore merely illustrates that an oligomer mixture with a low intrinsic viscosity, obtained by depolymerising post-consumer polyester through alcoholysis can be fed directly into a finisher. A reactive oligomeric ester with a high CEG number as obtainable with the method of the present invention may even reduce the residence time in the finisher since the polymerisation can take place even at a higher reaction speed.

10

In this example a direct comparison is made between a process based on prior art technology as depicted in figure 3, versus a process using the set-up of figure 4, i.e. where the oligomer mixture resulting from the depolymerisation of a stream of polyester waste material is fed directly into a finisher. For this comparison a lab-type finisher was used, being able to process a liquid up to an IV of 0.3-0.35. It is estimated that in order to arrive at an IV of about 0.6 in an industrial finisher about twice the amount of time is needed. However, this extra time needed is expected to be fully compensated by the fact that in an industrial finisher a pressure as low as 1-2 mbar can be obtained whereas in the laboratory set-up this was about 10 mbar. This means that the time needed in the laboratory finisher to reach an IV of about 0.3 is expected to be the same as needed in an industrial finisher to reach an IV of about 0.6.

For the comparison experiment a polyester material, consisting of PET granules (RamaPET N180; IV 0.8 dL/g), was melted and depolymerised with monoethylene glycol into a liquid mixture of oligomeric esters having an average polymerisation grade between 5 and 20 (5-20 subunits of BHET per molecule) at a throughput of about 30 kg/hr. Since the filling level in the CSTR was maintained at ca. 48%, the average residence of the partially depolymerised polyester material in the CSTR was 30 minutes. In these depolymerisation and repolymerisation trials, the virgin polyester material was used as such, and, thus, was not dried beforehand.

In a first experiment, the resulting oligomer was repolymerised in the set-up of figure 2, thus the process being in line with that as shown in figure 3. In a second series of experiments the resulting oligomer was repolymerised by directly feeding the oligomer mixture into the finisher, as shown in figure 4. In the latter series the amount of MEG as used in the depolymerisation process was varied in order to arrive at oligomers with a

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varying degree of polymerisation. In this respect it is noted that the use of about 10% MEG leads to an x (= degree of polymerisation = number of subunits in the oligomer) of about 8-10; 7.5% MEG leads to an x of about 11-12; 4.5-6% MEG leads to an x of about 15-16 and 2.5% MEG leads to an x of about 20.

5

Melting and depolymerisation of the polyester material and subsequent repolymerisation of the liquid depolymerised polyester material were executed under conditions depicted in Table 1. For each of these experiments the depolymerisation process as described in WO 2022/003084 was used. In the first extruder the temperature was kept in each case to about 288°C, no MEG was added. The amount of MEG added to the second extruder was in each case 2.4% and the temperature was kept at about 268°C. In the CSTR the amount of MEG added is indicated in the table here below. The temperature in de condensation reactor was about 258°C. In the finisher the temperature was kept to about 271°C.

15

Table 2 De- and repolymerisation experiments

Exp	MEG (%)	Cond. Reactor (h)	Finisher (h)	IV (dL/g)	L*a*b
1	7.6	3.7	5.3	0.31	Above Threshold
2	5.1	-	1.0	0.31	64.6/-1.7/7.8
3	5.1	-	1.0	0.29	63.3/-0.8/8.8
4	5.1	-	0.5	0.34	72.4/-1.9/5.5
5	5.1	-	0.5	0.37	65.7/-2.3/4.9
6	5.1	-	0.5	0.33	66.3/-2.4/4.9
7	5.1	-	0.5	0.32	68.0/-2.4/4.9
8	5.1	-	0.5	0.30	67.6/-2.4/4.5
9	3.4	-	1.0	0.31	71.0/-2.3/6.3
10	1.7	-	1.0	0.31	68.8/-1.4/7.3
11	1.7	-	1.0	0.33	62.4/0.2/11.8
12	1.7	-	1.0	0.33	63.0/-1.3 /8.2
13	1.7	-	1.0	0.34	64.2/-2.1 /7.4
14	1.7	-	1.0	0.35	66.2/-2.0/6.9
15	0.0	-	2.0	0.35	60.0/-3.6/9.8
16	0.0	-	2.0	0.35	63.0/-3.6/8.1

