

POLYMERIC MATERIALS

This invention relates to polymeric materials and particularly, although not exclusively, relates to compositions and composite materials which comprise a polymeric material.

It is well known to compound polymeric materials with fillers in order to provide composite materials having properties which are improved, at least in some respects, over the polymeric materials alone. For example, a polyaryletherketone such as polyetheretherketone is compounded with up to 30 wt% of glass fibres or carbon fibres. Such materials have been commercially available for many years from Victrex Plc under the names VICTREX PEEK 150GL30 and 150CA30 respectively. These materials include polyetheretherketone having an MV of 0.15 kNsm^{-2} and 30 wt% of fibrous filler.

It is difficult to incorporate greater than 30 wt% of filler materials into a polymeric material such as polyetheretherketone because the molten composite is too viscous for standard melt processing equipment and/or due to difficulties in fully wetting out filler materials. These problems have been addressed in the prior art as discussed further below.

US 4541884 (Cogswell) recognises the difficulties associated with achieving rapid impregnation of a fibre tow or roving if the viscosity of the melt of a polymer used is too high. The problem is solved by drawing a plurality of continuous filaments through a melt comprising a mixture of a thermoplastic polymer and a

relatively high level of plasticizer for the polymer which is thermally stable but which can be volatilised from the composition. Use of the plasticizer plasticizes the polymer in the melt and gives a melt of reduced viscosity compared with the melt viscosity of the polymer alone. The document describes, in Example 1, the use of a mixture of polyetheretherketone (70 wt%) having a MV of 110 Ns/m² and diphenylsulphone (30 wt%) as plasticizer; and also in Example 3, the use of polyetheretherketone (100 parts by weight (pbw)) having a MV of 25 Ns/m², and diphenylsulphone (100 pbw). Fibre loadings as high as 69 wt% are described. Disadvantageously, use of the process described requires use (and disposal of) large amounts of plasticizer with consequential increased costs of the process.

US 5213889 (Cogswell) solves the same problem by using a thermoplastic polymer having a very low melt viscosity, of less than 30 Ns/m² and preferably in the range 1 to 10 Ns/m² to enable wetting of the filaments. The disclosure envisages processing steps to increase the molecular weight of the polymer, after preparation of the composite, to improve its properties.

More recently, US 5844036 (Hughes) has addressed the problem of providing highly filled composites of polyaryletherketones to improve their properties. The solution involves using a polyaryletherketone matrix and two types of fillers each said to provide unique properties. The first filler is a reinforcing filler which provides high strength and stiffness. The second filler is a non-thermoplastic immobilizing filler to immobilise the amorphous portion of the partially crystalline

polyaryletherketone polymer and provide resistance to high temperature absorption. The document describes the use of polyetheretherketone grade PEEKTM 150FP from ICI Victrex which has an MV of 0.15 kNsm⁻². Disadvantageously, Hughes
5 is limited in its application to the use of two different types of fillers having two specific properties described.

It is an object of the present invention to address problems associated with polymeric materials and
10 particularly, although not exclusively, with filled composite materials.

According to a first aspect of the invention, there is provided a method of preparing a composite material, the
15 method comprising:

- (i) selecting polymeric material having a melt viscosity (MV) in the range 0.05 to 0.12 kNsm⁻²;
- (ii) contacting said polymeric material having said
20 MV in the range 0.05 to 0.12 kNsm⁻² with a filler means;

wherein said polymeric material is of a type which includes: unsubstituted phenyl moieties, carbonyl moieties
25 and ether moieties in the polymeric backbone of said polymeric material.

MV is suitably measured using capillary rheometry operating at 400°C at a shear rate of 1000s⁻¹ using a
30 tungsten carbide die, 0.5x3.175mm.

Although the invention is described in terms of MV this may be equated approximately to IV (measured as described in EP0001879B) in accordance with figure 1 hereinafter.

5 In the method at least 1 kg, preferably at least 5 Kg, more preferably at least 10 Kg, especially at least 25 Kg of said polymeric material is selected. In the method, at least 1 Kg, preferably at least 5 Kg, more preferably at least 10 Kg, especially at least 25 kg of said filler
10 means is selected.

Suitably at least 5 kg (preferably at least 10 kg, especially at least 25 kg) of said polymeric material is selected and contacted with at least 5 kg (preferably at
15 least 10 kg, especially at least 25 kg) of said filler means.

In the method a batch of composite material may be prepared having a weight of at least 10 kg, preferably at
20 least 20 kg, especially at least 50 kg.

The method may comprise forming said composite material into a particulate form, for examples granules or pellets. The particulate form may comprise particles having an
25 average weight of at least 0.5mg, preferably at least 1.0mg, more preferably at least 1.5mg. The average weight may be less than 100mg, suitably less than 60mg, preferably less than 40mg.

30 The particulate form may have an average volume in the range 5 to 100mm³, preferably 10 to 50mm³, more preferably 15 to 35mm³.

The mass of composite material in said particulate form may be provided in a pack. Said pack may contain at least 10,000 suitably at least 50,000, preferably at least 250,000 particles of said composite material in said
5 particulate form. The pack may contain less than 1,000,000 particles.

Said polymeric material suitably has a MV of at least 0.06 kNsm^{-2} , preferably has a MV of at least 0.07 kNsm^{-2} , more
10 preferably at least 0.08 kNsm^{-2} .

Said polymeric material may have a MV of less than 0.11 kNsm^{-2} , preferably less than 0.10 kNsm^{-2} .

15 Said polymeric material may have a MV in the range 0.07 to 0.12 kNsm^{-2} , preferably in the range 0.08 to 0.11 kNsm^{-2} , more preferably in the range 0.08 to 0.10 kNsm^{-2} .

20 Said polymeric material preferably has a MV in the range 0.07 to 0.10 kNsm^{-2} , more preferably in the range 0.08 to 0.10 kNsm^{-2} , especially in the range 0.085 to 0.095 kNsm^{-2} .

Said polymeric material may have a tensile strength,
25 measured in accordance with ASTM D790 of at least 80 MPa. The tensile strength is preferably in the range 80-110 MPa, more preferably in the range 80-100 MPa.

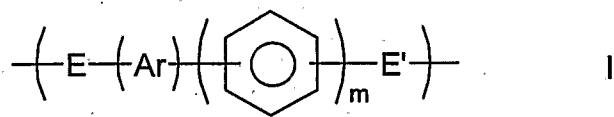
Said polymeric material may have a flexural strength,
30 measured in accordance with ASTM D790 of at least 145 MPa. The flexural strength is preferably in the range 145-180 MPa, more preferably in the range 145-165 MPa.

