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(54) Title: ORIENTED POLYMERIC FILM COMPRISING AT LEAST ONE COPOLYETHERESTER

(57) Abstract: An oriented polymeric film comprising one or more copolyetherester(s) wherein the film is oriented in at least one direction; and a waterproof moisture vapour permeable fabric comprising a substrate, for instance a woven or knit material comprising polyester or nylon, the oriented polymeric film, and optionally an adhesive or primer layer or coating between the substrate and the copolyetherester-containing oriented film.

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ORIENTED POLYMERIC FILM COMPRISING AT LEAST ONE COPOLYETHERESTER

This invention relates to an oriented polymeric film comprising one or more copolyetherester(s) which is useful in the manufacture of waterproof moisture vapour permeable materials. The invention further relates to a fabric comprising substrate and an oriented polymeric film comprising one or more copolyetherester(s).

BACKGROUND

Waterproof moisture vapour permeable membranes are of use in the manufacture of, inter alia, apparel, materials for use in healthcare and packaging.

So-called breathable fabrics composed of a film of a polymeric material that is permeable to moisture vapour bonded to a textile material are known. The most notable and successful material that transmits moisture vapour therethrough is a film of microporous polytetrafluoroethylene that is adhered to a textile material. Although this product has been very successful, it is rather expensive and the pores tend to be blocked by dirt, body oils and detergents. It is known that other polymers can be formed into films that have a high moisture vapour transmission rate (MVTR) and, when covered with textile materials such as nylon or poly(ethylene terephthalate), can be used to make waterproof and water vapour permeable garments. U.S. Patent No. 4,493,870 discloses waterproof garments made of a textile material covered with a single layered film of a copolyetherester made from a dicarboxylic acid, an aliphatic diol and a poly(alkylene oxide)glycol wherein at least 70% of the glycol has a carbon to oxygen ratio of 2.0-2.4.

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US Patent No. 4,725,481 discloses a waterproof water vapour permeable film for use as surgical drape and in waterproof garments having rapid transmission of moisture vapour through the film toward the exterior or weather-side of the garment, while minimising the transmission of moisture vapour in the opposite direction, making the garment more comfortable to wear due to the increase in the MVTR away from the wearer while protecting the wearer from water, liquid and vapour from exterior sources. In particular, US Patent No. 4,725,481 discloses a bicomponent film of a hydrophobic layer and a hydrophilic layer of copolyetherester elastomers bonded together which permits

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differential transfer of moisture vapour to prevent build-up of moisture. These bicomponent films behave like a permeability valve.

One disadvantage with known waterproof moisture vapour permeable fabrics, such as GORETEX®, is that they are not stretchable. It would be desirable to impart some stretchability to materials of this type while at the same time ensuring that the fabric also has the characteristic of elasticity or stretch recovery, i.e. when the material is stretched it returns to its original dimensions.

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SUMMARY OF INVENTION

Oriented polymeric film comprising one or more copolyetherester(s), wherein the film is oriented in at least one direction. Fabric comprising such oriented polymeric film and substrate. Processes for making such oriented polymeric film and fabric.

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DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

A preferred oriented film in accordance with the present invention is a waterproof moisture vapour permeable oriented film and fabric having good mechanical properties (such as toughness, tensile strength, flex performance and tear resistance), preferably having good elasticity or stretch recovery, and preferably having good thermal properties.

In a preferred embodiment, the film has a thickness of less than 50 μm , and preferably less than 20 μm . In a further preferred embodiment the film is a clear film.

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Preferred oriented films may also retain an MVTR comparable to a cast film comprising one or more copolyetherester(s). Generally, orientation of a film would be expected to reduce the MVTR of the film in relation to an unoriented film.

The MVTR of the film is primarily dependent upon its chemical composition and thickness, and these parameters can be adjusted to tailor a film so that it is suitable for a particular end-use, as required. In a preferred embodiment of the invention, the MVTR of the copolyetherester is at least about 2500, preferably at least about 3500, and more

preferably from about 3500 to about 20000, gm.mil/m²/24hrs according to ASTM E96-66 (Procedure BW).

Formation of a film according to the invention is preferably effected by extrusion. In
5 general terms the process comprises the steps of extruding a layer of molten polymer, quenching the extrudate and orienting the quenched extrudate in at least one direction.

The polymeric film may be uniaxially oriented, but is preferably biaxially oriented by drawing in two mutually perpendicular directions in the plane of the film to achieve a
10 satisfactory combination of mechanical and physical properties. Orientation may be effected by any process known in the art for producing an oriented film, for example a tubular or flat film process.

In a preferred tubular process, simultaneous biaxial orientation may be effected by
15 extruding a thermoplastics polyester tube which is subsequently quenched, reheated and then expanded by internal gas pressure to induce transverse orientation, and withdrawn at a rate which will induce longitudinal orientation.

