

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 288 771 B1

(12)

EUROPEAN PATENT SPECIFICATION

- (45) Date of publication of patent specification: **15.01.92** (51) Int. Cl.⁵: **A42B 3/00**, C08G 18/10,
C08G 18/79, C08L 75/04,
C08K 3/00
- (21) Application number: **88105186.6**
- (22) Date of filing: **30.03.88**

- (54) **Protective helmets consisting of composite materials essentially based on a polyisocyanuric matrix.**

- (30) Priority: **01.04.87 IT 1992587**
- (43) Date of publication of application:
02.11.88 Bulletin 88/44
- (45) Publication of the grant of the patent:
15.01.92 Bulletin 92/03
- (84) Designated Contracting States:
AT BE DE ES FR GB NL SE
- (56) References cited:
EP-A- 0 226 176
DE-A- 2 014 899
US-A- 3 817 939

- (73) Proprietor: **ECP ENICHEM POLIMERI S.r.l.**
16, Piazza della Repubblica
I-20124 Milano(IT)
- (72) Inventor: **Bianchin, Eugenio**
7, via Monfenera
I-31100 Treviso(IT)
Inventor: **Longoni, Luigi**
72, via S. Alessandro
I-24100 Bergamo(IT)
- (74) Representative: **Weinhold, Peter, Dr. et al**
Patentanwälte Dr. V. Schmied-Kowarzik
Dipl.-Ing. G. Dannenberg Dr. P. Weinhold Dr.
D. Gudel Dipl.-Ing. S. Schubert Dr. P. Barz
Siegfriedstrasse 8
W-8000 München 40(DE)

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

Description

This invention relates to protective helmets consisting of composite materials essentially based on a polyisocyanuric matrix.

It is known that the helmets for motor-cyclists and/or motorists are usually manufactured from particular reinforced-type resins which are utilized in the plastic materials industry.

Such reinforced resins utilized in the plastic materials industry mainly consist of thermosetting resins which, under the manufacturing conditions, lead to particular chemical reactions, such as cross-linking etc.

Many of the physical and thermomechanical properties of the manufactured articles come just from the cross-linked structure of the polymer chain.

Thermosetting polymeric matrices suited to provide materials reinforced with glass fibres or other inorganic or organic fillers are known since long.

Thus, manufactured articles having excellent mechanical properties, i.e. articles with so-called "structural" characteristics, are obtained. In particular, these articles exhibit a flexural modulus at 23° C higher than 8000 MPa and a heat distortion temperature (HDT at 1.82 MPa) higher than 200° C.

Examples of such resins are: phenol-formaldehyde resins, unsaturated polyester resins, epoxy resins, vinylester resins, etc.

These resins, after mixing with organic and/or inorganic fillers, can be processed according to the sheet molding technique (SMC = sheet molding compound), the bulk molding technique (BMC = bulk molding compound), the resin transfer molding technique (RTM = resin transfer molding) or the reaction injection molding technique (RIM = reaction injection molding).

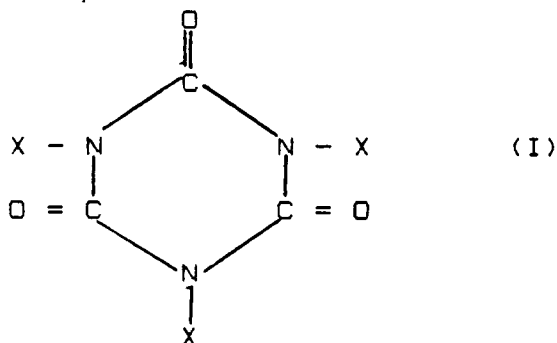
According to these technologies, a glass fibre cloth or a cloth made of another material, or fibres of considerable length (> 10 mm) are impregnated with a resin susceptible of being polymerized and cross-linked when it is subjected to the action of heat and pressure.

These types of resin and of technology have been used to prepare high-performance helmets for motor-cyclists and motorists.

For example, it is possible to produce helmets endowed with good characteristics by using the resin transfer molding polymerization technique (RTM) by using preformed molds with matrices of the vinyl ester type.

