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(57) Abstract

The present invention provides a process for crystallising polyethylene naphthalate copolymer in the absence of a devolatilization step comprising: a) copolymerising carboxylic acids made up of at least 60 mole % of 2,6–naphthalene dicarboxylic acid; with polyols comprising at least 80 mole % ethylene glycol and from 2 to 20 mole % of a polyol having three or more carbon atoms, based on the total moles of polyols, to form PEN copolymer solids; and b) subsequently crystallising said solids comprising heating said solids to at least their sticking temperature at an average rate of at least 10 °C/min, to form agglomerate–free crystallised solids. In another embodiment of the invention, there is provided a process wherein said crystallising solids are subsequently solid state polymerised.

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PROCESS FOR CRYSTALLISING POLYETHYLENE NAPHTHALATE COPOLYMERS IN THE ABSENCE OF A DEVOLATILIZATION STEP

Field of the Invention

The invention relates to a process for crystallising polyethylene naphthalate copolymers in the absence of a devolatilization step.

Background of the Invention

High molecular weight polyesters are commonly produced from low molecular weight polyesters of the same composition by solid state polymerisation. The low molecular weight polyesters which are used in such solid state polymerisations are generally prepared by conventional melt polymerisations. Solid state polymerisation is generally considered advantageous in that the handling of high molecular weight ultra-high viscosity molten polymers during the polymerisation phase is eliminated. Thermal degradation is also essentially avoided during the solid state portion of the polymerisation.

The low molecular weight polyesters utilised in solid state polymerisations are generally in the form of pellets or chips. Such pellets can vary greatly in size; however, as a general rule, the smaller the size of the pellets of polyester the faster the solid state polymerisation will proceed. Very fast rates of solid state polymerisation can be attained by utilizing polyesters which are in the form of porous pills.

Most thermoplastic polyesters, including polyethylene terephthalate (PET) and polyethylene naphthalate (PEN), produced by melt-phase polymerisation are almost completely amorphous in nature. Such amorphous polyesters which are prepared by melt polymerisation are normally converted from the amorphous state to the crystalline state prior to solid state polymerisation to raise their sticking temperature. This is done to prevent the polyester pellets or chips from sticking together as a solid mass during solid state polymerisation.

When an amorphous polyester is heated from ambient temperature to above its glass transition temperature (Tg), it will soften and become sticky before it starts to crystallise. The sticking temepratue of an amorphous polyester is usually about 20°C above its Tg. The crystallisation rate of the polyester will not be fast enough to be practical until its temperature is further raised to about 30°C above its sticking temperature. To achieve the maximum crystallisation rate, the temperature of the polyester must be raised even higher. For example, PET has a Tg of 74°C and a sticking temperature of about 95°C. The crystallisation rate of PET is rather low until the temperature is raised above 125°C, and in practice, PET is usually crystallised at temperatures between 150°C and 190°C.

PEN has promising properties for fibre and packaging applications. PEN has a Tg of about 118°C and a crystalline melting point T_m of 268°C. It exhibits a crystallisation peak between 180°C and 220°C. Its sticking temperature is about 140°C when in the amorphous state. According to conventional wisdom, the best crystallisation temperature range for PEN polymer would be between 180°C and 220°C.

During the crystallisation process, the PEN polyester undergoes a sticky stage. This takes place within the period of time the polyester temperature exceeds the sticking (softening) temperature and the time the polyester becomes well crystallised. To mitigate the agglomeration and lumping effect as the PEN polyester pellets rise through their sticking temperature to their crystallisation temperature, commercial-scale crystallisers for continuous crystallisation of polyester can be equipped with means to provide vigorous agitation. In a batch process, a variable speed, variable temperature rotating vessel can be used. With respect to PET polyester polymers, two types of continuous crystallisers have been widely used, namely, agitated vessels and fluidized beds.

