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(54) Title: MICROSPHERES

(57) Abstract: The invention relates to thermally expandable thermoplastic microspheres comprising a polymer shell made from ethylenically unsaturated monomers encapsulating a propellant, said ethylenically unsaturated monomers comprising at least one first cross- linking monomer having two or more carbon-to carbon double bonds and at least one second cross-linking monomer having two or more carbon-to-carbon double bonds, said at least one first cross-linking monomer having a reactivity Q greater than 0.2 and said at least one second cross-linking monomer having a reactivity Q less than 0.2, the reactivity Q being defined in accordance with the Alfrey-Price Q-e scheme, the amount of said at least one second cross-linking monomer being less than 0.8 mol% of the total amount of ethylenically unsaturated monomers. The invention further relates to production and use of such microspheres.

MICROSPHERES

The present invention relates to thermally expandable thermoplastic microspheres, its production and use.

Expandable thermoplastic microspheres comprising a thermoplastic polymer shell encapsulating a propellant are commercially available under the trademark EXPANCEL® and are used as a foaming agent in many different applications.

In such microspheres, the propellant is normally a liquid having a boiling temperature not higher than the softening temperature of the thermoplastic polymer shell. Upon heating, the propellant evaporates to increase the internal pressure at the same time as the shell softens, resulting in significant expansion of the microspheres. The temperature at which the expansion starts is called T_{start}, while the temperature at which maximum expansion is reached is called T_{max}. Expandable microspheres are marketed in various forms, e.g. as dry free flowing particles, as an aqueous slurry or as a partially dewatered wet-cake.

Expandable microspheres can be produced by polymerising ethylenically unsaturated monomers in the presence of a propellant. Usually the monomers mainly comprise monomers with one carbon-to-carbon double bond together with small amounts of cross-linking monomers having two or more carbon-to-carbon double bonds. Detailed descriptions of various expandable microspheres and their production can be found in, for example, US Patents 3615972, 3945956, 4287308, 5536756, 6235800, 6235394 and 6509384, 6617363 and 6984347, in US Patent Applications Publications US 2004/0176486 and 2005/0079352, in EP 486080, EP 1230975, EP 1288272, EP 1598405, EP 1811007 and EP 1964903, in WO 2002/096635, WO 2004/072160, WO 2007/091960, WO 2007/091961 and WO 2007/142593, and in JP Laid Open No. 1987-286534 and 2005-272633.

One important application for expandable microspheres is as a foaming agent for processing of polymeric materials, for example in injection moulding, extrusion and others. In some cases it is desirable to have microspheres with a high T_{start} in combination with a T_{max} that is not too high, for example when microspheres are pre-processed together with a polymer and optionally various additives in order to make a well mixed formulation that later can be used in injection moulding, extrusion, thermoforming etc. This mixing step, e.g. compounding, must take place at sufficiently high temperature for the polymer to melt but without pre-expansion of the microspheres, which, for example, could block an extruder or significantly reduce the expansion capacity of the final formulation.

It is an object of the invention to provide expandable microspheres with high expansion capability having a comparatively high T_{start} and high resistance against pre-expansion, combined with a distinct expansion at a temperature relatively close to T_{start}.

It is another object of the invention to provide expandable microspheres useful as foaming agent in thermoplastic materials.

It has surprisingly been found possible to fulfil these objects by providing expandable microspheres in which the monomers comprise at least two different kinds of cross-linking monomers, one kind having high reactivity and one kind having low reactivity.

Thus, one aspect of the invention concerns thermally expandable thermoplastic microspheres comprising a polymer shell made from ethylenically unsaturated monomers encapsulating a propellant, said ethylenically unsaturated monomers comprising at least one first cross-linking monomer having two or more carbon-to carbon double bonds and at least one second cross-linking monomer having two or more carbon-to-carbon double bonds, said at least one first cross-linking monomer having a reactivity Q greater than 0.2 and said at least one second cross-linking monomer having a reactivity Q less than 0.2, the reactivity Q being defined in accordance with the Alfrey-Price Q-e scheme, the amount of said at least one second cross-linking monomer being less than 0.8 mol% of the total amount of ethylenically unsaturated monomers.

The Alfrey-Price Q-e scheme as a way of quantifying the reactivity of monomers is well established in the field of polymers and is described in Robert Z. Greenley, Polymer Handbook, Fourth Edition, Brandrup, Immergut and Grulke, John Wiley & Sons, New York, NY, (1999) pp. 309-319. In the Q-e scheme, Q represents the reactivity of a monomer and e represents the polarity of a monomer. A high value for Q indicates that a monomer has a relatively high reactivity and a low value for Q indicates that a monomer has a relatively low reactivity. In the above document Q values for several monomers are explicitly listed, and for those monomers not listed the Q values can be estimated based on the values for similar monomers.

Preferably the at least one first cross-linking monomer has a reactivity Q from greater than 0.2 to 10 or from 0.4 to 2. The at least one second cross-linking monomer preferably has a reactivity Q from 0.001 to less than 0.2 or from 0.002 to 0.15.

The amount of the at least one first cross-linking monomer, i.e. those having high reactivity, is preferably from 0.01 to 1.0 mol% or from 0.03 to 0.4 mol% of the total amount of ethylenically unsaturated monomers. The at least one first cross-linking monomer may be a mixture of two or more monomers having high reactivity. The amount of the at least one second cross-linking monomer, i.e. those having low reactivity, is preferably from 0.01 to 0.75 mol% or from 0.03 to 0.6 mol% of the total amount of

ethylenically unsaturated monomers. The at least one second cross-linking monomer may be a mixture of two or more monomers having low reactivity. The total amount of the first and second cross-linking monomers is preferably from 0.02 to 1.75 mol% or from 0.06 to 1.0 mol% of the total amount of ethylenically unsaturated monomers. The first and second cross-linking monomers may have two, three, four or more carbon-carbon double bonds, although two or three usually are preferred.

