solubility, and thus, industrial application thereof was limited.

Disclosure of Invention

Aspects of the invention are defined in the independent claims. Some optional features of the invention are defined in the dependent claims.

In accordance with one aspect of the present invention, there is provided a polyester resin comprising a repeating unit obtained by copolymerizing:

(a) a divalent acid component; and

(b) a diol component comprising isosorbide and a cycloaliphatic diol,

wherein the polyester resin has a glass transition temperature of 80°C or higher, wherein the diol component further comprises at least one compound selected from the group consisting of ethylene glycol, diethylene glycol, triethylene glycol, propanediol, 1,4-butanediol, pentanediol, hexanediol, neopentyl glycol, 1,2-cyclohexanediol, 1,4-cyclohexanediol, 1,2-cyclohexanedimethanol, 1,3-cyclohexanedimethanol, 1,4-cyclohexanedimethanol, and tetramethyl cyclobutanediol in an amount of 19 to 80 mol% on the basis of the total number of moles of the diol component, and wherein the diol component further comprises neopentyl glycol, and the molar ratio of the sum of the isosorbide and the cycloaliphatic diol and the neopentyl glycol in the diol component is 0.5 to 2.5 : 1.

In accordance with another aspect of the present invention, there is provided a coating composition comprising the above-described polyester resin and an organic solvent.

Advantageous Effects of Invention

According to the present invention, it may be possible to prepare a polyester resin comprising isosorbide which has high heat-resistance with a glass transition temperature

of 80°C or higher and good solubility in solvents widely used in the industry. In addition, it may be possible to provide a coating composition comprising the polyester resin which shows improved solubility to overcome the low solvent-solubility limitation of a conventional polyester resin containing isosorbide. The coating composition may be usefully used as a coating material for cans, electronic products, exterior materials of a building, and films, and as an adhesion material. It may be possible to provide a coating composition comprising the polyester resin which has excellent heat-resistance and solvent-solubility and is capable of forming a coating film having good hardness.

Best Mode for Carrying out the Invention

The polyester resin of the present invention comprises a repeating unit obtained by copolymerizing (a) a divalent acid component, and (b) a diol component comprising isosorbide and a cycloaliphatic diol, and the polyester resin has a glass transition temperature of 80°C or higher.

The diol component includes isosorbide which has a hard molecular structure and shows high heat-resistance, and a cycloaliphatic diol for improving heat-resistance and solvent-solubility of a resin. For example, the diol component may include 1 to 50 mol% of the isosorbide and 1 to 80 mol% of the cycloaliphatic diol on the basis of the total number of moles of the diol component. Particularly, the diol component may include 10 to 50 mol% of the isosorbide and 10 to 50 mol% of the cycloaliphatic diol on the basis of the total number of moles of the diol component. More particularly, the diol component may include 20 to 45 mol% of the isosorbide and 20 to 30 mol% of the cycloaliphatic diol on the basis of the total number of moles of the diol component.

The cycloaliphatic diol may be a diol derivative of at least one tricycloC_{7-14}alkane, for example, a diol derivative of a compound selected from the group consisting of tricyclooctane, tricyclononane, tricyclodecane, tricycloundecane, tricyclododecane, tricycloheptane, tricyclotridecane, and tricyclotetradecane, or a mixture thereof.

Particularly, the cycloaliphatic diol may be a diol derivative of a compound

selected from the group consisting of tricyclo[3.2.1.$0^{2,6}$]octane, tricyclo[4.2.1.$0^{2,6}$]nonane, tricyclo[5.2.1.$0^{2,6}$]decane, tricyclo[6.2.1.$0^{2,6}$]undecane, tricyclo[7.2.1.$0^{2,6}$]dodecane, tricyclo[4.2.1.$1^{2,5}$]decane, tricyclo[4.3.1.$1^{2,5}$]decane, tricyclo[4.4.1.$1^{2,5}$]decane, tricyclo[2.2.1.$0^{2,6}$]heptane, tricyclo[2.2.2.$0^{2,6}$]octane, tricyclo[3.2.2.$0^{2,6}$]nonane, tricyclo[3.3.1.$1^{3,6}$]decane, tricyclo[3.2.1.$1^{3,7}$]nonane, tricyclo[4.2.2.$2^{2,5}$]dodecane, tricyclo[4.3.2.$2^{2,5}$]tridecane, tricyclo[4.4.2.$2^{2,5}$]tetradecane, tricyclo[4.2.1.$0^{3,7}$]nonane, tricyclo[4.4.1.$1^{1,5}$]dodecane, tricyclo[6.2.1.$0^{2,7}$]undecane, tricyclo[5.2.2.$0^{2,6}$]undecane, tricyclo[6.2.2.$0^{2,7}$]dodecane, tricyclo[4.3.2.$0^{2,5}$]undecane, tricyclo[4.2.2.$0^{2,5}$]decane, and tricyclo[5.5.1.$0^{3,11}$]tridecane, or a mixture thereof. More particularly, the cycloaliphatic diol may be a dimethanol derivative of a compound selected from the group consisting of tricyclo[7.2.1.$0^{2,6}$]dodecane, tricyclo[4.2.2.$2^{2,5}$]dodecane, tricyclo[4.4.1.$1^{1,5}$]dodecane, and tricyclo[6.2.2.$0^{2,7}$]dodecane, or a mixture thereof.