Heretofore, in the continuous crystallisation process of particulate polyesters, PET in particular, polyester pellets are charged at ambient temperature directly into the crystalliser without any pretreatment. The heat transfer medium in a crystalliser used in a continuous process is generally hot air, hot nitrogen, or hot oil to subject the polyester pellets to a fast rate of temperature rise and maintain a constant crystallisation temperature. Under appropriate operating conditions, the PET polyester pellets can be crystallised without lumping or agglomeration.

Unlike PET pellets, however, when PEN pellets are exposed to crystallisation conditions wherein the rate of temperature rise toward the crystallisation temperature climbs quickly, the pellets "popcorn" by undergoing a sudden and rapid expansion as they are heated to near the crystallisation temperature. The puffed up skins of the pellets are very sticky and, within seconds, the pellets agglomerated tightly into big lumps, vigorous agitation notwithstanding. The popcorning phenomena indicates that those conventional PET crystallisation processes in which the rate of temperature rise in a crystalliser is high, are not suitable for those desiring to crystallise PEN polyesters in large scale commercial production.

The sudden expansion of PEN pellets during crystallisation heat-up may be due to the total internal vapour pressure of volatile material (such as water) within the pellet exceeding atmospheric pressure when the temperature reaches the softening point of the PEN pellet. Once the pellet is softened, the pressurised volatile materials within the pellet can escape and diffuse from the PEN pellet. Since the softening point of PEN is above the boiling point of the moisture trapped within the pellet, the vapour pressure build up of volatiles within the pellet exceeds atmospheric pressure while the pellet morphology, structure, and/or barrier properties are intact. Without an avenue for escape, such as by diffusion through a softened pellet, the volatized materials puff up the pellet when it does reach the point at which the pellet is sufficiently soft to be deformed.

The popcorning effect is not observed in PET pellets because the Tg and the softening point of PET is generally below the boiling point of water. Accordingly, the vapour pressure of internal moisture within the pellet does not have a change to build up and exceed atmospheric pressure. Since the PET pellet is softened before the vapour pressure of moisture within the pellet exceed atmospheric pressure, the moisture can escape (diffuse) out of the softened pellet as the temperature reaches the boiling point of water.

The sudden expansion of PEN pellets during heat up to crystallisation is discussed in U.S. Patent No. 4,963,644. According to this patent, the cause for the sudden expansion of PEN pellets during crystallisation was investigated by subjecting a PEN pellet to a DTA scan. Its DTA thermogram exhibited an endotherm near the onset of the crystallisation exotherm. The endotherm was believed to arise from the sudden vaporisation and/or release of volatiles, whose total internal vapour pressure exceeded atmospheric pressure, trapped inside the pellet as the PEN is softened near its crystallisation temperature. This phenomenon explained the sudden expansion of PEN pellets as they were exposed to standard crystallisation temperatures of 180°C to 220°C.

The volatile material trapped inside of PEN pellets arise from a number of different sources, such as contaminants entering the process during melt polymerisation or the formation of by-products generated during melt polymerisation. Due to the higher temperature at which the melt of PEN polymer is held during melt polymerisation compared to the temperature at which PET is held during melt polymerisation, the number and quantity of by-products generated in PEN melt polymerisation is greater than in PET melt polymerisation. Degradation of PEN could generate water, ethylene glycol, acetaldehyde and the like. Because of the very high melt viscosity of PEN, these by-products are difficult to remove during pelletizing. Furthermore, PEN is often pelletized under nitrogen pressure. In this case, nitrogen could also be trapped inside the the pellets. PET, on the other hand, generates fewer by products, is more stable in its melt state, and its melt viscosity if lower than that of PEN. The quantity of by-products generated in PET are relatively small and are more easily removed during pelletizing. Therefore, very little volatile material is trapped inside PET pellets to cause lumping and sticking problems during crystallisation.

