

Description

This invention relates to cyanoacrylate adhesive compositions which are improved in toughness and flexibility by incorporation therein of selected polyester polymers.

Cyanoacrylate compositions are well known as excellent adhesives. Known advantages for these compositions are they can be used as a single component, are convenient and easy to use since they cure rapidly at room temperature without an external energy source and they have the ability to bond a wide variety of substrates making them useful in numerous bonding operations. Despite these attributes, cyanoacrylate adhesives do have their limitations and one primary shortcoming is in the area of impact resistance and toughness.

Attempts to change and improve the properties of cyanoacrylate compositions have included the addition of various thickeners, fillers, toughening agents and other modifiers and additives. US-A-4,102,945 discloses a cyanoacrylate adhesive composition thickened by a copolymer or terpolymer resin capable of being dissolved or solvated by the cyanoacrylate monomer and resulting in significantly improved peel strength.

US-A-4,105,715 discloses a cyanoacrylate adhesive composition which is made thixotropic by incorporating powdered organic fillers such as polycarbonate, polyvinylidene fluoride, polyethylene and acrylic block copolymer resins containing saturated elastomer segments.

US-A-4,425,471 involves cyanoacrylate adhesive compositions containing an alkyl 2-cyanopenta-2,4-dienoate which have improved resistance to heat and water and exhibit suitable peel and impact strengths.

US-A-4,440,910 discloses cyanoacrylate adhesive compositions containing elastomeric polymers such as acrylic rubbers as fillers and exhibit substantially increased toughness.

US-A-4,560,723 discloses a cyanoacrylate adhesive composition containing a toughener such as a core-shell thermoplastic/rubber copolymer which is treated to remove impurities which cause premature polymerization of cyanoacrylates and a compatible organic compound having one or more aryl groups, such as diphenylmethane, to provide improved retention of peel strength and toughness.

JP-A-63 284 279 is concerned with a cyanoacrylate adhesive composition comprising ethyl 2-cyanoacrylate and a saturated copolyester. The composition is said to exhibit improved tensile shear strength, impact resistance and peel strength. The material obtained according to this reference, however, lacks in flexibility and proves to be too rigid for particular applications.

The present invention provides cyanoacrylate adhesive compositions wherein selected high molecular weight, hydroxyl terminated, low Tg polyesters are added to provide improved impact resistance and toughness with good flexibility.

More particularly, this invention relates to cyanoacrylate adhesive compositions having improved toughness and flexibility and consisting essentially of:

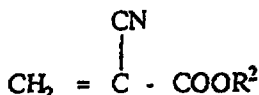
a) a cyanoacrylate monomer; and

b) from about 0.1 to 10% by weight of a saturated, hydroxy terminated polyester polymer derived from a dibasic aliphatic or aromatic carboxylic acid and a glycol and having repeating units of the structure:



where R is the organic residue of the dibasic aliphatic or aromatic carboxylic acid and R¹ is the organic residue of the glycol, the polyester having a weight average molecular weight of from about 30,000 to 60,000 and a Tg of from about -40 to +30°C.

The advantages of this invention may be achieved with essentially all adhesive compositions based upon cyanoacrylate esters. More particularly, the esters have the formula:

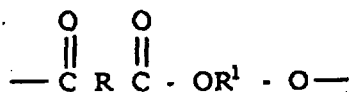


where R² represents a C₁₋₁₆ alkyl, cycloalkyl, alkenyl, cycloalkenyl, phenyl or heterocyclic (such as furfuryl) radical. The R² group can contain any substituents or linkages which do not adversely effect the monomer in the performance of its intended function in the cyanoacrylate adhesive composition. For purposes of this invention, the preferred monomers are those wherein R² is a C₁ to C₆ alkyl or alkenyl radical or a cyclohexyl radical. Most preferred are methyl and ethyl cyanoacrylates. The cyanoacrylate monomer can be used singly or in admixture.

Methods for preparing the above monomeric esters of 2-cyanoacrylic acid are well known in the art as, for example,

described in US-A-2,467,927 and US-A-3,254,111.

The polyester polymers added to the cyanoacrylate adhesive compositions in accordance with this invention are polyesters derived from dibasic carboxylic acids and glycols. More particularly, the polyester polymers are derived from dibasic aliphatic or aromatic carboxylic acids and glycols and have repeating units characterized by the formula:



where R is the organic residue of the dibasic aliphatic or aromatic carboxylic acid and R¹ is the organic residue of the glycol.