In this case, the obtained manufactured articles, although they have the impact strength characteristics required for the homologation of the material, exhibit, besides the high cost deriving from the type of the starting material utilized, a high shrinkage which adversely affects the surface appearance and favours the forming of cracks. These cracks mainly appear if the synthesis occurs at a high temperature, from 100° to 140° C. This is a necessary condition in order to have short demolding times.

It has now been found by the Applicant that protective helmets, in particular protective helmets for motor-cyclists and/or motorists, free from the abovesaid drawbacks are obtainable by using high-density composite materials based on an essentially polyisocyanuric matrix, having a density equal to or higher than 500 and preferably than 1000 kg/cm³, containing reinforcing fillers, in which the polyisocyanuric matrix derives from a repeating structural unit having the formula:



wherein at least one X group represents the group -R₁-NCO and at least one X group represents the group:

-R₁-NH-CO-OR₂-(-OCO-NH-R₁-NCO)_n,

where n is an integer from 1 to 8, preferably from 1 to 3, R₁ is an aliphatic, cycloaliphatic, aromatic or

mixed radical and R_2 , like or different from R_1 , is an aliphatic, cycloaliphatic, aromatic or mixed group, or a carbonic, siloxane, silane or mixed group.

According to a preferred embodiment, in a repeating structural unit of formula (I), on the average, two X groups represent the group $-R_1NCO$ and the third X represents the radical $R_1-NH-CO-OR_2-(-OCO-NH-R_1-NCO)_n$, wherein the symbols own the meaning hereinbefore.

The amount of reinforcing filler in the composite material ranges from 5 to 85% by weight, preferably from 30 to 70% by weight.

Said composite materials show an exceptional value with respect to their technology and own in particular the following characteristics:

- flexural elastic modulus (ASTM D 790/81) equal to or higher than 4000 N/mm², preferably higher than 5000 N/mm² and, even more preferably, higher than 10,000 N/mm²;
- absorbed energy (ASTM D 790/81) equal to or higher than 1 J, preferably higher than 2 J, and even more preferably higher than 4 J.

The use of the abovesaid composite materials has enabled to manufacture protective helmets, for example for motor-cyclists or motorists, which, while retaining the high mechanical properties, in particular the impact strength, exhibit a low shrinkage, an excellent surface appearance, an excellent paintability and the absence of cracks.

The composite materials utilized for the production of the protective helmets of the present invention, are described in detail in the European patent application No. 86. 117 195.7 of the same Applicant.

According to what is described in said application, the process for preparing these composite materials comprises the use of particular prepolymers, produced by partial addition of polyisocyanates and polyols, which remain fluid at room temperature, also in the presence of cross-linking catalysts, at least for a few days and in any case for a time more than sufficient to carry out the impregnation of the glass fibre and/or of another filler and up to the time when molding takes place.

In particular, the process for preparing the above-said composite materials comprises a first step in which a partially polymerized urethane system (prepolymer) is prepared by condensing a polyisocyanate, such as for example 4,4'-diphenyl-methane-di-isocyanate and/or its 2,4' isomer, with polyols having a functionality equal to at least 2 and having a wide range of molecular weights, with an equivalent ratio of polyisocyanate to polyol higher than 1.2:1. Usually, in the preparation of thermosetting resins, polyols having a functionality equal to or higher than 3, in particular triols derived from glycerine or from trimethylolpropane, are utilized. Then, in a second step, the resulting prepolymer is mixed with a cross-linking catalyst, which is active at temperatures higher than 80 °C and can be of organic, inorganic, metallorganic or metallic nature. The thus prepared matrix is utilized to impregnate a support consisting of cut glass fibres or of glass fibre fabrics or of another reinforcing material (for example carbon fibres or polyamide or aramide fibres). If cut fibres are utilized as a reinforcing material, it is possible to prepare first a concentrate, for example with 85% by weight of fibres, and then to dilute the concentrate with the pure prepolymer until the desired concentration is obtained. It is generally preferred to use glass fibres superficially coated with substances capable of imparting compatibility with the matrix, said fibres having a diameter of 8-30 micrometer (preferably of 10-18 micrometer) and a length of 1-100 mm (preferably of 5-50 mm).