In a preferred flat film process, the layer-forming polymer is extruded through a slot die
20 and rapidly quenched upon a chilled casting drum to ensure that the polymer is quenched to the amorphous state. Orientation is then effected by stretching the quenched extrudate in at least one direction at a temperature above the glass transition temperature of the polymer. Sequential orientation may be effected by stretching a flat, quenched extrudate firstly in one direction, usually the longitudinal direction, i.e. the forward direction through
25 the film stretching machine, and then in the transverse direction. Forward stretching of the extrudate is conveniently effected over a set of rotating rolls or between two pairs of nip rolls, transverse stretching then being effected in a stenter apparatus. Stretching is effected to an extent determined by the nature of the polymer. Stretching is usually effected so that the dimension of the stretched film is from 2 to 5, more preferably 2.5 to 4.5 times its
30 original dimension in the stretched direction, or each direction of stretching. Greater draw ratios (for example, up to about 8 times) may be used if orientation in only one direction is required. It is not necessary to stretch equally in the machine and transverse directions although this is preferred if balanced properties are desired.

The stretched film may be, and preferably is, dimensionally stabilised by heat-setting under dimensional restraint at a temperature above the glass transition temperature of the polymer but below the melting temperature thereof, to induce crystallisation. In applications where film shrinkage is not of significant concern, the film may be heat set at relatively low temperatures or not at all. On the other hand, as the temperature at which the film is heat set is increased, the tear resistance of the film may change. Thus, the actual heat set temperature and time will vary depending on the composition of the film and its intended application but preferably should not be selected so as to substantially degrade the tear resistant properties of the film. Within these constraints, a heat set temperature of about 135° to 205°C is generally desirable.

According to a further aspect of the invention, there is provided a process for the preparation of an oriented film comprising one or more copolyetherester(s), said process preferably comprising the steps of extruding the copolyetherester(s), quenching the extrudate, stretching the quenched extrudate and optionally heat-setting the oriented film.

The film contains preferably at least 50 weight percent, more preferably at least 65 weight percent, more preferably at least 80 weight percent, more preferably at least 90 weight percent, and even more preferably at least 99 weight percent of the copolyetherester(s). The copolyetherester(s) are generally hydrophilic, as described in more detail below.

The viscosity of the copolyetheresters is preferably less than about 3000 Pa.s and preferably at least 20 Pa.s, measured according to the standard ISO11443. Preferably, the viscosity is in the range from about 20 to about 2000 Pa.s, more preferably from about 40 to about 1000 Pa.s, and more preferably from about 50 to about 700 Pa.s, measured according to the standard ISO11443. The viscosity in Pa.s is measured according to the standard ISO 11443 as a function of shear rate in sec^{-1} and temperature. The temperatures used in the measurement of viscosity are from a minimum of just above the melting (or softening) point of the polymer (typically from about 200 to about 210°C) up to a maximum of just above the temperatures (typically from about 230 to about 260°C, particularly from about 240 to about 250°C) used in the processing methods (for example, coextrusion, injection moulding and lamination) of thermoplastic materials. The

temperatures used in the processing of thermoplastics are generally from about 20 to about 50°C, and particularly from about 40 to about 50°C, above the melting point of the thermoplastic. The shear rates used in the measurement of viscosity were from about 10 to about 10000 sec⁻¹, which encompass those typically encountered in the processing methods
5 of thermoplastic materials.

In a preferred embodiment of the invention, the viscosity of the copolyetheresters is preferably less than about 3000 Pa.s, preferably at least 20 Pa.s, preferably from about 20 to about 2000 Pa.s, more preferably from about 40 to about 1000 Pa.s, and more preferably
10 from about 50 to about 700 Pa.s, in the temperature range from about 200 to about 250°C, as measured according to the standard ISO11443.

Preferably, the melting point of the copolyetherester(s) is greater than 120°C, usually from about 120°C to above about 220°C. If the melting point of the copolyetherester is less than
15 about 120°C, then the polymer is tacky and difficult to handle in film form; and if the melting point is more than about 220°C, then the films become excessively stiff. The melting points are determined by differential scanning calorimetry (DSC) in accordance with the standard ISO 3146.

20 According to another aspect of the invention, an oriented polymeric film comprises one or more copolyetherester(s) wherein the film is oriented in at least one direction and has a set value less than a corresponding unoriented polymeric film. Preferably, the set value is less than 75% of that of a corresponding unoriented film.

25 According to a further aspect of the invention, there is provided a waterproof moisture vapour permeable fabric comprising a substrate and an oriented polymeric film comprising one or more copolyetherester(s) as herein described.

The substrate of the fabric may be any suitable fabric known in the art. The substrates may
30 be any woven, non-woven (including spun-bonded) or knit material, and preferably a woven or knit material. Preferably the substrate comprises polyester or nylon. Blends of other fibres may also be used, such as Lycra® or cotton.

In a preferred embodiment, the fabric comprises an adhesive or primer layer or coating between the substrate and copolyetherester-containing film. The adhesive or primer may be any conventional adhesive known in the art, such as a polyurethane-based adhesive. A suitable adhesive is LIOFOL® (UK4501; Henkel). The adhesive or primer is generally applied to the substrate layer. The adhesive or primer layer may be continuous or discontinuous, but should not significantly affect the breathability properties of the fabric. Preferably the adhesive layer is a discontinuous layer.

