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(54) RESINES DE POLYESTER AUX CARACTERISTIQUES AMELIOREES

(54) POLYESTER RESINS HAVING IMPROVED PROPERTIES

(57) Aromatic polyester resins having improved mechanical and hydrolysis resistant properties, including a phenoxy resin, a dianhydride of a tetracarboxylic acid and liquid crystals.

ABSTRACT

Aromatic polyester resins having improved mechanical and hydrolysis resistant properties, including a phenoxy resin, a dianhydride of a tetracarboxylic acid and liquid crystals.

DESCRIPTION

The present invention refers to aromatic polyester resins having improved mechanical and hydrolysis resistant properties.

The aromatic polyester resins find a wide application both in the fiber and film production as well as in the injection and blow molding.

The hydrolysis resistance of the resins is not however sufficiently high; in conditions of excessive hydrolysis, the resins become weak with a remarkable loss of the tensile properties (elongation, ultimate tensile stress and strength).

It is known that the addition of liquid crystals (PLC) to the polyester resins does not bring about a significant improvement of the mechanical properties of the fibers and films obtained from them: it is necessary to submit fibers and films to sufficiently high stretching ratios in order to obtain such an orientation of the macromolecules as to cause significant increases of the tensile properties. Sufficiently high stretching ratios are not however applicable because of the poor melt strength of the resins.

It has been found (WO-A-94/26821) that the mechanical properties of fibers and films obtained from aromatic polyester resins added with even small quantities of liquid crystals (less than 5% by weight) can be remarkably improved even under non-excessive stretching conditions if the resins undergo a solid state polyaddition (SSPA) in the presence of polyfunctional compounds such as the dianhydrides of tetracarboxylic acids able to react with the resin end groups. The pyromellitic dianhydride (PMDA) is a representative compound.

The addition of liquid crystals to the polyester resins does not determine considerable improvements of the mechanical properties both in the resins after extrusion and in the resins subjected to solid state polycondensation treatments. The presence of the liquid crystals has however a beneficial effect on the hydrolysis resistance.

The addition of dianhydrides such as PMDA to resins containing liquid crystals does not improve the situation of both the hydrolysis resistance and the mechanical properties of the resin after extrusion; the mechanical properties and the hydrolysis resistance are considerably improved if the resin undergoes a solid state polycondensation treatment.

It has been now unexpectedly found that it is possible to obtain aromatic polyester resins having improved mechanical and hydrolysis resistant properties if the resins are added with:

a) polymeric liquid crystals (PLC) in quantity from 0.5 to 30% by weight on the resin, preferably 5-20% by weight;
b) a dianhydride of tetracarboxylic acids, preferably aromatic, in quantity between 0.05 and 2% by weight on the resin, preferably 0.1-0.5% by weight;
c) a phenoxy resin in quantity from 0.1 to 5% by weight, preferably 0.2-1% by weight. The improvement is more

marked if the resins are subjected to solid state polyaddition treatments (SSPA).

Fibers and films obtained from the above resins show particularly high mechanical properties even under normal stretching conditions.

The aromatic polyester resins used in the preparation of the resins of this invention are formed of the product of the polycondensation of an aromatic bicarboxylic acid, or a dialkyly esterthered, with an aliphatic diol with 2-12 carbon atoms.

Terephthalic acid and naphthalenedicarboxylic acids, or their dimethylic esters, are representative compounds.

Examples of aliphatic diols are ethylene glycol, 1,4-butandiol and 1,4-dimethylolcycloexan.

Preferred polyester resins are polyethyleneterephthalate, polybuthyleneterephthalate and polyalkyleneterephthalic copolymers, wherein from 1 to 20% by mols of the units deriving from terephthalic acid are replaced by units deriving from isophthalic acid and/or from a naphthalendicarboxylic acid.

The polyester resins can be added with polymers such as polyamides, polycaprolacton, polycarbonates and polyolefins, generally in quantities lower than 20% by weight.

The resins can contain additives such as antioxidants, heat stabilizers, dyes, pigments, flame retardant compounds, plasticizers.

The intrinsic viscosity of the resins before the SSPA treatment in general ranges from 0.6 to 0.8 dl/g.

The viscosity can be increased up to values of 1-1.8 dl/g by the SSPA treatment.

The usable phenoxy resins are formed of poly(hydroxy) ethers, poly(hydroxy) esters-ethers and poly(hydroxy) amino-ethers.