Useful cross-linking monomers having high reactivity (Q greater than 0.2) includes vinyl monomers such as (meth)acrylic esters or (meth)acrylamides or vinyl aromatic monomers having two or more carbon-to carbon double bonds. It is to be understood that whenever a chemical name herein contains “(meth)acryl” it refers to both “methacryl” and “acryl”.

Examples of preferred cross-linking monomers having high reactivity include derivatives of (meth)acrylates such as trimethylolpropane tri(meth)acrylate, ethylene glycol di(meth)acrylate, di(ethylene glycol) di(meth)acrylate, 1,4-butanediol di(meth)acrylate, di(trimethylolpropane) tetra(meth)acrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, dipentaerythritol penta(meth)acrylate, dipentaerythritol hexa(meth)acrylate and tris[2-acryloyloxy)ethyl] isocyanurate. Particularly preferred are derivatives of methacrylates, such as trimethylolpropane trimethacrylate, ethylene glycol dimethacrylate, di(ethylene glycol) dimethacrylate, 1,4-butanediol dimethacrylate, di(trimethylolpropane) tetramethacrylate, pentaerythritol trimethacrylate, pentaerythritol tetramethacrylate, dipentaerythritol pentamethacrylate and dipentaerythritol hexamethacrylate.

Other examples of useful cross-linking monomers having high reactivity include tri(ethylene glycol) di(meth)acrylate, tetra(ethylene glycol) di(meth)acrylate, poly(ethylene glycol) di(meth)acrylate, PEG #200 di(meth)acrylate, PEG #400 di(meth)acrylate, PEG #600 di(meth)acrylate, propylene glycol di(meth)acrylate, di(propylene glycol) di(meth)acrylate, tri(propylene glycol) di(meth)acrylate, tetra(propylene glycol) di(meth)acrylate, poly(propylene glycol) di(meth)acrylate, 1,3-propanediol di(meth)acrylate, 1,3-butanediol di(meth)acrylate, tri(butanediol) di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, 1,8-octanediol di(meth)acrylate, 1,9-nonanediol di(meth)acrylate, 1,10-decanediol di(meth)acrylate, neopentyl glycol di(meth)acrylate, 3-methyl-1,5-pentanediol di(meth)acrylate, 2,4-diethyl-1,5-pentanediol di(meth)acrylate, glycerol di(meth)acrylate, glycerol tri(meth)acrylate, allyl (meth)acrylate, vinyl (meth)acrylate, triacrylformal, divinylbenzene, divinyltoluene, divinylnaphthalene, N,N’-ethylene bisacrylamide.

Further examples of cross-linking monomers having high reactivity include alkyl ether diol di(meth)acrylates (represented by the formula (-R1-O-R2-) constructed of

aliphatic carbons R_1, R_2 and an ether bond, such as 3-oxo-1,6-hexanedioldi(meth)acrylate; and alkyl ester diol di(meth)acrylates (represented by the formula (-R1-COO-R2-) composed of aliphatic carbons R_1, R_2 and an ester bond) such as hydroxypivalic acid neopentyl glycol di(meth)acrylate.

Useful cross-linking monomers having low reactivity (Q less than 0.2) include monomers having two or more allylic double bonds, vinyl ether double bonds, vinylsilane double bonds or non-conjugated olefinic double bonds or other types of carbon carbon double bonds having low reactivity. Examples of cross-linking monomers having low reactivity are polyvinyl or polyallyl ethers of ethylene glycol, of propylene glycol, di-, tri-, tetra-, or poly-ethylene glycol and propylene glycol, of glycerol, of butanediol, of erythritol, of pentaerythritol, of dipentaerythritol, hexanediol, octanediol, cyclohexanediol, cyclohexanetriol, xylitol, sorbitol, mannitol, glucose, sucrose, cellulose, hydroxyl cellulose, methyl cellulose, and of resorcinol.

Other examples of cross-linking monomers having low reactivity include polyvinyl or polyallyl esters of e.g. polycarboxylic acids, of carbonic acid, cyanuric acid, and of isocyanuric acid. Further examples include allyl ethers like pentaerythritol diallyl ether, pentaerythritol triallyl ether, pentaerythritol tetraallyl ether, trimethylolpropane diallyl ether, trimethylolpropane triallyl ether, polyallyl sucrose, polyallyl glucose, p-diallyl ether bisphenol A, o-diallyl ether bisphenol A, glycerol diallyl ether and tetra(allyloxy)ethane. Still further examples include allyl monomers like triallyl cyanurate, triallyl isocyanurate, triallyl melamine, isocyanuric acid diallyl ester, isocyanuric acid diallyl *n*-propyl ester diallyl carbonate, di(ethylene glycol) diallyl dicarbonate, di- or tri- allyl trimesate, di- or tri allyl mellitate, diallyl phthalate, diallyl isophthalate, diallyl terephthalate, diallyl maleate, diallyl fumarate, diallyl succinate, diallyl malonate, diallylmalonic acid diethyl ester, diallylmalonic acid dimethyl ester, diallyl oxalate, diallyl adipate, diallyl sebacate, diallyl tartrate, diallyl silicate, di- or tri- allyl tricarballylate, di- or tri- allyl citrate, di- or tri- allyl phosphate, diallyl chlorendate, allyl crotonoate, diallyl monoethyleneglycol citrate, 1,1'-diallyl-2,2'-bis-imidazolin, diallyl propylene urea, diallyl ethylene urea, diallylurea, diallylthiourea, methyldiallylamine, di- or tri- allylamine, N,N-diallylethanolamine, tetraallylethylenediamine, tartaric acid diallylamide, tetraallyl tin, diphenyldiallyl tin, diallylformal, 5,5-diallylbarbituric acid, diallylphenol, diallyloxybenzene, diallylbenzene and triallylbenzene. Still further monomers include di or polyvinyl ethers such as di(ethylene glycol) divinyl ether, tri(ethylene glycol) divinyl ether, tetra(ethylene glycol) divinyl ether, poly(ethylene glycol) divinyl ether, 1,4-butanediol divinyl ether, divinyl ether, cyclohexane-1,4-dimethanol divinyl ether, poly(ethylene glycol) divinyl ether, poly(propylene glycol) divinyl ether and poly(tetramethylene glycol) divinyl ether. Still further monomers include di or poly vinyl esters such as divinyl-oxalate, -malonate, -succinate, -glutamate, -adipate,

