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(54) Title: POLYESTER COMPOSITIONS SUITABLE FOR THE MANUFACTURE OF FIBRES AND FILMS WITH HIGH ELASTIC MODULUS

(57) Abstract

Polyester resins containing up to 5 % by weight of a polymeric liquid crystal and an upgrading agent capable of increasing the I.V. of the resin by polyaddition reaction in the solid state with the end groups of the resin. Fibres, films and biaxially oriented articles obtained from the resins.

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POLYESTER COMPOSITIONS SUITABLE FOR THE MANUFACTURE OF FIBRES AND FILMS WITH HIGH ELASTIC MODULUS

The present invention relates to polyester compositions, containing polymeric liquid crystals (LCP) suitable for the preparation of stretched articles such as films and fibres endowed with high mechanical properties and particularly of high elastic modulus.

It is known that the liquid crystals (LCP) are used as reinforcing material of thermoplastic polymers to improve their mechanical properties.

The improvement is shown when the LCP quantity is at least 10% by weight on the polymeric matrix.

Quantities lower than 5% determine under the conditions of experimental use only marginal increases.

The lowest concentrations used in literature do not arrive to values lower than 1-2% by weight. This is due to the fact that with these low concentrations and under the experimental use conditions there is no improvement of the resin mechanical properties.

The improvements moreover depend on the degree of stretching carried out.

Stretching ratios of at least 20:1 are necessary in the case of cooled filaments at the extruder exit to obtain the highest increases.

In the case of films where the practicable stretching ratios are generally included between 2:1 and 10:1 there are no significant improvements in consequence of the insufficient molecular orientation obtainable (A.M. Sukhadia et al. - Intern. Polymer Processing VII (1992) 3, 218-228).

It has been unexpectedly found that it is possible to obtain oriented articles such as fibres, films and bioriented containers endowed with high mechanical properties particularly with high elastic modulus starting from polyester resins mixed with a polyfunctional upgrading compound capable to increase the molecular weight of the resin by polycondensation and/or polyaddition reactions in the solid state with the end groups of the resin and containing in the polymer matrix relatively small quantities, lower than 5% by weight of a liquid polymeric crystal.

The formed article has to be subjected to stretching to obtain the desired effect.

The stretching ratio is of at least 2:1 and is generally comprised between 2:1 and 10:1.

The stretching temperature is a little higher than the Tg of the polymer in the case of stretching of films and bioriented articles.

Suitable temperatures are comprised between 80 and 120°C.

Regarding the fibres, the stretching can be carried out in two phases; in the first one the stretching is carried out at temperatures lower than Tg, in the second phase the stretching is carried out at higher temperatures.

In the case of films the stretching ratio is preferably comprised between 4:1 and 9:1; in the case of fibres between 2:1 and 6:1.

The LCP crystals are incorporated into the polyester resin under such mixing conditions, as to assure a homogeneous distribution of the same in the polymer matrix.

The preferred method comprises mixing of the liquid crystals in the melted polymer mass at a temperature between 250 and 320°C.

The temperature is chosen in accordance with the processability temperature of the liquid crystal; it generally increases when the latter increases.

Twin screw extruders are preferably used; counter rotating and intermeshing twin screw extruders are particularly suitable.

The residence time in the extruder is generally comprised between 20 and 200 sec.

The polymer mixture coming out of the extruder can be pelletized and the chips used for the preparation of the stretched articles or the blend is sent to feed directly the filming or spinning apparatus.

The invention polyester resins are converted into fibres and stretched films or in other bioriented articles according to the conventional techniques.

Examples of bioriented articles are the sheets in which the biorientation is obtained by calendering and the bioriented containers are obtained by injection blow molding.

The liquid crystals are preferably used in a quantity lower than 2% by weight on the resin; preferably in quantities between 0,5 and 1,5% by weight.

The quantity of upgrading agent is generally included between 0,1 and 2% by weight.

It is preferably lower than 1% by weight.

The polymeric liquid crystals LCP are polymers that tend to maintain a crystal order also in the molten state.