Preferred resins contain repeating units [$O-CH_2-CHOH-CH_2-R-CH_2-CHOH-CH_2-O-R^1$], where R is a bivalent radical chosen among bis(4-oxyphenyl) dimethylmethane, bis(4-oxyphenyl) sulphoxide, bis(1,3-dicarboxyl) dimethylmethane wherein the free valences of the radical are on the oxygen atoms of the benzenic ring or on the oxygen of the carboxylic groups, or R is the radical $>N-CH_2-CH_2OH$; R^1 is the bivalent radical bis (4-phenylen) dimethylmethane or 1,3-phenylene.

The resins contain at least 50 repeating units with the above mentioned formula.

The most preferred resins are formed of poly(hydroxy) amino-ethers wherein, in the above mentioned repeating units, R is the bivalent radical $>N-CH_2-CH_2OH$ and R^1 is bis (4-phenylen) dimethylmethane.

The polymeric liquid crystals are polymeric substances that tend to maintain a crystalline order also at the melt state.

Usable representative liquid crystals are:

- Poly(oxybenzoil-co-ethyleneterephthalate) (PHBA/ET:4/1) produced by Eastman Chemical & Unitika and commercialized under the trade mark of Rodrum (melting point 230°C);
- Poly(oxybenzoil-co-biphenylterephthalate) (PHBA/TA:2/1) produced by Amoco Performance Products and commercialized under the trade mark of Xydar;
- Poly(oxybenzoil-co-oxynaphtoil) (PHBA/HNA:7/3) produced by Hoechst/Celanese and commercialized under the trade mark of Vectra A 950 (melting point 275°C);
- Poly(phenyl-para-phenylenterephthalate) produced by DuPont (melting point 340°C).

Crystals of the above mentioned type are described in US-A-3 804 760, US-A-4 161 470, US-A-4 093 593, US-A-4 447 577, US-A-4 668 760 and US-A-4 360 658 whose descriptions are hereby incorporated by reference.

Vectra A 950 liquid crystals of Hoechst/Celanese are preferred.

Representative dianhydrides of the tetracarboxylic acids are pyromellitic dianhydride, that is the most preferred one, the dianhydride of benzophenontetracarboxylic acid, the dianhydride of tetrahydrophurantetracarboxylic acid and the dianhydrides of cyclopentanetetracarboxylic and cyclobutanetetracarboxylic acids.

The dianhydrides can be used in the form of adducts with ethylene glycol or polyalkyleneglycols in the ratio of two mols of anhydride for one of the glycol compound.

The liquid crystals are incorporated in the polyester resin under such mixing conditions as to assure a homogeneous distribution of the same in the polymeric matrix.

The preferred method consists in mixing the liquid crystals in the molten mass of the resin working at a temperature between 250° and 380°C. The temperature is chosen in function of the workability temperature of the liquid crystals.

Twin screw extruders are preferably used. The residence time in the extruders generally ranges from 20 to 200 seconds.

The dianhydride of the tetracarboxylic acid and the phenoxy resin can be incorporated contemporaneously with the liquid crystals or the liquid crystals and the phenoxy resin are previously mixed in an extruder utilizing for example 5-10% of the phenoxy resin and using then such a quantity of liquid crystals as to introduce the desired quantity of the phenoxy resin.

The polyester resins of the invention are converted into fibers and films or into bioriented items according to conventional methods.

Examples of bioriented items are sheets, whose biorientation is obtained through calendering, and containers obtained through injection blow molding.

The stretching ratio applied to fibers and films usually ranges from 2:1 to 20:1. The stretching temperature is a little higher than the polymer Tg in the case of film and bioriented items stretching. Suitable temperatures range from 80° to 120°C.

In the case of fibers, the stretching can be made in two steps: in the first at temperatures lower than the Tg; in the second at higher ones. In the case of films, the stretching ratio preferably ranges from 4:1 to 9:1, in the case of fibers, from 2:1 to 10:1.

Fibers, films and oriented objects that can be obtained from the resins of the inventions find application in all those sectors where high mechanical properties and good hydrolysis resistance are required, and also where gas barrier properties are required.

As already indicated, the resins of the invention remarkably improve their mechanical and hydrolysis resistance properties after solid state polyaddition treatment.

The treatment temperature generally ranges from 160 to 220°C, preferably 180-210°C.

The residence times (generally from 1 to more hours) are chosen in function of the desired increase of the intrinsic viscosity of the resin. It is operated under inert gas (nitrogen) atmosphere.

