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(54) **BRUSH CONTAINING MONO-FILAMENTS CONTAINING POLYAMIDE-410**

BÜRSTE AUS EINZELFILAMENTE MIT POLYAMID-410

BROSSE DE MONO-FILAMENTS CONTENANT LE POLYAMIDE 410

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Description

[0001] This invention relates to a brush containing mono-filaments containing polyamide, especially a toothbrush containing these mono-filaments.

[0002] A brush containing mono-filaments containing polyamide, also known as nylon, is known and is for example described in GB800610A. GB800610A describes a brush containing nylon mono-filaments and mentions mono-filaments of nylon-66 and nylon-610 for this application. For application in a brush and especially in a toothbrush, so-called "wet bend recovery" is an essential feature for a mono-filament. "Wet bend recovery" is the ability of a material to return to its original shape after deformation while being wet. If the wet bend recovery is high, this means that the mono-filaments easily return to its original shape, which allows for example longer use of a brush containing these mono-filaments.

[0003] An object of the present invention is to thus to provide a brush containing mono-filaments of polyamide, which mono-filaments exhibit high wet bend recovery.

[0004] This object surprisingly has been achieved by providing a brush containing mono-filaments containing a polyamide which comprises polyamide-410 in an amount of at least 40 wt.% based on the total amount of polyamide.

[0005] Monofilaments containing a polyamide which comprises PA-410 are known from WO 00/09586. However in WO 00/09586 nothing is said about the properties of the filaments under wet conditions, nor about their use in brushes.

Polyamide-410

[0006] Polyamide-410 is here understood to be a polyamide containing monomer units derived from a dicarboxylic acid with 10 carbon atoms and a diamine with 4 carbon atoms. Preferably as the dicarboxylic acid 1,10 decandioic acid is used. As the diamine preferably 1,4-butanediamine is used. PA-410 may comprise up to 30 wt. % of further monomeric units, for example dicarboxylic acids with less than 10 carbon atoms or diamines with more than 4 carbon atoms, with respect to the total amount of polyamide. Preferably the PA-410 used in the mono-filament used in the brush according to the invention comprises at least 80 wt. % with respect to the total amount of polyamide of the dicarboxylic acid with a chain of 10 carbon atoms between the carboxylic acid groups and a the diamine with 4 carbon atoms, more preferably at least 90 wt. % with respect to the total amount of polyamide, even more preferably at least 95 wt. % with respect to the total amount of polyamide, even more preferably at least 99 wt. %, most preferably at least 99.9 wt. %, with respect to the total amount of polyamide.

[0007] The mono-filament used in the brush according to the invention is produced from a polyamide comprising at least 40 wt% of polyamide-410 with respect to the total amount of polyamide, more preferably at least 50 wt % of polyamide-410, and most preferred at least 60 wt% of polyamide-410. Most preferably the polyamide consists essentially of PA-410. In a preferred embodiment the mono-filament containing the polyamide contains no further polymer.

[0008] Another important improvement is that the mono-filament according to the invention is no longer fully based on fossil carbon, since polyamide-410 may be at least partly based on renewable resources. This is especially an advantage, even if the polyamide of the mono-filament only contains a fraction of polyamide-410 and also a further polymer. Employing PA410 in mono-filaments which is at least partly based on monomers originating from natural resources already provides an important decrease in the production of green house gases and CO₂ in particular for mono-filament industry and its applications thereof.

[0009] A further advantage of the mono-filament used in the brush according to the invention is that the stiffness retention when wet is good. "Stiffness retention when wet" is here understood to be the ability to retain stiffness, usually measured as tensile modulus in MPa under humid conditions, i.e. under 50% relative humidity, compared to dry conditions, such as for example 0% relative humidity according to ISO5271A. A high stiffness retention when wet allows for pleasant brushing experience when applied in a toothbrush, as this is usually performed under wet conditions. The mono-filament can thus advantageously be employed in bristles for toothbrushes, as it combines very good wet bend recovery with good stiffness retention when wet.