Representative liquid crystals LCP include following types:

- Poly(oxybenzoyl-co-ethylenterephthalate) (PHBA/ET:4/1)
  Produced by Eastman Chemical & Unitika
  sold under the Rodrum trademark
  (melting point 230°C)
- Poly(oxybenzoyl-co-biphenylterephthalate)(PHBA/TA:2/1/1)
  Produced by Amoco Performance Products
  sold under the Xydar trademark
  (melting point 420°c)
- Poly(oxybenzoyl-co-oxynaphtoil) (PHBA/HNA:7/3)
  Produced by Hoechst Celanese
  sold under the Vectra trademark
  (melting temperature 275°C)
- Poly(phenil-para-phenylenterephthalate) (PPHQ/TA)
  Produced by DuPont

(melting point 340°C)

Liquid crystals of these types are described in the USP patents 3,804,805; 3,637,595; 4,161,470; 4,093,595; 4,447,577; 4,668,760; 4,360,658 whose description is herewith incorporated by reference.

The preferred liquid crystal is Vectra A900 of Hoechst / Celanese.

The polyfunctional upgrading agents are preferably compounds containing two or more groups capable of addition reactions with the OH and COOH end groups of the polyester resin.

The most preferred compounds are the dianhydrides of tetracarboxylic aromatic acids. The preferred compound is the dianhydride of pyromellitic acid.

Other usable dianhydrides are tetrahydrofuran dianhydride, bis (3, 4 dicarboxyphenil) thither dianhydride, dianhydride of (diphenil tetracarboxyl) sulfone, dianhydride of benzophenonetetracarboxylic acid, dianhydride of cyclopentanetetracarboxylic acid.

Addition compounds of one mole of an alkylene glycol or polyalkylene glycol with two moles of pyromellitic dianhydride or other dianhydrides are also usable.

The polyester resins usable for the preparation of the invention compositions include the polycondensation products of an aromatic bicarboxylic acid with a diol containing 1-12 carbon atoms.

Representative acids are terephthalic acid, naphtalenebicarboxylic acid, biphenylbicarboxylic acids and their esters; representative glycols are ethyleneglycol, butyleneglycol 1,4 dimethylol-cyclohexane.

In the definition of polyester resin are included the copolyesters containing terephthalic acid units and units from other acids such as isophtalic acid and elastomeric copolyesters including sequences deriving from terephthalic acid or from another bicarboxylic acid and sequences deriving from a polyalkylene glycol.

The polyester resins may contain, suitably blended, polymers such as polyamides, polycaprolactones, polycarbonates, polyolefines.

The resins can be blended with the conventional additives normally added to the resins; examples of these additives are the antioxidants, thermal stabilizers, dyes and pigments, flame retardant compounds, plasticizers.

Reinforcing charges such as glass fibres or other types of charges can be used.

The usable quantities are those normally used in the polyester resins.

The resins intrinsic viscosity for fibres and films is generally comprised between 0,6 and 0,8 dl/g. Higher viscosities can be used.

The required viscosity values can be obtained by subjecting the resin to polycondensation/reactions in the solid state without using upgrading agents or to polyaddition/polycondensation reactions in the presence of an upgrading agent of the above mentioned type.

It has been found, and this is another aspect of the invention, that significant improvements of the films and stretched fibres mechanical properties, even if lower than those obtainable with the combined used of the liquid crystals and an upgrading agent, can be obtained when the polyester resin is mixed with liquid crystals alone without upgrading agents, in a quantity lower than about 2% by weight on the resin.

Remarkable results are obtained with a quantity lower than 1% by weight, for example 0,5% by weight.

The fibres, films and bioriented articles of the invention find wide application in all those sectors where high mechanical properties are required and also in sectors where high properties of gas barrier are required.

The following examples are given to illustrate but not to limit the invention.

EXAMPLE 1

10 kg/h of a mixture at 99,5% by weight of Polyethyleneterephthalate (PET) having I.V. of 0,61 dl/g and 0,5% by weight of vectra A 950 (Hoechst Celanese) previously vacuum dried at 140°C for 10h and containing 0,3% by weight of pyromellitic dianhydride (PMDA) was fed into a counter rotating and intermeshing extruder and then pelletized.

