

Crosslinking of polyaryletherketones

The invention relates to a method for producing a molded article from polyaryletherketones (PAEK) and a crosslinker. The invention also relates to molded articles obtainable by the method and sealing articles.

State of the art

Polyaryletherketones (PAEK), such as polyetheretherketones (PEEK), are partially crystalline high-performance polymers which have a high temperature and media resistance. They consist of alternating keto, ether and aryl groups. One advantage of PAEK is the thermoplastic processability. However, thermoplastics have an intrinsically given limit in terms of temperature resistance. In order to increase the temperature resistance and the mechanical stability of the PAEK, it was proposed to crosslink the polymer chains. In the prior art, methods are used for crosslinking, in which the PAEKs are crosslinked with diamines. Imine bonds (Schiff's bases) here are formed, which can give the crosslinked polymers a greater stability. The disadvantage here is that such crosslinked polymers are not flowable. They cannot therefore easily be processed thermoplastically from a melt of the polymer.

The method for chemical crosslinking of polyetheretherketones (PEEK) with diamines was first described by Thompson and Farris (Journal of Applied Polymer Science, 1988, Vol. 36, 1113-1120). Here, polyetheretherketone is first modified in diphenylsulfone as a solvent by attaching para-phenylenediamine. The solvent must then be removed by drying and further cleaning. The problem is that cross-links are already formed with the method described, and here also with covalent attachment. Here, the glass transition temperature and the temperature resistance increase and the thermoplastic processability is lost. The polymer mass obtained is therefore not crosslinked thermoplastically from the melt, but rather by hot pressing.

Yurchenko et al. (2010, Polymer 51, 14-1220) investigated in more detail the method and the products described by Thompson and Farris. They describe an analogous reaction of PEEK and phenylenediamine in diphenyl sulfone as a solvent, in which the PAEK is modified and, after removal of the solvent and cleaning by hot pressing, is crosslinked and characterized. A thermoplastic processing is also not described. The investigation shows

that the products have a higher stability than uncrosslinked PEEK, which, however, is still in need of improvement.

WO 2010/011725 A2 describes a large number of aminic crosslinkers for crosslinking PAEK. However, the document contains only a single synthesis example which describes the crosslinking of PAEK with diphenylamine according to the literature cited above, in which a reaction initially takes place in diphenyl sulfone as solvent.

Methods for crosslinking PAEK with non-amine crosslinkers are described in US 6,887,408 B2.

In order to crosslink PAEK, it has also been proposed in the prior art to functionalize the polymers themselves with crosslinkable amino groups. Such methods are described, for example, in US 2017/0107323 A1. The disadvantage here is that the functionalization of the PAEK with amino groups is relatively expensive. In addition, the crosslinking of functionalized PAEK cannot be controlled as easily and variably as with a low molecular weight crosslinker.

The methods described in the prior art for crosslinking PAEK with diamines with low molecular weight crosslinkers are carried out in the presence of a high proportion of solvent, wherein the production of the molded articles takes place through hot pressing (compression molding). The products are more temperature stable than comparable non-crosslinked PAEK. However, it is disadvantageous that PAEK crosslinked in this way have a relatively low rigidity, since the crystallinity of the PAEK is lost when the polymers are dissolved in solvent. During the further processing, the crystallinity can only be recovered to a small extent because of the intrinsic steric hindrance of the chains through the crosslinking points. In addition, it is disadvantageous that the methods as a whole are very complex because they also require a large number of work steps because of the removal of the solvent. Another disadvantage is that the molded articles are produced by hot pressing, which limits the application possibilities compared to the thermoplastic processing. Hot pressing and comparable methods are carried out with non-flowable materials which cannot be converted into thermoplastic melts. This limits the deformability and it is not possible to produce thin-walled or complex molded articles. For these reasons, such methods can only be automated to a very limited extent. Therefore, no

efficient and cost-effective industrial production can take place on the basis of the known solvent-based methods.

WO 2010/011725 A2 also proposes theoretically to produce crosslinked PAEK by
5 extrusion. However, there is no evidence that PAEK can be extruded with low molecular weight crosslinkers, let alone that products here with advantageous properties can be obtained. There is also no reasonable expectation of success for this. On the one hand, it is problematic that at the required high melting temperatures, at which the components have to be mixed and processed, the crosslinking already begins. On the other hand, it is
10 not to be expected that PAEK are miscible and processable with such amine crosslinkers in the absence of a solvent. In practice, when low molecular weight components are incorporated into polymers, demixing processes are often observed. The homogeneous distribution of the crosslinker in the polymer is, however, absolutely necessary for obtaining a stable product.

15 Another disadvantage is that handling volatile diamines at high temperatures is associated with considerable hazards for the user and a high level of environmental pollution.

It would therefore be desirable to provide methods and molded articles which overcome
20 the disadvantages described.

Object of the invention

The invention is based on the object of providing methods and products which overcome
25 the disadvantages described above.

In particular, materials based on PAEK are to be provided, which have a high stability and a good processability. In particular, the materials should have a high temperature resistance and a high rigidity (module) at high temperatures. In addition, they should have
30 a good resistance to chemicals and a low flammability. In addition, the materials should have a low tendency to creep and a rubber-elastic behavior in the high temperature range.

In particular, the invention is based on the object of providing materials which have a high stability but are nevertheless easy to process. Here, the materials should be able to be

produced efficiently and inexpensively in a simple manner. Here, it would be particularly advantageous if the materials can be processed thermoplastically. In particular, inefficient methods such as hot pressing should be here avoided.

- 5 The methods should also be as environmentally friendly as possible and without endangering the user.