[0010] Polyamide-410 can be prepared as for example described in the examples. For mono-filaments, preferably the viscosity number (VN) of polyamide-410 is at least 100 ml/g, more preferably at least 110 ml/g, even more preferably at least 120 ml/g and most preferred at least 140 ml/g. Higher viscosities will lead to improved mechanical properties of the mono-filaments. Preferably the viscosity number is at most 200 ml/g. If the viscosity number is too high, the throughput of the spinning machine is limited. The viscosity number is measured according to ISO 307, version 2007 in formic acid (90 wt%) in a concentration of 0.005 g/ml at 25 °C.

Mono-filaments

[0011] The mono-filaments used in the brush according to the invention preferably have an average diameter of between 1 micrometer and 1.5 mm. Preferably, the mono-filaments have an average diameter of between 15 micrometer and 1.2 mm. Mono-filaments can be prepared by melting the polyamide and subsequently pushing it through a die. After

leaving the die, the mono-filament is cooled down, preferably in a quench bath. In order to produce high quality mono-filaments, it is desirable to keep the threads separated from each other. This may be effected by a separating guide or a comb. The length of the air gap, i.e. the distance between the spinning plate and water surface, can influence the surface of the mono-filaments and the mechanical properties. Dependent upon the properties required of the mono-filament, either at least a single or at least a two stage drawing step can be performed in for example a hot water bath or in a hot air or infra-red oven. The second stage of a two stage drawing process usually takes place in a hot air oven and requires temperatures which are higher than the temperature in the first stage. It is preferable to use a water bath for the first stage if very close tolerances are required.

[0012] The drawing ratio and the applied temperatures influence the physical structure of the molecules in a mono-filament. As a number of properties such as tensile strength, elongation, e-modulus, heat resistance and dyeability with nonreactive dyestuffs, depend on the physical structure, the drawing process has a wide and varying influence on the properties of the mono-filament.

[0013] As an optional third step mono-filament properties such as, heat stability, tensile strength, elongation at break and dyeability can be trimmed to the desired level by fixation or relaxation. The percentage of relaxation allowed and the applied temperatures strongly depend on the final property requirements. To achieve proper fixation/relaxation the temperature of the mono-filament during the third step should at least equal, but more usually exceed, the temperature acquired during drawing. Temperature setting for the oven are very dependent on line speed, mono-filament diameter, oven length, and air velocity.

[0014] The mono-filament used in the brush according to the invention preferably comprises pigments, such as titanium oxide, to give the mono-filament a white appearance. The mono-filament according to the invention may also comprise lubricants, such as ethylene bis stearylamine (EBA), for higher transparency.

[0015] The mono-filament can be advantageously employed for bristles, preferably bristles for toothbrushes. The invention thus also relates to a toothbrush comprising the mono-filaments. The toothbrush combines good wet bend recovery and stiffness retention when wet. This allows longer use of the toothbrush before it needs to be discarded. Moreover, it also is advantageous in CO₂-reduction both from a longer use, as well as at least part of the toothbrush is made of renewable sources.

Examples

Preparation of PA-410

[0016] In an inert 2L autoclave reactor a 45% 410-salt solution was prepared. At 65 °C 230 ml of a 67.5% 1,4-diaminobutane solution was added to 540 ml of water prior to adding 348.2 g of solid 1,10-decanedioic acid. The maximum pressure of the reactor was set to 2 barA. The salt solution was heated up to 153 °C in 60 minutes. During this process the excess of water was distilled off until a water concentration of 10% was reached at 153 °C. The pressure of the reactor was set at 12 barA. The 410-salt solution was heated up in 15 minutes to reach a pressure of 12 barA, thereby polymerizing the salt solution. While maintaining 12 barA, more water is distilled off until a polymer melt was obtained and the temperature reached 250 °C. At 250 °C, the reactor was depressurized to 1.02 barA while heating up to 265 °C in 60 minutes, while further polymerizing the polymer melt. The polymer melt was further heated to 290 °C and kept at that temperature and 1.02 barA for 16 hours. The water of the polymer melt was stripped off with a small nitrogen flow. After the polycondensation phase the reactor was emptied into a water bath to get a polymer strand, which was off-line cut into granules. The PA-410 polymer had a solution viscosity of 179 ml/g in 90% formic acid.

