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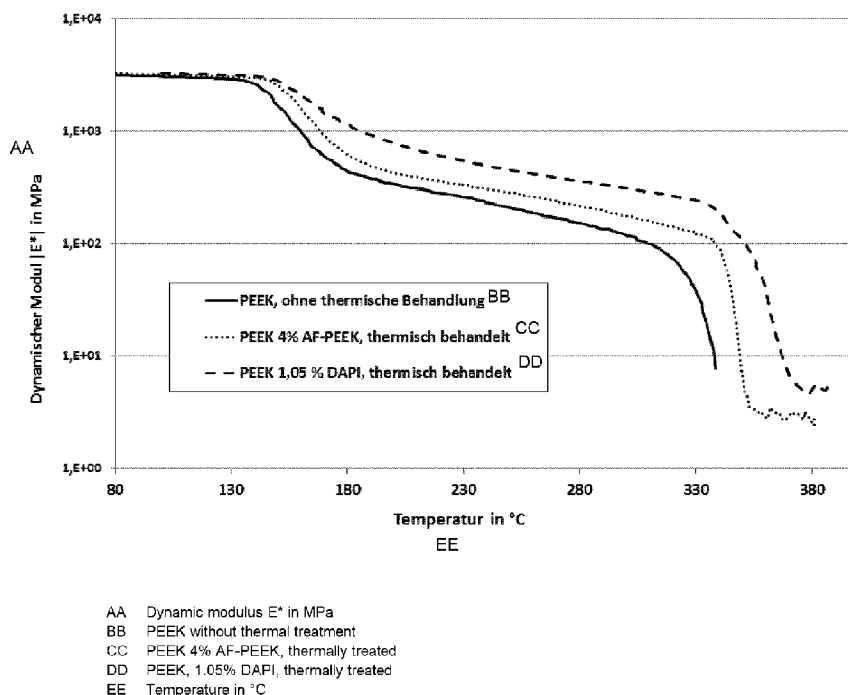
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(54) Titre : RETICULATION DE POLYARYLETHERCETONES
(54) Title: CROSSLINKING OF POLYARYLETHERCETONES

Figur 1:



(57) **Abrégé/Abstract:**

The invention relates to a method for producing a crosslinked moulded article containing polyaryletherketones (PAEK), said method comprising the steps: (a) providing a mixture containing a PAEK and a crosslinking agent; (b) producing a moulded article from the mixture; and (c) thermally treating the moulded article at a temperature at which PAEK is crosslinked to obtain the crosslinked moulded article, wherein the crosslinking agent is a di(aminophenyl) compound in which the two aminophenyl rings are connected to each other via an aliphatic group which has a carbocyclic group. The invention also relates to moulded articles obtainable using the method, and to sealing articles.

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ABSTRACT

The invention relates to a process for the production of a crosslinked moulding comprising polyaryletherketones (PAEK), comprising the steps of:

- (a) provision of a mixture comprising a PAEK and a crosslinking agent,
- (b) production of a moulding made of the mixture, and
- (c) thermal treatment of the moulding at a temperature at which PAEK is crosslinked, with resultant production of the crosslinked moulding, and

where the crosslinking agent is a di(aminophenyl) compound in which the two aminophenyl rings have bonding to one another by way of an aliphatic group comprising a carbocyclic moiety. The invention also relates to mouldings obtainable by the process, and to sealing items.

CROSSLINKING OF POLYARYLEETHERKETONES

5 The invention relates to processes for the production of a moulding made of polyaryletherketones (PAEK) and to a crosslinking agent. The invention also relates to mouldings obtainable by using the process, and to sealing items.

Prior Art

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Polyaryletherketones (PAEK), for example polyetheretherketones (PEEK), are semicrystalline engineering polymers which have high resistance to heat and to solvents. They consist of alternating keto groups, ether groups and aryl groups. PAEK have the advantage of thermoplastic processability. However, thermoplastics have an intrinsic limit
15 in respect of heat resistance. Crosslinking of the polymer chains of PAEK has been proposed in order to increase heat resistance and mechanical stability. The crosslinking is achieved in the prior art by processes that use diamines to crosslink the PAEK. Imine bonds (Schiff bases) are thus formed, which can provide relatively high stability to the crosslinked polymers. It is disadvantageous here that these crosslinked polymers are not
20 flowable. They cannot therefore readily be processed thermoplastically from a melt of the polymer.

The process for the chemical crosslinking of polyetheretherketones (PEEK) with diamines was first described by Thompson and Farris (Journal of Applied Polymer Science, 1988,
25 Vol. 36, 1113-1120). This process begins by modifying polyetheretherketone by linkage to *para*-phenylenediamine in diphenyl sulfone as solvent. The solvent must then be removed by drying and further purification. Problems arise because crosslinking occurs already in the process described, and therefore also during the covalent linkage. Glass transition temperature and heat resistance thus rise, and thermoplastic processability is lost. The
30 resultant polymer composition is therefore not crosslinked thermoplastically from the melt, but instead is crosslinked via compression moulding.

Yurchenko et al. (2010, Polymer 51, 14-1220) have undertaken a more detailed study of the process described by Thompson and Farris, and of the products. They describe an

analogous reaction of PEEK and phenylenediamine in diphenyl sulfone as solvent, where the PAEK is modified and, after removal of the solvent and purification, crosslinked via compression moulding, and characterized. Again, no thermoplastic processing is described. The study shows that the products have higher stability than uncrosslinked PEEK, but the said stability still requires improvement.

WO 2010/011725 A2 describes a wide variety of aminic crosslinking agents for crosslinking of PAEK. However, the document comprises only a single synthesis example describing the crosslinking of PAEK with diphenylamine in accordance with the literature cited above, beginning with the reaction in diphenyl sulfone as solvent.

US 6,887,408 B2 describes processes for the crosslinking of PAEK with non-aminic crosslinking agents.

In another process proposed in the prior art for crosslinking of PAEK, the polymers themselves are functionalized with crosslinkable amino groups. Processes of this type are described by way of example in US 2017/0107323 A1. It is disadvantageous here that the functionalization of the PAEK with amino groups is relatively complicated. Furthermore, control of the crosslinking of functionalized PAEK is less simple and less flexible than when a low-molecular-weight crosslinking agent is used.

The processes described in the prior art for the crosslinking of PAEK with diamines with low-molecular-weight crosslinking agents are carried out in the presence of a high proportion of solvent, where the production of the mouldings is achieved via hot pressing (compression moulding). The products have better heat resistance than comparable uncrosslinked PAEK. However, it is disadvantageous that PAEK thus crosslinked has relatively low stiffness, because the crystallinity of the PAEK is lost when the polymers are dissolved in solvent. The proportion of the crystallinity that can be regained during further processing may be at most small, because of the intrinsic steric hindrance of the chains caused by the crosslinking points. It is moreover disadvantageous that the processes overall are very complicated, because they also require a large number of operations on account of the removal of the solvent. A further disadvantage is that the mouldings are produced by compression moulding, which limits possible applications in comparison with thermoplastic processing. Compression moulding and comparable processes use non-

flowable materials which cannot be converted to thermoplastic melts. This restricts mouldability, and it is impossible to produce thin-walled or complex mouldings. For these reasons it is also very difficult to automate such processes. The known solvent-based processes cannot therefore form any basis for efficient, low-cost industrial production.

