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(54) Title: LOW MELTING POINT COPOLYESTER AND PROCESS FOR PREPARING THE SAME

(57) Abstract: A copolyester having a broad amorphous region is disclosed, which is prepared from terephthalic acid, isophthalic acid and a dibasic alcohol component as well as an ether bond-containing dihydroxy compound as basic materials, wherein the acid component comprises 10-30 mol% isophthalic acid and 70-90 mol% terephthalic acid, by the steps of: formulating the components in a molar ratio of total acid/total alcohol equal to 1.05-2.0 to obtain a uniform slurry, followed by esterification and polycondensation reaction, to thereby result in a low melting point copolyester without obvious melting peak, and having a broad amorphous region, as determined by DSC. The process of the present invention can be put into industrial production by using the existing semi-continuous and continuous production lines of polyester. The polyester prepared by the process of the present invention can be used for the production of packaging film, sheet, hot-melt adhesive, and etc. It is especially suitable for making heat shrinkable film for use as packaging material or as label, to substitute polyvinyl chloride (PVC) film presently used in the market.



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## **Low Melting Point Copolyester and Process for Preparing the Same**

### **Technical field**

The present invention relates to a process for preparing a copolyester having a relatively low melting point and a relatively low crystallinity through acid modification of a polyester by using a third component, and alcohol modification of the polyester by using a fourth component.

### **Background art**

Heat shrinkable film has been widely used in different fields. Polyethylene, polyester, polyvinyl chloride (PVC) and etc. all can be used to make heat shrinkable film. However, it is very difficult to print on polyethylene film, and polyester heat shrinkable film requires a relatively high shrink temperature (usually above 100°C). While PVC heat shrinkable film has become the most widely used heat shrinkable film on the market at present due to its excellent processability, shrink property, good transparency and low cost, the use of PVC shrinkage film also engenders serious problems in environment protection. Thus, there is a need to develop a new type of material, in place of PVC, for the production of heat shrinkable film that simultaneously possesses the excellent properties of PVC heat shrinkable film.

Polyethylene terephthalate is a widely used polyester. The performance of polyester is differently required for different use, and to make a polyester have preferable service performance by modification is always one goal that people pursues. Isophthalic acid has been used, in place of partial terephthalic acid, for acid modification of PET, to thereby obtain a copolyester that has a far lower melting point than that of PET and excellent mechanical properties. The copolyester has been widely used for the production of various products such as polyester bottle, polyester sheet and polyester film. Presently, the processes used for the production of polyester or copolyester are very mature esterification (transesterification), polycondensation processes. In general, a

dibasic acid is reacted with a dibasic alcohol (direct esterification) to produce ester monomer, or a dibasic acid alkyl ester is reacted with a dibasic alcohol (transesterification) to produce ester monomer. At the stage of polycondensation, the ester monomer undergoes condensation reaction under vacuum condition in the presence of a polycondensation catalyst, while removing dibasic alcohol produced in the reaction, to obtain the desired polyester or copolyester.

In the prior art, a low melting point copolyester is generally prepared by a process comprising the steps of: esterification of terephthalic acid (PTA), isophthalic acid (IPA), adipic acid (AA), ethylene glycol (EG) and 1,4-butanediol (BDO) in the presence of a catalyst to obtain an esterified product, and then polymerization of the esterified product under vacuum condition in the presence of a catalyst. The shortcoming of this process is that relatively serious side reactions are present in the esterification step.

Japanese patent application Laid-open 10-298271 discloses that the shortcoming of the existing process is that relatively serious side reactions are present in the esterification step. The side reaction of 1,4-butanediol produces a quite high ratio of tetrahydrofuran, which enables the ratios of various monomers to deviate from the estimated ratios, and thereby affects the performance of the product. Meanwhile, this also affects the degree of esterification, leads to difficult polycondensation, and is then disadvantageous for the production control.

WO97/45470 discloses a process preparing a copolyester comprising 55-95 mol% alkylene glycol terephthalate monomer and 5-45 mol% alkylene glycol isophthalate monomer, and a polyester film thereof, by using terephthalic acid (PTA), isophthalic acid (IPA) and ethylene glycol (EG) as basic materials, in the presence of an antimony-free titanium catalyst. In which, diethylene glycol is added as an inhibitor, in an amount of 100 to 200 ppm. Since titanium catalyst is quite instable, its activity is seriously affected, so that its use in production is greatly limited.

Chinese patents CN 1239612C and CN 1399656A respectively disclose a new type of polyester mixture and a heat shrinkable film produced thereby, and a new type of copolyester for heat shrinkable film. It is described in these two patents that the heat shrinkable films have similar thermal shrinkage properties to PVC heat shrinkable film. However, both of the patents utilize 1,4-cyclohexane dimethanol (CHDM) as an alcohol modifier. At present, CHDM has not yet been produced in a large scale in China, and is only available by importation. Moreover, it is expensive.

### **Summary of the invention**

The present invention provides a new type of low melting point copolyester with a melting point of 170-220°C, and a process for preparing it. By using suitable monomers to participate in copolymerization, the problems including serious side reactions during the reaction and instable property of product are solved. All the monomers used can be produced in a large scale in China, so that the production cost is greatly reduced.

The present invention relates to a copolyester comprising terephthalic acid, isophthalic acid and alcohol components, wherein the molar ratio of terephthalic acid alcohol ester unit to isophthalic acid alcohol ester unit is 90-70:10-30; 3-25 mol% an ether bond-containing dihydroxy compound is added in the alcohol components for alcohol modification, the remaining alcohol component being dibasic alcohol.

In one embodiment, the present invention relates to a new type of copolyester, which comprises:

1. an acid residual moiety, comprising about 70-90 mol% terephthalic acid and about 10-30 mol% isophthalic acid; and
2. a dibasic alcohol residual moiety, comprising about 75-97 mol% alcohol component selected from ethylene glycol, 1,3-propanediol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 2,2-dimethyl-1,3-propanediol or 1,4-cyclohexane dimethanol, and about 3-25 mol% an ether bond-containing

dihydroxy compound selected from diethylene glycol, triethylene glycol, dipropylene glycol, polyethylene glycol 200, polyethylene glycol 300, polyethylene glycol 400, polyethylene glycol 600.