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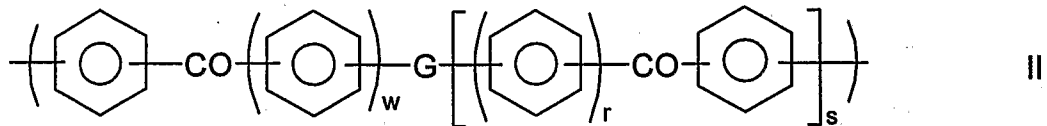
Said polymeric material may have a flexural modulus, measured in accordance with ASTM D790, of at least 3.5 GPa. The flexural modulus is preferably in the range 3.5-4.5 GPa, more preferably in the range 3.5-4.1 GPa.

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Preferably, said polymeric material has a moiety of formula



10 and/or a moiety of formula

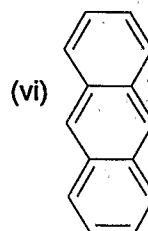
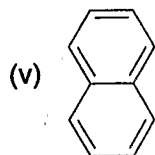
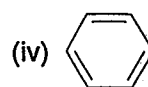
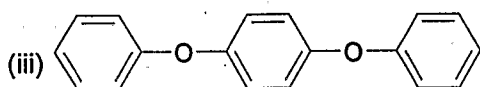
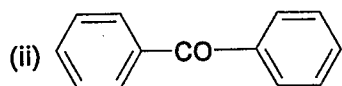
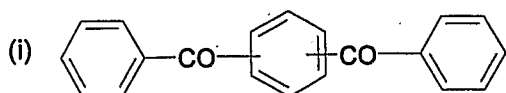


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wherein m, r, s and w independently represent zero or a positive integer, E and E' independently represent an oxygen atom or a direct link, G represents an oxygen atom, a direct link or a -O-Ph-O- moiety where Ph represents a phenyl group and Ar is selected from one of the following moieties (i) to (vi) which is bonded via one or more of its phenyl moieties to adjacent moieties

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Unless otherwise stated in this specification, a phenyl moiety has 1,4-, linkages to moieties to which it is bonded.

In (i), the middle phenyl may be 1,4- or 1,3-substituted. It is preferably 1,4-substituted.

10 Said polymeric material may include more than one different type of repeat unit of formula I; and more than one different type of repeat unit of formula II. Preferably, however, only one type of repeat unit of formula I or II is provided.

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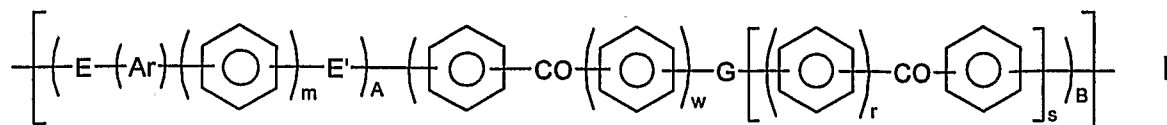
Said moieties I and II are suitably repeat units. In the polymeric material, units I and II are suitably bonded to

one another - that is, with no other atoms or groups being bonded between units I and II.

Where w is greater than zero, the respective phenylene moieties may independently have 1,4- or 1,3-linkages to the other moieties in the repeat units of formulae II. Preferably, said phenylene moieties have 1,4- linkages.

Suitably, "a" represents the mole % of units of formula I in said polymeric material, suitably wherein each unit I is the same; and "b" represents the mole % of units of formula II in said polymeric material, suitably wherein each unit II is the same. Preferably, a is in the range 45-100, more preferably in the range 45-55, especially in the range 48-52. Preferably, b is in the range 0-55, more preferably in the range 45-55, especially in the range 48-52. Preferably, the ratio of a to b is in the range 0.9 to 1.1 and, more preferably, is about 1. Suitably, the sum of a and b is at least 90, preferably at least 95, more preferably at least 99, especially about 100. Preferably, said polymeric material consists essentially of moieties I and II.

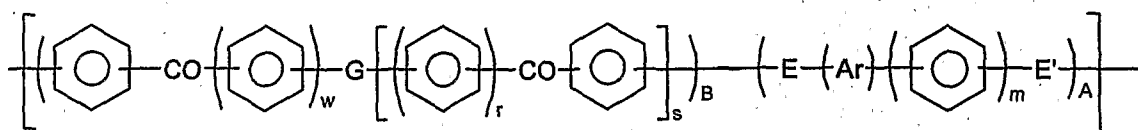
Said polymeric material may be a homopolymer having a repeat unit of general formula



or a random or block copolymer of at least two different units of IV, wherein A and B independently represent 0 or 1

and E, E', G, Ar, m, r, s and w are as described in any statement herein.

As an alternative to a polymeric material comprising
 5 unit(s) IV discussed above, said polymeric material may be a homopolymer having a repeat unit of general formula



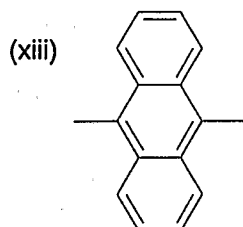
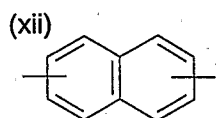
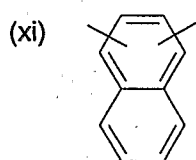
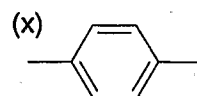
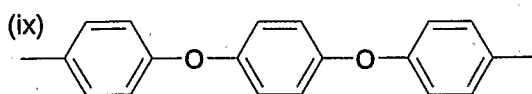
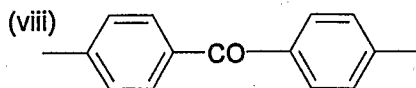
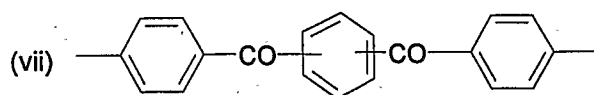
or a random or block copolymer of at least two different
 10 units of IV* wherein A and B, independently represent 0 or 1 and E, E', G, Ar, m, r, s and w are as described in any statement herein.

Preferably, m is in the range 0-3, more preferably 0-2,
 15 especially 0-1. Preferably, r is in the range 0-3, more preferably 0-2, especially 0-1. Preferably, s is 0 or 1. Preferably, w is 0 or 1.

Preferably, said polymeric material is a homopolymer having
 20 a repeat unit of general formula IV.

Preferably Ar is selected from the following moieties (vii) to (xiii):

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In (vii), the middle phenyl may be 1,4- or 1,3-substituted. It is preferably 1,4-substituted.

- 5 Preferably, (xi) is selected from a 1,2-, 1,3-, or a 1,5-moiety; and (xii) is selected from a 1,6-, 2,3-, 2,6- or a 2,7- moiety.

Suitable moieties Ar are moieties (i), (ii), (iii) and (iv)
 10 and, of these, moieties (i), (ii) and (iv) are preferred.
 Other preferred moieties Ar are moieties (vii), (viii),

(ix) and (x) and, of these, moieties (vii), (viii) and (x) are especially preferred.