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WO 2010/011725 A2 also contains the theoretical proposal of crosslinked PAEK production via extrusion. However, there is no proof that the PAEK can be extruded with low-molecular-weight crosslinking agents, or that products with advantageous properties can thus be obtained. Nor is there any reasonable expectation of success here. Problems firstly arise with the fact that crosslinking begins to occur at the high melting temperatures at which the components must be mixed and processed. Secondly, it is unlikely that PAEK can be mixed and processed with these aminic crosslinking agents in the absence of any solvent. Demixing processes are frequently observed in practice when low-molecular-weight components are incorporated into polymers, whereas homogeneous distribution of the crosslinking agent in the polymer is an absolute necessity if a stable product is to be obtained.

Another disadvantage is that the handling of volatile diamines at high temperature is attended by considerable risks to the user and by a high level of environmental pollution.

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It would therefore be desirable to provide processes and mouldings which overcome the disadvantages described.

Object of the Invention

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

A particular intention is to provide materials which are based on PAEK and which have high stability and good processability. The materials are in particular intended to have high heat resistance and to have high stiffness (modulus) at high temperatures. They are moreover intended to have good resistance to chemicals and low combustibility. The materials are moreover intended to have little susceptibility to creep and to have elastomeric behaviour at high temperature.

In particular, the invention is based on the object of providing materials which have high stability but nevertheless are easy to process. The materials here are intended to be amenable to easy, efficient, low-cost production. In particular, thermoplastic processability
 5 of the materials would be advantageous here. A particular intention here is to avoid inefficient processes, for example compression moulding.

The processes are also intended to be very environmentally friendly and to involve no risk to users.

Disclosure of the invention

Surprisingly, the object on which the invention is based is achieved via processes, mouldings and sealing items according to the claims.

The invention provides a process for the production of a crosslinked moulding comprising polyaryletherketones (PAEK), comprising the steps of:

- (a) provision of a mixture comprising a PAEK and a crosslinking agent,
- (b) production of a moulding made of the mixture, and
- 20 (c) thermal treatment of the moulding at a temperature at which PAEK is crosslinked, with resultant production of the crosslinked moulding, and

where the crosslinking agent is a di(aminophenyl) compound in which the two aminophenyl rings have bonding to one another by way of an aliphatic group comprising a carbocyclic moiety.

Polyetherketones (PEK) are polymers 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 (1,4)-position respectively between the functional groups. PAEK have a rigid, semicrystalline structure that gives the materials comparatively high glass transition
 30 temperatures and comparatively high melting points.

The process relates to a crosslinking reaction in which the polymer chains of the PAEK are bonded covalently and intermolecularly to one another. Step (a) provides a mixture comprising the PAEK and the crosslinking agent. It is preferable here to set the

temperature in step (a) in a manner such that no substantial reaction between the PAEK and the crosslinking agent yet takes place during this step. It is advantageous here that the aminic crosslinking of PAEK with the crosslinking agents described according to the invention begins only when higher temperatures are reached. The simple process
 5 according to the invention does not require covalent linkage of the crosslinking agent to the PAEK of the type described in the prior art.

Step (b) produces a moulding made of the mixture. Step (b) of the moulding-production process here comprises all of the measures via which the mixture is converted to the
 10 three-dimensional shape that is retained in the hardened, crosslinked state. It is preferable that the moulding is produced by means of thermoplastic shaping processes. It is preferable here that the production of the moulding takes place before and/or during the crosslinking. It is particularly preferable that the shaping takes place before step (c), because before the crosslinking, it is advantageously possible to achieve thermoplastic
 15 processing and moulding of the mixture, in particular via compression moulding, extrusion and/or injection moulding.

Step (c) comprises the thermal treatment of the moulding at a temperature at which PAEK is crosslinked, thus giving the crosslinked moulding.

20 During the crosslinking, two imine bonds are formed between two keto groups of the PAEK chains and the two amino groups of the crosslinking agent. Another term used for the resultant imine bridge is Schiff base, because the imine nitrogen bears no hydrogen atom but instead has bonding to an organic molecule. The extent of crosslinking here is
 25 maximized in a manner that maximizes the number of amino groups of the diamine used that react with the carbonyl groups of the PAEK. Complete crosslinking has the advantage of increased heat resistance and increased stiffness (modulus). Nevertheless, the term "crosslinked" is also intended to encompass crosslinking that is merely partial. Crosslinking that is merely partial can be present when the quantity of diamine used has
 30 not been sufficient for complete bonding of all of the PAEK chains into the network. In this case, the tensile strain at break of the material is generally higher than that of the completely crosslinked material. The imine bonds give the moulding high stability. According to the invention, it is preferable that the moulding is a moulding based on PAEK. The expression "based on PAEK" here means that the PAEK is the substantial

structure-providing polymer component of the moulding. In one embodiment, it is preferable that the PAEK is the sole polymer component of the moulding. In another embodiment, the PAEK is in a mixture with other polymers, in particular thermoplastic polymers. Preferred other polymers are polyphenylene sulphide (PPS), polyamideimide (PAI), polyphthalamide (PPA), semiaromatic polyamides, thermoplastic polyimide (TPI), and liquid-crystalline polyesters (LCP). Preferred ratios by mass here of PAEK and other polymers, in particular other thermoplastic polymers, are from 1:1 to 100:1, preferably from 5:1 to 100:1, particularly preferably from 10:1 to 100:1. The moulding can moreover comprise fillers, for example fibres, and/or conventional additives, for example processing aids, and/or functional components. The crosslinked PAEK forms a matrix here in which there are optionally uniformly distributed additives present.

The crosslinking agent is a di(aminophenyl) compound. These compounds have two aminophenyl rings bonded to one another. The compounds are therefore primary diamines. In one embodiment of the invention, each phenyl ring here has only a single amino group. However, it is equally conceivable that the phenyl rings mutually independently have two or three amino groups. The compounds have low molecular weight and are not polymers. The phenyl rings can have other substituents alongside the amino groups, examples being alkyl groups and halogen groups. The two aminophenyl rings have bonding to one another by way of an aliphatic group. Aliphatic groups consist only of carbon and hydrogen, and are not aromatic. It is preferable that the crosslinking agents have, other than in the two phenyl rings, no double or triple bonds. The aliphatic group comprises a carbocyclic moiety. Carbocyclic moieties are hydrocarbon rings which here can by way of example have from 4 to 7 carbon atoms, preferably 5 or 6 carbon atoms. The carbocyclic moiety here can encompass double bonds of the phenyl rings. It is preferable that the carbocyclic group comprises only a single aliphatic hydrocarbon ring. The aliphatic group preferably has a total of from 5 to 15 carbon atoms, in particular from 6 to 8 carbon atoms. By virtue of the aliphatic group between the carbocyclic moieties, the two phenyl rings are not conjugated.

