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(54) Title: HIGH MOLECULAR WEIGHT COPOLYESTER RESINS HAVING LOW MELTING POINTS

(57) Abstract

Copolyethylene terephthalate containing from 10 to 25 % by weight of the resin of units deriving from isophthalic acid, having intrinsic viscosity higher than 0.85 dl/g, melting point lower than 220 °C and crystallization properties such as to solidify from the melt to the amorphous form also by low cooling rate (1 °C/min).
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High molecular weight copolyester resins having low melting points

The present invention relates to high molecular weight copolyester resins having low melting points and peculiar crystallization behaviour and the process for preparing the resins.

It is well known that the molecular weight of the polyester resins can be increased by solid state polycondensation reaction.

The possibility however to upgrade polyester resins having low melting points, e.g. lower than 220°C presents serious process difficulties due to the sticking problems on the walls of the reactor caused by the high upgrading temperatures used.

The known solid state polycondensation processes need high upgrading temperature due to the low kinetic of the upgrading reactions. Usually, the solid state polycondensation reactions of polyester resins are performed by temperatures higher than 180°C; mainly higher than 195°C (see page 3295 of Journal of Applied Polym. Cs. 28 3289 – 3300, 1989).

The possibility of preparing polyester resins with low melting points and having sufficiently high values of the intrinsic viscosity, which are particularly suitable for extrusion blow applications, is a not yet solved problem.

In Applicant's previous pending European application No. 89119049.8 a solid state upgrading process is described in which the resin is upgraded at temperatures higher than 170°C and in general in the range of 170°C - 220°C, using a dianhydride of an aromatic tetracarboxylic acid.

The resins subjected to upgrading comprise copolyethylenterephtalates (COPETs). Amongs the COPETs use is exemplified of copolimers containing at most 10% in
mols of units deriving from isophthalic acid on the total of the acid units. Except the melting point of the resin after upgrading and intrinsic viscosity values no other indications are given regarding the upgraded polymer.

It has now been found that it is possible to upgrade polyester resins having melting points lower than 220°C without having sticking problems and that the upgraded resin presents valuable properties particularly from the viewpoint of the crystallization behaviour.

The resins subjected to upgrading are the copolyethylenenterephthalates containing from 10 to 25% by weight on the total resin weight of units deriving from isophthalic acid (COPETs).

According to the process of the present invention, the COPET is upgraded at temperature lower than 170°C and higher than the TG of the resin, preferably comprised between 130° and 160°C using an upgrading additive selected from the group consisting of the dianhydrides of aromatic, aliphatic cycloaliphatic tetracarboxylic acids.

Unexpectedly, the upgraded COPETs present, besides the high IV values (higher than 0.85 dl/g) and molding points lower than 220°C, other valuable properties.

In particular the crystallization behaviour of the resins is remarkable from the viewpoint of the molding applications, because the resin does not show any crystallinity also by slow cooling from the melt; the COPETs give clear, transparent amorphous solids also by very slow cooling rate, e.g. 1°C/min.

It is worthwhile to note that the resin crystallizes when heated in the solid state for instance at 150°C for 40 mins.

Another interesting property of the resin is its gel-free characteristic.

Particularly interesting is the COPET containing about 15% weight of the resin of isophthalic acid units,
melting point of 212°C. This COPET gives clear highly
transparent amorphous solid by cooling its melt also at
very slow cooling rate (1°C/min). Pyromellitic dianhydride
is the preferred upgrading compound.

Other suitable dianhydrides are the dianhydrides of
1, 2, 3, 4-cyclobutanetetracarboxylic acid,
3,4-dicarboxy-1,2,3,4-tetrahydro-1-naphthalenesuccinic
acid and 3,3',44' benzophenone tetracarboxylic acid.

The preferred dianhydride from the cycloaliphatic
acids is 1,2,3,4 cyclobutantetracarboxylic acid
dianhydride.

Interesting results are also obtainable with the
dianhydride of 3,4 dicarboxy - 1,2,3,4 -
tetrahydro-1-naphthalene succinic acid and bicyclo (2,2,2)
oct-7-ene 2,3,5,6 - tetracarboxylic acid.

The preferred concentration of the additive with
respect to the polyester resin is 0,05-1% by weight.

