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(21) International Application Number: PCT/EP92/01368 (22) International Filing Date: 16 June 1992 (16.06.92) (30) Priority data: 9101082 24 June 1991 (24.06.91) NL (71)(72) Applicant and Inventor: PONNET, Tom, Paul, Marthe, Ghislain [BE/BE]; Statiestraat 92, B-2600 Antwerpen (BE). (74) Agent: SIEMENS, Andreas, Meinhard, Ernest; Siemens & Cie., Roskam 8, NL-4813 GZ Breda (NL). (81) Designated States: AU, CA, JP, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LU, MC, NL, SE).		Published <i>With international search report.</i>
(54) Title: A MATERIAL AND SPLINT FOR ORTHOPAEDICAL, SURGICAL AND VETERINARY USE (57) Abstract <p>A thermoplastic material, mainly to be used for splints and supports in the orthopaedical, surgical and veterinary practice, is proposed for the fixation of body parts, said material consisting of a copolymer of ε-caprolactone, polyurethane, ethylene-butylene-styrene-copolymer mixed with triallylcyanurate and oleic acid-imide, said copolymer-mixture being gamma-irradiated after processing, such that a degree of cross-linking of the molecules and a partial crystalline configuration results in a reproducible flexibility, elasticity and reciprocal stretch properties.</p>		

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A material and splint for orthopaedical, surgical and veterinary use.

The present invention relates to a thermoplastic polymer material to be applied for orthopaedical, surgical and veterinary use, shaped as splints, artificial parts, prothesis, bandages and dressings.

The material ought to be used in suitable shapes for said practices as
5 a supporting gird or splint and it shall comply with special requirements, which are not claimed for other plastic articles.

Polymer plastic materials have been proposed already for similar purposes, in order to forestall the disadvantages of gypsum splints.

In U.S.-A-3,692,023 polymers or mixtures of poly- ϵ -caprolactone and
10 polyvinylethylether are described, which can be put upon fabric or gauze.

This material was to be wrapped, in a warmed condition, around broken limbs, and after cooling down it formed a relatively hard supporting means, which could be removed again manually by warming up same.

In U.S.-A-4,175,177 orthopaedical bandages were described, consisting
15 of copolymers of ϵ -caprolactone and acrylates.

Now more suitable materials have been sought in order to control the flexibility, bending strength, reciprocal elasticity and tensile strength in a reproducible manner.

The materials, which are already known, have been studied and compared
20 with each other.

From these investigations it became apparent, that the following requirements should be met merely in an accurate way:

1. Application of a thermoplastic polymer without any supporting material.
2. The material must have the property to be deformed easily.
- 25 3. The material shall be fit for repeated use.
4. The material should have a high compression strength.
5. The material should have a defined elasticity.

6. The material should have a resistance to remaining elongation. The phenomena of elasticity and resistance to elongation, as well as the compression strength, depend from the degree of crystallinity, the cross-linking index and the shape of the molecular chains.

5 A suitable material for surgical and orthopaedical practice, consisting of a composite of layers of poly- ϵ -caprolactone and a polyester with an upper layer of polyurethane foam with open cells has been described in European patent 0 263 552 of applicant.

10 A novel mixture of improved copolymers with a plasticizer has now been developed.

Hereby use was made of insight and further reflections on the structure of materials obtained by fundamental research. The structure of the materials is shown on page 5.

15 The process to obtain the present material according to the invention is characterized by a copolymerization by heating equimolecular weight-quantities of ϵ -caprolactone, polyurethane of polyoxypropylene-glycol and toluene-di-isocyanate with ethylene-butylene-styrene-copolymer, while during the formation of this mixed copolymer triallyl-cyanurate in an amount of 0.3 to 3.5% wt./wt., related to the total mass, and

20 about 1% wt./wt. of oleic acid imide as a plasticizer are added, and the product, cast in shapes of block sections or sheeting is then irradiated by Gamma radiation up to 2.5 Mrad during a short period.

By this method a material is obtained, which by its partial cross-linking of bundles of macromolecular chains with an isotactic structure and

25 its partial crystallinity of 5-10% can be processed successfully in injection moulds with an inner coating of polytetrafluorethylene, to obtain desired shapes for practical surgery and orthopaedy.

To a small part of the above raw materials during the last step some water can be added, such that a soft foamed layer with open cells is

30 formed, which at the elevated temperature is attaching to the surface of the shapes in a thickness of 0.5 to 1.0 mm.

The temperature of the copolymerization reaction is ranging from 45° to 180°C, depending from the plasticizer contents.

The elasticity, crystallinity and stretch properties depend from the

35 enthalpy of deformation. A measure for this quantity has been developed by Mooney and Rivlin, described in "Journal of Applied Physics", Vol. II, (1940), pages 582 a.f.

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A review of the evaluation of similar materials is represented in "Elasticity and Structure of Polyurethane Networks", Dissertation of R. Blokland, Delft Technical University, 1968.

5 A stretched elastomeric copolymer of the type of the present material has properties in accordance with the formula of Mooney and Rivlin:

$$F = (C_1 + \lambda^{-1} C_2) \cdot (\lambda - \lambda^{-2}),$$

Wherein the following parameters appear:

F = strain force [dyn/cm²].

C₁ = constant for basic polymer [Kg/cm²].

10 C₂ = Constant for copolymer [Kg/cm²].

λ = Stretch.