3. Metal titanium atom, antimony atom, germanium atom as catalyst; phosphoric acid, phosphate or phosphate ester as stabilizer; and toner.

In one preferred embodiment, the ether bond-containing dihydroxy compound is selected from the group consisting of diethylene glycol, triethylene glycol, dipropylene glycol, polyethylene glycol 200, polyethylene glycol 300, polyethylene glycol 400, polyethylene glycol 600.

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In one preferred embodiment, the ether bond-containing dihydroxy compound is selected from the group consisting of diethylene glycol, triethylene glycol, polyethylene glycol 200.

In one preferred embodiment, the alcohol components is selected from ethylene glycol, 1,3-propanediol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 2,2-dimethyl-1,3-propanediol or 1,4-cyclohexane dimethanol.

In one preferred embodiment, the alcohol components is selected from ethylene glycol, 1,3-propanediol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol or 2,2-dimethyl-1,3-propanediol.

In one preferred embodiment, the alcohol components is selected from ethylene glycol, 1,3-propanediol, 1,3-butanediol or 1,4-butanediol.

In one preferred embodiment, the copolyester has an intrinsic viscosity of not less than 0.55 dl/g.

In one preferred embodiment, the copolyester has an intrinsic viscosity of 0.6 to 0.8 dl/g.

In one preferred embodiment, the copolyester is a low melting point copolyester without obvious melting peak, and having a broad amorphous region, as determined by DSC.

In one preferred embodiment, the copolyester has a melting temperature in the range of 170-220°C.

The present invention also relates to a process for preparing the copolyester, which comprises the steps of:

- (a) reacting terephthalic acid, isophthalic acid and alcohol component other than ether bond-containing dihydroxy compound in an esterification kettle,
- (b) further reacting the reaction product obtained in step (a) with an ether bond-containing dihydroxy compound to obtain a reaction mixture, and
- (c) polycondensing the reaction mixture obtained in step (b).

In one preferred embodiment, the molar ratio of the alcohol components to the sum of terephthalic acid and isophthalic acid in step (a) is 1.05-2.0:1.

In one preferred embodiment, step (c) is carried out in the presence of a catalyst.

In one preferred embodiment, the catalyst used is titanium catalyst, antimony catalyst, germanium catalyst, titanium-antimony composite catalyst or titanium-antimony-germanium composite catalyst.

In one preferred embodiment, the titanium-antimony composite catalyst

includes tetrabutyl titanate, isopropyl titanate and antimony glycolate, antimony acetate or antimony trioxide.

The present invention further relates to use of the copolyester for the production of packaging film, sheet, hot-melt adhesive.

In one preferred embodiment, the packaging film is a heat shrinkable film.

### **Description of the figures**

Fig. 1 shows a tensile stress-strain curve of PVC film.

Fig. 2 shows a tensile stress-strain curve of a new type of low melting point copolyester.

Fig. 3 shows thermodynamic (DSC) analysis of three samples in example 3.

### **Mode of carrying out the invention**

The technical solution used in the present invention comprises esterification 1 reaction stage, esterification 2 reaction stage and polycondensation reaction stage.

Esterification 1 reaction stage:

A slurry is formulated using terephthalic acid/isophthalic acid and dibasic alcohol component as principal materials, which is then subjected to esterification reaction. The molar ratio of acid/alcohol in the slurry is 1:1.05-2.0. The acid component includes 10-30 mol% isophthalic acid and 70-90 mol% terephthalic acid. Then, a stabilizer is added in an amount of 25-100 ppm, based on the weight of the copolymer. The esterification reaction is carried out at a pressure ranging from normal pressure to 0.15 MPa and a temperature of 230-260°C for 1.5 to 4 hours, until the amount of water produced from the esterification reaches the theoretical value.

The amounts of terephthalic acid, isophthalic acid and dibasic alcohol for formulating the slurry can be calculated according to the following formulae:

The amount of isophthalic acid (mole) =  $A \times$  total amount of dicarboxylic acids (mole)

The amount of terephthalic acid (mole) =  $(1-A) \times$  total amount of dicarboxylic acids (mole)

wherein  $A$  is a molar coefficient of proportionality, which ranges from 0.10 to 0.30, preferably from 0.10 to 0.18.

The amount of dibasic alcohol (mole) =  $M \times$  total amount of dicarboxylic acids (mole), the dibasic alcohol is selected from ethylene glycol, 1,3-propanediol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 2,2-dimethyl-1,3-propanediol or 1,4-cyclohexane dimethanol, preferably ethylene glycol; wherein  $M$  is a molar coefficient of proportionality, which ranges from 1.05 to 2.0, preferably from 1.12 to 1.30.

The stabilizer is selected from phosphoric acid, phosphate and phosphate ester, such as phosphoric acid, trimethyl phosphate, triethyl phosphate, and etc., preferably phosphoric acid.

Esterification 2 reaction stage:

The product obtained in esterification 1 reaction stage is fed the esterification 2 reaction stage. The ether bond-containing dihydroxy compound is fed to the esterification reaction product in the esterification 1 reaction stage with continuous stirring at a temperature of 230-270°C and a pressure of 0-100 kPa, and further reacted for 10-30 minutes, and then an antimony-titanium composite catalyst and a toner are added to obtain a prepolymer.

The amount of the ether bond-containing dihydroxy compound can be calculated according to the following formula:

The amount of ether bond-containing dihydroxy compound (mole) =  $B \times$  total amount of dicarboxylic acids (mole)

wherein B is a molar coefficient of proportionality, which ranges from 0.03 to 0.25, preferably from 0.05 to 0.20, preferably from 0.07 to 0.19, more preferably from 0.07 to 0.18, more preferably from 0.10 to 0.18, and more preferably from 0.12 to 0.18.