The extrusion conditions were as follows:

- Screw ratio L/D = 36
- Screw rotation speed = 45 rpm
- Barrel temperature = 260°C
- Chips feed speed = 10 Kg/h
- Die type = circular with 3 mm dia.

Comparative example 1

The preparation of example 1 was repeated with the difference that it was used PET alone without Vectra A950 and PMDA.

EXAMPLE 2

The preparation of example 1 was repeated with the difference that it was used PET mixed only with 0,5% by weight of Vectra A950.

EXAMPLE 3

The preparation of example 1 was repeated with the difference that it was used a blend of 94.7% by weight of PET, 5% by weight of Vectra A950 and 0,3% by weight of PMDA.

EXAMPLE 4

The preparation of example 3 was repeated with the difference that it was used a blend of 98% by weight of PET and 2% by weight of Vectra A 950.

EXAMPLE 5

Chip samples prepared from the mixtures according to the previous examples, were extruded continuously in a filming equipment including a monoscrew extruder provided with a die suitable for cast film production.

The extrusion conditions were as follows:

- Screw ratio L/D = 28
- Screw rotation speed = 80 rpm
- Barrel temperature = 265°C
- Head temperature = 275°C

The extruded film was collected on slow chilled rollers, then on slow heated rollers and on stretching rollers V1 and V2.

The preparation conditions were as follows:

- Screw speed = 60 rpm
- V1 roller speed = 5
- V2 roller speed = 15.20.25.30.35.40.45.
- Stretch ratio = 3. 4. 5. 6. 7. 8. 9.
- Cooled roller (temp.) = 7°C
- Heated roller (temp.) = 87°C

The obtained films properties are shown in tables A, B, C, D, E

Table A

(PET/0,5% VECTRA/0,3% PMDA-Ex. 1)

Stretch ratio	Modulus (GPa)	Tensile strength (MPa)	Strain at break (%)
4	6.3	247	31
5	10.0	430	13
6	6.4	551	13
7	7.1	518	10
8	6.8	258	13
9	5.6	414	13
10	5.8	379	13

Table B

(PET/5% VECTRA/0,3% PMDA-Ex. 3)

Stretch ratio	Modulus (GPa)	Tensile strength (MPa)	Strain at break (%)
3	4.3	148	48
4	5.3	250	41
5	7.8	372	48
6	5.4	448	32
7	5.1	670	13

Table C

(PET/0,5% VECTRA-Ex. 2)

Stretch ratio	Modulus (GPa)	Tensile strength (MPa)	Strain at break (%)
4	4.4	204	67
5	3.9	484	15
6	5.9	314	42
7	6.2	294	26

Table D

(PET/2% VECTRA-Ex. 4)

Stretch ratio	Modulus (GPa)	Tensile strength (MPa)	Strain at break (%)
3	2.2	68	41
4	4.4	143	57
5	3.2	86	47
6	5.3	158	23
7	5.2	165	26

Table E

(PET Comparative ex. 1)

Stretch ratio	Modulus (GPa)	Tensile strength (MPa)	Strain at break (%)
4	2.0	192	32
5	2.5	253	20

Analytical determinations

The intrinsic viscosity was determined in a solution of 0,5 g of resin in 100 ml of a solution at 60/40 by weight of phenol and tetrachlorethane operating at 25°C according to ASTM-D 4603-86.

The film tensile properties were determined according to ASTM-D 882, using an INSTRON tensile tester (Mod. 4505).

CLAIMS

1. Polyester resins mixed with a polyfunctional upgrading agent capable of increasing the molecular weight of the resin by polyaddition/polycondensation reaction in the solid state with the end groups of the resin and containing, dispersed in the polymer matrix, a polymeric liquid crystal in a quantity up to about 5% by weight on the resin.

2. Polyester resins according to claim 1 where in the upgrading agent is chosen among the dianhydrides of tetracarboxylic acids.

3. Polyester resins according to claim 2 where the dianhydride is the pyromellitic dianhydride.

4. Polyester resins according to claims 2 or 3 where the dianhydride is present in a quantity from 0,05 to 2% by weight.

5. Polyester resins according to the previous claims 1, 2, 3 or 4 where the liquid crystal is a copolyester chosen between poly (oxybenzoyl-co-ethylenterephtha-late) and poly (oxybenzoyl-co-oxynaphtoil).