Surprisingly, it has been found according to the invention that PAEK crosslinked with these di(aminophenyl) compounds has particularly advantageous properties. In particular, the crosslinked PAEK has particularly high thermal stability and mechanical stability, in particular together with particularly high glass transition temperature and stiffness. Without

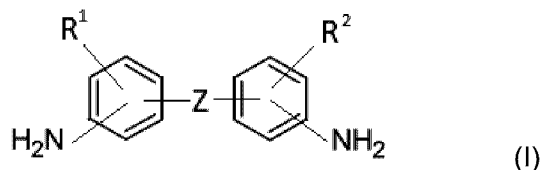
adoption of any theory, it is believed that the carbocyclic moiety can promote the formation of a particularly rigid, semicrystalline polymer structure that gives the product high stability. It is also assumed here that an advantageous and regular spacing of the PAEK polymer chains can be achieved by way of the crosslinking agent having the carbocyclic moiety. It appears overall that these crosslinking agents cause little impairment of the crystalline structure of the PAEK, or indeed advantageously promote the said structure.

In a preferred embodiment, the crosslinking agent is an annellated compound in which only one of two phenyl rings has been annellated with the carbocyclic moiety. Annellation (condensation) means the coalescence of a further ring with a ring of a cyclic molecule. The two annellated rings share two carbon atoms, and thus share a carbon-carbon double bond of the phenyl ring. The use of these annellated crosslinking agents has the advantage of permitting formation of a particularly rigid and regular connection between the PAEK chains, thus permitting achievement of particularly high heat resistance and stiffness of the products.

The amino groups can in principle be present at any desired positions on the phenyl group, i.e. in *ortho*-, *meta*- or *para*-position in relation to the aliphatic connection between the two phenyl rings. In the embodiment where each phenyl group has only a single amino group, it is preferable to maximize the distance between the two amino groups. This can be achieved if the attachment of the two amino groups is at the *para*-position in relation to the aliphatic connection and/or at the 4- and 4'-position of the phenyl rings. In a preferred embodiment, the diaminodiphenyl compound is therefore a 4,4'-diaminodiphenyl compound. The advantage of maximized distance between the amino groups can generally consist in a reduced extent of undesired intramolecular reactions in which a crosslinking agent forms two bonds to the same PAEK polymer chain. These intramolecular reactions with the crosslinking agent can, while having no crosslinking effect, disrupt the crystalline structure of the PAEK, and thus reduce the stability of the product.

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

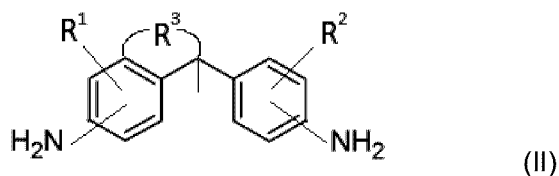
In a preferred embodiment of the invention, the crosslinking agent is a compound of the general formula (I):



- 5 where R^1 and R^2 are selected mutually independently from H, substituted or unsubstituted alkyl having from 1 to 20 carbon atoms, in particular having from 1 to 4 carbon atoms, in particular methyl or ethyl, substituted or unsubstituted aryl having from 5 to 12 carbon atoms, F and Cl, and where Z is the aliphatic group comprising a carbocyclic moiety. Each phenyl ring here can have, selected mutually independently, one, two or three moieties R^1
- 10 or R^2 . Preference is given to a phenyl ring having only one moiety R^1 and/or R^2 . The moieties R^1 and R^2 are particularly preferably respectively H. Crosslinking agents without additional moieties R^1 and R^2 have relatively good availability and can be processed to give very stable crosslinked PAEK.
- 15 There can be two, or one, bond(s) between the moiety Z and each phenyl moiety. It is preferable that there are two bonds between the moiety Z and one phenyl moiety and that there is one bond between the moiety Z and the second phenyl moiety.

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

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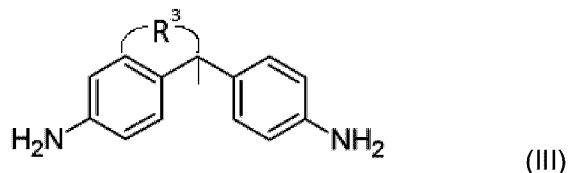


- where R^1 and R^2 are selected mutually independently from H, substituted or unsubstituted alkyl having from 1 to 20 C atoms, in particular having from 1 to 4 C atoms, in particular methyl or ethyl, substituted or unsubstituted aryl having from 5 to 12 C atoms, F and Cl,
- 25 and
- where R^3 is a carbocyclic moiety which comprises from 2 to 3 ring carbon atoms and which can have substitution by at least one alkyl group having from 1 to 4 carbon atoms,

in particular methyl or ethyl. The moieties R^1 and R^2 are particularly preferably respectively H. The carbocyclic moiety R^3 is therefore a pentyl or hexyl moiety. These crosslinking agents have the advantage that they can give a particularly good combination of heat resistance and mechanical stability of the crosslinked PAEK.

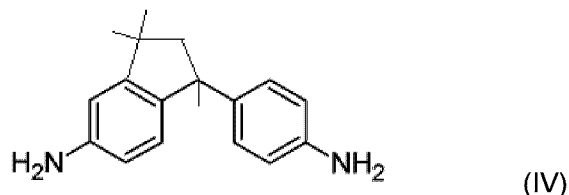
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In a preferred embodiment, the crosslinking agent is a compound of the general formula (III):



10 where selection of R^3 is as stated above. These crosslinking agents have the advantage that they can give a particularly good combination of heat resistance and mechanical stability of the crosslinked PAEK.

In a preferred embodiment, the crosslinking agent has the formula (IV):

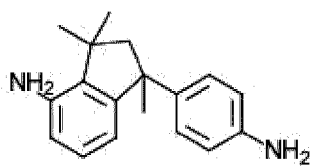


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The compound led to a particularly advantageous combination of heat resistance and mechanical stability of the crosslinked PAEK in the experiments carried out. The chemical name is 1-(4-aminophenyl)-1,3,3-trimethylindan-5-amine (CAS No. 54628-89-6).

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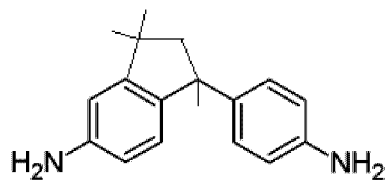
In another preferred embodiment, the crosslinking agent has the formula (V):



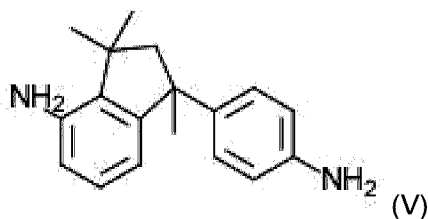
(V)

The compound likewise leads to a particularly advantageous combination of heat resistance and mechanical stability of the crosslinked PAEK in the experiments carried out. The chemical name is 1-(4-aminophenyl)-1,3,3-trimethylindan-6-amine.