The ether bond-containing dihydroxy compound is selected from the group consisting of diethylene glycol, triethylene glycol, dipropylene glycol, polyethylene glycol 200, polyethylene glycol 300, polyethylene glycol 400, polyethylene glycol 600, preferably diethylene glycol (DEG).

The amount of the catalyst added: as calculated in the metal atomic weight of the catalyst, based on the weight of the copolymer, the amount of titanium is 10-150 ppm, the amount of antimony is 20-300 ppm, and the amount of germanium is 50-200 ppm; most preferably, based on the weight of the copolymer, the amount of titanium is 10-50 ppm, and the amount of antimony is 50-300 ppm.

Wherein, the compound of titanium as the catalyst is selected from the group consisting of inorganic titanates such as sodium titanate and lithium titanate, and organic titanates such as tetrabutyl titanate, isopropyl titanate, tetramethyl titanate, tetrahexyl titanate, and etc., preferably tetrabutyl titanate and triethanolamine titanate. The compound of antimony as the catalyst is selected from the group consisting of antimony trioxide, antimony acetate, antimony glycolate, preferably antimony glycolate. The compound of germanium as the catalyst is selected from the group consisting of germanium trioxide, germanium peroxide, and etc, preferably germanium trioxide.

The toner is selected from organic dyes such as anthraquinone dyes or inorganic dyes such as cobalt acetate.

The polycondensation reaction stage includes stage of establishing vacuum and stage of high vacuum:

A. Stage of establishing vacuum: delivering the prepolymer to a polycondensation reactor, and reducing the vacuum degree of the reactor with

stirring till an absolute pressure of below 1 kPa, while keeping the temperature in the range of 250-275°C. This stage shall be accomplished within 40-100 minutes.

B. Stage of high vacuum: after establishing vacuum, further reducing the vacuum degree the reactor till an absolute pressure of below 100 Pa, and performing the reaction while keeping the reaction temperature in the range of 260-285°C for 3-6 hours. When the power of stirring machine in the reactor reaches a predetermined value, the reaction is terminated. The final product obtained has an intrinsic viscosity (IV) of not less than 0.55 dl/g, preferably 0.6-0.9 dl/g, more preferably 0.6-0.85 dl/g, more preferably 0.65-0.85 dl/g, more preferably 0.65-0.8 dl/g, more preferably 0.7-0.8 dl/g, more preferably 0.65-0.75 dl/g.

In the present invention, DEG is introduced into the alcohol to participate in the esterification and polycondensation reactions. DEG mainly acts to destroy the regularity of molecular chain of PET, and lower its melting point; and meanwhile acts to introduce flexible segments into the polyester, which benefits the movement of the molecular chain, reduces the crystallization rate of the polyester, and increases the amorphous region of the copolyester.

At the polycondensation reaction stage of the present invention, the antimony catalyst used is preferably antimony glycolate; the titanium catalyst used is preferably tetrabutyl orthotitanate or triethanolamine titanate. In the production of the copolyester, antimony catalyst exhibits a relatively low activity, which results in a very long polycondensation time, and is not suitable for industrial production. While titanium catalyst exhibits a relatively strong activity, it results in a copolymer having a relatively yellow color value. Then, an antimony-titanium composite catalyst system is used, which can not only assure a relatively quick polycondensation reaction rate, but also improve the color value of the product. Therefore, the most preferred catalyst system used herein is an antimony-titanium composite catalyst system.

The copolyester produced by using the process of the present invention is

especially suitable for making heat shrinkable film for use as packaging material or as label. By using the presently known processes of producing polyester film such as tubular film production process or planar film production process, the copolyester can be conveniently processed into a polyester film or a polyester heat shrinkable film. In the tubular film production process, a thermoplastic polyester tubular film is melt-extruded, and then subjected to cooling, secondary heating, blowing up to induce transversal orientation, and further drawing at a certain rate to induce longitudinal orientation. In the planar film production process, a copolyester film is extruded through a slit die, and then subjected to quenching, and further drawing respectively in longitudinal and transverse directions at a temperature above the glass transition temperature of the copolyester. Meanwhile, the drawn film may be further subjected to heat setting at a temperature above the glass transition temperature of the copolyester but lower than its melting temperature. This copolyester film may be used to substitute for PVC film presently used in the market.

The new type of low melting point copolyester and PVC were respectively made into films by using the same tubular film production process. The heat shrink properties of the films were tested and compared under the same conditions, with the data listed in Table 1:

The heat shrink time is 20 seconds, and the drawing ratio is 2 folds.

Table 1

| Temperature (°C)                               |              | Shrinkage |    |    |     |    |
|------------------------------------------------|--------------|-----------|----|----|-----|----|
|                                                |              | 50        | 60 | 70 | 80  | 90 |
| PVC film                                       | Transverse   | 0         | 5  | 49 | 51  | 51 |
|                                                | Longitudinal | 0         | 0  | 2  | 2   | 3  |
| New type of low melting point copolyester film | Transverse   | 0         | 35 | 48 | 52  | 58 |
|                                                | Longitudinal | 0         | 2  | 3  | 2.5 | 3  |

The low melting point copolyester film and the PVC film produced by the same tubular film production process had closely similar shrinkage to each other under the same testing conditions.

