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(54) Method of manufacturing a synthetic-resin fibre and molecularly oriented synthetic-resin fibre, and a molecularly oriented synthetic-resin fibre obtained by this method.

(57) The invention provides a method of manufacturing a synthetic-resin fibre, in which decomposition of the polymer molecules is avoided, and in which no solvents have to be used. A starting material which comprises at least an oligomeric compound is extruded from the melt to form a liquid thread, after which the starting material is polymerized by subjecting it to actinic radiation.

The method is particularly suitable for the manufacture of a molecularly oriented synthetic-resin fibre, for which purpose the liquid thread is subjected to an elongational flow, after which the thus oriented oligomeric compound is polymerized. The synthetic-resin fibre obtained by this method has a particularly high density of cross-links between the polymer chains.

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Method of manufacturing a synthetic-resin fibre and a molecularly oriented synthetic-resin fibre, and a molecularly oriented synthetic-resin fibre obtained by this method.

The invention relates to a method of manufacturing a synthetic-resin fibre.

The invention further relates to a method of manufacturing a molecularly oriented synthetic-resin fibre and to a molecularly oriented synthetic-resin fibre manufactured by this method.

Due to their great strength and rigidity, synthetic-resin fibres, in particular those formed from oriented polymers, are frequently used in, for example, textile fibres, as a reinforcing means in optical telecommunication cables and as a filler in synthetic-resin composite materials. The expression "molecularly oriented" is to be understood to mean herein that the material concerned contains anisotropic molecules having a preferred orientation. In a molecularly oriented synthetic-resin fibre, the polymer molecules are elongated, the preferred orientation being the longitudinal direction of the fibre. In a non-oriented synthetic-resin, the polymer molecules generally have the shape of an isotropic cluster or coil.

In accordance with a known method of manufacturing a synthetic-resin fibre, as described in, for example, the published European Patent Application EP 145745, a molten polymer is extruded through a narrow aperture after which the liquid thread is led through a cooling means in which the polymer solidifies to form a solid thread. Due to the high temperature of the melt chemical decomposition in the melting and extrusion process is hard to avoid.

However, an alternative method of manufacturing a synthetic-resin fibre is known, in which the fibre is spun from a polymer solution at a relatively low temperature. In the said method, the solvent is evaporated or, in accordance with an alternative method, the solution is introduced into a medium in which the polymer coagulates. In the case of polymers which have a high molecular weight, there is only a limited number of suitable solvents. Frequently, the use of solvents is undesirable, for example, in view of contamination of the environment, safety during use and the energy required for the evaporation process.

It is an object of the invention to provide a method of manufacturing a synthetic-resin fibre which can be used at such a low temperature that chemical decomposition of the polymer molecules does not have any adverse effects. A further object of the invention is to provide a method in which no solvents have to be used.

This object is achieved in accordance with the invention by a method in which a starting material which comprises at least one oligomeric compound is extruded from the melt to form a liquid thread, after which the starting material is polymerized by subjecting it to actinic radiation. Besides a lower melting point and, thus, a lower processing temperature, an oligomeric compound also has a lower viscosity than the corresponding polymeric compound. This has the additional advantage that the oligomeric compound can be extruded at a lower pressure than the corresponding polymeric compound. The oligomeric compound may be a monomeric compound or a compound consisting of a small number of monomeric units. It should be noted, however, that the compound is not polymerized until the desired fibre shape has been imparted to the starting material.

As a quick solidification of the starting material is desired, polymerization is not started by means of a thermal treatment but by means of actinic radiation. The term actinic radiation is to be understood to mean herein radiation using light, in particular UV-light, X-rays, gamma-rays or radiation using high-energetic particles, such as, electrons or ions.

If desired, the starting material may comprise a mixture of various oligomeric compounds. Besides, the starting material may comprise one or more other suitable components, such as, for example, catalysts, -(light sensitive) initiators, stabilizers, co-reacting monomers and surface-active compounds.

In accordance with a known method of manufacturing an oriented synthetic-resin fibre, as described in, for example, the published European Patent Application EP 145745, a synthetic-resin fibre is stretched. The said fibre is manufactured in the usual way, for example, by spinning from a melt. In this process, creep and relaxation of the stretched polymer molecules is precluded in a known manner by fixing the stretched conformation by means of cross-links between the polymer molecules. Such a cross-linking reaction may be caused, for example, by radiation using high-energetic particles, such as electrons.

It is an object of the invention to provide a method of manufacturing a molecularly oriented synthetic-resin fibre by means of which a product can be obtained having a very regular molecular structure and a great strength due to the fact that the method yields an extremely high degree of molecular orientation.