In another preferred embodiment, the crosslinking agent has a mixture of compounds of the formulae:



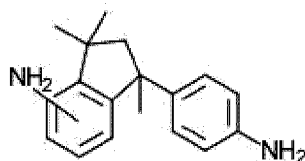
(IV) and



(V)

This crosslinking agent likewise leads to a particularly advantageous combination of heat resistance and mechanical stability of the crosslinked PAEK in the experiments carried out.

In another preferred embodiment, the crosslinking agent has the formula (VI):



(VI)

This crosslinking agent likewise leads to a particularly advantageous combination of heat resistance and mechanical stability of the crosslinked PAEK in the experiments carried out. The chemical name is 1-(4-aminophenyl)-1,3,3-trimethylindanamine (CAS No. 68170-20-7). The amino group here can occur at any position on the aromatic ring of the indane. Mixtures of 1-(4-aminophenyl)-1,3,3-trimethylindanamines in which the amino group is situated at different positions on the aromatic ring of the indane are likewise encompassed.

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According to the invention, it is preferable to use a single specific crosslinking agent, in order to maximize uniformity of properties of the material. However, it is also possible to use mixtures of two or more crosslinking agents.

The quantity of the crosslinking agent is established with a view to the desired degree of crosslinking. The proportion of the crosslinking agent, based on the PAEK, can thus be from 0.05% by weight to 15% by weight, in particular from 0.1% by weight to 5% by weight. In a preferred embodiment, the proportion of the crosslinking agent is from 0.1 to 1.5% by weight. It has been found that with this proportion of crosslinking agent the stability of the product can be particularly advantageous. In particular, when the quantity of crosslinking agent is established within the said range it is possible to achieve significantly improved tensile strain at break.

In a preferred embodiment, the boiling point of the crosslinking agent is above 300°C, in particular above 350°C or above 400°C. This is advantageous because the vapour pressure of these crosslinking agents at the required high crosslinking temperatures is relatively low. The boiling point of the crosslinking agent is preferably from 300°C to 500°C, in particular from 350°C to 500°C. The melting point of the crosslinking agent is

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advantageously below the melting point of the PAEK. This achieves good processability and little risk to users.

In principle, any desired polyaryletherketones can be used as polymer components.
 5 Polyaryletherketones are characterized by linear polymer chains made of aryl groups, of ether groups and of keto groups. The compounds in this class of substance differ via different arrangement of the said groups and their ratio in the molecule. The PAEK here can by way of example be a polyetheretherketone (PEEK), a poly(etherketoneketone) (PEKK), a poly(etheretheretherketone) (PEEEK) or a poly(etheretherketoneketone)
 10 (PEEKK). The compounds in this class of substance have keto groups which can undergo bonding to form imine bonds. It is also possible here to use mixtures of various polyaryletherketones. It is preferable to use a single PAEK, because this can achieve high crystallinity and, associated therewith, heat resistance.

15 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 melting range from 335°C to 345°C. It has been found that PEEK which is crosslinked according to the invention has particularly advantageous properties in respect of heat resistance and mechanical stability.

20 The melt viscosity of the polyaryletherketone (PAEK) at 380°C is preferably 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 made in accordance with DIN ISO 1130, where the material is melted at 380°C and subjected to loading by a 5 kg ram, whereupon flowability is
 25 determined. 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 this melt viscosity is advantageous because according to the invention good thermoplastic processability and miscibility are achieved while it is also possible to obtain a homogeneous product with high stability, and in particular here high
 30 stiffness. It is particularly preferable here to use this PAEK, in particular PEEK with melt viscosity as mentioned above, and a quantity of from 0.1% by weight to 5% by weight of the crosslinking agent, in particular from 0.1% by weight to 1.5% by weight based on the PAEK, in particular PEEK. With this ratio and these properties of the starting materials, it is possible to achieve particularly good processability and heat resistance of the products.

In particular, stiffness is particularly high, characterized by a high tensile modulus. This PAEK, in particular PEEK, can moreover be processed at a temperature that still permits thermoplastic mixing, while excessively rapid progress of the crosslinking reaction during this process is avoided. A moulding composition is thus obtained that is amenable to very
 5 successful thermoplastic further processing.

The mixture provided in step (a) can be produced by conventional compounding processes. In these processes, the mixture is intensively mixed, preferably in the form of melt, for example in a screw-based system. The temperatures in the mixing device are
 10 preferably set in a manner such that the mixture has good processability and has a viscosity that is suitable for the compounding procedure. The compounding procedure can give an intermediate product, for example a granulate.

The mixture here is preferably produced at a temperature at which no crosslinking, or no
 15 substantial crosslinking, yet takes place. According to the invention, there is no requirement that, as in the processes described in the prior art, covalent linkage of the crosslinking agents to the PAEK by way of aminic bonding takes place at this early stage. This is advantageous because according to the invention it is possible to omit this additional reaction step, which would require precise control in order to prevent undesired
 20 further reaction of the intermediates and resultant premature crosslinking.

During the production of the mixture, intensive mixing by suitable means, for example stirring equipment or kneading equipment, takes place in order to achieve uniform distribution of the crosslinking agent in the polymer. This is very important for obtaining
 25 uniform stability properties in the material. In a preferred embodiment, production is a step of the process that takes place before step (a), in a step (a0). After production, the crosslinkable mixture is preferably further processed in step (b) without further intermediate steps that alter the composition.

30 In a particularly preferred embodiment of the invention, the mixture comprises no solvent. Surprisingly, it has been found according to the invention that mixtures of the PAEK with the crosslinking agent can be processed without use of any solvent, while intimate mixing is achieved.

The mixture is preferably heated to a temperature at which it is in liquid form. In order to obtain a homogeneous mixture, it is preferable here to select a temperature and residence time in a manner such that no significant crosslinking takes place here.

- 5 In a preferred embodiment, the crosslinking agent is added continuously to the PAEK. The components here can be in liquid or solid form. It is thus possible to obtain a particularly uniform mixture. The addition of the crosslinking agent preferably takes place here with intimate mixing, for example with stirring and/or kneading. In a preferred embodiment, the crosslinking agent is introduced in the form of a concentrate. This has the advantage of
 10 being able to improve metering of the crosslinking agent, with resultant improved uniformity of the mixture. The overall effect with continuous addition of the crosslinking agent is that a particularly homogeneous mixture may be obtained, and thus particularly well-controlled crosslinking is achieved. It is thus possible to avoid production of regions with a high or low level of crosslinking that can lead to damage to the product on exposure
 15 to thermal or mechanical stress. Particularly good properties in respect of heat resistance and mechanical stability can thus be achieved.