The solution proposed in U.S. Patent No. 4,963,644 to the lumping and sticking problem of PEN pellets during crystallisation was to slowly remove the volatiles trapped inside the pellets at temperatures below its sticking temperature prior to the crystallisation step. This process incorporated a devolatilization step before the crystallisation step. This patent calls for a devolatilization step involving (1) heating the amorphous polyethylene naphthalate to a temperature which is within the range of 80°C to 140°C in the presence of a stream of inert gas or under a vacuum to devolatilize the amorphous polyethylene naphthalate; and (2) subsequently heating the devolatilized polyethylene naphthalate to a temperature which is within the range 150°C to 260°C while providing agitation to produce the crystallised polyethylene naphthalate.

It would be desirable, in the interest of improving the processing speed, to find a way to avoid the need for subjecting the PEN pellets to the slow devolatilization step without sacrificing the advantage of abating the tendency of the pellets to lump together into a large mass. We would desire to rapidly heat up PEN pellets during the heat up phase in a crystallisation step comparable to the rapid heat up to

PET pellets in crystallisers, such as fluidized or agitated bed crystallisers, without experiencing the popcorning effect.

Summary of the Invention

The present invention provides a process for crystallising polyethylene naphthalate copolymer in the absence of a devolatilization step comprising:

a) copolymerising carboxylic acids made up of at least 60 mole % of 2,6-naphthalene dicarboxylic acid; with polyols comprising at least 80 mole % ethylene glycol and from 2 to 20 mole % of a polyol having three or more carbon atoms, based on the total moles of polyols, to form PEN copolymer solids; and
b) subsequently crystallising said solids comprising heating said solids to at least their sticking temperature at an average rate of at least 10°C/min, to form agglomerate-free crystallised solids.

In another embodiment of the invention, there is provided a process wherein said crystallising solids are subsequently solid state polymerised.

The process of the present invention avoids the need to conduct a devolatilization step as described in U.S. Patent No. 4,963,644, wherein a stream of inert gas must be passed over the pellets for a period of time effective to remove volatiles at a temperature below the sticking point of the pellets, or the pellets are subjected to a vacuum.

Detailed Description of the Invention

A composition of PEN copolymerised with 2,7-naphthalenedicarboxylic acid, diethylene glycol, 1,4-cyclohexanedimethanol, isophthalic acid or terephthalic acid has been described in WO90/03993. This publication describes the modification of PEN with one of these monomers to lower the melting point of PEN to enable it to be more easily processed by injection stretch blow moulding, reheat stretch blow moulding or extrusion blow moulding. This publication is silent with regard to the processing techniques used crystallise the PEN polymer, if at all, other than to state that conventional polymer processing techniques can be used to make the described polyester. This publication found that all of the described co-monomers worked well in its process, which was concerned with lowering the melt point of PEN.

With respect to the crystallisation of PEN pellets, the known and/or patented techniques used to crystallise PEN involve the removal of trapped moisture within the pellet by slowly heating the pellets to their sticking temperature to sufficiently dry the pellets to avoid a signification amount of puffing under agitation, or to subject the pellets to a vacuum or a stream of inert gas in a discrete devolatilization step for a period of time below their sticking point. Each of these processes are inadequate because they slow the processing speed. However, a process was unexpectedly discovered comprising a rapid heat up towards the sticking point of a PEN copolyester by subjecting a PEN copolymerised with an alkylene glycol other than ethylene glycol, such as diethylene glycol to the rapid heat up without suffering the drawback of lumping or agglomeration. Other comonomers, such as terephthalic acid described in WO90/3993 as equally useful to diethylene glycol to lower the melt point of PEN, failed to provide PEN copolymer useful in a process herein for a rapid heat up without experiencing lumping and agglomeration, even under agitation.

The polyethylene naphthalate copolymer (PEN copolymer) utilised in accordance with the present invention is typically prepared by standard melt polymerisation techniques, either in a continuous or a batch process. Such melt polymerisations result in the formation of a PEN copolymer which is essentially amorphous in nature. By this we mean that the PEN copolymer is virtually totally amorphous even though it may contain small regions where crystallinity exists.