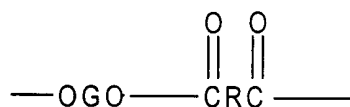
The fabric of the invention should preferably display good durability after washing, i.e. the fabric should retain good structural integrity after repeated washing.

Formation of the fabric according to the invention may be effected by conventional techniques well-known in the art. In a preferred embodiment, the fabric is formed using conventional laminating techniques, for example by lamination of a preformed copolyetherester-containing layer with the substrate, or by casting. Typically, such lamination techniques would involve thermal lamination of the respective layers on hot roll calendering equipment, and with the application of sufficient pressure, the layers become bonded.

Preferred copolyetherester(s) are now described.

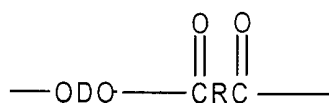
In a preferred embodiment of the invention, the copolyetherester elastomer(s) are selected from those described in US Patent No 4,725,481, the disclosure of which is incorporated herein by reference.

In another preferred embodiment, the copolyetherester elastomer(s) have a multiplicity of recurring long-chain ester units and short-chain ester units joined head-to-tail through ester linkages, said long-chain ester units being represented by the formula:



(I)

and said short-chain ester units being represented by the formula:



(II)

wherein

- 5 G is a divalent radical remaining after the removal of terminal hydroxyl groups from a poly(alkylene oxide)glycol having an average molecular weight of about 400-3500, wherein the amount of ethylene oxide groups incorporated in said one or more copolyetheresters by the poly(alkylene oxide)glycol is from about 20 to about 68 weight percent, preferably from about 25 to about 68 weight percent, based upon the total weight
 10 of the copolyetherester(s);
- R is a divalent radical remaining after removal of carboxyl groups from a dicarboxylic acid having a molecular weight less than about 300;
- D is a divalent radical remaining after removal of hydroxyl groups from a diol having a molecular weight less than about 250;
- 15 wherein said copolyetherester(s) contain from about 25 to about 80 weight percent short-chain ester units.

As used herein, the term "ethylene oxide groups incorporated in the copolyetherester(s)" means the weight percent in the total copolyetherester(s) of (CH₂-CH₂-O-) groups in the
 20 long-chain ester units. The ethylene oxide groups in the copolyetherester that are counted to determine the amount in the polymer are those derived from the poly(alkylene oxide)glycol and not ethylene oxide groups introduced into the copolyetherester by means of a low molecular weight diol.

- 25 As used herein, the term "long-chain ester units" as applied to units in a polymer chain refers to the reaction product of a long-chain glycol with a dicarboxylic acid. Suitable long-chain glycols are poly(alkylene oxide)glycols having terminal (or as nearly terminal as possible) hydroxy groups and having a molecular weight of from about 400 to about 3500, particularly from about 600 to about 1500.

The poly(alkylene oxide)glycols used to make the copolyetheresters should preferably contain ethylene oxide groups in amounts that result in a copolyetherester having from about 20 to about 68, preferably from about 25 to about 68, more preferably from about 30 to about 55, weight percent ethylene oxide groups, based on the total weight of the copolyetherester. The ethylene oxide groups cause the polymer to have the characteristic of being readily permeable to moisture vapour and, generally, the higher the percentage of ethylene oxide in the copolyetherester, the higher degree of water permeability. Random or block copolymers of ethylene oxide containing minor portions of a second poly(alkylene oxide)glycol can be used. Generally, if a second monomer is present, the second monomer will constitute less than about 30 mol percent of the poly(alkylene oxide)glycols, and usually less than about 20 mol percent. Representative long-chain glycols include poly(ethylene oxide)glycol, ethylene-oxide capped polypropylene oxide glycol, mixtures of poly(ethylene oxide)glycol with other glycols such as ethylene oxide capped poly(propylene oxide)glycols and/or poly(tetramethylene oxide)glycol provided the resulting copolyetherester has an amount of ethylene oxide groups of at least about 25 weight percent. Copolyetheresters prepared from poly(ethylene oxide)glycols having a molecular weight of from about 600 to 1500 are preferred because they provide a combination of superior moisture vapour permeability and limited water swell and, when formed into a film, they exhibit useful properties over a wide temperature range.

20

The term "short-chain ester units" as applied to units in a polymer chain of the copolyetheresters refers to low molecular weight compounds or polymer chain units having molecular weights less than about 550. They are made by reacting a low molecular weight diol or a mixture of diols (MW below about 250) with a dicarboxylic acid to form ester units represented by Formula (II) above.

25

Included among the low molecular weight diols which react to form short-chain ester units suitable for use for preparing copolyetheresters are acyclic, alicyclic and aromatic dihydroxy compounds. Preferred compounds are diols with 2-15 carbon atoms such as ethylene, propylene, isobutylene, tetramethylene, 1,4-pentamethylene, 2,2-dimethyltrimethylene, hexamethylene and decamethylene glycols, dihydroxycyclohexane, cyclohexane dimethanol, resorcinol, hydroquinone, 1,5-dihydroxynaphthalene, etc. Especially preferred diols are aliphatic diols containing 2-8 carbon atoms, most especially

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1,4-butanediol. Included among the bisphenols which can be used are bis(p-hydroxy)diphenyl, bis(p-hydroxyphenyl)methane, and bis(p-hydroxyphenyl)propane. Equivalent ester-forming derivatives of diols are also useful (e.g., ethylene oxide or ethylene carbonate can be used in place of ethylene glycol). The term "low molecular weight diols" as used herein should be construed to include such equivalent ester-forming derivatives; provided, however, that the molecular weight requirement pertains to the diol and not to its derivatives.

