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(54) Titre : COMPOSITION A BASE DE POLYESTER
(54) Title: POLYESTER COMPOSITION

(57) **Abrégé/Abstract:**

Process for making a shaped article composed of a biodegradable hydroxybutyrate-co-valerate and 5-25 phr of at least one plasticiser selected from high-boiling esters of polybasic acids such as specified adipates and citrates, polyoxyalkylenes terminally esterified or etherified, epoxy derivatives, ricinoleates and polymeric esters.



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ABSTRACT

Process for making a shaped article composed of a biodegradable hydroxybutyrate-co-valerate and 5-25 phr of at least one plasticiser selected from high-boiling esters of polybasic acids such as specified adipates and citrates, polyoxyalkylenes terminally esterified or etherified, epoxy derivatives, ricinoleates and polymeric esters.

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Process of making a Shaped Article substantially composed of Biodegradable Polyester

5 THIS INVENTION relates to a process of making a shaped article composed substantially of biodegradable polyester in particular containing biodegradable polyester and plasticiser.

10 Biodegradable polyesters for example the microbiologically produced polyhydroxyalkanoates can be adapted by the use of plasticiser compounds for applications where improved impact strength, improved elongation to break and improved ductility are important. Since such compounds should preferably also be biodegradable, many of the plasticisers used in synthetic polymer processing are not suitable for biodegradable polymers. Most commonly glycerol triacetate is used, but it is more volatile than is ideal during melt processing or storage at high ambient temperatures. International Publication WO 94/04607 describes that acetyl tri-n-butyl citrate has been
15 introduced for polyhydroxy-alkanoates. This is an improvement over triacetin, but, alternatives to these compounds are continually sought for further improvements in physical properties of the polymer, improvements in the biodegradability and resistance to migration in the polymer, improvements in flexibility, mobility and permanence, and economic benefits.
20 In looking for new plasticisers the applicants have unexpectedly found that a number of plasticisers or materials used in conventional plasticised systems are useful plasticisers of biodegradable polyesters.

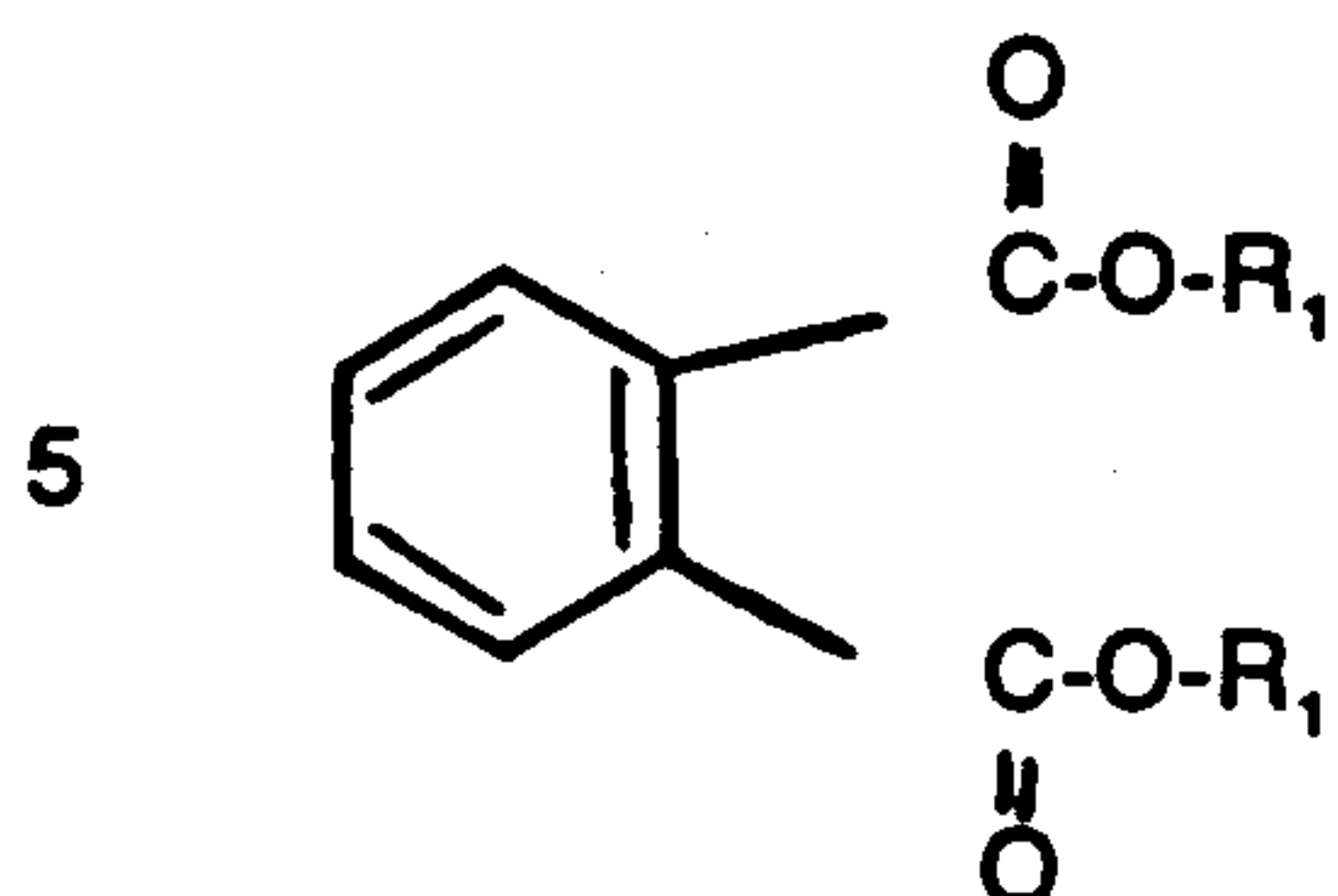
25 Thus, according to the present invention there is provided a process for making, by extrusion, injection moulding, injection blow moulding, compression moulding, film or fibre formation or coating, a shaped article substantially composed of biodegradable polyester, characterised by:

- (a) using as said polyester a (hydroxybutyrate-co-valerate) containing 70-98 mol percent of hydroxybutyrate; and
- (b) having present in said polyester 5-25 phr w/w of at least one
30 plasticiser selected from the group:

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A high-boiling esters selected from phthalates of the formula