The intrinsic viscosity of the resins is measured in a solution (40/60 by weight) of phenol/tetrachloroethane at 25°C (0.5 g of resin in 100 ml of solvent).

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

EXAMPLE 1

5 kg/hr of a mixture (previously vacuum dried at 140°C for 12 hours) of PET from dimethylterephthalate (IV = 0.62 dl/g) and 0.4% of pyromellitic dianhydride (PMDA) has been fed in continuous to an intermeshing counter-rotating conic twin screw extruder together with 10% by weight of Vectra A 950 liquid crystal of Hoechst Celanese previously mixed in a monoscrew extruder with 7.5% by weight of Paphen phenoxy resin of Union Carbide.

Extrusion Conditions

Rotation of the screw: 100 rpm
Temperature of the cylinder: 285°C
Feeding throughput: 5 kg/hr
Average residence time in the extruder: 2 minutes
PMDA feeding: 0.25 kg/hr

The obtained pellets are vacuum dried at 140°C for at least 12 hours and then injection extruded at 280-285°C to produce Dumbells specimens (3 mm thick).

The IV after extrusion was 0.62 dl/g.

Comparison Example 1

Example 1 is repeated with the difference that 5 kg/hr of PET and 0.25 kg/hr of PMDA are fed to the twin screw extruder.

Comparison Example 2

Example 1 is repeated with the difference that 5 kg/hr of PET are fed to the twin screw extruder.

Comparison Example 3

Example 1 is repeated with the difference that 5 kg/hr of PET mixed with 10% by weight of Vectra A 950 are fed to the twin screw extruder.

Comparison Example 4

Example 1 is repeated with the difference that 5 kg/hr of PET mixed with 0.4% by weight of PMDA and 10% by weight of Vectra A 950 are fed to the twin screw extruder.

The Dumbell specimens of all examples have been subjected to hydrolysis resistance tests at 90° and 120°C for 16 hours using a batch reactor.

The Dumbell specimens have been also subjected to solid state polyaddition (SSPA) at 180°C for 60 hours before the hydrolysis treatment.

The tensile properties have been determined on the specimens (both after extrusion and SSPA) after the hydrolysis treatment.

The results are reported in Table 1.

The therein reported breaking energy is a quantity reflecting both the breaking stress and the elongation at break: the higher the energy, the tougher the material; on the contrary, low values of breaking energy show fragility of the material.

Table 1

Mechanical properties of Dumbell specimens as such after injection (Specimens 1) and after SSPA at 180°C (Specimens 2). The specimens have been subjected to an hydrolysis treatment at 90°C for 16 hours (Specimens A) and at 120°C for 16 hours (Specimens B).

Example	Specimens	Module (GPa)	Breaking Stress (MPa)	Elongation %	Breaking Energy J/mm
1.	1A	2.5	120	7.0	7.0
	1B	3.4	110	3.3	2.7
	2A	2.7	172	8.3	9.7
	2B	3.1	130	4.8	4.0
Comp.Ex. 1	1A	2.6	69	6.0	3.0
	1B	3.2	32	1.0	0.2
	2A	3.0	110	4.3	3.1
	2B	3.2	32	2.6	0.2
Comp.Ex. 2	1A	2.4	60	8.0	3.1
	1B	2.9	32	1.0	0.2
	2A	2.8	120	4.0	3.7
	2B	2.9	32	1.0	0.2
Comp.Ex. 3	1A	2.7	120	7.0	7.0

	1B	3.4	110	3.3	2.0
	2A	3.0	130	4.3	3.1
	2B	3.4	89	3.6	1.3
Comp.Ex. 4	1A	2.7	124	6.0	7.0
	1B	3.4	94	2.8	2.0
	2A	2.8	160	5.8	5.3
	2B	3.4	122	3.8	2.9

The properties of the specimens as such (Specimens A), after SSPA (Specimens B) and prior to the hydrolysis treatment are reported in Table 2:

Table 2

Example	**Specimens**	**Module** (GPa)	**Breaking Stress** (MPa)	**Elongation** %	**Breaking Energy** J/mm
1.	A	2.5	120	7.0	7.0
	B	2.7	180	8.3	10.4
Comp.Ex. 1	A	2.6	69	6.0	3.0
	B	3.0	132	4.9	4.2
Comp.Ex. 2	A	2.4	60	6.0	3.1
	B	2.9	130	5.3	4.4
Comp.Ex. 3	A	2.7	113	6.0	7.0
	B	3.0	131	4.5	3.4
Comp.Ex. 4	A	2.7	114	6.0	7.0
	B	2.9	150	5.8	5.5

EXAMPLE 2

The composition of Example No. 1, previously dried at 140°C for 12 hours, has been extruded in an intermeshing counter-rotating conic twin screw extruder equipped with a 30 mm wide flat die and filmed with various stretching ratios using winding cylinders cooled at 5°C.

