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Process for the manufacture of stretched rope.

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FR-A- 2 053 180

References cited :
GB-A- 2 042 414
GB-A- 2 051 667
US-A- 2 911 384
US-A- 3 266 232

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Description

The invention relates to a process for the manufacture of a rope comprising polymeric filaments manufactured according to the gel spinning process.

By 'rope' is understood in the present application: rope, cord, cable, string and similar structures comprising filaments or filaments and fibres.

The gel spinning process as known from GB-A-2,042,414 and GB-A-2,051,667 substantially consists in preparing a solution of a polymer, transforming the solution to filaments above the dissolution temperature of the polymer, cooling the filaments to below the dissolution temperature so that gelation occurs, and complete or partial removal of the solvent. The filaments can subsequently be stretched while the rest of the solvent is removed.

Such filaments show a high stiffness and a high tensile strength compared with filaments manufactured in a different manner from the same polymer by spinning.

A rope containing filaments that have been manufactured according to the gel spinning process also shows a high stiffness and a high strength. That is precisely why such a rope is used in situations where these properties are of much importance. It is therefore desirable to increase the stiffness and the strength of the rope still further.

The object of the invention is to provide a process for the manufacture of a rope containing polymeric filaments manufactured according to the gel spinning process, with a higher stiffness and a higher tensile strength than the known ropes. This is achieved by stretching a rope containing polymeric filaments manufactured according to the gel spinning process.

Such a rope shows a stiffness and a tensile strength which, depending on the degree of stretching, are significantly higher than the stiffness and the tensile strength of the original rope.

It is surprising that the stretching causes the stiffness and the tensile strength of the rope to increase because the filaments of which the rope is made are already stretched maximally during the spinning.

The tensile strength and the stiffness of the filaments increase with increasing degree of stretching during the spinning process.

The degree of stretching cannot be augmented unrestrictedly because rupture of the filaments during the production process occurs with increasing frequency as the degree of stretching is increased. It is easy to determine experimentally at what degree of stretching rupture of the filaments occurs with such a frequency that the corresponding frequency with which the process has to be interrupted is acceptable. This degree of stretching is called the maximum degree of stretching of the filaments.

It is possible to stretch such filaments somewhat further under very special conditions, for instance at

a very low rate, but such further stretching hardly yields an increase in the stiffness and the strength of the filaments.

From the maximally stretched filaments thus obtained, yarns can be manufactured by the known processes for that purpose, such as bundling, twisting and/or twining.

From the yarns a rope can be manufactured by the known processes for that purpose, such as twisting, twining, plaiting and/or laying up.

Besides filaments produced according to the gel spinning process, the rope may also contain other filaments or fibres.

By stretching the rope its stiffness and tensile strength increase. The stretching is preferably effected at elevated temperature, but below the melting point of the filaments. At elevated temperature the stretching can be effected with less force or, using the same force, a higher rate of stretching is achieved.

The stretching of the rope can also be effected in several steps.

Polymers that can be processed to filaments with good results by means of the gel spinning process are for instance polyalkenes, polyvinylalcohol and polyacrylonitrile.

The polyalkenes preferably have a weight average molecular weight higher than 400,000.

Good results are obtained if polyethylene (PE) is chosen as polyalkene. This PE may contain a minor quantity, preferably at most 5 mol.%, of one or more alkenes that can copolymerize with it, such as propene, butene, pentene, hexene, octene and 4-methylpentene, and possess 1 to 10, preferably 2-6, methyl or ethyl groups per 1000 carbon atoms.

Other polyalkenes can also be considered, such as for instance propene homo- and copolymers. Further, the polyalkenes used may contain minor quantities of one or more other polymers, in particular alkene-1 polymers.

By 'polyvinylalcohol' are also understood copolymers containing vinylalcohol and minor quantities, preferably at most 5 mol.%, of one or more other monomers, such as vinylacetate, ethene and other alkenes. By 'polyacrylonitrile' are also understood copolymers containing acrylonitrile and minor quantities, preferably at most 5 mol.%, of one or more other monomers, such as methacrylates, acrylates, vinylacetate.