The polyester polymers used in this invention are generally formed from the esterification or condensation of dicarboxylic acids with dihydroxy alcohols. The dicarboxylic acid used in preparing the ester may be an aliphatic acid having 2 to 22 carbon atoms or an aromatic acid having 6 to 14 carbon atoms. More particularly the dicarboxylic acid will be an aliphatic acid, preferably containing 2 to 14 carbon atoms, and an aromatic acid, preferably containing 6 to 10 carbon atoms. These dicarboxylic acids may include the alicyclic or cycloaliphatic acids and also the anhydrides of such acids. Illustrative of the dicarboxylic acids which may be used include: adipic acid, azelaic acid, sebacic acid, succinic acid, dodecanoic acid, terephthalic acid, isophthalic acid and phthalic acid.

The dihydroxy alcohols or glycols which may be used in preparing the polyesters used in this invention are aliphatic diols having from 2 to 12 carbons and preferably aliphatic diols having 2 to 5 carbon atoms. These aliphatic diols or glycols include the polyglycols having repeating units of respective glycols such as polyethylene glycol and polypropylene glycols. Also included as useful dihydroxy compounds are the saturated cycloaliphatic diols. Examples of such useful dihydroxy alcohols include: ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, propylene glycol, polypropylene glycol, 1,3-butanediol, 1,4-butanediol, 1,6-hexanediol, 2,2-dimethyl, 1,3-propanediol and 1,4-cyclohexane dimethanol.

The polyesters of this invention, as described above, may be modified by the incorporation therein of monocarboxylic acids, monohydroxy alcohols and even small amounts of polycarboxylic acids or polyhydroxy alcohols.

The polyesters which are linear have a glass transition temperature, T_g, of from about -40 to 30°C, preferably from about -30 to 15°C. The polyesters, many of which are commercially available, may be prepared using known procedures by esterification or condensation of selected dicarboxylic acids and dihydroxy alcohols. Typical procedures are described in "Organic Polymer Chemistry" by K. K. Saunders, Chapman and Hall Ltd., 1973, pp. 203-244 and in "Encyclopedia of Polymer Science and Engineering," 2nd Edition, Vol. 12, 1985, pp. 217 to 234.

The polyesters are generally added to the adhesive in a solution prepared by dissolving the polyester in an appropriate solvent such as tetraglyme, toluene or 2,4-pentanedione at solids concentrations of 20 to 40%, by weight, preferably about 30% by weight.

The amount of polyester polymer added to the cyanoacrylate compositions will comprise from about 0.1 to 10% by weight, based on the weight of cyanoacrylate, preferably from about 0.5 to 8% by weight.

Other known additives for use in cyanoacrylate adhesives, such as fillers, thickeners, anionic polymerization inhibitors, free radical stabilizers, pigments, dyes, adhesion promoters, heat resistant promoters, water resistance promoters, etc., may be included in the compositions of this invention. One additive which has been found particularly useful in these compositions is carbon black pigment. The types and amounts of such additives are well known to those skilled in the art.

The following examples are further illustrative of this invention and are not intended to be construed as limitations thereof. In the examples, all parts and percentages are by weight and all temperatures in degrees Celsius unless otherwise noted.

EXAMPLE I

Polyester polymers were prepared having the following composition and properties by combining the respective dicarboxylic acids and glycols:

Polyester Polymer			
(Mole %)			
Component	A	B	C
azelaic acid	24	18	24

Continuation of the Table on the next page

(continued)

Polyester Polymer			
(Mole %)			
Component	A	B	C
terephthalic acid	16	32	14
isophthalic acid	10	--	12
ethylene glycol	50	23	50
2,2-dimethyl-1,3 propanediol	--	27	--
wt. no. molecular weight	42,400	47,500	48,700
Tg, °C	-28	15	-28

EXAMPLE II

A solution of polyester polymer A (30% by wt.) in tetraglyme was prepared and a pigment dispersion obtained by adding 25% by weight of carbon black pigment under high shear. An adhesive formulation was obtained by adding 5% by weight (solids) of the polyester dispersion to ethyl cyanoacrylate monomer.

EXAMPLE III

A solution of polyester polymer A in 2,4 pentanedione was prepared and a pigment dispersion obtained by adding 18% of carbon black under high shear mixing. An adhesive formulation was obtained by adding 10% by weight (solids) of the polyester dispersion to ethyl cyanoacrylate monomer.