The PEN copolymer is generally produced by melt polymerising carboxylic acids made up of at least 60 mole %, preferably at least 80 mole %, and more preferably from 85 to 100 mole %, most preferably from 90 to 100 mole %, of naphthalene dicarboxylic acid; with polyols comprising at least 80 mole % of ethylene glycol, preferably from 90 mole % to 96 mole %, and from 2 mole % to 20 mole % of a polyol having three or more carbon atoms, each based on the total moles of polyols. By an "acid" or a "dicarboxylic acid", when used with reference to a polyester monomer, is meant the free acid monomer, its lower alkyl esters, and other derivatives thereof which can be reacted with a glycol to produce a repeating units of naphthalene-glycol ester linkages, such as the anhydrides or the acid halides of these acids. Many conventional melt polymerisation processes, however, employ the free acids, thereby avoiding the need to remove the lower alcohol by-products from the reaction mixture.

In preferred embodiments, the naphthalene dicarboxylic acid comprises a 2,6-naphthalene dicarboxylic acid. Generally, the amount of 2,6-naphthalene dicarboxylic acid will range from 85 mole % to 95 mole %, based on the moles of acid. The naphthalate units are beneficial to enhance the gas barrier properties of the polyester.

Other types of di or polycarboxylic acids can be copolymerised with naphthalene dicarboxylic acid. One example of such an additional acid in terephthalic acid, which can be added in an amount of from about 4 mole % to 40 mole %, based on the weight of all polymerisable carboxylic acids. Since it is preferred to keep the number of naphthalate units high, the preferred amount of additional di or polycarboxylic acid, preferably dicarboxylic acid, ranges from 4 to 15 mole %, based on the total moles of polymerising acids, more preferably from 5 to 10 mole % of terephathalic acid. Other examples of carboxylic acids include isophthalic-, succinic-, adipic-, 1,4- and 1,3-cyclohexane-, suberic-, glutaric-, sebacic, 1,12-dodecane-, dicarboxylic acids.

The combination of the polyol having three or more carbon atoms during PEN copolymerisation is necessary to avoid the devolatilisation step and produce agglomerate-free crystalline solids. The amount of the polyol having three or more carbon atoms preferably ranges from 2 mole %, more preferably 3 mole %, to 20 mole %, more preferably 10 mole %, most preferably to 7 mole %, based on the total moles of polyols.

Suitable types of polyols having three or more carbon atoms are the aliphatic, cycloaliphatic, and aromatic diol and higher hydroxyl functional polyols, including the glycol ethers. The polyol having three or more carbon atoms may or may not contain heteroatom(s) such as oxygen or nitrogen in the backbone of the molecule. Examples of the polyols having three or more carbon atoms are diethylene glycol, dipropylene glycol, 1,4-dihydroxyethoxy benzene, trimethylene glycol, tetramethylene glycol, neopentyl glycol, propylene glycol, 1,3-propane diol, triethylene glycol, 2,4-dimethyl-2-ethylhexane-1,3-diol, 2-ethyl-2-butyl-1,3-propane diol, 2-ethyl-2-isobutyl-1,3-propane diol, 1,3-butane diol, 1,4-butane diol, 1,5-pentane diol, 1,6-hexane diol, 1,2-, 1,3- and 1,4-cyclohexane dimethanol, 2,2,4,4-tetramethyl-1,3-cyclobutane diol, 1,4-xylylenediol, trimethylolethane, 1,2,6-hexanetriol, alpha-methyl glucoside, glycerine, sucrose, trimethylol propane, sorbitol, pentaerythritol, and the higher molecular weight polyoxyalkylene polyether adducts made by reacting these polyols with alkylene oxides.