where R_1 is C_{1-20} alkyl,

adipates of the formula $R_1-O-C(O)-(CH_2)_4-C(O)-OR_2$ where

10 R_1 and R_2 which may be the same or different are C_{2-12} alkyl or C_{2-12} alkoxyalkyl;

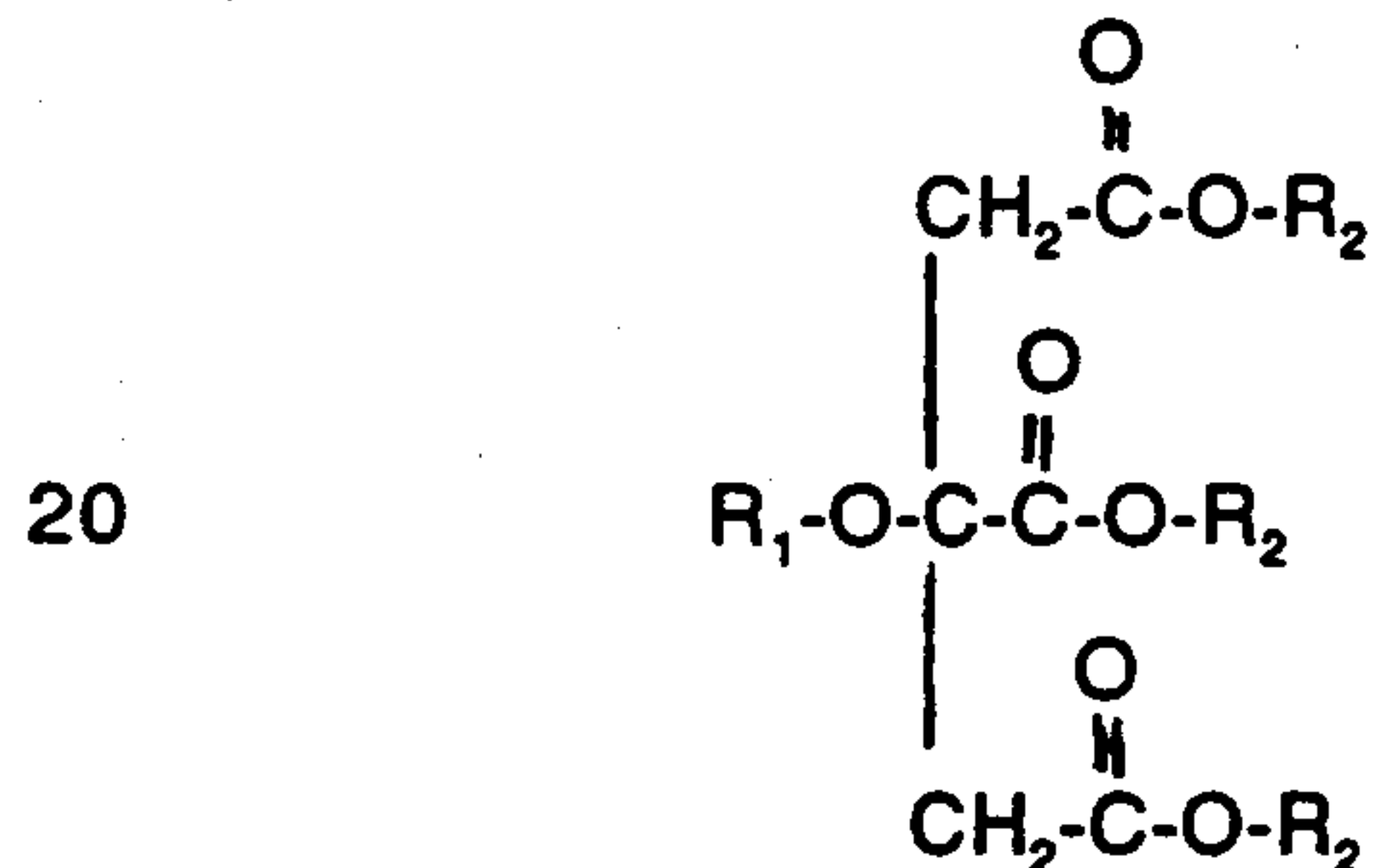
sebacates of the formula $R_1-O-C(O)-(CH_2)_8-C(O)-O-R_1$

where R_1 is C_{2-15} alkyl or C_{2-15} alkoxyalkyl;

azelaates of the formula $R_1O-C(O)-(CH_2)_7-C(O)-OR_1$

15 where R_1 is C_{2-12} alkyl, benzyl, or C_{2-12} alkoxy-alkyl;

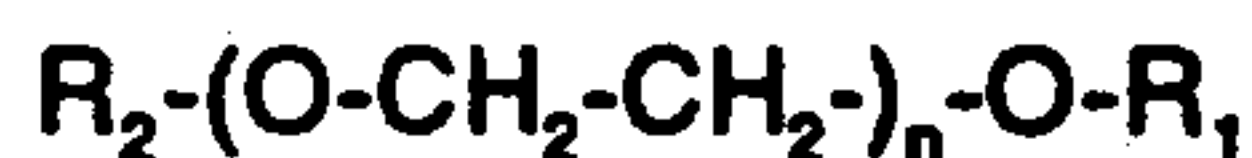
citrate esters of the formula:



where R_1 is hydrogen or C_{1-10} alkyl, and

R_2 is C_{1-10} alkyl or C_{1-10} alkoxyalkyl;

25 B alkyl ethers/esters of general formula



where R_1 is alkyl or $-C(O)$ -alkyl;

R_2 is alkyl; and

n is 2 or more; or

30 where R_1 is hydrogen; and either:

R_2 is alkylphenyl where the alkyl is C_{2-12} alkyl, and

n is 2 to 100; or

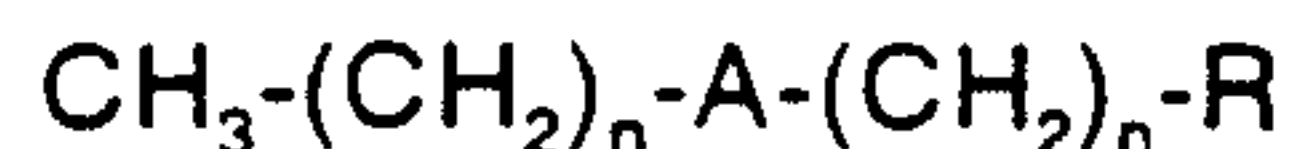
R_2 is $CH_3-(CH_2)_{10}-C(O)-$ and n is 10, 5 or 15; or

R_2 is $CH_3-(CH_2)_7CH=CH-(CH_2)_7-C(O)-$ and n is 5 or 15.

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C epoxy derivatives of the formula



in which the A is an alkene containing one or more double bonds,

5 n is up to 25 and

R is C₂₋₁₅ alkyl; and

D ricinoleate esters;

E polymeric esters of formula



10 in which R₁ and R₂ are both independently C₂₋₁₂ alkylene.

in which R₁ and R₂ are both independently C₂₋₁₂ alkylene.

In the description, examples and claims herein a * indicates a tradename or registered trademark. Where a structural formula containing symbols such as R, m and n is given, the meaning of such symbols applies only to the particular compounds referred to.

The majority of plasticisers used in this invention are known in the art as plasticisers of other materials. A plasticiser is a material which when added to a polymer composition makes an improvement in the ductility of the polymer. It is generally the case with most plasticised polymer systems that the extent of the plasticising effect is in direct correlation with the glass transition temperature (T_g) of the plasticised material, i.e. the lower the T_g, the greater the plasticising effect. It has now been found that in the biodegradable polyesters of the present invention, the glass transition temperature is not a predictor of the extent of beneficial effect of the plasticiser of the polymer, and surprisingly the plasticisers of the present invention are unexpectedly useful with the biodegradable polyesters of the present invention.

The polyesters are PHAs having units of formula I:



30 where n is 2m and m is 3 or 4 and there are units with m = 3 and m = 4 copolymerised together and with respectively a C₁ and C₂ side chain on the carbon next to oxygen in the chain. Particular polyesters contain 4-20 mol% of m = 4 units. The molecular weight of the PHA is preferably over 50000, especially over 300000.

35 The PHA may also be a blend of two or more copolymers differing in

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their relative values of m . An example contains

- (a) PHA consisting essentially of Formula I units in which 2-5 mol% of units have $m = 4$, the rest $m = 3$; and
- (b) PHA consisting essentially of Formula I units in which 5-30 mol% of units have $m = 4$, the rest $m = 3$.