An especially preferred class of polymeric material are
5 polymers (or copolymers) which consist essentially of
phenyl moieties in conjunction with ketone and/or ether
moieties. That is, in the preferred class, the polymeric
material does not include repeat units which include -S-, -
SO₂- or aromatic groups other than phenyl. Preferred
10 polymeric materials of the type described include:

(a) a polymer consisting essentially of units of
formula IV wherein Ar represents moiety (iv), E
and E' represent oxygen atoms, m represents 0, w
15 represents 1, G represents a direct link, s
represents 0, and A and B represent 1 (i.e.
polyetheretherketone).

(b) a polymer consisting essentially of units of
20 formula IV wherein E represents an oxygen atom, E'
represents a direct link, Ar represents a moiety
of structure (i), m represents 0, A represents 1,
B represents 0 (i.e. polyetherketone);

(c) a polymer consisting essentially of units of
25 formula IV wherein E represents an oxygen atom, Ar
represents moiety (i), m represents 0, E'
represents a direct link, A represents 1, B
represents 0, (i.e. polyetherketoneketone).

30 (d) a polymer consisting essentially of units of
formula IV wherein Ar represents moiety (i), E and
E' represent oxygen atoms, G represents a direct

link, m represents 0, w represents 1, r represents 0, s represents 1 and A and B represent 1. (i.e. polyetherketoneetherketoneketone).

5 (e) a polymer consisting essentially of units of formula IV, wherein Ar represents moiety (iv), E and E' represents oxygen atoms, G represents a direct link, m represents 0, w represents 0, s, r, A and B represent 1 (i.e. polyetheretherketoneketone).

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(f) a polymer comprising units of formula IV, wherein Ar represents moiety (iv), E and E' represent oxygen atoms, m represents 1, w represents 1, A represents 1, B represents 1, r and s represent 0 and G represents a direct link (i.e. polyether-diphenyl-ether-phenyl-ketone-phenyl-).

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Said polymeric material is preferably semi-crystalline.

20 The level and extent of crystallinity in a polymer is preferably measured by wide angle X-ray diffraction (also referred to as Wide Angle X-ray Scattering or WAXS), for example as described by Blundell and Osborn (Polymer 24, 953, 1983). Alternatively, crystallinity may be assessed

25 by Differential Scanning Calerimetry (DSC).

The level of crystallinity in said polymeric material may be at least 1%, suitably at least 3%, preferably at least 5% and more preferably at least 10%. In especially

30 preferred embodiments, the crystallinity may be greater than 30%, more preferably greater than 40%, especially greater than 45%.

The glass transition temperature (T_g) of said polymeric material may be at least 140°C, suitably at least 144°C. In some cases it may be greater than 154°C, 160°C, 164°C, 170°C, 190°C or greater than 250°C or even 300°C. In a preferred embodiment, the glass transition temperature is in the range 140°C to 145°C.

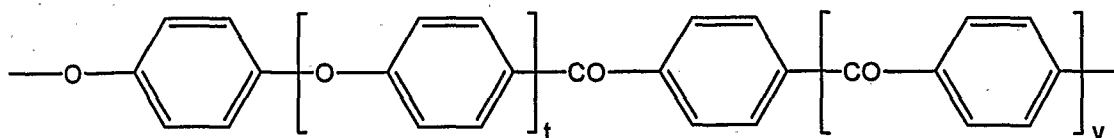
The main peak of the melting endotherm (T_m) for said polymeric material (if crystalline) may be at least 300°C.

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Said polymeric material may consist essentially of one of units (a) to (f) defined above. Alternatively, said polymeric material may comprise a copolymer comprising at least two units selected from (a) to (f) defined above.

15 Preferred copolymers include units (a). For example, a copolymer may comprise units (a) and (f); or may comprise units (a) and (e).

Said polymeric material preferably comprises, more preferably consists essentially of, a repeat unit of formula



25 where t and v independently represent 0 or 1. Preferred polymeric materials have a said repeat unit wherein either $t=1$ or $v=0$; $t=0$ and $v=0$; or $t=0$ and $v=1$. More preferred have $t=1$ and $v=0$; or $t=0$ and $v=0$. The most preferred has $t=1$ and $v=0$.

30

In preferred embodiments, said polymeric material is selected from polyetheretherketone, polyetherketone and polyetherketoneketone. In a more preferred embodiment, said polymeric material is selected from polyetherketone
5 and polyetheretherketone. In an especially preferred embodiment, said polymeric material is polyetheretherketone.

Said filler means may include a fibrous filler or a non-
10 fibrous filler. Said filler means may include both a fibrous filler and a non-fibrous filler.

A said fibrous filler may be continuous or discontinuous. In preferred embodiments a said fibrous filler is
15 discontinuous.

A said fibrous filler may be selected from inorganic fibrous materials, non-melting and high-melting organic fibrous materials, such as aramid fibres, and carbon
20 fibre.

A said fibrous filler may be selected from glass fiber, carbon fibre, asbestos fiber, silica fiber, alumina fiber, zirconia fiber, boron nitride fiber, silicon nitride
25 fiber, boron fiber, fluorocarbon resin fibre and potassium titanate fiber. Preferred fibrous fillers are glass fibre and carbon fibre.

A fibrous filler may comprise nanofibres.
30

A said non-fibrous filler may be selected from mica, silica, talc, alumina, kaolin, calcium sulfate, calcium carbonate, titanium oxide, ferrite, clay, glass powder,

zinc oxide, nickel carbonate, iron oxide, quartz powder, magnesium carbonate, fluorocarbon resin, graphite, carbon powder, nanotubes and barium sulfate. The non-fibrous fillers may be introduced in the form of powder or flaky particles.

Said composite material could be prepared as described in PCT/GB2003/001872, the contents of which are incorporated herein by reference. Preferably, in the method, said polymeric material and said filler means are mixed at an elevated temperature, suitably at a temperature at or above the melting temperature of said polymeric material. Thus, suitably, said polymeric material and filler means are mixed whilst the polymeric material is molten. Said elevated temperature is suitably below the decomposition temperature of the polymeric material. Said elevated temperature is preferably at or above the main peak of the melting endotherm(T_m) for said polymeric material. Said elevated temperature is preferably at least 300°C and more preferably is at least 350°C. Advantageously, the molten polymeric material can readily wet the filler and/or penetrate consolidated fillers, such as fibrous mats or woven fabrics, so the composite material prepared comprises the polymeric material and filler means which is substantially uniformly dispersed throughout the polymeric material.

The composite material may be prepared in a substantially continuous process. In this case polymeric material and filler means may be constantly fed to a location wherein they are mixed and heated. An example of such a continuous process is extrusion. Another example (which may be particularly relevant wherein the filler means comprises a

fibrous filler) involves causing a continuous filamentous mass to move through a melt comprising said polymeric material. The continuous filamentous mass may comprise a continuous length of fibrous filler or, more preferably, a plurality of continuous filaments which have been consolidated at least to some extent. The continuous fibrous mass may comprise a tow, roving, braid, woven fabric or unwoven fabric. The filaments which make up the fibrous mass may be arranged substantially uniformly or randomly within the mass.

