

METHOD OF CONTROLLING WALL THICKNESS OF RE-DISPERSIBLE POLYUREA MICROCAPSULES

BACKGROUND

Field

[0001] Embodiments of the present disclosure relate to methods of controlling wall thickness of re-dispersible polyurea microcapsules.

Description of Related Art

[0002] Encapsulation of functionally active materials is an attractive way of storing the active materials as well as protecting the active materials from environment until required for fulfilling appropriate applications. Microencapsulated substances can be utilized for sustained drug release, electro rheological fluids, intumescent fire retarding powders, preservation of flavors, electrophoretic display applications, textiles, biotechnology and inorganic metal salt catalyst and so on.

BRIEF SUMMARY

[0003] The following summary presents a simplified summary in order to provide a basic understanding of some aspects of the present disclosures discussed herein. This summary is not an extensive overview of the present disclosure discussed herein. It is not intended to identify critical elements or to delineate the scope of such disclosure. Its sole purpose is to present some concepts in a simplified form as a prelude to the more detailed description that is presented later.

[0004] In accordance with one aspect of the present disclosure, provided is a method of controlling a wall thickness of a polyurea microcapsule including mixing a surfactant and a cross-linking agent to make a first mixture; adding an isocyanate compound to a solvent to make a second mixture; combining the first mixture with the second mixture to make a third mixture; and emulsifying the third mixture to make the polyurea microcapsule. When making the wall thickness of the polyurea microcapsule larger, an amount of the isocyanate in the third mixture is increased. When making the wall thickness of the polyurea microcapsule smaller, the amount of the isocyanate in the third mixture is decreased. The amount of the isocyanate in the third

mixture can be 1 weight percent to 50 weight percent. The amount of the isocyanate in the third mixture can be 1.9 weight percent to 31.2 weight percent. The wall thickness of the polyurea microcapsule can be 35 nm to 500 nm.

[0005] In accordance with one aspect of the present disclosure, provided is a method of controlling a wall thickness of a polyurea microcapsule including mixing a surfactant and a cross-linking agent to make a first mixture; adding an isocyanate compound to a solvent to make a second mixture; combining the first mixture with the second mixture to make a third mixture; and emulsifying the third mixture to make the polyurea microcapsule. When making the wall thickness of the polyurea microcapsule larger, an amount of the cross-linking agent in the third mixture is increased. When making the wall thickness of the polyurea microcapsule smaller, the amount of the cross-linking agent in the third mixture is decreased. The amount of the cross-linking agent in the third mixture can be 1.85 weight percent to 23.19 weight percent. The wall thickness of the polyurea microcapsule can be 140 nm to 473 nm.

[0006] In accordance with one aspect of the present disclosure, provided is a method of controlling a wall thickness of a polyurea microcapsule including mixing a surfactant and a cross-linking agent to make a first mixture; adding an isocyanate compound to a solvent to make a second mixture; combining the first mixture with the second mixture to make a third mixture; and emulsifying the third mixture to make the polyurea microcapsule. When making the wall thickness of the polyurea microcapsule larger, an amount of the isocyanate and an amount of the cross-linking agent in the third mixture are increased. When making the wall thickness of the polyurea microcapsule smaller, the amount of the isocyanate and the amount of the cross-linking agent in the third mixture are decreased. The amount of the isocyanate in the third mixture can be 1.9 weight percent to 31.2 weight percent, and the amount of the cross-linking agent in the third mixture can be 1.85 weight percent to 23.19 weight percent. The wall thickness of the polyurea microcapsule is 62 nm to 464 nm. A mole ratio of the isocyanate to the cross-linking agent in the third mixture is 0.75.