The thus obtained pre-impregnated materials are then molded according to conventional techniques and are polymerized in a mold at 80 °-200 °C (preferably at 100-150 °C), and in any case at temperatures, respectively which depend on the type of catalyst, the type of isocyanate utilized, the polyols and the pressure, which should be high enough to remove the surface defects of the composite articles. Furthermore it is necessary to reduce to a minimum any possible absorption of water atmospheric humidity by operating in protected environments. Prior to molding it is possible to add additives of the common type, for example pigments and/or antifiame agents and the like.

As to the operative conditions of the first step, during which the partially polymerized urethane system (prepolymer) is prepared, it is advisable to work at 50-90 °C, preferably under vacuum or in an inert atmosphere, such as N₂, during a period of time from 5 minutes to 3 hours, using reactive mixtures where the polyisocyanate is present in a stoichiometric excess with respect to the polyol.

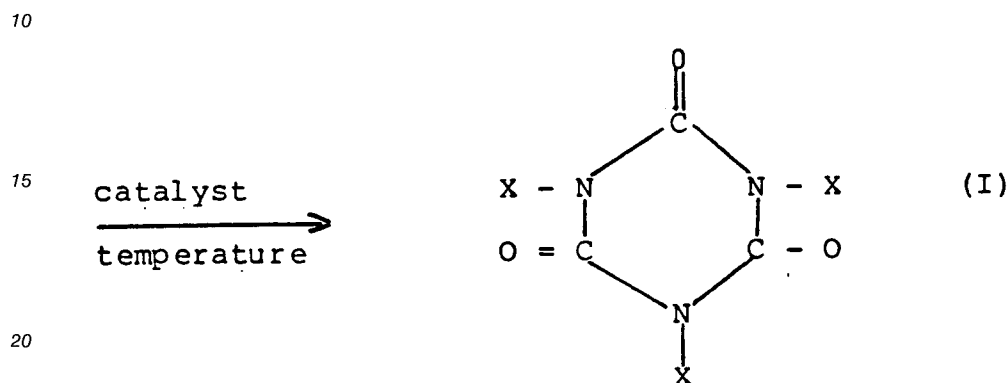
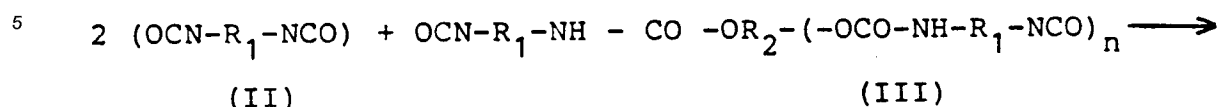
Under these conditions, an A + B blend, referred to as prepolymer, is obtained, wherein:

A = OCN - R₁ - NCO (polyisocyanate in the free state) (IV)

B = OCN - R₁ - NH - CO - OR₂ - (-OCO - NH - R₁ - NCO)_n (urethane compound) (V).

Subsequently, under the effect of heat and after addition of a cross-linking catalyst (activator), of reinforcing fillers and/or of inert fillers and, optionally, of other additives, the blends are converted into a

compound having a prevailing polyisocyanuric structure, the structural unit of which can be represented by the following scheme:



wherein X is the same as hereinabove.

25 The final structure is a tridimensional lattice resulting from the polyaddition of structural unit (I), according to mechanisms analogous with the described one, until a practically complete conversion of the remaining -NCO groups is obtained. In other words, in the first two process steps, a preimpregnated material is obtained which, in the molding step at a high temperature, is cross-linked in a very short time (0.5-4 minutes).

As an alternative to the above-described process, it is possible to prepare a blend containing a polyisocyanate of formula (IV), an urethane compound of formula (V), and one or more reinforcing materials, optionally along with organic and/or inorganic fillers and with plastic and/or elastomeric materials. The thus obtained blend, after addition of a cross-linking catalyst which acts at a temperature higher than 80° C, is molded and heated at a temperature ranging from 80° to 200° C. Also in this case, the added amount of reinforcing material ranges from 5 to 85% by weight and preferably from 30 to 70% by weight.