6. Polyester resins according to the previous claims 1, 2, 3, 4 or 5 where the liquid crystal is present in a quantity from 0,1 to 2% by weight.

7. Stretched fibres and films and bioriented articles obtained from polyester resins of the previous claims.

8. Fibres, films and bioriented articles according to claim 7, where in the stretch is carried out at temperatures higher than the glass transition temperature Tg of the resin and lower than about 130°c and where the stretch ratio is higher than 2:1 and between 2:1 and 12:1.

9. Fibres obtained from the resin according to previous claim 8 where in the stretch is carried out in two stages, one at a temperature lower than Tg, the other one at a temperature higher than Tg, but lower than about 130°C and the stretch ratio is between 2:1 and 10:1.

10. Bioriented containers obtained from the resin according to claims 1-6, prepared by injection-blow moulding.

11. Fibres and films in polyester resin having an elastic modulus higher of about 6 GPa containing up to about 5% by weight of a polymeric liquid crystal, dispersed in the polymer matrix.

12. Fibres and films according to claim 11 where the liquid crystal is the product sold under the name Vectra A 950 of Hoechst/Celanese.

13. Polyester resin containing a polymeric liquid crystal dispersed in the polymer matrix in a quantity not higher than 2% by weight.

14. Polyester resins according to claim 13 where the liquid crystal is the product sold under the name Vectra 950 of Hoechst/Celanese.

15. Stretched fibres and films and bioriented articles obtained from the resins according to claim 15, where the stretch is carried out at temperatures higher than the resin Tg and lower than 130°C and the stretch ratio is higher than 2:1 and comprised between 2:1 and 12:1.

AMENDED CLAIMS

[received by the International Bureau on 4 October 1994 (04.10.94);
original claims 4 and 5 amended; remaining claims unchanged (1 page)]

1. Polyester resins mixed with a polyfunctional upgrading agent capable of increasing the molecular weight of the resin by polyaddition/polycondensation reaction in the solid state with the end groups of the resin and containing, dispersed in the polymer matrix, a polymeric liquid crystal in a quantity up to about 5% by weight on the resin.

2. Polyester resins according to claim 1 where in the upgrading agent is chosen among the dianhydrides of tetracarboxylic acids.

3. Polyester resins according to claim 2 where the dianhydride is the pyromellitic dianhydride.

4. Polyester resins according to claim 2 or 3 where the dianhydride is present in a quantity from 0,05 to 2% by weight.

5. Polyester resins according to the previous claims 1, 2, 3 or 4 where the liquid crystal is a copolyester chosen between poly (oxybenzoyl-co-ethyleneterephthalate) and poly (oxybenzoyl-co-oxynaphtol).

6. Polyester resins according to the previous claims 1, 2, 3, 4 or 5 where the liquid crystal is present in a quantity from 0,1 to 2% by weight.

INTERNATIONAL SEARCH REPORT

International Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C08L67/02 D01F6/92 C08J5/18 //C08L67:02

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 5 C08L D01F C08J

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	EP,A,0 314 785 (TORAY INDUSTRIES, INC.) 10 May 1989 see the whole document ---	11-15
X	EP,A,0 041 327 (IMPERIAL CHEMICAL INDUSTRIES LIMITED) 9 December 1981 see the whole document ---	11-15
X	CHEMICAL ABSTRACTS, vol. 97, no. 24, 13 December 1982, Columbus, Ohio, US; abstract no. 199462h, ASAHI CHEMICAL IND. CO., LTD. 'Polyester blend fibers' page 69 ;column 2 ; see abstract & JP,A,82 101 020 (...) 23 June 1982 --- -/--	11

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

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search 27 July 1994	Date of mailing of the international search report - 4. 08. 94
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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 422 282 (PHOBOS N. V.) 17 April 1991 ---	
A	US,A,3 553 157 (ALBERT JAN DIJKSTRA ET AL.) 5 January 1971 -----	

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Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
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