The tensile properties of the low melting point copolyester film and the PVC film produced by the same tubular film production process were further tested

under the same conditions. Three groups of films were tested, wherein the first group was standard PVC film for use as label, and the second and third groups were films made by the new type of low melting point copolyester, with the data listed in Table 2:

Test apparatus: Instron tensile tester

Tensile moment: 100 N

Tensile speed: 50 mm/min

Table 2

| Name of sample | PVC                 | Tensile speed                               |                            | 50mm/min           |               |
|----------------|---------------------|---------------------------------------------|----------------------------|--------------------|---------------|
| Sample No.     | Maximum load<br>(N) | Tensile stress at the maximum load<br>(MPa) | Elongation at break<br>(%) | Thick ness<br>(mm) | Width<br>(mm) |
| 1              | 12.72               | 52.98                                       | 168.56                     | 0.040              | 6.00          |
| 2              | 13.39               | 55.81                                       | 156.57                     | 0.040              | 6.00          |
| 3              | 12.33               | 51.39                                       | 155.49                     | 0.040              | 6.00          |
| 4              | 13.08               | 54.50                                       | 104.91                     | 0.040              | 6.00          |
| Average        | 12.88               | 53.67                                       | 146.38                     |                    |               |

| Name of sample | New type of low melting point copolyester | Tensile speed                               |                            | 50mm/min           |               |
|----------------|-------------------------------------------|---------------------------------------------|----------------------------|--------------------|---------------|
| Sample No.     | Maximum load<br>(N)                       | Tensile stress at the maximum load<br>(MPa) | Elongation at break<br>(%) | Thick ness<br>(mm) | Width<br>(mm) |
| 1              | 13.12                                     | 50.84                                       | 393.95                     | 0.042              | 6.00          |
| 2              | 12.34                                     | 45.71                                       | 400.99                     | 0.042              | 6.00          |
| 3              | 14.04                                     | 55.72                                       | 389.52                     | 0.042              | 6.00          |
| 4              | 12.83                                     | 50.92                                       | 408.95                     | 0.042              | 6.00          |
| Average        | 13.08                                     | 50.80                                       | 398.35                     |                    |               |

| Name of sample | New type of low melting point copolyester | Tensile speed                               |                            | 50mm/min           |               |
|----------------|-------------------------------------------|---------------------------------------------|----------------------------|--------------------|---------------|
| Sample No.     | Maximum load<br>(N)                       | Tensile stress at the maximum load<br>(MPa) | Elongation at break<br>(%) | Thick ness<br>(mm) | Width<br>(mm) |
| 1              | 21.84                                     | 53.54                                       | 253.94                     | 0.090              | 6.00          |
| 2              | 21.79                                     | 53.40                                       | 282.10                     | 0.068              | 6.00          |
| 3              | 31.18                                     | 76.43                                       | 329.03                     | 0.068              | 6.00          |
| Average        | 24.94                                     | 61.12                                       | 288.36                     |                    |               |

As could be seen from the test results, the tensile stress indexes of the films made by the new type of low melting point copolyester film were similar to or exceeded those of the standard PVC films for use as label, while their elongations at break were far higher than those of the standard PVC films for use as label.

As could be seen from the tensile stress-strain curve of the two materials, the new type of low melting point copolyester had a strain hardening zone that was not possessed by PVC, which indicated that the new type of low melting point copolyester had a self-healing function during drawing operation, could be made into a film having a very even thickness more conveniently than PVC, and could serve to make a film having a larger width than PVC by using a conventional production process, and meanwhile it was favorable to the realization of large scale industrial production with high efficiency and high energy saving.

The new type of low melting point copolyester can be made into a composite film or a composite sheet.

By using conventional heat-sealing apparatus and conditions, the new type of low melting point copolyester film is adapted to be heat sealed onto itself or a PET polyester film, while PVC film does not have this property.

The new type of low melting point copolyester film has excellent printability, does not need corona treatment, and has a surface tension of above 38 dyn/cm, as determined by a dyne pen. In other words, print can be performed on the film just with a common printing ink.

At present, PETG film occurs in the market to substitute for PVC film, but the PETG film is very expensive. In contrast, all the raw materials for preparing the new type of low melting point copolyester can be produced in a large scale, and the industrial production of the copolyester can be just realized by slightly modifying the existing apparatus for producing PET. Thus, the copolyester has a very stronger competitive advantage than the PETG. Moreover, the existing

apparatus for producing PVC film, after slight modification, just can be used for the production of the new type of low melting point copolyester film, which saves a lot of investment in apparatus.

### **Examples**

The present invention is further illustrated by reference to the following examples, but it shall be understood that these examples are not intended to limit the scope of the invention.

In the following examples, various properties are determined according to the methods described below.

#### **Intrinsic viscosity**

Method as described in Section 6.2 of GB17931-2003: dissolving a sample in a phenol-tetrachloroethane solvent, determining viscosity of the obtained solution by using an Ubbelohde viscometer in a thermostatic bath at 25°C, and then, based on the solution's viscosity, calculating the intrinsic viscosity.

#### **Melting point**

DSC method: as described in Section 6.7 of GB17931-2003.

Microscopic method: as described in Section 6.2.6.1 of GB17931-1999 (the method as described in ISO3146 may be used equivalently).

#### **Color value**

Method as described in Section 6.4 of GB17931-2003.

#### **Shrinkage of film**

A sample in a square of 100 mm x 100 mm is marked with longitudinal and

transverse lines respectively. The sample is placed flatwise in a thermostatic bath. After 20 seconds, it is taken out, and cooled down to room temperature, and then its longitudinal and transverse lengths are respectively measured along the marked lines. The heat shrinkage is calculated according to the following formula:

$$S = (L_0 - L_1) / L_0 \times 100\%$$

wherein S is heat shrinkage, %

$L_0$  is length before heating, mm

$L_1$  is length after heating, mm.

#### Example 1

A semi-continuous polymerization process was utilized. The test apparatus used was a 50 kg/batch semi-continuous bench-test polymerization apparatus, including a slurry kettle, an esterification 1 kettle, an esterification 2 kettle, a polycondensation kettle, and a vacuum system.

##### First step: formulation of slurry

33.75 kg of PTA, 11.25 kg of IPA, 21.5 kg of EG and 5 g phosphoric acid were charged into a slurry kettle, and stirred thoroughly to obtain a slurry. In the slurry, the molar ratio of PTA: IPA was 75: 25, the molar ratio of acid: alcohol was 1: 1.28, and the amount of the stabilizer was 100 ppm.