Alternatively, the composite material may be prepared in a discontinuous process. In this case, a predetermined amount of said polymeric material and a predetermined amount of said filler means may be selected and contacted and a composite material prepared by causing the polymeric material to melt and causing the polymeric material and filler means to mix to form a substantially uniform composite material.

The composite material may be formed into a particulate form for example into pellets or granules. Pellets or granules may have a maximum dimension of less than 10mm, preferably less than 75mm, more preferably less than 50mm.

Preferably, said filler means comprises one or more fillers selected from glass fibre, carbon fibre, carbon black and a fluorocarbon resin. More preferably, said filler means comprises glass fibre or carbon, especially discontinuous, for example chopped, glass fibre or carbon fibre. Preferred discontinuous fibres have an average length before contact with the polymeric material, of less than 10mm, preferably less than 7mm. The average length

may be greater than 1mm, preferably greater than 2mm. Preferably, a fibrous filler means consists essentially of fibers having a length, before contact with the polymeric material, of less than 10mm.

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Said composite material may comprise one or more different polymeric materials of a type described above with MV as described. Preferably, said composite material comprises only a single type of polymeric material. Said single
10 type is preferably polyetheretherketone.

Said composite material suitably includes 70wt% or less, suitably 65 wt% or less, preferably 55 wt% or less, more preferably 45 wt% or less, especially 35 wt% or less of
15 said polymeric material (especially polyetheretherketone). Said composite material suitably includes at least 35 wt%, preferably at least 45 wt%, more preferably at least 55 wt%, especially at least 65 wt% of filler means which may include different types of fillers (in which case the wt%
20 refers to the sum of the wt% of each filler present), but preferably comprises the same type of filler.

Said composite material suitably includes 20 to 60wt% of polymeric material having a MV as described, (which is
25 preferably a single type of polymeric material, especially polyetheretherketone) and 40 to 60wt% of filler means. Preferably, said composite material comprises 20 to 50wt% of polymeric material and 50 to 80wt% of filler means. More preferably, said composite material comprises 20 to
30 45wt% of polymeric material and 55 to 80wt% of filler means.

The ratio of the wt% of said polymeric material having a MV as described to the wt% of filler means may be in the range 0.6 to 1.6, preferably 0.65 to 1.5. Preferably the ratio of the wt% of said polymeric material having a MV as described is 1, or preferably less than 1.

A mixture, prepared after contacting said polymeric materials and said filler means suitably includes less than 1 wt%, preferably less than 0.9 wt%, more preferably less than 0.7 wt%, especially less than 0.5 wt% of a plasticizer for the polymeric material (e.g. a material which will enable a melt to be obtained from a said polymeric material having a lower melt viscosity than that of the polymeric material alone measured under the same conditions), for example diphenylsulphone. Preferably, in the method, substantially no plasticizer, for example diphenylsulphone, is added to either the polymeric material or a mixture comprising said polymeric material.

A mixture, prepared after contacting said polymeric material and said filler means, suitably includes less than 0.005 parts by weight (pbw) of an alkaline salt of a Group I or Group II metal per 100 pbw of said polymeric material. Said mixture preferably does not include any salt present at concentrations of greater than 0.005 pbw per 100 pbw of said polymeric material. Preferably, said mixture includes less than 0.004 pbw, more preferably less than 0.003 pbw, especially less than 0.001 pbw. Preferably, no salt, for example an alkaline salt of a Group I or Group II metal, is added to the mixture or any component thereof used to make the composite material in the method.

The method of the first aspect preferably produces a composite material which includes a low level of Group I or Group II metal ions. Said composite material suitably includes less than 1000 ppm, preferably less than 500 ppm, 5 more preferably less than 150 ppm of any alkali metal cation (e.g. Na^+ , Li^+ or K^+) in it, said ppm being based on the amount of said polymeric material in said composite. Said composite material suitably includes less than 1000 ppm, preferably less than 500 ppm, more preferably less 10 than 150 ppm of any Group II metal cation (e.g. Ca^{2+}) in it, said ppm being based on the amount of said polymeric material in said composite. Preferably, the sum of the ppm of all Group I and Group II metal cations in said composite material is less than 2000 ppm, preferably less 15 than 1000 ppm, more preferably less than 500 ppm, especially less than 250 ppm.

The levels of ions in ppm described may be assessed using ICPAES (Inductive Coupling Plasma Atomic Emission 20 Spectroscopy).

According to a second aspect of the invention, there is provided a composite material prepared or preparable as described according to the first aspect *per se*.

25

A said composite material preferably comprises:

- (i) a polymeric material having a melt viscosity (MV) in the range of 0.05 to 0.12 kNsm^{-2} ; and
- 30 (ii) a filler means;

wherein said polymeric material is of a type which includes unsubstituted phenyl moieties, carbonyl moieties

and ether moieties in the polymeric backbone of said polymeric material.

The composite material of the second aspect may have any
5 feature of the composite material of the first aspect.

A preferred composite material comprises:

- 10 (i) a polymeric material having a MV in the range 0.06 to 0.11 kNsm⁻², preferably a material selected from polyetheretherketone, polyetherketone and polyetherketoneketone;
- (ii) at least 45 wt%, preferably at least 55 wt%, of
15 a filler means, preferably a fibrous filler means, more preferably a discontinuous fibrous filler means;

wherein the composite material includes less than 1000 ppm
of any Group I metal cation; and less than 1000 ppm of any
20 Group II metal cation.

The composite material may advantageously be used in injection moulding or extrusion to manufacture components. Thus, according to a third aspect of the invention, there
25 is provided a method of making a component, the method comprising extruding or injection moulding a composite material as described according to the first and/or second aspects.

30 Said composite material may have any feature of said composite material described according to any of the above aspects.

Said method preferably involves selecting a precursor material from which to make the component wherein said precursor material comprises a said composite material and
5 subjecting the precursor material to a temperature to melt polymeric material in said composite material in an extrusion or injection moulding apparatus. Suitably, said precursor material is heated to a temperature of greater than 300°C, preferably greater than 340°C. It is suitably heated to a temperature not exceeding 450°C.

10

Said precursor material may consist essentially of a said composite material described herein.

Suitably, in the method, at least 0.5g, preferably at
15 least 1g, more preferably at least 5g, especially at least 12g is selected in order to make the component.

Preferably, the component made comprises at least 25g, more preferably at least 50g of said composite material.

20

The method may be used to make components having relatively thin walls. Thus, the invention, in a fourth aspect relates to a method of making a component which has a wall which includes a region having a thickness of 3mm
25 or less, the method comprising:

(A) selecting a precursor material as described according to the third aspect.

30 AND

(B) treating said precursor material, thereby to form said component.