This object is achieved by a method in accordance with the invention, in which a starting material which at least comprises one oligomeric compound is extruded from the melt to form a liquid thread, after which the starting material is polymerized by subjecting it to actinic radiation, which method is further characterized in that the oligomeric compound is oriented immediately after the extrusion process by subjecting the liquid thread to an elongational flow, after which the starting material is polymerized prior to relaxation of the oriented oligomeric compound.

The invention is based on the experimentally established phenomenon that in a liquid having a relatively low viscocity an orientation can be brought about very effectively by means of an elongational flow. The not yet polymerized molecules are small enough to form regular, almost crystalline structures, which in the case of a polymer is possible only to a limited extent, in particular, if there are cross-links between the molecules in the said polymer.

In order to maintain the molecular orientation, it is necessary to carry out the polymerization process without delay and at a sufficiently high rate, for this reason actinic radiation is used to start the polymerization process. In this case, actinic radiation is not used to form cross-links in an existing polymeric material, but to form the polymer. An additional advantage of the method in accordance with the invention is the efficient use of actinic radiation when it is simultaneously used to form the polymer and to form cross-links between the polymer molecules. In this case it is not necessary to carry out a separate operation after a fibre has been formed, in which operation the fibre is reinforced and cross-links are formed.

A further advantage of the method in accordance with the invention is that, as a result of the regular molecular structure, it is possible to form very many cross-links in the polymeric material, as a result of which a very strong fibre is obtained which is hardly subject to creep.

Many common monomeric compounds can not be used as a starting material in the method in accordance with the invention, because, for example, it is difficult to orient small molecules, even when they are anisotropic, and because small molecules have a very high relaxation rate, i.e. when an orienting force ceases to exist an unoriented situation quickly developes.

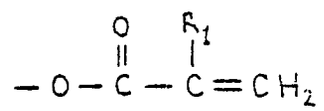
In a very efficient embodiment of the method in accordance with the invention, the oligomeric compound used and the processing temperature are selected so that the oligomeric compound exhibits liquid crystalline proporties at the processing temperature.

In an embodiment of the method in accordance with the invention, in which use is made of the dielectric anisotropy of the molecules, the orientation is enhanced by applying an electric or magnetic field. Dependent upon the orientation of the dipole moment, i.e. whether it is applied longitudinally or perpendicularly to the molecules, the field is applied longitudinally or perpendicularly to the fibre to be manufactured. Due to this measure, the relaxation time of the molecules is increased and the curing time is less critical.

Examples of suitable compounds are aromatic polyamides and polyesters on the basis of p-hydroxybenzoic acid. These materials are liquid crystalline with the mesogenic or smectic group in the main chain of the polymer. Further, it is possible to select a fast-curing starting material which comprises a mixture of oligomers, for example, a mixture in which the polymerization reaction is a reaction between a vinyl group and a thiol group.

In an alternative method in accordance with the invention, in which a high polymerization rate can be obtained and the polymer molecules form a network, the oligomeric compound used is selected from the group formed by oligo-esteracrylates and oligoetheracrylates having a molecular weight of less than 3000 and comprising at least two acrylate-ester groups per molecule.

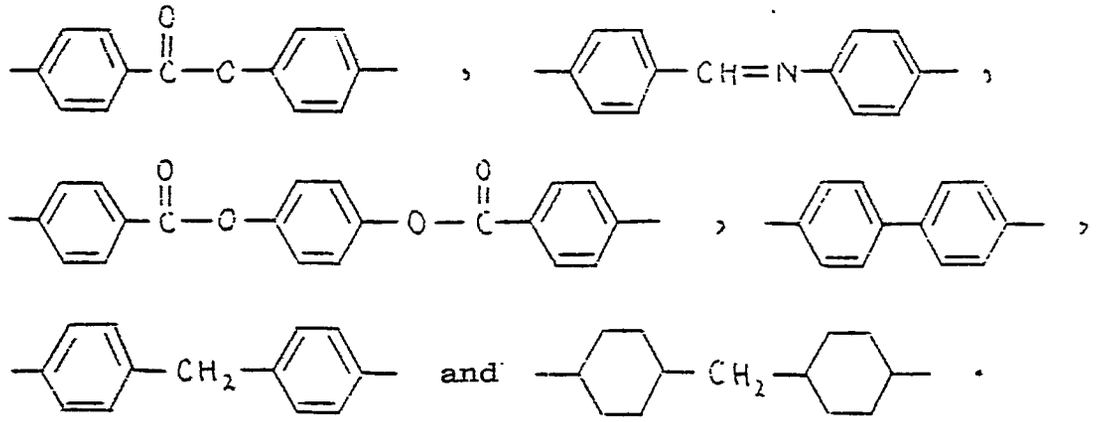
Acrylate-ester groups are to be understood to mean groups having the following structural formula:



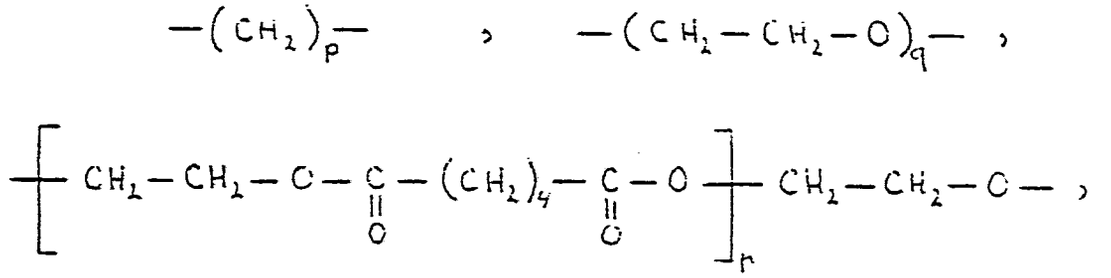
where $R_1 = H$ or CH_3 (acrylate and methacrylate, respectively).

In a suitable embodiment of the method in accordance with the invention, an oligomeric compound is used which consists of unbranched chains containing 1 to 12 rod-like, rigid chemical groups which enhance liquid crystalline properties, and 2 to 15 flexible chemical groups, and in which the acrylate-ester groups are attached to the chains via such flexible groups. A high degree of molecular orientation is possible because the chains are unbranched and because of the presence of the rigid chemical groups in the main chains of the polymer molecules. The acrylate-ester groups permit a high polymerization rate, consequently, these groups must possess a certain degree of mobility. A polymer network can be formed because there are at least two polymerizing acrylate-ester groups in each molecule.

The rod-liked, rigid chemical groups are preferably selected from the group formed by :



The flexible chemical groups are preferably selected from the group formed by :



in which p has a value of from 2 to 10, q has a value of from 1 to 10 and r has a value of from 1 to 6.

The chemical groups can be interconnected in the linear molecular chain in various ways, for example, directly, via oxygen atoms (ether bond), via ester groups or via urethane groups.

It is an object of the invention to provide a molecularly oriented synthetic-resin fibre having a large modulus of elasticity in the longitudinal direction of the fibre, and having a great breaking strength, in which fibre the molecular orientation remains intact over a wide temperature range.

This object is achieved in accordance with the invention by a synthetic-resin fibre which is manufactured by the method in accordance with the invention, which fibre is further characterized in that the number of cross-links between the polymer molecules is more than 10^{20} per cm^3.

An embodiment of the method in accordance with the invention and of the product obtained is explained in more detail with reference to a drawing, in which

Figure 1 is a structural formula of an oligoesteracrylate suitable for use in the method in accordance with the invention, and in which

Figure 2 is a schematic representation of an arrangement for carrying out the method in accordance with the invention.

EXAMPLE OF AN EMBODIMENT

Figure 1 is the structural formula of an oligoesterurethane acrylate which is suitable for use in the method in accordance with the invention, and which has 2 rigid, rod-like chemical groups per molecule, different types of flexible groups, urethane groups as coupling elements and 2 acrylate-ester groups per molecule. Due to the regular construction of the molecules, this material is crystalline in a non-polymerized condition at room temperature. In order to be able to cure the material by subjecting it to UV-light, it is mixed with 2 % by weight of 1-hydroxy-1-methyl-ethylphenylketone by stirring the components together at a temperature of 70°C. The viscocity of the mixture at 80°C is almost independent of the rate of shear and

amounts to 5 to 6 Pa.s. If desired, the starting material may contain mono-or polyfunctional acrylate compounds which are incorporated into the polymer network. Such compounds increase the rate of the polymerization reaction and reduce the viscocity of the starting material. Suitable examples are 2-phenoxy-ethylacrylate, hexanedioldiacrylate and trimethylolpropanetriacrylate.

The starting material is extruded at a temperature of 80°C, in an arrangement as shown in Figure 2, from a vessel 10 which is provided with heating elements 11 and a plunger 12. A stable liquid thread 13 is obtained, for example, under the following conditions : the bore of the nozzle 14 has a diameter of 0.5 mm and a length of 5 mm, the liquid pressure is 1.73 MPa and the rate of flow is 102 mm^3/s.