[0007] In accordance with one aspect of the present disclosure, provided is a method of controlling a wall thickness of a polyurea microcapsule including mixing a surfactant and a cross-linking agent to make a first mixture; adding an isocyanate compound to a solvent to make a second mixture; combining the first mixture with the second mixture to make a third mixture; and emulsifying the third mixture to make the polyurea microcapsule. When making the wall

thickness of the polyurea microcapsule smaller, a homogenization speed in the emulsifying is increased within a range from 5,500 rpm to 9,500 rpm. When making the wall thickness of the polyurea microcapsule larger, the homogenization speed in the emulsifying is decreased within a range from 9,500 rpm to 5,500 rpm.

[0008] In accordance with one aspect of the present disclosure, provided is a method of controlling a wall thickness of a polyurea microcapsule including mixing a surfactant and a cross-linking agent to make a first mixture; adding an isocyanate compound to a solvent to make a second mixture; combining the first mixture with the second mixture to make a third mixture; and emulsifying the third mixture to make the polyurea microcapsule. When making the wall thickness of the polyurea microcapsule smaller, an amount of the surfactant is increased within a range from 0.5 weight percent to 5 weight percent in the third mixture. When making the wall thickness of the polyurea microcapsule larger, the amount of the surfactant is decreased within a range from 5 weight percent to 0.5 weight percent in the third mixture.

[0009] In accordance with one aspect of the present disclosure, provided is a method of controlling a wall thickness of a polyurea microcapsule including mixing a surfactant and a cross-linking agent to make a first mixture; adding an isocyanate compound to a solvent to make a second mixture; combining the first mixture with the second mixture to make a third mixture; and emulsifying the third mixture to make the polyurea microcapsule. When making the wall thickness of the polyurea microcapsule smaller, a molecular weight of the surfactant is increased within a range from 70,000 to 1,000,000. When making the wall thickness of the polyurea microcapsule larger, the molecular weight of the surfactant is decreased within a range from 1,000,000 to 70,000.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] Fig. 1 is a flow chart showing a process of an embodiment of preparing polyurea microcapsules of the present disclosure.

[0011] Fig. 2 is a flow chart showing a process of an embodiment of preparing polyurea microcapsules of the present disclosure.

[0012] Fig. 3 includes a graph showing an effect of amount of isocyanate on wall thickness of microcapsule.

[0013] Fig. 4 includes SEM (Scanning Electron Microscope) images in 1,000x magnification and in 20,000x magnification of polyurea microcapsules prepared by a process of embodiment 1 of the present disclosure with different amounts of isocyanate as described in Fig. 3.

[0014] Fig. 5 includes a graph showing an effect of amount of cross-linking agent on wall thickness of microcapsule.

[0015] Fig. 6 includes SEM images in 1,000x magnification and in 20,000x magnification of polyurea microcapsules prepared by a process of embodiment 2 of the present disclosure with different amounts of cross-linking agent as described in Fig. 5.

[0016] Fig. 7 includes a graph showing an effect of amount of isocyanate and cross-linking agent on wall thickness of microcapsule.

[0017] Fig. 8 includes SEM images in 1,000x magnification and in 20,000x magnification of polyurea microcapsules prepared by a process of embodiment 3 of the present disclosure with different amounts of isocyanate and cross-linking agent as described in Fig. 7.

[0018] Fig. 9 includes a graph showing an effect of amount of solvent on wall thickness of microcapsule.

[0019] Fig. 10 includes SEM images in 1,000x magnification and in 20,000x magnification of polyurea microcapsules prepared by a process of embodiment 4 of the present disclosure with different amounts of solvent as described in Fig. 9.

[0020] Fig. 11 includes a graph showing an effect of homogenization speed in emulsifying on wall thickness of microcapsule.

[0021] Fig. 12 includes SEM images in 1,000x magnification and in 20,000x magnification of polyurea microcapsules prepared by a process of embodiment 5 of the present disclosure with different homogenization speeds in emulsifying as described in Fig. 11.

[0022] Fig. 13 includes a graph showing an effect of amount of surfactant on wall thickness of microcapsule.