[0017] Mono-filaments with a diameter of 0.2 mm were obtained by melting the PA-410 to a temperature of 270 °C and subsequently pressing it through a die.

Measurements

Viscosity number (VN).

[0018] The viscosity number was determined according to ISO 307, version 2007, by dissolving the PA-410 samples in formic acid (90 wt. %) in a concentration of 0.005 g/ml and determining of the viscosity number by an Ubelohde viscometer by measuring at 25 °C the times of flow of the solvent (t₀) and of the solution (t₁) and calculating the viscosity number by the formulae $VN = [(t_1/t_0) - 1] \times 200 \text{ ml/gram}$.

Pinch bend recovery tests

[0019] Bend recovery tests were performed on various mono filaments with the so called pinch hole bend recovery method. This method uses metal plates holes of various sizes (plates A, B and C with holes of 1.5 mm, 2.5 mm and 3.5

mm, respectively). The following procedure was applied:

Mono-filaments were immersed in water at a temperature of 20 ± 1 °C for 18 hours. The mono-filament was centrally laid across the hole and gently pressed into the hole using a blunt instrument, on order not to kink the mono-filament.

The mono-filament was positioned in such a way that it did not protrude by more than the radius of the hole.

[0020] The metal plate including the mono-filament was immersed in water at of 50 ± 2 °C for 2 minutes, then in water at of 20 ± 2 °C for 30 seconds. The plate was removed from the water and the mono-filament from the hole. The mono-filament was placed in a petri dish full of water at of 20 ± 2 °C. After 15 minutes of immersion, the mono-filament was removed and the included angle was measured, while ensuring that the mono-filament was lying flat on a smooth surface.

[0021] The percentage recovery was calculated using formula [1]:

$$\text{Recovery} = \text{Included angle} \times 100/180 \% \quad [\text{formula 1}]$$

Results are shown in Table 1.

[0022]

Table 1 Pinch bend recovery tests

Experiment number	Material	Recovery [%]		
		hole diameter 1.5 mm	hole diameter 2.5 mm	hole diameter 3.5mm
Exp 1	PA-410	81	86	88
Exp 2	PA-410 and 0.4 wt% titane dioxide	81	84	84
Comp. A	PA-66	77	84	85
Comp. B	PA-6	71	83	79
Comp. C	PA-610	67	74	78
Comp. D	PA-612	66	64	66

[0023] Table 1 surprisingly shows that PA-410 exhibits high percentage of recovery for all three diameters, especially compared to PA-610 and PA-612, which are usually employed in filaments for tooth brushes.

Mandrel bend recovery tests

[0024] Also mandrel bend recovery tests were performed, in which a filament was attached to and wound ten times around a mandrel with a diameter of 2.5 mm. After this the filament around the mandrel was left in this position for 1 hour at room temperature, after which the filament was cut off from the mandrel and allowed to recover in a dish of water for one hour. The mandrel bend recovery, expressed in %, is the number of turns wrapped on the mandrel versus the number of turns in the fiber at the end of recovery period. Results are shown in Table 2.

Table 2 Mandrel bend recovery tests

Experiment number	Material	Recovery [%]
Exp 4	PA-410	98.0
Exp 5	PA-410 and 0.4 wt% titanium dioxide	97.3
Comp. E	PA-66	97.3
Comp. F	PA-6	99.2
Comp. G	PA-610	96.8
Comp. H	PA-612	96.2

[0025] Also these tests show that mono-filaments from PA-410 show very high recovery, especially compared to polyamide-610 and polyamide-612, which are usually employed in filaments for tooth brushes.

[0026] Tensile modulus was measured according to ISO 527 1A for PA-410 plates and compared to other polyamides. Results are shown in Table 3.

Table 3 Tensile modulus and stiffness retention

Experiment no.	Material	Dry	Conditioned*	Stiffness retention [%]
Exp 1	PA-410	3100	1700	55
Comp. A	PA-66	3300	1500	45
Comp. B	PA-6	3000	1000	33
Comp. C	PA-610	2400	1400	58
Comp. D	PA-612	2300	1500	65
* at 50% relative humidity at 23 °C; Stiffness retention is calculated by dividing tensile modulus conditioned and tensile modulus dry x 100%.				