Preferably, the component includes a region having a thickness of 2mm or less, more preferably 1mm or less.

- 5 Said treatment described in (B) preferably involves melt processing said precursor material. Melt processing is preferably carried out by extrusion or injection moulding.

Suitably, said component includes a region having an area
10 of at least 0.5cm^2 , preferably at least 1cm^2 , more preferably at least 5cm^2 having a thickness as described. Thus, in one embodiment, said component may include a region of at least 0.5cm^2 which has a thickness of 3mm, preferably of 2mm or less.

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- A said polymeric material as described herein may be made by any suitable method. An electrophilic process may be used as described in US6566484B2; or a nucleophilic process may be used as described in EP00001879B or PCT/GB99/02833.
20 A nucleophilic process is preferred.

MV may be controlled as described in EP 0001879B.

- Any feature of any aspect of any invention or embodiment
25 described herein may be combined with any feature of any aspect of any other invention or embodiment described herein mutatis mutandis.

- Specific embodiments of the invention will now be described
30 by way of example, with reference to the accompanying figure which is a plot illustrating the relationship between MV and IV.

VICTREX PEEK 150P (Trade Mark), Victrex PEEK 150GL30 (Trade Mark) and Victrex PEEK 150CA30 may be obtained from Victrex Plc, UK.

- 5 All chemicals referred to herein were used as received from Sigma-Aldrich Chemical Company, Dorset, UK, unless otherwise stated.

Example 1 - Preparation of polyetheretherketone

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A 250ml flanged flask fitted with a ground glass Quickfit lid, stirrer/stirrer guide, nitrogen inlet and outlet was charged with 4,4'-difluorobenzophenone (22.48g, 0.103 mole), hydroquinone (11.01g, 0.1 mole) and
15 diphenylsulphone (49g) and purged with nitrogen for over 1 hour. The contents were then heated under a nitrogen blanket to between 140 and 150°C to form an almost colourless solution. While maintaining a nitrogen blanket, dried sodium carbonate (10.61g, 0.1 mole) and
20 potassium carbonate (0.278g, 0.002 mole) was added. The temperature was raised to 200°C and held for 1 hour; raised to 250°C and held for 1 hour; raised to 315°C and maintained for 2 hour.

- 25 The reaction mixture was allowed to cool, milled and washed with acetone and water. The resulting polymer was dried in an air oven at 120°C producing a powder. The polymer had a melt viscosity at 400°C, 1000sec⁻¹ of 0.089 kNsm⁻².

30

The polymer was compression moulded at 400°C in a press (20tonnes, 5 minutes) into a thin film approximately 0.2mm thick and cooled from 400°C to 120°C in 30 minutes to

induce complete crystallisation and then allowed to cool to room temperature.

The film was then hinged through 180° followed by hinging through 360°C. This process was repeated 5 times and the film survived without breaking and was therefore considered to be tough.

Example 2a-d - Preparation of samples of
polyetheretherketone with different melt viscosities

The procedure described in Example 1 was repeated except the polymerisation time was varied to produce polyetheretherketone with different melt viscosities. The details are given in Table 1 below.

Table 1

Example	Reaction Time (mins)	Melt Viscosity (kNsm ⁻²)	Toughness Test
1	120	0.089	Tough
2a	180	0.150	Tough
2b	160	0.117	Tough
2c	90	0.075	Brittle
2d	60	0.06	Brittle

Example 3 - Large Scale production of polyetheretherketone

The procedure described in Example 1 was repeated on a larger scale to produce sufficient material to carry out mechanical and melt flow testing. Five batches were produced, Examples 3a-e, with Melt Viscosities measured at 400°C and 1000s⁻¹ of 0.144, 0.110 0.089, 0.076 and 0.059kNsm⁻² respectively.

10 Example 4a-d - Melt Flow Index of polyetheretherketones

The Melt Flow Index of the polyetheretherketone samples from Examples 3c,3e, a sample of Victrex PEEK 150P and blends of Examples 3d and 3a in a weight ratio of 77 : 23 and Examples 3e and 3a in a weight ratio of 64 : 36 were measured on a CEAST Melt Flow Tester 6941.000. The polymer was placed in the barrel of the Melt Flow Tester apparatus and heated to 400°C. The polymer was then extruded under a constant shear stress by inserting a weighted piston (2.16kg) into the barrel and extruding through a tungsten carbide die, 2.095mm bore x 8.000mm. The MFI (Melt Flow Index) is the average mass of polymer (in g) extruded in 10 min. The results are detailed in Table 2 below.

Table 2

Example	Polyetheretherketone Sample	Melt Viscosity (kNsm ⁻²)	Melt Flow Index (g/10mins)
4a	Example 3c	0.089	87
4b	Example 3e	0.059	117
4c	Example 3d (77wt%) + Example 3a (23wt%)	0.09	83
4d	Example 3e (64wt%) + Example 3a (36wt%)	0.09	78
4e	Victrex PEEK 150P	0.150	41

5 Example 5 - Spiral Flow of Low viscosity polyetheretherketones

Spiral flow measurements were made on a spiral flow mould at a melt temperature of 370 and 390°C and 1 and 2mm mould
 10 depth at a mould temperature of 185°C with an injection pressure of 140Bar and the flow length determined. The results are detailed in Table 3 below.

Table 3

Example	Polyetheretherketone Sample	Mould Temperature (°C)	Mould Depth	Flow Length (mm)
5a	Ex3e (64wt%) + Ex3a (36wt%)	370	1mm	302
5b	Victrex PEEK 150P	370	1mm	239
5c	Ex3e (64wt%) + Ex3a (36wt%)	370	2mm	834
5d	Victrex PEEK 150P	370	2mm	514
5e	Ex3e (64wt%) + Ex3a (36wt%)	390	1mm	315
5f	Victrex PEEK 150P	390	1mm	263
5g	Ex3e (64wt%) + Ex3a (36wt%)	390	2mm	>1000
5h	Victrex PEEK 150P	390	2mm	727

5 Examples 6a-e - Mechanical Properties of Low Viscosity polyetheretherketones

Samples of polyetheretherketone from Examples 3c, 3d, 3e, Victrex PEEK 150P, the 60:40wt% blend of Example 3d and 3b
 10 the 30:30:30:10wt% blend of Examples 3b, 3c, 3d and 3e, the 77:23wt% blend of Example 3d and 3a and the 64:36wt% blend of Example 3e and 3a were injection moulded using a barrel temperature of 350-360°C, nozzle temperature 365°C, mould temperature 145-155°C, holding pressure 30Bar,
 15 injection pressure of 140Bar and a screw speed of 45rpm to

produce standard test pieces for mechanical property evaluation. The results are detailed in Table 4 below.