In experiment 1 partial depolymerisation of the molten virgin polyester material went smoothly in the presence of 10 w/w% MEG versus PET in total for Extruder II and CSTR, in a time frame of about 20-25 minutes. Intermediate sampling before repolymerisation showed that a white depolymerised polyester material with a degree of polymerisation (DP) ca. 8-10 (or molecular weight Mw 1500-1950 Dalton) was formed. The liquid depolymerised polyester oligomer was repolymerised in the set-up of figure 2 yielding a pale, yellow liquid recycled polyester material (Lab value above threshold) with an intrinsic viscosity IV 0.31 dL/g after about 9 hours of polymerisation. The yellow colouration was indicative of significant thermal degradation.

In the experiments 2-16 various continuous depolymerisation-repolymerisation experiments were performed, excluding the standard condensation reactor and directly feeding the liquid oligomer mixture into the finisher, thus, without the contribution of a pre-polymerisation reactor. The obtained liquid recycled polyester material was cooled down in a water bath and cut into solid polyester granules. In these experiments, apart from assessing the total time needed to arrive at the same degree of polymerisation as arrived at in the first experiment, the influence of the amount of MEG during the depolymerisation step and residence time in the finisher on the physical properties of the obtained polymer as expressed in intrinsic viscosity, and colour values was investigated. The conditions and settings of the individual reactors in the continuous depolymerisation-repolymerisation line and the result of this experiment in terms of intrinsic viscosity (IV) and colour values ($L^*a^*b^*$) are listed in the table as far as relevant.

Experiments 2 and 3 in the table show that a reduction in the amount of MEG to 5.1 w/w% in the CSTR and therewith, the total amount of MEG to 7.5 w/w%, yield recycled polyester material from liquid polyester oligomers at a residence of about 1 hour in the finisher. Apart from the omitting the pre-polymerisation reactor, the one hour residence is significantly shorter than the 5 hours in experiment 1. From the recycled polyester material polyester granules were obtained with intrinsic viscosities of about 0.3 dL/g (at the level of viscosity of the recycled polyester material obtained in the repolymerisation process comprising a pre-polymerisation reactor and finisher; experiment 1) but at a significantly reduced time and at significantly reduced colour, indicating less thermal degradation.

A reduction in residence time to 0.5 hour in the finisher (see experiments 4 to 8) while maintaining the total amount of MEG of 7.5 w/w% for the partial depolymerisation reaction in Extruder II and the CSTR to polyester oligomers, yields recycled polyester granules with intrinsic viscosities that are higher when compared to experiments 2 and 3. The reduction in residence time in the finisher improves the colour of the recycled polyester granules as indicated by the lower b^* values of around 5.

In experiments 9 and 10 to 14, the amount of MEG in the CSTR is reduced to 3.4 and 1.7 w/w%, respectively, thereby reducing the total amount of MEG that is used in the partial depolymerisation reaction ≤ 5.8 w/w%. Repolymerisation of these polyester oligomers for 1 hour in the finisher and subsequent granulation yields recycled polyester granules with intrinsic viscosities that are slightly higher than in previous experiments, varying around 0.33 dL/g, and also higher b^* values.

An increase in residence time for the repolymerisation process to 2 hours was investigated in experiments 15 and 16. In addition, also the amount of MEG in the CSTR was reduced to 0 w/w%. Repolymerisation of depolymerised polyester material with a DP 20 to 25 over the course of 2 hours showed a further increase in intrinsic viscosity to 0.35 dL/g of the obtained recycled polyester granules. The polyester granules appeared more yellowish than in experiments 4 to 9, as confirmed by the higher b^* values of about 9.

These experiments show that faster repolymerisation can be achieved when using only a finisher in the repolymerisation of polyester oligomers. The recycled polyester granules show comparable viscosities in significantly shorter residence times. The colour values of the recycled polyester granules shows that a shorter residence of polyester oligomers in the finisher leads to less thermal degradation.