Another method of producing the protective helmets, subject of the present invention, comprises preparing a partially polymerized urethane system (prepolymer) by condensing a polyisocyanate with polyols having a functionality equal to at least 2, with a polyisocyanate/polyol equivalent ratio higher than 1.2:1; admixing the prepolymer with a cross-linking catalyst which is active at a temperature higher than 80° C; and feeding the resulting mixture to a closed mold, whereinto a reinforcing agent has been previously introduced. The reinforcing agent can be a cloth or a "preform" obtained from cut and/or continuous non-woven fibres bonded by an adhesive material so as to form a shape having the form and dimensions of the helmet (preform).

Because of the pressure employed when feeding the blend or generated by the mold, the blend flows
45 through the gaps existing between the mold walls and the reinforcing agent and through the passages in the
reinforcing agent until all the free spaces are filled. The mold is then heated at a temperature ranging from
80° to 150° C, preferably from 90° to 110° C.

The reinforcing agent content is such that said agent is present in the finished article in an amount from 5 to 85% by weight and preferably from 30 to 70% by weight. The finished article consists of a 50 tridimensional-lattice composite material having high physical, applicative and aesthetic properties.

Different polyols are utilizable for preparing the matrix, optionally in admixture with proper antioxidants; as a matter of principle, any diol, triol or polyol with four or more hydroxyl end groups can be advantageously used; excellent results are obtainable by using polyols-polyethers deriving from the condensation of glycerine, of trimethylolpropane or of pentaerythritol with alkylene oxides, such as ethylene, propylene, butylene oxide, etc., or with polyoxyalkylene chains (polyoxyethylene, polyoxypropylene, polyoxybutylene chains, oxyethylene-oxypropylene mixed chains, etc.). It is also possible to use mixtures containing two triols having an average molecular weight from 250 to 10,000, preferably from 250 to 7,000, wherein:

- i) a first triol, having a lower molecular weight than the second triol, is consisting of glycerine and/or trimethylolpropane condensed with propylene oxide and/or ethylene oxide;
- ii) a second triol, having a higher molecular weight than the first triol, is consisting of glycerine and/or trimethylolpropane, esterified with oxyethylene-oxypropylene mixed chains, with propylene oxide/ethylene oxide weight ratios ranging from 95/5 to 20/80; the weight ratio:

triol of type i)

triol of type ii)

preferably ranging from 70:30 to 10:90.

As it is known to those skilled in the art, the above-cited polyols can be replaced by analogous compounds in which the hydroxyl end groups are replaced by aminic groups (NH₂); furthermore, the abovesaid polyols-polyethers can be replaced by polyols-polyesters, by polyols-polythioethers and by all the other polyols which are cited, for example, in European patent publication 12,417.

Different are also the utilizable polyisocyanates; suitable polyisocyanates are 4,4' - and 2,4'-diphenylmethane diisocyanate, toluene diisocyanates (TDI), 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, para- or metaphenylene diisocyanate, 1-chlorophenylene-2,4-diisocyanate, 1,5-naphthalene diisocyanate, diphenyl-4,4'-diisocyanate, 1,4- or 1,2-cyclohexylene diisocyanate, and/or polyisocyanates having more than 2 functional groups, such as polyphenylmethane polyisocyanate.

A necessary condition for the obtainment of isocyanuric structures of formula (I) is that the equivalent ratio: polyisocyanate/polyol be equal to or higher than 1.2:1 and preferably higher than 2:1.

At last, various cross-linking activators (or catalysts) of organic, inorganic, metallorganic or metallic nature are utilizable for the molding of the pre-impregnated materials. Suggested are preferably the lead compounds and the bismuth compounds described by J.W. Britain and P. G. Gemeinhardt in 1960 in J. Appl. Polym. Sci. (Vol. 4, pages 207-211), or particular metallorganic compounds based on Ti, V, Co, Ni, Sn, optionally in admixture with amines. Excellent results were obtained by using lead stearate, oleate and 2-ethyl-hexanoate.