In each such PHA there are side chains as above mentioned. The proportions in such a blend are preferably such as give an average $m = 4$ content in the range 4 - 18 mol %.

In each such PHA having units with $m = 3$ and $m = 4$ there may be very small, typically fractional, percentages of units having higher values of m .

Especially preferred are the (R)-3-hydroxy forms of PHBV.

The composition may contain a blend of at least 50% w/w of PHA with another polymer, particularly poly-caprolactone, polylactic acid, and cellulose esters particularly PHBV and polycaprolactone and PHBV and cellulose esters.

The PHA is preferably a fermentation product, especially of a microbiological process in which a microorganism lays down PHA during normal growth or is caused to do so by cultivation in the absence of one or more nutrients necessary for cell multiplication. The microorganism may be wild or mutated or may have had the necessary genetic material introduced into it. Alternatively the necessary genetic material may be harboured by a eukariote, to effect the microbiological process.

A suitable microbiological process is described in for Formula I material with $m = 3$ or $m =$ partly 3, partly 4 : EP-A-69497 (Alcaligenes eutrophus); US 4101533 (Alcaligenes eutrophus H-16) EP-A-144017 (Alcaligenes latus);

The PHA can be extracted from the fermentation product cells by means of an organic solvent, or the cellular protein material may be decomposed leaving microscopic granules of polymer. For specialised end uses the cellular protein may be partly or wholly allowed to remain with the PHA, but preferably subjected to cell breakage.

Alternately, the PHA can be a product of synthetic chemistry. PHBV can be made by the method of Bloembergen, Holden, Bluhm, Haymer and

Marchessault, Macromolecules 1989, Vol 22, p1663-1669)

Examples of suitable plasticisers are

- (A) high-boiling esters of polybasic acids, such as
- (i) phthalates of the above formula where R_1 is preferably C_{5-11} alkyl, especially isoheptyl, isooctyl, isononyl, isodecyl and isoundecyl, for example di-isodecylphthalate (JaflexTM DIDP*), di-isooctylphthalate (JayflexTM DIOP*), diisoheptyl-phthalate (JayflexTM 77 DHIP*), di-heptylphthalate, di-undecylphthalate, di-isononylphthalate (JayflexTM DNIP*), di-isoundecylphthalate (JayflexTM DUIP*), di-isodecylphthalate (ReomolTM DiDP*), or possibly di-isobutyl-phthalate (ReomolTM DiBP*) or di-tridecyl-phthalate;
- (ii) citrate esters of the above formula where R_1 and R_2 selected from methyl, ethyl and straight or branched chain propyl, butyl, pentyl and hexyl; also ethoxyethyl, propoxy-ethyl, butoxyethyl, butoxyiso-propyl and butoxy-ethoxyethyl are encompassed by the present invention. Particular examples are : triethyl-citrate, trimethylcitrate, n-butyl tri-n-hexyl-citrate (CitroflexTM B6), tri-n-butylcitrate (CitroflexTM 4).
- (iii) adipates, such as those of the formula $R_1-O-C(O)-(CH_2)_4-C(O)-OR_2$ where R_1 and R_2 which may be the same or different are C_{2-12} alkyl (e.g. butyl), C_{2-12} alkoxyalkyl (e.g. butoxyethyl), for example, di-2-ethyl-hexyl adipate (ReomolTM DOA*), di-isodecyl adipate, di-isononyl adipate, dioctyl adipate; other esterified radicals may be for example $C_1 - C_{12}$ alkyl, aryl, aralkyl or alkaryl.
- (iv) sebacates of the formula $R_1-O-C(O)-(CH_2)_8-C(O)-O-R_1$ where R_1 is C_{2-15} alkyl or C_{2-15} alkoxyalkyl, for example, di-octyl sebacate, di-dodecyl sebacate, di-butoxyethyl sebacate, or di-n-butyl sebacate;
- (v) azelaates of the formula $R_1-O-C(O)-(CH_2)_7-C(O)-R_1$ where R_1 is C_{2-12} alkyl, benzyl, or C_{2-12} alkoxy-alkyl, for example, di-n-butyl azelaate and di-i-octyl azelaate;
- (vi) polyesters such as ReoplexTM 346*, ReoplexTM 1102*, ReomolTM MD

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(ester of mixed adipic, glutaric and succinic acids with isodecanol);

- (B) alkyl ethers/esters of general formula $R_2-(O-CH_2-CH_2)_n-O-R_1$, where R_1 is alkyl or $-C(O)$ -alkyl, R_2 is alkyl and n is 2 or more, for example Morton TP90BTM where R_2 is C_4H_9 - and n is 2, Reomol BCD or BCFTM where R_1 is $-C(O)$ -alkyl, R_2 is C_4H_9 - and n is 2; or Morton TP759TM; where R_2 is C_4H_9 , n is 2 and R_1 is $[-C(O)-]_2$ alkyl in the form of the residue of adipic acid; or,
- where R_1 is hydrogen; and either R_2 is alkylphenyl where the alkyl is C_{2-12} alkyl, and n is 2 to 100, for example, Igepal CA210TM where the alkyl is C_8 alkyl and n is 2, Igepal CA510TM which is the same as CA210 except that n is 5, Triton X-100TM and Triton X-405TM which is the same as Igepal CA510TM except that n is 10 and 40 respectively; or R_2 is
- $CH_3-(CH_2)_{10}-C(O)$ - and n is 10, 5 or 15 as in Plasthall CPH27NTM, CPH30N and CPH39 respectively; or R_2 is $CH_3-(CH_2)_7-CH=CH-(CH_2)_7-C(O)$ - and n is 5 or 15 as in Plasthall CPH39NTM and CPH41NTM respectively.
- (C) epoxy derivatives such as the compounds of formula $CH_3-(CH_2)_n-A-(CH_2)_n-R$ in which the A is an alkene containing one or more double bonds (i.e. unsaturated fatty acids), n is up to 25 and R is C_{2-15} alkyl, epoxidised esters of fatty acids, epoxidised soya bean oil, epoxidised linseed oils, epoxidised octyl tallate, epoxidised glycololeate, e.g. Lankro EDGTM, Lankro GETM, Paraplex G60TM, Paraplex G62TM, Plasthall E50TM, Reoplas 39TM and Lankro LTM;
- (D) ricinoleic esters such as butyl acetyl ricinoleate (BAR) or castor oil;
- (E) polymeric esters such as those of the formula $-O-C(O)-R_1-C(O)-O-R_2-O-$ in which R_1 and R_2 are both independently C_{2-12} alkylene; R_2 may be derived from a diol such as 1,2-propanediol, 1,3-butanediol, 1,4-butanediol or 1,6-hexanediol; for example;
- (i) polyester glutarates having molecular weights from 2000 to 20,000, e.g. Plasthall 550TM, Plasthall 7046TM, Plasthall 7092TM Paraplex P550TM, Paraplex P7035TM;
- (ii) polyester adipates having a molecular weight from 200 to 20000

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for example Plasthall 643TM, Plasthall 650TM, poly(propylene) adipate
 example LANKROFLEX PLATM, LANKROFLEX PPLTM, LANKROFLEXTM
 PPA/3TM, Paraplex G56TM, Paraplex G59TM, Diolpate 214TM, Diolpate 917TM;

(iii) polyester succinates;

5 (iv) polyester sebacates having a molecular weight from 4000 to 10000,
 preferably 8000, for example, Plasthall 1070TM;

(v) Diolpate OL1696TM, Diorex 570TM;

(vi) lactone copolymers of the formula $[-(O-C(O)-R_1-C(O)-O)-(R_2-O)]_m-$
 $[(C(O)-R_3-O)]_n$ where R_1 and R_2 are both independently C_{2-12}
 10 alkylene; R_2 may be derived from a diol such as 1,2-propanediol, 1,3-
 butanediol, 1,4-butanediol or 1,6-hexanediol, and R_3 is $-(CH_2)_5-$
 (based on caprolactone);

Generally it is preferred that the plasticiser should be biodegradable.