The solid state upgrading process comprises the steps
of blending the COPET resin in a molten state with the
upgrading additive, converting the melt into granules,
crystallizing the granulate at temperatures higher than
the TG of the resin but lower than 180°C and then upgradi-
ing the crystallized resin at a temperature comprised in
the range from the TG of the resin and 180°C, particularly
from 130" and 170 °C.

The process is preferably carried out in continuous
way using continuous crystallizers and upgrading reactors
where the chips can move counter currently with a stream
of a heated gas, e.g. air, nitrogen and carbon dioxide.

Apparatus suitable for the crystallization and
upgrading steps can be those described in USP 4,064,112
and 4,161,578 whose description is herewith enclosed for
reference.

The recycling of the inert gas streams can be carried
out according to European application 86830340.5 whose
description is herewith enclosed for reference.

The blending of the polyester resin with the additive is carried out in an equipment capable to perform reactive extrusion such as corotating or counter rotating intermeshing or not intermeshing twin screw extruder with or without venting capability at a temperature between 200° and 350°C, depending on the melting point of the polyester.

A counter rotating non intermeshing twin screw extruder vented or not vented is preferred.

The use of such kind of extruder allows to perform a good distribution of the additive in the melt and to avoid problems of local high concentrations of the additive due to its high reactivity.

The extruder may be directly fed with molten COPET from a plant in which the COPET is produced by polycondensation in the molten state.

The extruder may also be fed with solid COPET granulates produced in another plant.

The extruder is preferably connected to a high vacuum oil seal pump to maintain a vacuum higher than 2 torr for the devolatilization of the reactive blend and for obtaining a resin with a low content of acetaldehyde. However, the blending could be also performed without the use of vacuum.

The residence time in the extruder could be comprised between 10 and 120 sec., preferably 15-30 sec.

To avoid random local concentration of additive in the melt it is advisable to dilute the additive with crystallised PET powder (1 part of additive to 5 parts of PET powder). This procedure will ensure a homogeneous distribution of PMDA in the melt leading to a better reproducibility of the end product intrinsic viscosity and inhibiting the gel formation.

The dianhydride could be also diluted using blends of
the dianhydride and crystallized PET-chips (1 part additive to 10 parts PET chips). The dilution could be performed in a fanned blender using about 0.1% of polyethylenglycol or polycaprolactone, as adhesives, and using blending temperature at about 150°C.

The reactive melt coming out of the twin screw extruder is continuously palletized using an underwater pelletizer or a strand pelletizer system.

According to another aspect of this invention, the new COPETs may be modified by blending with polymers like polybutylenterephthalate, polycarbonate, polycaprolactone, polyester elastomers, phenoxy resins in amount up to about 20% by weight of the total resins, directly before the extrusion processing. The addition has the effect of improving the mechanical properties of the composition as well as the processing conditions without sacrificing the transparency of the end product.

Analytical Procedures

The intrinsic viscosity was determined on a solution of 0.5 g of COPET in 100 ml of 60/40 mixture by weight of phenol and tetrachloroethane at 25°C according to ASTM D 4603 - 86.

The acetaldehyde content was determined with a gas chromatographic method according to ASTM D 4526-85, using a Perkin Elmer 8700 gas chromatograph. (Perkin Elmer model HS 101).

The extraction conditions were 150°C for 90 min.

Example 1

30 Kg/h random COPET melt (15% isophthalic acid in weight, melting point 212°C, IV = 0.75 dl/g) having a content of 110 ppm acetaldehyde were fed continuously from the finisher of PET melt polycondensation pilot plant to a counter rotating not intermeshing 30 mm twin screw extruder with venting capability.

220 g/h of a mixture of 20% weight of pyromellitic
acid dianhydride in crystallized COPET powder (IV: 0.75 dl/g, 15% weight isophthalic acid) were fed to the extruder using a gravimetric feeder.

The test conditions were as follows:
- pyromellitic acid dianhydride in the COPET melt = 0.15% by weight
- screw speed: 415 RPM
- ratio length/diameter (L/D): 24
- average residence time: 18 - 25 sec.
- barrel temperature: 235°C
- product melt temperature: 290°C
- vacuum: 1 - 5 torr

A die with double holes was used as extruder die (Diameter: 7 mm).

A strand pelletizer was used to obtain the COPET-chips which had a cylindrical shape with a diameter of 3 mm and a length of 5 mm, and with an intrinsic viscosity IV = 0.85 ± 0.01 dl/g.

