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(54) Title: A POLYURETHANE ELASTIC FIBER WITH HIGH HEAT SETTABLE PROPERTY

(57) Abstract: The present invention relates to a process for preparing polyurethane and polyurethane elastic yarns made therefrom, wherein an amount of 1,3-diaminopropane contained in a chain extender is 40 mol % or more based on the total chain extender and the chain extender further comprises at least one selected from a group consisting of ethylene diamine, 1,2- diaminopropane, 1,4-diaminobutane, 2,3-butanediamine, 1,5-pentanediamine, 1,6-hexandiamine and 1,4-cyclohexanediamine. The polyurethane elastic yarns show excellent heat settable property at low temperature and a fabric using the elastic yarns may be heat-set at low temperature to prevent edge curling and to improve fabric hand value of a knitted fabric.

Description

A POLYURETHANE ELASTIC FIBER WITH HIGH HEAT SETTABLE PROPERTY

Technical Field

[1] The present invention relates to a process for preparing polyurethane and an elastic fabric comprising polyurethane elastic yarns made therefrom and, particularly, to polyurethane prepared by adding diamine of chain extender at a predetermined rate and polyurethane elastic yarns made therefrom having excellent heat settable property.

[2] More particularly, the present invention relates to a knitted fabric consisting of the elastic fabric having excellent heat settable property at low temperature and a heat-sensitive fiber such as nylon, silk, wool, polypropylene, rayon and polytrimethylene terephthalate. The knitted fabric may be heat-set at low temperature to prevent heat degradation of the heat-sensitive fiber and edge curling of the knitted fabric.

Background Art

[3] Polyurethane is customarily prepared by reacting a polyol with an excessive amount of diisocyanate to prepare a prepolymer, dissolving the prepolymer in an organic solvent and then adding diamine or diol of chain extender to the resulting solution and reacting with chain terminator such as mono-alcohol and monoamine to form a polyurethane spinning solution which is then dry- or wet-spun to make the polyurethane elastic fiber.

[4] The polyurethane fiber is characterized by its high elasticity and widely used in a variety of areas. As its usage has expanded, there is a growing demand for developing extra features of polyurethane fibers.

[5] Generally, polyurethane fibers is heat-set at high temperature during a post-process after knitting and the high temperature causes heat degradation of heat-sensitive fibers such as nylon, cotton, silk, wool, polypropylene, rayon and polytrimethylene terephthalate. In order to prevent heat degradation and improve fabric hand value, it is increasingly necessary to develop a polyurethane fiber to be heat-set at low temperature.

[6] In the related art, efforts to improve the heat settable property of polyurethane fibers have been continued. For examples, Japanese Patent Publication No. S63-53287, Japanese Patent Publication No. S63-53288, Japanese Patent Publication No. S43-639, Japanese Patent Publication No. H7-316922, Korean Patent Publication No. 2001-5854, Korean Patent Publication No. 2001-16788 disclose processes for improving heat settable property of polyurethane elastic yarns. Furthermore, U.S. Patent No. 6,472,494, U.S. Patent No. 6,403,682, U.S. Patent No. 6,376,071, U.S.

Patent No. 6,063,892, U.S. Patent No. 5,981,686, U.S. Patent No. 5,948,875 disclose processes for improving the heat settable property of polyurethane elastic yarns. Due to the lack of heat settable property at a low temperature, however, heat-sensitive fibers have not been applicable to the processes disclosed in the prior arts.

Disclosure of Invention

Technical Problem

[7] The object of the present invention is to prepare polyurethane elastic yarns having excellent heat settable property with appropriate amine. According to the present invention, the polyurethane elastic yarns are knitted with a heat-sensitive fiber such as nylon, cotton, silk, wool, polypropylene, rayon and polytrimethylene terephthalate. The knitted fabric may be heat-set at low temperature to prevent fabric degradation of the heat-sensitive fiber which in turn improves fabric hand value and to provide the knitted fabric without edge curling.

Technical Solution

[8] According to a preferred embodiment of the present invention, a process for preparing polyurethane elastic yarns having excellent heat settable property and an elastic fabric made therefrom are produced by reacting polyols with an excessive amount of diisocyanate to prepare a prepolymer, dissolving the prepolymer in an organic solvent and reacting the resulting solution with a chain extender in order to prepare polyurethane elastic yarns, wherein an amount of 1,3-diaminopropane contained in the chain extender is 40 mol% or more based on the total chain extender.