-sebacate, -maleate, -fumarate, -citraconate, -tartrate and –mesaconate. Still further monomers include mixture compounds such as ethyleneglycol vinyl allyl citrate and allyl vinyl maleate. Still further monomers include non-conjugated alkenes (two or more isolated double bonds not conjugated with carbonyl, nitrile or similar, with carbon carbon double bonds, or with aromatic systems such as benzene) such as trivinylcyclohexane, divinylcyclohexane, 1,4-pentadiene, 2-methyl-1,4-pentadiene, 3-methyl-1,4-pentadiene,1,4-hexadiene, 1,5-hexadiene, 2-methyl-1,5-hexadiene, 3-methyl-1,5-hexadiene, 1,5-hexadiene-3,4-diol, 1,5-heptadiene, 2-methyl-1,6-heptadiene-3-ol, 1,6-heptadiene, 1,6-heptadiene-4-ol, 1,7-octadiene, 7-methyl-1,6-octadiene, 1,8-nonadiene, 1,9-decadiene, 1,5,9-decatriene, 1,10-undecadiene, 1,11-dodecadiene, 1,13-tetradecadiene, 1,19-eicosadiene, citronellene, 1,5-cyclooctadiene, dicyclopentadiene and 2,5-norbornadiene, and the corresponding substituted monomers. Still further monomers include silicone compounds such as 1,3-divinyltetramethyldisiloxane, 1,3-diallyltetramethyldisiloxane, 1,3-dimethyl-1,1,3,3-tetravinyl disiloxane, 1,3-divinyl-1,3-dimethyl-1,3-dichlorodisiloxane, 1,3-divinyl-1,3-diphenyl-1,3-dimethyldisiloxane, 1,3-divinyltetraethoxydisiloxane, pentavinylpentamethylcyclopentasiloxane, 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane, 2,4,6-trimethyl-2,4,6-trivinylcyclotrisiloxane, 1,3,5-trivinyl-1,1,3,5,5-pentamethyltrisiloxane, diphenyldivinylsilane, dimethyldivinylsilane, methyltrivinylsilane, tetravinylsilane, 1,3-divinyl-1,1,3,3-tetramethyldisilazane, 1,3-divinyl-1,3-diphenyl-1,3-dimethyldisilazane, diallyldimethylsilane, diallyldiphenylsilane, diallyloxydimethylsilane, methyltriallylsilane, phenyltriallylsilane, tetraallyloxysilane, tetraallylsilane and triallylsilane. Still further monomers include the group represented by di or polyvinyl ethers of ethylene, propylene, butylene, and the like, glycols, glycerine, pentaerythritol, sorbitol, di or poly allyl compounds such as those based on glycols, glycerine, and the like, or combinations of vinyl allyl cycloaliphatic and heterocyclic compounds. Still further monomers include divinyl propylene urea, divinyl ethylene urea and 3,9-divinyl-2,4,8,10-tetraoxaspiro[5.5]undecane.

Examples of preferred cross-linking monomers having low reactivity include triallyl cyanurate, trivinylcyclohexane, 1,4-butanediol divinyl ether, diallyl carbonate, pentaerythritol triallyl ether, trimethylolpropane diallyl ether and triallyl trimesate.

The major part of the ethylenically unsaturated monomers comprise only one carbon-to-carbon double bound and will hereinafter be referred to as non-crosslinking monomers. The amount of such monomers is preferably from 98 to 99.98 mol% or from 99 to 99.94 mol% of the total amount of ethylenically unsaturated monomers.

The non-crosslinking monomers may, for example, be nitrile containing monomers such as acrylonitrile, methacrylonitrile, α-chloroacrylonitrile, α-

ethoxyacrylonitrile, fumaronitrile or crotonitrile; acrylic esters such as methyl acrylate or ethyl acrylate; methacrylic esters such as methyl methacrylate, isobornyl methacrylate, ethyl methacrylate or hydroxyethylmethacrylate; vinyl halides such as vinyl chloride; vinylidene halides such as vinylidene chloride; vinyl pyridine; vinyl esters such as vinyl acetate; styrenes such as styrene, halogenated styrenes or α-methyl styrene; unsaturated carboxylic compounds like acrylic acid, methacrylic acid and salts thereof; or other unsaturated monomers like acrylamide, methacrylamide or N-substituted maleimides. Any mixtures of the above mentioned monomers may also be used.

Preferably the non-crosslinking monomers comprise nitrile containing monomers, most preferably in a high amount, for example from 50 to 100 mol% or from 70 to 100 mol%, preferably from 80 to 100 mol%, or from 95 to 100 mol% of the ethylenically unsaturated non-crosslinking monomers.

The nitrile containing monomers are preferably mainly selected from one or more of acrylonitrile and methacrylonitrile. If other ethylenically unsaturated monomers are present, they are preferably selected from one or more of acrylic esters or methacrylic esters or methacrylic acid. It is also most preferred to only use non-halogen containing monomers.

The softening temperature of the polymer shell, normally corresponding to its glass transition temperature (T_g), is preferably within the range from 50 to 250°C or from 100 to 200°C.

Preferably the polymer shell constitutes from about 50 to about 95 wt% or from about 60 to about 90 wt% of the total microsphere.

The propellant is normally a liquid having a boiling temperature not higher than the softening temperature of the thermoplastic polymer shell and may comprise hydrocarbons such as n-pentane, isopentane, neopentane, cyclopentane, cyclohexane, n-butane, isobutane, n-hexane, isohexane, neohexane, n-heptane, isoheptane, n-octane, isooctane, isodecane, isododecane, or mixtures thereof. Aside from them, other hydrocarbon types can also be used, such as petroleum ether, or chlorinated or fluorinated hydrocarbons, such as methyl chloride, methylene chloride, dichloroethane, dichloroethylene, trichloroethane, trichloroethylene, trichlorofluoromethane, perfluorinated hydrocarbons, etc. Particularly preferred propellants comprise at least one of isopentane, isooctane, and isododecane.

