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(71) Applicant: KEMIRA OYJ [FI/FI]; Energiakatu 4, 00180 Helsinki (FI).

(72) Inventors: HIETANIEMI, Matti; Tulvatie 10 A, 02780 Espoo (FI). KARPPI, Asko; Solmukatu 18, 20540 Turku (FI). RAUTIAINEN, Jukka; c/o Kemira Oyj, R&D Center, PL 44, 02271 Espoo (FI).

(74) Agent: BERGGREN OY; PO Box 99, 20521 Turku (FI).

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(54) Title: POLYMERIC STRUCTURE AND ITS USE

(57) Abstract: The present invention relates to a water-soluble polymeric structure, which is obtainable by polymerisation of a non-ionic monomer, such as (meth)acrylamide, and at least a charged first monomer in a polymerisation medium comprising at least one host polymer, which is a copolymer of a non-ionic monomer, such as (meth)acrylamide, and at least a charged second monomer. The first monomer and the second monomer are oppositely charged. The polymeric structure has a total ionicity in a range of 3 – 50 mol-%, preferably 3 – 40 mol-%, more preferably 3 – 20 mol-%, and a charge density in a range from 0.05 to 3.0 meq/g, preferably from 0.05 to 1.2 meq/g at pH 2.8 and a charge density from -1.0 to +1.0 meq/g, preferably -0.8 to +0.6 meq/g, at pH 7.



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POLYMERIC STRUCTURE AND ITS USE

The present invention relates to a polymeric structure and its use according to the preambles of enclosed independent claims.

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Use of recycled fibre raw material has been steadily increasing in the manufacture of paper, board or the like, and a large portion of the fibre raw material is recycled more than once. Paper or board, which is made from stock comprising extensive amounts of recycled fibres, has typically low dry strength properties, because the
10 quality of the fibres is reduced during the recycling. For example, each time the fibres are repulped, the average fibre length tends to be reduced. Various chemicals are added to the fibre suspension before the web forming in order to minimise the effects of deteriorating fibre properties and for increasing, maintaining and improving the dry strength properties of the final paper or board
15 product.

Compression strength and burst strength are important dry strength properties for paper and board, especially for board grades, which are used for packaging. Compression strength is often measured and given as Short-span Compression
20 Test (SCT) strength, which may be used to predict the compression resistance of the final product, e.g. cardboard box. Burst strength indicates paper's or board's resistance to rupturing, and it is defined as the hydrostatic pressure needed to burst a sample when the pressure is applied uniformly across the side of the sample. Both the compression strength and burst strength are negatively affected
25 when the amount of recycled fibres in the stock increases.

The extensive recycling affects also quality of water, which is used in the manufacturing process of paper, board and the like. Nowadays the water circulations are practically closed or nearly closed in majority of paper and board
30 mills and the use of fresh water is minimised in paper and board making. Together with the use of recycled fibre raw material the closure of water circulations leads to increase in the concentration of charged species, such as ions, organic compounds, and other components in the water circulation.

There is a need for efficient and cost-effective dry strength additives that are suitable for use even in processes where the concentration of ionic species in the process water may be high. Furthermore, the dry strength additives should be safe
5 to use in paper and board grades that are intended for food contact.

The object of the present invention is to minimize or even eliminate the disadvantages existing in the prior art.

10 One object of the present invention is to provide a water-soluble polymeric structure, which is effective in increasing the dry strength properties of paper, board or the like, especially burst strength and SCT strength.

These objects are attained with the invention having the characteristics presented
15 below in the characterising parts of the independent claims.

Some preferable embodiments of the invention are presented in the dependent claims. The features recited in the dependent claims are freely combinable with each other unless otherwise explicitly stated.

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A typical water-soluble polymeric structure according to the present invention is obtainable by polymerisation of a non-ionic monomer, such as (meth)acrylamide, and at least a charged first monomer in a polymerisation medium comprising at least one host polymer, which is a copolymer of a non-ionic monomer, such as
25 (meth)acrylamide, and at least a charged second monomer, the first monomer and the second monomer being oppositely charged,
wherein the polymeric structure has

- a total ionicity in the range of 3 – 50 mol-%, preferably 3 – 40 mol-%, more preferably 3 – 20 mol-%, and
- 30 - a charge density in a range from 0.05 to 3.0 meq/g, preferably from 0.05 to 1.2 meq/g, when measured at pH 2.8; and from -1.0 to +1.0 meq/g, preferably -0.8 to +0.6 meq/g, when measured at pH 7.

A typical use of the polymeric structure according to the present invention is in making of paper, board, tissue or the like as a strength agent, retention agent, drainage agent, sludge dewatering agent or fixation agent, emulsifier for hydrophobic sizing agent, preferably as strength agent.

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Now it has been surprisingly found that a polymeric structure, which is formed by polymerising a non-ionic monomer, such as (meth)acrylamide, and at least one charged first monomer in a polymerisation medium comprising at least one host polymer, provides an unexpected improvement in the dry strength properties of paper or board, when the obtained polymeric structure is amphoteric, i.e. contains both anionic and cationic groups. It is assumed, without wishing to be bound by a theory, that the presence of both anionic and cationically charged groups, which provide a carefully defined ionicity and charge density for the polymeric structure, produces at the same time an improvement in one or more strength properties as well as a beneficial effect on the obtained bulk values. It is speculated that the anionic groups of the polymeric structure are straightened out in the fibre stock and improve the bulk of the produced paper or board. At the same time the presence of cationic groups in the polymeric structure provide sufficient bonding to and between the fibres, which usually have an anionic surface charge. Thus, an improvement in strength properties is obtained.

In the present context the concept “polymeric structure” denotes a structure or a polymeric material or a polymer that comprises at least two polymer networks which are at least partially or wholly interlaced with each other. The polymer networks are at least partially interlaced with each other on a molecular scale but not covalently bonded to each other. The individual polymer networks of the polymeric structure cannot be separated from each other unless chemical bonds are broken. This means that the individual polymers forming the polymeric structure of the present invention cannot be separated from each other without breaking the individual polymer chains and thus the polymeric structure. In the present context the term “interlacing polymer” is used to denote the polymer, which is formed by polymerisation of (meth)acrylamide and at least one charged first monomer in a polymerisation medium comprising at least one host polymer.

It has been observed that the polymeric structure according to the present invention, which is obtainable by polymerisation of a non-ionic monomer and a first monomer in a polymerisation medium comprising at least one host polymer, provides better stability for the obtained polymeric structure. Especially the viscosity properties of the obtained polymeric structure are stable, which means that the viscosity of the obtained polymeric structure does not change during storage.

Preferably both the host polymer(s) and interlacing polymer are obtained by free radical polymerisation, more preferably by solution polymerisation or gel polymerisation. The polymerisation is preferably carried out in one phase system.

The non-ionic monomers used for the polymerisation of the host polymer and for the polymerisation of the interlacing polymer may be same or different. The host polymer and/or the interlacing polymer may also be obtained by polymerisation of two or more different non-ionic monomers. Preferably the non-ionic monomer both in the host polymer and in the interlacing polymer is methacrylamide and/or acrylamide, more preferably acrylamide.

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The pH value of the polymeric structure may be < 7.5 , for example in the range of 2.5 – 7.0, preferably 2.8 – 5.0, more preferably in the range of 2.8 – 4.0, even more preferably 2.8 – 3.5, at 1 weight-% concentration. The pH value is determined by diluting or dissolving, if the polymeric structure is in dry particulate form, the polymeric structure to pure water at 1 weight-% solids concentration. It is assumed that the acidity of the polymeric structure improves its storage stability by inhibiting or reducing the possibility of its self-complexation, thereby controlling the solution viscosity and inhibiting or reducing its increase during the storage. The pH of the polymeric structure changes, i.e. rises, when it is diluted to the use concentration. For example, at 0.1 weight-% concentration the pH of the polymeric structure may be in a range of 3.1 – 7, preferably 3.2 – 5.5, more preferably 3.3 – 4.5. According to one embodiment, the polymeric structure may have its isoelectric point, where the polymeric structure is electrically neutral in the statistical mean, in

a pH range around 3.9 – 4.8. Preferably the pH of the polymeric structure solution for use is adjusted to a value below the pH area of the isoelectric point. When the polymeric structure comes into a contact with the stock, its pH further rises due to the dilution by the stock water. The anionic charges in the polymeric structure are
5 activated, thus leading to effective interaction with the stock constituents.

According to one embodiment of the invention the polymeric structure may be obtained by solution polymerisation of non-ionic monomers, such as (meth)acrylamide, and at least one charged first monomer in the polymerisation
10 medium. Non-ionic monomers, e.g. (meth)acrylamide, and the selected first monomer(s) are added to the aqueous polymerisation medium, which comprises at least one host polymer, and the reaction mixture is polymerised in presence of initiator(s) by using free radical polymerisation. The temperature during the polymerisation may be 60 – 100 °C, preferably 70 – 90 °C. The pH of the
15 polymeric structure during the polymerisation is usually acidic, for example pH is from 2.5 to 7, preferably in the range of 3.0 – 7.0, more preferably in the range of 3.0 – 5.0. At the end of polymerisation, the polymeric structure is in form of a solution, which has a dry solids content of 10 – 25 weight-%, typically 15 – 20 weight-%

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According to another embodiment of the invention the polymeric structure may be obtained by gel polymerisation of non-ionic monomer, such as (meth)acrylamide, and at least one charged first monomer in the polymerisation medium. Non-ionic monomers, e.g. (meth)acrylamide, and the first monomer(s) are polymerised in
25 presence of initiator(s) by using free radical polymerisation. The monomer content in the polymerisation medium at the beginning of the polymerisation may be at least 20 weight-%. The temperature in the beginning of the polymerisation may be less than 40 °C or less than 30 °C. Sometimes the temperature in the beginning of the polymerisation may be even less than 5 °C or less than 0 °C. The temperature
30 during polymerisation may increase, for example to 100 °C, or for example to 140 °C, but typically the temperature remains below 100 °C during the polymerisation. The pH of the polymerisation medium is usually acidic, for example the pH is from 2.5 to 7. Preferably the polymerisation medium has pH value ≤ 4.5 , more

preferably in the range of 3 – 4.5. It has been observed that the low pH during polymerisation improves the solubility of the polymeric structure.