##### Second step: esterification 1 reaction

The slurry was added in batch to an esterification 1 kettle, in which a half of esterified liquid of the previous lot was remained, for carrying out esterification reaction at a normal pressure, and a temperature of 230-255°C; after reacting for 2 hours, the amount of water discharged from fractionating tower of esterification reached about 9.75 kg. The esterification reaction was terminated.

##### Third step: esterification 2 reaction

Nitrogen was charged into the esterification 1 kettle, and a half of the esterified

liquid was pushed into an esterification 2 kettle through a middle material pipe (another half of the esterified liquid was remained in the esterification 1 kettle). By controlling a normal pressure in the esterification 2 kettle and keeping the materials therein at a temperature of 240-250°C, 1.5 kg of DEG (which corresponded to 5 mol% of the amount of reactive alcohols), 0.05 g of toner, 10 g of antimony glycolate, and 4 g of tetrabutyl titanate were added in sequence to the esterified liquid with stirring. After 15 minutes, the reaction was terminated.

#### Fourth step: polycondensation reaction

Nitrogen was charged into the esterification 2 kettle, and the materials in the kettle were totally delivered to a polycondensation kettle. A stirrer was started up, and its frequency was set to be 50 Hz. The materials in the kettle were heated gradually up to 273°C, and then the kettle was vacuumized uniformly to a pressure below 1 kPa over a period of 50 minutes.

Then, the reaction entered into a high vacuum stage. The frequency of the stirrer was adjusted to 25 Hz. As the reaction proceeded, the reaction temperature gradually reached 280°C since the polycondensation reaction was an exothermic reaction. After 3.5 hours, the current of the stirrer reached 6.9 A, and the reaction was terminated.

After de-vacuumizing, nitrogen was charged to the polycondensation kettle to a pressure of 0.15 MPa (gauge pressure), cast strip was opened, and the reaction product (melt) was discharged, cooled down, and then cut into granules.

By analysis, the product had the following properties:

Intrinsic viscosity (IV): 0.76 dl/g

Melting point (MP): none (DSC) 175-201°C (microscope)

Color value: L 82 a 0.5 b 3.5

#### Example 2

A semi-continuous polymerization process was adopted. The test apparatus used was a 50 kg/batch semi-continuous bench-test polymerization apparatus, including a slurry kettle, an esterification 1 kettle, an esterification 2 kettle, a polycondensation kettle, and a vacuum system.

First step: formulation of slurry

38.92 kg of PTA, 6.08 kg of IPA, 22.6 kg of EG and 5 g of phosphoric acid were charged into a slurry kettle, and stirred thoroughly to obtain a slurry. In the slurry, the molar ratio of PTA: IPA was 86.5: 13.5, the molar ratio of acid: alcohol was 1: 1.345, and the amount of the stabilizer was 100 ppm.

Second step: esterification 1 reaction

The slurry was added in batch to an esterification 1 kettle, in which a half of esterified liquid of the previous lot was remained, for carrying out esterification reaction at a normal pressure, and a temperature of 250-260°C; after reacting for 2 hours, the amount of water discharged from fractionating tower of esterification reached about 9.75 kg. The esterification reaction was terminated.

Third step: esterification 2 reaction

Nitrogen was charged into the esterification 1 kettle, and a half of the esterified liquid was pushed into an esterification 2 kettle through a middle material pipe (another half of the esterified liquid was remained in the esterification 1 kettle). By controlling a normal pressure in the esterification 2 kettle and keeping the materials therein at a temperature of 240-250°C, 4.5 kg of DEG (which corresponded to 15 mol% of the amount of reactive alcohols), 0.05 g of toner, 10 g of antimony glycolate, and 3.5 g of tetrabutyl titanate were added in sequence to the esterified liquid with stirring. After 20 minutes, the reaction was terminated.

Fourth step: polycondensation reaction

Nitrogen was charged into the esterification 2 kettle, and the materials in the

kettle were totally delivered to a polycondensation kettle. A stirrer was started up, and its frequency was set to be 50 Hz. The materials in the kettle were heated gradually up to 273°C, and then the kettle was vacuumized uniformly to a pressure below 1 kPa over a period of 50 minutes.

Then, the reaction entered into a high vacuum stage. The frequency of the stirrer was adjusted to 25 Hz. As the reaction proceeded, the reaction temperature gradually reached 275°C since the polycondensation reaction was an exothermic reaction. After 2.5 hours, the current of the stirrer reached 7.3 A, and the reaction was terminated.

After de-vacuumizing, nitrogen was charged to the polycondensation kettle to a pressure of 0.15 MPa (gauge pressure), cast strip was opened, and the reaction product (melt) was discharged, cooled down, and then cut into granules.

By analysis, the product had the following properties:

Intrinsic viscosity (IV): 0.74 dl/g

Melting point (MP): none (DSC) 175-200°C (microscope)

Color value: L 85 a -0.1 b 4

After drying, the granules were extruded with a known process to obtain a copolyester film. The film was cooled down to room temperature, and then heated to a temperature 15°C above the glass transition temperature of the copolyester, followed by drawing in tubiform by 2 folds. The heat shrinkable film obtained was subjected to heat shrinkage test within a temperature range of 55-95°C, with the data listed in Table 3.

Table 3

| Temperature (°C) | Shrinkage |    |    |    |     |     |    |    |    |    |
|------------------|-----------|----|----|----|-----|-----|----|----|----|----|
|                  | 50        | 55 | 60 | 65 | 70  | 75  | 80 | 85 | 90 | 95 |
| Transverse       | 0         | 18 | 35 | 42 | 50  | 51  | 51 | 51 | 51 | 52 |
| Longitudinal     | 0         | 0  | 2  | 2  | 2.5 | 2.5 | 3  | 3  | 3  | 3  |

As compared with the heat shrinkage data disclosed in patent documents CN 1239612C (EASTMAN CHEM CO, "Polyester blend and heat shrinkable film produced thereby", cf. page 3 of the drawings in the specification) and CN 1399656A (EASTMAN CHEM CO, "Reactor grade copolyesters for shrink film applications", cf. Figs. 1 and 2 at pages 1-2 of the drawings in the specification), it could be found that: despite of their similarity in term of total shrinkage, the heat shrinkable film produced in the present invention had a relatively low shrink starting temperature than the films disclosed in said patent documents. The heat shrinkable film produced in the present invention just could reach a shrinkage of 40% at 65°C, which indicated that said film could produce the expected effect at a relatively low shrink operation temperature.