Disclosure of the invention

- 10 Surprisingly, the object on which the invention is based is achieved by methods, molded articles and sealing articles according to the claims.

Subject of the invention is a method for producing a crosslinked molded article containing polyaryletherketones (PAEK), said method comprising the steps:

- 15 (a) providing a mixture containing a PAEK and a crosslinker;
(b) producing a molded article from the mixture; and
(c) thermally treating the molded article at a temperature at which PAEK is crosslinked, whereby the crosslinked molded article is obtained, and
wherein the crosslinker is a di(aminophenyl) compound in which the two aminophenyl
20 rings are connected to each other via an aliphatic group which has a carbocyclic residue.

- Polyetherketones (PEK) are polymers which are composed of alternating ketone (R-CO-R) and ether groups (R-O-R). In the case of polyaryletherketones (PAEK) there is an aryl group linked in the (1,4) position between the functional groups. The PAEK have a
25 partially crystalline, rigid structure that gives the materials comparatively high glass transition and melting temperatures.

- The method concerns a crosslinking reaction in which the polymer chains of the PAEK are covalently and intermolecularly linked to each another. In step (a) a mixture is provided
30 which contains the PAEK and the crosslinker. It is here preferred that the temperature in step (a) is set in such a way that no significant reaction takes place between the PAEK and the crosslinker. It is advantageous here that the aminic crosslinking of PAEK with the crosslinker described according to the invention only starts at higher temperatures. A

covalent attachment of the crosslinker to the PAEK, as described in the prior art, is not necessary in the simple method according to the invention.

In step (b) a molded article is produced from the mixture. The step (b) of producing the
5 molded article comprises here all measures by which the mixture is brought into the three-dimensional shape which is retained in the cured, crosslinked state. The molded article is preferably produced by means of thermoplastic molding methods. It is preferred here that the molded article is produced before and/or during the crosslinking. It is particularly preferable for the shaping to take place before step (c), because the mixture can
10 advantageously be thermoplastically processed and shaped before crosslinking, in particular by hot pressing, extrusion and/or injection molding.

Step (c) comprises the thermal treatment of the molded article at a temperature at which PAEK is crosslinked, whereby the crosslinked molded article is obtained.

15 During the crosslinking, two imine bonds are formed between two keto groups of the PAEK chains and the two amino groups of the crosslinker. The resulting bridge in the form of an imine is also called Schiff's base, since the imine nitrogen does not carry a hydrogen atom, but is connected to an organic molecule. The crosslinking takes place here as
20 completely as possible, so that as far as possible all amino groups of the diamine used react with the carbonyl groups of the PAEK. The advantages of a complete crosslinking are an increased heat resistance and an increased rigidity (module). Nonetheless, only partial crosslinking should also be included in the term "crosslinked". There may be only partial crosslinking if a sufficient amount of diamine was not used for complete integration
25 of all PAEK chains into the cross-linking. In this case, the material usually has a higher elongation at break than the fully crosslinked material. The imine bonds give the molded article a high level of stability. According to the invention, the molded article is preferably a molded article based on PAEK. Here, "based on PAEK" means that the PAEK is the essential structure-giving polymer component of the molded article. In an embodiment it is
30 preferred that the PAEK is the single polymer component of the molded article. In a further embodiment, the PAEK is present in the mixture with further polymers, in particular thermoplastic polymers. Preferred further polymers are polyphenylene sulfide (PPS), polyamideimide (PAI), polyphthalamide (PPA), partially aromatic polyamides, thermoplastic polyimide (TPI), liquid crystalline polyesters (LCP). Preferred mass ratios

between PAEK and further polymers, in particular thermoplastic further polymers, are here 1:1 to 100:1, preferably 5:1 to 100:1, particularly preferably 10:1 to 100:1. Furthermore, the molded body can contain fillers such as fibers and/or customary additives such as processing aids and/or functional components. The cross-linked PAEK forms here a
5 matrix in which any additives which may be present are evenly distributed.

The crosslinker is a di(aminophenyl) compound. Such compounds have two aminophenyl rings linked together. The compounds are therefore primary diamines. Here, in one embodiment of the invention, each phenyl ring has only a single amino group. However, it
10 is also conceivable that the phenyl rings have two or three amino groups independently of one another. The compounds are low molecular and not polymers. In addition to the amino groups, the phenyl rings can have further substituents, such as alkyl or halogen groups. The two aminophenyl rings are linked to one another via an aliphatic group. Aliphatic groups consist only of carbon and hydrogen and are not aromatic. Apart from the
15 two phenyl rings, the crosslinkers preferably have no further double or triple bonds. The aliphatic group has a carbocyclic residue. Carbocyclic residues are hydrocarbon rings which here for example can have 4 to 7 carbon atoms, preferably 5 or 6 carbon atoms. The carbocyclic residue can here comprise double bonds of the phenyl rings. The carbocyclic group preferably has only a single aliphatic hydrocarbon ring. The aliphatic
20 group preferably has a total of 5 to 15 carbon atoms, in particular 6 to 8 carbon atoms. Because of the aliphatic group between the carbocyclic residues, the two phenyl rings are not conjugated.