Preferred plasticisers are the polymeric esters (E), polyoxyalkylenes

15 (B), epoxidised soyabean oils (C), adipates, sebacates, phthalates, citrates
 (A), and castor oil (D).

Particularly preferred are the epoxidised natural oils, phthalate
 derivatives, polypropylene adipates, polymeric esters, especially
 polypropylene glycol adipate, substituted polyethylene glycol (B), polyester
 20 glutarate and epoxidised soyabean oil.

Plasticisers which are particularly preferred for conferring improved
 impact properties are high molecular weight glycols of general formula R_2-
 $(O-CH_2-CH_2)_n-OR_1$, for example Reomol BCDTM, adipates, for example di-
 isodecyl adipate, mixed polyesters, for example Reomol MDTM, polyester
 25 glutarate, for example Paraplex 550TM, and citrates.

In a further aspect of the invention the polyester composition may
 contain at least two plasticisers selected from those defined herein. In a yet
 further aspect of the present invention the polyester composition may
 contain one or more plasticisers selected from those defined herein and
 30 may additionally contain one or more plasticisers previously known to
 plasticise polyhydroxyalkanoates, for example, citrates containing doubly

esterified hydroxycarboxylic acids having at least 3 ester groups in the molecule, glycerol triacetate and glycerol diacetate. Of particular interest is a polyester composition containing as plasticisers acetyl tri-n-butyl citrate (EstaflexTM) and any of the plasticisers defined herein, especially acetyl tri-n-butyl citrate (EstaflexTM) and epoxidised soya bean oil.

The composition can contain the usual polymer processing additives such as fillers, fibres, nucleants, for example boron nitride, and pigments such as titanium dioxide. It can be in the form of mouldings, extrudates, coatings, films or fibres, including multilayer coatings, films or fibres. The nucleant is generally present in amounts from 0.1 phr to 10 phr w/w, preferably 1 to 5 phr w/w.

The invention provides methods of making the composition by mixing its components. If desired, this may be effected in a solvent, such as a halogenated hydrocarbon or alkylene carbonate. Such a method is convenient for coating or for centrifugal spinning of fibres. More conveniently, the plasticiser is mixed with powdered dry polymer and the mixture is treated in conditions of shear, such as in a plastic mill or extruder. The product is then granulated and used as feed for a shaping operation such as extrusion, injection moulding, injection blow-moulding or compression moulding.

The composition is especially useful for making the following shaped articles: films, especially for packaging, fibres, non-woven fabrics, extruded nets, personal hygiene products, bottles and drinking vessels, agricultural and horticultural films and vessels, ostomy bags, coated products (such as paper, paperboard, non-woven fabrics), agricultural and horticultural films and vessels, slow-release devices.

The invention is now further described, but is not limited by, the following examples. In the following examples the tests were conducted with PHBV of the (R)-3-hydroxy form.

- (iv) DiolpateTM OL1696[°], DiorexTM 570[°];
- (v) lactone copolymers of the formula $[-(O-C(O)-R_1-C(O)-O)-(R_2-O)]_m-[(C(O)-R_3-O)]_n$, where R_1 and R_2 are both independently C_{2-12} alkyl, or R_2 may be derived from a diol such as 1,2-propanediol, 1,3-butanediol, 1,4-butanediol or 1,6-hexanediol, and R_3 is $-(CH_2)_5-$ (based on caprolactone);
- (vi) polyesters such as ReoplexTM 346[°], ReoplexTM 1102[°], Reomol MD (ester of mixed adipic, glutaric and succinic acids with isodecanol), polycaprolactone triol (PCL TriolTM (300)[°]);
- (J) Wolflex-But[°];

Generally it is preferred that the plasticiser should be biodegradable.

Preferred plasticisers are the polymeric esters, high-boiling glycols, polyglycols, polyoxyalkylenes and glycerol each optionally substituted and optionally terminally esterified, epoxidised soyabean oils, adipates, sebacates, phosphate esters, phthalates, citrates, castor oil, chlorinated paraffins and toluene sulphonamide derivatives.

Particularly preferred are epoxidised natural oils, phthalate derivatives, polypropylene adipates, phosphoric acid derivatives, polymeric esters. Especially polypropylene glycol adipate, substituted polyethylene glycol, polyester glutarate and epoxidised soyabean oil.

Plasticisers which are particularly preferred for conferring improved impact properties are high molecular weight glycols of general formula $R_2-(O-CH_2-CH_2-O-CH_2-CH_2-O)_n-R_1$, for example ReomolTM BCD, adipates, for example di-isodecyl adipate, mixed polyesters, for example ReomolTM MD, polyester glutarate, for example ParaplexTM 550, and citrates.

In a further aspect of the invention the polyester composition may contain at least two plasticisers selected from those defined herein. In a yet further aspect of the present invention the polyester composition may contain one or more plasticisers selected from those defined herein and may additionally contain one or more plasticisers previously known to plasticise polyhydroxyalkanoates, for example, citrates containing doubly esterified hydroxycarboxylic acids having at least 3 ester groups in the molecule, glycerol triacetate and glycerol diacetate. Of particular interest

is a polyester composition containing as plasticisers acetyl tri-n-butyl citrate (Estaflex[™]) and any of the plasticisers defined herein, especially acetyl tri-n-butyl citrate (Estaflex[™]) and epoxidised soya bean oil.

5 The invention further provides for the use of any of the plasticisers defined above for plasticising a biodegradable polyester composition as defined above.

10 The composition can contain the usual polymer processing additives such as fillers, fibres, nucleants, for example boron nitride, and pigments such as titanium dioxide. It can be in the form of mouldings, extrudates, coatings, films or fibres, including multilayer coatings, films or fibres. The nucleant is generally present in amounts from 0.1 phr to 10 phr w/w, preferably 1 to 5 phr w/w.

15 The invention provides methods of making the composition by mixing its components. If desired, this may be effected in a solvent, such as a halogenated hydrocarbon or alkylene carbonate. Such a method is convenient for coating or for centrifugal spinning of fibres. More conveniently, the plasticiser is mixed with powdered dry polymer and the mixture is treated in conditions of shear, such as in a plastic mill or extruder. The product is then granulated and used as feed for a
20 shaping operation such as extrusion, injection moulding, injection blow-moulding or compression moulding.

25 The composition is especially useful for making the following shaped articles: films, especially for packaging, fibres, non-woven fabrics, extruded nets, personal hygiene products, bottles and drinking vessels, agricultural and horticultural films and vessels, ostomy bags, coated products (such as paper, paperboard, non-woven fabrics), agricultural and horticultural films and vessels, slow-release devices. Alternatively, the polymer composition with suitable additives can be used as an adhesive.