Preferably, the polyol having three or more carbon atoms will have 3 to 12 carbon atoms, and more preferably 3 to 8 carbon atoms, and is a diol or triol. Examples of the more preferred diols and triols having between 3 and 8 carbon atoms are trimethylene glycol, or tetramethylene glycol, diethylene glycol, dipropylene glycol, neopentyl glycol, 1,3-propane diol, triethylene glycol, 2,4-dimethyl-2-ethylhexane-1,3-diol, 1,3-butane diol, 1,4-butane diol, 1,5-pentane diol, 1,6-hexane diol, 1,2-trimethylolethane, 1,2,6-hexanetriol, glycerine, and trimethylol propane. The intrinsic viscosity (IV) of the PEN copolymer is not limited. The PEN copolymer will generally have an initial starting IV of at least about 0.2 dl/g as measured in a 60:40 phenol:tetrachloroethane solvent system at a temperature of 30°C and at a concentration of 0.4 g/dl. The amorphous PEN copolymer will preferably have an initial or starting IV of from 0.3 to 0.7 dl/g. The amorphous PEN copolymer will more preferably have an initial IV of 0.4 to 0.5 dl/g.

The glass transition temperature (Tg) of the PEN copolymer is also not limited. In general, the Tg of the copolymer is above 100°C, and will often range from 105°C to 130°C. Preferably, the Tg of the copolymer ranges from 115°C to 125°C.

In the process described in U.S. Patent No. 4,963,644, the devolatilisation step comprised heating the PEN prepolymer to a temperature below the sticking temperature of the PEN prepolymer (80°C to 140°C) in the presence of a stream of an inert gas or under a vacuum to devolatilize the amorphous PEN copolymer for a period of time (typically one to four hours) sufficient to remove most of the volatile materials, such as water, ethylene glycol, acetaldehyde, etc. from the PEN copolymer. This step is now eliminated in the process of this invention. The PEN copolymer may be added directly to a crystalliser, heated to any temperature throughout the range of 150°C to 260°C, wherein the temperature rise of the PEN copolymer climbs at a rapid average rate of at least 10°C/min up to at least the sticking point of the PEN copolymer.

The average pellet temperature rise of at least 10°C/min is measured throughout the heat cycle from the temperature at which the pellet is introduced into the crystalliser to the sticking temperature of the PEN copolymer. To take full advantage of processing speeds, the average temperature rise of at least 10°C occurs throughout and up to 150°C, and more preferably throughout and up to the crystallisation temperature of the PEN copolymer. In another embodiment, the average rate of temperature rise up to the sticking point of the

PEN copolymer is at least 15°C/min, and more preferably at least 18°C.

Since the PEN copolymer is not devolatized according to the process described in U.S. Patent No. 4,963,644, its volatiles content when introduced to the crystallisation step can advantageously be at least substantially the same as or greater than its volatiles content upon solidification at the conclusion of the melt polymerisation step. In other words, the PEN copolymer solid does not need to be treated, such as by drying or devolatilization, to reduce its volatiles content between its solidification at the end of the melt polymerisation step and the crystallisation step. Volatiles are defined as any agent within the PEN copolymer which vaporises at temperatures below the sticking temperature of the PEN copolymer under atmospheric pressure. Typical volatiles include water, ethylene glycol, acetaldehyde, and nitrogen. In general, the volatiles content of the PEN copolymer solids is within the range of 0.1% to 0.7%. The exact volatiles content will vary depending upon the purity of monomers and stability of the melt polymerisation conditions, as well as the environmental pelletising conditions to which the pellets are exposed, which also vary from season to season. The process of the invention is particularly useful for crystallising pellets having high volatiles content, such as from 0.2 wt.% or more.

PEN homopolymer pellets which have not been devolatized or dried for significant periods of time undergo significant expansion and puffing as visible to the eye at the conclusion of crystallisation, resulting in an agglomerate that does not break apart into the individual pellets, in many cases even when subjected to agitation. However, during and at the conclusion of the crystallisation step, the PEN copolymer pellets as described herein will not agglomerate, and in most cases, there is no pellet expansion or puffing visible to the eye.