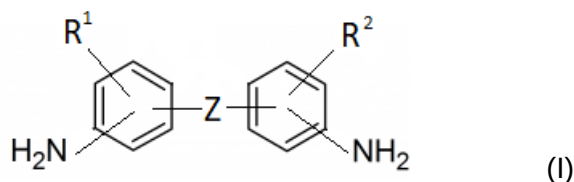
According to the invention it was surprisingly found that PAEK which is crosslinked with
25 such di(aminophenyl) compounds has particularly advantageous properties. In particular, the crosslinked PAEK has a particularly high thermal stability and mechanical stability, and in particular a particularly high glass transition temperature and rigidity. Without being bound by theory, it is assumed that the carbocyclic residue can support the formation of a particularly rigid, partially crystalline polymer structure, which gives the product a high
30 level of stability. It is here also assumed that an advantageous and regular spacing of the PAEK polymer chains can be set via the crosslinker with the carbocyclic residue. Overall, the crystalline structure of the PAEK seems to be little impaired or even supported in an advantageous manner by such crosslinkers.

In a preferred embodiment, the crosslinker is an annulated compound in which only one of the two phenyl rings is annulated to the carbocyclic residue. Annulation (condensation) refers to the addition of a further ring to a ring of a cyclic molecule. The two annulated rings share two carbon atoms and thus a C-C double bond of the phenyl ring. The use of such annulated crosslinkers has the advantage that a particularly rigid and regular connection can be formed between the PAEK chains, whereby a particularly high temperature stability and rigidity of the products can be achieved.

The amino groups can in principle be present at any position of the phenyl group, that is to say in *ortho*, *meta* or *para* position with respect to the aliphatic connection of the two phenyl rings. In the embodiment that each phenyl group has only a single amino group, it is preferred that the two amino groups are as far apart as possible. This can be achieved if the two amino groups are attached to the *para* position with respect to the aliphatic compound and/or to the 4 and 4' positions of the phenyl rings. In a preferred embodiment, the diaminodiphenyl compound is therefore a 4,4'-diaminodiphenyl compound. In general, the advantage of amino groups that are as widely spaced as possible from one another can be that the formation of undesired intramolecular reactions in which a crosslinker forms two bonds with the same PAEK polymer chain is reduced. Such intramolecular reactions with the crosslinker can disrupt the crystalline structure of the PAEK without being effective for crosslinking and thereby reduce the stability of the product.

In a preferred embodiment of the invention, the crosslinker is an asymmetrical compound.

In a preferred embodiment of the invention, the crosslinker is a compound of the general formula (I):

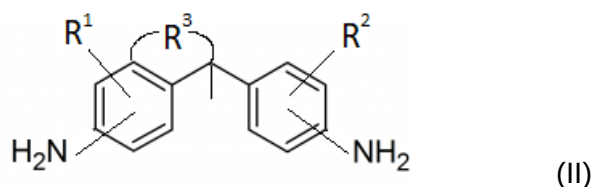


wherein R^1 and R^2 are independently of one another selected from H, substituted or unsubstituted alkyl with 1 to 20 carbon atoms, in particular with 1 to 4 carbon atoms, in particular methyl or ethyl, substituted or unsubstituted aryl with 5 to 12 carbon atoms, F and Cl, and wherein Z is the aliphatic group which has a carbocyclic residue. Here, each

phenyl ring can have one, two or three residues R^1 or R^2 , which are selected independently of one another. A phenyl ring preferably has only one residue R^1 and/or R^2 . The residues R^1 and R^2 are particularly preferably each H. Crosslinkers without additional R^1 and R^2 residues are relatively readily available and can be processed into highly stable crosslinked PAEK.

The residue Z can be linked to each phenyl residue via two bonds or via one bond. The residue Z is preferably connected to a phenyl residue via two bonds and to the second phenyl residue via one bond.

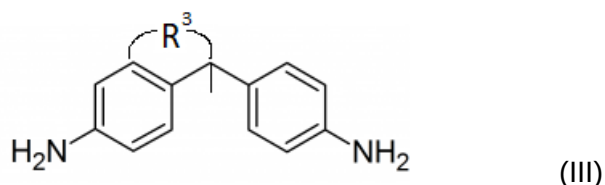
In a preferred embodiment, the crosslinker is a compound of the general formula (II):



wherein R^1 and R^2 are independently of one another selected from H, substituted or unsubstituted alkyl with 1 to 20 carbon atoms, in particular with 1 to 4 carbon atoms, in particular methyl or ethyl, substituted or unsubstituted aryl with 5 to 12 carbon atoms, F and Cl, and

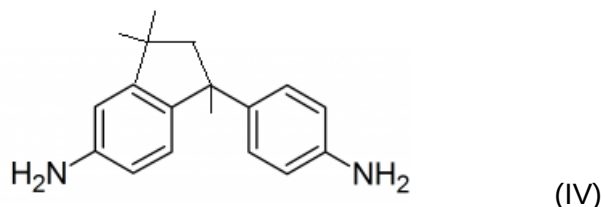
wherein R^3 is a carbocyclic residue which has 2 to 3 carbon ring atoms and which can be substituted by at least one alkyl group with 1 to 4 carbon atoms, in particular methyl or ethyl. The residues R^1 and R^2 are particularly preferably each H. The carbocyclic residue R^3 is therefore a pentyl or hexyl residue. Such crosslinkers have the advantage that a particularly good combination of temperature stability and mechanical stability of the crosslinked PAEK can be obtained.

In a preferred embodiment, the crosslinker is a compound of the general formula (III):



wherein R³ is selected as indicated above. Such crosslinkers have the advantage that a particularly good combination of temperature stability and mechanical stability of the crosslinked PAEK can be obtained.