30 The invention is now further described, but is not limited by, the following examples. In the following examples the tests were conducted with PHBV of the (R)-3-hydroxy form.

Example 1

Compositions were prepared by mixing PHBV copolymer (10% HV) (500 g) with 1 phr boron nitride (as nucleant) and 20 phr of

plasticiser. The mixture was extruded in a Betol 2520TM extruder under these conditions: Zone 1 = 130°C; Zone 2 = 140°C; Zone 3 = 150°C; Die = 150°C; Screw Speed = 100 rpm.

5 The extrudate, a single 4mm lace, was crystallised at 50-60°C in a water bath, dried in a current of air and cut into granules.

The granules were then injection moulded (Boy 15S) into tensile bars, dumbbell shaped according to ISO R 537/2, their prismatic part measuring 40 x 5 x 2 mm. The bars were numbered as they came out of the mould, then allowed to cool at ambient temperature.

10 Injection moulding conditions were: Barrel Zone 1 = 130°C; Barrel Zone 2 = 130°C; Nozzle = 130°C; Mould heater temperature = 74-77°C; Mould temperature = 60°C; Pressure hold on time = 12 sec; Cooling time = 30 sec; Injection pressure 45 bar; Screw speed = 250 rpm.

15 Tensile testing was carried out using an Instron 1122TM fitted with a Nene data analysis system. The jaw separation used was 50 mm and crosshead speed was 10 mm/min⁻¹. The samples were measured after 30 days for elongation at break. The results are presented in Table 1 in percentage elongation to break (E%) relative to the starting gauge length of 40mm.

Glass transition temperature (T_g) measurement

25 The blends were prepared by dispersing the plasticiser (20 phr) onto 10g of PHBV copolymer (10% HV). The plasticiser was dissolved in 20-25ml methanol (or chloroform if immiscible with methanol) and the polymer powder fully wetted. The solvent was allowed to evaporate off at room temperature for 3-4 hours before the blend was finally dried at 60°C for 30 minutes.

30 The T_g measurement was carried out by differential scanning calorimetry (DSC) analysis using a Perkin Elmer DSC7 under a nitrogen atmosphere. 10mg samples were used in the following temperature regime : melt sample at 200°C for 2 minutes, cool rapidly to -80°C and hold at this temperature until the system has equilibrated. Heat at 20°C min⁻¹ from -80°C to 50°C. The T_g was reported as the point of inflection (in the trace) for the second heating step.

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Table 1

	Plasticiser	T _g /°C	E (%)
	No plasticiser	0	8.5
	poly(ethylene glycol) (PEG 200)	-19.5	10
5	poly(ethylene glycol) (PEG 300)	-20.5	11.75
	poly(propylene glycol) (PPG 1000)	-10.19	12.75
	ditridecyl phthalate	-10.92	12.75
	poly(oxyethylene)(4)lauryl ether (Brij 30)	-9.3	13.75
10	poly(oxyethylene)(20)sorbitan monolaurate (Tween TM 20)	-16.6	14
	di-isodecylphthalate (Jayflex TM DIUP)	-8.38	14.5
	polycaprolactone triol (PCL (Mw 300))	-8.3	15.75
	poly(propylene glycol) (PPG 425)	-23.13	16.75
15	di-isononylphthalate (Jayflex TM DINP)	-12.77	16.75
	di-isoheptylphthalate (Jayflex TM 77 DIHP)	-19.42	20
	poly(propylene glycol) (PPG 725)	-14.2	21.5
	di-iso-octylphthalate (Jayflex TM DIOP)	-15.84	22
	di-isodecylphthalate (Jayflex TM DIDP)	-10.06	22.5
20	epoxidised soya bean oil (Reoplast TM 39)	-9.5	34.25

The plasticisers used in this example are available from commercial suppliers (BDH, Aldrich Chemicals, Exxon Chemicals, and Ciba Geigy).

Example 2

25 Compositions were prepared by mixing PHBV copolymer (11% HV) (500 g) with 1 phr boron nitride (as nucleant) and 100g (20 phr) of

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plasticiser. The mixture was extruded in a Betol 2520[™] extruder under these conditions: Zone 1 = 115°C; Zone 2 = 133°C; Zone 3 = 153°C; Die = 158°C = Screw Speed = 100 rpm.

5 The extrudate, a single 4mm lace, was crystallised at 50-60°C in a water bath, dried overnight at a low temperature (40°C) and cut into granules.

10 The granules were then injection moulded (Boy 15S) into tensile bars, dumbbell shaped according to ISO R 537/2, their prismatic part measuring 40 x 5 x 2 mm. The bars were numbered as they came out of the mould.

15 Injection moulding conditions were: Barrel Zone 1 = 130°C; Barrel Zone 2 = 130°C; Nozzle = 134°C; Mould heater temperature = 74-77°C; Mould temperature = 60°C; Pressure hold on time = 12 sec; Cooling time = 12 sec; Injection pressure = 45 bar; Screw speed = 250 rpm.

20 Tensile testing was carried out using an Instron 1122[™] fitted with a Nene data analysis system. The jaw separation used was 50 mm and crosshead speed was 10 mm/min⁻¹. The samples were measured after 90 days for elongation at break. The results are presented in Table 2 as percentage elongation to break relative to the starting gauge length of 40 mm.

25 The T_g tests of this example were carried out on samples taken from the extruded lace. The DSC analysis was conducted as in Example 1 except for the following conditions: sample size = 7-10 mg; sample cooled rapidly to -50°C at 100°C min⁻¹; allowed to equilibrate at -50°C; heated at 20°C min⁻¹ to 205°C.

The plasticisers used in this example are available from commercial suppliers (Unichema International, Akzo Chemie, FMC Corporation, C.P. Hall, ICI, Kemira Polymers).

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Table 2

	Plasticiser	T _g /°C	E (%)
	No plasticiser	0.8	13.5
	D-A Sebacate	-8.7	16.5
5	glycerol diacetate (Estol TM 1582)	-12.9	19.5
	toluene sulphonamide (Ketjenflex TM 3)	-8.6	21.8
	toluene sulphonamide (Ketjenflex TM 7)	-10.2	24
	di-2-ethylhexyl adipate (Reomol TM DOA)	-10.7	26.5
	butyl acetyl ricinoleate (BAR)	-8.5	28.3
10	di-isobutylphthalate (Reomol TM DiBP)	-16	28.5
	diester ether alkyl (Plashall TM 7050)	-26.3	29.3
	toluene sulphonamide (Ketjenflex TM 8)	-7.8	29.3
	triethylene glycol diacetate (Estol TM 1593)	-28	32
	triethylene glycol caprylate (Plasthall TM 4141)	-24	34
15	alkyl aryl phosphate (Ketjenflex TM 141)	-17.8	34.5
	toluene sulphonamide (Ketjenflex TM 15)	-7.4	38
	chlorinated paraffin (Cereclor TM 56L)	-7.2	41.5
	polyester (Reoplex TM 346)	-16.4	42.3
	di-isodecylphthalate (Reomol TM DiDP)	-6.6	43.8
20	adipic polyester (Plasthall TM 643)	-11.4	45
	butyl benzyl phthalate (Ketjenflex TM 160)	-13.8	45.3
	chlorinated paraffin (Cerechlor 552)	-11.8	51.5
	Wolflex-But	-9.8	52.8
	glutaric polyester (Plasthall TM 550)	-7.8	52.8