The desired molecular orientation is obtained by means of an elongational flow at the location of the arrow 15, for example, under the influence of gravity but, preferably, by drawing the fibre 16, for example, via one or more rollers 17 after the fibre has cured. The diameter of the liquid thread decreases from 0.5 to 0.2 mm, in which region the liquid thread is exposed to UV-light having a wavelength of from 300 to 400 nm, for example, by means of an electrodeless mercury lamp 18, marketed by Fusion System Inc., in combination with an elliptical-cylindrical mirror 19.

The molecular orientation of the cured fibre can be made visible in a polarization microscope having crossed polarizers.

In the table some material properties of the molecularly oriented synthetic-resin fibre are compared with the corresponding properties of an isotropically polymerized body of the same starting material.

Table

	oriented fibre	Isotropic material
Modulus of elasticity in GPa		
axial, -40°C	34.2	1.8
axial, 25°C	14.6	0.6
axial, 80°C	0.3	0.018
radial, 25°C	0.6	0.6
Breaking strength in MPa	> 60	28
Linear coefficient of expansion in $10^{-5}/°C$		
axial	2.6	13
axial	8.0	13

The oriented synthetic-resin fibre distinguishes itself by a large modulus of elasticity in the longitudinal direction (axially), a great breaking strength and a small thermal coefficient of expansion.

The oriented material exhibits 8.7 x 10^{20} cross-links per cm^3 between the polymer chains, which corresponds to a degree of conversion of 95 % of the acrylate-ester groups.

Claims

1. A method of manufacturing a synthetic-resin fibre, characterized in that a starting material which comprises at least one oligomeric compound is extruded from the melt to form a liquid thread, after which the starting material is polymerized by subjecting it to actinic radiation.

2. A method as claimed in Claim 1 for the manufacture of a molecularly oriented synthetic-resin fibre, characterized in that the oligomeric compound is oriented immediately after the extrusion process by subjecting the liquid thread to an elongational flow, after which the starting material is polymerized prior to relaxation of the oriented oligomeric compound.

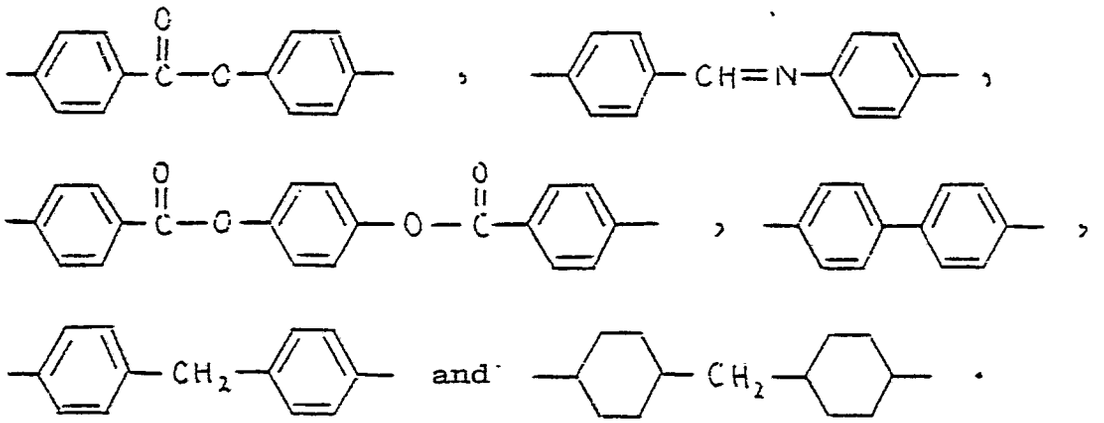
3. A method as claimed in Claim 2, characterised in that the oligomeric compound used and the processing temperature are selected so that the oligomeric compound exhibits liquid crystalline properties at the processing temperature.

4. A method as claimed in Claim 3, characterized in that the orientation is enhanced by applying an electric or magnetic field.