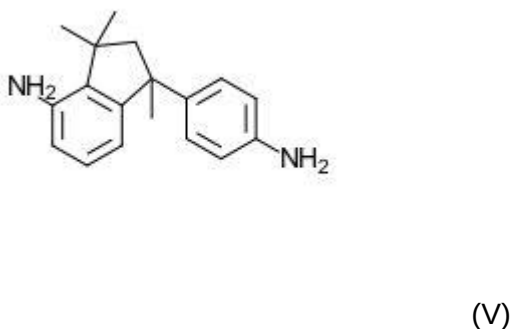
- 5 In a preferred embodiment, the crosslinker has the formula (IV):



In the tests carried out, the connection led to a particularly advantageous combination of temperature stability and mechanical stability of the crosslinked PAEK. The chemical name is 1-(4-aminophenyl)-1,3,3-trimethyl-indan-5-amine (CAS No. 54628-89-6).

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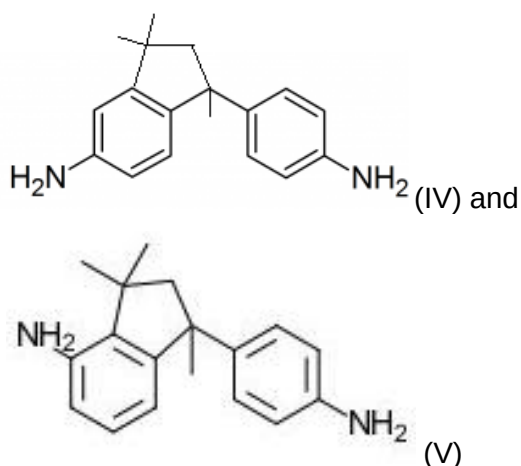
In a further preferred embodiment, the crosslinker has the formula (V):



- 15 In the tests carried out, the connection also leads to a particularly advantageous combination of temperature stability and mechanical stability of the crosslinked PAEK. The chemical name is 1-(4-aminophenyl)-1,3,3-trimethyl-indan-6-amine.

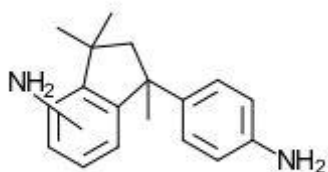
In a further preferred embodiment, the crosslinker has a mixture of compounds of the formula:

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In the tests carried out, this crosslinker also leads to a particularly advantageous combination of temperature stability and mechanical stability of the crosslinked PAEK.

In a further preferred embodiment, the crosslinker has the formula (VI):



(VI)

In the tests carried out, this crosslinker also leads to a particularly advantageous combination of temperature stability and mechanical stability of the crosslinked PAEK. The chemical name is 1-(4-aminophenyl)-1,3,3-trimethyl-indan-amine (CAS No. 68170-20-7). Here, the amino group on the aromatic ring of the indane can occur in all positions. Also included are mixtures of 1-(4-aminophenyl)-1,3,3-trimethyl-indane-amines in which the amino group on the aromatic ring of the indane is in different positions.

It is preferred according to the invention to use a single specific crosslinker in order to obtain material properties which are as uniform as possible. However, it is also possible to use mixtures of two or more crosslinkers.

The amount of crosslinker is adjusted with a view to the desired degree of crosslinking. Here, the proportion of the crosslinker in relation to the PAEK can be 0.05% by weight to 15% by weight, in particular 0.1% by weight to 5% by weight. In a preferred embodiment, the proportion of the crosslinker is 0.1 to 1.5% by weight. It has been found that the stability of the product with such a crosslinker content can be particularly advantageous. In particular, if the amount of crosslinker is set in this range, a significant improvement in elongation at break can be achieved.

In a preferred embodiment, the crosslinker has a boiling point which is greater than 300°C, in particular greater than 350°C or greater than 400°C. This is advantageous because such crosslinkers have only a relatively low vapor pressure at the required high crosslinking temperatures. The boiling point of the crosslinker is preferably between 300°C and 500°C, in particular between 350°C and 500°C. The melting point of the crosslinker is advantageously below the melting point of the PAEK. This results in good processability and low risk to the user.

In principle, any desired polyaryletherketones can be used as the polymer component. Polyaryletherketones are characterized by linear polymer chains made up of aryl, ether and keto groups. The compounds in this class of substances differ in the arrangement of these groups and their ratio in the molecule. The PAEK can be, for example, a polyetheretherketone (PEEK), a poly (etherketoneketone) (PEKK), a poly (etheretheretherketone) (PEEEK) or a poly (etheretherketoneketone) (PEEKK). The compounds of this class of substances have keto groups which can be linked to form imine bonds. Mixtures of different polyaryletherketones can also be used here. It is preferred to use a single PAEK because this allows a high crystallinity and the associated temperature stability to be achieved.

In a preferred embodiment, the polyaryletherketone (PAEK) is a polyetheretherketone (PEEK, CAS number 29658-26-2). The polyaryletherketone (PAEK) is particularly preferably a polyetheretherketone PEEK with a melting range of 335°C to 345°C. It has been found that PEEK which is crosslinked according to the invention has particularly advantageous properties with regard to temperature and mechanical stability.

The polyaryletherketone (PAEK) preferably has a melt viscosity at 380°C in the range from 5 cm³/10 min to 250 cm³/10 min, in particular from 50 cm³/10 min to 200 cm³/10 min. The measurement is carried out in accordance with DIN ISO 1130, wherein the material is melted at 380°C and loaded with a 5 kg punch, after which the flowability is determined.