Dicarboxylic acids which are reacted with the foregoing long-chain glycols and low molecular weight diols to produce the copolyetheresters are aliphatic, cycloaliphatic or aromatic dicarboxylic acids of a low molecular weight, i.e., having a molecular weight of less than about 300. The term "dicarboxylic acids" as used herein includes acid equivalents of dicarboxylic acids having two functional carboxyl groups which perform substantially like dicarboxylic acids in reaction with glycols and diols in forming copolyetherester polymers. These equivalents include esters and ester-forming derivatives, such as acid halides and anhydrides. The molecular weight requirement pertains to the acid and not to its equivalent ester or ester-forming derivative. Thus, an ester of a dicarboxylic acid having a molecular weight greater than 300 or an acid equivalent of a dicarboxylic acid having a molecular weight greater than 300 are included provided the acid has a molecular weight below about 300. The dicarboxylic acids can contain any substituent groups or combinations which do not substantially interfere with the copolyetherester polymer formation and use of the polymer in the compositions of this invention.

The term "aliphatic dicarboxylic acids", as used herein, means carboxylic acids having two carboxyl groups each attached to a saturated carbon atom. If the carbon atom to which the carboxyl group is attached is saturated and is in a ring, the acid is cycloaliphatic. Aliphatic or cycloaliphatic acids having conjugated unsaturation often cannot be used because of homopolymerization. However, some unsaturated acids, such as maleic acid, can be used.

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Aromatic dicarboxylic acids, as the term is used herein, are dicarboxylic acids having two carboxyl groups attached to a carbon atom in a carbocyclic aromatic ring structure. It is not necessary that both functional carboxyl groups be attached to the same aromatic ring

and where more than one ring is present, they can be joined by aliphatic or aromatic divalent radicals or divalent radicals such as $-O-$ or $-SO_2-$.

Representative aliphatic and cycloaliphatic acids which can be used are sebacic acid, 1,3-cyclohexane dicarboxylic acid, 1,4-cyclohexane dicarboxylic acid, adipic acid, glutaric acid, 4-cyclohexane-1,2-dicarboxylic acid, 2-ethylsuberic acid, cyclopentanedicarboxylic acid, decahydro-1,5-naphthylene dicarboxylic acid, 4,4,'-bicyclohexyl dicarboxylic acid, decahydro-2,6-naphthylene dicarboxylic acid, 4,4,'-methylenebis(cyclohexyl) carboxylic acid, 3,4-furan dicarboxylic acid. Preferred acids are cyclohexane-dicarboxylic acids and adipic acid.

Representative aromatic dicarboxylic acids include phthalic, terephthalic and isophthalic acids, bibenzoic acid, substituted dicarboxy compounds with two benzene nuclei such as bis(p-carboxyphenyl)methane, p-oxy-1,5-naphthalene dicarboxylic acid, 2,6-naphthalene dicarboxylic acid, 2,7-naphthalene dicarboxylic acid, 4,4,'-sulfonyl dibenzoic acid and C_1 - C_{12} alkyl and ring substitution derivatives thereof, such as halo, alkoxy, and aryl derivatives. Hydroxyl acids such as p-(beta-hydroxyethoxy)benzoic acid can also be used providing an aromatic dicarboxylic acid is also present.

Aromatic dicarboxylic acids are a preferred class for preparing the copolyetherester polymers useful for this invention. Among the aromatic acids, those with 8-16 carbon atoms are preferred, particularly terephthalic acid alone or with a mixture of phthalic and/or isophthalic acids.

The copolyetheresters contain about 25-80 weight percent short-chain ester units corresponding to Formula (II) above, the remainder being long-chain ester units corresponding to Formula (I) above. When the copolyetheresters contain less than about 25 weight percent short-chain ester units, then the crystallisation rate becomes very slow and the copolyetherester is tacky and difficult to handle. When more than about 80 weight percent short-chain ester units are present, then the copolyetheresters generally become too stiff. The copolyetheresters preferably contain about 30-60, preferably about 40-60, weight percent short-chain ester units the remainder being long-chain ester units. In general, as percent short-chain ester units in the copolyetherester are increased, the

