

Process for batchwise production of superabsorbent particles by polymerization of an aqueous monomer solution dispersed in a hydrophobic solvent

Description

The present invention relates to a process for batchwise production of superabsorbent particles by polymerizing an aqueous monomer solution dispersed in a hydrophobic solvent, wherein the reaction is conducted in a stirred vessel, the stirred vessel in each case can be heated or cooled and the hydrophobic solvent fed to the stirred vessel, immediately prior to entry into the stirred vessel, is at a temperature of at least 45°C.

The production of superabsorbent particles is described in the monograph "Modern Superabsorbent Polymer Technology", F. L. Buchholz and A. T. Graham, Wiley-VCH, 1998, pages 69 to 117.

Being products that absorb aqueous solutions, superabsorbent particles are used to produce diapers, tampons, sanitary napkins and other hygiene articles, but also as water-retaining agents in market gardening.

The properties of the superabsorbent particles can be adjusted via the degree of crosslinking. As the level of crosslinking increases, gel strength increases and absorption capacity decreases.

To improve the use properties, for example saline flow conductivity in a swollen gel bed (SFC) in the diaper and absorbency under load (AUL), superabsorbent particles are generally surface postcrosslinked. This increases only the level of crosslinking of the particle surface, and in this way it is possible to at least partly decouple absorbency under load (AUL) and centrifuge retention capacity (CRC).

JP 2012-7062 A2, US 5,807,916 A and WO 2008/084031 A1 disclose processes for producing superabsorbent particles by polymerizing a dispersed aqueous monomer solution.

US 2015/0080539 describes a batchwise process using a specific stirred vessel for shortening the heating or cooling operation.

It was an object of the embodiments disclosed herein to provide an improved process for batchwise production of superabsorbents by polymerizing an aqueous monomer solution dispersed in a hydrophobic solvent, particularly with shortening of the batch times.

The object was achieved, in an aspect, by a process for batchwise production of superabsorbent particles by polymerization of an aqueous monomer solution dispersed in a hydrophobic solvent, comprising

- i) initially charging a stirred vessel with a mixture of a hydrophobic solvent and a dispersing aid,
- ii) optionally heating the mixture from step i),
- iii) optionally cooling mixture from step i) or step ii),
- iv) metering an aqueous monomer solution into the mixture from step i), ii) or iii) to obtain a dispersed monomer solution and
- v) polymerizing the dispersed monomer solution to obtain dispersed polymer particles,

wherein the hydrophobic solvent is metered into the stirred vessel alone or together with the dispersing aid and the hydrophobic solvent immediately prior to entry into the stirred vessel is at a temperature of at least 45°C.

The temperature of the hydrophobic solvent prior to entry into the stirred vessel is preferably at least 60°C, more preferably at least 70°C, most preferably at least 75°C.

It is also possible to further heat the hydrophobic solvent in the stirred vessel; for example, the hydrophobic solvent may have a temperature of 60°C prior to entry into the stirred vessel and be heated to 90°C in the stirred vessel.

The dispersing aid is used for dispersion of the aqueous monomer solution in the hydrophobic solvent and of the superabsorbent particles that form.

The dispersing aid may be mixed with the hydrophobic solvent even prior to entry or be metered into the stirred vessel separately from the hydrophobic solvent.

Comparatively high temperatures are typically needed for dissolution of the dispersing aid. If the dispersing aid is not dissolved until within the stirred vessel, it may therefore be advantageous to heat the hydrophobic solvent to a higher temperature. After the dispersing aid has dissolved and before the aqueous monomer solution is metered in, cooling is then advantageous.

Hydrophobic solvents used are typically hydrocarbons and hydrocarbon mixtures.

The hydrocarbons or hydrocarbon mixtures preferably boil within the range from 50 to 150°C, more preferably within the range from 60 to 130°C, very particularly within the range from 70 to 110°C.

In a preferred embodiment of the present disclosure, the hydrophobic solvent, before being metered into the stirred vessel, is heated by means of a heat exchanger. Suitable heat exchangers are, for example, shell and tube heat exchangers or plate heat exchangers.