### Example 3

#### Preparation of sample

A1 sample was a new type of polyester produced according to the formulation and process provided in Example 2.

A2 sample was a polyester produced according to the process provided in Example 2, without the addition of DEG.

A3 sample was a polyester produced according to the process provided in Example 2, by adding 30.15 kg of PTA and 14.85 kg of IPA (the molar ratio of PTA: IPA = 67:33), without the addition of DEG.

The properties of the three samples were shown in Table 4.

Table 4

| Sample No. | Intrinsic viscosity (dl/g) | Melting point (DSC) °C | Melting point (microscope) °C | Color value      |
|------------|----------------------------|------------------------|-------------------------------|------------------|
| A1         | 0.73                       | none                   | 175—200                       | L85 a -0.1 b 4.0 |
| A2         | 0.75                       | 213.5                  | 228                           | L87 a -0.2 b 3.5 |
| A3         | 0.75                       | none                   | 155-185                       | L83 a -0.1 b 3.8 |

The heat shrinkage data of the three samples was listed in Table 5:

Table 5

| Sample No. | Draw ratio | Temperature (°C) | 50                                                                          | 55 | 60 | 65 | 75  | 80  | 85 | 90  | 95  |
|------------|------------|------------------|-----------------------------------------------------------------------------|----|----|----|-----|-----|----|-----|-----|
| A1         | 2          | Transverse %     | 0                                                                           | 18 | 35 | 42 | 50  | 51  | 51 | 51  | 51  |
|            | 0          | Longitudinal %   | 0                                                                           | 0  | 2  | 2  | 2.5 | 2.5 | 3  | 3   | 3   |
| A2         | 2          | Transverse %     | 0                                                                           | 3  | 7  | 15 | 22  | 28  | 31 | 33  | 35  |
|            | 0          | Longitudinal %   | 0                                                                           | 0  | 0  | 1  | 2   | 2   | 2  | 2.5 | 2.5 |
| A3         | 2          | Transverse %     | Since the films were too brittle, they could not undergo secondary drawing. |    |    |    |     |     |    |     |     |
|            | 0          | Longitudinal %   |                                                                             |    |    |    |     |     |    |     |     |

The comparison between A1 sample and A2 sample indicated that the introduction of ether-bond segment into a macromolecule could further destroy the regularity of the molecular chain, and enlarge the amorphous region. As could be seen from DSC curve, A2 sample had a melting point peak, while A1 sample did not. Just for having a larger amorphous region than A2 sample, A1 sample could obtain a higher shrinkage at the temperature of 90°C.

The comparison between A1 sample and A3 sample indicated that, due to the addition of IPA in a large quantity, A3 sample could also have an amorphous region similar to that of A1 sample. However, the addition of IPA in a large quantity simultaneously reduced the properties of the copolyester in terms of flexibility and strength, which accordingly led to difficulty in processing. Whereas, at the same time of reducing the melting point and enlarging the amorphous region of the copolyester, the addition of DEG (the introduction of ether bond) also improved the properties of the copolyester in terms of flexibility and strength.

To sum up, the present invention utilizes IPA and an ether bond-containing

dihydroxy compound to modify polyester, to thereby obtain a new type of copolyester having a relatively low melting point and a broad amorphous region. The heat shrinkable film produced from the copolyester has identical heat shrinkage with PVC film, can be directly printed, and has a heat-sealing property that is not possessed by PVC film. Thus, the heat shrinkable film produced by using the new type of copolyester of the present invention can be used to substitute for PVC shrinkable film.

## Claims

1. A copolyester comprising terephthalic acid, isophthalic acid and alcohol components, wherein the molar ratio of terephthalic acid alcohol ester unit to isophthalic acid alcohol ester unit is 90-70:10-30; 3-25 mol% an ether bond-containing dihydroxy compound is added in the alcohol components for alcohol modification, the remaining alcohol component being dibasic alcohol.
2. The copolyester according to claim 1, wherein the ether bond-containing dihydroxy compound is selected from the group consisting of diethylene glycol, triethylene glycol, dipropylene glycol, polyethylene glycol 200, polyethylene glycol 300, polyethylene glycol 400, polyethylene glycol 600.
3. The copolyester according to claim 2, wherein the ether bond-containing dihydroxy compound is selected from the group consisting of diethylene glycol, triethylene glycol, polyethylene glycol 200, polyethylene glycol 300, polyethylene glycol 400, polyethylene glycol 600.
4. The copolyester according to claim 3, wherein the ether bond-containing dihydroxy compound is selected from the group consisting of diethylene glycol, triethylene glycol, polyethylene glycol 200, polyethylene glycol 300.
5. The copolyester according to claim 4, wherein the ether bond-containing dihydroxy compound is selected from the group consisting of diethylene glycol, triethylene glycol, polyethylene glycol 200.
6. The copolyester according to claim 1, wherein the alcohol components is selected from ethylene glycol, 1,3-propanediol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 2,2-dimethyl-1,3-propanediol or 1,4-cyclohexane dimethanol.
7. The copolyester according to claim 6, wherein the alcohol components is selected from ethylene glycol, 1,3-propanediol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol or 2,2-dimethyl-1,3-propanediol.