It is normally preferred to conduct the crystallisation at a temperature which is within the range of from 160°C to 220°C. It is typically more preferred for the crystallisation temperature to be within the range of from 170°C to 200°C. While agitation is not necessary to prevent agglomeration of the PEN pellets into an inseparable mass, it is preferred to agitate the PEN solids during the crystallisation step to reduce their potential for lumping. The preferred form of agitation can be provided by utilising a crystalliser which has a fluidised bed. In such fluidised bed crystallisers, air or an inert gas is typically allowed to flow through the crystalliser at a rate sufficient to maintain the chips or pellets in the fluidised state. It is, of course, also possible to perform the crystallisation step in an agitated vessel. The crystallisation step can be carried out as a batch or a continuous operation.

The optimum period of time required for crystallisation is dependent upon the equipment utilised, the type of PEN copolymer, and the size and shape of the pellets or chips. The time required for crystallisation will typically be within the range of 1 minute to 4 hours. In a continuous process, the crystallisation step will normally take 2 minutes to 30 minutes, preferably from 2 minutes to 10 minutes. The PEN copolymer will usually be subjected to crystallisation conditions until the solids attain a degree of crystallinity of 15% or more, more preferably 20% or more. Regardless of the residence time in the crystalliser, whether in a continuous or batch process, the average heat up rate should be as described herein until the temperature reaches at least the sticking temperature of the PEN copolymer pellet, after which any desired heat up profile can be employed.

After the PEN copolymer has been crystallised, it can be solid state polymerised in a batch or continuous process. Suitable solid state polymerisation temperatures can range from a temperature just above the threshold temperature of the polymerisation reaction up to a temperature within a few degrees of the sticking temperature of the PEN copolymer, which can be well below its melting point.

The solid state polymerisation temperature utilised will typically be from 1°C to 50°C below the melting point of the crystallised PEN copolymer. The optimum solid state reaction temperature will differ somewhat for polymers of different composition or degree of polymerisation. As a general rule, the optimum solid state polymerisation temperature for the PEN copolymer will be from 5°C to 20°C below its melting point. For example, in the solid state polymerisation of crystalline PEN copolymer, the temperature employed normally ranges from 210°C to 265°C. Generally, the crystalline PEN copolymer will be solid state polymerised at a temperature of from 230°C to 265°C. In most cases, PEN copolymer will be solid state polymerised at a temperature of from 240°C to 260°C.

As the solid state polymerisation of the PEN copolymer proceeds, its sticking temperature can increase. Thus, the solid state polymerisation temperature can be incrementally increased during the course of the polymerisation. For example, U.S. Patent No. 3,718,621, describes such a technique in the solid state polymerisation of PET.

The solid state polymerisation is conducted under a vacuum or in the presence of a stream of an inert gas. Normally such solid state polymerisations are conducted in the presence of an inert gas stream. It is highly desirable for the inert gas to flow uniformly throughout the solid state polymerisation zone which is filled with the polyester which is being polymerised. In order to help insure that the inert gas flows homogeneously or uniformly through the solid state polymerisation zone without bypassing certain areas in it, a device for dispersing the inert gas is generally used. Thus, a good polymerisation reactor will be designed in such a way that the inert gas will flow homogeneously through the polyester in it. It should be noted that the inert gas actually flows around the pellets or chips of polyester as it streams through the solid state polymerisation zone.

Some suitable inert gases for use in the solid state polymerisation process of this invention include nitrogen, carbon dioxide, helium, argon, neon, krypton, zenon, and certain industrial waste gases. Various combinations or mixtures of different inert gases can also be used. In most cases nitrogen will be used as the inert gas. In a continuous process, the mass flow ratio of PEN copolymer to nitrogen gas will be within the range of 1:0.25 to 1:1.