The heat exchanger typically has a greater effective internal surface area than the stirred vessel. The effective internal surface area is the internal surface area utilizable for heat exchange. The quotient of effective internal surface area of the heat exchanger and effective internal surface area of the stirred vessel is preferably at least 2, more preferably at least 3, most preferably at least 4.

The heat exchanger is typically heated with steam or hot water. The steam used is at a positive pressure relative to ambient pressure of preferably 0.5 to 20 bar, more preferably of 1 to 10 bar, most preferably of 1.5 to 6 bar.

In a preferred embodiment of the present disclosure, the dimensions of the heat exchanger are such that the metering of the hydrophobic solvent into the stirred vessel is not delayed.

In a further preferred embodiment of the present disclosure, the reaction mixture, after the polymerization, is azeotropically dewatered at a temperature of at least 45°C, preferably at least 60°C, more preferably at least 70°C, even more preferably at least 75°C, and then the superabsorbent particles are separated off by means of filtration.

The filtrate obtained in the filtration is at a temperature of at least 45°C, preferably at least 60°C, more preferably at least 70°C, even more preferably at least 75°C, and is recycled into the polymerization as hydrophobic solvent.

The present disclosure enables shortening of the batch times and hence, in a simple and inexpensive manner, an increase in capacity of existing plants.

The production of the superabsorbent particles is elucidated hereinafter:

The aqueous monomer solution used for production of the superabsorbent particles typically comprises

- a) at least one ethylenically unsaturated monomer which bears acid groups and may have been at least partly neutralized,
- b) at least one crosslinker,
- c) at least one initiator,
- d) optionally one or more ethylenically unsaturated monomers copolymerizable with the monomers mentioned under a) and
- e) optionally one or more water-soluble polymers.

The monomers a) are preferably water-soluble, i.e. their solubility in water at 23°C is typically at least 1 g/100 g of water, preferably at least 5 g/100 g of water, more preferably at least 25 g/100 g of water and most preferably at least 35 g/100 g of water.

Suitable monomers a) are, for example, ethylenically unsaturated carboxylic acids, such as acrylic acid, methacrylic acid, maleic acid and itaconic acid. Particularly preferred monomers are acrylic acid and methacrylic acid. Very particular preference is given to acrylic acid.

Further suitable monomers a) are, for example, ethylenically unsaturated sulfonic acids, such as styrenesulfonic acid and 2-acrylamido-2-methylpropanesulfonic acid (AMPS).

The proportion of acrylic acid and/or salts thereof in the total amount of monomers a) is preferably at least 50 mol%, more preferably at least 90 mol%, most preferably at least 95 mol%.

5 The acid groups of the monomers a) may have been partly neutralized. The neutralization is conducted at the monomer stage. This is typically accomplished by mixing in the neutralizing agent as an aqueous solution or else preferably as a solid. The degree of neutralization is preferably from 25 to 95 mol%, more preferably from 30 to 80 mol% and most preferably from 40 to 75 mol%, for which the customary neutralizing agents can be used, preferably alkali metal hydroxides, alkali metal oxides, alkali metal carbonates or alkali metal hydrogencarbonates and also mixtures thereof. Instead of alkali metal salts, it is also possible to use ammonium salts. Particularly preferred alkali metals are sodium and potassium, but very particular preference is given to sodium hydroxide, sodium carbonate or sodium hydrogencarbonate and also mixtures thereof.

15 The monomers a) typically comprise polymerization inhibitors, preferably hydroquinone monomethyl ether (MEHQ), as storage stabilizer.

20 Suitable crosslinkers b) are compounds having at least two groups suitable for crosslinking. Such groups are, for example, ethylenically unsaturated groups which can be polymerized free-radically into the polymer chain, and functional groups which can form covalent bonds with the acid groups of the monomer a). In addition, polyvalent metal salts which can form coordinate bonds with at least two acid groups of the monomer a) are also suitable as crosslinkers b).

25 Initiators c) used may be all compounds which generate free radicals under the polymerization conditions, for example thermal initiators, redox initiators or photoinitiators.

30 Ethylenically unsaturated monomers d) copolymerizable with the ethylenically unsaturated monomers a) bearing acid groups are, for example, acrylamide, methacrylamide, hydroxyethyl acrylate, hydroxyethyl methacrylate, dimethylaminoethyl methacrylate, dimethylaminoethyl acrylate, dimethylaminopropyl acrylate, diethylaminopropyl acrylate, dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate.