[0023] Fig. 14 includes SEM images in 1,000x magnification and in 20,000x magnification of polyurea microcapsules prepared by a process of embodiment 6 of the present disclosure with different amounts of surfactant as described in Fig. 13.

[0024] Fig. 15 includes a graph showing an effect of molecular weight of surfactant on wall thickness of microcapsule.

[0025] Fig. 16 includes SEM images in 1,000x magnification and in 20,000x magnification of polyurea microcapsules prepared by a process of embodiment 7 of the present disclosure with different molecular weights of surfactant as described in Fig. 15.

[0026] Fig. 17 includes a graph showing an effect of pH of third mixture on wall thickness of microcapsule.

[0027] Fig. 18 includes SEM images in 1,000x magnification and in 20,000x magnification of polyurea microcapsules prepared by a process of embodiment 8 of the present disclosure with different pH levels as described in Fig. 17.

[0028] Fig. 19 is a flow chart showing an example process of preparing polyurea microcapsules.

DETAILED DESCRIPTION

[0029] Embodiments of the present disclosure relate to methods of controlling a wall thickness of a polyurea microcapsule. Encapsulation of functionally active materials is an attractive way of storing of the active materials as well as protecting the active materials from environment until they are required for fulfilling appropriate applications. An ideal amount of the functionally active material in each microcapsule and an ideal speed for releasing the functionally active material depends on the material characteristics of the functionally active material and the goal to achieve. Some functionally active material should be released within a few hours while some functionally active material should be constantly released over several days or several months. For the long-term release microcapsule, the ideal amount of the functionally active material in each microcapsule tends to be more than 30 percent of the total content weight of the microcapsule.

[0030] The amount of functionally active material and the release speed can be controlled by the wall thickness of the microcapsules, and re-dispersed polyurea microcapsules prepared by a method of controlling a wall thickness of a polyurea microcapsule of the present disclosure demonstrate high encapsulation efficiency with a wide range of active ingredients in a wide range of wall thickness as compared to the microcapsules prepared by conventional methods. Re-dispersion of polyurea microcapsules prepared by the method of the present disclosure in a wide range of wall thickness in water can be effectively achieved in an ideal time period for a wide variety of needs.

[0031] The present disclosure will now be described with reference to the drawings, wherein like reference numerals are used to refer to like elements throughout. It is to be appreciated that the various drawings are not necessarily drawn to scale from one figure to another nor inside a given figure, and in particular that the size of the components are arbitrarily drawn for facilitating the understanding of the drawings. In the following description, for purposes of explanation, numerous specific details are set forth in order to provide a thorough understanding of the present disclosure. It may be evident, however, that the present disclosure can be practiced without these specific details. Additionally, other embodiments of the disclosure are possible, and the disclosure is capable of being practiced and carried out in ways other than as described. The terminology and phraseology used in describing the disclosure is employed for the purpose of promoting an understanding of the disclosure and should not be taken as limiting.

[0032] Fig. 19 illustrates a flow chart showing an example process of preparing polyurea microcapsules. Specific methods of making such microcapsules are disclosed in U.S. Patent Application Publication No. 2013/0330292, 2013/0230574, 2013/0295149, 2011/0077188, 2006/0115604, 2002/0064656, 2002/0079599, and US Patent No. 5,635,211, which are hereby incorporated by reference. Fig. 1 illustrates a flow chart showing a process of an embodiment of preparing polyurea microcapsules of the present disclosure. Fig. 2 illustrates a flow chart showing another process of an embodiment of preparing polyurea microcapsules of the present disclosure. The process of the present disclosure includes mixing a surfactant and a cross-linking agent to make a first mixture, adding an active ingredient and an isocyanate compound to a solvent to make a second mixture, combining the first mixture with the second mixture to make a third mixture, emulsifying the third mixture, curing the emulsified third mixture, filtering the

cured third mixture, and drying the filtered third mixture. In the present disclosure, a cross-linking agent is mixed with a surfactant and added to a mixture of solvent, active ingredients, and an isocyanate before emulsification of the mixture as shown in Figs. 1 and 2.