In the gel polymerisation the free radical polymerisation of the first monomers in the polymerisation medium comprising at least one host polymer produces a polymeric structure, which is in form of gel or highly viscous liquid. The total polymer content in the obtained polymeric structure may be at least 60 weight-%, for example at least 70 weight-%. The remaining may be various auxiliaries, monomer residues, salts and/or moisture. After the gel polymerisation, the obtained polymeric structure is mechanically comminuted, such as shredded or chopped, as well as dried, whereby a particulate polymeric structure is obtained. Depending on the used reaction apparatus, shredding or chopping may be performed in the same reaction apparatus where the polymerisation takes place. For example, polymerisation may be performed in a first zone of a screw mixer, and the shredding of the obtained polymer composition is performed in a second zone of the said screw mixer. It is also possible that the shredding, chopping or other particle size adjustment is performed in a treatment apparatus, which is separate from the reaction apparatus. For example, the obtained water-soluble polymeric structure in gel form may be transferred from the second end of a reaction apparatus, which is a belt conveyor, through a rotating hole screen or the like, where it is shredded or chopped into small particles. After shredding or chopping the comminuted polymeric structure is dried, milled to a desired particle size and packed for storage and/or transport. According to one embodiment the polymeric structure may be dried to a solids content of at least 85 weight-%, preferably at least 90 weight-%, more preferably at least 95 weight-%. The obtained dry polymeric structure is easy to store and transport and provides an excellent storage stability and long self-life.

The polymerisation medium comprises, irrespective of polymerisation type, already at the start of the polymerisation, at least one host polymer, and possibly one, two or more successive host polymers. The polymerisation medium thus comprises at least one host polymer, which is a copolymer of non-ionic monomer, such as (meth)acrylamide, and at least a charged second monomer. The

- polymerisation medium may further comprise one, two or more successive host polymers, which are structurally different from the first host polymer, i.e. they are formed from different monomers. The successive host polymers are not necessarily copolymers of (meth)acrylamide. Successive host polymer(s) may be
- 5 synthetic polymer(s) and/or natural polymer(s). Examples of successive host polymer that are synthetic polymers are polyvinyl alcohol, polyepiamine, polyvinylamine, homo- and copolymers of diallyldimethylammonium chloride, DADMAC. Examples of successive host polymers that are natural polymers are degraded starch, as well as anionic and/or cationic derivatives of undegraded or
- 10 degraded starch, preferably cationic degraded starch. Starch may be degraded chemically, e.g. by acid hydrolysis or by oxidation, enzymatically, thermally or mechanically. According to one embodiment the polymerisation medium comprises only host polymer(s) that are copolymers of (meth)acrylamide.
- 15 Preferably any host polymer and/or successive host polymer has at most a moderate charge density, preferably between -5 and +5 meq/g. In general, host polymer(s) and polymerisation conditions, especially pH, are selected and/or adjusted so that complex formation between the host polymer(s) and interlacing polymer during polymerisation of the interlacing polymer is minimised or
- 20 completely avoided. Preferably the host polymer(s) do not partake the polymerisation reaction involving the monomers of the interlacing polymer. Chemical reactions, grafting, etc., between the host polymer(s) and monomers of the interlacing polymer are preferably avoided.
- 25 In the present context the polymerisation medium is an aqueous polymerisation medium, which is preferably essentially free of oil(s) and/or hydrocarbon solvents. Preferably, polymerisation medium is water, and preferably the polymerisation medium is free of polyvalent salts. The aqueous polymerisation medium comprises at least one host polymer, dissolved and uniformly distributed in the aqueous
- 30 polymerisation medium. The polymerisation medium may further comprise pH adjustment agents, chelating agents and/or compounds, additives or residual substances associated with the host polymer or its production, such as reaction products of used initiators. If desired, the polymerisation medium may comprise

chain transfer agent(s). However, according to one preferable embodiment of the invention, the polymerisation medium is free of chain transfer agent(s).

The pH of the aqueous polymerisation medium may be acidic, for example the pH
5 of the polymerisation medium may be from 2.5 to 7. Preferably the aqueous polymerisation medium has pH value in a range of 3 – 5 or 3 – 4.5. It has been observed that the low pH during the polymerisation reactions improves the solubility of the obtained polymeric structure.

10 A cross-linker may be optionally present during the polymerisation of any host polymer and/or the interlacing polymer. The amount of cross-linker may be less than 0.1 mol-%, preferably less than 0.05 mol-%. Polymeric structures obtained by gel polymerisation may be polymerised in the presence of a cross-linker, wherein the preferred amount of optional cross-linker is less than 0.002 mol-%, preferably
15 less than 0.0005 mol-%, more preferably less than 0.0001 mol-%.

The polymeric structure of the present invention is essentially water-soluble. The term “water-soluble” is understood in the present context that the polymeric structure is miscible with water. When mixed with an excess of water, the
20 polymeric structure is preferably fully dissolved, and the obtained polymer solution is preferably essentially free from discrete polymer particles or granules. Excess of water means that the obtained polymer solution is not a saturated solution. In order to determine water-solubility the following method may be used: 0.5 weight-% of polymeric structure (calculated as dry) is mixed with 1500 ml of deionized
25 water mixed with a magnetic stirrer for 60 min. NaCl is added to the sample solution, to obtain salt concentration of 5 weight-%, and mixed for further 5 minutes. Insoluble particles are measured using a stainless steel sieve with aperture 500 microns. The sieve is filled with 1500 ml of the aqueous sample and allowed to drain. The sieve is washed with 1000 ml of cold water. Total drainage
30 time does not exceed 5 minutes. Gels and/or particles remaining on the sieve are visually counted. In one preferable embodiment water-soluble means that there exists at most 500 insoluble particles/1500 ml, more preferably at most 50 insoluble particles/1500 ml.

According to the present invention the polymeric structure has a charge density in the range from -1.0 to +1.0 meq/g, preferably from -0.8 to +0.6 meq/g, measured at pH 7. The charge density of the polymeric structure is measured when the polymeric structure is in form of an aqueous solution, or the polymeric structure is dissolved into water to form an aqueous solution, and the pH of the solution is adjusted to pH 7.0. In case the polymeric structure is in form of solid or powderous product, the polymeric structure is first dissolved into water and the pH is adjusted to the defined level before the charge density measurement. Charge density is measured by using Mutek PCD-03 tester, titrator PCD-T3. The charge density value of the polymeric structure at pH 7 may be preferably in the range from -0.6 to +0.5 meq/g, more preferably from -0.4 to +0.4 meq/g, measured at pH 7. This means that the polymeric structure may have a slight anionic or cationic charge at pH 7, as desired. It has been found that this carefully defined charge density of the polymeric structure may provide an improvement in dry strength of the final paper or board product, especially in the SCT strength and burst strength. If the charge density is too high, the polymeric structure may interact with the ionic material present in the stock and thus be consumed without desired strength improvement effect.

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The polymeric structure furthermore has a charge density in the range from 0.05 to 3.0 meq/g, preferably from 0.05 to 1.2 meq/g, measured at pH 2.8. The charge density of the polymeric structure is measured at pH 2.8 in principle in the same manner as described above, i.e. when the polymeric structure is in form of an aqueous solution or the polymeric structure is dissolved into water to form an aqueous solution, and the pH of the solution is adjusted to pH 2.8. Charge densities are measured again by using Mutek PCD-03 tester, titrator PCD-T3. The charge density value of the polymeric structure at pH 2.8 may be preferably in the range from 0.1 to 1.0 meq/g, more preferably from 0.3 to 1.0 meq/g. This means that the polymeric structure may preferably have at least a slight cationic charge at pH 2.8. It has been found that the slight cationic charge at pH 2.8 improves the storage stability of the polymeric structure and reduces the risk that the oppositely

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charged groups in the polymeric structure would react with each other during the storage.

The polymeric structure according to the present invention may have a total ionicity in the range of 3 – 50 mol-%, preferably 3 – 40 mol-%, more preferably 3 – 20 mol-%. The total ionicity is here understood as the percentage of total molar amount of charged monomers, both anionic and cationic, calculated from the total molar amount of non-ionic monomers, such as (meth)acrylamide, and of the charged monomers, both anionic and cationic. According to one embodiment of the invention the polymeric structure may have a total ionicity in the range 4 – 16 mol-%, preferably 5 – 14 mol-%. It is possible that the polymeric structure may have a total ionicity in the range of 4 – 50 mol-%, preferably 4 – 40 mol-%, more preferably 4 – 20 mol-%. Alternatively, the polymeric structure may have a total ionicity of 3 – 16 mol-% or 3 – 14 mol-%. Relatively low total ionicity provides a polymeric structure, which shows good attachment to the fibres, and produces a maximal dry strength effect for the final paper/board product. The low total ionicity also reduces the risk for flocculation of anionic trash and other disturbing substances, and the risk for zeta potential problems, i.e. positive zeta potential values.

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According to one embodiment the polymeric structure, preferably obtained by a gel polymerisation, may have a standard viscosity SV in the range of 1.3 – 5.0 mPas, preferably 1.4 – 4.5 mPas, more preferably 1.5 – 4.0 mPas, measured at 0.1 weight-% solids content in an aqueous NaCl solution (1 M), at 25 °C, at pH 3, using Brookfield DV1 viscometer equipped with UL adapter, at 60 rpm. An exemplary procedure for standard viscosity measurement has been described in the experimental section of this application.

According to one embodiment the polymeric structure, preferably obtained by solution polymerisation, may have a bulk viscosity in the range of 500 – 20 000 mPas, preferably 1000 – 15 000 mPas, more preferably 3000 – 15 000 mPas, measured from 15 weigh-% aqueous solution at pH 3, at 25 °C. The bulk viscosity values are measured by using Brookfield DV1 viscometer, equipped with small

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sample adapter, maximum rpm. Spindle SC4-18 is used. If the viscosity value measured with spindle SPC-18, exceeds 1000 mPas, spindle SC4-31 is used for the bulk viscosity measurement. Maximum rotation speed is used in the determination to get maximum torque value in each determination.

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The polymeric structure, irrespective if it is obtained by gel polymerisation or solution polymerisation, preferably has a molecular weight which provides a bulk viscosity of > 500 mPas, preferably > 1000 mPas, more preferably > 3000 mPas, and a standard viscosity of <5 mPas, preferably <4.5 mPas, more preferably <4.0 mPas. Bulk and standard viscosities are measured as defined above.