As reinforcing materials to be used in the preparation of the pre-impregnated materials according to the present invention it is possible to utilize, besides the glass fibres and/or fabrics, any other type of organic or inorganic fibre or fabric, for example carbon fibres or polyamide fibres (in particular of aromatic polyamides), crystalline polyolefine fibres, polyester fibres, mineral wool, etc.; furthermore it is possible to use inorganic or organic fillers such as talc, calcium carbonate or sulphate, silicas, aluminas, kieselguhrs, cements, zeolites, wood flours, celluloses, amides etc. With a view to improving some mechanical characteristics it may be useful to incorporate plastic and/or elastomeric materials of various nature. In particular, the incorporation of plastic materials or of elastomers, optionally cross-linked, such as ABS, polycarbonates, polyesters, polyamides, elastomeric polyesters, butadiene rubber or SBR, polyurethane elastomers, nitrile rubbers, ethylene-propylene rubbers, acrylic rubbers etc., in the form of discrete particles (average diameter: 0.01 - 10 micrometer) permits to obtain final articles endowed with an improved impact strength.

The following examples are given to illustrate the present invention without limiting however the scope thereof.

EXAMPLE 1

70 g of 4,4'-diphenylmethane diisocyanate (MDI) were condensed at 80 °C for 2.5 hours with 20 g of a trifunctional polyol polyether having a molecular weight of about 5,000, consisting of glycerine etherified with mixed oxyethylene-oxypropylene chains, and with 10 g of a trifunctional polyol polyether based on oxypropylene having a molecular weight of about 300, prepared by condensing glycerine with propylene oxide, the product was then deaerated under vacuum at 70 °C, thereby obtaining a prepolymer having a viscosity from 7,000 to 8,000 mPa.s (at 23 °C) with a content of free NCO groups equal to about 18% by weight.

The preparation of the composite material was carried out by laminating eight glass fabric layers weighing 600 g/sq.m, impregnated with the matrix of the abovesaid modified polyisocyanate containing the catalyst, in such amount as to obtain a final article containing 63% of glass reinforcement.

A sheet measuring 35 x 35 x 0.5 cm, to be utilized to determine the physico-mechanical characteristics, was then molded in a vertical press, at 45 bar, during 3.5 minutes.

Polymerization of the modified polyisocyanate, to produce an essentially polyisocyanuric resin, was conducted under the following conditions:

- 5 - temperature of the mold: 95 °C
- Pb stearate catalyst: 0.8% parts by weight with respect to the resin
- curing: 24 minutes.

The physico-mechanical characteristics of the manufactured article were as follows:

- Flexural tests (ASTM D 790/81):
 - 10 . Flexural elastic modulus at 23 °C 15,000 MPa
 - . Maximum stress (σ) at the break point 280 MPa
 - . Absorbed energy 4.2 J

The absorbed energy was determined according to ASTM D 790/81, method 1, procedure A, under the following conditions:

- 15 - transverse speed: 10 mm/minute
- distance between the supports: 150 mm
- specimen thickness: 4.7 mm.

EXAMPLE 2

20 The same matrix of example 1 was utilized for producing protective caps, suited to be used as helmets for motor-cyclists.

The articles were molded by impregnating a glass fabric, of the type and in the amounts as indicated in example 1, which had been suitably placed before into a heated mold.

25 The heat yielded by the mold caused the polymerization of the matrix, once the impregnation of the glass fabric had occurred.

Operating with a mold at a temperature of 98 °C and with a catalyst content equal to 0.8% parts by weight with respect to the matrix, a demolding time was obtained from 8 to 12 minutes.

30 Under these conditions there were obtained the impregnation of the entire fabric, a good polymerization, the absence of cracks in the manufactured article and an excellent surface appearance.

By operating as described above, caps were produced which, after having been assembled according to a standard model, were characterized with regard to the impact strength.

All the caps passed the tests prescribed by standard ECE 22.02.