EXAMPLE IV

A solution of polyester polymer A was prepared as in Example II using toluene as the solvent. The polyester was added at a level of 5% by weight (solids).

Adhesive properties were determined in accordance with ASTM D950-82 for impact resistance, D 1876-72 for T-peel (90° peel), D 903 for 180° peel adhesion test and D 1002-72 for lap shear test. The control formulation contained no polyester. For further comparison, a commercially available toughened cyanoacrylate adhesive (Loctite 410) was also tested. It is believed this product is prepared according to the teachings of US-A-4,102,945.

ADHESIVES PROPERTIES OF FORMULATED ADHESIVES

Adhesive	Ex. II	Ex. III	Ex. IV	Control	'410
Cyanoacrylate	Ethyl	Ethyl	Ethyl	Ethyl	Ethyl
Thickener	PMMA ⁽¹⁾	PMMA	PMMA	PMMA	Unknown
Additive	Polyester	Polyester	Polyester	-----	Unknown
Additive Level	5%	10%	5%	-----	Unknown
Impact Resistance N _m /cm ² (Ft. Lbs/in ²)	1.26 (6.0)	1.26 (6.0)	1.26 (6.0)	0.42 (2.0)	1.05 (5.0)
Lap Shear After 2 min @ RT, N/m ² (psi)	1.17·10 ⁷ (1700)	1.10·10 ⁷ (1600)	1.17·10 ⁷ (1700)	9.66·10 ⁶ (1400)	1.80·10 ⁶ (260)
After 15 min @ RT, N/m ² (psi)	1.31·10 ⁷ (1900)	1.31·10 ⁷ (1900)	1.31·10 ⁷ (1900)	1.52·10 ⁷ (2200)	1.66·10 ⁷ (2400)
After 24 hrs. @ RT, N/m ² (psi)	2.41·10 ⁷ (3500)	2.28·10 ⁷ (3300)	2.28·10 ⁷ (3300)	2.00·10 ⁷ (2900)	2.41·10 ⁷ (3500)
T-peel, N/cm (Lbs/in)	8.76 (5) (CF)	8.76 (5) (CF)	8.76 (5.0) (CF)	10.5 (6.0) (AF)	7.0 (4) (CF)
180° peel, N/cm (Lbs/in)	19.3 (11) (CF)	17.5 (10) (CF)	26.3 (15.0) (CF)	17.5 (10.0) (AF)	NA

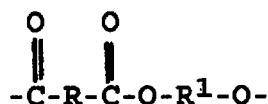
- (1) polymethylmethacrylate
AF = Adhesive Failure
CF = Cohesive Failure

These results show the improved toughness properties, evidenced especially by impact resistance, for the polyester containing cyanoacrylate adhesive formulation. Similar results should be obtained using other polyester compositions meeting the molecular weight and Tg requirements described herein including those polyesters designated "B" and "C" in Example I.

Claims

1. A cyanoacrylate adhesive composition having improved toughness and flexibility and consisting essentially of:

- a) a cyanoacrylate monomer; and
b) from about 0.1 to 10% by weight of a saturated, hydroxy terminated polyester polymer derived from a dibasic aliphatic or aromatic carboxylic acid and a glycol and having repeating units of the structure:



where R is the organic residue of the dibasic carboxylic acid and R¹ is the organic residue of the glycol, the polyester having a weight average molecular weight of from about 30,000 to 60,000 and a Tg of from about -40 to 30°C.

2. The composition of Claim 1 wherein R is an organic residue of an aliphatic acid having 2 to 22 carbon atoms or an aromatic acid having 6 to 14 carbon atoms and R¹ is the organic residue of a glycol comprising an aliphatic diol of 2 to 12 carbon atoms or a polyglycol comprising repeating units of an aliphatic diol of 2 to 12 carbon atoms.
3. The composition of Claim 2 wherein the polyester is linear and has a Tg of from about -30 to 15°C.
4. The composition of Claim 3 wherein the cyanoacrylate is methyl cyanoacrylate or ethyl cyanoacrylate.



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After 15 min @ RT, N/m ² (psi)	1.31·10 ⁷ (1900)	1.31·10 ⁷ (1900)	1.31·10 ⁷ (1900)	1.52·10 ⁷ (2200)	1.66·10 ⁷ (2400)
After 24 hrs. @ RT, N/m ² (psi)	2.41·10 ⁷ (3500)	2.28·10 ⁷ (3300)	2.28·10 ⁷ (3300)	2.00·10 ⁷ (2900)	2.41·10 ⁷ (3500)
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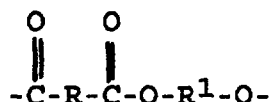
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where R is the organic residue of the dibasic carboxylic acid and R¹ is the organic residue of the glycol, the polyester having a weight average molecular weight of from about 30,000 to 60,000 and a Tg of from about -40 to 30°C.