Table 4

5

Example	Polyetheretherketone Sample	Melt Viscosity (kNsm ⁻²)	Tensile Strength (MPa) ^(a)	Flexural Strength (MPa) ^(b)	Flexural Modulus (GPa) ^(b)
6a	Example 3c	0.089	90.0	157.9	4.0
6b	Example 3d	0.076	98.1	149.8	3.7
6c	Example 3b (40wt%) + Example 3d (60wt%)	0.09		154.6	4.1
6d	Example 3e	0.059	100.6	149.2	3.7
6e	Ex3b (30wt%)+ Ex3c (30wt%)+ Ex3d (30wt%)+ Ex3e (10wt%)+	0.092	107.6	154.6	4.0
6f	Example 3d (77wt%) + Example 3a (23wt%)	0.09	98.3	147.7	3.7
6g	Example 3e (64wt%) + Example 3a (36wt%)	0.09	97.8	149.0	3.7
6h	Victrex PEEK 150P	0.150	98.5	149.1	3.9

(a) ASTM D638

(b) ASTM D790

10 Example 7a - d - Melt Flow Index and Mechanical Properties
of filled, low viscosity polyetheretherketones

The polyetheretherketone from the 64:36wt% blend of Example 3e and 3a was compounded separately with 30wt% glass fibre (Owens Corning OCP CS D165-11C) and 30wt%

carbon fibre (SGL Sigrafil C25 S006 APS) on a ZSK 25 WLE Twin Screw Extruder, Examples 7a and 7c respectively. The Melt Flow Index of the two compounds at 400°C and 2.16kg was determined and compared to Victrex PEEK 150GL30 and 150CA30 which are commercial grades of polyetheretherketone containing 30wt% glass fibre and carbon fibre respectively. The results are detailed in Table 5 below.

Compounds Example 7a and 7d were injection moulded using a barrel temperature of 370-380°C, nozzle temperature 380°C, mould temperature 180-200°C, holding pressure 30Bar, injection pressure 140Bar and a screw speed of 45rpm into standard test pieces and their mechanical properties determined and compared to those of to Victrex PEEK 150GL30 and 150CA30. The results are detailed in Table 5 below.

Table 5

Example	Polyetheretherketone Sample	Melt Flow Index (g/10min)	Tensile Strength (MPa) ^(a)	Flexural Strength (MPa) ^(b)	Flexural Modulus (GPa) ^(b)
7a	Blend [3e(64wt%) +3a(36wt%)] (70wt%) + Glass Fibre (30wt%)	30	155.8	242.1	10.2
7b	Victrex PEEK 150GL30	14	163.5	252.5	10.0
7c	Blend [3e(64wt%) +3a(36wt%)] (70wt%) + Carbon Fibre (30wt%)	30	202.4	304.5	16.9
7d	Victrex PEEK 150CA30	12	208.6	312.7	18.7

(a) ASTM D638

(b) ASTM D790

Example 8a - g - Melt Flow Index and Mechanical Properties of highly filled, low viscosity polyetheretherketones

The polyetheretherketone from the 64:36wt% blend of Example 3e and 3a was compounded separately with 40wt%, 50wt%, 60wt% and 70wt% glass fibre (Owens Corning OCF D165A-11C) and 40wt%, 50wt% and 60wt% carbon fibre (SGL Sigrafil C25 S006 APS) on a ZSK 25 WLE Twin Screw Extruder, Examples 8a - 8g respectively. The Melt Flow Index of the compounds at 400°C and 2.16kg was determined and compared to Victrex PEEK™ 150GL30 and 150CA30 which are commercial grades of polyetherketone containing 30wt% glass fibre and carbon fibre respectively. The results are detailed in Tables 6a and 6b below.

Compounds Example 8a - 8g were injection moulded using a barrel temperature of 370-380°C, nozzle temperature 380°C, mould temperature 180-200°C, holding pressure 30Bar and a screw speed of 45rpm into standard test pieces and their mechanical properties determined and compared to those of Victrex PEEK 150GL30 and 150CA30. The results are detailed in Table 6a and 6b below.

Table 6a

Example	Polyetheretherketone Sample (%wt) ^(a)	Glass Fibre (wt%)	Melt Flow Index (g/10min)	Tensile Strength (MPa) ^(b)	Flexural Strength (MPa) ^(c)	Flexural Modulus (GPa) ^(c)	Notched Izod (kJ/m ²) ^(d)
8a	60	40	26.9	211	314	13.7	12.6
8b	50	50	17.9	228	327	17.4	13.4
8c	40	60	11.9	227	342	21.8	12.5
8d	30	70	7.8	198	320	26.0	8.9
Victrex PEEK 150GL30			14	163.5	252.5	10.0	8.8

- (a) Polyetheretherketone sample Blend
3e (64wt%)+3a (36wt%)
- (b) ISO 527
- (c) ISO 178-1993(E)
- 5 (d) ISO 180

Table 6b

Example	Polyetheretherketone Sample (%wt) ^(a)	Carbon Fibre (wt%)	Melt Flow Index (g/10min)	Tensile Strength (MPa) ^(b)	Flexural Strength (MPa) ^(c)	Flexural Modulus (GPa) ^(c)	Notched Izod (kJ/m ²) ^(d)
8e	60	40	17	229	338	25.1	7.8
8f	50	50	6.5	229	354	31.3	6.8
8g	40	60	4.8	221	357	36.8	6.3
Victrex PEEK 150CA30			12	208.6	312.7	18.7	7.9

- (a) Polyetheretherketone sample Blend
- 10 3e (64wt%)+3a (36wt%)
- (b) ISO 527
- (c) ISO 178-1993(E)
- (d) ISO 180

15 Example 9a - b - Melt Flow Index and Mechanical Properties
of mica filled, low viscosity polyetheretherketones

The polyetheretherketones from the 64:36wt% blend of Examples 3e and 3a, and Victrex 150P were compounded with 30wt% mica (CAMP, microns mica 325 mesh) on a ZSK 25 WLE

20 Twin Screw Extruder, Examples 9a - 9b respectively. The Melt Flow Index of the compounds at 400°C and 2.16kg was determined. The results are detailed in Table 7 below.

Compounds Example 9a - 9b were injection moulded using a

25 barrel temperature of 370-380°C, nozzle temperature 380°C,

mould temperature 180-200°C, holding pressure 30Bar and a screw speed of 45rpm into standard test pieces and their mechanical properties determined. The results are detailed in Table 7.