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The polymeric structure may comprise 3 – 50 weight-%, preferably 5 – 40 weight-%, more preferably 7 – 40 weight-%, of at least one host polymer, calculated from the total polymer content, as dry.

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The polymeric structure is amphoteric, which means that it comprises charged groups originating from first monomers and charged groups originating from second monomers, which groups are oppositely charged. The polymeric structure may also contain a plurality of different first and second monomers. For example, the host polymer may be a copolymer of (meth)acrylamide and two or more charged second monomers and/or the interlacing polymer may be a copolymer of (meth)acrylamide and two or more charged first monomers. The polymeric structure may also comprise plurality of host polymers that are different from each other.

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Even if the polymeric structure itself is amphoteric, the host polymer and interlacing polymer are preferably non-amphoteric, i.e. the host polymer is either anionic or cationic and the interlacing polymer is either anionic or cationic, as long they have opposite charge. The polymeric structure is thus formed at least from two individual polymers which are oppositely charged.

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Preferably the polymeric structure of the present invention comprises an interlacing polymer or a host polymer, which is has an anionic net charge.

The polymeric structure may be obtained by polymerisation, preferably by solution polymerisation, of a non-ionic monomer, such as (meth)acrylamide, and at least one cationically charged first monomer, wherein the polymerisation medium may

5 comprise at least one host polymer, which is a copolymer of non-ionic monomer, such as (meth)acrylamide, and at least an anionically charged second monomer. According to one embodiment, especially if the polymeric structure is obtained by solution polymerisation, the polymeric structure may be obtained by copolymerisation of non-ionic monomer, preferably (meth)acrylamide, and 0.2 – 20

10 mol-%, preferably 0.2 – 15 mol-%, more preferably 0.5 – 12 mol-%, even more preferably 0.6 – 12 mol-%, of at least one cationically charged first monomer, calculated from total dry weight of non-ionic monomers, such as (meth)acrylamide, and the charged monomers of the polymeric structure. According to another embodiment, the polymeric structure may be obtained by copolymerisation of non-

15 ionic monomer, preferably (meth)acrylamide, and 3 - 20 mol-%, preferably 3 – 15 mol-%, more preferably 5 – 10 mol-%, of at least one cationically charged first monomer, calculated from total dry weight of non-ionic monomer, such as (meth)acrylamide, and the charged monomers of the polymeric structure.

20 According to another embodiment of the invention the polymeric structure may be obtainable by polymerisation of non-ionic monomer, such as (meth)acrylamide, and at least one anionically charged first monomer, wherein the polymerisation medium may comprise at least one host polymer, which is a copolymer of non-ionic monomer, preferably (meth)acrylamide, and at least a cationically charged

25 second monomer. Preferably, the polymeric structure may be obtained by copolymerisation of non-ionic monomer, preferably (meth)acrylamide, and 0.1 – 20 mol-%, more preferably 0.1 – 15 mol-%, even more preferably 5 – 10 mol-%, of at least one anionically charged first monomer, calculated from total dry weight of non-ionic monomer, such as (meth)acrylamide, and the charged monomers of the

30 polymeric structure.

According to one embodiment of the invention the polymeric structure may be obtained by polymerisation, preferably by gel polymerisation, of non-ionic

monomer, such as (meth)acrylamide, and at least one anionically charged first monomer and at least one cationically charged first monomer. This means that the interlacing polymer, which is polymerised in the polymerisation medium, is in itself amphoteric and comprises both anionically and cationically charged groups, originating from the respectively charged first monomers. The interlacing polymer, even if it comprises both anionic and cationic groups, has preferably a net anionic charge, for example amount of anionically charged groups may preferably be higher than the amount of cationically charged groups. The polymerisation medium typically comprises a host polymer which is obtained by polymerisation of (meth)acrylamide and cationically charged second monomers.

According to a further embodiment the polymeric structure may comprise at least one host polymer, which is a copolymer of non-ionic monomer, such as (meth)acrylamide, and a cationically charged second monomer and an anionically charged second monomer, i.e. the host polymer itself is amphoteric. The interlacing polymer may be obtained by polymerisation of (meth)acrylamide and at least one anionically charged first monomer and/or at least one cationically charged first monomer.

The host polymer may have a weight average molecular weight of at least 5000 g/mol and $\leq 1\,000\,000$ g/mol, preferably $\leq 500\,000$ g/mol, more preferably $\leq 200\,000$ g/mol. The weight average molecular weight of the host polymer may be in the range of 3000 – 1 000 000 g/mol, preferably 10 000 – 500 000 g/mol, more preferably 10 000 – 200 000 g/mol or 20 000 – 200 000 g/mol. These weight average molecular weight values, and especially the preferred ranges, are high enough so that the host polymer remains within the polymeric structure, and low enough to facilitate easy polymerisation of the interlacing polymer, and within the range which has been found to improve water-solubility of the polymeric structure.

The first and/or second monomer may be selected from anionically charged monomers, which are selected from unsaturated mono- or dicarboxylic acids, such as acrylic acid, methacrylic acid, maleic acid, itaconic acid, crotonic acid, isocrotonic acid; unsaturated sulfonic acids, such as 2-acrylamido-2-

methylpropane sulfonic acid (AMPS), methallylsulfonic acid; vinyl phosphonic acids; and any of their mixtures, and their salts. According to one preferable embodiment the anionically charged monomer is acrylic acid.

- 5 The first and/or second monomer may be selected from the cationically charged monomers, which are selected from cationic vinyl monomers, such as 2-(dimethylamino)ethyl acrylate (ADAM), [2-(acryloyloxy)ethyl] trimethylammonium chloride (ADAM-Cl), 2-(dimethylamino)ethyl acrylate benzylchloride, 2-(dimethylamino)ethyl acrylate dimethylsulphate, 2-dimethylaminoethyl
- 10 methacrylate (MADAM), [2-(methacryloyloxy)ethyl] trimethylammonium chloride (MADAM-Cl), 2-dimethylaminoethyl methacrylate dimethylsulphate, [3-(acryloylamino)propyl] trimethylammonium chloride (APTAC), [3-(methacryloylamino)propyl] trimethylammonium chloride (MAPTAC), and diallyldimethylammonium chloride (DADMAC). According to one embodiment the
- 15 monomers with quaternary groups, such as [2-(acryloyloxy)ethyl] trimethylammonium chloride, [2-(methacryloyloxy)ethyl] trimethylammonium chloride, diallyldimethylammonium chloride, [3-(acryloylamino)propyl] trimethylammonium chloride, [3-(methacryloylamino)propyl] trimethylammonium chloride, are preferable as cationic monomers as their cationicity is independent
- 20 from prevailing pH conditions.

According to one preferable embodiment the polymeric structure comprises acrylamide and acrylic acid and ADAM-Cl as first and/or second monomers, or alternatively acrylamide and acrylic acid and DADMAC as first and/or second

25 monomers.

The molar ratio of the first monomers:second monomers in the polymeric structure may be in the range of 1:1.5 – 1:10, preferably 1:1.5 – 1:4. It is advantageous that there is a sufficient difference in the molar amounts of the first and second

30 monomers. In this manner the risk of self-contraction of the polymeric structure is minimised, and maximal outreach of the structure may be obtained.

According to one embodiment of the invention the host polymer in the polymerisation medium has a higher absolute charge density than the interlacing polymer, which is obtained by polymerisation of non-ionic monomer, such as (meth)acrylamide, and at least a first charged monomer.

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According to one embodiment of the invention the polymeric structure may comprise at least 60 mol-%, preferably at least 70 mol-%, more preferably at least 80 mol-%, even more preferably at least 85 mol-% of non-ionic monomer, preferably (meth)acrylamide, calculated from total dry weight of non-ionic
10 monomer, such as (meth)acrylamide, and the charged monomers of the polymeric structure.

The polymeric structure may be obtained by two-stage polymerisation process. In the first stage at least the host polymer of the polymerisation medium is obtained
15 by polymerising (meth)acrylamide and at least a charged second monomer. After this it is possible to add successive host polymers to the polymerisation medium. In the second stage (meth)acrylamide and at least a charged first monomer polymerisation is added to the polymerisation medium, and the polymerisation process is started to obtain the desired polymeric structure. The polymeric
20 structure may comprise residual monomers, such as residual (meth)acrylamide, DADMAC or acrylic acid, in amount of < 1000 mg/kg or < 500 mg/kg, preferably < 100 mg/kg, more preferably < 50 mg/kg, sometimes even < 25 mg/kg. The given amounts apply for each monomer, separately. Even if the host polymer would contain residual monomers after the first polymerisation stage, these residual
25 monomers are usually consumed in great amount during the polymerisation of the interlacing polymer and thus become incorporated into the polymeric structure. The two-stage polymerisation provides an efficient use of raw materials with low amount of non-polymerised monomers, as well as safe products for end-use. The low amounts of the residual monomers make the use of polymeric structure
30 especially suitable for use in making of food grade paper or board.

Furthermore, the polymeric structure is suitable for use in making of paper, board, tissue or the like as retention agent, drainage agent, sludge dewatering agent,

fixation agent, flotation agent, or emulsifier for hydrophobic sizing agents, such as ASA. Preferably the polymeric structure is used as a strength agent in making of paper, board, tissue or the like.

- 5 The polymeric structure may be used as dry strength agent in making of paper, board, tissue or the like. It improves especially the tensile strength, burst strength and short span compression test (SCT) strength values, Concora medium test (CMT) values, ring crush test (RCT) values and z-directional tensile test (ZDT) values of the final paper or board.

10

According to one embodiment of the invention the polymeric structure is especially suitable as dry strength agent for making paperboard, such as liner, fluting, folding boxboard (FBB), white lined chipboard (WLC), solid bleached sulphate (SBS) board, solid unbleached sulphate (SUS) board or liquid packaging board (LPB),
15 but not limited to these. The basis weight or grammage of the board may be from 120 to 550 g/m² or from 120 to 500 g/m².

20

According to one embodiment of the invention the polymeric structure is especially suitable for improving dry strength properties of paper, board, or the like, which
20 comprises recycled fibres. The paper, board, or the like, may be prepared from fibre stock, which may contain at least 30 weight-%, preferably at least 60 weight-%, even 100 weight-% of recycled fibres, calculated as dry from the total weight of the fibres. Additionally, the fibre stock may comprise fibres originating from broke.