35 EXAMPLE 3 (comparative test)

In this example, the same procedure of example 2 was followed, with the exception that one utilized a matrix of the vinyl ester type, placed on the market by ATLAS under the trademark ATLAC 580.05.

40 Polymerization was performed at a temperature of 80 °C in the presence of 2 parts of methylethylketone peroxide, as a catalyst, and of 0.17 parts of cobalt octoate, as an accelerator, for 100 parts of resin.

Under these conditions, the demolding time was similar to the one of example 2.

The caps, assembled according to a standard model, got through the impact tests prescribed by standard ECE 22. 02.

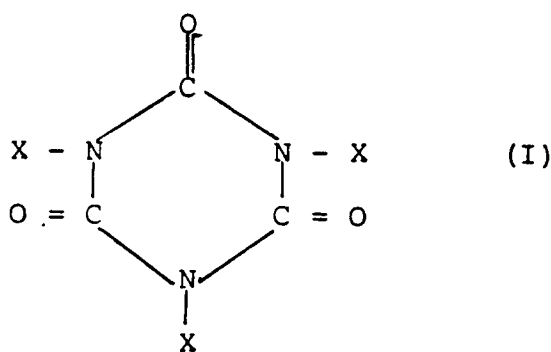
45 With respect to example 2, due to the higher shrinkage of the matrix and to the synthesis thermal conditions, an article was obtained, which exhibited:

- worse surface appearance, as to the finishing (roughness and "orange peel" on the surface) and
- presence of cracks.

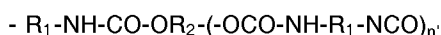
Claims

- 50 1. Protective helmets for motor-cyclists and/or motorists consisting of high-density composite materials based on an essentially polyisocyanuric matrix, having a density equal to or higher than 500 and preferably higher than 1,000 kg/m³, containing reinforcing fillers, wherein the polyisocyanuric matrix derives from a repeating structural unit having the formula:

55



15 wherein at least one X group represents the group $-R_1-NCO$ and at least one X group represents the group:



20 where n is an integer from 1 to 8, preferably from 1 to 3, R_1 is an aliphatic, cycloaliphatic, aromatic or mixed radical and R_2 , like or different from R_1 , is an aliphatic, cycloaliphatic, aromatic or mixed group, or a carbonic, siloxane, silane or mixed group.

25 **2.** The helmets according to claim 1, characterized in that in the repeating structural unit of formula I, two X groups on the average represent group $-R_1-NCO$ and the third X group represents group $-R_1-NH-CO-OR_2-(-OCO-NH-R_1-NCO)_n-$, wherein the symbols have the same significance as in claim 1.

3. The helmets according to claims 1 and 2, characterized in that the amount of reinforcing fillers in the composite material ranges from 5 to 85% by weight, preferably from 30 to 70% by weight.

30 **4.** The helmets according to any one of the preceding claims, wherein the reinforcing fillers are selected from: glass fibres and/or fabrics, carbon fibres, polyamide fibres, in particular aromatic polyamide fibres, crystalline polyolefinic fibres, polyester fibres and mineral wool.

35 **5.** The helmets according to any one of the preceding claims 1 through 3, wherein the reinforcing fillers consists of a continuous fabric.

6. The helmets according to any one of the preceding claims 1 through 3, wherein the reinforcing fillers consist of cut or continuous non-woven fibres bonded by an adhesive and having the shape of the helmet (preform).

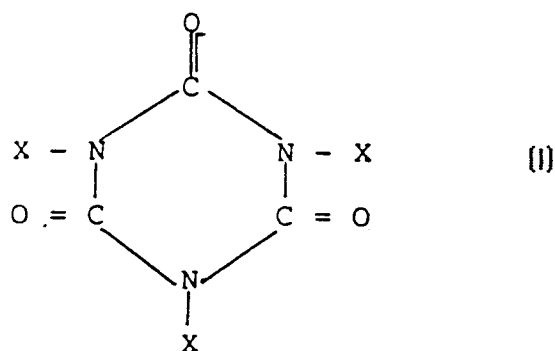
40 **7.** The helmets according to any one of the preceding claims, wherein the composite materials contain also organic and/or inorganic fillers and/or plastic materials or elastomers, optionally cross-linked.