5 Commercially available PAEK, in particular PEEK variants, are generally suitable. The melt viscosity generally correlates with the molecular weight of the polymer chains. It has been found that such a melt viscosity is advantageous because, according to the invention, not only good thermoplastic processability and miscibility are achieved, but also a homogeneous product with high stability, and here in particular high rigidity, can be
10 obtained. It is particularly preferred here to use such a PAEK, in particular PEEK with a melt viscosity as mentioned above, and the crosslinker in an amount of 0.1% by weight to 5% by weight, in particular between 0.1% by weight to 1.5% by weight, related to the PAEK, in particular PEEK. With such a ratio and properties of the starting materials, particularly good processability and temperature stability of the products can be achieved.
15 In particular, the rigidity is particularly high, which is characterized by a high tensile module. Furthermore, such a PAEK, in particular PEEK, can be processed at a temperature which still allows thermoplastic mixing without the crosslinking reaction proceeding too quickly during this process. This results in a mold mass that can be further processed thermoplastically very well.

20 The mixture provided in step (a) can be produced by customary compounding methods. In such methods, the mixture is intensively mixed, preferably as a melt, for example in a screw. The temperatures in the mixing device are preferably set so that the mixture is easy to process and has a viscosity suitable for compounding. When compounding, an
25 intermediate product can be obtained, for example a granulate.

The mixture is here preferably produced at a temperature at which no or no substantial crosslinking takes place. According to the invention, it is not necessary, as in the case of the methods described in the prior art, for the crosslinkers to be covalently bound to the
30 PAEK via aminic bonds. This is advantageous because according to the invention such an additional reaction step can be omitted, which would have to be precisely controlled in order to prevent an undesired further reaction of the intermediates and a premature crosslinking resulting therefrom.

During the preparation of the mixture, intensive mixing takes place by suitable means, such as stirring or kneading devices, in order to achieve a uniform distribution of the crosslinker in the polymer. This is of great importance in order to obtain uniform material properties with regard to stability. In a preferred embodiment, the production is a step of the method which takes place before step (a) in a step (a0). After production, the crosslinkable mixture is preferably processed further in step (b) without further intermediate steps which change the composition.

In a particularly preferred embodiment of the invention, the mixture does not contain any solvent. According to the invention, it was surprisingly found that mixtures of the PAEK and the crosslinker can be processed without the use of a solvent, wherein an intimate mixing takes place.

The mixture is preferably heated to a temperature at which it is in liquid form. In order to obtain a homogeneous mixture, it is here preferred to choose the temperature and residence time so that here no significant crosslinking takes place.

In a preferred embodiment, the crosslinker is given continuously to the PAEK. Here, the components can be in liquid or solid form. In this way a particularly uniform mixture can be obtained. The adding of the crosslinker takes place here preferably under intimate mixing, for example under stirring and/or kneading. In a preferred embodiment, the crosslinker is supplied in the form of a concentrate. This has the advantage that the crosslinker can be better dosed, whereby the uniformity of the mixture can be improved. Overall, a particularly homogeneous mixture can be obtained with continuous addition of the crosslinker, so that particularly regular crosslinking is achieved. This can prevent areas of strong or low cross-linking from developing, which can lead to damage to the product in the event of thermal or mechanical stress. In this way, particularly good properties with regard to temperature stability and mechanical stability can be achieved.

In step (b), a molded article is produced from the mixture. In a preferred embodiment, the molded article is produced in step (b) through thermoplastic shaping. This means that the mixture can be formed from the melt in a non-crosslinked and/or at least not significantly crosslinked state, since otherwise thermoplastic processing would no longer be possible. If there are too many crosslinking points, the PAEK intermediate product is no longer

flowable and can no longer be readily thermoplastically formed. Before molding, the mixture should only be exposed to the high processing temperatures for a short period of time. The thermoplastic processing is therefore preferably carried out in such a way that the residence time of the mixture in the device is as short as possible. It is here preferred
5 that the processing is carried out in such a way that the essential part of the crosslinking reaction, and here for example more than 80%, more than 90% or more than 95% of the crosslinks, only takes place after molding, i.e. in step (c) .

In a preferred embodiment, the mixture is processed in step (b) by extrusion, hot pressing
10 and/or injection molding and is here shaped. These methods are particularly suitable for the simple and efficient processing of thermoplastic polymer compositions.

The extrusion can be here carried out by known methods. During extrusion, solid to
15 viscous hardenable materials are continuously pressed out of a molding opening (also known as a nozzle, die or mouthpiece) under pressure. Here, this creates bodies with the cross-section of the opening, called extrudate, in theoretically any length. The extrusion is preferably carried out at a temperature of at least 320°C, preferably at least 350°C; preferably between 320°C and 400°C, and in particular between 350°C and 390°C.

Hot pressing is a method in which the molding material is introduced into the previously
20 heated cavity. The cavity is then closed using a pressure piston. The pressure gives the molding material the shape specified by the tool. The hot pressing is preferably carried out at a temperature of at least 300°C, preferably at least 350°C; preferably between 320°C and 400°C, and in particular between 350°C and 400°C.

Injection molding (often referred to as injection molding or injection molding process) is a
25 molding method which is used in plastics processing. Here, the plastic is plasticized with an injection molding machine and injected into a mold, the injection molding tool, under pressure. In the tool, the material returns to its solid state when it cools down and is
30 removed as a molded article after the tool is opened. The hollow space (cavity) of the tool determines the shape and surface structure of the product.

Processing is particularly preferably carried out by extrusion and subsequent injection molding. The mixture of the PAEK and the crosslinker is melted in this method if it is not yet in liquid form.

- 5 In step (b), the mixture is preferably introduced into an extruder, an injection molding machine or a hot press, melted at high temperatures, for example in the range from 300°C to 400°C, and brought into a desired shape.

10 In step (c), the molded article is thermally treated at a temperature at which PAEK is crosslinked, whereby the crosslinked molded article is obtained. This allows the PAEK to be crosslinked intermolecularly with the crosslinker. The temperature in step (c) can be set relatively high, since the crosslinkers which can be used according to the invention have relatively high melting and boiling points. This is advantageous because such crosslinking reactions are generally favored at high temperature. However, the
15 temperature is preferably below the melting range of PAEK.