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	polyester (Reoplex TM 1102)	-13.5	53.5
	polymeric ester (Diorex TM 570)	-14	54.3
	polymeric ester (Diolpate TM OL1696)	-15	54.8
5	tri-isopropyl phenyl phosphate (Reofos TM 95)	-9.2	55.3
	phosphate ester (Reomol TM 249)	-17.3	60.8

Example 3

10 Compositions were prepared by mixing PHBV copolymer (6.6% HV, Mw of 680,000) with 1 phr boron nitride (as nucleant) and 20 phr of plasticiser. The mixture was blended for 10 minutes then extruded in a Betol 2520 extruder under the following conditions:

Zone 1 = non-plasticised 140°C; plasticised 130°C;

Zone 2 = non-plasticised 150°C; plasticised 140°;

15 Zone 3 = non-plasticised 160°C; plasticised 140°C;

Die = non-plasticised 160°C; plasticised 150°C;

The extrudate, a single 4mm lace, was crystallised at 50-60°C in a water bath, dried overnight at a low temperature (40°C) and cut into granules.

20 The granules were then injection moulded (Boy 305) into tensile bars, dumbbell shaped according to ISO R 537/2, their prismatic part measuring 40 x 5 x 2 mm. The bars were numbered as they came out of the mould.

Injection moulding conditions were:-

25 Zones 1 to 3 temperature = as for the extrusion process ;

Injection time = 16 seconds;

Nozzle temperature = 150°C;

Mould heater temperature = 60-70°C;

Mould temperature = 60°C;

30 Pressure hold on time = 16 sec;

Cooling time = 16 sec;

Screw speed = 240 rpm.

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Tensile testing was carried out using an Instron 4501 instrument system. The jaw separation used was 50 mm and crosshead speed was 10 mm/min⁻¹. The samples were measured after 30 days for elongation at break. The results are presented in Table 3 as percentage elongation to break relative to a starting gauge length of 40mm.

The T_g tests of this example were carried out on samples from the injection moulded test pieces. The DSC analysis was conducted as in Example 1 except for the following conditions: sample size = 7-10 mg; sample cooled rapidly to -80°C at 100°C min⁻¹; allowed to equilibrate at -80°C; heated at 20°C min⁻¹ to 200°C.

The results are presented in Table 3 as percentage elongation to break relative to a starting gauge length of 40mm.

Impact testing was carried out on a notched impact test piece of 11.8mm x 1.3mm x 4mm using a Zwick Izod impact tester at 28°C. The results are presented in Table 3. Where a T_g is available for the material this is placed alongside the result in the Table.

Table 3

Plasticiser	%E	T _g	Plasticiser	IZOD	T _g
None	15.4		None	70.8	
.1	15.4		5	71	
2	18.5		53	98.8	
3	16.7		44	104	
4	17.0		4	105	
5	17.4		18	107.8	-8.3
6	17.7	-11.9	38	110	
7	18.9		41	110.3	1.39
8	18.9		17	111.3	
9	19.1	-13.5	26	111.8	

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Plasticiser	%E	T _g	Plasticiser	IZOD	T _g
32	30.2		63	166.3	-3.5
33	30.3	-17.9	49	166.8	-15.8
34	30.8	-6.5	58	166.8	
35	31.1		43	167.3	
36	31.3		16	167.8	
37	31.3	-18.3	6	169.4	-11.9
38	31.7		29	170.8	-21.5
39	33.3	-26.2	62	182.3	-6.6
40	34.2		33	183.3	-17.9
41	34.3	-1.4	56	185	
42	34.4	-22.0	13	186.6	-12.7
43	35.3	-10.8	45	187.3	-6.3
44	35.4		31	192.8	-6.1
45	36	-6.3	2	195.4	
46	36.4	-2.1	67	197.5	-3.1
47	38.5		19	197.8	-12.6
48	38.6	-3.7	61	197.8	
49	39	-15.8	59	198.8	-13
50	40.5		57	200.8	-4.2
51	40.6		68	201.8	-25.3
52	42.9		14	202.8	-18.6
53	47.6		35	204.8	

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	Plasticiser	%E	T _g	Plasticiser	IZOD	T _g
	54	48.4	-14.5	25	215.8	-3.8
	55	48.4	-1.2	9	220.8	-13.5
	56	48.6		37	227.3	-18.3
5	57	55.7	-4.2	38	227.8	
	58	59.3		42	228.3	-22
	59	60.7	-13.0	39	231.8	-26.2
	60	68.9		11	235.6	-19.6
	61	82.3		55	241	-1.2
10	62	96.6	-6.56	20	243.3	-8.5
	63	162.7	-3.49	30	251.8	-18.5
				69	257.8	-1.5
				54	271.3	-14.5
				22	273.8	
15				46	301.3	-2.1
				12	265.8	

Key

- 1 1,4-butane diol adipic acid (S102250) available from Occidental Chemical
- 2 1,4-butane diol adipic acid (S102250) (35phr)
- 3 polyethylene glycol 2000 available from Aldrich Chemical
- 4 polycaprolactone (Tone 301) available from Union Carbide
- 5 polyethylene glycol 6000 available from Aldrich Chemical
- 6 Triton X100 (polyethoxyethanol) available from Aldrich Chemical
- 7 1,4-butane diol adipic acid (S1063210) available from Occidental Chemical

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	Plasticiser	%E	T _g	Plasticiser	IZOD	T _g
	54	48.4	-14.5	25	215.8	-3.8
	55	48.4	-1.2	9	220.8	-13.5
	56	48.6		37	227.3	-18.3
5	57	55.7	-4.2	38	227.8	
	58	59.3		42	228.3	-22
	59	60.7	-13.0	39	231.8	-26.2
	60	68.9		11	235.6	-19.6
	61	82.3		55	241	-1.2
10	62	96.6	-6.56	20	243.3	-8.5
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				69	257.8	-1.5
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				22	273.8	
15				46	301.3	-2.1
				12	265.8	

Key

- 1 1,4-butane diol adipic acid (S102250) available from Occidental
Chemical
- 2 1,4-butane diol adipic acid (S102250) (35phr)
- 3 polyethylene glycol 2000 available from Aldrich Chemical
- 4 polycaprolactone (Tone 301) available from Union Carbide
- 5 polyethylene glycol 6000 available from Aldrich Chemical
- 6 Triton X100 (polyethoxyethanol) available from Aldrich Chemical
- 7 1,4-butane diol adipic acid (S1063210) available from Occidental
Chemical