35 The water-soluble polymers e) used may be polyvinyl alcohol, polyvinylpyrrolidone, starch, starch derivatives, modified cellulose, such as methyl cellulose or hydroxyethyl cellulose, gelatin, polyglycols or polyacrylic acids, preferably starch, starch derivatives and modified cellulose.

40 For optimal action, the preferred polymerization inhibitors require dissolved oxygen. The monomer solution can therefore be freed of dissolved oxygen before the polymerization by inertization, i.e. flowing an inert gas through, preferably nitrogen or carbon dioxide. The oxygen content of the monomer solution is preferably lowered before the polymerization to less than 1 ppm by weight, more preferably to less than 0.5 ppm by weight, most preferably to less than 0.1 ppm by weight.

45 If the polymerization is conducted under adequate reflux, the inertization can be dispensed with. In this case, the dissolved oxygen is removed from the stirred vessel together with the evaporating solvent.

50 For polymerization, the aqueous monomer solution is dispersed in the hydrophobic solvent.

55 Usable hydrophobic solvents are all the solvents known to the person skilled in the art for use in the inverse method of suspension polymerization. Preference is given to using aliphatic hydrocarbons, such as n-hexane, n-heptane, n-octane, n-nonane, n-decane, cyclohexane or mixtures thereof. Hydrophobic solvents have a solubility in water at 23°C of less than 5 g/100 g, preferably less than 1 g/100 g, more preferably less than 0.5 g/100 g.

The ratio between hydrophobic solvent and aqueous monomer solution is 0.5 to 3, preferably 0.7 to 2.5 and very preferably from 0.8 to 2.2.

60 The mean diameter of the aqueous monomer solution droplets in the dispersion, if no agglomeration is conducted, is preferably at least 100 µm, more preferably from 100 to 1000 µm, more preferably from 150 to 850 µm, most preferably from 300 to 600 µm, the droplet diameter being determinable by light scattering and signifying the volume-average mean diameter.

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The diameter of the aqueous monomer solution droplets can be adjusted via the stirrer energy introduced and through suitable dispersing aids.