8. The copolyester according to claim 7, wherein the alcohol components is selected from ethylene glycol, 1,3-propanediol, 1,3-butanediol or 1,4-butanediol.
9. The copolyester according to claim 1, wherein the copolyester has an intrinsic viscosity of not less than 0.55 dl/g.
10. The copolyester according to claim 9, wherein the copolyester has an intrinsic viscosity of 0.6 to 0.9 dl/g.
11. The copolyester according to claim 1, wherein the copolyester is a low melting point copolyester without obvious melting peak, and having a broad amorphous region, as determined by DSC.
12. The copolyester according to claim 1, wherein the copolyester has a melting temperature in the range of 170-220°C.
13. A process for preparing the copolyester according to any of claims 1 to 12, which comprises the steps of:
  - (a) reacting terephthalic acid, isophthalic acid and alcohol component other than ether bond-containing dihydroxy compound in an esterification kettle,
  - (b) further reacting the reaction product obtained in step (a) with an ether bond-containing dihydroxy compound to obtain a reaction mixture, and
  - (c) polycondensing the reaction mixture obtained in step (b).
14. The process according to claim 13, wherein the molar ratio of the alcohol components to the sum of terephthalic acid and isophthalic acid in step (a) is 1.05-2.0:1.
15. The process according to claim 13, wherein step (c) is carried out in the presence of a catalyst.

16. The process according to claim 15, wherein the catalyst is titanium catalyst, antimony catalyst, germanium catalyst, titanium-antimony composite catalyst or titanium-antimony-germanium composite catalyst.

17. The process according to claim 16, wherein the titanium-antimony composite catalyst includes tetrabutyl titanate, isopropyl titanate and antimony glycolate, antimony acetate or antimony trioxide.

18. Use of the copolyester according to any of claims 1 to 12 for the production of packaging film, sheet, hot-melt adhesive.