- polymer has a higher tensile strength and modulus, and the moisture vapour transmission rate decreases. Most preferably, at least about 70% of the groups represented by R in Formulae (I) and (II) above are 1,4-phenylene radicals and at least about 70% of the groups represented by D in Formula (II) above are 1,4-butylene radicals and the sum of the
- 5 percentages of R groups which are not 1,4-phenylene radicals and D groups which are not 1,4-butylene radicals does not exceed 30%. If a second dicarboxylic acid is used to make the copolyetherester, isophthalic acid is the acid of choice and if a second low molecular weight diol is used, 1,4-butenediol or hexamethylene glycol are the diols of choice.
- 10 A blend or mixture of two or more copolyetherester elastomers can be used. The copolyetherester elastomers used in the blend need not on an individual basis come within the values disclosed hereinbefore for the elastomers. However, the blend of two or more copolyetherester elastomers must conform to the values described herein for the copolyetheresters on a weighted average basis. For example, in a mixture that contains
- 15 equal amounts of two copolyetherester elastomers, one copolyetherester can contain 60 weight percent short-chain ester units and the other copolyetherester can contain 30 weight percent short-chain ester units for a weighted average of 45 weight percent short-chain ester units.
- 20 The MVTR of the copolyetheresters can be regulated by various means. The thickness of a layer of copolyetherester has an effect on the MVTR in that the thinner the layer the higher the MVTR. An increase in the percent of short-chain ester units in the copolyetherester results in a decrease in the MVTR, but also results in an increase in the tensile strength of the layer due to the fact the polymer is more crystalline.
- 25 The Young's moduli of the copolyetherester elastomers preferably are from 1000 to 14,000 psi, usually 2000 to 10,000 psi, as determined by ASTM Method D-412. The modulus can be controlled by the ratio of short-chain segments to long-chain segments of the copolyetherester elastomer, and comonomer choice for preparation of the copolyetherester.
- 30 Copolyetheresters having a relatively low modulus generally confer better stretch recovery and aesthetics to the laminate structure where the stiffness and drape of the structure are important.

Preferably, the copolyetherester elastomers are prepared from esters or mixtures of esters of terephthalic acid and isophthalic acid, 1,4-butanediol and poly(tetramethylene ether)glycol or ethylene oxide-capped polypropylene oxide glycol, or are prepared from esters of terephthalic acid, e.g. dimethylterephthalate, 1,4-butanediol and poly(ethylene oxide)glycol. More preferably, the copolyetherester elastomers are prepared from esters of terephthalic acid, e.g. dimethylterephthalate, 1,4-butanediol and poly(ethylene oxide)glycol.

The dicarboxylic acids or their derivatives and the polymeric glycol are incorporated into the final product in the same molar proportions as are present in the reaction mixture. The amount of low molecular weight diol actually incorporated corresponds to the difference between the moles of diacid and polymeric glycol present in the reaction mixture. When mixtures of low molecular weight diols are employed, the amounts of each diol incorporated is largely a function of the amounts of the diols present, their boiling points, and relative reactivities. The total amount of glycol incorporated is still the difference between moles of diacid and polymeric glycol. The copolyetherester elastomers described herein can be made conveniently by a conventional ester interchange reaction. A preferred procedure involves heating the ester of an aromatic acid, e.g., dimethyl ester of terephthalic acid, with the poly(alkylene oxide)glycol and a molar excess of the low molecular weight diol, 1,4-butanediol, in the presence of a catalyst at 150°-160°C, followed by distilling off methanol formed by the interchange reaction. Heating is continued until methanol evolution is complete. Depending on temperature, catalyst and glycol excess, this polymerization is complete within a few minutes to a few hours. This product results in the preparation of a low molecular weight prepolymer which can be carried to a high molecular weight copolyetherester by the procedure described below. Such prepolymers can also be prepared by a number of alternate esterification or ester interchange processes; for example, the long-chain glycol can be reacted with a high or low molecular weight short-chain ester homopolymer or copolymer in the presence of catalyst until randomization occurs. The short-chain ester homopolymer or copolymer can be prepared by ester interchange from either the dimethyl esters and low molecular weight diols as above, or from the free acids with the diol acetates. Alternatively, the short-chain ester copolymer can be prepared by direct esterification from appropriate acids, anhydrides or acid chlorides, for example, with diols or by other processes such as reaction of the acids

with cyclic ethers or carbonates. Obviously the prepolymer might also be prepared by running these processes in the presence of the long-chain glycol.

The resulting prepolymer is then carried to high molecular weight by distillation of the
5 excess of short-chain diol. This process is known as "polycondensation". Additional ester interchange occurs during this distillation to increase the molecular weight and to randomize the arrangement of the copolyetherester units. Best results are usually obtained if this final distillation or polycondensation is run at less than 1 mm pressure and 240°-260°C for less than 2 hours in the presence of antioxidants such as 1,6-bis-(3,5-di-tert-
10 butyl-4-hydroxyphenyl)propionamido]-hexane or 1,3,5-trimethyl-2,4,6-tris[3,5-ditertiary-butyl-4-hydroxybenzyl]benzene. Most practical polymerization techniques rely upon ester interchange to complete the polymerization reaction. In order to avoid excessive hold time at high temperatures with possible irreversible thermal degradation, it is advantageous to employ a catalyst for ester interchange reactions. While a wide variety of catalysts can be
15 used, organic titanates such as tetrabutyl titanate used alone or in combination with magnesium or calcium acetates are preferred. Complex titanates, such as derived from alkali or alkaline earth metal alkoxides and titanate esters are also very effective. Inorganic titanates, such as lanthanum titanate, calcium acetate/antimony trioxide mixtures and lithium and magnesium alkoxides are representative of other catalysts which can be
20 used.