[9] According to another preferred embodiment of the present invention, a process for preparing polyurethane elastic yarns is provided wherein the chain extender further comprises at least one selected from a group consisting of ethylene diamine, 1,2- diaminopropane, 1,4-diaminobutane, 2,3-butanediamine, 1,5-pentanediamine, 1,6-hexandiamine and 1,4-cyclohexanediamine.

[10] According to another preferred embodiment of the present invention, a process for preparing polyurethane elastic yarns is provided wherein the prepolymer contains 1.56 wt% to 4.29 wt% of isocyanate based on the total prepolymer.

Advantageous Effects

[11] By using the polyurethane elastic yarns produced in accordance with the present invention, a knitted fabric may be heat-set at lower temperature after knitting compared to the prior arts. Hence, heat degradation of the heat-sensitive fiber may be prevented which in turn improves fabric hand value. It also prevents edge curling of the knitted fabric.

Best Mode for Carrying Out the Invention

[12] Hereinafter, polyurethane elastic yarns having excellent heat settable property

according to the present invention will be described.

[13] Segmented polyurethane used in the present invention is made by reacting organic diisocyanate with polymer diol to prepare a prepolymer, dissolving the prepolymer in an organic solvent and then reacting with diamine and monoamine.

[14] Examples of organic diisocyanate used in the present invention may include at least one selected from a group consisting of diphenylmethane-4,4-diisocyanate, 1,5-naphthalenediisocyanate, 1,4-phenylenediisocyanate, hexamethylenediisocyanate, 1,4-cyclohexanediisocyanate, 4,4'-dicyclohexylmethanediisocyanate and isophorone diisocyanate.

[15] Examples of polymer diol used in the present invention may include polytetramethylen-etherglycol, polypropylene-etherglycol and polycarbonatediol. Diamine may be used as chain extender from at least one selected from a group consisting of ethylenediamine, 1,2-diaminopropane, 1,6-hexamethylendiamine and 1,3-diaminopropane. The content of 1,3-diaminopropane based on the total chain extender should be 40 mol% or more preferably. If it is less than 40 mol %, the heat settable property of polyurethane elastic yarn considerably deteriorates.

[16] Examples of amine having one functional group used in the present invention to control molecule weight of polyurethaneurea may include diethyl amine, monoethanolamine, dimethyleamine and so on.

[17] Furthermore, in order to prevent discoloration and deterioration of spandex under certain environmental conditions such as ultraviolet rays and smog and possibly in the heat-setting process, sterically hindered phenolic compounds, benzofuran-on compounds, semicarbazide compounds, benzotriazole compounds and polymeric tertiary amine stabilizer may be added in combination into a spinning solution.

[18] The polyurethane elastic yarns in the present invention may further include additives such as titanium dioxide and magnesium stearate.

Mode for the Invention

[19] A better understanding of the present invention may be obtained in light of the following Examples which are set forth to illustrate, but are not to be construed to limit the present invention.

[20] As described below in the Examples and Comparative Examples, the heat settable property of polyurethane yarns and the edge curling of polyurethane fibers were measured using the following methods.

[21]

[22] Evaluation of heat settable property of polyurethane yarns

[23] After being stretched to 100% (from 125 mm to 250 mm) in the air, the produced yarns was dry-heated at 170°C for one minute and then the yarns were cooled to room

temperature. The length of the yarns was measured, and heat settable property was calculated according to the following formula:

[24]

[25] Heat settable property(%)= {(heat-set length - original length)}/ (stretched length - original length)} x 100

[26]

[27] Evaluation of edge curling

[28] Spandex heat-set at low temperature were knitted with nylon to prepare a circular-knitted fabric. After drawing a regular triangle whose side is 5 cm long on the knitted fabric, two sides of the triangle were cut it out with scissor, and water-sprayed on it and dried. After drying, the edge curling the knitted fabric was calculated according to the following formula.

[29]

[30] Edge curling(%)= (the area of triangle being curled/ the initial area of the triangle) x 100

[31]

[32] [Example 1]

[33] 550g of diphenylmethane-4,4-diisocyanate and 2328g of polytetramethylene etherglycol(the molecular average weight was 1800) were reacted with agitation in a nitrogen gas atmosphere at 80°C for 90 minutes to produce a polyurethane prepolymer having isocyanate at both ends thereof. The prepolymer was cooled to room temperature, and 4122g of dimethylacetamide was added and dissolved to produce a polyurethane prepolymer solution. Subsequently, 46.08g(0.622 mol) of 1,3-diaminopropane, 16.01g(0.266 mol) of ethylenediamine and 5.2g of diethylamine were dissolved in 894g of dimethylacetamide, and added to the prepolymer solution below 10°C to produce a polyurethane solution.