The boiling point of the propellant at atmospheric pressure may be within a wide range, preferably from about -20 to about 200°C, most preferably from about -20 to about 150°C. It is particularly preferred that the propellant has a boiling point or boiling point range so a temperature above 50°C, more preferably above 60°C, most preferably above

70°C, but preferably not higher than about 150°C, would be required to evaporate at least 50 wt%, preferably at least 80 wt% of the propellant at atmospheric pressure.

In an embodiment the propellant preferably comprises isooctane, for example in an amount of at least 25 wt%, or at least 50 wt%, preferably at least 60 wt% or at least 70 wt%, or possibly even up to 85 wt% or substantially consists of isooctane. The propellant may further comprise, such as up to totally 75 wt% or up to 50 wt%, preferably up to 40 wt% or up to 30 wt% or up to 15 wt%, of one or more of butanes, pentanes, hexanes, heptanes, petroleum distillates, isododecane or other liquids giving a suitable boiling point range of the propellant. Particularly preferred hydrocarbons for use in combination with isooctane are isobutane, isopentane, isohexane, n-pentane, n-hexane, petroleum ether, isododecane and n-heptane. In an embodiment the propellant comprise from 85 to 99 wt% or from 90 to 95 wt% of isooctane and from 1 to 15 or from 5 to 10 wt% of isopentane.

The propellant may, for example constitute from about 5 to about 50 wt % or from about 10 to about 40 wt% of the microspheres.

Apart from the polymer shell and the propellant the microspheres may comprise further substances added during the production thereof, normally in an amount from about 1 to about 20 wt%, preferably from about 2 to about 10 wt%. Examples of such substances are solid suspending agents, such as one or more of silica, chalk, bentonite, colloidal clays, boron nitride, starch, gum agar, modified polysaccharides, for example methyl cellulose, hydroxypropyl methylcellulose, carboxy methylcellulose, starch ethers, starch esters, crosslinked polymers, polymer particles, for example polyamides, polycarbonates, polyethers, polyethylenes, polypropylenes, polystyrene, polyacrylates, and/or one or more salts, oxides or hydroxides of metals like Al, Ca, Mg, Ba, Fe, Zn, Ni and Mn, Ti, for example one or more of calcium phosphate, calcium carbonate, magnesium hydroxide, barium sulphate, calcium oxalate, titanium dioxide, and hydroxides of aluminium, iron, zinc, nickel or manganese. If present, these solid suspending agents are normally mainly located to the outer surface of the polymer shell. However, even if a suspending agent has been added during the production of the microspheres, this may have been washed off at a later stage and could thus be substantially absent from the final product.

Preferably the microspheres of the composition have a comparatively high T_{start} and T_{max}. T_{start} is preferably from 150 to 230°C, most preferably from 180 to 200°C. T_{max} is preferably from 170 to 260°C, most preferably from 200 to 240°C.

The expandable microspheres preferably have a volume median diameter from 1 to 500 µm, more preferably from 5 to 100 µm, most preferably from 10 to 50 µm.

A further aspect of the invention concerns a process for the production of expandable thermoplastic microspheres as described above. The process comprises polymerising ethylenically unsaturated monomers as described above in a preferably aqueous suspension in the presence of a propellant to yield microspheres comprising a polymer shell encapsulating said propellant. Regarding the kinds and amounts of monomers and propellant, the above description of the expandable microspheres is referred to. The production may follow the same principles as described in the earlier mentioned patent publications.

In an embodiment of the invention the microspheres are produced in a batchwise process and the polymerisation may then be conducted as described below in a reaction vessel. For 100 parts of monomer phase (suitably including monomers and propellant, the proportions of which determine proportions of monomers in the polymer shell and the amount of propellant in the final product), one or more polymerisation initiator, e.g. in an amount from 0.1 to 5 parts, aqueous phase, e.g. in an amount from 100 to 800 parts, and one or more preferably solid colloidal suspending agent, e.g. in an amount from 1 to 20 parts, are mixed and homogenised. The size of the droplets of the monomer phase obtained determines the size of the final expandable microspheres in accordance with the principles described in e.g. US Patent 3615972 that can be applied for all similar production methods with various suspending agents. The temperature is suitably maintained from 40 to 90°C, preferably from 50 to 80°C, while the suitable pH depends on the suspending agent used. For example, a high pH, preferably from 5 to 12, most preferably from 6 to 10, is suitable if the suspending agent is selected from salts, oxides or hydroxides of metals like Ca, Mg, Ba, Zn, Ni and Mn, for example one or more of calcium phosphate, calcium carbonate, magnesium hydroxide, magnesium oxide, barium sulphate, calcium oxalate, and hydroxides of zinc, nickel or manganese. A low pH, preferably from 1 to 6, most preferably from 3 to 5, is suitable if the suspending agent is selected from starch, methyl cellulose, hydroxypropyl methylcellulose, hydroxypropyl methylcellulose, carboxy methylcellulose, gum agar, silica, colloidal clays, or oxide or hydroxide of aluminium or iron. Each one of the above agents has different optimal pH, depending on, for example, solubility data.

In order to enhance the effect of the suspending agent, it is also possible to add small amounts of one or more promoters, for example from 0.001 to 1 wt%. Usually, such promoters are organic materials and may, for example, be selected from one or more of water-soluble sulfonated polystyrenes, alginates, carboxymethylcellulose, tetramethyl ammonium hydroxide or chloride or water-soluble complex resinous amine condensation products such as the water-soluble condensation products of diethanolamine and adipic acid, the water-soluble condensation products of ethylene oxide, urea and formaldehyde,

polyethylenimine, polyvinylalcohol, polyvinylpyrrolidone, polyvinylamine, amphoteric materials such as proteinaceous, materials like gelatin, glue, casein, albumin, glutin and the like, non-ionic materials like methoxycellulose, ionic materials normally classed as emulsifiers, such as soaps, alkyl sulfates and sulfonates and long chain quaternary ammonium compounds.