- 5 Suitable dispersing aids are, for example, anionic, cationic, nonionic or amphoteric surfactants, or natural, semisynthetic or synthetic polymers.
- 10 Anionic surfactants are, for example, sodium polyoxyethylene dodecyl ether sulfate and sodium dodecyl ether sulfate. A cationic surfactant is, for example, trimethylstearyl ammonium chloride. An amphoteric surfactant is, for example, carboxymethyl dimethylcetyl ammonium. Nonionic surfactants are, for example, sucrose fatty acid esters, such as sucrose monostearate and sucrose dilaurate, sorbitan esters such as sorbitan monostearate, polyoxyalkylene compounds based on sorbitan esters, such as polyoxyethylenesorbitan monostearate.
- 15 Natural or semisynthetic polymers are, for example, cellulose derivatives such as cellulose ethers, for example ethyl cellulose, and cellulose esters, for example cellulose acetate. Synthetic polymers are, for example, polyvinyl alcohols, polyvinyl alcohol derivatives, maleic acid-butadiene copolymers and quaternary salts, such as styrene dimethylaminoethyl methacrylate.
- 20 The dispersing aid is typically dissolved or dispersed in the hydrophobic solvent.
- The dispersing aid is used in amounts between 0.01% and 10% by weight, preferably between 0.2% and 5% by weight and more preferably between 0.5% and 2% by weight, based on the aqueous monomer solution.
- 25 The reaction is preferably conducted under reduced pressure, for example at a pressure of 800 mbar. The pressure can be used to set the boiling point of the reaction mixture to the desired reaction temperature.
- 30 After the polymerization has ended, the dispersed superabsorbent particles obtained can be agglomerated by addition of further aqueous monomer solution and another polymerization. The aqueous monomer solution may have a composition different than the first monomer solution. The agglomeration can also be conducted more than once.
- 35 Subsequently, the dispersed superabsorbent particles obtained are azeotropically dewatered and separated from the hydrophobic solvent by means of filtration. In a preferred embodiment of the present invention, the dispersion obtained after the azeotropic dewatering has not or not completely cooled. The still-warm filtrate is recycled into the polymerization as hydrophobic solvent.
- 40 To further improve the properties, the superabsorbent particles can be surface postcrosslinked. Suitable surface postcrosslinkers are compounds comprising at least two groups that can form covalent bonds with the carboxylate groups of the hydrogel. Suitable compounds are, for example, alkoxysilyl compounds, polyaziridines, polyamines, polyamidoamines, di- or
- 45 polyepoxides (for example Denacol® EX810), as described in EP 83 022 A2, EP 543 303 A1 and EP 937 736 A2, di- or polyfunctional alcohols as described in DE 33 14 019 A1, DE 35 23 617 A1 and EP 450 922 A2, or β -hydroxyalkylamides as described in DE 102 04 938 A1 and US 6,239,230.
- 50 Additionally described as suitable surface postcrosslinkers are cyclic carbonates in DE 40 20 780 C1, 2-oxazolidone and its derivatives, such as 2-hydroxyethyl-2-oxazolidone in DE 198 07 502 A1, bis- and poly-2-oxazolidinones in DE 198 07 992 C1, 2-oxotetrahydro-1,3-oxazine and its derivatives in DE 198 54 573 A1, N-acyl-2-oxazolidones in DE 198 54 574 A1, cyclic ureas in DE 102 04 937 A1, bicyclic amide acetals in DE 103 34 584 A1, oxetanes and
- 55 cyclic ureas in EP 1 199 327 A2 and morpholine-2,3-dione and its derivatives in WO 2003/31482 A1.
- The amount of surface postcrosslinker is preferably 0.01% to 1% by weight, more preferably 0.05% to 0.5% by weight and most preferably 0.1% to 0.2% by weight, based in each case on the polymer.
- 60 In a preferred embodiment of the present invention, polyvalent cations are applied to the particle surface in addition to the surface postcrosslinkers.
- 65 The polyvalent cations usable in the process of the invention are, for example, divalent cations such as the cations of zinc, magnesium, calcium and strontium, trivalent cations such as the

cations of aluminum, iron, chromium, rare earths and manganese, tetravalent cations such as the cations of titanium and zirconium. Possible counterions are chloride, bromide, sulfate, hydrogensulfate, carbonate, hydrogencarbonate, nitrate, phosphate, hydrogenphosphate, dihydrogenphosphate and carboxylate, such as acetate and lactate. Aluminum sulfate is preferred.

The amount of polyvalent cation used is, for example, 0.001% to 0.5% by weight, preferably 0.005% to 0.2% by weight and more preferably 0.02% to 0.1% by weight, based in each case on the polymer.

The surface postcrosslinking can be effected in two different ways.

For instance, it is possible to filter and optionally dry the dewatered dispersion, and only then to surface postcrosslink the superabsorbent particles thus obtained (surface postcrosslinking A).

The surface postcrosslinking here is typically conducted by spraying a solution of the surface postcrosslinker and optionally a solution of the polyvalent cation onto the superabsorbent particles. The spray application is followed by thermal drying, and the surface postcrosslinking reaction may take place either before or during the drying.

The spraying of a solution of the surface postcrosslinker is preferably performed in mixers with moving mixing tools, such as screw mixers, paddle mixers, disk mixers, plowshare mixers and shovel mixers. Particular preference is given to vertical mixers, very particular preference to plowshare mixers and shovel mixers. Suitable mixers are, for example, Lödige mixers, Bepex mixers, Nauta mixers, Processall mixers and Schugi mixers.

The thermal drying is preferably conducted in contact driers, more preferably paddle driers, most preferably disk driers. Suitable driers are, for example, Bepex driers and Nara driers. Moreover, fluidized bed driers may also be used.

The drying can be effected in the mixer itself, by heating the jacket or blowing in warm air. Equally suitable is a downstream drier, for example a shelf drier, a rotary tube oven or a heatable screw. It is particularly advantageous to effect mixing and drying in a fluidized bed drier.