[0033] The emulsification can be done by homogenizing the mixture of the cross-linking agent, surfactant, active ingredients, and isocyanate at certain speed. Contrary to the preparation methods of the present disclosure, in an example method as shown in Fig. 19, a cross-linking agent is added to a mixture of an active ingredient and isocyanate after the mixture is emulsified. By adding the cross-linking agent before emulsification of the mixture, the polyurea microcapsules of the present disclosure can have an excellent dispersion, excellent reproducibility and good stability in dry condition as well as suspension form, and high encapsulation efficiency without any additives or catalyst.

[0034] In one embodiment of the present disclosure, an amount of isocyanate is changed to control a wall thickness of the microcapsule. In one embodiment of the present disclosure, an amount of cross-linking agent is changed to control a wall thickness of the microcapsule. In one embodiment of the present disclosure, amounts of isocyanate and cross-linking agent are changed to control a wall thickness of the microcapsule. In one embodiment of the present disclosure, a homogenization speed in the emulsifying is changed to control a wall thickness of the microcapsule. In one embodiment of the present disclosure, an amount of surfactant is changed to control a wall thickness of the microcapsule. In one embodiment of the present disclosure, a molecular weight of surfactant is changed to control a wall thickness of the microcapsule. Unless otherwise specified in the present disclosure, the methods of the present disclosure are conducted at room temperature, *i.e.*, between 1 °C and 30 °C.

[0035]

(Isocyanate compound)

Any suitable isocyanate compound can be used in the process of preparing the polyurea microcapsules of the present disclosure as long as the isocyanate compound can produce the polyurea microcapsules. The isocyanate compound has the general structure $\text{O}=\text{C}=\text{N}-\text{R}-\text{N}=\text{C}=\text{O}$. The isocyanate compound can be aromatic, aliphatic, linear, branched, or cyclic. In one embodiment, the isocyanate compound can have, on average, 2 to 4 $-\text{N}=\text{C}=\text{O}$ groups. In

particular embodiments, the isocyanate compound contains at least three isocyanate functional groups.

[0036] In one embodiment, the process of preparing the polyurea microcapsules of the present disclosure uses one or more aromatic polyisocyanate and/or aliphatic polyisocyanate or its derivatives having free isocyanate group and containing adduct, trimer and biuret or combinations thereof. Examples of aromatic polyisocyanate include diphenylmethane diisocyanate, such as COSMONATE[®] M-100 (Mitsui Chemicals, Inc.), COSMONATE[®] M-200 (Mitsui Chemicals, Inc.), COSMONATE[®] PH (Mitsui Chemicals, Inc.), COSMONATE[®] PH-G (Mitsui Chemicals, Inc.), toluene diisocyanate, such as COSMONATE[®] T-65 (Mitsui Chemicals, Inc.), COSMONATE[®] T-80 (Mitsui Chemicals, Inc.), and COSMONATE[®] T-100 (Mitsui Chemicals, Inc.). Examples of aliphatic polyisocyanate include xylylene diisocyanate, such as TAKENATE[®] D-110N (Mitsui Chemicals, Inc.), TAKENATE[®] D-120N (Mitsui Chemicals, Inc.), TAKENATE[®] D-131-N (Mitsui Chemicals, Inc.), TAKENATE[®] D-127N (Mitsui Chemicals, Inc.), hexamethylene diisocyanate, such as TAKENATE[®] D-160N (Mitsui Chemicals, Inc.), TAKENATE[®] D-165N (Mitsui Chemicals, Inc.) and isophorone diisocyanate, such as TAKENATE[®] D-140N (Mitsui Chemicals, Inc.).