Surprisingly, it was found that in the system according to the invention the crosslinking reactions take place even below the melting range of the polymer and of the molded article. This was unexpected, since it is generally assumed that crosslinking reactions only
20 take place at temperatures above the melting range of the polymer and of the molded article.

In the prior art, it is also assumed that such crosslinking reactions take place relatively quickly within minutes or a few hours. According to the invention, however, it has been
25 found that the crosslinked PAEK can have particularly advantageous properties if the heating of the molded article in step (c) is carried out over a longer period of time, preferably of at least 6 hours, for example from 6 hours to 30 days. It has been found that the thermal stability and the mechanical stability can be significantly improved by such a thermal treatment.

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In particular, it was found that the thermal treatment can improve the rigidity of the samples at elevated temperatures. It was observed that a thermal treatment for a certain duration can significantly improve the rigidity, wherein saturation can subsequently occur, so that the rigidity is not or only insignificantly improved with further thermal post-

treatment. However, further thermal post-treatment shows an improvement in the thermoform resistance. It has been found that the thermoform resistance can increase even with prolonged thermal post-treatment, so that a significant improvement can still be observed even after 14 days.

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In a preferred embodiment, the molded article obtained in step (b) is subjected to a thermal treatment for at least 6 h, in particular for more than 2 days or for more than 2.5 days. In a preferred embodiment of the invention, the thermal treatment is carried out over a period of 2 to 30 days, in particular for 2.5 to 20 days. This is advantageous because the homogeneity of the products, and thereby the thermal and mechanical stability, can be improved. The thermal treatment is preferably carried out with the exclusion of oxygen.

In a preferred embodiment, the thermal treatment in step (c) takes place at a temperature of at least 250°C, preferably at least 300°C. The temperature in step (c) is preferably between 280°C and 415°C, particularly preferably between 300°C and 400°C. At such temperatures, efficient three-dimensional crosslinking can take place sufficiently quickly without the thermoplastically produced articles being impaired, for example by decomposition and/or undesired deformation of the molded articles.

20 The molded articles are cooled after crosslinking and can be used or further processed.

The mixture and the molded article can contain customary additives. For example, additives can be used in an amount of up to 20% by weight, for example from 0.1% by weight to 20% by weight and/or from 0.1% by weight to 18% by weight, respectively related to the total weight of the mixture and/or molded articles. Typical additives are, for example, dyes and processing aids.

The mixture and the molded article can contain conventional fillers such as, in particular, tribologically active and/or flexibilizing fillers and/or reinforcing fibers. For example, the fillers can be used in an amount of up to 80% by weight, for example from 0.1% by weight to 80% by weight and/or from 0.1% by weight to 60% by weight, respectively related to the total weight of mixture and/or molded article.

Subject of the invention is also a molded article based on polyaryletherketones (PAEK) which has a crosslinked matrix made of PAEK, wherein the PAEK is crosslinked with a linker L, which is a diphenyl residue in which the two phenyl rings are connected to one another via an aliphatic group which has a carbocyclic residue, wherein the PAEK is connected to the phenyl rings of the linker via imine bonds.

The molded article can be obtained in particular by the methods according to the invention which are described in the context of this invention. The molded article preferably has the advantageous properties which are described in the context of this invention for the crosslinked PAEK. In the context of this invention, the term molded article refers to products made from crosslinked PAEK which have a defined three-dimensional shape. It is not necessary here for the molded article to be a defined object, rather it can also be a coating, for example. The molded article can consist of the crosslinked PAEK or contain this, for example as a composite material or laminate.

The molded articles according to the invention can have advantageous, increased rigidity which is characterized by a high tensile module. The molded article preferably has a tensile module of at least 350 MPa, in particular of at least 400 MPa, and particularly preferably of at least 450 MPa. In particular, the tensile module is between 350 MPa and 600 MPa or between 400 MPa and 550 MPa. The tensile module is preferably determined at 240°C according to DIN EN ISO527-2.

It may be desirable not to completely crosslink the polymer in the molded article, since the elongation at break of the material can decrease as the crosslinking increases. The degree of crosslinking is therefore preferably set with a view to the desired application, for example via the proportion of crosslinker and the type and duration of the thermal treatment.

Here, the degree of crosslinking is preferably not measured directly, but rather it is determined by suitable test methods, such as a high-temperature tensile test, whether the molded article has the desired properties. At very high temperatures, it is advisable to determine the dynamic module.

The molded articles can be used in particular in technical fields in which high temperature resistance and mechanical stability, and here in particular high rigidity, are required. They are particularly suitable for applications as sealing articles, in particular sealing and O-rings, bushings, bearings, back-up rings, valves, thrust washers, snap hooks, pipes or lines, cables, casings and sheaths, housings of an electrical or chemical application or as a component thereof. They are particularly suitable for applications in which high chemical resistance and resistance to abrasion are required. This applies in particular to applications in the oil and gas transportation, the aviation and aerospace technology and the chemical industry, and here the manufacture of safety-relevant parts, and the field of energy generation and the automotive industry. Likewise conceivable applications are connectors and insulators in the electronics field, since the cross-linking leads to good insulation properties.

Subject of the invention is also a sealing article consisting of or containing a molded article according to the invention. The sealing article can be used for static or dynamic applications and here in particular for dynamic applications in which it is exposed to high mechanical loads. In particular, the sealing article is suitable for sealing applications in which it is in contact with fluids, such as lubricants, and in which it is exposed to high temperatures, for example above 150°C, and in particular in the range from 180°C to 400°C.

