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(54) Title: HIGH SHRINKAGE POLYESTER FIBRES

(57) Abstract: The present disclosure relates to a polyester fibre having shrinkage capacity in the range of 20 to 22 % at a temperature of 130 °C. The polyester fibre of the present disclosure further comprises at least one co-monomer up to 2 w/w%.

HIGH SHRINKAGE POLYESTER FIBRES

FIELD:

The present disclosure relates to shrinkable polyester fibres. The present disclosure also relates to a polymeric blend comprising the shrinkable polyester fibres.

DEFINITIONS:

In the context of the present disclosure the terms "high shrinkage" or "high shrinkable" includes a polymer having a shrinkage capacity of at least 20 %; and the terms "low shrinkage" or "low shrinkable" includes a polymer having a shrinkage capacity below 5 %.

The tenacity of the fibers is expressed in the units of grams per denier (gpd).

The size of the fibers is expressed in Denier (D).

BACKGROUND:

Polyester fibres are employed in a wide variety of applications such as in manufacturing bedspreads, sheets, pillows, carpets and curtains. Shrinkage property is one of the factors in deciding the application of the polyester fibres. For instance, polyester fibres with low shrinkable property may not be suitable for applications where high shrinkable acrylic acids are used. The reason being the aesthetic look of the polyester fibres may be affected due to repeated use or exposure to adverse conditions. Due to this problem associated with polyester fibres, acrylic fibres are preferred over the polyester fibres in certain applications due its enhanced shrinkable property. Further, in certain applications it is also required to blend low shrinkable acrylic fibres with high shrinkable acrylic fibres to produce a product having properties suitable for that particular application; however, the cost of acrylic fibre is very high. Therefore, there is a need for economic polyester fibres having high shrinkable property so that the costly acrylic fibres are replaced with

economical polyester fibres. Several attempts have been made in the past to provide high shrinkable polyester fibres.

JPH09-296056 suggests polyethylene terephthalate fibres having heat shrinkage capacity in the range of 1.5 to 35 %. The polyethylene terephthalate contains 2 to 20 mol% isophthalic acid component.

Japanese Patent No. JPH02104722 suggests high-shrinkage polyethylene terephthalate fibres which are copolymerized with 4.0-10.0mol% of isophthalic acid.

Japanese Patent No. JPH08113825 suggests high shrinkage polyester fibres containing 2-20 mol % biphenyl 2, 2' dicarboxylic acid or its ester.

The shrinkage capacity of these polyester fibres is unacceptable for niche applications.

Therefore, there is felt a need for high shrinkable polyester fibres that contain relatively low amounts of isophthalic acid component and possesses an acceptable shrinkage capacity.

OBJECTS:

Some of the objects of the present disclosure, which at least one embodiment herein satisfies, are as follows:

An object of the present disclosure is to provide polyester fibres having high shrinkage capacity.

Another object of the present disclosure is to provide polyester fibres containing lower amounts of co-monomer.

Still another object of the present disclosure is to provide polyester fibres which can be easily processed to achieve the desired dye depth.

Still another object of the present disclosure is to provide polyester fibres having the desired denier size.

Still another object of the present disclosure is to provide polyester fibres which can be used to at least partially substitute acrylic fibres.

Yet another object of the present disclosure is to provide a process for preparing polyester fibres having high shrinkage capacity.

Further object of the present disclosure is to provide a blend of polyester fibres having high shrinkage capacity.

SUMMARY:

Polyester fibres having acceptable level of shrinkage capacity and containing at least one co-monomer not more than 2 wt% is provided which can be replaced for high shrinkable acrylic fibres in textile applications. The dyeability of the polyester fibres of the present disclosure can be adjusted to match with the dyeability of the component in which it is blended or mixed so that the resulting product possesses uniformly dyed. The shrinkage capacity of the polyester fibres of the present disclosure ranges from 20 to 22 % whereas the denier size is in the range of 1.2 to 4. The polyester from which the fibres of the present disclosure are prepared may contain at least one co-monomer to give polyester fibres having co-monomer in the specified range. Such polyester may be recycled polyester from polyethylene terephthalate bottles. Alternatively, if fresh polyester is used then at least one co-monomer may be added in an amount to yield polyester fibre having co-monomer in the specified range.