The COPET chips had an acetaldehyde content of 5 - 8 ppm. During the test period, the IV of the product was constant over the period of 2 weeks.

The melting point of the product was 212°C.

The COPET-chips were then fed continuously to a solid state upgrading pilot plant using the apparatus and the inert gas recycling conditions set forth in European application EP 86830340.5.

The crystallization temperature was 150°C and the residence time was 40 min.

The temperature of the solid state upgrading reactor was 150°C and the residence time was 12 h.

The IV of the upgraded products was 0.94 ± 0.02 dl/g.

The product was free from gel, with acetaldehyde content of 0.60 ppm.

In comparison, there was no upgrading of COPET not containing pyromellitic dianhydride (starting IV = 0.75
using the same conditions for crystallization and upgrading as in this example.

The crystallization behaviour of the COPET in comparison with standard PET is shown in figure 1.

Fig. 1 shows the crystallization kinetic of COPET prepared according to this example in comparison with standard bottle grade polyethyleneterephthalate. The crystallization kinetic was determined under isothermal conditions at 120°C.

It is interesting that although this COPET is crystallizing in the solid state (150°C/40 min), its melt does not bring about any crystallization by cooling, and gives a clear transparent amorphous solid also by very slow cooling rate.

Table 1 shows the data relating to crystallization by cooling of COPET of example 1 in comparison to standard PET.

All the crystallization data are obtained by DSC measurements performed with Mettler Thermal Analyzer YC 11.

Fig. 2 reports the DSC curves of COPET versus the cooling rate of the melt, starting from a rate of 10°C/min changing then to 5 and 3°C/min = curves A, B, and C respectively. Curve 1 refers to standard PET cooled to a rate of 10°C/min wherein the increase of the heat of crystallization is 11.8 J/g.

**TABLE 1**

Heat of melting of PET samples crystallized with different cooling rates.

Heats are in joule/gram.
<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>QUENCHING</th>
<th>COOLING RATE (deg/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>COPET</td>
<td>2.1 (a)</td>
<td>N</td>
</tr>
<tr>
<td>STANDARD PET</td>
<td>30.0 (b)</td>
<td>34.1 (c)</td>
</tr>
</tbody>
</table>

N = no crystallization

a) crystallization during melting 1.6 J/g
b) crystallization during melting 29.1 J/g
c) crystallization during melting 12.2 J/g

Example 2

30 Kg/h random COPET melt (15% isophthalic acid in weight, melting point 212°C, IV = 0.75 dl/g) having a content of 110 ppm acetaldehyde were fed continuously from the finisher of a PET melt polycondensation pilot plant to a counter rotating not intermeshing 30 mm twin screw extruder with venting capability.

220 g/h of a mixture of 20% weight of 1, 2, 3, 4-cyclobutanetetracarboxylic acid dianhydride in crystallized COPET powder (IV: 0.75 dl/g, 15% weight isophthalic acid) were fed into the extruder using a gravimetric feeder. The test conditions were as follows:

- Cyclobutane tetracarboxylic acid dianhydride in the COPET melt = 0.15% by weight
- Screw speed: 415 RPM
- Ratio length-diameter (L/D): 24
- Average residence time: 18 - 25 sec.
- Barrel temperature: 235°C
- Product melt temperature: 290°C
- Vacuum: 1 - 5 torr.

A die with double holes was used as extruder die (Diameter: 7 mm).

A strand pelletizer was used to obtain the COPET-chips which had a cylindrical shape with a diameter of 3
mm and a length of 5 mm, and with an intrinsic viscosity IV = 0.865 ± 0.01 dl/g.

The COPET chips had an acetaldehyde content of 6 - 9 ppm. During the test period, the IV of the product was constant over a period of 2 weeks.

The melting point of the product was 212°C.

The modified COPET-chips were then fed continuously into a solid state polycondensation pilot plant using the apparatus and the inert gas recycling conditions described in European application EP 86830340.5.

The crystallization temperature was 150°C and the residence time in the crystallizer was 40 min. The solid state temperature in the reactor was 150°C and the residence time was 10 h. The IV of the upgraded product was 0.965 dl/g. The product was free from gel, with an acetaldehyde content of 0.60 ppm.

In comparison, there was no upgrading of COPET not containing the dianhydride (starting IV = 0.75 dl/g), using the same conditions for crystallization and upgrading as in this example.