25

The polymeric structure is added in an aqueous fibre stock in amount of 500 - 5000 g/ton dry stock. In the present context the fibre stock is understood to comprise not only water and fibres, but also fillers and other inorganic or organic material used for making of fibrous webs, such as paper, board or tissue. Before
30 addition to the fibre stock the polymeric structure is dissolved and/or diluted to the suitable addition concentration, e.g. concentration of around 0.05 – 0.1 weight-%, and it may be added to the thick stock and/or thin stock, preferably at least to the thick stock. Preferably the polymeric structure is added to the stock in form of an aqueous solution, and the aqueous dissolved and/or diluted solution of the

- polymeric structure has pH of 3.1 – 7, preferably 3.2 – 5.5, more preferably 3.3 – 4.5 at the time of addition to the fibre stock. This application pH allows the molecules of polymeric structure to form larger entities, and thus improving the performance of the polymeric structure. It has been observed that the said
- 5 application pH is especially beneficial for improvement of strength results obtained.

EXPERIMENTAL

- 10 This experimental section describes polymerisation of various polymeric structures as well as their use in paper and board making applications.

Polymerisation Examples

15 **Used methods for characterisation of polymeric structures**

Procedure for standard viscosity measurement

- Weigh 300 g $\pm$ 1 g deionised water at room temperature into a 500 ml squat beaker. Set the paddle in the centre of the solution and stir at 250 $\pm$ 5 rpm.
- 20 Calculate the weight of polymeric structure by using the formula:
Weight of polymeric structure = 0.33 x (100/% dry weight)
For example, for a polymeric structure with 90% dry weight, the weight of the required polymeric structure is 0.367 g.
- Weigh out the required weight of polymeric structure to $\pm$ 0.001 g accuracy.
- 25 Sprinkle the polymeric structure into the sides of the vortex ensuring that no agglomerates are formed and that all the polymeric structure is fully wetted. If any agglomerates form, discard the solution and start again. Stir for 1 minute, then reduce stirring speed to 200 $\pm$ 5 rpm and continue stirring for two hours. After 2 hours, add 17.5 $\pm$ 0.1 g of sodium chloride and if needed, adjust pH to pH 3.
- 30 Continue stirring at the same speed for an additional 20 minutes. Ensure that all the sodium chloride is dissolved. If not, discard and start again. Filter the obtained solution of polymeric structure through a 250-micron stainless steel sieve,

diameter 10 cm. Ensure that the sieve is clean and not blind as this could affect the viscosity.

Rinse out the measuring cylinder with 20 ml of the filtered solution and use a
5 further 20 ml to rinse out the UL adapter. Measure a 16 ml aliquot of filtered
solution of the polymeric structure on a Brookfield DV1 viscometer using the UL
adapter at 25°C at 60 rpm. Take 3 readings on this first aliquot. Ignore the first
reading and, provided that the following two readings are within 0.05 cp from each
other, average the two readings. If the readings are more than 0.05 cp apart then
10 discard the first aliquot, and repeat the process using a second aliquot from the
filtered solution. Record results with 2 decimals.

Method for bulk viscosity measurements

Viscosity is measured at 25 °C, at pH 3. Viscosity of polymer solution is
15 determined by Brookfield DV1 viscometer, which is equipped with a small sample
adapter, spindle 31, and by using maximum applicable rotation speed.

Dry content

Dry content of the polymeric structure is determined by drying a known weight of
20 polymeric structure in an oven at 110 °C for three hours and then weighing the
amount of dried material. The dry content of the polymeric structure is calculated
by the equation: $\text{dry content} = 100 * (\text{dried material, g} / \text{original known weight of polymeric structure, g})$.

25 pH

pH is determined at 25 °C by a pH meter Knick Portamess Type 911 pH.

Determination of molecular size of cationic polymers by size exclusion chromatography (SEC)

30

Molecular size is determined with a gel permeation chromatography, GPC, system
equipped with integrated autosampler, degasser, column oven and refractive index
detector. Eluent is a buffer solution containing 0.3125 M CH₃COOH + 0.3125 M

CH₃COONa, flow rate 0.5 ml/min, at 35 °C. The column set consisted of a precolumn and two columns (a TSKgel PWXL guard column and two TSKgel GMPWXL columns from Tosoh Biosciences). A refractive index detector is used for detection. The molecular weights and polydispersities are determined by using a conventional (column) calibration with poly(ethyleneoxide)/poly(ethylene glycol) narrow molecular weight distribution standards (PSS Polymer Standards Service GmbH, Germany). The injection volume is 50 µl with a sample concentration of about 0.1 – 4 mg/ml, depending on the sample. Ethylene glycol (1mg/ml) is used as a flow marker.

Determination of molecular size of anionic polymers by size exclusion chromatography (SEC)

Molecular size is determined with a gel permeation chromatography, GPC, system equipped with integrated autosampler, degasser, column oven and refractive index detector. Eluent is an aqueous solution containing 2.5 weight-% of acetonitrile and 0.1 M sodium nitrate, flow rate 0.8 ml/min, at 35 °C. The column set consisted of a precolumn and three columns (Ultrahydrogel precolumn, Ultrahydrogel 2000, Ultrahydrogel 250 and Ultrahydrogel 120, all columns by Waters Corporation, USA). A refractive index detector is used for detection. The molecular weights and polydispersities are determined using conventional (column) calibration with poly(ethyleneoxide)/poly(ethylene glycol) narrow molecular weight distribution standards (PSS Polymer Standards Service GmbH, Germany). The injection volume is 50 µl with a sample concentration of between 0.1 – 4 mg/ml depending on the sample. Ethylene glycol (1mg/mL) is used as a flow marker.

Monomer residuals

Acrylamide and acrylic acid residues are analysed by Shimadzu Nexera XR HPLC, equipped with Kinetex 5 µm, 4.6x250 mm (Phenomenex) column and using UV-detection with 200 nm wavelength for acrylic acid and 225 nm for acrylamide. Eluent is 0.025 M NaH₂PO₄ pH 3, flow rate 1 ml/min. Injection volume is 5 µl. Quantification is done using external standard calibration (ESTD) with authentic standards and the identity of the peaks is confirmed with positive UV-spectral

recognition. A sample of polymeric structure, weight 2.00 g, is diluted with purified water and 0.5 ml phosphoric acid (85 %) to 50 ml total volume. The sample is sonicated in ultrasound bath for 7 min, mixed and filtered with 0.5 µm syringe filter before HPLC analysis.

5

Polymerisation Example 1: Preparation of polymeric structure in solution form, anionic host polymer

Three different aqueous polymeric structures in solution form are produced by a two-stage polymerisation process. The first polymerisation stage is identical for all polymeric structures. The monomers and their amounts used at the second stage vary and are explained below.

First polymerisation stage

15 The anionic host polymer is first polymerised according to the following procedure: 387 g of de-ionized water is dosed into a reactor equipped with an agitator and a jacket for heating and cooling. The water is heated to 100 °C. Monomer solution is prepared by mixing 525 g of acrylamide (37.5 weight-%), 0.5 g of sodium hypophosphite, 50 g of acrylic acid and 0.5 g of diethylenetriamine-penta-acetic acid, penta sodium salt (40 %). The monomer mixture is purged with nitrogen gas for 15 min. Initiator solution is prepared by dissolving 2 g of ammonium persulfate in 34 g of de-ionized water. Dosages of the monomer solution and the initiator solution to the reactor are started at the same time. Dosing time of the monomer solution is 60 min and dosing time of the initiator solution is 105 min, under constant agitation. Temperature is kept at 100 °C during dosing. When the dosing of the initiator solution is completed, then the agitation is continued for 30 min at 100 °C. Obtained solution of host polymer A is then cooled to 25 °C. Characteristics of the host polymer A solution are given in Table 1.

Table 1 Characteristics of the host polymer A solution

Characteristic	Value
Dry Content [%]	25.5
Bulk Viscosity [mPas]	1230
pH	4.15
Residual Acrylamide [mg/kg]	43
Residual Acrylic Acid, [mg/kg]	<10
Weight Average Molecular Weight, MW _r [g/mol]	133 000
Number Average Molecular Weight, MW _n [g/mol]	15 200
Peak Molecular Weight, MW _p [g/mol]	106 000
Polydispersity Index, PDI *	8.75

*PDI = MW_r/MW_n

Second polymerisation stage: Production of polymeric structure A, involving a cationic monomer

In the second polymerisation stage a second monomer mixture is polymerized in a polymerisation medium comprising the host polymer solution.

A mixture of 525 g of de-ionized water, 145 g of host polymer A solution and 1 g citric acid is prepared in the reactor described in production of the host polymer in the first polymerisation stage. The mixture is purged with nitrogen for 15 min and then heated to 80 °C. A second monomer solution is prepared by mixing 227 g of acrylamide (37.5 weight-%), 32 g of acryloyloxyethyltrimethylammonium chloride (80 weight-%) and 0.5 g of diethylenetriamine-penta-acetic acid, penta sodium salt (40 %). The second monomer solution is purged with nitrogen gas for 15 min. Initiator solution is made by dissolving 0.5 g of ammonium persulfate in 34 g of de-ionized water. Dosages of the second monomer solution and the initiator solution to the reactor are started at the same time. Dosing time of the second monomer solution is 60 min and dosing time of the initiator solution is 90 min, under agitation. Temperature is kept at 80 °C during dosing. When dosing of the initiator solution is completed, then the agitation is continued for 30 min at 80 °C. Then an aqueous solution of 0.25 g of ammonium persulfate and 37 g of de-ionized water is dosed into the reactor at one time. The reaction is continued at 80 °C for 30 min. Obtained polymeric structure A is then cooled to 25 °C. Characteristics of the

polymeric structure A, which is a net cationic polymeric structure, are given in Table 2.

Second polymerisation stage: Production of polymeric structure B, involving an anionic monomer

A net anionic polymeric structure B is prepared in a similar way as the net cationic polymeric structure A, except the second monomer solution comprised 257 g of acrylamide (37.5 weight-%) and 18 g of acryloyloxyethyltrimethylammonium chloride (80 weight-%). Initiator solution comprised 1.2 g of ammonium persulfate and 34 g of de-ionized water. Characteristics of the polymeric structure B, which is a net anionic polymeric structure, are given in Table 2.