In addition, the diol component additionally includes at least one compound selected from the group consisting of ethylene glycol, diethylene glycol, triethylene glycol, propanediol, 1,4-butanediol, pentanediol, hexanediol, neopentyl glycol, 1,2-cyclohexanediol, 1,4-cyclohexanediol, 1,2-cyclohexanedimethanol, 1,3-cyclohexanedimethanol, 1,4-cyclohexanedimethanol, and tetramethyl cyclobutanediol, in an amount of 19 to 80 mol% on the basis of the total number of moles of the diol component. For example, the propanediol may be 1,2-propanediol or 1,3-propanediol. In addition, the hexanediol may be 1,6-hexanediol. Particularly, the diol component additionally includes neopentyl glycol, and the molar ratio of the sum of the isosorbide and the cycloaliphatic diol and the neopentyl glycol in the diol component is 0.5 to 2.5 : 1. More particularly, the molar ratio of the sum of the isosorbide and the cycloaliphatic diol and the neopentyl glycol in the diol component may be 0.5 to 1.8 : 1, 0.5 to 1.5 : 1, or 0.5 to 1.3 : 1.

The divalent acid component may include at least one C_8-C_{14} aromatic dicarboxylic

acid, and may include a compound selected from the group consisting of terephthalic acid, isophthalic acid, naphthalene dicarboxylic acid, diphenyl dicarboxylic acid, a derivative thereof, and a mixture thereof. When an aliphatic dicarboxylic acid, instead of the aromatic dicarboxylic acid, is used as the divalent acid component, the glass transition temperature decreases, and thus, it is difficult to prepare a polyester resin with

performed under reduced pressure conditions of 1.0 mmHg at 270°C, and the polymerization reaction was terminated when viscosity reached a constant value (intrinsic viscosity of 0.36 dl/g) to obtain a target polyester resin.

Examples 2 to 4 and Comparative Examples 1 to 4

Polyester resins were prepared by performing the same procedure described in Example 1 except for using the component and amount listed in the following Table 1.

[Table 1]

Material name	Divalent acid component (g)		Diol component (g)			
	TPA	IPA	NPG	EG	TCDDM	ISB
Example 1	157	157	59	9	82	194
Example 2	157	157	61	12	91	175
Example 3	159	159	116	14	93	98
Example 4	166	166	141	14	48	112
Comparative Example 1	141	141	-	17	265	87
Comparative Example 2	174	174	68	32	-	226
Comparative Example 3	172	172	118	27	-	165
Comparative Example 4	170	170	150	33	52	78

Experimental Example 1: Evaluation of performance of polyester resin

Performance evaluation methods of the polyester resins prepared in the above examples and comparative examples are as follows.

(1) Components (Component ratio of (TCDDM + ISB)/NPG)

A nuclear magnetic resonance (NMR, 600 MHz) analysis was utilized. A polyester resin was dissolved in chloroform-D, and proton NMR was measured to confirm the component ratio (molar ratio) of (TCDDM + ISB) mol%/NPG mol%.

[Table 2]

	IV (dl/g)	Tg (°C)	Mn	(TCDDM + ISB)/NPG component ratio (molar ratio)	Solvent-solubility		
					cyclohexanone: K-100 = 50:50 by volume ratio	toluene:MEK = 50:50 by volume ratio	MEK
Example 1	0.36	120	12,000	2.2	O	O	X
Example 2	0.39	112	14,000	1.9	O	O	X
Example 3	0.44	93	16,000	0.8	O	O	O
Example 4	0.41	87	15,000	0.5	O	O	O
Comparative Example 1	0.37	111	13,000	-	O	O	X
Comparative Example 2	0.38	112	13,000	1.7	O	X	X
Comparative Example 3	0.48	98	17,000	0.7	O	O	X
Comparative Example 4	0.52	79	20,000	0.3	O	O	O

As shown in Table 2, when compared with Comparative Examples 2 and 3 not using TCDDM which is a cycloaliphatic diol, all polyester resins of Examples 1 to 4 had a high glass transition temperature of 80°C or higher, and solubility thereof in various solvents was good.