45 **8.** The helmets according to any one of the preceding claims, wherein the composite materials have a flexural elastic modulus equal to or higher than $4,000 \text{ N/mm}^2$ and an absorbed energy equal to or higher than 1 J.

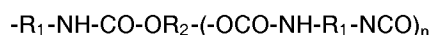
50 **9.** The helmets according to claim 8, wherein the composite materials have a flexural modulus equal to or higher than $5,000 \text{ N/mm}^2$, preferably higher than $10,000 \text{ N/mm}^2$, and an absorbed energy equal to or higher than 2 J, preferably higher than 4 J.

Revendications

55 **1.** Casques de protection pour motocyclistes et/ou automobilistes consistant en matériaux composites de haute densité à base de matrice essentiellement polyisocyanurique, ayant une densité égale ou supérieure à 500 kg/cm^3 et de préférence supérieure à $1,000 \text{ kg/cm}^3$, contenant des charges de renforcement, dans lesquels la matrice polyisocyanurique dérive d'une unité structurale répétée ayant la formule:

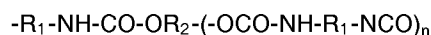


15 dans laquelle au moins un groupe X représente le groupe $-R_1-NCO$ et au moins un groupe X représente le groupe:



20 dans lequel n est un entier de 1 à 8, de préférence de 1 à 3, R_1 est un radical aliphatique, cycloaliphatique, aromatique ou mélangé et R_2 , identique ou différent R_1 , est un groupe aliphatique, cycloaliphatique, aromatique ou mélangé, ou un groupe carbonique, siloxane, silane ou mélangé.

- 25 2. Casques suivant la revendication 1, caractérisés en ce que dans l'unité structurale répétée de formule (I), deux groupes X en moyenne représentent un groupe $-R_1-NCO$ et le troisième groupe X représente le groupe:



30 dans laquelle les symboles sont tels que définis dans la revendication 1.

- 35 3. Casques suivant la revendication 1 et la revendication 2, caractérisés en ce que la quantité de charges de renforcement présente dans le matériau composite est de l'ordre de 5 à 85% en poids, de préférence de 30 à 70% en poids.

- 40 4. Casques suivant l'une quelconque des revendications précédentes, caractérisés en ce que les charges de renforcement sont choisies parmi des fibres et/ou tissus de verre, des fibres de carbone, des fibres de polyamide, en particulier des fibres de polyamide aromatique, des fibres polyoléfiniques cristallines, des fibres de polyester et de la laine minérale.

- 45 5. Casques suivant l'une quelconque des revendications précédentes 1 à 3, caractérisés en ce que les charges de renforcement consistent en tissu continu.

6. Casques suivant l'une quelconque des revendications précédentes 1 à 3, caractérisés en ce que les charges de renforcement consistent en fibres non tissées coupées ou continues liées par un adhésif et ayant la forme du casque (pré-forme).

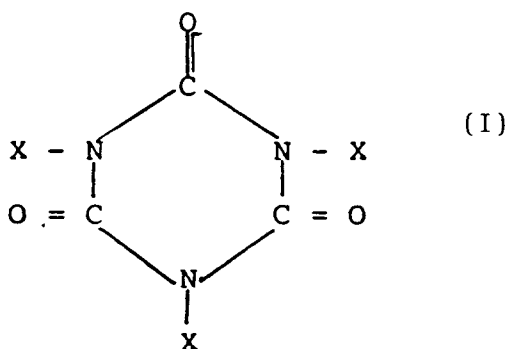
7. Casques suivant l'une quelconque des revendications précédentes, caractérisés en ce que les matériaux composites contiennent aussi des charges organiques et/ou inorganiques et/ou des matières plastiques ou des élastomères éventuellement réticulés.

8. Casques suivant l'une quelconque des revendications précédentes, caractérisés en ce que les matériaux composites ont un module élastique de flexion égal ou supérieur à 4.000 N/mm^2 et une énergie absorbée égale ou supérieure à 1 J.