Second polymerisation stage: Production of polymeric structure C, involving a cationic monomer

A net cationic polymeric structure C is prepared in the same way as the polymeric structure A, except that a mixture of 359 g of de-ionized water, 193 g of host polymer A solution and 1 g citric acid is prepared in the reactor. The second monomer solution comprised 303 g of acrylamide (37.5 wt-%) and 42.5 g of acryloyloxyethyltrimethylammonium chloride (80 wt-%). Characteristics of the polymeric structure C, which is a net anionic polymeric structure, are given in Table 2.

Table 2 Characteristics of polymeric structures A, B and C.

Characteristics	Polymeric Structure		
	A (net cationic)*	B (net anionic)*	C (net cationic)*
Charge Density at pH 2.8 [meq/g dry]	0.88	0.49	0.88
Charge Density at pH 7.0 [meq/g dry]	0.19	-0.21	0.19
Total Ionicity [mol-%]	13	9	13
Dry Solids [%]	14.9	14.9	20.9
Bulk Viscosity [mPas]	4130	4020	3440
pH	3.2	2.9	3.3
Residual Acrylamide [mg/kg]	65	80	18
Residual Acrylic Acid [mg/kg]	< 10	< 10	< 10

*at pH 7

Polymerisation Example 2: Preparation of polymeric structure in solution form, cationic host polymer

- 5 An aqueous polymeric structure in solution form are produced by a two-stage polymerisation process.

First polymerisation stage

The cationic host polymer is polymerised according to the following procedure:

- 10 350 g of de-ionized water is dosed into a reactor equipped with an agitator and a jacket for heating and cooling. The water is heated to 100 °C. Monomer solution is prepared by mixing 477 g of acrylamide (37.5 weight-%), 104 g of diallyldimethylammonium chloride (DADMAC, 65 weight-%), 1 g of citric acid and 0.6 g of diethylenetriamine-penta-acetic acid, penta sodium salt (40 %). The
- 15 monomer mixture is purged with nitrogen gas for 15 min. Initiator solution is prepared by dissolving 2 g of ammonium persulfate in 34 g of de-ionized water. Dosages of the monomer solution and the initiator solution to the reactor are started at the same time. Dosing time of the monomer solution is 90 min and dosing time of the initiator solution is 120 min, under constant agitation.
- 20 Temperature is kept at 100 °C during dosing. When the dosing of the initiator solution is completed, then the agitation is continued for 30 min at 100 °C. The obtained host polymer B is diluted with 31 g of de-ionized water and cooled to 25 °C. Characteristics of the host polymer B solution are given in Table 3.
- 25 The amount of residual DADMAC is determined by NMR technique, which is well-known as such for persons skilled in polymerisation techniques and polymer analysis. NMR spectrum of the host polymer B showed proportion of polymerised DADMAC 98 mol-% and DADMAC monomer 2 mol-%. The amount of residual DADMAC was thus 1350 mg/kg.

Table 3 Characteristics of host polymer B.

Characteristic	Values
Dry Solids, %	25.8
Bulk Viscosity, mPas	310
pH	4.2
Residual Acrylamide, mg/kg	56
Residual DADMAC, mg/kg *	1350
Weight Average Molecular Weight, MW _r , g/mol	103 000
Number Average Molecular Weight, MW _n , g/mol	26 000
Peak Molecular Weight, MW _p , g/mol	101 000
Polydispersity Index, PDI **	4.0

*Residual DADMAC is determined by NMR.

**PDI = MW_r/MW_n

5 *Second polymerisation stage: Production of polymeric structure D, involving an anionic monomer*

In the second polymerisation stage a second monomer mixture is polymerised in a polymerisation medium comprising the host polymer solution.

- 10 A mixture of 525 g of de-ionized water, 143 g of host polymer B solution and 1 g of citric acid is prepared to the reactor described in production of the host polymer B in the first polymerisation stage. The mixture is purged with nitrogen for 15 min and then heated to 100 °C. A second monomer solution is prepared by mixing 277 g of acrylamide (37.5 weight-%), 6.7 g of acrylic acid, 0.14 mg of methylenebis-
- 15 acrylamide and 0.5 g of diethylenetriamine-penta-acetic acid, penta sodium salt (40 %). The second monomer solution is purged with nitrogen gas for 15 min. Initiator solution is prepared by dissolving 0.13 g of ammonium persulfate in 34 g de-ionized water. Dosages of the second monomer solution and the initiator solution to the reactor are started at the same time. Dosing time of the second
- 20 monomer solution is 90 min and dosing time of the initiator solution is 100 min, under agitation. Temperature is kept at 100 °C during dosing. When dosing of the initiator solution is completed, then the agitation is continued for 15 min at 100 °C. Then an aqueous solution of 0.5 g of ammonium persulfate and 10 g de-ionized water 10 g is dosed into the reactor at one time. The reaction is continued at 100
- 25 °C for 30 min. Obtained polymeric structure D is then cooled to 25 °C.

Characteristics of the polymeric structure D, which is a net anionic polymeric structure at pH 7, are given in Table 4.

Table 4. Characteristics of polymeric structure D

Characteristic	Values
Charge Density at pH 2.8 [meq/g dry]	0.42
Charge Density at pH 7.0 [meq/g dry]	-0.2
Total Ionicity [mol-%]	8
Dry Solids [%]	14.1
Bulk Viscosity [mPas]	2725
pH	4.2
Residual Acrylamide [mg/kg]	20
Residual Acrylic acid [mg/kg]	9

5

DADMAC monomer signals was not detected in the polymeric structure D by using NMR technique. This indicates that the residual DADMAC monomer present in host polymer B was reacted in the second polymerisation stage.

10 **Polymerisation Example 3: Preparation of water-soluble amphoteric polymeric structures in dry form**

Several amphoteric polymeric structures in powder form are prepared by gel polymerisation of acrylamide and charged monomer(s) in an aqueous solution of a
15 host polymer.

Following cationic host polymers are used in the preparation of polymeric structures:

H1: an aqueous solution of copolymer of diallyldimethylammonium chloride, DADMAC, (14.2 mol-%) and acrylamide (85.8 mol-%), obtained by solution polymerisation and having charge density of about 1.67 meq/g dry polymer, dry solids content of 38.3 weight-%, and bulk viscosity 69 mPas, and containing residual acrylamide less than 1 ppm; or

H2: an aqueous solution of copolymer of [2-(acryloyloxy)ethyl] trimethylammonium chloride, ADAM-Cl, (9.8 mol-%) and acrylamide (90.2 mol-%), obtained by solution
25

polymerisation and having charge density of about 1.17 meq/g dry polymer, dry solids content of 30.8 weight-%, and bulk viscosity 2900 mPas, and containing residual acrylamide less than 10 ppm.

- 5 A reactant solution is prepared by mixing acrylamide, charged monomer(s) and the aqueous solution of the selected host polymer H1 or H2. Na-hypophosphite, diethylenetriaminepentaacetic acid Na-salt, adipic acid and citric acid are added for adjusting the pH of the reactant solution and for controlling the molecular weight of the polymeric structure to be formed. The obtained mixture is stirred until
- 10 the solid substances are dissolved. pH is adjusted to about pH 3 – 4 by using sulfuric acid (conc. 50 weight-%). The initiator system comprised of a thermal initiator 2,2'-azobis(2-methylpropionamidine)dihydrochloride (typical dose 0.5 g) and a redox pair comprising ammonium persulfate (typical dose 0.01 g) and ferrous ammonium sulphate (typical dose 0.01 g). After the reactant solution is
- 15 prepared, thermal initiator is added (dissolved in 5 ml of water) and the reactant solution is degassed by nitrogen gas at low temperature, typically from -8 to +2 °C, more typically from -7 to -4 °C. The redox pair is then injected (each dissolved in 5 ml of water) to the reactant solution to start the radical adiabatic gel polymerisation. After the maximum temperature of the exothermic reaction has
- 20 been reached, the obtained gel is moved to postpolymerisation in an oven at temperature of about 85 °C, and then cut mechanically by running through a meat grinder and dried to a moisture content less than 10 % in an oven at temperature of about 60 °C. The dried polymer is then ground and sieved and particle size range of 0.5 – 1.0 mm is collected.

25

Amphoteric reference polymers are prepared essentially in the same way but without using any host polymer.

- Characteristics of the amphoteric polymeric structures and reference polymers are
- 30 given in Tables 5 and 6.

Table 5 Characteristics of the amphoteric polymeric structures and reference polymer R-1.

	R-1 (ref.)	A-1	A-3	A-7	A-8	A-13	A-14	A-16
Acrylamide* [mol-%]	89.0	89.0	89.0	91.0	91.0	91.0	91.0	91.0
Acrylic Acid, Na-salt* [mol-%]	7.0	7.0	7.0	6.0	6.0	6.0	6.0	6.0
ADAM-Cl [mol-%]*	4.0	-	2.0	2.0	0.8	2.0	2.0	0.8
Host Polymer	-	H1	H1	H1	H1	H2	H1	H2
DADMAC [mol-%]*, **	-	4.0	2.0	1.0	2.2	-	1.0	-
ADAM-Cl [mol-%]*, **	-	-	-	-	-	1.0	-	2.2
Amount of Host [w-% of polymeric structure]	0.0	29.6	14.7	7.4	16.6	11.0	7.9	24.5
Standard Viscosity, SV [cP]	3.0	2.2	2.6	2.8	2.8	2.5	2.8	2.4
Weight Average Molecular Weight, M _w [MDa]	4	3	4	4	4	4	4	4
Total Ionicity [mol-%]	11	11	11	9	9	9	9	9
Charge Density at pH 2.8 [meq/g]	0.52	0.52	0.52	0.40	0.40	0.42	0.40	0.45
Charge Density at pH 7 [meq/g]	-0.38	-0.40	-0.39	-0.39	-0.40	-0.37	-0.39	-0.34

*mol-% calculated from total polymeric structure

**originating from the host polymer

5

Table 6 Characteristics of the amphoteric polymeric structures and reference polymer R-2.