- The production of a moulding made of the mixture takes place in step (b). In a preferred embodiment, a thermoplastic forming process is used to produce the moulding in step (b).
 20 This means that the mixture, in non-crosslinked or at least not significantly crosslinked condition, can be moulded from the melt, since otherwise thermoplastic processing would no longer be possible. If an excessive number of crosslinking sites are present, the intermediate PAEK product is no longer flowable, and no longer readily thermoplastically mouldable. The period for which the mixture is exposed to the high processing
 25 temperatures before the shaping procedure should be short. The thermoplastic processing is therefore preferably carried out in a manner that minimizes the residence time of the mixture in the device. It is preferable here that the processing is carried out in a manner such that the substantial portion of the crosslinking reaction, for example more than 80% here, more than 90% or more than 95% of the crosslinking, takes place only after the
 30 shaping procedure, i.e. in step (c).

In a preferred embodiment, the mixture is processed, and thus subjected to a forming process, via extrusion, compression moulding and/or injection moulding in step (b). These

processes are particularly suitable for the easy and efficient processing of thermoplastic polymer compositions.

5 The extrusion here can take place by known processes. In the extrusion procedure, solid to high-viscosity-liquid curable compositions are extruded under pressure continuously from a shaping aperture (also termed die). This produces products known as extrudate with the cross section of the aperture, in theoretically any desired length. The extrusion procedure preferably takes place at a temperature of at least 320°C, preferably of at least 350°C, preferably from 320°C to 400°C, and in particular from 350°C to 390°C.

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Compression moulding is a process in which the moulding composition is introduced into the preheated cavity. A plunger is then used to close the cavity. The pressure forces the moulding composition into the shape prescribed by the mould. The compression moulding procedure preferably takes place at a temperature of at least 300°C, preferably at least 350°C, preferably from 320°C to 400°C, and in particular from 350°C to 400°C.

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Injection moulding (or injection-moulding process) is a shaping process used in plastics processing. Here, an injection-moulding machine is used to plastify the plastic, which is injected under pressure into a mould, the injection mould. Within the mould, cooling causes the material to return to the solid state, and after opening of the mould it is removed in the form of moulding. The cavity of the mould here determines the shape and surface structure of the product.

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Particular preference is given to processing via extrusion followed by injection moulding. If the mixture of the PAEK with the crosslinking agent is not already liquid, it is melted in these processes.

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

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In step (c), the moulding is thermally treated at a temperature at which PAEK is crosslinked, and the crosslinked moulding is thus obtained. By this means, the PAEK can be intermolecularly crosslinked by the crosslinking agent. The temperature during step (c)

can be set to be relatively high, because the crosslinking agents that can be used according to the invention have relatively high melting points and boiling points. This is advantageous because high temperature generally assists these crosslinking reactions. However, the temperature is preferably below the melting range of PAEK.

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Surprisingly, it has been found that in the system according to the invention the crosslinking reactions actually take place below the melting range of the polymer and of the moulding. This was unexpected, because it is generally assumed that crosslinking reactions take place only at temperatures above the melting range of the polymer and of

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In the prior art, it is moreover assumed that crosslinking reactions of this type take place relatively rapidly within minutes or a few hours. However, it has been found according to the invention that the crosslinked PAEK can have particularly advantageous properties

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when the heating of the moulding in step (c) is carried out over a prolonged period, preferably of at least 6 hours, for example of from 6 hours to 30 days. It has been found that this type of thermal treatment can substantially improve thermal stability and mechanical stability.

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In particular, it has been found that the thermal treatment can improve stiffness of samples at elevated temperatures. It has been observed here that thermal treatment for a defined period can significantly improve stiffness, whereupon then saturation can occur, resulting in no, or only insubstantial, improvement of stiffness on further thermal post-treatment. However, further thermal post-treatment is found to improve heat resistance. It has been

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found that heat resistance can also rise during prolonged thermal post-treatment, and therefore that even after 14 days it is still possible to observe a significant improvement.

In a preferred embodiment, the moulding obtained in step (b) is subjected to thermal treatment for at least 6 h, in particular for more than 2 days or for more than 2.5 days. In a

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preferred embodiment of the invention, the thermal treatment is carried out over a period of from 2 to 30 days, in particular for from 2.5 to 20 days. This is advantageous because it is possible to improve the homogeneity of the products and thus thermal, and mechanical stability. The thermal treatment preferably takes place with 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 from 280°C to 415°C, particularly preferably from 300°C to 400°C. At these temperatures, efficient three-dimensional crosslinking can proceed sufficiently rapidly without any impairment of the thermoplastically produced items, for example due to the decomposition and/or undesired deformation of the mouldings.

After crosslinking, the mouldings are cooled and can be available for use or can be further processed.

The mixture, and the moulding, can comprise conventional additives. By way of example, it is possible for a quantity of up to 20% by weight of additives, for example from 0.1% by weight to 20% by weight or from 0.1% by weight to 18% by weight, based in each case on the total weight of mixture and/or moulding. Examples of conventional additives are dyes and processing aids.

The mixture and the moulding can comprise conventional fillers, for example in particular tribologically active and/or flexibilizing fillers, and/or reinforcing fibres. By way of example, it is possible for a quantity of up to 80% by weight of the fillers, for example from 0.1% by weight to 80% by weight or from 0.1% by weight to 60% by weight, based in each case on the total weight of the mixture and/or moulding.

The invention also provides a moulding which is based on polyaryletherketones (PAEK) and which has a crosslinked matrix made of PAEK, where the PAEK has been crosslinked with a linker L that is a diphenyl moiety in which the two phenyl rings have bonding to one another by way of an aliphatic group comprising a carbocyclic moiety, where the PAEK has bonding by way of imine bonds to the phenyl rings of the linker.

The moulding is in particular obtainable via the processes according to the invention, which are described in the context of this invention. The moulding preferably has the advantageous properties which are described for the crosslinked PAEK in the context of this invention. In the context of this invention, the term moulding means products made of crosslinked PAEK which have a defined three-dimensional shape. There is no requirement here that the moulding is a defined article; it can by way of example also

instead be a coating. The moulding can consist of the crosslinked PAEK or comprise the same, for example in the form of composite material or laminate.

The mouldings according to the invention can have advantageous, increased stiffness values, characterized by a high tensile modulus. The tensile modulus of the moulding is preferably at least 350 MPa, in particular at least 400 MPa, and particularly preferably at least 450 MPa. In particular, the tensile modulus is from 350 MPa to 600 MPa or from 400 MPa to 550 MPa. The tensile modulus is preferably determined at 240°C in accordance with DIN EN ISO 527-2.

It can be desirable to avoid complete crosslinking of the polymer in the moulding, because the tensile strain at break of the material can decrease with increasing crosslinking. The degree of crosslinking is therefore preferably established with a view to the desired use, for example by way of the proportion of the crosslinking agent and the nature and duration of the thermal treatment.

It is preferable here instead of direct measurement of the degree of crosslinking to use suitable test methods, for example a high-temperature tensile test, to determine whether the moulding has the desired properties. In the case of very high temperatures, determination of the dynamic modulus is an attractive possibility.