The stretching ratios have been calculated using the ratio between the area of the die and the cross section of the films.

The extrusion conditions were:

Rotation of the screw: 100 rpm
Temperature of the cylinder: 285°C
Residence time: 2 minutes.

The mechanical properties of the film are reported in Table 3.

<u>Comparison Example 5</u>

The composition of Comparison Examples 1, 2, 3 and 4 have been fed to the twin screw extruder of Example 2 and filmed with various stretching ratios.

In the case of the PET of Comparison Example 2, it was not possible to use a stretching ratio of 17:1 because of the insufficient melt strength of the material.

The mechanical properties of the film are reported in Table 3.

EXAMPLE 3

Fibers from PET (IV = 0.6 dl/g) containing 0.4% of PMDA and 20% of Vectra A 950 with and without phenoxy resin have been prepared. The above mentioned percentages are by weight.

The mechanical properties of the fibers were the following:

	Module (GPa)	**Stress** (MPa)
1) PET + 0.4% PMDA + 20% Vectra	3.9	22
2) 0.25% phenoxy resin + PET + 0.4% PMDA + 20% Vectra	7.4	48
3) As in 2) but with phenoxy resin 0.5%	11.1	92
4) As in 2) but with phenoxy resin 0.75%	16.7	165
5) As in 2) but with phenoxy resin 1%	9.0	72
6) As in 2) but with phenoxy resin 2%	6.2	45

Table No. 3

Film	**Stretching Ratio**	**Module** (GPa)	**Breaking Stress** (MPa)	**Elongation** %
Ex. 1	2.5	3.9	88	11
	10.0	5.2	110	4
	17.0	5.9	115	4
Comp.Ex. 1	2.5	1.8	43	270
	10.0	1.8	42	300
	17.0	1.7	46	240
Comp.Ex. 2	2.5	1.7	42	320
	10.0	1.8	44	310
	17.0	1.8	41	320
Comp.Ex. 3	2.5	2.8	51	16
	10.0	3.7	57	11
Comp.Ex. 4	2.5	3.4	71	14
	10.0	4.5	92	19
	17.0	5.5	115	4

CLAIMS

1. Aromatic polyester resins comprising:
   a) from 0.5 to 30% by weight of polymeric liquid crystal:
   b) from 0.05 to 2% by weight of a dianhydride of a tetracarboxylic acid;
   c) from 0.05 to 5% by weight of a phenoxy resins elected from the group consisting of poly(hydroxy) ethers, poly(hydroxy) ethers-esters, poly(hydroxy) amino-ethers.

2. Polyester resins according to claim 1 wherein the liquid crystals are present in quantity from 5 to 20% by weight, the dianhydride from 0.1 to 0.5% by weight and the phenoxy resin from 0.1 to 1% by weight.

3. Resins according to claims 1 and 2 wherein the dianhydride is pyromellitic dianhydride.

4. Resin according to claims 1, 2 or 3 wherein the phenoxy resin is formed of at least 50 repeating units [-O-CH_2-CHOH-CH_2-R-CH_2-CHOH-CH_2O R^1] where R is a bivalent radical selected from bis(4-oxyphenyl) dimethylmethane, bis(4-oxyphenyl) sulphoxide, 1,3-dioxyphenyl and bis(1,3-dicarboxylphenyl) dimethylmethane, wherein the free valences of the radical are on the oxygen atoms of the benzenic ring or on the oxygen of the carboxylic groups, R^1 is a bivalent radical selected from bis (4-phenylen) dimethylmethane and 1,3-phenylene.

5. Resins according to claims 1, 2, 3 or 4 wherein the

polyester resin is selected from polyethyleneterephthalate, polybuthyleneterephthalate and polyethyleneterephthalic copolymers, wherein from 1 to 20% by mols of units deriving from terephthalic acid are replaced by units deriving from isophthalic acid and/or naphthalenedicarboxylic acids.

6. Resins according to previous claims, subjected to a solid state polyaddition treatment.

7. Fibers and films obtained from the resins of the previous claims.