19. The use according to claim 18, wherein the packaging film is a heat shrinkable film.

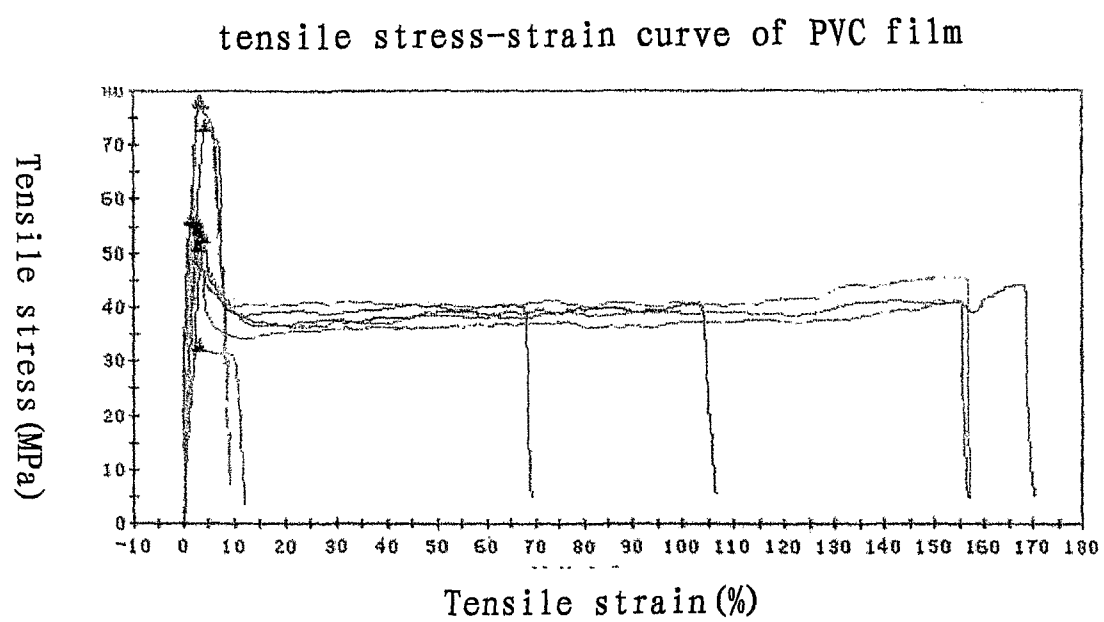


Fig. 1

tensile stress-strain curve of a new type  
of low melting point copolyester

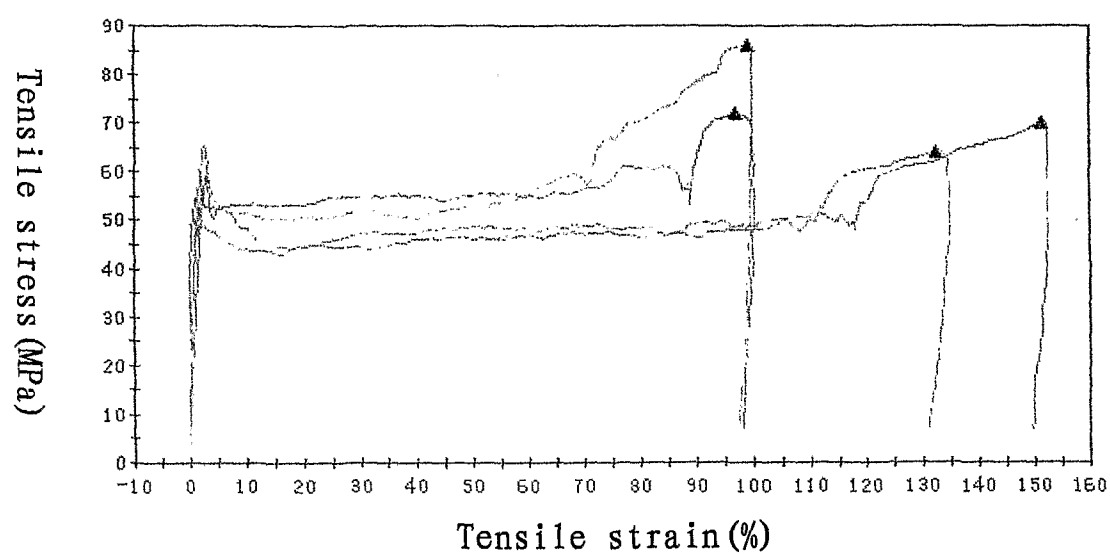


Fig. 2

thermodynamic (DSC) analysis of three samples in example 3

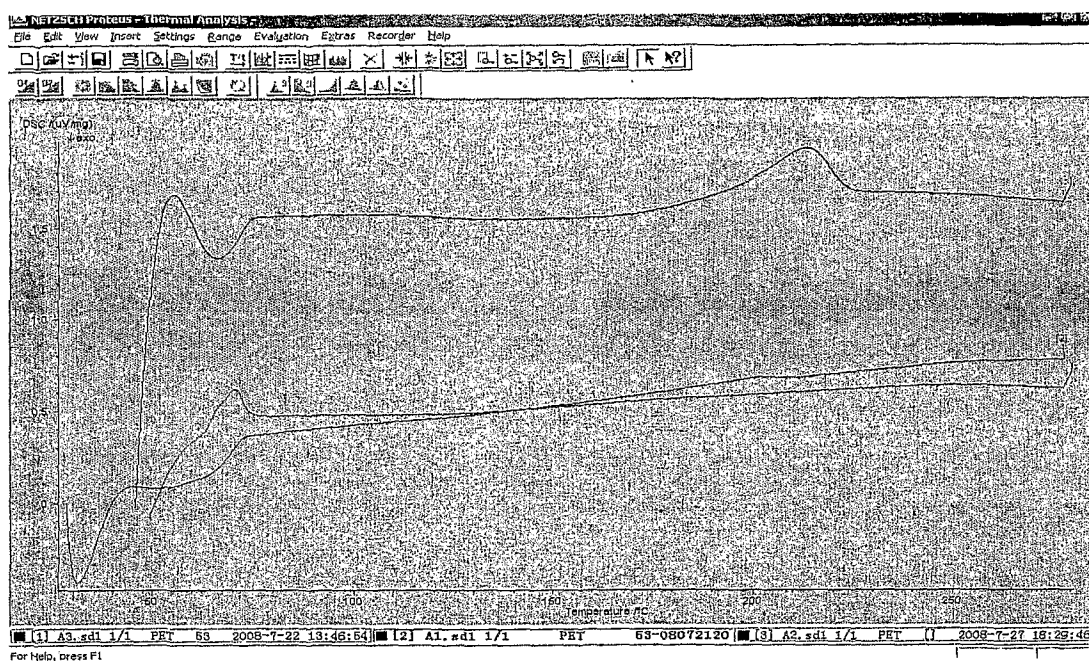


Fig. 3

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2009/000511

## A. CLASSIFICATION OF SUBJECT MATTER

See the extra sheet

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: C08G63-; C08J5-; B29C;B32B

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)

CPRS,CNKI, WPI, EPODOC, PAJ: ??POLYESTER? IPA OR (ISOPHTHALIC W ACID?) OR +ISOPHTHALATE? TPA OR PTA OR +TEREPHTHALATE? OR (TEREPHTHALIC W ACID?) DEG OR TEG OR DPG OR (DIETHYLENE W GLYCOL?) OR (TRIETHYLENE W G LYCOL?) OR (DIPROPYLENE W GLYCOL?) OR (POLYETHYLENE W GLYCOL+) (HEAT OR THERMAL??) W SHRINK????

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|------------------------------------------------------------------------------------|-----------------------|
| X         | JP2289627A(KANEBO LTD)29 Nov. 1990(29.11.1990)<br>See examples 1-3 and claim 1     | 1-19                  |
| X         | JP3045631A(GUNZE KK et al)27 Feb. 1991(27.02.1991)<br>See example 1 and claim 1    | 1-19                  |
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☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

|                                                                                                                                                                          |                                                                                                                                                                                                                                                  |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| * Special categories of cited documents:                                                                                                                                 | “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                                              |
| “A” document defining the general state of the art which is not considered to be of particular relevance                                                                 | “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                                                                     |
| “E” earlier application or patent but published on or after the international filing date                                                                                | “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 |
| “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) | “&”document member of the same patent family                                                                                                                                                                                                     |
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| “P” document published prior to the international filing date but later than the priority date claimed                                                                   |                                                                                                                                                                                                                                                  |

|                                                                                                                                                                                                              |                                                                                        |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------|
| Date of the actual completion of the international search<br>20 Jul. 2009(20.07.2009)                                                                                                                        | Date of mailing of the international search report<br><b>06 Aug. 2009 (06.08.2009)</b> |
| Name and mailing address of the ISA/CN<br>The State Intellectual Property Office, the P.R.China<br>6 Xitucheng Rd., Jimen Bridge, Haidian District, Beijing, China<br>100088<br>Facsimile No. 86-10-62019451 | Authorized officer<br><b>HE Fang</b><br>Telephone No. (86-10)62084472                  |

**INTERNATIONAL SEARCH REPORT**

International application No.

PCT/CN2009/000511

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages            | Relevant to claim No. |
|-----------|-----------------------------------------------------------------------------------------------|-----------------------|
| X         | US5407752A(MITSUBISHI RAYON CO LTD)18 Apr. 1995(18.04.1995)<br>See example 5                  | 1,6-10,18-19          |
| X         | CN1408000A(WELLMAN INC) 02 Apr. 2003(02.04.2003)<br>See claims 3 and 17                       | 1-8,18                |
| PX        | CN101338023A(UNIV ZHEJIANG SCI TECH) 07 Jan. 2009(07.01.2009)<br>See claims 1-2 and example 1 | 1-3,6-11              |

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

International application No.  
PCT/CN2009/000511

| Patent Documents referred<br>in the Report | Publication Date | Patent Family  | Publication Date |
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| CN101338023A                               | 07.01.2009       | NONE           |                  |

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International application No.

PCT/CN2009/000511

## CLASSIFICATION OF SUBJECT MATTER

C08G63/672(2006.01)i

C08G63/86(2006.01)i

C08G63/85(2006.01)i

C08J5/18(2006.01)i