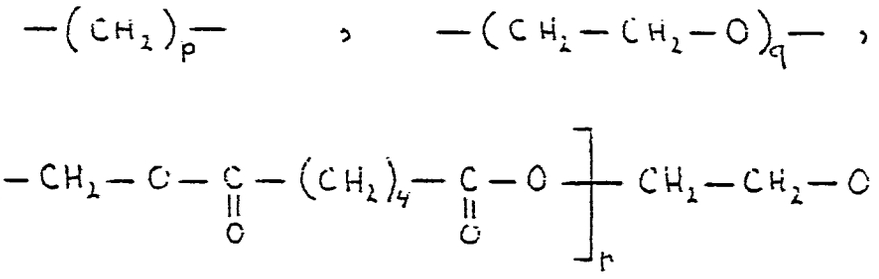
5. A method as claimed in any one of the Claims 2 up to and including 4, characterized in that the oligomeric compound used is selected from the group formed by oligo-esteracrylates and oligoetheracrylates having a molecular weight of less then 3000 and comprising at least 2 acrylate-ester groups per molecule.

6. A method as claimed in Claim 5, characterized in that an oligomeric compound is used which consists of unbranched chains containing 1 to 12 rod-like, rigid chemical groups which enhance liquid-crystalline properties, and 2 to 15 flexible chemical groups, and in which the acrylate-ester groups are attached to the chains via such flexible groups.

7. A method as claimed in Claim 6, characterized in that the rod-like, rigid chemical groups are selected from the group formed by :

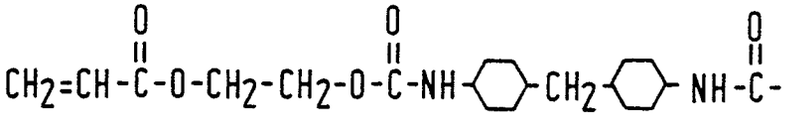


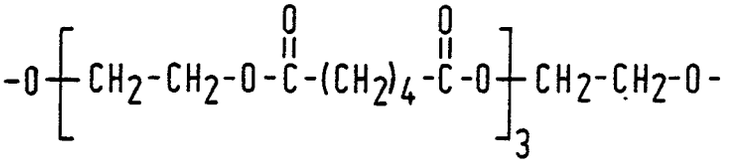
8. A method as claimed in Claim 6 or 7, characterized in that the flexible chemical groups are selected from the group formed by :



in which p has a value of from 2 to 10, q has a value of from 1 to 10 and r has a value of from 1 to 6.

9. A molecularly oriented synthetic-resin fibre manufactured by the method as claimed in any one of the Claims 2 up to and including 8, characterized in that the number of cross-links between the polymer chains is more than 10^{24} per cm^3.





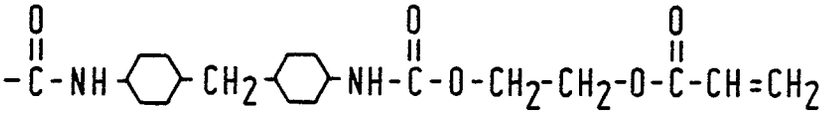


FIG.1

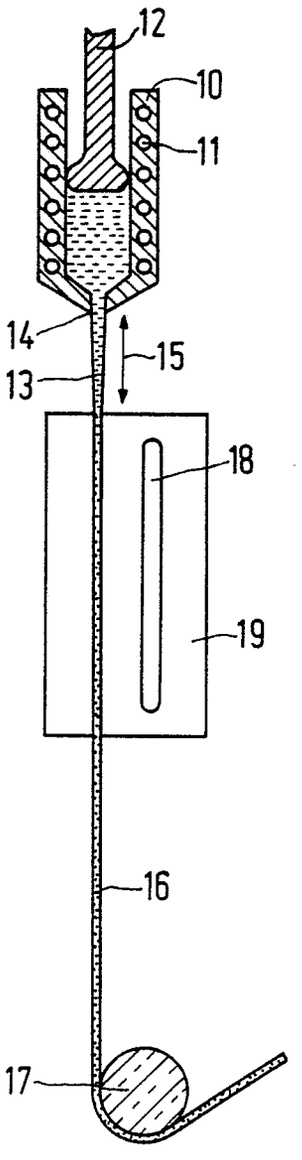


FIG.2

European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 87 20 0155

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	FR-A-2 080 737 (VEB CHEMIEFASERKOMBINAT SCHWARZA "WILHELM PIEK") * Whole document *	1-9	D 01 D 5/00 D 01 F 6/78
A	PATENT ABSTRACTS OF JAPAN, vol. 9, no. 228 (C-303)[1951], 13th September 1985; & JP-A-60 88 112 (MATSUSHITA DENKI SANGYO K.K.) 17-05-1985		
A	PATENT ABSTRACTS OF JAPAN, vol. 8, no. 138 (C-231)[1575], 27th June 1984; & JP-A-59 47 411 (TEIJIN K.K.) 17-03-1984		

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

D 01 D
C 08 F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	06-05-1987	VAN GOETHEM G.A.J.M.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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