Ester interchange polymerizations are generally run in the melt without added solvent, but inert solvents can be used to facilitate removal of volatile components from the mass at low temperatures. This technique is especially valuable during prepolymer preparation, for
25 example, by direct esterification. However, certain low molecular weight diols, for example, butanediol, are conveniently removed during polymerization by azeotropic distillation. Other special polymerization techniques for example, interfacial polymerization of bisphenol with bisacylhalides and bisacylhalide capped linear diols, may be useful for preparation of specific polymers. Both batch and continuous methods can be
30 used for any stage of copolyetherester polymer preparation. Polycondensation of prepolymer can also be accomplished in the solid phase by heating finely divided solid prepolymer in a vacuum or in a stream of inert gas to remove liberated low molecular weight diol. This method has the advantage of reducing degradation because it must be

used at temperatures below the softening point of the prepolymer. The major disadvantage is the long time required to reach a given degree of polymerization.

Although the copolyetheresters possess many desirable properties, it is sometimes

5 advisable to stabilize these compositions further against heat or light produced degradation.

This is readily achieved by incorporating stabilizers in the copolyetherester compositions.

Satisfactory stabilizers preferably comprise phenols, especially hindered phenols and their derivatives, amines and their derivative, especially arylamines.

10 Representative phenol derivatives useful as stabilizers include 4,4,'-bis(2,6-di-tertiarybutylphenol); 1,3,5-trimethyl-2,4,6-tris[3,5-ditertiary-butyl-4-hydroxybenzyl]benzene and 1,6-bis[3,5-di-tert-butyl-4-hydroxyphenyl]propionamido]hexane. Mixtures of hindered phenols with co-stabilizers such as diaurylthiodipropionate or phosphites are particularly useful. Improvement in light
15 stability occurs by the addition of small amounts of pigments or the incorporation of a light stabilizer, such as benzotriazole ultraviolet light absorbers. The addition of hindered amine photostabilizers, such as bis(1,2,2,6,6-pentamethyl-4-piperidiny) n-butyl-(3,5-di-tert-butyl-4-hydroxybenzyl)malonate, usually in amounts of from 0.05-1.0% by weight of the copolyetherester, are particularly useful in preparing compositions having resistance to
20 photodegradation.

Various conventional fillers can be added to the copolyetheresters usually in amounts of from about 1-10 percent by weight of the copolyetherester(s). Fillers such as clay, talc, alumina, carbon black and silica can be used, the latter being preferred, and white and light
25 coloured pigments can be added to the polymers. In general, these additives have the effect of increasing the modulus at various elongations.

EXAMPLES

The invention is further illustrated by the following examples. It will be appreciated that the examples are for illustrative purposes only and are not intended to limit the invention
5 as described above. Modification of detail may be made without departing from the scope of the invention.

EXAMPLES 1-5

10 In Examples 1-5, the following test procedures were used:

MVTR is measured according to standard test NF G52-019 ("up-cup" method at a temperature of 32°C).

15 Hydrohead is measured according to standard test ISO 20811.

Tensile strength and elongation at break are measured according to standard test ISO 527-3.

20 Tear strength is measured according to standard test ASTM D1922.

In the following discussion, "MD" refers to the machine direction and "TD" refers to the transverse direction.

25 The copolyetherester used in Examples 1-5 contained 45 weight percent 1,4-butylene terephthalate, and 55 weight percent ethylene oxide/propylene oxide copolyether terephthalate. The copoly(alkylene oxide) glycol used to make the copolyetherester was obtained by end-capping poly(propylene ether) glycol with 64 weight percent ethylene oxide, and had a molecular weight of about 2100. The copolyetherester had a calculated
30 ethylene oxide content of 33 weight percent, and contained 45 weight percent short-chain ester units. The polymer had a melting point of 200 degrees Centigrade.

Example 1

The copolyetherester was extruded through a film-forming die onto a water-cooled rotating quenching drum to yield a cast extrudate. The cast extrudate was heated to a temperature of about 40°C and then stretched longitudinally at a forward draw ratio of 3.0:1. The sheet
5 was passed into a stenter oven, where the sheet was heated to about 80°C and stretched in the sideways direction to approximately 3.0 times its original dimensions. The biaxially stretched sheet was heat-set at a temperature of 160°C. The final thickness of the sheet was 13µm. The sheet was analysed as described herein and demonstrates the following properties:

10	MVTR:	3676g/m ² /day
	Hydrohead:	>1000 cm
	Tensile strength at break:	1.4 daN (MD) 0.7 daN (TD)
	Elongation at break:	111% (MD) 15 220% (TD)
	Tear Strength:	464 mN (MD) 352 mN (TD)

Example 2

20 The procedure of Example 1 was repeated except that the film was heated to a temperature of 60°C in the forward draw.

Example 3

The procedure of Example 1 was repeated except that the forward draw ratio was 1 and the
25 sideways draw ratio was between 3 and 4.2.

Example 4

The procedure of Example 1 was repeated except that the forward draw ratio was 2.5 and the sideways draw ratio was between 2.5 and 3.