Further, it has surprisingly been found that rope manufactured from not maximally stretched filaments, preferably manufactured from filaments with a degree of stretching of 50% or more, significantly gains stiffness and strength when stretched, and can be given the same stiffness and strength as the rope manufactured from maximally stretched filaments and subsequently stretched.

The invention will be elucidated in the following by means of a number of examples with ropes made

from polyethylene, polypropene and Kevlar (TM).

Rope 1 is laid up using 1600 denier polyethylene yarn, type Dyneema (TM) SK 60, manufactured according to the gel spinning process, and has the following structure: 7 x 19 x 2 x 1600. The strength of the rope, measured according to DIN 83305, is 73.8 kN. The tensile strength of the yarn, measured according to DIN 53834, is 3.20 GPa.

Rope 2 is laid up using 2000 denier polyethylene yarn, type Dyneema (TM) SK 60, manufactured according to the gel spinning process, the filaments not being stretched maximally but to 80%. Rope 2 has the following structure: 7 x 19 x 2 x 2000.

Rope 3 is laid up using Kevlar (TM) 29 1600 denier yarn and has the following structure: 7 x 19 x 2 x 1600. The strength of the rope is 51.7 kN.

Rope 4 is a randomly chosen rope made of polypropene filaments; it has a strength of 9.78 kN.

Example I

Rope 1 is clamped in in a Zwick (TM) tensile tester. The clamp-to-clamp distance is 60 cm.

The rope is loaded at room temperature to 50% of the measured strength for 10 days. At the end of that period the rope shows an elongation of 5% and its strength is 99 kN.

Example II

Rope 1 is stretched at 120°C at a rate of 20 mm/min until the elongation of the rope is 5%. The subsequent strength of the rope is 87.8 kN.

Example III

Rope 1 is stretched at 140°C at a rate of 5 mm/min until the elongation of the rope is 5%. The subsequent strength of the rope is 90.9 kN.

Example IV

Rope 1 is stretched at 140°C at a rate of 5 mm/min until the elongation of the rope is 7.5%. The subsequent strength of the rope is 102 kN.

Example V

Rope 1 is loaded 5000 times for a few seconds to 50% of its measured strength. The subsequent strength is 87.2 kN.

Example VI

Rope 2 is stretched at 140°C at a rate of 5 mm/min until the elongation of the rope is 23%. The subsequent strength of the rope is 91 kN.

Comparative Experiment A

Rope 3 is for 10 days loaded to 50% of its measured strength. The subsequent strength is 51.3 kN.

Comparative Experiment B

Rope 3 is loaded 5000 times for a few seconds to 50% of its measured strength. The subsequent strength is 49.6 kN.

Comparative Experiment C

Rope 4 is stretched at 150°C at a rate of 1 mm/min until the elongation of the rope is 5%. The subsequent strength of the rope is 9.06 kN.

Examples I, II, III, IV and V show that stretching of Rope 1 causes the initial strength to increase from 73.8 kN to 99, 87.8, 90.8, 102 and 87.2 kN respectively. It is clear that at elevated temperatures higher tensile strengths can be reached faster.

Example VI shows that yarns made of the polyethylene filaments which initially have not been stretched to their maximum strength can be laid up to form Rope 2, which after stretching at the same temperature and with the same rate of stretching as in Example III has acquired a similar higher tensile strength as Rope 1 in Example III, the filaments of which had been maximally stretched before manufacture of the rope.

The Kevlar Rope 3 of Comparative Experiment A, treated in the same way as Rope 1 of Example I, after stretching shows a decrease in tensile strength from 51.7 to 51.3 kN.

The polypropene Rope 4 of Comparative Experiment C also shows a decrease in tensile strength, from 9.78 to 9.06.

It is surprising that the ropes according to the invention gain tensile strength, while other ropes even show a decrease in tensile strength. This cannot be attributed to further stretching of the filaments, as appears from the following tests.

Test I

The strength of Dyneema (TM) SK 60 1600 denier yarn is determined according to DIN 53834. The strength of the yarn is 3.20 GPa. The yarn is stretched at 120°C at a rate of 20 mm/min until the elongation is 5%. The strength then is 3.28 GPa. The stretching has not brought about a significant increase in the strength of the yarn, nor consequently in that of the filaments.