[0027] Stiffness retention for PA-410 is shown to be higher than for PA-6 and PA-66. Due to the intrinsically higher stiffness of PA-410 however, the stiffness under wet conditions of PA-410 is also higher than the stiffness of PA-610- and PA-612. These data, combined with the wet bend recovery results show that mono-filaments according to the invention exhibit best combination of these properties, as required for applications in for example bristles for tooth brushes.

Claims

- Brush containing a mono-filament containing a polyamide, **characterized in that** the polyamide comprises polyamide-410 in an amount of at least 40 wt.% based on the total amount of polyamide.
- Brush according to claim 1, wherein the amount of polyamide-410 is at least 50 wt.% based on the total amount of polyamide.
- Brush according to claim 1 wherein the polyamide consists essentially of polyamide-410.
- Brush according to any of the claims above, wherein the viscosity number of polyamide-410 is at least 100 ml/g.
- Brush according to any of the claims above, wherein the viscosity number of polyamide-410 is at least 120 ml/g.
- Brush according to any of the claims above, wherein the viscosity number of polyamide-410 is at least 140 ml/g.
- Brush according to any one of the claims above, wherein the mono-filaments further comprise titanium oxide.
- Brush according to any one of the claims above, wherein the brush is a toothbrush.

Patentansprüche

- Ein Polyamid enthaltendes Monofilament enthaltende Bürste, **dadurch gekennzeichnet, dass** das Polyamid Polyamid-410 in einer auf die Polyamidgesamtmenge bezogenen Menge von mindestens 40 Gew.-% umfasst.
- Bürste nach Anspruch 1, bei der die auf die Polyamidgesamtmenge bezogene Menge an Polyamid-410 mindestens 50 Gew.-% beträgt.
- Bürste nach Anspruch 1, bei der das Polyamid im Wesentlichen aus Polyamid-410 besteht.
- Bürste nach einem der vorhergehenden Ansprüche, bei der beim Polyamid-410 die Viskositätszahl bei mindestens 100 ml/g liegt.

5. Bürste nach einem der vorhergehenden Ansprüche, bei der beim Polyamid-410 die Viskositätszahl bei mindestens 120 ml/g liegt.
- 5 6. Bürste nach einem der vorhergehenden Ansprüche, bei der beim Polyamid-410 die Viskositätszahl bei mindestens 140 ml/g liegt.
7. Bürste nach einem der vorhergehenden Ansprüche, bei der die Monofilamente ferner Titanoxid umfassen.
- 10 8. Bürste nach einem der vorhergehenden Ansprüche, bei der es sich um eine Zahnbürste handelt.

Revendications

- 15 1. Brosse contenant un monofilament contenant un polyamide, **caractérisée en ce que** le polyamide comprend du polyamide 410 dans une quantité d'au moins 40 % en poids relativement à la quantité totale de polyamide.
2. Brosse selon la revendication 1, dans laquelle la quantité de polyamide 410 est d'au moins 50 % en poids relativement à la quantité totale de polyamide.
- 20 3. Brosse selon la revendication 1, dans laquelle le polyamide se compose essentiellement de polyamide 410.
4. Brosse selon l'une quelconque des revendications ci-dessus, dans laquelle l'indice de viscosité du polyamide 410 est d'au moins 100 ml/g.
- 25 5. Brosse selon l'une quelconque des revendications ci-dessus, dans laquelle l'indice de viscosité du polyamide 410 est d'au moins 120 ml/g.
6. Brosse selon l'une quelconque des revendications ci-dessus, dans laquelle l'indice de viscosité du polyamide 410 est d'au moins 140 ml/g.
- 30 7. Brosse selon l'une quelconque des revendications ci-dessus, dans laquelle les monofilaments comprennent en outre de l'oxyde de titane.
8. Brosse selon l'une quelconque des revendications ci-dessus, dans laquelle la brosse est une brosse à dents.
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REFERENCES CITED IN THE DESCRIPTION

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