The solid state polymerisation reactor employed can have a fixed bed, a static bed, a fluidized bed, or a moving bed. In most cases, it is preferred to utilise a cylindrical polymerisation reactor wherein the PEN copolymer flows through the reactor for the desired residence time. Such cylindrical reactors have a substantially uniform cross-section and a sufficient height to allow the PEN copolymer to flow by reason of the force of gravity from the top to the bottom of the reactor in the desired residence time. In other words, the PEN copolymer moves from the top to the bottom of such a cylindrical polymerisation reactor in a partially dammed state. The rate of flow through such a reactor can be controlled by regulating discharge at the bottom of the reactor. It is generally preferred to allow an inert gas to flow countercurrently (upwardly) through the reactor at a gas velocity well below the turbulence point so that the pellets or chips of PEN copolymer are not fluidized (always remain in contact with each other). The pellets or chips of PEN copolymer remain in substantially the same physical form throughout the solid state polymerisation process.

The PEN copolymer will be solid state polymerised for a time sufficient to increase its molecular weight or IV to that of the high molecular weight PEN copolymer resin desired. It will be desirable for the high molecular weight PEN copolymer resin being prepared to have an IV of at least 0.5 dl/g. In most cases the high molecular weight resin will have an IV of at least 0.65 dl/g and for some applications will preferably have an IV of at least 0.8 dl/g. The polymerisation time needed will normally range from 1 to 36 hours and in most cases will range from 6 to 24 hours.

This invention is illustrated by the following examples which are merely for the purpose of illustration and are not to be regarded as limiting the scope of the invention or the manner in which it can be practiced. Unless specifically indicated otherwise all parts and percentages are given by weight.

Comparative Example 1

In each example, the crystlliser used was an agitated fluidized bed made of a glass tube 3.18 cm (1.25 inches) in diameter and 50.8 cm (20 inches) in length. The crystalliser had a cone-shaped bottom which was fitted with a purge gas (dried air or nitrogen) supply tube. During the crystallisation test, two thirds of the length of the crystalliser was immersed in a transparent hot oil bath whose temperature was controlled at 180°C and a stream of nitrogen, preheated to 180°C, was passed through the crystalliser at a flow rate of 0.45 m^3 per hour (16 standard cubic feet per hour). A metal rod was used to agitate the pellets being crystallised. The crystallisation residence time in each case was 15 minutes. The average rate of temperature rise from the temperature of the pellets introduced into the crystalliser (ambient) up to the time at which the pellets reached their sticking temperature was at least 10°C/min. Although the crystalliser used was a simple batch fluidized bed, it is capable of projecting the difficulty or ease with which polyester pellets are crystallised in commercial scale continuous crystallisers.

5 grams of melt polymerised PEN homopolymer pellets having an IV of 0.47 dl/g, a Tg of 120°C, a melting point of 270°C, and a moisture content of 0.54% was charged into the crystalliser whose temperature was maintained at 180°C. Within a short time, as the

temperature of the PEN pellets reached the softening temperature, they visibly puffed up and agglomerated into a tight lump which could not be separated, even under agitation.

Comparative Example 2

5 grams of melt polymerized 95/5 PEN/T copolymer pellets (95 mole % of reacted naphthalene dicarboxylic acid and 5 mole % of reacted terephthalic acid, each based on the moles of all polymerisable acid monomers) was crystallised in the same fashion as in Example 1. These PEN/T copolymer pellets had an IV of 0.45 dl/g, a Tg of 119°C, a melting point of 262°c, and a moisture content of 0.47%. Again, visible to the eye, the pellets puffed up and agglomerated into a tight lump which could not be separated after the crystallisation.

Comparative Example 3

5 grams of melt polymerised 90/10 PEN/T copolymer pellets having an IV of 0.46 dl/g, a Tg of 118°C, a melting point of 255°C, and a moisture content of 0.28% was crystallised in the same fashion as in Example 1. During crystallisation, the pellets expanded substantially and tended to lump, but agglomeration was prevented, albeit with difficulty, by agitation. After 15 minutes of crystallisation, pearl-shaped pellets were obtained.