2. The composition of Claim 1 wherein R is an organic residue of an aliphatic acid having 2 to 22 carbon atoms or an aromatic acid having 6 to 14 carbon atoms and R¹ is the organic residue of a glycol comprising an aliphatic diol of 2 to 12 carbon atoms or a polyglycol comprising repeating units of an aliphatic diol of 2 to 12 carbon atoms.
3. The composition of Claim 2 wherein the polyester is linear and has a Tg of from about -30 to 15°C.
4. The composition of Claim 3 wherein the cyanoacrylate is methyl cyanoacrylate or ethyl cyanoacrylate.

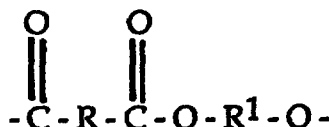


5. The composition of Claim 4, which contains a carbon black pigment.

Patentansprüche

1. Cyanoacrylatklebstoffzusammensetzung mit verbesserter Zähigkeit und Flexibilität, die im wesentlichen besteht aus:

- a) einem Cyanoacrylatmonomer und
b) etwa 0,1 bis 10 Gew.-% eines gesättigten hydroxyterminierten Polyesterpolymers, das sich von einer zweibasischen aliphatischen oder aromatischen Carbonsäure und einem Glycol ableitet und wiederkehrende Einheiten folgender Struktur aufweist:



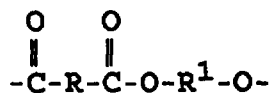
in der R der organische Rest der zweibasischen Carbonsäuren und R¹ der organische Rest des Glycols ist, wobei der Polyester ein gewichtsgemittelter Molekulargewicht von etwa 30000 bis 60000 und eine Tg von etwa -40 bis +30°C aufweist.

2. Zusammensetzung nach Anspruch 1, bei der R ein organischer Rest einer aliphatischen Säure mit 2 to 22 Kohlenstoffatomen oder einer aromatischen Säure mit 6 bis 14 Kohlenstoffatomen und R¹ der organische Rest eines Glycols einschließlich eines aliphatischen Diols mit 2 bis 12 Kohlenstoffatomen oder eines Polyglycols mit wiederkehrenden Einheiten eines aliphatischen Diols mit 2 bis 12 Kohlenstoffatomen ist.
3. Zusammensetzung nach Anspruch 2, bei der der Polyester linear ist und eine Tg von etwa -30 bis 15°C aufweist.
4. Zusammensetzung nach Anspruch 3, bei der das Cyanoacrylat Methylcyanoacrylat oder Ethylcyanoacrylat ist.
5. Zusammensetzung nach Anspruch 4, die ein Rußpigment enthält.

Revendications

1. Composition adhésive à base de cyanoacrylate, présentant une ténacité et une flexibilité améliorées et consistant essentiellement en :

- a) un monomère cyanoacrylate ; et
b) environ 0,1 à 10 % en poids d'un polyester saturé à terminaison hydroxy dérivé d'un diacide carboxylique aliphatique ou aromatique et d'un glycol et comprenant des motifs répétés de formule structurale :



dans laquelle R représente le résidu organique du diacide carboxylique et R¹ représente le résidu organique du glycol, le polyester ayant une moyenne pondérale du poids moléculaire d'environ 30 000 à 60 000 et une Tg d'environ -40 à 30°C.

2. Composition suivant la revendication 1, dans laquelle R représente un résidu organique d'un acide aliphatique ayant 2 à 22 atomes de carbone ou d'un acide aromatique ayant 6 à 14 atomes de carbone et R¹ représente le résidu organique d'un glycol comprenant un diol aliphatique de 2 à 12 atomes de carbone ou un polyglycol comprenant les motifs répétés d'un diol aliphatique de 2 à 12 atomes de carbone.
3. Composition suivant la revendication 2, dans laquelle le polyester est linéaire et a une Tg d'environ -30 à 15°C.
4. Composition suivant la revendication 3, dans laquelle le cyanoacrylate consiste en cyanoacrylate de méthyle ou



cyanoacrylate d'éthyle.

5. Composition suivant la revendication 4, qui contient un pigment consistant en noir de carbone.

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