30

Example 5

The procedure of Example 1 was repeated except that the forward draw ratio was 2.5, the sideways draw ratio was between 2.5 and 3, and the heat-set temperature was 120°C.

EXAMPLE 6

Example 6 illustrates advantageous elastic and stretch recovery properties of preferred
5 embodiments of this invention.

The copolyetherester that was used in Example 6 contained 45 weight percent 1,4-butylene
terephthalate, and 55 weight percent ethylene oxide/propylene oxide copolyether
terephthalate. The copoly(alkylene oxide) glycol used to make the copolyetherester was
10 obtained by end-capping poly(propylene ether) glycol with 64 weight percent ethylene
oxide, and had a molecular weight of about 2100. The copolyetherester had a calculated
ethylene oxide content of 33 weight percent, and contained 45 weight percent short-chain
ester units. The polymer had a melting point of 200 degrees Centigrade.

15 Samples of 28 micron and 100 micron film of the copolyetherester were prepared as
follows. The copolyetherester was fed to the feed throat of a 38 mm diameter extruder at a
temperature of 220°C which was run at 20 rpm. The output of this melt was passed
through a 35 cm wide film die block that was heated to 220°C. The output from the die
was directed onto a chill roll, and then to a wind up roll. The roll speeds were varied to
20 make the different thickness film samples.

The 100 micron film was cut into 10 cm x 10 cm squares and drawn biaxially in a long
stretcher stenter frame. It was drawn simultaneously in both directions at a rate of
9000%/min. In one experiment, the film was drawn to 4.0 times the original length and 4.0
25 times the original width. On being released from the grips, it relaxed down to 2.1 times the
original length and 2.1 times the original width. In another experiment, the film was drawn
to 3.0 times the original length and 3.0 times the original width; and on being released
from the grips, it relaxed down to 1.8 times the original length and 1.8 times the original
width. The thicknesses of the resulting films were 24 microns and 45 microns.

30

Small dumbbells were died out of the 28 micron unoriented film and both of the
oriented films (24 microns and 45 microns). They were tested in an Instron machine at a
strain rate of 12.5 cm/min. Hysteresis curves were obtained by drawing dumbbells to 20%,

30%, 50%, or 100% elongation, retracting to the original length, drawing again, and retracting again. In addition, samples were drawn to break after two cycles of the 50% hysteresis curves, and tensile strength and percent elongation were measured according to ASTM D638. In each case, the amount of set was determined by calculating the
5 elongation at which the force dropped to zero in the unload curve. The following results were obtained:

Property	Unoriented Film (28 micron)	Oriented Film (45 micron)	Oriented Film (24 micron)
% Set in 20% hysteresis cycles	3	1	1
% Set in 30% hysteresis cycles	6	2.5	2.5
% Set in 50% hysteresis cycles	13	6.5	6
% Set in 100% hysteresis cycles	41	22	22
Tensile Strength at Break (MPa)	14.6	21.0	18.0
Elongation at Break	400%	200%	144%

While this invention has been described with respect to what is at present considered to be
10 the preferred embodiments, it is to be understood that the invention is not limited to the disclosed embodiments. To the contrary, the invention is intended to cover various modifications and equivalent arrangements included within the spirit and scope of the appended claims. The scope of the following claims is to be accorded the broadest interpretation so as to encompass all such modifications and equivalent formulations and
15 functions.

CLAIMS

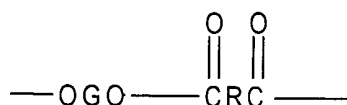
1. An oriented polymeric film comprising one or more copolyetherester(s) wherein the film is oriented in at least one direction.

5

2. A film according to claim 1 wherein the thickness of the film is from about 5 μm to about 100 μm .

3. A film according to claim 1 comprising at least 90 weight percent of the
10 copolyetherester(s).

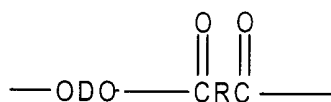
4. A film according to claim 1 wherein the copolyetherester elastomer(s) have a multiplicity of recurring long-chain ester units and short-chain ester units joined head-to-tail through ester linkages, said long-chain ester units being represented by the formula:



15

(I)

and said short-chain ester units being represented by the formula:



20

(II)

wherein

G is a divalent radical remaining after the removal of terminal hydroxyl groups from a poly(alkylene oxide)glycol having an average molecular weight of about 400-3500, wherein the amount of ethylene oxide groups incorporated in said one or more
25 copolyetheresters by the poly(alkylene oxide)glycol is from about 25 to about 68 weight percent based upon the total weight of the copolyetherester(s);

R is a divalent radical remaining after removal of carboxyl groups from a dicarboxylic acid having a molecular weight less than about 300;

D is a divalent radical remaining after removal of hydroxyl groups from a diol having a molecular weight less than about 250;

wherein said copolyetherester(s) contain from about 25 to about 80 weight percent short-chain ester units.

5

5. A film according to claim 1 wherein said copolyetheresters(s) have a moisture vapour transmission rate (MVTR) of at least about 2500 gm.mil/m²/24hrs according to ASTM E96-66 (Procedure BW).