	A-19	A-20	A-21	A-22	A-23	A-25	R-2 (ref)
Acrylamide* [mol-%]	91.0	91.0	91.0	91.0	91.0	90.0	92.1
Acrylic Acid, Na-salt* [mol-%]	6.0	6.0	6.0	6.0	6.0	7.0	7.1
ADAM-Cl* [mol-%]	0.4	0.9	0.8	0.8	0.6	0.6	0.8
Host Polymer	H1	H1	H1	H1	H1	H1	-
DADMAC [mol-%]*, **	2.6	2.1	2.2	2.2	2.4	2.4	-
Amount of Host [w-% of polymeric structure]	19.7	15.6	16.6	16.6	17.7	17.6	0.0
Standard Viscosity, SV [cP]	2.8	3.1	2.5	3.1	2.6	3.1	3.0
Weight Average Molecular Weight, M _w [MDa]	4	5	4	5	4	5	5
Total Ionicity [mol-%]	9	9	9	9	9	9	7.9
Charge Density at pH 2.8 [meq/g]	0.40	0.38	0.40	0.40	0.40	0.40	0.10
Charge Density at pH 7 [meq/g]	-0.40	-0.42	-0.40	-0.40	-0.40	-0.53	-0.87

*mol-% calculated from total polymeric structure

**originating from the host polymer

10

Application Experiments

Application Experiments 1 – 6 provide information about the behaviour and effect of different dry strength compositions comprising polymeric structures according to the invention in paper or board making. Table 7 gives methods and standards used for pulp characterisation and sheet testing in the Application Experiments.

15

Table 7 Standards and methods used for pulp characterisation and sheet testing in application examples 1 – 6.

Property	Device	Standard
pH	Knick Portamess 911	-
Conductivity (mS/cm)	Knick Portamess 911	-
Zeta potential (mV)	Mütek SZP-06	-
Consistency (g/l)	-	ISO 4119
Basis weight	Mettler Toledo	ISO 536
Thickness, bulk	Lorentzen & Wettre	ISO 534
Ash content, 525°C	-	ISO 1762
Scott bond	Huygen	Tappi T 569
Z-directional tensile (ZDT)	Lorentzen & Wettre	ISO 15754
Short span compression test (SCT)	Lorentzen & Wettre	ISO 9895
Concora medium test, 30 min (CMT30)	IDM test, PTA Group	ISO 7263:1994
Burst strength	IDM test, PTA Group	ISO 2758
Tensile strength, tensile stiffness, elastic modulus	Lorentzen & Wettre	ISO 1924-3

5 Application Example 1

This application example simulates preparation of multi-ply board, such as folding boxboard or liquid packaging board. Test sheets are made with Formette-dynamic hand sheet former manufactured by Techpap.

- 10 Test fibre stock is made from 80 % of bleached dried CTMP having Canadian standard Freeness of 500 ml and from 20 % of dry base paper broke from manufacture of folding box board. Test pulp is disintegrated according to ISO 5263:1995, at 70 °C. Test fibre stock is diluted to 0.6 % consistency with de-ionized water, pH adjusted to 7, and conductivity is adjusted to 1.5 mS/cm with a
- 15 salt mixture containing 70 % calcium acetate, 20 % sodium sulphate and 10 % sodium bicarbonate. Same salt mixture is added water to obtain 1.5 mS conductivity for water, which is used to fill drum of Formette with 5.4 litres for each sheet.
- 20 Starch is added to test pulp before addition of polymeric structure solutions. Used starch is native cationised potato starch having substitution degree 0.035. Starch is cooked at 1% concentration at 97 °C for 60 min.

The polymer structure A-3 and a reference polymeric structure R-1 are dissolved at 0.8 weight-% concentration and diluted to obtain 0.08 weight-% solutions. pH of the polymeric structure solutions is adjusted to pH 3.5 before dosing.

5

Pulp mixture is added to Formette to obtain 110 g/m² basis weight. Chemical additions are made to the mixing tank of Formette according to Table 7. All chemical amounts are given as kg dry chemical per ton dry fibre stock. Water is drained out after all the pulp has been sprayed. Drum is operated with 1400 rpm, mixer for pulp and chemicals preparation 650 rpm and 200 rpm for sheet spraying, 10 pulp pump 1100 rpm, number of sweeps is 29 and scoop time is 60 s. Used retention aid is Fennopol K 3500P (cationic polyacrylamide, Kemira Oyj) which is dissolved at 0.5 weight-%, diluted to 0.05 weight-% concentration, and dosed in amount of 150 g/t pulp mixture 15 s before sheet spraying. Used retention 15 microparticle is FennoSil 442 (colloidal silica, Kemira Oyj) which is diluted to 0.1 weight-% concentration and dosed in amount of 300 g/t pulp mixture 10 s before sheet spraying. Sheet is removed from the drum between wire and 1 blotting paper on the other side of the sheet. Wetted blotting paper and wire are removed. Sheets are wet pressed (Techpap nip press) with 9 bar pressure with 2 passes 20 having new blotting paper each side of the sheet. Before each pass wetted paper machine felts are used both sides in contact with press nip rolls. Sheets are dried in STFI restrained dryer at 130 °C, 10 min. Dry content is determined from the pressed sheet by taking a part of the sheet for weighing and drying in oven for 4 h at 110 °C. Before testing in the laboratory, the sheets are pre-conditioned for 24 h 25 at 23 °C in 50 % relative humidity, according to ISO 187.

The results are shown in Table 8. In Table 8 the geometrical mean value, GM, is a square root of MD strength*CD strength. GM value can be used to evaluate strength properties of sheets with fibre orientation. It is seen from the results in 30 Table 8 that the elastic modulus of the formed sheet is not significantly improved only by addition of starch. Polymeric structures R-1 (reference) and A-3 are net anionic, which means that they change the zeta potential of the pulp towards the anionic direction. Based on zeta potential changes the polymeric structures are

well adsorbed to fibre surface, which is needed to retain the anionic chemicals to web. A-3 is obtained by polymerising anionic and cationic second monomers in the presence of cationic host polymer. This means that A-3 has cationic groups originating both from the host polymer and the second monomer. The results show that a clear improvement in the elastic modulus is obtained with A-3. Good elastic modulus is needed, for example, to improve bending stiffness of board.

Table 8 Results for Application Example 1.

Time [s]	-60	-30	-30	Zeta Potential [mV]	Elastic Modulus GM [Gpa]
Test	Starch [kg/t dry]	R-1 (reference) [kg/t dry]	A-3 [kg/t dry]		
1-1	0	-	-	-15.4	0.81
1-2	14.3	-	-	5.9	0.94
1-4	14.3	1.5	-	0.8	1.03
1-5	14.3	-	1.5	1.0	1.05

10 Application Example 2

This application example simulates preparation of multi-ply board, such as folding boxboard, white top liner or liquid packaging board. Test sheets are made with Rapid Köthen type sheet former.

Test fibre stock is prepared from 80 % of bleached birch kraft pulp refined to SR 25° and 20 % of bleached pine kraft pulp refined to SR 25°. Test pulp is disintegrated according to ISO 5263:1995, at 70 °C. Test fibre stock is diluted to 0.6 % consistency with de-ionized water, pH adjusted to 7, and conductivity to 1.5 mS/cm in the same manner as in Application Example 1. Same salt mixture is added water to obtain 1.5 mS conductivity for water, which is used to fill hand sheet machine dilution water tank to 4 litres volume.

Starch is the same as in the Application Example 1. Starch is cooked at 1 % concentration at 97 °C for 90 min.

25

“SP Ref” is amphoteric copolymer of anionic, cationic and non-ionic monomers that has similar charge density, dry solids content and bulk viscosity than

polymeric structure D. "SP Ref" is thus a copolymer, which contains both anionic and cationic groups, whereas polymeric structure D is obtained by polymerising the anionic polymer in the presence of cationic host polymer as explained above. Both "SP Ref" and polymeric structure D are diluted to 0.1 % concentration and pH
5 adjusted to 3.5 before dosing.

Handsheets having basis weight of 80 g/m² are formed by using Rapid Köthen sheet former, according to ISO 5269-2:2012. Added retention aid is Fennopol K 3500P (cationic polyacrylamide, Kemira Oyj) dissolved at 0.5 weight-%, diluted to
10 0.05 weight-% concentration and dosed in amount of 150 g/t pulp mixture 15 s before sheet forming. Added retention microparticle is FennoSil 442 (colloidal silica, Kemira Oyj) diluted to 0.1 weight-% and dosed 300 g/t pulp mixture 10 s before sheet forming. The handsheets are dried in vacuum dryer for 6 minutes at 92 °C, at 1000 mbar. Before testing in the laboratory, the sheets are pre-
15 conditioned for 24 h at 23 °C in 50 % relative humidity, according to ISO 187.

Results are shown in Table 9. In Table 9 the index values are obtained by dividing the strength result by basis weight of the prepared sheet. The Application Example 2 provides a comparison between polymeric structure according to invention, a
20 cationic wet end starch and conventional amphoteric dry strength copolymer. The polymeric structure D provides good tensile stiffness, which is an important parameter for machine runnability and dimension stability at printing houses. At the same time, the polymeric structure D provides a significant improvement in SCT strength, which is an important parameter for box strength. With improved
25 SCT strength, the boxes can take more load, or they might be manufactured from lower basis weight board.

Table 9 Results for Application Example 2.

Time [s]	-60	-30	-30		
Test	Starch [kg/t dry]	Polymeric Structure D [kg/t dry]	SP Ref (reference) [kg/t dry]	Tensile Stiffness index [kNm/g]	SCT index [Nm/g]
2-1	0	-	-	7.1	29.7
2-2	9.5	-	-	7.3	31.4
2-3	9.5	2.5	-	7.4	33.5
2-4	9.5	-	2.5	7.4	32.6

Application example 3

This application example simulates preparation of multi-ply board, such as folding
 5 boxboard or liquid packaging board. Test sheets are made with Formette-dynamic
 hand sheet former manufactured by Techpap.

Same test fibre stock and starch as in Application Example 1 are used.

- 10 The polymeric structures A-8, A-20 and A-22 are dissolved at 0.8 weight-%
 concentration and diluted to 0.08 weight-% solutions. pH of the polymeric structure
 solutions is adjusted to 3.5 before dosing.

The sheets are prepared with Formette in the same manner as in Application
 15 Example 1, except that in wet pressing wetted paper machine felts are used in the
 first pass on both sides in contact with the press nip rolls, and the second pass is
 made without felts.

The addition times for starch and polymeric structure solutions are given in Table
 20 10.

The results are also shown in Table 10. It can be seen that the polymeric
 structures A-8, A-20 and A-22 are improving the tensile strength, Scott bond and
 ZDT values. Scott bond and ZDT are important parameters to prevent
 25 delamination of the board structure in drying, in coating or in printing. Tensile
 strength can be important strength parameter for paper grades. Furthermore, the
 results indicate that it is possible that the polymeric structures according to

invention may improve press dewatering. Usually also dryness after forming stays on good level.