DETAILED DESCRIPTION:

Though the aesthetic look of polyester fibres is acceptable it cannot be used in certain applications due to other un-suitable properties. For instance, polyester fibres cannot be

used in textiles where high shrinkage property is desirable. Instead, acrylic fibres are used even if they are costly and not so aesthetic in appearance as compared to polyester fibres. Thus, it would be advantageous to develop polyester fibres having high shrinkage capacity. Accordingly, the present disclosure provides polyester fibres having shrinkage capacity in the range of 20 to 22 % at a temperature of 130 ^{o}C for a time period of 30 minutes. The polyester in the polyester fibres of the present disclosure is recycled polyester or is obtained from a polymerization reaction. The polyester fibres of the present disclosure comprise at least one co-monomer up to 2 w/w%.

Examples of co-monomer useful for the purpose of the present disclosure include but are not limited to, isophthalic acid, 2-methyl-1,3-propanediol, trimethylene glycol and cyclohexane dimethanol.

Examples of polyester in the polyester fibre include but are not limited to polyethylene terephthalate, polybutylene terephthalate and polyethylene naphthalate. It is observed that polyethylene terephthalate is specifically useful for the purpose of the present disclosure as it is readily available or can be prepared economically. Further, polyethylene terephthalate provides the desired characteristics to the polyester fibres of the present disclosure.

Another property that also characterizes the polyester fibres of the present disclosure is denier size of the final fibre. The denier size of the polyester fibres of the present disclosure is in the range from 1.2 to 4 denier.

The present disclosure is further described in light of the following experiments which are set forth for illustration purpose only and not to be construed for limiting the scope of the disclosure.

Example 1:

Polyester fibres of the present disclosure were prepared in five steps as follows:

Step 1:- Esterification stage

In a continuously run process, pure Terephthalic acid was reacted with mono ethylene glycol in the presence of 1.8 wt% isophthalic acid at a temperature of 250 to 290 °C to obtain an oligomer.

400 ppm of antimony trioxide as the catalyst and 0.3 wt % of titanium dioxide as a dulling agent were added to the oligomer.

Step 2:- Polymerization

The oligomer obtained in step 1 was subjected to polymerization at a temperature of 270 to 290°C and at a pressure in the range of 0.1 to 3.0 mm Hg to obtain polyethylene terephthalate.

Step 3:- Spinning and drawing

Polyethylene terephthalate obtained in step 2 was fed to a spinning machine and the entire downstream operation was carried out in a staple line involving spinning and drawing to make fibres having shrinkage level of 20 %. The tenacity of the obtained fibres was 4.2 gpd and the size of the fibres was 2.5D.

Example 2:

15 tons of polyethylene terephthalate flakes (obtained from recycled PET) containing 1.8 wt% isophthalic acid component, was dried at 150 °C for 7 to 9 hrs. and spun at 265 to 290°C using a staple line. Tow was further processed to obtain polyethylene terephthalate fibres having 22 % of shrinkage. The tenacity of the obtained fibres was 4 gpd and the size of the fibres was 2.8D.

Shrinkage Test: A tow of predetermined denier is cut to a certain length, and preweighed. Thereafter, it is subjected to a temperature of 130 °C for 30 min. The length

of the heated fibre is now measured and the length difference noted, the shrinkage value is calculated.

Throughout this specification the word "comprise", or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated element, integer or step, or group of elements, integers or steps, but not the exclusion of any other element, integer or step, or group of elements, integers or steps.

The use of the expression "at least" or "at least one" suggests the use of one or more elements or ingredients or quantities, as the use may be in the embodiment of the disclosure to achieve one or more of the desired objects or results.