[0037]

(Cross-Linking Agent)

A cross-linking agent is used to make an encapsulating wall of polyurea microcapsules. Amine can be used as a cross-linking agent for synthesis of polyurea microcapsules. Other cross-linking agents are guanidine and its salts which are applied for the synthesis of microcapsules in the presence of catalyst. Examples of cross-linking agents include salts of guanidine including guanidine carbonate salt, guanidine hydrochloride salt, guanidine nitrate salt, guanidine sulfate salt, guanidine acetate salt, a salt of guanidine phosphate. Inorganic bases are applied for adjusting the pH including alkali metal oxide or alkaline earth metal oxide such as sodium oxide, potassium oxide, calcium oxide, and cerium oxide. Other polyamine cross-linking agents include one or more NH₂ group per molecule that can be tris (2-aminoethyl) amine, triethylene tetra amine, tetra ethylene pentamine, pentaethylene hexamine, or combinations thereof.

[0038] In one embodiment, the process of preparing the polyurea microcapsules of the present disclosure uses one or more cross-linking agents. In another embodiment, guanidine

carbonate salt is mixed with a surfactant and then mixed with a solvent, isocyanate compound, and active ingredients. This procedure can facilitate reducing one step of addition of cross-linking agent after emulsification which is common in conventional preparation processes.

[0039] By adding the cross-linking agent to the mixture of solvent, active ingredients, and isocyanate compound before emulsification, the polyurea microcapsules of the present disclosure demonstrates stable dispersion of microcapsules in water and re-dispersion which are not observed in comparative preparation processes. Any suitable amount of cross-linking agent can be employed as long as the polyurea microcapsules of the present disclosure can be prepared with the cross-linking agent.

[0040]

(Surfactant)

In one embodiment, the process of preparing the polyurea microcapsules of the present disclosure uses one or more surfactants. Examples of the surfactants include anionic and non-ionic surfactants. Specific examples of anionic surfactant include poly(sodium 4-tyrenesulfonate) with different weight average molecular weight (Mw: 70, 000 to 1,000, 000) and non-ionic surfactant includes Polysorbate. The poly(sodium 4- styrenesulfonate) may have a weight average molecular weight of 70,000, 200,000, or 1,000, 000. The molecular weight is a mass (gram) of 1 mole of the substance. Unless specified in the present disclosure, the molecular weights disclosed in the present disclosure are average molecular weights.

[0041] Any suitable amount of surfactant can be employed as long as the polyurea microcapsules of the present disclosure can be prepared with the surfactant. In one embodiment, the amount of surfactant is 0.5 to 10 weight percent. In another embodiment, the amount of surfactant is 0.5 to 5 weight percent. In another embodiment, the amount of surfactant is 0.1 to 2 weight percent.

[0042] The amount of cross-linking agent can affect the dispersion of polyurea microcapsule powder in water. The higher the amounts of guanidine carbonate salt, the better the dispersion of the microcapsules in water is observed. The amount of cross-linking agent further can affect re-dispersion of polyurea microcapsules.

[0043]

(Solvent)

In one embodiment, the process of preparing the polyurea microcapsules of the present disclosure uses one or more solvent. Any suitable solvent can be used as long as the solvent dissolves active ingredients and isocyanate compound to make the second mixture. Examples of solvent include glyceryl tributyrate, caprylic triglyceride, capric triglyceride, diethyl phthalate, dimethyl phthalate, methyl cocoate, and methyl cocoate or combinations thereof.

[0044]

(Active Ingredients)

In one embodiment, the process of preparing the polyurea microcapsules of the present disclosure uses one or more active ingredients. Examples of active ingredients include insecticide and insect repellent. Specific examples of active ingredients include para-menthane-3, 8-diol (CITREPEL[®] Chemian Technology Ltd, UK), eucalyptus oil, citronella oil (SIGMA ALDRICH[®]), geraniol oil, lemongrass oil, neem, basil oil, camphor oil, cinnamon oil, clove oil, castor oil, etofenprox, diiodomethyl-p-tolylsulfone (DMTS), and 3-Iodo-2-propynyl N-butylcarbamate (IPBC). Depending on what active ingredient is contained in the microcapsules, the microcapsules may be used to manufacture different final products, such as mosquito repellent, anti-mold product, in forms of a spray, a detergent, a fabric softener, a laundry starch, a shampoo, a hair conditioner, a body wash, a hygiene product, a paint, or a coating and so on.