**Example 3**

The same COPET was used as in Example 1, but in the form of crystallized COPET granules of IV = 0.75 dl/g.

The crystallized COPET chips were dried and fed into the twin screw.

The IV of the product was 0.845 ± 0.02 dl/g.

The same conditions were used as in Example 1; only the average residence time was about 25 sec.

The solid state conditions were 130° - 140°C in the crystallizer and 140°C in the polyaddition reactor. The residence time in the reactor was 10 hours. The chips intrinsic viscosity was 0.92 ± 0.015 dl/g. The acetaldehyde content was 0.67 ppm.

**Example 4**

The following table reports the extrusion blow
moulding conditions and the apparatus used for the production of the bottles up to 1500 ml:
mould: rotative distributor / 2 moulds
head: PET covered mono parison
screw length: 24 L/D
screw size: 65 mm
screw type: standard PVC
article: round bottle
volume: up to 1500 ml
output: 50.4 Kg/h (depends on the bottle volume)
parison length: up to 40 cm
production: 960 bottles/hour
cycle: 8.0 seconds
temperature
barrel: 250°C
profile head: 280°C
die: 290°C

The COPET was dried to a content of water less than 0.005% using dried air with Dew point between -30°C and -40°C.

The following table gives the blowing conditions and the results obtained using the COPET of example 1.

<table>
<thead>
<tr>
<th>RESIN</th>
<th>BARREL / HEAD / DIE</th>
<th>BOTTLE / HOURS</th>
<th>BOTTLE</th>
<th>OUTPUT</th>
<th>SCREW</th>
<th>ACA</th>
<th>DROP</th>
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<td></td>
<td>TEMP.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>°C</td>
<td>No.</td>
<td>gr</td>
<td>Kg/h</td>
<td>rpm</td>
<td>ppm</td>
<td>cm</td>
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<tr>
<td>COPET</td>
<td>230  270  280  960</td>
<td>42</td>
<td>1</td>
<td>50.4</td>
<td>48</td>
<td>3.6</td>
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</table>

ACA = acetaldehyde

Example 5

This example describes the extrusion blowing of COPET produced according to example and mixed before blowing with polybutylenetherphthalate (General Electric) (PBT); IV
= 1.220 d1/g in amount of 3.5% by weight.

This mixture was dried and blowed according to the general description of example 4.

The following table gives the blowing conditions and the results obtained.

<table>
<thead>
<tr>
<th>RESIN</th>
<th>BARREL / HEAD / DIE</th>
<th>BOTTLE / HOURS</th>
<th>BOTTLE</th>
<th>OUTPUT</th>
<th>SCREW</th>
<th>ACA</th>
<th>DROP</th>
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<tr>
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<td>TEMP.</td>
<td>WEIGHT</td>
<td>SPEED</td>
<td>TEST</td>
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<tr>
<td></td>
<td>°C</td>
<td>gr</td>
<td>Kg/h</td>
<td>rpm</td>
<td>ppm</td>
<td>cm</td>
<td></td>
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<tr>
<td>COPET</td>
<td>[240, 280, 300, 960]</td>
<td>42</td>
<td>1</td>
<td>50.4</td>
<td>52</td>
<td>3.7</td>
<td>70</td>
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</table>

Example 6

This example describes the extrusion blowed of COPET of example 1 and mixed before blowed with 5% by weight of polycarbonate (Dow Chem.).

This mixture was then dried and blowed according to the general description of example 4.

The following table reports the conditions and the obtained results.

<table>
<thead>
<tr>
<th>RESIN</th>
<th>BARREL / HEAD / DIE</th>
<th>BOTTLE / HOURS</th>
<th>BOTTLE</th>
<th>OUTPUT</th>
<th>SCREW</th>
<th>ACA</th>
<th>DROP</th>
</tr>
</thead>
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<tr>
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<td>TEMP.</td>
<td>WEIGHT</td>
<td>SPEED</td>
<td>TEST</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>°C</td>
<td>gr</td>
<td>Kg/h</td>
<td>rpm</td>
<td>ppm</td>
<td>cm</td>
<td></td>
</tr>
<tr>
<td>COPET</td>
<td>[240, 290, 300, 960]</td>
<td>42</td>
<td>1</td>
<td>50.4</td>
<td>52</td>
<td>3.7</td>
<td>70</td>
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</tbody>
</table>

Example 7

This example describes the extrusion blowed of COPET of example 1 mixed before blowed with 5% by weight of phenoxy resin (Union Carbide).