Any discussion of documents, acts, materials, devices, articles or the like that has been included in this specification is solely for the purpose of providing a context for the disclosure. It is not to be taken as an admission that any or all of these matters form a part of the prior art base or were common general knowledge in the field relevant to the disclosure as it existed anywhere before the priority date of this application.

The numerical values mentioned for the various physical parameters, dimensions or quantities are only approximations and it is envisaged that the values higher/lower than the numerical values assigned to the parameters, dimensions or quantities fall within the scope of the disclosure, unless there is a statement in the specification specific to the contrary.

While considerable emphasis has been placed herein on the particular features of this disclosure, it will be appreciated that various modifications can be made, and that many changes can be made in the preferred embodiments without departing from the principles of the disclosure. These and other modifications in the nature of the disclosure or the preferred embodiments will be apparent to those skilled in the art from the disclosure herein, whereby it is to be distinctly understood that the foregoing descriptive matter is to be interpreted merely as illustrative of the disclosure and not as a limitation.

The foregoing description of the specific embodiments will so fully reveal the general nature of the embodiments herein that others can, by applying current knowledge, readily modify and/or adapt for various applications such specific embodiments without departing from the generic concept, and, therefore, such adaptations and modifications should and are intended to be comprehended within the meaning and range of equivalents of the disclosed embodiments. It is to be understood that the phraseology or terminology employed herein is for the purpose of description and not of limitation. Therefore, while the embodiments herein have been described in terms of preferred embodiments, those skilled in the art will recognize that the embodiments herein can be practiced with modification within the spirit and scope of the embodiments as described herein.

TECHNICAL ADVANCES:

The present disclosure described herein above has several technical advantages including, but not limited to, the realization of:

- Providing polyester fibres having high shrinkage capacity
- Replacing at least a portion of acrylic high shrinkable component by the fiber of the present disclosure
- Providing a normal shrinkable component having tensile properties and dyeability closely matching with that of the high shrinkable component of polyester.

CLAIMS:

1. A polyester fibre having shrinkage capacity in the range of 20 to 22 % at a temperature of 130 ^{o}C, wherein said polyester fibre comprises at least one co-monomer in a quantity less than 2 w/w%.

2. The polyester fibre as claimed in claim 1, wherein the polyester in the polyester fibre is formed from at least one polymer selected from the group consisting of polyethylene terephthalate, polybutylene terephthalate and polyethylene naphthalate.

3. The polyester fibre as claimed in claim 2, wherein the polymer is fresh, recycled or a combination thereof.

4. The polyester fibre as claimed in claim 1, wherein the co-monomer is at least one selected from the group consisting of isophthalic acid, 2-methyl-1,3-propanediol, trimethylene glycol and cyclohexane dimethanol.

5. The polyester fibre as claimed in claim 1, characterized by denier size in the range from 1.2 to 4.

INTERNATIONAL SEARCH REPORT

International application No.
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A. CLASSIFICATION OF SUBJECT MATTER
D01F6/62 Version=2015.01

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)

D01F

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

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

IPO Internal Database, PATSEER

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US5567796 A (NAKATSUKASA Sigeki et al.) October 22, 1996. Whole document	1-5
X	EP0207489 A2 (SHIMAZU Takumi et al.) January 7, 1987. Whole document	1-5

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent 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
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

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Citation	Pub.Date	Family	Pub.Date
US 5567796 A	22-10-1996	CN 1069353 C	08-08-2001
		CN 1113392 A	13-12-1995
		CN 1310253 A	29-08-2001
		CN 1664195 A	07-09-2005
		CN 1664199 A	07-09-2005
		DE 69418848 D1	08-07-1999
		DE 69418848 T2	27-01-2000
		EP 0664351 A1	26-07-1995
		EP 0664351 A4	22-01-1997
		EP 0664351 B1	02-06-1999
		WO 1995004846 A1	16-02-1995
EP 0207489 A2	07-01-1987	EP 0207489 A3	13-01-1988