CLAIMS

1. A process to enable the recycling of a stream of polyester waste material by depolymerising the polyester present in the stream of polyester waste material into a reactive oligomeric ester, the process comprising providing the polyester in a liquid form in a reactor, and feeding an alcohol to the reactor to subject the polyester to alcoholysis to depolymerise the polyester, while at the same time adding an amount of water and an amount of carboxylic acid, to form the reactive oligomeric ester.
2. A process according to claim 1, characterised in that the amount of water and the amount of carboxylic acid are each independently chosen from an amount between 0.1 and 5% w/w with respect to the amount of polyester.
3. A process according to claim 1 or 2, characterised in that the amount of water is between 0.1 and 2% w/w, preferably between 0.2 and 1% w/w, and the amount of carboxylic acid is between 0.2 and 3% w/w, preferably between 0.5 and 2% w/w.
4. A process according to any of the preceding claims, wherein the polyester is based on a diol and a diacid, characterised in that the carboxylic acid is a dicarboxylic acid.
5. A process according to any of the preceding claims, characterised in that the process comprises a first stage of feeding the polyester waste material into an extruder to melt the polyester and a consecutive second stage wherein the polyester is depolymerised into the reactive oligomeric ester.
6. A process according to claim 5, characterised in that the second stage is comprised of a first sub-stage wherein the molten polyester is subjected to alcoholysis, and a consecutive second sub-stage wherein the partly broken-down polyester is further subjected to alcoholysis while at the same time adding the amount of water and the amount of carboxylic acid.
7. A process according to claim 6, characterised in that the first sub-stage is performed in an extruder and the second sub-stage is performed in a continuous stirred tank reactor (CSTR).
8. A process according to any of the preceding claims, wherein the polyester is

polyethylene terephthalate (PET), characterised in that the reactive oligomeric ester for over 50% w/w, preferably over 60, 70, 80 or even 90% w/w, comprises oligomers of 5 to 20 Bis(2-Hydroxyethyl) terephthalate (BHET) units, preferably 6 to 15 (BHET) units, most preferably, 8 to 10 BHET units.

5

9. A process according to any of the preceding claims, characterised in that the reactive oligomeric ester is fed directly into a finishing polymerisation reactor for repolymerisation.

10 10. A process according to claim 9, characterised in that the reactive oligomeric ester comprises from 5 to 20 subunits, preferably from 5 to 14 subunits such as from 8 to 10 subunits.

11. A process according to any of the claims 9 and 10, characterised in that the reactive
15 oligomeric ester is repolymerised into a polyester having an intrinsic viscosity of at least 0.4 dL/g, preferably at least 0.5 or even 0.6 dL/g in less than 100 minutes, preferably less than 80 minutes, most preferably in less than 60 minutes.

12. A process for polymerising an oligomeric ester, comprising feeding a liquid mixture
20 comprising the reactive oligomeric ester obtainable in a method according to any of the claims 1 to 8 in a continuous manner to a finishing polymerisation reactor.

13. A process for obtaining a polyester polymer, comprising mixing the reactive
oligomeric ester obtained in a method according to any of the claims 1 to 8 from a
25 stream of polyester waste material, and a virgin pre-polyester material, and reacting the oligomeric ester and the virgin pre-polyester to form the polyester polymer.

14. System for recycling a stream of polyester waste material, the system comprising in
consecutive order 1) an extruder, 2) a depolymerisation reactor and 3) a finishing
30 polymerisation reactor, wherein the system is constituted such that polyester waste material is fed from the extruder to the depolymerisation reactor while at the same time alcohol, water and a carboxylic acid are independently fed to the depolymerisation reactor, wherein the extruder, the depolymerisation reactor and the finishing reactor are operatively coupled such that a stream of polyester waste material is able to flow from
35 an entrance of the extruder to an outlet of the finishing polymerisation reactor in a continuous manner.

15. A system according to claim 14, characterised in that the depolymerisation reactor comprises a first sub-reactor to which at least part of the alcohol is fed, and a second sub-reactor to which the remaining part of the alcohol is fed as well as the water and
- 5 carboxylic acid.