Conventional radical polymerisation may be used and initiators are suitably selected from one or more of organic peroxides such as dialkyl peroxides, diacyl peroxides, peroxy esters, peroxy dicarbonates, or azo compounds. Suitable initiators include dicetyl peroxydicarbonate, di(4-tert-butylcyclohexyl) peroxydicarbonate, dioctanoyl peroxide, dibenzoyl peroxide, dilauroyl peroxide, didecanoyl peroxide, tert-butyl peracetate, tert-butyl perlaurate, tert-butyl perbenzoate, tert-butyl hydroperoxide, cumene hydroperoxide, cumene ethylperoxide, diisopropylhydroxy dicarboxylate, 2,2'-azobis(2,4-dimethyl valeronitrile), 2,2'-azobis(isobutyronitrile), 1,1'-azobis(cyclohexane-1-carbonitrile), dimethyl 2,2'-azobis(2-methylpropionate), 2,2'-azobis[2-methyl-N-(2-hydroxyethyl)propionamide] and the like. It is also possible to initiate the polymerisation with radiation, such as high energy ionising radiation.

When the polymerisation is essentially complete, microspheres are normally obtained as an aqueous slurry or dispersion, which can be used as such or dewatered by any conventional means, such as bed filtering, filter pressing, leaf filtering, rotary filtering, belt filtering or centrifuging to obtain a so called wet cake. However, it is also possible to dry the microspheres by any conventional means, such as spray drying, shelf drying, tunnel drying, rotary drying, drum drying, pneumatic drying, turbo shelf drying, disc drying or fluidised bed-drying.

If appropriate, the microspheres may at any stage be treated to reduce the amount of residual unreacted monomers, for example by any of the procedures described in the earlier mentioned WO 2004/072160 or US 4287308.

The microspheres of the invention are useful as foaming agent in various application, such as for thermoplastic materials and particularly for high melting thermoplastic materials.

A particular aspect of the invention concerns use of expandable microspheres as described above in an expandable formulation comprising a thermoplastic polymer matrix and expandable microspheres. The formulation optionally further comprise one or more additives like colorants, stabilisers, reinforcements etc. Examples of expandable formulations include mouldable composite sheets and compounds for use in injection moulding, extrusion, blow moulding, rotational moulding, thermoforming or the like. The amount of expandable microspheres is preferably from 0.5 to 15 wt% or from 1 to 5 wt%. The polymer may, for example, be polypropylene, polystyrene, polyethylene,

thermoplastic polyurethanes, styrene-ethylene-butylene-styrene co-polymer, styrene-butadiene-styrene co-polymer, polyvinyl chloride, ethylene-vinylacetate co-polymer or copolymers thereof, or another polymer with similar melting point.

The invention also concerns an expandable formulation as described above comprising a thermoplastic polymer matrix and expandable microspheres as described above and optional further additives as described above.

The invention furthermore concerns a process for its preparation comprising mixing a thermoplastic polymer with expandable microspheres as described above at a temperature above, and optionally further additives as mentioned above, at a temperature above the melting point of the polymer but below the expansion temperature (T_{start}) of the microspheres.

The invention will be further described in connection with the following Examples which, however, are not to be interpreted to limit the scope of the invention. If not otherwise stated, all parts and percentages refer to parts and percent by weight. Mol% of cross-linking monomers always refers to mol% of total amount of ethylenically unsaturated monomers.

The expansion properties of the microspheres were evaluated on Mettler Toledo TMA/SDTA 841^e using a heating rate of 20°C / min and a load (net.) of 0.06 N. T_{start} is the temperature at which the expansion starts, T_{max} is the temperature at which maximum expansion is obtained and TMA-density is the density of the microspheres at T_{max}.

The pre-expansion resistance properties of certain microspheres with high expansion temperatures were evaluated on TMA using a step wise temperature profile as described in Table 1. Temperature steps 1 and 2 are pre-heating steps during which microspheres with good pre-expansion resistance should have no or a very small degree of expansion, while temperature steps 3 and 4 are expansion steps during which the microspheres should expand to a high degree. Dmax (pre) and Dmax (exp) are the maximum probe displacements due to the dimension changes of the microspheres during the preheating steps (steps 1 and 2) and the expansion steps (steps 3 and 4), respectively. Dmax (pre) may in some cases have negative value due to an initial shrinkage of the microspheres before the expansion starts. The TMA-curves were normalized to a sample amount of 0.70 mg of microspheres.

Table 1. Temperature profile in the TMA for the evaluation of pre-expansion resistance.

Temperature step	Temperature profile
1	30°C → 180°C, 20°C/min
2	180°C, 10 min
3	180°C → 220°C, 20°C/min
4	220°C, 10 min

As the particle size and the amount of propellant have an influence on T_{start}, all comparisons have been made for particles having essentially the same amount of propellant and having similar particle sizes.

The particle size and size distribution was determined by laser light scattering on a Malvern Mastersizer Hydro 2000 SM apparatus on wet samples. The particle size is presented as the volume median diameter D(0.5).

The amount of propellant was determined by thermal gravimetric analysis (TGA) on a Mettler Toledo TGA/SDTA851e. All samples were dried prior to analysis in order to exclude as much moisture as possible and if present also residual monomers. The analyses were performed under an atmosphere of nitrogen using a heating rate at 20°C / min starting at 30°C.

Example 1: A reaction mixture containing $Mg(OH)_2$-stabilised organic droplets in water was created by mixing the phases and stirring vigorously until a suitable droplet size had been achieved. The water dispersion contained 5.0 parts of $Mg(OH)_2$ and 371 parts of water. The organic droplets contained 2.0 parts of dilauroylperoxide, 25 parts of isooctane, 65 parts of acrylonitrile, 35 parts of methacrylonitrile, and 0.52 parts (0.09 mol%) of trimethylolpropane trimethacrylate. Polymerisation was performed at 62°C in a sealed reactor under agitation during 20 h. After cooling to room temperature a sample of the obtained microsphere slurry was removed for determination of the particle size distribution. After filtration, washing and drying the particles were analysed by TMA. The dry particles contained about 22% by weight of isooctane and had a mean particle size of about 37 µm. The TMA-results are found in Tables 3 and 4.