Preferred drying temperatures are in the range of 100 to 250°C, preferably 120 to 220°C, and more preferably 130 to 210°C. The preferred residence time at this temperature in the reaction mixer or drier is preferably at least 10 minutes, more preferably at least 20 minutes, most preferably at least 30 minutes.

It is alternatively possible to add the surface postcrosslinkers and optionally the polyvalent cations to the optionally dewatered dispersion, preferably as an aqueous solution (surface postcrosslinking B). This is then followed by thermal surface postcrosslinking. For this purpose, preference is given to using reactive surface postcrosslinkers, such as di- or polyepoxides. The thermal surface postcrosslinking is optionally followed by azeotropic dewatering, filtering and drying.

Examples

The process from comparative example 1 of US 2015/0080539 was used for the calculations. The effective internal surface area of the stirred vessel is 31.3 m². It was further assumed that the n-heptane is heated by means of a shell and tube heat exchanger during the metered addition to the stirred vessel. The shell and tube heat exchanger is heated by means of steam (5 bar). The effective internal surface area of the shell and tube heat exchanger was chosen such that the metering of the n-heptane into the stirred vessel is not delayed. These data were used to calculate the heating times in the first heating step.

Tab.: Influence of preheating on heating time

Example	Temperature before entry into the stirred vessel	Effective internal surface area of the shell and tube heat exchanger	Time taken for heating to 90°C in the stirred vessel
1*)	25°C	---	113 minutes
2	50°C	62 m ²	73 minutes
3	55°C	75 m ²	70 minutes
4	60°C	87 m ²	65 minutes
5	65°C	99 m ²	60 minutes

6	70°C	112 m ²	53 minutes
7	75°C	124 m ²	46 minutes
8	80°C	137 m ²	38 minutes
9	85°C	149 m ²	23 minutes
10	90°C	161 m ²	0 minutes

*) comparative example

Claims

1. A process for batchwise production of superabsorbent particles by polymerization of an aqueous monomer solution dispersed in a hydrophobic solvent, comprising
 - i) initially charging a stirred vessel with a mixture of a hydrophobic solvent and a dispersing aid,
 - ii) optionally heating the mixture from step i),
 - iii) optionally cooling mixture from step i) or step ii),
 - iv) metering an aqueous monomer solution into the mixture from step i), ii) or iii) to obtain a dispersed monomer solution and
 - v) polymerizing the dispersed monomer solution to obtain dispersed superabsorbent particles,

wherein the hydrophobic solvent is metered into the stirred vessel alone or together with the dispersing aid and the hydrophobic solvent immediately prior to entry into the stirred vessel is at a temperature of at least 45°C.
2. The process according to claim 1, wherein the hydrophobic solvent immediately prior to entry into the stirred vessel is at a temperature of at least 60°C.
3. The process according to claim 1 or 2, wherein the hydrophobic solvent immediately prior to entry into the stirred vessel is at a temperature of at least 70°C.
4. The process according to any of claims 1 to 3, wherein the hydrophobic solvent is a hydrocarbon or hydrocarbon mixture.
5. The process according to claim 4, wherein the hydrocarbon or hydrocarbon mixture boils within the range from 50 to 150°C.
6. The process according to any of claims 1 to 5, wherein the hydrophobic solvent is heated by means of a heat exchanger before being metered into the stirred vessel.
7. The process according to claim 6, wherein the quotient of effective internal surface area of the heat exchanger and effective internal surface area of the stirred vessel is at least 2.
8. The process according to claim 6 or 7, wherein the heat exchanger is heated with steam or hot water.
9. The process according to claim 8, wherein the steam is at a pressure in the range from 0.5 to 20 bar.

10. The process according to claim 8, wherein the steam is at a pressure in the range from 1.5 to 6 bar.
- 5 11. The process according to any of claims 1 to 10, wherein the reaction mixture after the polymerization is azeotropically dewatered and filtered at a temperature of at least 45°C.
12. The process according to claim 11, wherein the filtrate is at a temperature of at least 45°C and is recycled into the polymerization as hydrophobic solvent.
- 10 13. The process according to any of claims 1 to 12, wherein the aqueous monomer solution comprises at least one monomer a), at least one crosslinker b) and at least one initiator c).