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- 8 neopentylglycol-adipic acid-caprolactone (S1063210) available from Occidental Chemical
- 9 triethylcitrate (Citroflex 2) available from Morflex Inc.
- 10 polyester adipate (MW = 2000) (Plasthall P643) available from C.P. Hall
- 5 11 Morton TP95 (polyether) available from Morton Thiokol Inc
- 12 di-isononyladipate (JayflexTM DINA2) available from Exxon Chemical
- 13 ReomolTM 249 (phosphate ester) available from FMC Corporation
- 14 MonoplexTM 573 (epoxidised octyl tallate) available from C.P. Hall
- 10 15 PEG 600 monolaurate (Plasthall CPH43N) available from C.P. Hall
- 16 Epoxidised soyabean oil (Plasthall ESO) available from C.P. Hall
- 17 PEG 200 Monolaurate (Plasthall CPH27N) available from available from C.P. Hall
- 18 Epoxidised soya bean oil (ParaplexTM G60) available from C.P. Hall
- 15 19 acetyl tri-n-butyl citrate (CitroflexTM A4) available from Morflex Inc
- 20 acetyl triethyl citrate (CitroflexTM A2) available from Morflex Inc
- 21 polyester sebecate (Plasthall P1070) available from C.P. Hall
- 22 neopentylglycol-adipic acid-caprolactone (S1063210) (35phr) available from Occidental Chemical
- 20 23 F1040250 trifunctional polyester adipates available from Occidental Chemical
- 24 polypropylene glycol adipate (low MW) (LankroflexTM PPL) available from Harcros Chemicals
- 25 25 di isooctylazelate (Reomol DIOZ) available from FMC Corporation
- 26 polyester adipate (MW = 1200) (Plasthall P650) available from C.P. Hall
- 27 Butyl carbitol ether/ester (Reomol BCF) available from FMC Corporation
- 28 epoxidised linseed oil (LankroflexTM L) available from Harcros Chemicals
- 29 epoxidised ester of fatty acid (LankroflexTM ED6) available from Harcros Chemicals
- 30 30 tri-n-butylcitrate (CitroflexTM 4) available from Morflex Inc
- 31 epoxidised soyabean oil (ParaplexTM G62) available from C.P. Hall
- 32 polyoxyethylene laurate (PlasthallTM CPH 376N) available from C.P. Hall
- 33 Morton TP759 available from Morton Thiokol

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- 34 dioctyladipate (Jayflex DOA2)TM available from Exxon Chemical
- 35 polyester glutarate (Plasthall P7092)TM available from C.P. Hall
- 36 polyester adipate (Diolpate 917)TM available from Kemira Chemical
- 37 butyl carbitol ether/ester (Reomol BCD)TM available from FMC
5 Corporation
- 38 octylphenyl substituted PEG (Igepal CA520)TM
- 39 Morton TP90B available from Morton Thiokol
- 40 trifunctional polyester adipates (F1040250) (35phr) available from
Occidental Chemical
- 10 41 epoxidised soya bean oil (Lankroflex GE)TM available from Harcros
Chemical
- 42 acetyltributylcitrate (Estaflex[®])TM available from Akzo Chemie
- 43 acetyltrimethylcitrate available from Morflex Inc
- 44 PEG 600 monooleate (Plasthall CPH41N)TM available from C.P. Hall
- 15 45 butyl-tri-n-hexyl citrate (Citroflex B6) available from Morflex Inc
- 46 di-isodecyladipate (Jayflex DIDA2)TM available from Exxon Chemical
- 47 polyester adipate (Diolpate 214)TM available from Kemira Polymers
- 48 epoxidised soya bean oil (Reoplas 39) available from Ciba Geigy
- 49 di-n-butyl sebecate (Reomol DBS)TM available from Ciba Geigy
- 20 50 polyester adipate (MW = 4200) (Diolpate 214)TM available from Kemira
Polymers
- 51 epoxidised glycol oleate (Monoplex S75) available from C.P. Hall
- 52 PEG 400 Monolaurate (Plasthall CPH30N)TM available from C.P. Hall
- 53 Castor oil available from Aldrich Chemical
- 25 54 Estaflex[®]/epoxidised soyabean oil (Reoplas 39) (50/50) available from
Akzo Chemie/Ciba Geigy
- 55 polyester glutarate (Paraplex P550)TM available from C.P. Hall
- 56 S1069285 (35phr) available from Occidental Chemical
- 57 PPG phthalate/adipate blend (Lankroflex 828)TM available from Harcros
30 Chemical
- 58 polyester adipate (Paraplex G59)TM available from C.P. Hall
- 59 tri-isopropyl phenyl phosphate (Reofos 95)TM available from FMC
Corporation
- 60 polypropylene adipate (Diolpate PPA350)TM available from Kemira

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much poorer elongation to break of 26.8%.

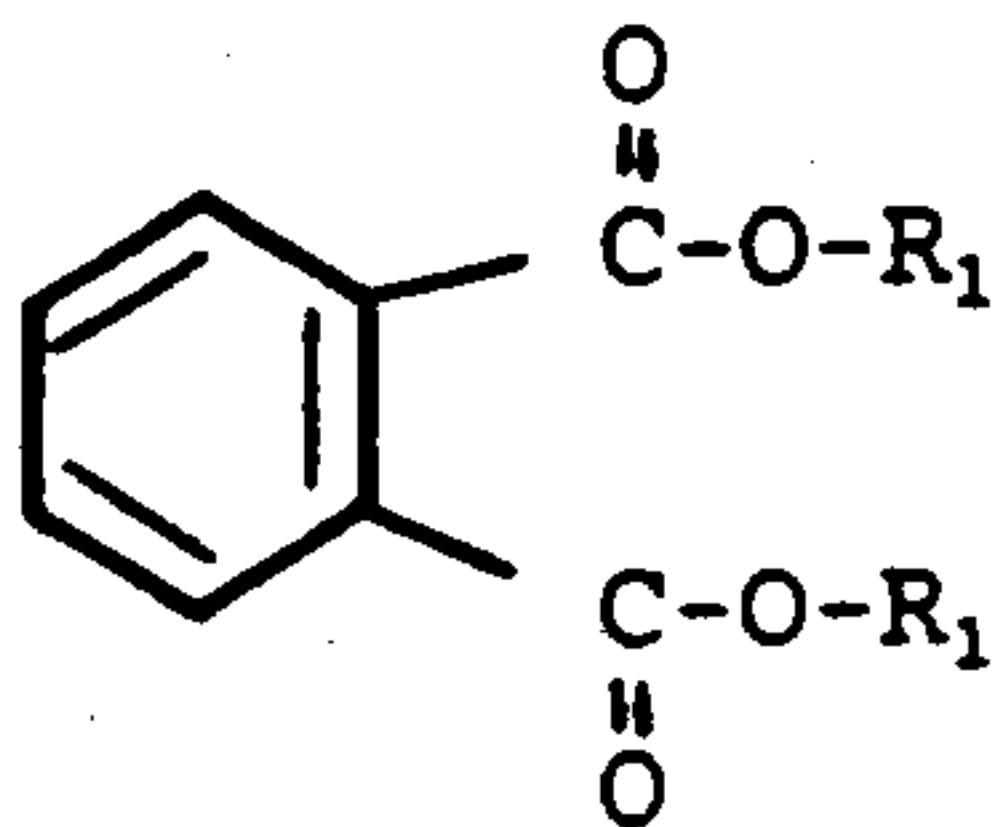
The Izod impact performance demonstrates a better correlation with T_g . Substituted PEGs such as Reomol BCD and the Morton range of plasticisers gave good results. Citrate esters were also highly effective.