Table 10 Results for Application Example 3.

Time [s]	-60	-30	-30	-30	Dryness forming [%]	Dryness pressing [%]	Bulk [g/cm ³]	Tensile index [Nm/g]	Scott Bond [J/m ²]	ZDT [kPa]
Test	Starch [kg/t dry]	A-8 [kg/t dry]	A-20 [kg/t dry]	A-22 [kg/t dry]						
3-1	10	0	-	-	14	57	3.1	27	74	141
3-2	10	2	-	-	14	62	3.1	28	82	167
3-3	10	-	1	-	16	58	3.2	28	76	148
3-4	10	-	2	-	16	58	3.2	29	80	161
3-5	10	-	-	2	14	60	3.2	28	81	152

5

Application Example 4

The test furnish and the sheet preparation are similar to Application Example 1.

10 The polymeric structures A-22, R-2 and H1 are dissolved at 0.8 weight-% concentration and diluted to 0.08 weight-% solutions. pH is adjusted to 3.5 before dosing.

15 Polymer H1 corresponds to the host polymer of A-22, and polymer R-2 is obtained polymerising similar monomers than those which are polymerised in the presence of host polymer for polymeric structure A-22. This example thus provides comparison between separately added polymers to the polymeric structure according to invention, where monomers are polymerised in the presence of host polymer.

20 The results are shown in Table 11. It is seen that an addition of 1.3 kg/t of polymeric structure A-22 according to invention gives significantly higher tensile strength and higher Scott bond than the separately added polymers H1 and R-2 in the same total amount of 1.3 kg/t. The ratio between polymers H1 and R-2 corresponds to their theoretical ratio in A-22. This Application Example clearly

indicates that polymeric structures according to invention provides unexpected possibilities to generate improved strength properties.

Table 11 Results for Application Example 4.

Time [s]	-30	-30	-30	Tensile index GM [Nm/g]	Scott bond [J/m ²]
Test	A-22 [kg/t dry]	R-2 [kg/t dry]	H1 [kg/t dry]		
1	-	-	-	10.0	55
2	1.3	-	-	10.8	60
3	-	1.092	0.208	10.3	57

5

Application example 5

This Application Example simulates preparation of testliner and fluting. Test sheets are made with Formette-dynamic hand sheet former manufactured by Techpap.

- 10 Test fibre stock is made from dry test liner originated from the United States, produced from 100 % OCC. Ash content of stock is 7 %. Test pulp is disintegrated according to ISO 5263:1995, at 70 °C. Test fibre stock was diluted to 0.6 % consistency with deionized water, pH adjusted to 7, and conductivity is adjusted to 1.2 mS/cm with a salt mixture containing 70 % calcium acetate, 20 % sodium sulphate and 10 % sodium bicarbonate. Same salt mixture is added water to
15 obtain 1.2 mS conductivity for water, which was used to fill the drum of Formette with 8.5 litres for each sheet.

Following chemicals are used in the Application Example 5:

- 20 CPAM: 10 mol-% cationic polyacrylamide, weight average molecular weight 1 MDa, diluted to 0.1 weight-% concentration before use.

- Starch-HC: cationic waxy starch of 0.055 degree of substitution, cooked at 1 % concentration at 97 °C for 60 min, diluted to 0.1 weight-% concentration before
25 use.

GPAM: cationic glyoxylated polyacrylamide, charge density 2.8 meq/g, weight average molecular weight 0.5 MDa, diluted to 0.1 weight-% concentration before use.

“SP Ref2”: reference, amphoteric copolymer of anionic, cationic and non-ionic monomers that has similar charge density, dry solids content and bulk viscosity than polymeric structure A, diluted to 0.08 weight-% concentration, pH adjusted to 3.5 before dosing.

The polymeric structures A-1 and A-3 are dissolved at 0.8 weight-% concentration. All polymeric structure solutions are diluted to 0.08 weight-% solutions. pH for all polymeric structure solutions is adjusted to 3.5 before dosing.

10

Pulp mixture is added to Formette to obtain 110 g/m² basis weight. Chemical additions are made to the mixing tank of Formette according to Table 12. All chemical amounts are given as kg dry chemical per ton dry fibre stock. Water is drained out after all the pulp is sprayed. Drum is operated with 1400 rpm, mixer for pulp and chemicals preparation 650 rpm and 200 rpm for sheet spraying, pulp pump 1100 rpm, number of sweeps until all material is sprayed and scoop time 60 s. Added retention aid is Fennopol K 3500P (cationic polyacrylamide, Kemira Oyj), dissolved at 0.5 weight-%, diluted to 0.05 weight-% concentration and dosed in amount of 400 g/t pulp mixture 15 s before spraying. Added retention microparticle is FennoSil 2180 (structured aluminized silica, Kemira Oyj) diluted to 0.1 weight-% and dosed in amount of 400 g/t pulp mixture 10 s before sheet spraying. Sheet is removed from drum between wire and 1 blotting paper on the other side of the sheet. Wetted blotting paper and wire are removed. Sheets are wet pressed (Techpap nip press) with 9 bar pressure with 2 passes having new blotting paper each side of the sheet. Before first pass wetted paper machine felts are used both sides in contact with press nip rolls. Sheets are dried in STFI restrained dryer at 130 °C for 10 min. Dry content is determined from the pressed sheet by taking a part of the sheet for weighing and drying in oven for 4 h at 110 °C. Before testing in the laboratory, the sheets are pre-conditioned for 24 h at 23 °C in 50 % relative humidity, according to ISO 187.

The results are shown in Table 12. In Table 12 the geometrical mean value, GM, is a square root of MD strength*CD strength, and it can be used to evaluate

strength properties of sheets with fibre orientation. The index values in Table 12 are obtained by dividing the strength result by basis weight of the prepared sheets. It can be seen from the results that the polymeric structure A in test 5-3 provides better SCT values at the same dosage than the reference "SP Ref2", which is a conventional amphoteric polymer, see test 5-6. Improvement in SCT is beneficial for testliner and fluting, providing enhanced strength or lower weight for corrugated boxes. CMT30 strength is important parameter fluting strength. CMT30 is typically measured in machine direction, MD, because corrugator machines operate in that direction. CMT30 improvement indicates that fluting waves are stronger and that the waves do not collapse so easily in the corrugated board. Tests 5-4 and 5-5 show that improvement in CMT30 can be achieved when polymeric structure according to invention is combined with cationic strength agents.

Table 12 Results for Application Example 5.

Time [s]	-60	-60	-60	-40	-40	SCT index GM Nm/g	CMT30 index MD Nm ² /g
Test	CPAM [kg/t dry]	Starch-HC [kg/t dry]	GPAM [kg/t dry]	Polymeric structure A [kg/t dry]	SP ref2 [kg/t dry]		
5-1	-	-	-	-	-	24.2	1.63
5-2	2	2	-	-	-	26.0	1.72
5-3	-	-	-	3	-	28.1	1.76
5-4	2	2	-	3	-	26.1	1.94
5-5	-	-	4	3	-	25.9	1.82
5-6	-	-	-	-	3	25.3	1.60

Application example 6

This application example simulates preparation of testliner and fluting. Test sheets were made with Rapid Köthen type sheet former.

Test fibre stock is made from 50 % of dry testliner and 50 % of fluting originating from Germany, produced from 100 % recycled fibres. Ash content of furnish is 16 %. Test pulp is disintegrated according to ISO 5263:1995, at 70 °C. Test fibre stock is diluted to 0.6 % consistency with deionized water, pH adjusted to 7, and conductivity is adjusted to 3 mS/cm with a salt mixture containing 70 % calcium acetate, 20 % sodium sulphate and 10 % sodium bicarbonate. Same salt mixture

is added water to obtain 3 mS/cm conductivity for water which is used to fill hand sheet machine dilution water tank to 4 litres. Zeta potential of used test fibre stock is -6.5 mV.

- 5 Following chemicals are used in the Application Example 6:
Starch-HC: prepared from waxy starch of 0.055 degree of substitution, cooked at 1 weight-% concentration at 97 °C for 60 min, diluted to 0.1 weight-% concentration before use.
- 10 “SP Ref2”: amphoteric copolymer of anionic, cationic and non-ionic monomers that has similar charge density, dry solids content and bulk viscosity than polymeric structure A, diluted to 0.1 weight-% concentration, pH adjusted to 3.5 before dosing.
- 15 “SP Ref3”: amphoteric copolymer of anionic, cationic and non-ionic monomers, charge density 0.5 meq/g at pH 2.7, charge density 0.2 meq/g at pH 7. Dry solids content 20 weight-%, bulk viscosity 4000 mPas. Diluted to 0.1 %, pH adjusted to 3.5 before dosing.
- 20 The polymeric structure A is diluted to 0.1 weigh-% concentration, pH adjusted to 3.5 before dosing.

- Handsheets having basis weight of 110 g/m² are formed by using Rapid Köthen sheet former, according to ISO 5269-2:2012. Added retention aid is Fennopol K
- 25 3500P (cationic polyacrylamide, Kemira Oyj) dissolved at 0.5 weight-%, diluted to 0.05 weight-% concentration and dosed to pulp mixture 15 s before sheet forming. Basis weight and retention are kept constant by adjusting retention aid dosage. Added retention microparticle is FennoSil 2180 (structured aluminized silica, Kemira Oyj), diluted to 0.1 weight% and dosed 400 g/t pulp mixture 10 s before
 - 30 sheet forming. The handsheets are dried in vacuum dryers for 6 minutes at 92 °C, at 1000 mbar. Before testing in the laboratory, the sheets are pre-conditioned for 24 h at 23 °C in 50 % relative humidity, according to ISO 187.

Results are shown in Table 13. In Table 13 the index values are obtained by dividing the strength result by basis weight of the prepared sheets. It is seen from the results that polymeric structure A provide a clear improvement in burst strength and SCT strength in comparison to references "SP Ref2" and "SP Ref3". Burst strength and SCT strength are important parameters for a testliner to qualify for major market areas. "SP Ref3" has lower molecular weight than "SP Ref2", and it can be seen that the molecular weight does not influence the performance of these conventional amphoteric polymers very much. It is reasonable to assume that the interlacing structure gives different dimensions to the polymeric structure A than it is possible to achieve with conventional amphoteric polymers. In addition, tests 6-6 and 6-7 show that the combination of cationic strength agent and net anionic polymeric structure A may be useful for achieving burst strength and SCT strength. Depending on zeta potential level of the stock it is possible to select net cationic or net anionic polymeric structure. Net anionic polymeric structures are beneficial in higher zeta potentials. The experiments indicate also that the use of polymeric structures according to invention may lead to savings in retention polymer consumption.