Test II

The rope stretched as described in Example II is unravelled, so that the 1600 denier yarn is obtained

again. The strength of the yarn is 3.18 GPa. It appears that the strength of the yarn has not increased relative to the original yarn, while the strength of the rope has increased substantially as a result of the stretching.

Claims

1. Process for the manufacture of a rope containing polymeric filaments manufactured according to the gel spinning process, characterized in that the rope is stretched. 10
2. Process according to claim 1, characterized in that the stretching is carried out at elevated temperature, but below the melting temperature of the filaments. 15
3. Process according to claim 1 or 2, characterized in that the filaments are manufactured from polyalkene with a weight average molecular weight higher than 400,000. 20
4. Process according to claim 3, characterized in that polyethylene is used as polyalkene. 25
5. Process according to claim 1 or 2, characterized in that the filaments are manufactured from polyvinylalcohol. 30
6. Process according to claim 1 or 2, characterized in that the filaments are manufactured from polyacrylonitrile. 35
7. Process according to any one of the claims 1-6, characterized in that the rope is manufactured from unstretched filaments and subsequently stretched. 40
8. Process according to any one of the claims 1-6, characterized in that the rope is manufactured from partially stretched filaments and subsequently stretched. 45
9. Process according to any one of the claims 1-6, characterized in that the rope is manufactured from maximally stretched filaments and subsequently stretched. 50

Patentansprüche

1. Verfahren zur Herstellung eines nach dem Gelspinnverfahren hergestellte Polymerfäden enthaltenden Seils, dadurch gekennzeichnet, daß das Seil gestreckt wird. 55

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das Strecken bei erhöhter Temperatur, aber unterhalb des Schmelzpunktes der Fäden, durchgeführt wird.

3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß die Fäden aus Polyalken mit einem gewichtsmittleren Molgewicht von mehr als 400 000 hergestellt sind.

4. Verfahren nach Anspruch 3, dadurch gekennzeichnet, daß Polyäthylen als Polyalken verwendet wird.

5. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß die Fäden aus Polyvinylalkohol hergestellt sind.

6. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß die Fäden aus Polyacrylnitril hergestellt sind.

7. Verfahren nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß das Seil aus ungestreckten Fäden hergestellt und dann gestreckt wird.

8. Verfahren nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß das Seil aus teilweise gestreckten Fäden hergestellt und dann gestreckt wird.

9. Verfahren nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß das Seil aus maximal gestreckten Fäden hergestellt und dann gestreckt wird.

Revendications

1. Procédé pour la fabrication d'une corde renfermant des filaments polymères, fabriquée selon le procédé de filage en gel, caractérisé en ce que la corde est étirée.

2. Procédé selon la revendication 1, caractérisé en ce que l'étirage est effectué à température élevée, mais en dessous de la température de fusion des filaments.

3. Procédé selon la revendication 1 ou 2, caractérisé en ce que les filaments sont fabriqués à partir d'un polyalcène ayant une masse moléculaire moyenne en poids supérieure à 400 000.

4. Procédé selon la revendication 3, caractérisé en ce que le polyéthylène est utilisé en tant que polyalcène.

5. Procédé selon la revendication 1 ou 2, caractérisé en ce que les filaments sont fabriqués en alcool polyvinylique.
6. Procédé selon la revendication 1 ou 2, caractérisé en ce que les filaments sont fabriqués en polyacrylonitrile. 5
7. Procédé selon l'une quelconque des revendications 1 à 6, caractérisé en ce que la corde est fabriquée à partir de filaments non étirés et étirés ultérieurement. 10
8. Procédé selon l'une quelconque des revendications 1 à 6, caractérisé en ce que la corde est fabriquée à partir de filaments partiellement étirés et étirés ultérieurement. 15
9. Procédé selon l'une quelconque des revendications 1 à 6, caractérisé en ce que la corde est fabriquée à partir de filaments étirés au maximum et étirée ultérieurement. 20

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