Examples 2-10: Microspheres were prepared in a plurality of polymerisation experiments performed as in Example 1 except for cross-linking monomers which were added according to Table 3. Polymerisation was performed at 62°C as described in Example 1. Analytical results can be found in Tables 3 and 4.

Table 2. Cross linking monomers used in the Examples with estimated reactivity Q and abbreviations. The XL number given for each monomer is used in Tables 2-10

Name	Abbreviation	Q[a]	XL No.
Trimethylolpropane trimethacrylate	TMPTMA	0.78[b]	1
Triallyl cyanurate	TAC	0.14	2
Di(ethyleneglycol) dimethacrylate	DEGDMA	0.78[b]	3
Diallyl carbonate	DAK	0.031[c]	4
1,2,4-Trivinylcyclohexane	TVCH	0.035[d]	5
Triallyl trimesate	TATM	0.031[c]	6
Pentaerythritol triallyl ether	PEAE	0.005[e]	7
Triallyl isocyanurate	TAiC	0.035	8
Trimethylolpropane diallyl ether	TMP DAE	0.005[e]	9
1,4-Butanediol divinyl ether	BDDVE	0.018[f]	10
1,7-Octadiene	OD	0.035[d]	11
Citronellene	CIT	0.002[g]	12
Divinyltetramethyldisiloxane	DVTMDS	0.027[h]	13
Divinylbenzene	DVB	1.0[i]	14
Triacrylformal	TAF	0.23[j]	15

a) The reactivity of monomers has been quantified by the Alfrey-Price Q-e scheme in the earlier mentioned Polymer Handbook. Q values for most vinyl crosslinking monomers are not found explicitly in the Q-e scheme in Polymer Handbook. However, Q values for structurally similar monomers to those crosslinking monomers of interest can be found, and these values can be used as an estimation of the reactivity of the crosslinking monomers. b) estimated from methyl methacrylate c) estimated from diallyl phthalate d) estimated from 1-hexene e) estimated from allyl alcohol f) estimated from ethyl vinyl ether g) estimated from 2-butene h) vinyltrimethylsilane i) estimated from styrene j) estimated from acrylamide

Table 3. Analytical results for Examples 1-10 and amounts charged of cross-linking monomers used. 25 parts isooctane (IO) was used as blowing agent.

Ex.	XL 1 (mol%)	XL 2 (mol%)	Size (µm)	Propellant (wt% analysed)	T_{start} (°C)	T_{max} (°C)	TMA-density (g/l)
1	0.09		37	22	179	224	9.0
2	0.09	0.02	36	22	185	223	9.3
3	0.09	0.03	36	22	188	224	9.7
4	0.09	0.05	36	22	192	224	11.7
5	0.09	0.07	38	22	195	224	12.6
6	0.09	0.09	36	22	196	224	11.9
7	0.08	0.14	41	22	206	225	12.3
8	0.09	0.17	37	20	194	223	17.8
9		0.09	33	23	203	220	79.4
10		0.16	36	23	215	222	137

In Table 3 it can be seen that T_{start} increases significantly by combining the two cross-linking monomers of different type, TMPTMA having high reactivity and TAC having low reactivity. TAC alone gives high T_{start} but very poor expansion.

Table 4. Pre-expansion resistance for Examples 1, 3, 6-10 and amounts charged of cross linking monomers used.

Ex.	XL 1 (mol%)	XL 2 (mol%)	Dmax (pre) (µm)	Dmax (exp) (µm)
1	0.09		786	2045
3	0.09	0.03	373	2019
6	0.09	0.09	-2	1599
7	0.08	0.14	-6	1412
8	0.09	0.17	0	727
9		0.09	0	255
10		0.16	1	164

In Table 4 it is shown that by using both TMPTMA and TAC as cross-linking monomers both good pre-expansion resistance and good expansion can be achieved.

Examples 11-18: Microspheres were prepared in a plurality of polymerisation experiments performed as in Example 1 except for cross-linking monomers which were added according to Table 5. Polymerisation was performed at 62°C as described in Example 1. Analytical results can be found in Tables 5 and 6.

Table 5. Analytical results for Examples 11-18 and amounts charged of cross-linking monomers (XL) used. 25 parts of isooctane (IO) was used as blowing agent.

Ex.	XL 1 (mol%)	XL 3 (mol%)	Size (µm)	Propellant (wt% analysed)	T_{start} (°C)	T_{max} (°C)	TMA-density (g/l)
11	0.03		33	22	162	222	10.8
12	0.13		39	20	173	219	11.9
13	0.26		37	18	179	207	45.7
14	0.41		38	20	179	193	76.5
15		0.08	29	23	159	211	39.4
16		0.19	32	23	157	225	10.5
17		0.36	33	21	152	224	12.2
18		0.60	38	19	149	222	23.4

From Table 5 it appears that there is no or only a minor increase of T_{start} by increasing the amount of TMPTMA or DEGDMA, both having high reactivity, unless also a cross-linking monomer having low reactivity is used as exemplified in Table 3.

Table 6. Pre-expansion resistance for Examples 11-18 and amounts charged of cross-linking monomers used.

Ex.	XL 1 (mol%)	XL 3 (mol%)	Dmax (pre) (µm)	Dmax (exp) (µm)
11	0.03		414	738
12	0.13		755	1653
13	0.26		234	408
14	0.41		199	199
15		0.08	265	457
16		0.19	1049	2032
17		0.36	582	1504
18		0.60	407	673

As can be seen in Table 6 above, the pre-expansion resistance is poor for microspheres with only TMPTMA or DEGDMA as cross-linking monomers, also at levels comparable to the total amount of cross-linking monomers in Table 4. Microspheres containing too high or too low levels also show less good expansion during the expansion step (lower Dmax).