Table 13 Results for Application Example 6.

Time, [s]	-60	-60	-60	-60	-40	-15	-10		
Test	Starch-HC [kg/t dry]	Polymeric structure A [kg/t dry]	SP ref3 [kg/t dry]	SP ref2 [kg/t dry]	Polymeric structure A [kg/t dry]	Retention aid [kg/t dry]	Microparticle [kg/t dry]	Burst index [kPam ² /g]	SCT index [Nm/g]
6-1	-	-	-	-	-	0.4	0.4	1.92	19.2
6-2	-	1.5	-	-	-	0.15	0.4	2.20	21.5
6-3	-	3	-	-	-	0.1	0.4	2.32	21.8
6-4	-	-	1.5	-	-	0.15	0.4	2.11	20.8
6-5	-	-	3	-	-	0.15	0.4	2.10	21.6
6-6	1	-	-	-	1.5	0.1	0.4	2.13	21.0
6-7	1	-	-	-	3	0.1	0.4	2.24	21.3
6-8	-	-	-	1.5	-	0.15	0.4	2.00	20.6
6-9	-	-	-	3	-	0.15	0.4	2.23	21.1

Even if the invention was described with reference to what at present seems to be the most practical and preferred embodiments, it is appreciated that the invention shall not be limited to the embodiments described above, but the invention is intended to cover also different modifications and equivalent technical solutions

5 within the scope of the enclosed claims.

CLAIMS

1. A water-soluble polymeric structure, which is obtainable by polymerisation of a non-ionic monomer, such as (meth)acrylamide, and at least a charged first monomer in a polymerisation medium comprising at least one host polymer, which is a copolymer of a non-ionic monomer, such as (meth)acrylamide, and at least a charged second monomer, the first monomer and the second monomer being oppositely charged,
the polymeric structure having
- a total ionicity in a range of 3 – 50 mol-%, preferably 3 – 40 mol-%, more preferably 3 – 20 mol-%, and
 - a charge density in a range from 0.05 to 3.0 meq/g, preferably from 0.05 to 1.2 meq/g, at pH 2.8; and from -1.0 to +1.0 meq/g, preferably -0.8 to +0.6 meq/g, at pH 7.
2. Polymeric structure according to claim 1, **characterised** in that the polymeric structure has a total ionicity in the range 4 – 16 mol-%, preferably 5 – 14 mol-%.
3. Polymeric structure according to claim 1 or 2, **characterised** in that the polymeric structure has a charge density in the range from 0.1 to 1.0 meq/g, preferably from 0.3 to 1.0 meq/g, at pH 2.8; and from -0.6 to +0.5 meq/g, preferably from -0.4 to +0.4 meq/g, at pH 7.
4. Polymeric structure according to claim 1, 2 or 3, **characterised** in that the polymeric structure has a standard viscosity SV in the range of 1.3 – 5.0 mPas, preferably 1.4 – 4.5 mPas, more preferably 1.5 – 4.0 mPas, measured at 0.1 weight-% solids content in an aqueous NaCl solution (1 M), at 25 °C, at pH 3, using Brookfield DV1 viscometer with UL adapter.
5. Polymeric structure according to claim 1, 2 or 3, **characterised** in that the polymeric structure has a bulk viscosity in the range of 500 – 20 000 mPas, preferably 1000 – 15 000 mPas, more preferably 3000 – 15 000 mPas, measured

from 15 weigh-% aqueous solution at pH 3, 25 °C, measured by using Brookfield DV1 viscometer, small sample adapter (SSA), maximum rpm.

6. Polymeric structure according to any of claims 1 – 5, **characterised** in that the polymeric structure is obtained by polymerisation of non-ionic monomer, such as (meth)acrylamide, and at least a cationically charged first monomer, wherein the polymerisation medium comprises at least one host polymer, which is a copolymer of non-ionic monomer, such as (meth)acrylamide, and at least an anionically charged second monomer.
7. Polymeric structure according to any of claims 1 – 5, **characterised** in that the polymeric structure is obtained by polymerisation of non-ionic monomer, such as (meth)acrylamide, and at least an anionically charged first monomer, wherein the polymerisation medium comprises at least one host polymer, which is a copolymer of non-ionic monomer, such as (meth)acrylamide, and at least a cationically charged second monomer.
8. Polymeric structure according any of preceding claims 1 – 7, **characterised** in that the first and/or second monomer is
 - anionically charged monomer, which is selected from unsaturated mono- or dicarboxylic acids, such as acrylic acid, methacrylic acid, maleic acid, itaconic acid, crotonic acid, isocrotonic acid; unsaturated sulfonic acids, such as 2-acrylamido-2-methylpropane sulfonic acid (AMPS), methallylsulfonic acid; vinyl phosphonic acids, and any of their mixtures, and their salts; and/or
 - the cationically charged monomer, which is selected from cationic vinyl monomers, such as 2-(dimethylamino)ethyl acrylate (ADAM), [2-(acryloyloxy)ethyl] trimethylammonium chloride (ADAM-Cl), 2-(dimethylamino)ethyl acrylate benzylchloride, 2-(dimethylamino)ethyl acrylate dimethylsulphate, 2-dimethylaminoethyl methacrylate (MADAM), [2-(methacryloyloxy)ethyl] trimethylammonium chloride (MADAM-Cl), 2-dimethylaminoethyl methacrylate dimethylsulphate, [3-(acryloylamino)propyl] trimethylammonium chloride (APTAC), [3-(methacryloylamino)propyl] trimethylammonium chloride (MAPTAC), and diallyldimethylammonium chloride (DADMAC).

9. Polymeric structure according to any of preceding claims 1 – 8, **characterised** in that the polymeric structure is obtained by copolymerisation of non-ionic monomer, such as (meth)acrylamide, and 0.2 – 20 mol-%, preferably 0.2 – 15 mol-%, more preferably 0.5 – 12 mol-%, even more preferably 0.6 – 12 mol-% of cationically charged first monomer, calculated from total dry weight of non-ionic monomer, such as (meth)acrylamide, and the charged monomers of the polymeric structure.
10. Polymeric structure according to any of claims 1 – 9, **characterised** in that the polymeric structure is obtained by copolymerisation of non-ionic monomer, such as (meth)acrylamide, and 3 – 20 mol-%, preferably 3 – 15 mol-%, more preferably 5 – 10 mol-%, of cationically charged first monomer, calculated from total dry weight of non-ionic monomer, such as (meth)acrylamide, and the charged monomers of the polymeric structure.
11. Polymeric structure according to claim 9 or 10, **characterised** in that the polymeric structure is obtained by copolymerisation of non-ionic monomer, such as (meth)acrylamide, and 0.1 – 20 mol-%, preferably 0.1 – 15 mol-%, more preferably 5 – 10 mol-%, of anionically charged first monomer, calculated from total dry weight of non-ionic monomer, such as (meth)acrylamide, and the charged monomers of the polymeric structure.
12. Polymeric structure according to any of preceding claims 1 – 11, **characterised** in that the molar ratio of the first monomers:second monomers in the polymeric structure is in the range of 1:1.5 – 1:10, preferably 1:1.5 – 1:4.
13. Polymeric structure according to any of preceding claims 1 – 12, **characterised** in that the polymeric structure comprises 3 – 50 weight-%, preferably 5 – 40 weight-%, more preferably 7 – 40 weight-%, of at least one host polymer, calculated from the total polymer content, as dry.

14. Polymeric structure according to any of preceding claims 1 – 13, **characterised** in that the polymeric structure comprises at least 60 mol-%, preferably at least 70 mol-%, more preferably at least 80 mol-%, even more preferably at least 85 mol-% of non-ionic monomer, such as (meth)acrylamide, calculated from total dry weight of non-ionic monomer, such as (meth)acrylamide, and the charged monomers of the polymeric structure.

15. Use of the polymeric structure according to any of claims 1 – 14 in making of paper, board, tissue or the like as a strength agent, retention agent, drainage agent, sludge dewatering agent or fixation agent, emulsifier for hydrophobic sizing agents, preferably as strength agent.

16. Use according to claim 15, **characterised** in that the polymeric structure is added in a fibre stock in amount of 500 - 5000 g/ton dry stock.

17. Use according to claim 15 or 16, **characterised** in that the polymeric structure is in form of an aqueous solution having pH of 3.1 – 7, preferably 3.2 – 5.5, more preferably 3.3 – 4.5 at the time of addition to the fibre stock.

INTERNATIONAL SEARCH REPORT

International application No
PCT/FI2020/050448

A. CLASSIFICATION OF SUBJECT MATTER INV. D21H17/37 D21H21/06 D21H21/10 D21H21/16 D21H21/18 C08F220/56 ADD. According to International Patent Classification (IPC) or to both national classification and IPC											
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) D21H C08F Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data											
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%;">Category*</th> <th style="width: 70%;">Citation of document, with indication, where appropriate, of the relevant passages</th> <th style="width: 20%;">Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td>WO 2017/149200 A1 (KEMIRA OYJ [FI]) 8 September 2017 (2017-09-08) claims 1-4</td> <td style="text-align: center; vertical-align: top;">1-17</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td>WO 2018/109279 A1 (KEMIRA OYJ [FI]) 21 June 2018 (2018-06-21) claims 1-17</td> <td style="text-align: center; vertical-align: top;">1-17</td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	A	WO 2017/149200 A1 (KEMIRA OYJ [FI]) 8 September 2017 (2017-09-08) claims 1-4	1-17	X	WO 2018/109279 A1 (KEMIRA OYJ [FI]) 21 June 2018 (2018-06-21) claims 1-17	1-17
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.									
A	WO 2017/149200 A1 (KEMIRA OYJ [FI]) 8 September 2017 (2017-09-08) claims 1-4	1-17									
X	WO 2018/109279 A1 (KEMIRA OYJ [FI]) 21 June 2018 (2018-06-21) claims 1-17	1-17									
☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.											
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Date of the actual completion of the international search 22 September 2020		Date of mailing of the international search report 01/10/2020									
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Ponsaud, Philippe									

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/FI2020/050448

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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