[34] The solid additives to the solution may include 1.5 wt% of ethylenebis(oxyethylene)bis-(3-(5-ter-butyl-4-hydroxy-m-toyl)-propionate), 0.5 wt% of 5,7-di-t-butyl-3-(3,4-dimethylphenyl)-3H-benzofuran-2-one, 1 wt% of 1,1,1',1'-tetramethyl-4,4'-(methylene-di-p-phenylene)disemicarbazide, 1 wt% of poly(N,N-diethyl-2-aminoethyl methacrylate) and 0.1 wt% of titanium dioxide to produce a polyurethane spinning solution.

[35] The solution was then dry-spun at 250°C to produce polyurethane elastic yarns of 40 denier.

[36] Using the resulting polyurethane elastic yarns whose heat-set temperature is low and nylon fibers, a circular-knitted fabric was made using a circular-knitting machine(Mayer Co.) with 38 inches cylinder diameter, 28 gauge and 120 feeder. The nylon used in preparing the knitted fabric is 70 denier nylon and knitted with 40 denier

of elastic yarns produced by the process, and the content of the elastic yarns is 8 wt% based on the total fabric weight.

[37]

[38] [Example 2]

[39] 550.2g of diphenylmethane-4,4-diisocyanate and 2328g of polytetramethylene etherglycol(the molecular average weight was 1800) were reacted with agitation in a nitrogen gas atmosphere at 80°C for 90 minutes to produce a polyurethane prepolymer having isocyanate at both ends thereof. The prepolymer was cooled to room temperature, and 4122g of dimethylacetamide was added and dissolved to produce a polyurethane prepolymer solution. Subsequently, 32.92g(0.444 mol) of 1,3-diaminopropane, 16.01g(0.2664 mol) of ethylenediamine, 13.17g(0.1776 mol) of 1,2-diaminopropane and 5.2g of diethylamine were dissolved in 894g of dimethylacetamide, and added to the prepolymer solution below 10°C to produce a polyurethane solution. Additives having the same composition as those of Example 1 were added and the process for preparing yarns and fabric was carried out as in Example 1.

[40]

[41] [Example 3]

[42] 550.2g of diphenylmethane-4,4-diisocyanate and 2328g of polytetramethylene etherglycol(the number average molecular weight was 1800) were reacted with agitation in a nitrogen gas atmosphere at 80°C for 90 minutes to produce a polyurethane prepolymer having isocyanate at both ends thereof. The prepolymer was cooled to room temperature, and 4122g of dimethylacetamide was added and dissolved to produce a polyurethane prepolymer solution. Subsequently, 65.83g(0.888 mol) of 1,3-diaminopropane and 5.2g of diethylamine were dissolved in 900g of dimethylacetamide, and added to the prepolymer solution below 10°C to produce a polyurethane solution.

[43] Additives having the same composition as those of Example 1 were added and the process for preparing yarns and fabric was carried out as in Example 1.

[44]

[45] [Example 4 to 6 and Comparative Example 1 to 3]

[46] Example 4 to 6 and Comparative Example 1 to 3 were carried out as in Example 1, except the changes in the weight percent (wt%) of isocyanate, the type and mol percent(mol%) of chain extender as shown in Table 1.

[47] Table 1

	The wt% of isocyanate	The type of chain extender	The ratioof chain extender	Heat settable property (%)

Ex. 1	2.64	EDA/1,3-PDA	30/70	76
Ex. 2	2.64	EDA/1,2-PDA/1,3-PDA	30/20/50	72
Ex. 3	2.64	1,3-PDA	100	74
Ex. 4	2.64	EDA/1,3-PDA	60/40	72
Ex. 5	1.93	EDA/1,3-PDA	30/70	83
Ex. 6	4.29	EDA/1,3-PDA	30/70	70
Comp.Ex. 1	2.64	EDA/1,2-PDA	80/20	48
Comp.Ex. 2	2.64	EDA/1,2-PDA	30/70	52
Comp.Ex. 3	1.93	EDA/1,2-PDA	30/70	55

[48]

[49] As shown in Table 1, the polyurethane elastic yarns prepared with 1,3-diaminopropane as chain extender at 40 mol% or more resulted in an increase of heat settable property.