The methods, molded articles and sealing articles according to the invention achieve the object on which the invention is based. They have a high temperature resistance and high mechanical stability in connection with good processability. In particular, the molded articles have a high glass transition temperature and high rigidity, in particular above the glass transition temperature. The high rigidity is accompanied by reduced creep behavior at high temperatures. The improved temperature resistance is evident both at the maximum temperature and at the long-term use temperature, in particular in the range from 150°C to 400°C. The molded articles also show advantageous rubber-elastic behavior in the high temperature range. The products show here very good chemical resistance and reduced flammability, as the material does not melt due to the crosslinking and no burning material drips off.

In addition, the molded articles according to the invention can be produced in a simple and efficient manner by thermoplastic molding methods. So, for example, the production can be carried out by simple extrusion. The methods are also environmentally friendly and can be carried out without endangering the user, since the crosslinkers used have
5 relatively high boiling points and have low volatility.

Brief description of the figures:

FIG. 1 shows the development of the complex dynamic module with increasing
10 temperature of the molded article according to the invention (PEEK with 1.05% DAPI, thermally treated, dashed curve) in comparison to the standard base material (PEEK without thermal treatment, solid line), and to another material (PEEK, 4% AF-PEEK, thermally treated, dotted line).

15 FIG. 2 shows the development of the complex dynamic module with increasing temperature of the molded article 4 according to the invention (PEEK with 1% DAPI (CAS No. 68170-20-7), thermally treated, dashed curve) in comparison to the standard base material 1 (PEEK without thermal treatment, solid line).

20 Embodiments

Embodiment 1

Mixtures as indicated in Table 1 are produced. Amine-functionalized PEEK (hereinafter
25 referred to as "AF-PEEK") is produced using PEEK and p-phenylenediamine according to Thompson and Farris, 1988, and is ground to powder after diphenylsulfone and unreacted p-phenylenediamine have been completely leached out. The determination of the total nitrogen content according to Kjeldahl shows a conversion rate of 95% of the carbonyl groups of PEEK. DAPI (CAS No. 54628-89-6) in a purity of 98% was used as the
30 crosslinker.

Table 1: Mixtures

Example No.	Compound
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1 (comparison)	PEEK
2 (comparison)	PEEK, 4% by weight AF-PEEK
3	PEEK, 1.05% by weight DAPI

The mixtures from Table 1 are processed into test specimens by injection molding and then subjected to a thermal treatment for crosslinking.

5 Table 2: Thermal treatment and results of the tensile elongation test

Ex.	Compound	Thermal treatment	Stretch limit	Tensile strength	Elongation at break	Tensile module
Nr.			[MPa]	MPa	%	[MPa]
1	PEEK, no additive	Without	14.5	47.0	274	211
2 a	PEEK, 4% AF-PEEK	Without	18.5	41.0	204	241
2 b	PEEK, 4% AF-PEEK	With	25.2	25.2	20.8	310
3	PEEK, 1.05% DAPI	With	28.1	30.8	97	505

The tensile tests are carried out at 240°C in accordance with the DIN EN ISO527-2 standard.

10

The results show that the sample according to the invention becomes infusible by thermal treatment and that the tensile module of elasticity increases. This clearly shows the advantage of the homogeneity of the samples crosslinked with DAPI compared to the inhomogeneity of the PEEK crosslinked with AF-PEEK.

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Dynamic mechanical analysis (DMA)

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The dynamic mechanical analysis (DMA) is a thermal method to determine the physical properties of plastics. The temperature gradient (temperature sweep) shows the development of the dynamic module and thus also the rigidity over the measured temperature range. The glass transition area (T_g), the height of the plateau above the T_g , the position of the drop of the module when the crystalline phase melts, and the height of the plateau in the high temperature range are particularly important here.

This was carried out with thermally treated molded articles according to the embodiments described above (see Table 1). The temperature gradients were measured with test specimen strips (width approx. 3 mm, thickness approx. 3 mm) under the following conditions: heating rate 3 K/min, contact force 3N, mean elongation 0.5%, elongation ampl. +/-0.1%. The results are shown in FIG. 1 graphically.

FIG. 1 shows the development of the complex dynamic module with increasing temperature of the molded article 3 according to the invention (PEEK with 1.05 % DAPI, thermally treated, dashed curve) in comparison to the standard base material 1 (PEEK without thermal treatment, solid line).

As a further reference, the complex dynamic module over the temperature of a further material 2b (PEEK, 4% AF-PEEK, thermally treated, dotted line) is shown, which is made of standard PEEK, which was cross-linked with 4% AF-PEEK through thermal post-treatment. This AF-PEEK was produced by the method described by Thompson and Farris, and by Yurchenko et al. by modifying PEEK.

The results show that the crosslinked PEEK according to the invention has advantageous thermal properties. Here, for all molded articles according to the invention, improvements are achieved in the glass transition area (T_g), in the height of the plateau above the T_g , and in terms of the drop of the module when the crystalline phase melts, and in terms of the height of the plateau in the high temperature range. The glass transition temperature is increased, as is the rigidity at high temperature, in particular in the range above 150°C. The results also show that, particularly when combining DAPI with PEEK, optimum product properties can be achieved with regard to the height of the module and the height of thermoform resistance. The thermal properties can be significantly improved by extending the thermal treatment.

Embodiment 2

The DAPI isomer mixture with the CAS number 68170-20-7 (crosslinker with the formula VI) is mixed into a commercial PEEK of medium viscosity using a twin-screw compounder, as in the previous example 1, and the strand is chopped into granules.