The enthalpy of deformation of each component is:

$$\Delta G = \frac{1}{2} \cdot C \cdot (\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3)$$

wherein the symbols are the following:

15 ΔG = Enthalpy of deformation,

C = Constant of the component material,

λ_x = Stretch in x-direction,

λ_y = Stretch in y-direction,

λ_z = Stretch in z-direction.

20 The elastic deformation is leading to an increase of the crystallinity and of the enthalpy of deformation (decrease of the entropy).

For the polyurethane-copolymers with ethylene-butylene-styrene and caprolactone-components the values of the constants C at a standard temperature of 25°C are as follows:

25 Basic polymer : C₁ = 3,30 Kg/cm²

Copolymer : C₂ = 2,00 Kg/cm².

These values can be altered within ranges by the addition of the triallyl-cyanurate and of the oleic acid-imide, such that a variety of well-defined properties can be obtained.

30 By the gamma-irradiation a reverse effect to some extent is obtained, such that every desired mechanical property with this versatile polymer material according to the invention can be reached, which is very important

for the medical treatment.

It is important that the shaped material in practice will remain at its place as required, that it will not slide or slip and that it will not deform if no pressure is applied, and moreover that it will not stick at the skin of the patient.

The material as developed according to the present invention has a so-called "plastic memory", resulting from its special molecular and crystalline structure, as described, such that after adaptation in the adjusted shape as a splint or support, it will have some suppleness at a slightly elevated temperature and that it presses softly at the part of the body, the limb or the organism in question.

The product is not restricted in its application to orthopaedical or surgical possibilities of use, but it might be used as well for technical purposes, such as the manufacture of filter aids, membranes and sieves, because it can be made porous and specifically permeable in thin layers. This renders the possibility of use in specialized clinical and analytical apparatus.

Furthermore the possibility of recycling of the present material is important, because it can be reduced into the form of particles and it can be granulated and reshaped anew by extrusion and for injection moulding.

The present invention relates to the preparation, processing and applications of the described material.

For special paramedical applications, such as arch supports and suchlike or similar expedients, the polymer foam layer on the surface of the articles can be replaced partly or entirely by a surface treatment with a suspension of a neutral scourer, such as e.g. pumice powder.

The chemical structures of the organic building parts of the copolymer mixture are rendered in the enclosed formula sheet with formulae 1 to 5.

The copolymer mixture is innocuous for human and animal tissue.

As polycaprolactone is an aerobic-biodegradable material, the compositions according to the present invention are explicitly compatible with the environment.

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Claims:

1. A method for the production of a deformable material for orthopaedical, surgical, veterinary and technical applications, based upon poly- ϵ -caprolactone, characterized in that equimolecular weight amounts of ϵ -caprolactone, polyurethane prepared of polyoxypropyleneglycol and toluene-di-isocyanate, and ethylene-butylene-styrene-copolymer are
5 reacted together under heating, and with reflux-cooling of vapours during said reaction triallylcyanurate in an amount of 0.3 to 3.5% wt./wt. and slowly oleic acid-imide in an amount of about 1% wt./wt. of the total mass are added, and the reaction product is cooled down,
10 washed and granulated, and brought into the desired surgical or technical shape by injection moulding or extrusion, followed by irradiation with gamma-rays of up to 2.5 Mrad, to obtain a solid flexible shape of flexibility and elasticity, as required for practical use.
- 15 2. A method for the manufacture of orthopaedical and surgical splint- or supporting means consisting of thermoplastic polymer material, characterized in that a shaped product obtained according to claim 1 is coated with a thin layer of a scourer.
3. A method for the manufacture of articles according to claim 2,
20 characterized in that a thin layer of weak open-cell foam of polymer is spread upon the surface of the articles.
4. Orthopaedical and surgical supporting means for the fixation of body parts after a fracture or an operation, characterized in that
25 said means consist entirely of a material manufactured according to claim 2 or 3, or comprise partly such a material.

INTERNATIONAL SEARCH REPORT

PCT/EP 92/01368

International Application No

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. 5 A61L15/07; C08L67/04		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	A61L ; C08L	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	US,A,4 483 333 (WARTMAN) 20 November 1984 see column 3, line 28 - column 5, line 31; claims 1,10 ---	1
A	EP,A,0 235 500 (UCC) 9 September 1987 see page 7, line 1 - page 15, line 16; claims 1-6 ---	1
A	EP,A,0 087 329 (LABORATOIRES D'HYGIEINE ET DE DIETETIQUE) 31 August 1983 cited in the application ---	1
A	EP,A,0 263 552 (PONNET) 13 April 1988 cited in the application ---	1
<p>¹⁰ Special categories of cited documents : 10</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"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</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"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.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
03 SEPTEMBER 1992	11. 09. 92	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	BOURGONJE A. F. 	

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. EP 9201368
SA 61122**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 03/09/92

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4483333	20-11-84	None	
EP-A-0235500	09-09-87	US-A- 4784123 AU-B- 591212 AU-A- 6705386 CA-A- 1276336 JP-A- 63260551	15-11-88 30-11-89 09-07-87 13-11-90 27-10-88
EP-A-0087329	31-08-83	FR-A- 2519992 CA-A- 1210181 JP-A- 58171413 US-A- 4912174	22-07-83 19-08-86 08-10-83 27-03-90
EP-A-0263552	13-04-88	BE-A- 905570 BE-A- 905981 BE-A- 905798 DE-A- 3777521	08-04-87 19-06-87 21-05-87 23-04-92