CLAIMS:

1 Process for making, by extrusion, injection moulding, injection blow moulding, compression moulding, film or fibre formation or coating, a shaped article substantially composed of biodegradable polyester characterised by:

- (a) using as said polyester a (hydroxybutyrate-co-valerate) containing 70-98 mol percent of hydroxybutyrate; and
 (b) having present in said polyester 5-25 phr w/w of at least one plasticiser selected from the group:

A high-boiling esters selected from phthalates of the formula



where R_1 is C_{1-20} alkyl;

adipates of the formula $R_1-O-C(O)-(CH_2)_4-C(O)-OR_2$

where

R_1 and R_2 which may be the same or different are C_{2-12} alkyl or C_{2-12} alkoxyalkyl;

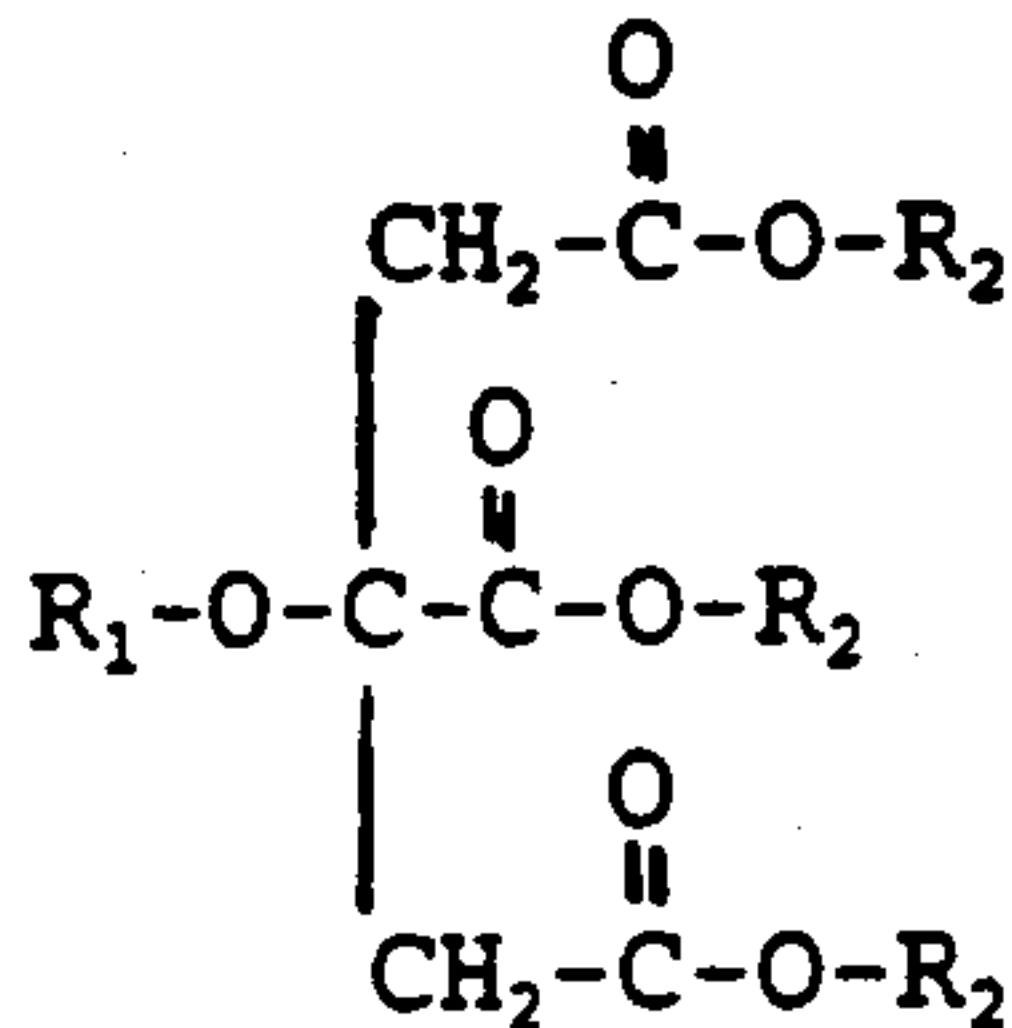
sebacates of the formula $R_1-O-C(O)-(CH_2)_8-C(O)-OR_2$

where R_1 is C_{2-15} alkyl or C_{2-15} alkoxyalkyl;

azelaates of the formula $R_1O-C(O)-(CH_2)_7-C(O)-OR_2$

where R_1 is C_{2-12} alkyl, benzyl, or C_{2-12} alkoxyalkyl; and

citrate esters of the formula:



where R_1 is hydrogen or C_{1-10} alkyl, and

R_2 is C_{1-10} alkyl or C_{1-10} alkoxyalkyl;

B alkyl ethers/esters of general formula

$R_2-(O-CH_2-CH_2-)_n-O-R_1$

where R_1 is alkyl or $-C(O)-$ alkyl;

R_2 is alkyl; and

- n is 2 or more; or
 where R₁ is hydrogen; and either:
 R₂ is alkylphenyl where the alkyl is C₂₋₁₂ alkyl, and
 n is 2 to 100; or
 R₂ is CH₃-(CH₂)₁₀-C(O)- and n is 10, 5 or 15; or
 R₂ is CH₃-(CH₂)₇CH=CH-(CH₂)₇-C(O)- and n is 5 or 15;
- C epoxy derivatives of the formula

$$\text{CH}_3-(\text{CH}_2)_n-\text{A}-(\text{CH}_2)_n-\text{R}$$
 in which the A is an alkene containing one or
 more double bonds,
 n is up to 25 and
 R is C₂₋₁₅ alkyl;
- D ricinoleate esters; and
- E polymeric esters of formula

$$-\text{O}-\text{CO}-\text{R}_1-\text{CO}-\text{O}-\text{R}_2-$$
 in which R₁ and R₂ are both independently C₂₋₁₂
 alkylene.
- 2 A process according to claim 1 in which the high-boiling ester is selected from
 diisodecyl phthalate,
 diisooctyl phthalate,
 diisodecyl adipate,
 di-n-butyl sebacate,
 dioctyl adipate,
 diisononyl adipate,
 diisooctyl azelaate, and
 isodecanol esters of adipic, glutaric and succinic
 acids.
- 3 A process according to claim 1 in which the citrate ester is selected from
 butyl-tri-n-hexyl citrate,
 triethylcitrate, and
 tri-n-butyl citrate.
- 4 A process according to claim 1 in which the alkyl ether/ester is selected from
 PEG 600 monooleate,
 PEG 400 monolaurate,
 PEG 600 monolaurate,
 PEG 200 monolaurate,
 butyl carbitol ether/ester, and
 octyl phenyl substituted polyethyleneglycol.

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- 5 A process according to claim 1 in which the ricinoleate ester is castor oil.
- 6 A process according to claim 1 in which the epoxy derivative is selected from the class consisting of
epoxidised esters of fatty acids;
epoxidised soya bean oil;
epoxidised linseed oil;
epoxidised octyl tallate; and
epoxidised glycololeate.
- 7 A process according to claim 1 in which the polymeric ester is selected from
glutaric polyesters having molecular weights from 2000 to 20,000;
adipic polyesters having a molecular weight from 200 to 20,000;
succinic polyesters; and
sebacic polyesters having a molecular weight from 4000 to 10,000.
- 8 A process according to any one of claims 1 to 7 in which at least two plasticisers selected from those defined in any of the preceding claims are used.
- 9 A process according to any one of claims 1 to 8 in which there is used additionally a plasticiser selected from citrates containing doubly esterified hydroxycarboxylic acids having at least 3 ester groups in the molecule, glycerol triacetate and glycerol diacetate.
- 10 A process according to claim 9 in which the additional plasticiser is acetyl tri-n-butyl citrate.