Table 3: Mixtures

Example no.	Compound
1 (comparison)	PEEK
4	PEEK + DAPI, CAS No.68170-20-7, thermally treated

The granules from the mixtures of Table 3 are processed into test specimens by injection molding and then likewise subjected to thermal post-treatment.

5

The samples are tested according to embodiment 1 by means of DMA in a T-sweep, wherein the result shown in FIG. 2 is obtained.

FIG. 2 shows the development of the complex dynamic module with increasing temperature of the molded article 4 according to the invention (PEEK mit 1 % DAPI (CAS No. 68170-20-7), thermally treated, dashed curve) in comparison to the standard base material 1 (PEEK without thermal treatment, solid line).

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Also here, the advantageous results discussed in relation to FIG. 1 are obtained in a comparable form.

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CLAIMS

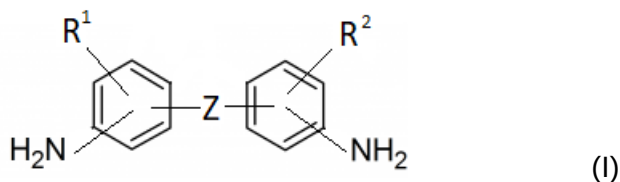
1. A method for producing a crosslinked molded article containing polyaryletherketones (PAEK), said method comprising the steps:

5 (a) providing a mixture containing a PAEK and a crosslinker;
(b) producing a molded article from the mixture; and
(c) thermally treating the molded article at a temperature at which PAEK is crosslinked, whereby the crosslinked molded article is obtained, and wherein the crosslinker is a di(aminophenyl) compound in which the two aminophenyl rings are connected to each other via an aliphatic group which has a carbocyclic residue.

2. The method according to claim 1, wherein the crosslinker is an annulated compound in which one of the two phenyl rings is annulated with the carbocyclic residue.

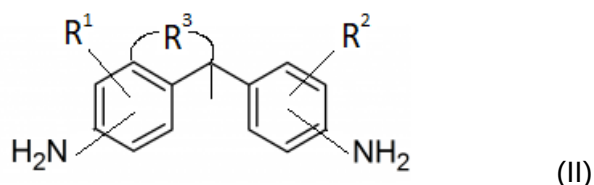
3. The method according to at least one of the preceding claims, wherein the crosslinker is a 4,4'-diaminodiphenyl compound and/or is an asymmetric compound.

4. The method according to at least one of the preceding claims, wherein the crosslinker is a compound of the general formula (I):



wherein R^1 and R^2 are independently of one another selected from H, substituted or unsubstituted alkyl with 1 to 20 carbon atoms, in particular with 1 to 4 carbon atoms, in particular methyl or ethyl, substituted or unsubstituted aryl with 5 to 12 carbon atoms, F and Cl, and wherein Z is the aliphatic group which has a carbocyclic residue.

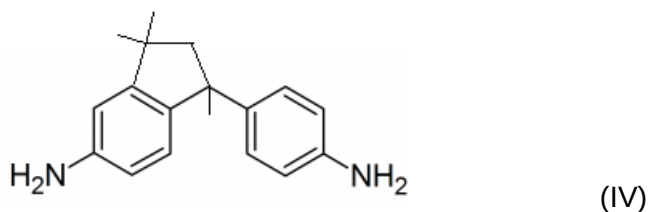
5. The method according to claim 4, wherein the crosslinker is a compound of the general formula (II):



wherein R^1 and R^2 are independently of one another selected from H, substituted or unsubstituted alkyl with 1 to 20 carbon atoms, in particular with 1 to 4 carbon atoms, in particular methyl or ethyl, substituted or unsubstituted aryl with 5 to 12 carbon atoms, F and Cl, and

wherein R^3 is a carbocyclic residue which has 2 to 3 carbon ring atoms and which can be substituted by at least one alkyl group with 1 to 4 carbon atoms, in particular methyl or ethyl.

6. The method according to claim 5, wherein the crosslinker is a compound of the formula (IV):



7. The method according to at least one of the preceding claims, wherein the polyaryletherketone (PAEK) is a polyetheretherketone (PEEK).
8. The method according to at least one of the preceding claims, wherein the polyaryletherketone (PAEK) at 380 °C has a melt viscosity in the range of 5 cm³/10 min to 250 cm³/10 min, measured according to DIN ISO 1130.
9. The method according to at least one of the preceding claims, wherein the mixture contains no solvent.
10. The method according to at least one of the preceding claims, wherein the temperature in step (b) is at least 300 °C.

11. The method according to at least one of the preceding claims, wherein the mixture in step (b) is processed by extrusion, hot pressing and/or injection molding.
12. The method according to claim 11, wherein the molded article obtained in step (b) is
5 subjected to a thermal treatment in step (c) for at least 6 h.
13. The method according to claim 12, wherein the thermal treatment in step (c) takes place at a temperature of at least 250 °C.
- 10 14. Molded articles based on polyaryletherketones (PAEK) which has a cross-linked matrix made of PAEK,
wherein the PAEK is crosslinked with a linker L, which is a diphenyl residue in which the two phenyl rings are connected to each other via an aliphatic group which has a carbocyclic residue,
15 wherein the PAEK is connected to the phenyl rings of the linker via imine bonds,
wherein the molded article can be obtained in particular by a method according to at least one of claims 1 to 13.
- 20 15. Sealing articles, thrust washers, back-up rings, valves, connectors, insulators, snap hooks, bearings, sockets, sealing and O-rings, pipes and lines, cables, casings and jackets, housings for an electrical or chemical application, consisting of or containing a shaped body according to claim 14.