The mouldings can in particular be used in technical sectors which require high heat resistance and mechanical stability, and at the same time in particular high stiffness. They are suitable in particular for applications as sealing items, in particular sealing rings and O-rings, bushes, bearings, back-up rings, valves, thrust washers, snap hooks, tubes or conduits, cables, sheaths and jackets, or housings for an electrical or chemical application, or as constituent thereof. They are in particular suitable for uses which require high chemicals resistance and resistance to abrasion. This relates in particular to applications in oil and gas production, aerospace engineering and chemical industry, and thereby in the production of parts relevant to safety, and to the field of energy generation and the automobile industry. Other conceivable applications are connectors and insulators in the electronics sector, because the crosslinking leads to good insulation properties.

The invention also provides a sealing item consisting of or comprising a moulding according to the invention. The sealing item can be useful for static or dynamic applications and in particular here for dynamic applications in which it has exposure to high mechanical loads. In particular, the sealing item is suitable for sealing applications in which it is in contact with fluids, for example lubricants, and in which it has exposure to high temperatures, for example above 150°C, and in particular in the range from 180°C to 400°C.

The processes, mouldings and sealing items according to the invention achieve the object on which the invention is based. They have high heat resistance and high mechanical stability in conjunction with good processability. In particular, the mouldings have high glass transition temperature and high stiffness, in particular above the glass transition temperature. The high stiffness is attended by reduced creep at high temperatures. The improved heat resistance is apparent not only from the maximal temperature but also from the long-term service temperature, in particular in the range from 150°C to 400°C. The mouldings also exhibit advantageous elastomeric behaviour at high temperature. The products here exhibit very good chemicals resistance and reduced combustibility because, on account of the crosslinking, the material does not melt and does not produce any burning drops.

The mouldings according to the invention can moreover be produced in a simple and efficient manner via thermoplastic shaping processes. By way of example, production can thus be achieved via simple extrusion. The processes are moreover environmentally friendly and can be carried out without risk to users, because the crosslinking agents used have relatively high boiling points and low volatility.

Brief description of the Figures

Figure 1 shows the development, with rising temperature, of the complex dynamic module of a moulding of the invention (PEEK with 1.05% of DAPI, thermally treated, broken-line curve) in comparison with the standard main material (PEEK without thermal treatment, continuous line), and also in comparison with another material (PEEK, 4% AF-PEEK, thermally treated, dotted line).

Figure 2 shows the development, with rising temperature, of the complex dynamic module of the moulding 4 of the invention (PEEK with 1% of DAPI (CAS No. 68170-20-7), thermally treated, broken-line curve) in comparison with the standard main material 1 (PEEK without thermal treatment, continuous line),

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Examples

Example 1

- 10 Mixtures are produced as indicated in Table 1. Amine-functionalized PEEK (hereinafter termed "AF PEEK") is produced by using PEEK and *p*-phenylenediamine according to Thompson and Farris, 1988 and, after extraction to remove all diphenyl sulfone and unreacted *p*-phenylenediamine, ground to give powder. Determination of total nitrogen content by the Kjeldahl method reveals 95% conversion of the carbonyl groups of the
- 15 PEEK. DAPI (CAS No. 54628-89-6), purity 98%, was used as crosslinking agent.

Table 1: Mixtures

Ex. No.	Compound
1 (Comparison)	PEEK
2 (Comparison)	PEEK, 4% by weight of AF PEEK
3	PEEK, 1.05% by weight of DAPI

- The mixtures from Table 1 are processed by injection moulding to give test samples and
- 20 then subjected to thermal treatment for crosslinking.

Table 2: Thermal treatment and results of tensile strain test

Ex.	Compound	Thermal Treatment	Yield point	Tensile strength	Tensile strain at break	Tensile modulus
No.			[MPa]	MPa	%	[MPa]
1	PEEK, no addition	without	14.5	47.0	274	211
2 a	PEEK, 4% of AF PEEK	without	18.5	41.0	204	241
2 b	PEEK, 4% of AF PEEK	with	25.2	25.2	20.8	310
3	PEEK, 1.05% of DAPI	with	28.1	30.8	97	505

The tensile tests are carried out at 240°C in accordance with the standard DIN EN ISO 527-2.

The results reveal that thermal treatment prevents possible melting of the sample according to the invention, and that the tensile modulus of elasticity rises. This clearly reveals the advantage of the homogeneity of the DAPI-crosslinked samples in contrast to the inhomogeneity of the AF PEEK-crosslinked PEEK.

Dynamic-mechanical analysis (DMA)

Dynamic-mechanical analysis (DMA) is a thermal method for determining the physical properties of plastics. The temperature gradient (temperature sweep) reveals the changes in dynamic modulus and thus likewise in stiffness over the temperature range tested. Important factors here are especially the glass transition range (T_g), the height of the plateau above the T_g , the position of the modulus decrease on melting of the crystalline phase, and also the height of the plateau at high temperature.

This was carried out with thermally treated mouldings according to the Examples described above (see Table 1). The temperature gradients were measured under the following conditions by using sample strips (width about 3 mm, thickness about 3 mm): heating rate 3 K/min, contact force 3N, average tensile strain 0.5%, tensile strain amplitude +/- 0.1%. FIG. 1 shows the results in a graph.

Figure 1 shows the development, with rising temperature, of the complex dynamic module of the moulding 3 of the invention (PEEK with 1.05% of DAPI, thermally treated, broken-line curve) in comparison with the standard main material (PEEK without thermal treatment, continuous line),

Presented as further reference is the complex dynamic module, plotted against temperature, of another material 2b (PEEK, 4% of AF-PEEK, thermally treated, dotted line) crosslinked from standard PEEK by thermal post-treatment crosslinking with 4% of AF-PEEK. This AF-PEEK was produced by the method described by Thompson and Farris, and also by Yurchenko et al., by modification of PEEK.

The results reveal that the PEEK crosslinked according to the invention have advantageous thermal properties. All the mouldings according to the invention here achieved improvements in the glass transition range (T_g), in the height of the plateau above T_g , and also in respect of the modulus decrease on melting of the crystalline phase, and also in respect of the height of the plateau at high temperature. Glass transition temperature is increased in a manner similar to stiffness at high temperature, in particular in the range above 150°C. The results also reveal that in particular in the case of the combination of DAPI with PEEK ideal product properties can be achieved in respect of the magnitude of the modulus and magnitude of the heat resistance value. A lengthened period of thermal treatment can provide a further considerable improvement of thermal properties.

Example 2

The DAPI isomer mixture with the CAS number 68170-20-7 (crosslinking agent with the formula VI) is mixed as in the preceding Example 1 into a commercially available PEEK of moderate viscosity by means of a twin-screw compounder, and the strand is chopped to give a granulate.