10 6. A waterproof moisture vapour permeable fabric comprising a substrate and an oriented polymeric film according to claim 1.

7. A fabric according to claim 6 wherein the substrate is a woven or knit material comprising polyester or nylon.

15

8. A fabric according to claim 6 further comprising an adhesive or primer layer or coating between the substrate and copolyetherester-containing film.

9. A fabric according to claim 8 wherein the adhesive or primer is a polyurethane-
20 based adhesive.

10. A process for the preparation of a fabric according to claim 6 comprising the steps of forming an oriented film comprising one or more copolyetherester(s) by extruding the copolyetherester(s), quenching the extrudate, stretching the quenched extrudate and
25 optionally heat-setting the oriented film, and laminating the oriented film to a pre-formed substrate.

11. An oriented polymeric film comprising one or more copolyetherester(s) wherein the film is oriented in at least one direction and has a set value less than a corresponding
30 unoriented polymeric film.

12. The oriented polymeric film of claim 11, wherein the set value is less than 75% of that of the corresponding unoriented film.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/35167

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08J5/18 B32B27/36 //C08L67:02

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 7 C08J B32B D06N C08G

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 practical, search terms used)

EPO-Internal, WPI Data, PAJ, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4 493 870 A (VROUENRAETS CORNELIUS M F ET AL) 15 January 1985 (1985-01-15) cited in the application claims 1,3 column 2, line 39 - line 48 column 5, line 16 -column 6, line 47 ---	1-10
Y	US 5 958 567 A (SUGIURA KATSUHIKO ET AL) 28 September 1999 (1999-09-28) claims 1,6,7 example 1 ---	1-10
X	US 4 342 806 A (KUTSCH HOWARD J) 3 August 1982 (1982-08-03) claims 1,4 column 3, line 39 -column 4, line 42 column 5, line 8 - line 10 --- -/--	1,3,4

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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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)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

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

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

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.

* & * document member of the same patent family

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INTERNATIONAL SEARCH REPORT

International Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 918 156 A (ROGERS JOHN H) 17 April 1990 (1990-04-17) claim 1 example 1 ----	1-3
X	DATABASE WPI Section Ch, Week 199421 Derwent Publications Ltd., London, GB; Class A23, AN 1994-173930 XP002163559 & JP 06 116486 A (TORAY IND INC), 26 April 1994 (1994-04-26) abstract ----	1-3
X	EP 0 005 510 A (TORAY INDUSTRIES) 28 November 1979 (1979-11-28) claim 1 example 1 ----	1, 3
A	US 4 725 481 A (OSTAPCHENKO GEORGE J) 16 February 1988 (1988-02-16) cited in the application claim 1 ----	1
A	EP 0 353 768 A (DU PONT) 7 February 1990 (1990-02-07) claim 1 ----	1
A	WO 97 37849 A (ICI PLC ;BRENNAN WILLIAM JAMES (GB); RHOADES GARY VICTOR (GB); LAW) 16 October 1997 (1997-10-16) claims 1,3,8 page 2, line 19 -page 3, line 34 -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/35167

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4493870	A	15-01-1985	AT 27471 T CA 1191439 A DE 3371803 D DE 8334353 U EP 0111360 A JP 1048872 B JP 1703474 C JP 59111847 A	15-06-1987 06-08-1985 02-07-1987 12-04-1984 20-06-1984 20-10-1989 14-10-1992 28-06-1984
US 5958567	A	28-09-1999	JP 11166045 A	22-06-1999
US 4342806	A	03-08-1982	CA 1157687 A DE 3163734 D DK 249381 A EP 0041709 A ES 268056 Y GR 74605 A IE 51299 B JP 57025545 A	29-11-1983 28-06-1984 10-12-1981 16-12-1981 16-11-1983 29-06-1984 26-11-1986 10-02-1982
US 4918156	A	17-04-1990	EP 0297423 A	04-01-1989
JP 6116486	A	26-04-1994	NONE	
EP 0005510	A	28-11-1979	JP 1375903 C JP 54148869 A JP 57005691 B DE 2961353 D	22-04-1987 21-11-1979 01-02-1982 21-01-1982
US 4725481	A	16-02-1988	CA 1321864 A CN 87107026 A DE 3773328 A EP 0265922 A JP 1859277 C JP 2139233 A JP 5079227 B KR 9105725 B JP 1600443 C JP 2020425 B JP 63116850 A	07-09-1993 08-06-1988 31-10-1991 04-05-1988 27-07-1994 29-05-1990 01-11-1993 02-08-1991 31-01-1991 09-05-1990 21-05-1988
EP 0353768	A	07-02-1990	US 4906729 A BR 8903929 A DE 68925445 D DE 68925445 T JP 2088632 A JP 2979066 B MX 169788 B	06-03-1990 27-03-1990 29-02-1996 05-09-1996 28-03-1990 15-11-1999 26-07-1993
WO 9737849	A	16-10-1997	AU 1935097 A CN 1214653 A DE 69703151 D EP 0892721 A	29-10-1997 21-04-1999 26-10-2000 27-01-1999