Examples 19-21: Microspheres were prepared in a plurality of polymerisation experiments performed as in Example 1 except for cross-linking monomers, which were added according to Table 7. As propellant a mixture of 12.5 parts of isopentane and 25.5 parts of isooctane was used The amounts of water and $Mg(OH)_2$ in the examples was 320 parts and 2.6 parts respectively. Polymerisation was performed at 62°C as described in Example 1. Analytical results can be found in Table 7.

Table 7. Analytical results for Examples 19-21 and amounts charged of cross-linking monomers, 38 parts of isopentane/isooctane (33/67 w/w) was charged as propellant.

Ex.	XL 1 (mol%)	XL 2 (mol%)	Size (µm)	Propellant (wt% analysed)	T_{start} (°C)	T_{max} (°C)	TMA-density (g/l)
19	0.06	0	18	28	155	193	9.3
20	0.06	0.03	18	28	160	192	10.4
21	0.06	0.09	18	28	165	192	10.2

In Table 7 it can be seen that an increasing amount of TAC gives higher T_{start} also when a mixture of isopentane and isooctane is used as propellant.

Examples 22-33: Microspheres were prepared in a plurality of polymerisation experiments performed as in Example 1 except for cross-linking monomers and propellants, which were added according to Table 8. The propellants used in the examples are isopentane (IP), isooctane (IO), and isododecane (ID). Polymerisation was performed at 62°C as described in Example 1. Analytical results can be found in Table 8.

Table 8. Analytical results for Examples 1, 8 and 22-33 and amounts charged of cross linking monomers and propellants used.

Ex.	XL 1 (mol%)	XL 2 (mol%)	IP (parts)	IO (parts)	ID (parts)	Size (µm)	Propellant (wt% analysed)	T_{start} (°C)	T_{max} (°C)	TMA-density (g/l)
22	0.09	0.17	25	0	0	52	21	120	177	13.7
23	0.09	0.17	19	7	0	50	19	133	183	13.8
24	0.09	0.17	12	13	0	39	20	148	189	14.2
25	0.09	0.17	6	19	0	39	20	170	203	15.4
26	0.09	0.17	2	23	0	37	21	180	215	15.8
8	0.09	0.17	0	25	0	37	20	194	223	17.8
27	0.09	0.17	0	13	12	45	23	230	236	42.2
28	0.09	0	25	0	0	40	20	117	198	7.3
29	0.09	0	19	7	0	38	20	123	197	7.5
30	0.09	0	12	13	0	37	21	129	198	8.5
31	0.09	0	6	19	0	41	22	136	206	9.0
32	0.09	0	2	23	0	36	21	162	214	8.3
1	0.09	0	0	25	0	37	22	179	224	9.0
33	0.09	0	0	13	12	55	23	182	225	23.7

IP = isopentane, IO = isooctane, ID = isododecane

In Table 8 it can be seen that TAC in combination with TMPTMA increases T_{start} for microspheres with various hydrocarbon mixtures as propellant. The effect on T_{start} is more pronounced when a propellant with higher boiling points is used.

Examples 34-57: Microspheres were prepared in a plurality of polymerisation experiments performed as in Example 1 except for cross-linking monomers, which were added according to Table 9. The amounts of water and $Mg(OH)_2$ in the examples varied between 323-371 parts and 2.1-5.0 parts respectively. This is due to small differences in the recipes in different polymerisation reactors but does not influence the thermal properties of the polymerised particles. Polymerisation was performed at 62°C as described in Example 1. Analytical results can be found in Tables 9 and 10.

Table 9. Analytical results for Examples 34-57 and amounts charged of cross-linking monomers, charging 25 parts of isooctane as propellant.

Ex.	XL 1 (mol%)	XL No.	Amount XL # (mol%)	Size (µm)	Propellant (wt% analysed)	T_{start} (°C)	T_{max} (°C)	TMA-density (g/l)
34	0.09	4	0.13	37	21	193	223	12.1
35	0.09	4	0.19	33	22	193	224	13.8
36	0	4	0.13	29	24	202	222	33.0
37	0.09	5	0.09	44	22	187	223	11.2

Ex.	XL 1 (mol%)	XL No.	Amount XL # (mol%)	Size (µm)	Propel-lant (wt% analysed)	T_{start} (°C)	T_{max} (°C)	TMA-density (g/l)
38	0.09	5	0.13	34	22	199	224	10.9
39	0	5	0.13	28	24	177	223	21.4
40	0.09	6	0.06	39	21	199	224	14.2
41	0.09	6	0.09	44	21	154	223	14.0
42	0.09	6	0.13	38	22	202	223	15.6
43	0	6	0.09	29	22	206	220	96.1
44	0.09	7	0.09	40	22	154	224	16.0
45	0.09	7	0.13	35	22	199	224	15.5
46	0	7	0.09	30	23	207	222	43.3
47	0.09	8	0.09	39	22	185	223	12.9
48	0.09	8	0.17	37	22	192	222	17.6
49	0.09	8	0.25	34	22	192	221	32.1
50	0	8	0.09	29	22	188	209	47.4
51	0.08	9	0.10	30	22	190	222	12.5
52	0.08	10	0.21	28	21	191	216	20.9
53	0.08	11	0.26	27	22	196	219	13.4
54	0.08	12	0.42	26	19	190	215	10.5
55	0.08	13	0.16	27	21	191	223	11.4
56	0.08	14	0.22	30	20	182	204	16.9
57	0.09	15	0.09	43	20	165	217	43.8

Table 10. Pre-expansion resistance for Examples 34-42, 44-45, 47-49, 51-57 and amounts of cross linkers used.