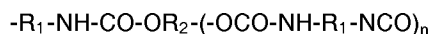
9. Casques suivant la revendication 8, caractérisés en ce que les matériaux composites ont un module élastique de flexion égal ou supérieur à 5.000 N/mm^2 , de préférence supérieur à 10.000 N/mm^2 et une énergie absorbée égale ou supérieure à 2 J, de préférence supérieure à 4 J.

Patentansprüche

1. Schutzhelme für Motorradfahrer und/oder Motorfahrzeugfahrer, bestehend aus einem hochdichten Verbundwerkstoff auf der Basis einer im wesentlichen aus Polyisocyanurat bestehenden Matrix mit einer Dichte gleich oder über 500 und vorzugsweise über 1000 kg/cm³, der verstärkende Füllstoffe enthält, worin die Polyisocyanuratmatrix sich von einer wiederkehrenden Struktureinheit der Formel ableitet:

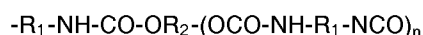


worin mindestens eine Gruppe X die Gruppe -R₁-NCO bedeutet und mindestens eine Gruppe X die Gruppe:



bedeutet, worin n eine ganze Zahl von 1 bis 8, vorzugsweise von 1 bis 3 ist, R₁ ein aliphatischer, cycloaliphatischer, aromatischer oder gemischter Rest ist und R₂, der von R₁ gleich oder verschieden sein kann, eine aliphatische, cycloaliphatische, aromatische oder gemischte Gruppe oder eine Carbon-, Siloxan-, Silan- oder gemischte Gruppe ist.

2. Helme gemäß Anspruch 1, dadurch gekennzeichnet, daß in der wiederkehrenden Struktureinheit der Formel I zwei Gruppen X durchschnittlich die Gruppe -R₁-NCO bedeuten und die dritte Gruppe X die Gruppe



bedeutet, wobei die Symbole die gleiche Bedeutung wie in Anspruch 1 haben.

3. Helme gemäß Anspruch 1 und 2, dadurch gekennzeichnet, daß die Menge der verstärkenden Füllstoffe im Verbundwerkstoff von 5 bis 85 Gew.-%, vorzugsweise von 30 bis 70 Gew.-%, beträgt.
4. Helme gemäß irgendeinem der vorhergehenden Ansprüche, worin die verstärkenden Füllstoffe aus Glasfasern und/oder -stoffen, Kohlefasern, Polyamidfasern, insbesondere aromatischen Polyamidfasern, kristallinen polyolefinischen Fasern, Polyesterfasern und Mineralwolle ausgewählt sind.
5. Helme gemäß irgendeinem der vorhergehenden Ansprüche 1 bis 3, worin die verstärkenden Füllstoffe aus einem kontinuierlichen Gewebe bestehen.
6. Helme gemäß irgendeinem der vorhergehenden Ansprüche 1 bis 3, worin die verstärkenden Füllstoffe aus geschnittenen oder kontinuierlichen nichtgewebten Fasern bestehen, die durch einen Klebstoff verbunden sind und die Form des Helmes (Vorformling) haben.
7. Helme gemäß irgendeinem der vorhergehenden Ansprüche, worin die Verbundwerkstoffe auch organische und/oder anorganische Füllstoffe und/oder Kunststoffmaterialien oder Elastomere, gegebenenfalls in vernetzter Form, enthalten.

8. Helme gemäß irgendeinem der vorhergehenden Ansprüche, worin die Verbundwerkstoffe einen Biegeelastizitätsmodul gleich oder größer als 4000 N/mm^2 und eine absorbierte Energie gleich oder größer als 1 J aufweisen.

5 9. Helme gemäß Anspruch 8, worin die Verbundwerkstoffe einen Biegemodul gleich oder größer als 5000 N/mm^2 , vorzugsweise größer als $10\,000 \text{ N/mm}^2$, und eine absorbierte Energie gleich oder größer als 2 J, vorzugsweise größer als 4 J, aufweisen.

10

15

20

25

30

35

40

45

50

55