Further, when compared with Comparative Example 2 having a similar glass transition temperature, the polyester resin of Example 2 was dissolved in a mixture solvent of toluene and MEK, showing improved solvent-solubility.

In addition, in Comparative Example 4 in which the (TCDDN + ISB)/NPG component ratio (molar ratio) was less than 0.5, the glass transition temperature was less than 80°C and heat-resistance was low. Further, when the (TCDDN + ISB)/NPG component ratio (molar ratio) was 2.5 or more, the reaction time rapidly increased, and defects such as difficulty in the synthesis of a polymer, cost increase, and solubility decrease were shown (results not shown).

Examples 5 to 8 and Comparative Examples 5 to 8: Preparation of coating composition

In a mixture solvent of cyclohexanone/solvent naphtha 100 (manufacturer of solvent naphtha 100: SK Energy, product name: Kocosol-100) (50/50 by weight ratio), each of the polyester resins of Examples 1 to 4 and Comparative Examples 1 to 4 was dissolved in a concentration of 40 wt% to prepare resin solutions. 208 g of the resin solution, 100 g of TiO_2 (rutile type), and 1.5 g of a wetting agent (manufacturer: BYK, product name: BYK-110) were mixed to prepare a dispersion mixture (mill base).

0.6 g of the resin solution, 30 g of the dispersion mixture, 1.4 g of a cross-linking agent (manufacturer: CYTEC, product name: CYMEL-303), 0.8 g of a curing catalyst (manufacturer: King Industries, product name: Nacure1953), 3 g of the mixture solvent, and 0.2 g of a smoothening agent (manufacturer: BYK, product name: BYK-355) were mixed to prepare a coating composition.

Experimental Example 2: Evaluation of physical properties of coating composition

The evaluation methods of the performance of the coating compositions prepared in Examples 5 to 8 and Comparative Examples 5 to 8 are as follows.

(6) Gloss

A zinc plated steel plate with a thickness of 0.5 mm was coated with a coating composition and dried using a hot air drier at 230°C for 5 minutes to manufacture a coated steel plate with the thickness of a coating film of 20 μm. The 60° surface gloss of the coated steel plate was measured using a gloss meter manufactured by BYK.

(7) MEK rubbing

The same coated steel plate used in (6) above was rubbed using a gauze sufficiently soaked with MEK to measure chemical-resistance, and the number of

rubbing was measured.

(8) Pendulum hardness

With respect to the same coated steel plate used in (6) above, pendulum hardness was measured using a pendulum hardness tester of T.Q.C by a Konig measurement method and ISO 1522 (2005). Particularly, a pendulum (weight: 200 g) was put on the surface of a coated steel plate, and a state where the pendulum was stopped was set to 0°. Then, the pendulum was pulled to an angle of 6°, pendulum movement was started, and a time period until the angle became 3° was measured three times.

(9) Pencil hardness

With respect to the same coated steel plate used in (6) above, scratch hardness of the coated film was measured using a Mitsubishi pencil. Pencils with diverse hardness were leaned against a test sample with an angle of 45 degrees. Then, the surface was scratched with a load of 750 g, and the hardness of the coated film was measured according to the damaged degree of the surface. Under the above-described conditions, the surface was scratched using a pencil with a specific hardness, and the maximum hardness value which did not generate scratches on the surface was recorded.

The measured results of physical properties are listed in the following Table 3.

[Table 3]

	Gloss (60°)	MEK rubbing (number)	Pendulum hardness (seconds, average of three times)	Pencil hardness
Example 5	90	>100	188	H
Example 6	87	>100	187	H
Example 7	91	>100	190	H
Example 8	91	>100	193	H
Comparative Example 5	96	>100	190	H
Comparative	61	>100	179	H

Example 6				
Comparative Example 7	90	>100	200	H
Comparative Example 8	92	>100	195	F-

As shown in Table 3, the coating composition of the present invention results in a coating film with good hardness, gloss, and scratch-resistance.