5

Table 7

Example	Polyetheretherketone Sample (%wt)	Mica (wt%)	Melt Flow Index (g/10min)	Tensile Strength (MPa) ^(c)	Flexural Strength (MPa) ^(d)	Flexural Modulus (GPa) ^(d)	Notched Izod (kJ/m ²) ^(e)
9a	70 ^(a)	30	61.2	84	139	7.5	2.9
9b	70 ^(b)	30	25.1	85	152	7.3	3.2

(a) Polyetheretherketone sample Blend

3e (64wt%) + 3a (36wt%)

(b) Victrex PEEK 150P

(c) ISO 527

10 (d) ISO 178-1993 (E)

(e) ISO 180

Example 10a - 10b- Melt Flow Index and Mechanical Properties of highly filled, low viscosity polyetheretherketones

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The polyetheretherketones from the 64:36wt% blend of Example 3e and 3a, and Victrex 150P were compounded with 15wt% carbon fibre (SGL Sigrafil C25 S006), 15wt% polytetrafluoroethylene (PTFE) (Asahi Glass Fluoropolymers Fluon FL 1650) and 21wt% polyethersulphone (PES) (BASF Ultrason E3010) on a ZSK 25 WLE Twin Screw Extruder, Examples 10a - 10b respectively. The Melt Flow Index of the compounds at 400°C and 10kg was determined. The results are detailed in Table 8a.

20

Table 8a

Example	Polyetheretherketone Sample (%wt)	PES (wt%)	Carbon Fibre (wt)	PTFE (wt%)	Melt Flow Index (g/10min)
10a	49 ^(a)	21	15	15	125.3
10b	49 ^(b)	21	15	15	58.5

(a) Polyetheretherketone sample Blend

3e (64wt%) + 3a (36wt%)

(b) Victrex PEEK 150P

5 (c) ISO 527

(d) ISO 178-1993 (E)

(e) ISO 180

Compounds Example 10a - 10b were injection moulded using a
 10 barrel temperature of 370-380°C, nozzle temperature 380°C,
 mould temperature 180-200°C, holding pressure 30Bar and a
 screw speed of 45rpm into standard test pieces and their
 mechanical properties determined. The results are detailed
 in Table 8b.

15

Table 8b

Example	Polyetheretherketone Sample (%wt)	PES (wt%)	Carbon Fibre (wt)	PTFE (wt%)	Tensile Strength (MPa) ^(c)	Flexural Strength (MPa) ^(d)	Flexural Modulus (GPa) ^(d)	Notched Izod (kJ/m ²) ^(e)
10a	49 ^(a)	21	15	15	152	217	9.8	4.4
10b	49 ^(b)	21	15	15	158	239	11.0	5.5

(a) Polyetheretherketone sample Blend

3e (64wt%) + 3a (36wt%)

(b) Victrex PEEK 150P

(c) ISO 527

20 (d) ISO 178-1993 (E)

(e) ISO 180

Example 11 - Preparation of polyetherketone

A 250ml flanged flask fitted with a ground glass Quickfit
5 lid, stirrer/stirrer guide, nitrogen inlet and outlet was
charged with 4,4'-difluorobenzophenone (33.49g, 0.153
mole), 4,4'-dihydroxybenzophenone (32.13g, 0.150 mole) and
diphenylsulphone (124.5g) and purged with nitrogen for
over 1 hour. The contents were then heated under a
10 nitrogen blanket to 160°C to form an almost colourless
solution. While maintaining a nitrogen blanket, dried
sodium carbonate (16.59g, 0.156 mole) was added. The
temperature was raised to 340°C at 1°C/min and held for 2
hour.

15

The reaction mixture was allowed to cool, milled and
washed with acetone and water. The resulting polymer was
dried in an air oven at 120°C producing a powder. The
polymer had a melt viscosity at 400°C, 1000sec⁻¹ of 0.12
20 kNsm⁻².

Example 12a-12d - Large Scale production of
polyetherketone

25 The procedure described in Example 11 was repeated on a
larger scale to produce sufficient material to carry out
mechanical and melt flow testing. Four batches were
produced, Examples 12a-d, with Melt Viscosities measured
at 400°C and 1000s⁻¹ of 0.12, 0.10 0.09 and 0.08kNsm⁻²
30 respectively.

Example 13a-13b Melt Flow Index of polyetherketone

The Melt Flow Index at 400°C and 2.16kg for the polyetherketone sample from Example 12c and a sample of Victrex PEK P22 were measured. The results are detailed in Table 9 below.

Table 9

Example	Polyetherketone Sample	Melt Viscosity (kNsm ⁻²)	Melt Flow Index (g/10mins)
13a	Example 12c	0.09	140
13b	Victrex PEK P22	0.21	30

Examples 14a-14e - Mechanical Properties of Low Viscosity polyetherketones

10

Samples of polyetherketones from Examples 12a, 12b, 12c, 12d and Victrex PEK 22P were injection moulded using a barrel temperature of 380-390°C, nozzle temperature 385°C, mould temperature 155-165°C, holding pressure 30Bar, injection pressure of 140Bar and a screw speed of 45rpm to produce standard test pieces for mechanical property evaluation. The results are detailed in Table 10 below.

15

Table 10

Example	Polyetherketone Sample	Melt Viscosity (kNsm ⁻²)	Tensile Strength (MPa) ^(a)	Flexural Strength (MPa) ^(b)	Flexural Modulus (GPa) ^(b)
14a	Example 12a	0.12	110	184	4.6
14b	Example 12b	0.10	111	183	4.6
14c	Example 12c	0.09	114	186	4.6
14d	Example 12d	0.08	112	184	4.5
14e	Victrex PEK 22P	0.21	104	175	4.2

(a) ASTM D638

(b) ASTM D790

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Example 15a - 15b - Melt Flow Index and Mechanical Properties of filled, low viscosity polyetherketones

The polyetherketone from Example 12c and Victrex PEK P22 were compounded with 30wt% glass fibre (Owens Corning OCF CS D165A-11C) on a ZSK 25 WLE Twin Screw Extruder, Examples 15a - 15b respectively. The Melt Flow Index of the compounds at 400°C and 2.16kg was determined. The results are detailed in Table 11 below.

Compounds Example 15a - 15b were injection moulded using a barrel temperature of 375-410°C, nozzle temperature 390°C, mould temperature 180-200°C, holding pressure 30Bar and a screw speed of 45rpm into standard test pieces and their mechanical properties determined. The results are detailed in Table 11 below.

20

Table 11

Example	Polyetherketone Sample (%wt)	Glass Fibre (wt%)	Melt Flow Index (g/10min)	Tensile Strength (MPa) ^(c)	Flexural Strength (MPa) ^(d)	Flexural Modulus (GPa) ^(d)	Notched Izod (kJ/m ²) ^(e)
8a	70 ^(a)	30	42	187	261	11.0	8.9
8b	70 ^(b)	30	12	175	278	10.0	10.4

(a) Polyetherketone Example 12c

(b) Victrex PEK P22

5 (c) ISO 527

(d) ISO 178-1993(E)

(e) ISO 180

10 Example 16a -16i - Viscosity and Mechanical Properties of highly filled, low viscosity polyetheretherketones

The polyetheretherketone from the 64:36wt% blend of Example 3e and 3a was compounded with 0, 3, 6, 9 and 12% of a liquid crystal polymer (LCP) polymer (Ticona T130, melt point 370°C, glass content 30%), and with additional glass fibre (Owens Corning D165-11C) to obtain total glass content 60%, on a ZSK 25 WLE Twin Screw Extruder, Examples 16a - 16e respectively. The LCP polymer was predried 16 hours at 150°C before compounding.