[50]

[51] [Example 7 to 10 and Comparative Example 4 to 6]

[52] Example 7 to 10 were carried out to produce a circular-knitted fabric with elastic yarns prepared in Example 1 and nylon, and Comparative Example 4 to 6 were carried out with elastic yarns prepared by Comparative Example 1 and nylon. They were then treated under the heat-setting conditions shown in Table 2. The edge curling(%) and fabric hand value of the resulting fabric are shown in Table 2.

[53]

[54] Table 2

	The temperature of pre-setting(°C)	The temperature of final-setting(°C)	Edge curling(%)	Fabric hand value
Ex. 7	170	160	0	excellent
Ex. 8	175	160	0	excellent
Ex. 9	165	155	0	excellent
Ex. 10	N/A	175	0	excellent
Comp.Ex. 4	175	165	100	excellent

Comp.Ex. 5	190	180	0	inferior
Comp.Ex. 6	180	170	100	excellent

[55]

[56] As shown in Table 2, in the process of preparing circular-knitted nylon fabric, the fabric of Example 7 to 10 prepared with yarns in Example 1 do not cause edge curling even at 20°C lower heat-setting temperature, compared to the fabric in Comparative Example 5 prepared with yarns in comparative Example 1. Meanwhile, no edge curling occurred in Comparative Example 5, but the fabric hand value was inferior because it was heat-set at high temperature. As shown in the Table, the fabric using spandex does not cause heat degradation of nylon with the heat-setting process at lower temperature and therefore the fabric may have excellent fabric hand value. Furthermore, as shown in Example 10, the process of pre-setting may be omitted.

[57] The present invention is specifically explained providing illustrative embodiments. It is to be appreciated that those skilled in the art may change or modify the embodiments without departing from the scope and sprit of the present invention. While the present invention has been described with reference to the particular illustrative embodiments, it is not to be restricted by the embodiments but only by the appended claims.

Industrial Applicability

[58] The polyurethane elastic yarns of the present invention show excellent heat settable property at low temperature. Therefore, the fabric comprising the elastic yarns prepared in the present invention do not cause edge curling with the heat-set process at low temperature, which resulted in excellent fabric hand value of the resulting knitted fabric available in various areas.

[59]

Claims

[1] A process for preparing polyurethane elastic yarns having excellent heat settable property, comprising the steps of:
(a) reacting polyols with an excessive amount of diisocyanate to prepare a prepolymer, (b) dissolving the prepolymer in an organic solvent and (c) reacting the resulting solution with a chain extender in order to prepare polyurethane elastic yarns, wherein an amount of 1,3-diaminopropane contained in the chain extender is 40 mol% or more based on the total chain extender.

[2] The process for preparing polyurethane elastic yarns according to the claim 1, wherein the chain extender further comprises at least one selected from a group consisting of ethylene diamine, 1,2- diaminopropane, 1,4-diaminobutane, 2,3-butanediamine, 1,5-pentanediamine, 1,6-hexandiamine and 1,4-cyclohexanediamine.

[3] The process for preparing polyurethane elastic yarns according to the claim 1 or 2, wherein the prepolymer contains 1.56 wt% to 4.29 wt% of isocyanate based on the total prepolymer.

[4] An elastic fabric containing the polyurethane elastic yarns made by the process of claim 1.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2007/003689

A. CLASSIFICATION OF SUBJECT MATTER

D01F 6/70(2006.01)i

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 6/70, 6/78, and C08G18/10, 18/32, 18/48, 18/66

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

Korean Utility models and applictions for Utility models since 1975
Japanese Utility models and applications for Utility models since 1975

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

eKIPASS(KIPO INTERNAL), Kyeword : "(polyurethane or spandex), diaminopropane, chain*"

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 20020028901 A1 (Pathiraja A. Gunatillake et al.) 7 March 2002 See the abstract and the claims	1-4
A	JP 02019511 A (E. I. Du Pont de Nemours and Company) 23 January 1990 See the abstract and the claims	1-4
A	KR 1020020095226 A (E. I. Du Pont de Nemours and Company) 20 December 2002 See the abstract and the claims	1-4
A	KR 1020050055740 A (Invista North America S.A.R.L.) 13 June 2005 See the abstract and the claims	1-4

☐ 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
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"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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INTERNATIONAL SEARCH REPORT

Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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