Claims:

[Claim 1]

A polyester resin comprising a repeating unit obtained by copolymerizing:

(a) a divalent acid component; and

(b) a diol component comprising isosorbide and a cycloaliphatic diol,

wherein the polyester resin has a glass transition temperature of 80°C or higher, wherein the diol component further comprises at least one compound selected from the group consisting of ethylene glycol, diethylene glycol, triethylene glycol, propanediol, 1,4-butanediol, pentanediol, hexanediol, neopentyl glycol, 1,2-cyclohexanediol, 1,4-cyclohexanediol, 1,2-cyclohexanedimethanol, 1,3-cyclohexanedimethanol, 1,4-cyclohexanedimethanol, and tetramethyl cyclobutanediol in an amount of 19 to 80 mol% on the basis of the total number of moles of the diol component, and

wherein the diol component further comprises neopentyl glycol, and the molar ratio of the sum of the isosorbide and the cycloaliphatic diol and the neopentyl glycol in the diol component is 0.5 to 2.5 : 1.

[Claim 2]

The polyester resin of claim 1, wherein the diol component comprises 1 to 50 mol% of the isosorbide and 1 to 80 mol% of the cycloaliphatic diol on the basis of the total number of moles of the diol component.

[Claim 3]

The polyester resin of claim 1, wherein the cycloaliphatic diol is one or more diol derivatives of tricycloC_{7-14}alkane.

[Claim 4]

The polyester resin of claim 3, wherein the cycloaliphatic diol is a diol derivative

of a compound selected from the group consisting of tricyclo[3.2.1.$0^{2,6}$]octane, tricyclo[4.2.1.$0^{2,6}$]nonane, tricyclo[5.2.1.$0^{2,6}$]decane, tricyclo[6.2.1.$0^{2,6}$]undecane, tricyclo[7.2.1.$0^{2,6}$]dodecane, tricyclo[4.2.1.$1^{2,5}$]decane, tricyclo[4.3.1.$1^{2,5}$]decane, tricyclo[4.4.1.$1^{2,5}$]decane, tricyclo[2.2.1.$0^{2,6}$]heptane, tricyclo[2.2.2.$0^{2,6}$]octane, tricyclo[3.2.2.$0^{2,6}$]nonane, tricyclo[3.3.1.$1^{3,6}$]decane, tricyclo[3.2.1.$1^{3,7}$]nonane, tricyclo[4.2.2.$2^{2,5}$]dodecane, tricyclo[4.3.2.$2^{2,5}$]tridecane, tricyclo[4.4.2.$2^{2,5}$]tetradecane, tricyclo[4.2.1.$0^{3,7}$]nonane, tricyclo[4.4.1.$1^{1,5}$]dodecane, tricyclo[6.2.1.$0^{2,7}$]undecane, tricyclo[5.2.2.$0^{2,6}$]undecane, tricyclo[6.2.2.$0^{2,7}$]dodecane, tricyclo[4.3.2.$0^{2,5}$]undecane, tricyclo[4.2.2.$0^{2,5}$]decane and tricyclo[5.5.1.$0^{3,11}$]tridecane, or a mixture thereof.

[Claim 5]

The polyester resin of claim 1, wherein the divalent acid component comprises one or more C_8-C_{14} aromatic dicarboxylic acids.

[Claim 6]

The polyester resin of claim 1, wherein the divalent acid component comprises a compound selected from the group consisting of terephthalic acid, isophthalic acid, naphthalene dicarboxylic acid, diphenyl dicarboxylic acid, a derivative thereof, and a mixture thereof.

[Claim 7]

The polyester resin of claim 6, wherein the divalent acid component comprises the terephthalic acid, the isophthalic acid, or a mixture thereof in an amount of 1 to 100 mol% on the basis of the total number of moles of the divalent acid component.

[Claim 8]

The polyester resin of claim 1, wherein the polyester resin has a number average molecular weight of 2,000 to 20,000, a hydroxyl value of 2 to 60 mgKOH/g, and an

acid value of 0.1 to 20 mgKOH/g.

[Claim 9]

The polyester resin of claim 1, wherein the polyester resin has a glass transition temperature of 80 to 150°C.

[Claim 10]

A coating composition, comprising:

the polyester resin according to any one of claims 1 to 9; and

an organic solvent.

[Claim 12]

The coating composition of claim 10, wherein the organic solvent is selected from the group consisting of an aromatic hydrocarbon solvent, a glycol ester solvent, a glycol ether solvent, a ketone solvent, an alcohol solvent, and a mixture thereof.

[Claim 12]

The coating composition of claim 10, wherein the coating composition comprises 10 to 40 wt% of the polyester resin and 60 to 90 wt% of the organic solvent.

[Claim 13]

The coating composition of claim 10, wherein the coating composition further comprises a component selected from the group consisting of a cross-linking agent, a curing catalyst, an additive for slip property, a smoothening agent, a defoaming agent, a