Example	XL 1 (mol% charged)	XL No.	Amount XL # (mol% charged)	Dmax (pre) (µm)	Dmax (exp) (µm)
34	0.09	4	0.13	599	1633
35	0.09	4	0.19	0	1698
36	0	4	0.13	1	536
37	0.09	5	0.09	797	1869
38	0.09	5	0.13	-4	2029
39	0	5	0.13	0	509
40	0.09	6	0.06	0	1793
41	0.09	6	0.09	-1	1458
42	0.09	6	0.13	0	1415
44	0.09	7	0.09	0	1665
45	0.09	7	0.13	0	1328
47	0.09	8	0.09	348	1446
48	0.09	8	0.17	294	1143

Example	XL 1 (mol% charged)	XL No.	Amount XL # (mol% charged)	Dmax (pre) (µm)	Dmax (exp) (µm)
49	0.09	8	0.25	160	737
51	0.08	9	0.10	1	1755
52	0.08	10	0.21	-1	1000
53	0.08	11	0.26	0	1679
54	0.08	12	0.42	2	1865
55	0.08	13	0.16	1	1905
56	0.08	14	0.22	496	961
57	0.09	15	0.09	293	301

In Tables 9 and 10 the results of combinations of different cross-linking monomers are shown. It appears that both high expansion and high resistance against pre-expansion can only be achieved when a cross-linking monomer having high reactivity is combined with a cross-linking monomer having low reactivity. In Examples 41 and 44 the values for T_{start} is lower than might be expected (see Table 9) as there was a small degree of expansion occurring at this relatively low temperature. This is probably due to the fact that the microspheres in these Examples had a relatively large particle size and in these analyses a fraction of the larger particles expands to some extent at a lower temperature. However, the resistance against pre-expansion is still very good as can be seen in Table 10. In Examples 56 and 57 when two cross-linking monomers having high reactivity are combined, the resistance against pre-expansion is poor.

CLAIMS

1. Thermally expandable thermoplastic microspheres comprising a polymer shell made from ethylenically unsaturated monomers encapsulating a propellant, said ethylenically unsaturated monomers comprising at least one first cross-linking monomer having two or more carbon-to carbon double bonds and at least one second cross-linking monomer having two or more carbon-to-carbon double bonds, said at least one first cross-linking monomer having a reactivity Q greater than 0.2 and said at least one second cross-linking monomer having a reactivity Q less than 0.2, the reactivity Q being defined in accordance with the Alfrey-Price Q-e scheme, the amount of said at least one second cross-linking monomer being less than 0.8 mol% of the total amount of ethylenically unsaturated monomers.

2. Microspheres as claimed in claim 1, wherein said at least one first cross-linking monomer has a reactivity Q from greater than 0.2 to 10.

3. Microspheres as claimed in any one of the claims 1-2, wherein said at least one second cross-linking monomer has a reactivity Q from 0.001 to less than 0.2.

4. Microspheres as claimed in any one of the claims 1-3, wherein the amount of said at least one first cross-linking monomer is from 0.01 to 1.0 mol% of the total amount of ethylenically unsaturated monomers.

5. Microspheres as claimed in any one of the claims 1-4, wherein the amount of said at least one second cross-linking monomer is from 0.01 to 0.75 mol% of the total amount of ethylenically unsaturated monomers.

6. Microspheres as claimed in any one of the claims 1-5, wherein said at least one first cross-linking monomers are selected from the group consisting of is one or more of (meth)acrylic esters or (meth)acrylamides or vinyl aromatic monomers.

7. Microspheres as claimed in claim 6, wherein said at least one first cross-linking monomers is one or more of trimethylolpropane tri(meth)acrylate, ethylene glycol di(meth)acrylate, di(ethylene glycol) di(meth)acrylate, 1,4-butanediol di(meth)acrylate, di(trimethylolpropane) tetra(meth)acrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, dipentaerythritol penta(meth)acrylate, dipentaerythritol hexa(meth)acrylate and tris[2-acryloyloxy)ethyl] isocyanurate.

8. Microspheres as claimed in any one of the claims 1-7, wherein said at least one second cross-linking monomers are selected from the group consisting of monomers having two or more allylic double bonds, vinyl ether double bonds, vinylsilane double bonds or non-conjugated olefinic double bonds.

9. Microspheres as claimed in any one of the claim 8, wherein said at least one second cross-linking monomers is one or more of triallyl cyanurate, trivinylcyclohexane,

1,4-butanediol divinyl ether, diallyl carbonate, pentaerythritol triallyl ether, trimethylolpropane diallyl ether and triallyl trimesate.

10. Microspheres as claimed in any one of the claims 1-9, wherein said ethylenically unsaturated monomers comprise non-crosslinking monomers in an amount from 98 to 99.98 mol% of the total amount of ethylenically unsaturated monomers.

11. Microspheres as claimed in claim 10, wherein said non-crosslinking monomers comprise nitrile containing monomers in an amount from 80 to 100 mol% of the ethylenically unsaturated non-crosslinking monomers.

12. Microspheres as claimed in any one of the claims 1-11 wherein said propellant comprises isooctane.

13. Microspheres as claimed in any one of the claims 1-12, wherein T_{start} of the expandable microspheres is from 150 to 230°C.

14. Process for the production of thermally expandable microspheres according to any one of the claims 1-13 comprising polymerising ethylenically unsaturated monomers in the presence of a propellant to yield microspheres comprising a polymer shell encapsulating said propellant, said ethylenically unsaturated monomers comprising at least one first cross-linking monomer having two or more carbon-to carbon double bonds and at least one second cross-linking monomer having two or more carbon-to-carbon double bonds, said at least one first cross-linking monomer having a reactivity Q greater than 0.2 and said at least one second cross-linking monomer having a reactivity Q less than 0.2, the reactivity Q being defined in accordance with the Alfrey-Price Q-e scheme, the amount of said at least one second cross-linking monomer being less than 0.8 mol% of the total amount of ethylenically unsaturated monomers.

15. Use of thermally expandable microspheres according to any one of the claims 1-13 in an expandable formulation comprising a thermoplastic polymer matrix and expandable microspheres.

16. Expandable formulation comprising a thermoplastic polymer matrix and expandable microspheres according to any one of the claims 1-13.

17. Process for the preparation of an expandable formulation according to claim 14 comprising mixing a thermoplastic polymer with expandable microspheres according to any one of the claims 1-13 at a temperature above the melting point of the polymer but below the expansion temperature of the microspheres.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2009/067486

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J13/14
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)
B01J

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 practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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