Example 4

About 5 grams of melt polymerised PEN copolymer pellets, prepared by adding 5 mole % of diethylene glycol to the ethylene glycol precursor, based on the moles of all polymerised hydroxyl functional compounds, was chopped into cylindrical pellets. The PEN/DEG copolymer had an IV of 0.446 dl/g, a Tg of 120°C, and a DSC melting point of 260°C. The pellets as prepared had a moisture content of 0.13%. About 5 grams of these pellets, without any pretreatment for devolatilisation, were crystallised in the same fashion as in Example 1. During and after the crystallisation, no visible puffing or expansion of the pellets was observed and agglomeration of the pellets was prevented with agitation. Well crystallised pellets with normal appearance were obtained within the 15 minute crystallisation cycle.

Example 5

The same PEN/DEG copolymer as prepared in Example 4 was exposed to ambient atmospheric moisture to absorb more water into the pellets. A week later, the moisture content in the pellets increased to 0.20%. These pellets with the higher moisture content were crystallised in the same fashion as in Example 1. Again, no visible puffing or expansion was observed during and at the conclusion of crystallisation. Well crystallised pellets with normal appearance were obtained.

Example 6

The same PEN/DEG copolymer as prepared in Example 4 was soaked in water at room temperature to maximise the moisture content. A week later, the moisture content increased to 0.52%. These pellets were then crystallised in the same fashion as in Example 1. During crystallisation, there was slight expansion of some of the pellets and the pellets were somewhat more sticky, but lumping and agglomeration was still prevented with agitation. Again, well crystallised pellets were obtained, although some of the crystallised pellets were slightly deformed.

There are many advantages associated with the process of this invention. As mentioned previously, if conventional PEN pellets are used, they tend to expand and agglomerate resulting in process upsets. If the PEN pellets are first devolatized, this adds a process step which increased cycle time, and in some cases, adds equipment. This invention eliminates such problems.

CLAIMS

1. A process for crystallising polyethylene naphthalate copolymer in the absence of a devolatilization step comprising:

    a) copolymerising carboxylic acids made up of at least 60 mole % of 2,6-naphthalene dicarboxylic acid; with polyols comprising at least 80 mole % ethylene glycol and from 2 to 20 mole % of a polyol having three or more carbon atoms, based on the total moles of polyols, to form PEN copolymer solids; and

    b) subsequently crystallising said solids comprising heating said solids to at least their sticking temperature at an average rate of at least 10°C/min, to form agglomerate-free crystallised solids.

2. The process of Claim 1, wherein the amount of 2,6-naphthalene dicarboxylic acid is at least 80 mole %.

3. The process of Claim 2, wherein the amount of polyol having 3 or more carbon atoms ranges from 3 to 10 mole %.

4. The process of Claim 1 or 3, wherein said polyol having three or more carbon atoms comprises diethylene glycol, dipropylene glycol, trimethylene glycol, tetramethylene glycol or triethylene glycol.

5. The process of Claim 4, wherein said polyol having three or more carbon atoms comprises diethylene glycol.

6. The process of Claim 1, wherein the volatiles content within said solids immediately prior to step b) ranges from 0.1 to 0.7%.

7. The process of Claim 1, wherein the solids are heated at an average rate of at least 15°C/min.

8. The process of Claim 1, wherein the IV of the copolymer ranges from 0.3 to 0.7 dl/g prior to crystallisation.

9. The process of any one of Claims 1-8 wherein said crystallising solids are subsequently solid state polymerised.

INTERNATIONAL SEARCH REPORT

Inte' ~tional Application No
PC i/EP 99/04699

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08G63/88 C08G63/189

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08G

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97 25364 A (DU PONT) 17 July 1997 (1997-07-17) page 12, line 27 - line 31; claims 1,5,6,14-20 -----	1-9

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

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

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

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Decocker, L

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 99/04699

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9725364 A	17-07-1997	US 5670606 A	23-09-1997
		AU 1570397 A	01-08-1997
		CA 2241961 A	17-07-1997
		EP 0871679 A	21-10-1998
		PL 327733 A	21-12-1998