This mixture was then dried and blowed according to the general description of example 4.

The following table reports the conditions and the results obtained.
<table>
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<tr>
<th>Resin</th>
<th>Barrel / Head / Die</th>
<th>Bottle / Hours</th>
<th>Bottle</th>
<th>Output</th>
<th>Screw</th>
<th>ACA</th>
<th>Drop</th>
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<td>Temp.</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>°C</td>
<td>No.</td>
<td>gr</td>
<td>Kg/h</td>
<td>rpm</td>
<td>ppa</td>
<td>cm</td>
<td></td>
</tr>
<tr>
<td>COPET</td>
<td>240 280 300 960</td>
<td>42</td>
<td>1</td>
<td>50.4</td>
<td>50</td>
<td>5.1</td>
<td>69</td>
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CLAIMS

1. Copolyethylterephthalate containing from 10 to 20% by weight of the resin of units deriving from isophthalic acid, having intrinsic viscosity higher than 0.85 dL/g, melting point lower than 220°C and solidifying from the melt to amorphous solid (cooling rate not less than 1°C/min).

2. Copolyethylterephthalate according to claim 1, containing about 15% by weight of the resin of units from isophthalic acid.

3. Copolyethylterephthalate according to claims 1 and 2, free from gel.

4. Copolyethylterephthalate according to claim from 1 to 3, obtained with a process comprising the steps of blending in the molten state a copolyethylterephthalate with intrinsic viscosity less than 0.85 dL/g with 0.05 - 1% by weight of a dianhydride of an aliphatic, cycloaliphatic, aromatic tetracarboxylic acid, pelletizing the melt, crystallizing and then upgrading the resin at temperatures higher than TG and lower than 170°C.

5. Copolyethylterephthalate according to claims 1 to 4, mixed with 1 - 20% by weight of a polymer selected from polycarbonate, polybutylterephthalate, epoxy resins.

6. Formed articles obtained from the copolyethylterephthalate of the previous claims.

7. Bottles obtained by blow molding the copolyethylterephthalates of the claims from 1 to 5.
FIG. 1

DEGREE OF CRYSTALLIZATION

TIME (min.)

--- STANDARD PET
--- COPET

1/2
**INTERNATIONAL SEARCH REPORT**

**I. CLASSIFICATION OF SUBJECT MATTER**

If several classification symbols apply, indicate all.°

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C08G63/181; C08G63/20; C08L67/02

**II. FIELDS SEARCHED**

<table>
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**III. DOCUMENTS CONSIDERED TO BE RELEVANT**

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of Document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to Claim No.</th>
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<tr>
<td>Y</td>
<td>LU, A, 56 112 (IMPERIAL CHEMICAL INDUSTRIES LIMITED) 9 September 1968 see claim I - I.1, I.2, I.3, I.4, I.16 see page 4, line 20 - line 40 see page 6, line 3 - line 27 see examples</td>
<td>1, 4</td>
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<tr>
<td>Y</td>
<td>FR, A, 2 250 782 (GENERAL ELECTRIC COMPANY) 6 June 1975 see claims 1, 9</td>
<td>1, 4</td>
</tr>
</tbody>
</table>

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- **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

- **I** 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
- **Y** document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step
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- **A** document member of the same patent family

**IV. CERTIFICATION**

Date of the Actual Completion of the International Search

15 JUNE 1992

International Searching Authority

EUROPEAN PATENT OFFICE

Date of Mailing of this International Search Report

13. 07. 92

Signature of Authorized Officer

K. Y. P. Miao

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<td>CHEMICAL ABSTRACTS, vol. 63, no. 9, 25 October 1965, Columbus, Ohio, US; M. MURANO; ET AL: 'Determination of the copolymerization ratio in poly(ethylene terephthalate-isophthalate) by high resolution nuclear magnetic resonance spectroscopy'; column 11714; J. Polymer Sci., Pt. A 3(7), 2698-700(1965)(Eng). see abstract</td>
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<td>CHEMICAL ABSTRACTS, vol. 89, no. 16, 16 October 1978, Columbus, Ohio, US; abstract no. 130514U, 'Thermoplastic polyester resin composition' page 44 column RIGHT; JP,A,78 71611 (TORAY INDUSTRIES, INC.) 26 June 1978 (26.06.78) see abstract</td>
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