Table 3: Mixtures

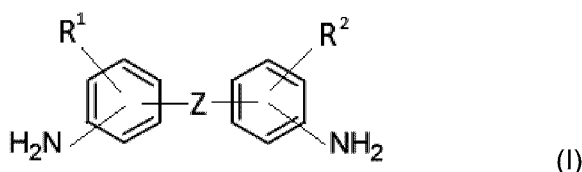
Example number	Compounded material
1 (Comparison)	PEEK
4	PEEK + DAPI, CAS No. 68170-20-7, thermally treated

- 10 The granulates made from the mixtures of Table 3 are injection-moulded to give test samples and then likewise subjected to a thermal post-treatment.
- The samples are tested as in Example 1 by DMA in temperature sweep, giving the result depicted in Figure 2.
- 15 Figure 2 shows the development, with rising temperature, of the complex dynamic module of the moulding 4 of the invention (PEEK with 1% of DAPI (CAS No. 68170-20-7), thermally treated, broken-line curve) in comparison with the standard main material 1 (PEEK without thermal treatment, continuous line),
- 20 Here again, the advantageous results obtained are comparable to those discussed in relation to Figure 1.

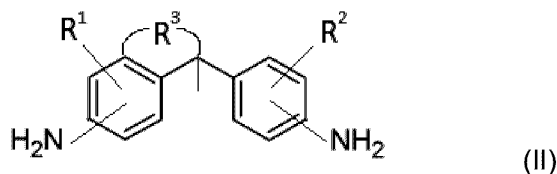
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Claims

1. Process for the production of a crosslinked moulding comprising polyaryletherketones (PAEK), comprising the steps of:
 - (a) provision of a mixture comprising a PAEK and a crosslinking agent,
 - (b) production of a moulding made of the mixture, and
 - (c) thermal treatment of the moulding at a temperature at which PAEK is crosslinked, with resultant production of the crosslinked moulding, and
 where the crosslinking agent is a di(aminophenyl) compound in which the two aminophenyl rings have bonding to one another by way of an aliphatic group comprising a carbocyclic moiety.
2. Process according to Claim 1, where the crosslinking agent is an annellated compound in which one of the two phenyl rings has been annellated with the carbocyclic moiety.
3. Process according to at least one of the preceding claims, where the crosslinking agent is a 4,4'-diaminodiphenyl compound and/or an asymmetric compound.
4. Process according to at least one of the preceding claims, where the crosslinking agent is a compound of the general formula (I):



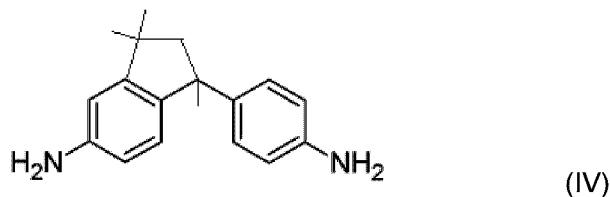
- where R^1 and R^2 are selected mutually independently from H, substituted or unsubstituted alkyl having from 1 to 20 carbon atoms, in particular having from 1 to 4 carbon atoms, in particular methyl or ethyl, substituted or unsubstituted aryl having from 5 to 12 carbon atoms, F and Cl, and where Z is the aliphatic group comprising a carbocyclic moiety.
5. Process according to Claim 4, where the crosslinking agent is a compound of the general formula (II):



where R^1 and R^2 are selected mutually independently from H, substituted or unsubstituted alkyl having from 1 to 20 C atoms, in particular having from 1 to 4 C atoms, in particular methyl or ethyl, substituted or unsubstituted aryl having from 5 to 12 C atoms, F and Cl, and

where R^3 is a carbocyclic moiety which comprises from 2 to 3 ring carbon atoms and which can have substitution by at least one alkyl group having from 1 to 4 carbon atoms, in particular methyl or ethyl.

6. Process according to Claim 5, where the crosslinking agent is a compound of the formula (IV):



7. Process according to at least one of the preceding claims, where the polyaryletherketone (PAEK) is a polyetheretherketone (PEEK).

8. Process according to at least one of the preceding claims, where the melt viscosity of the polyaryletherketone (PAEK) at 380°C is in the range from 5 cm³/10 min to 250 cm³/10 min, measured in accordance with DIN ISO 1130.

9. Process according to at least one of the preceding claims, where the mixture comprises no solvent.

10. Process according to at least one of the preceding claims, where the temperature in step (b) is at least 300°C.

11. Process according to at least one of the preceding claims, where the mixture is processed in step (b) via extrusion, compression moulding and/or injection moulding.
12. Process according to Claim 11, where the moulding obtained in step (b) is subjected in
5 step (c) to a thermal treatment for at least 6 h.
13. Process according to Claim 12, where the thermal treatment in step (c) takes place at a temperature of at least 250°C.
- 10 14. Moulding based on polyaryletherketones (PAEK) which comprises a crosslinked matrix made of PAEK,
where the PAEK has been crosslinked with a linker L that is a diphenyl moiety in which the two phenyl rings have bonding to one another by way of an aliphatic group comprising a carbocyclic moiety,
15 where the PAEK has bonding by way of imine bonds to the phenyl rings of the linker,
where the moulding in particular is obtainable via a process according to at least one of Claims 1 to 13.
15. Sealing items, thrust washers, back-up rings, valves, connectors, insulators, snap
20 hooks, bearings, bushes, sealing rings and O-rings, tubes and conduits, cables, sheaths and jackets, and housings for electrical or chemical use, consisting of or comprising a moulding according to Claim 14.

Figure 1:

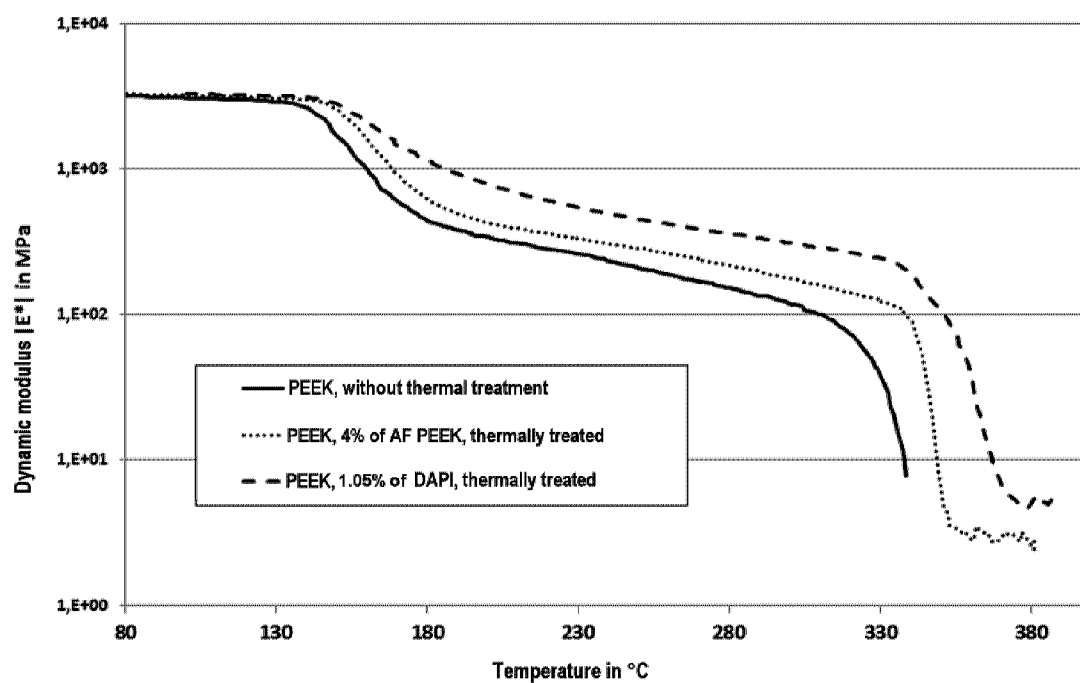
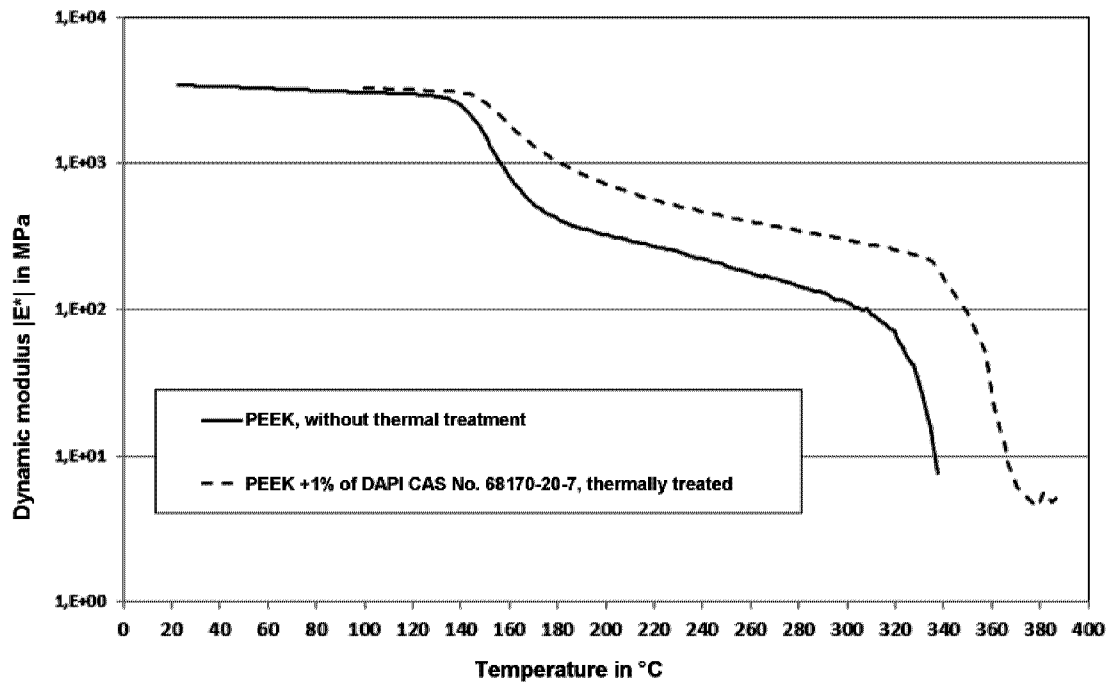
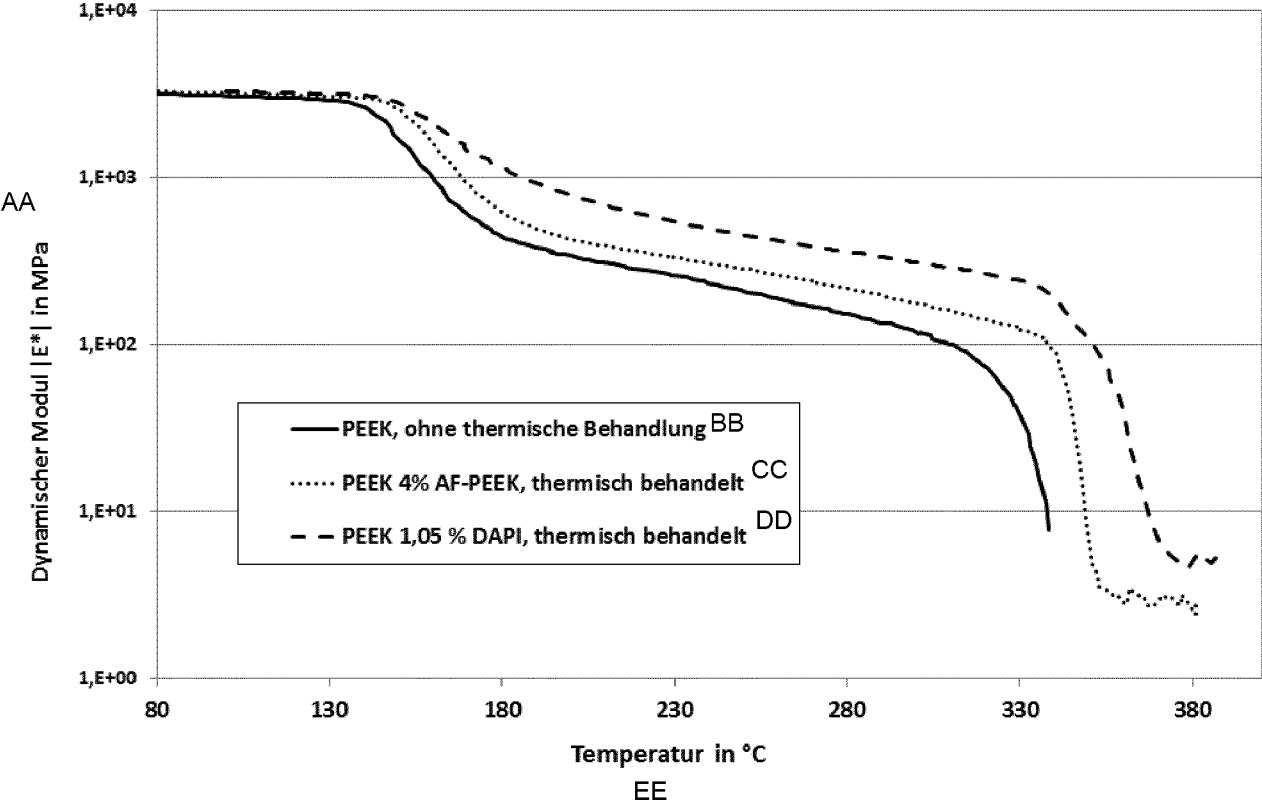


Figure 2:



Figur 1:



- AA Dynamic modulus E^* in MPa
BB PEEK without thermal treatment
CC PEEK 4% AF-PEEK, thermally treated
DD PEEK, 1.05% DAPI, thermally treated
EE Temperature in °C