20 The addition of LCP T130 was observed to decrease the extruder torque and to improve fibre wet out.

Comparative trials were carried out with Victrex 150P polyketone compounded with 0, 5, 10 and 15% of LCP T130 and with additional glass fibre to make the total glass content 30%; Examples 16f-16i respectively.

The Melt Viscosity of the compounds was determined at 380°C and 1000 s⁻¹, and the Melt Flow Index at 380°C and 2.16kg.

- 5 Compounds Example 16a-i were injection moulded using a barrel temperature of 350-360°C, nozzle temperature 365°C, mould temperature 145-155°C, holding pressure 30Bar and a screw speed of 45rpm into standard test pieces and their mechanical properties determined. The results are detailed
- 10 in Tables 12a and 12b below.

Table 12a

Example	PEEK (wt%)	LCP T130 (wt%)	Glass Fibre (wt%)	LCP in recipe, pphr	ZSK 25 torque %	Melt Flow Index, 380°C (g/10min)	Melt Viscosity 380°C (kNsm ⁻²)
16a	40 ^(a)	0	60	0	74	7.8	0.51
16b	37.9 ^(a)	3	59.1	5.25	57	7.4	0.29
16c	35.8 ^(a)	6	58.2	10.5	50	5.5	0.26
16d	33.7 ^(a)	9	57.3	15.75	50	5.3	0.23
16e	31.6 ^(a)	12	56.4	21	50	5.1	0.21
16f	70 ^(b)	0	30	0	65	8.5	0.33
16g	66.5 ^(b)	5	28.5	5	45	9.5	0.30
16h	63 ^(b)	10	27	10	39	9.6	0.20
16i	59.5 ^(b)	15	25.5	15	34	9.1	0.19

(a) PEEK sample Blend 3e (64wt%) + 3a (36wt%)

(b) Victrex PEEK 150P

Table 12b

Example	Tensile Strength (MPa) ^(a)	Flexural Strength (MPa) ^(b)	Flexural Modulus (GPa) ^(b)	Notched Izod kJ/m ² ^(c)	Unnotched Izod kJ/m ² ^(c)
16a	230	342	20.6	10.5	50.1
16b	234	349	21.2	14.0	52.9
16c	235	340	21.3	12.8	48.9
16d	212	323	21.3	12.5	45.6
16e	216	325	21.2	12.4	45.8
16f	174	265	9.8	9.1	60.4
16g	168	232	10.1	8.6	43.3
16h	163	231	10.4	7.3	38.6
16i	156	221	10.6	7.5	40.0

(a) ISO 527

(b) ISO 178-1993 (E)

5 (c) ISO 180

The invention is not restricted to the details of the foregoing embodiment(s). The invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

CLAIMS

1. A method of preparing a composite material, the method comprising:

5

(iii) selecting polymeric material having a melt viscosity (MV) in the range 0.05 to 0.12 kNsm⁻²;

(iv) contacting said polymeric material having said MV in the range 0.05 to 0.12 kNsm⁻² with a filler means;

10

wherein said polymeric material is of a type which includes: unsubstituted phenyl moieties, ketone moieties and ether moieties in the polymeric backbone of said polymeric material.

15

2. A method according to claim 1, wherein a batch of composite material is prepared having a weight of at least 10 Kg

20

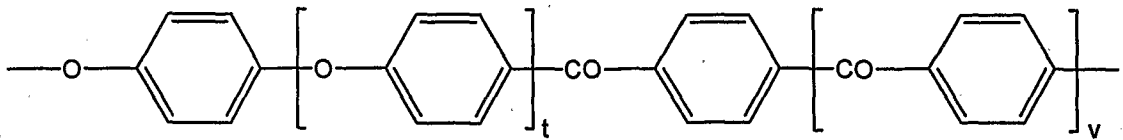
3. A method according to claim 1 or claim 2, which comprises forming said composite material into a particulate form.

25 4. A method according to any preceding claim, wherein said polymeric material has a MV in the range 0.08 to 0.11 kNsm⁻².

5. A method according to any preceding claim, wherein said polymeric material has a MV in the range 0.085 to 0.095 kNsm⁻².

30

6. A method according to any preceding claim, wherein said polymeric material comprises a repeat unit of formula



wherein t and v independently represent 0 or 1.

7. A method according to any preceding claim, wherein said polymeric material is polyetheretherketone.

8. A method according to any preceding claim, wherein said filler means includes a fibrous filler or a non-fibrous filler.

9. A method according to any preceding claim, which includes a discontinuous fibrous filler or a non-fibrous filler.

10. A method according to claim 9, wherein discontinuous fibres have an average length before contact with the polymeric material of less than 10mm.

11. A method according to any of claims 8 to 10, wherein said fibrous filler is selected from inorganic fibrous materials, non-melting and high-melting organic fibrous materials and carbon fibre.

12. A method according to any preceding claim, wherein said filler means comprises one or more fillers selected from discontinuous glass fiber, discontinuous carbon fibre, carbon black and a fluoro carbon resin.

13. A method according to any preceding claim, wherein said composite material is prepared in a process which comprises extruding a mixture comprising polymeric materials and filler means.

14. A method according to any preceding claim, wherein said composite material includes 65wt% or less of said polymeric material and at least 35wt% of filler means.

15. A method according to any preceding claim, wherein said composite material includes 20 to 60wt% of said polymeric material and 40 to 60wt% of filler means.

16. A method according to any preceding claim, which includes 20 to 50wt% of said polymeric material and 50 to 80wt% of filler means.

17. A method according to any preceding claim, wherein the ratio of the wt% of said polymeric material to said filler means is less than 1.

18. A composite material prepared or preparable in a method according to any preceding claim.

19. A composite material comprising a polymeric material and filler means, wherein said polymeric material has an MV in the range of 0.06 to 0.11 kNsm⁻² and is selected from polyetheretherketone, polyetherketone and polyetherketoneketone and said composite material comprises at least 45wt% of filler means selected from a discontinuous fibrous filler means and a non-fibrous filler means.

20. A composite material according to claim 18 or claim 19, wherein said polymeric material comprises polyetheretherketone having a MV in the range 0.085 to
5 0.095 kNsm⁻² and a discontinuous fibrous filler means.

21. A method of making a component which comprises extruding or injection moulding a composite material according to any of claims 18 to 20.

10

22. A method of making a component which has a wall which includes a region having a thickness of 3mm or less, the method comprising:

15 (a) selecting a composite material as described in any of claims 18 to 20;

and

(b) treating said composite material thereby to form said component.

20

23. A method according to claim 22, wherein said treatment referred to in (b) involves melt processing said precursor material.