[0045]

(Preparation Process)

[0046] A polyurea microcapsule of the present disclosure is prepared by the following process. A first mixture is prepared by mixing a surfactant solution with powder of cross-linking agent.

[0047] A second mixture is prepared by adding a solvent to an isocyanate compound followed by an active ingredient such as CITREPEL[®] which is liquid. If the active ingredient is solid, second mixture is prepared by adding an active ingredient to a solvent followed by an isocyanate compound.

[0048] A third mixture is prepared by combining the second mixture with the first mixture under homogenization speed of 2,800 rpm until it finishes the addition of second

mixture to the first mixture, for safety reason, these two solutions are not added at a high homogenization speed. This third mixture is emulsified by increasing the homogenization speed to 5,500 rpm or higher for 2 minutes at any suitable temperature (*e.g.*, room temperature).

[0049] The emulsified third mixture is cured at 55 °C for two hours under stirring.

[0050] The cured third mixture is filtered under vacuum by using ADVATEC quantitative filter paper No. 5C and washed with deionized water to remove unreacted chemicals and surfactant.

[0051] The filtered third mixture is dried at room temperature for 2 to 5 hours.

[0052]

(Embodiment 1)

<Effect of Amount of Isocyanate on Wall Thickness>

[0053] Polyurea microcapsules are prepared with nine different weight percent of isocyanate. The polyurea microcapsules are prepared by the process shown in Fig. 2. 20 ml of 1 % poly(sodium 4-styrene sulfonate) (SIGMA-ALDRICH[®]) and 0.4 g of guanidine carbonate salt (SIGMA-ALDRICH[®]) are mixed at room temperature in a first container to make a first mixture. In a second container, 6 g of glyceryl tributyrate (SIGMA-ALDRICH[®]), 3 g of CITREPEL[®] as an active ingredient, and 0.2 g (1.9 weight percent), 0.4 g (3.6 weight percent), 0.6 g (5.4 weight percent), 0.8 g (7.0 weight percent), 1 g (8.6 weight percent), 1.2 g (10.2 weight percent), 2.4 g (18.5 weight percent), 3.16 g (25.4 weight percent), or 4.8 g (31.2 weight percent) of TAKENATE[®] D-110N, respectively in each sample, are mixed to make a second mixture. The first mixture and the second mixture are combined to make a third mixture. The third mixture is emulsified by homogenizer (ULTRA TURRAX, T25 Basic, IKA) at 6,500 rpm for two minutes. The emulsified third mixture is stirred by at room temperature with 450 rpm for 10 minutes. The stirred third mixture is cured under stirring at 55 °C for 2 hours. The cured third mixture becomes a polyurea microcapsule slurry. The polyurea microcapsule slurry is filtered by applying vacuum using a vacuum filtration device (*e.g.*, Buchner flask and Buchner funnel). The filtered polyurea microcapsule slurry is placed on a paper and dried at room temperature for 2 to 5 hours to get polyurea microcapsule powder.

[0054] The polyurea microcapsules prepared with different weight percent of isocyanate are sandwiched between two layers of Scotch Magic Tape[®] (3M). The resultant sandwiched tape is sliced to 5 to 10 microns by using Microtome (Nippon Microtome Laboratory). These slices

are mounted on SEM sample holder for scanning the wall thickness. The results are shown in Fig. 3 for this condition. SEM images in 1,000x magnification and in 20,000x magnification of polyurea microcapsules prepared with different weight percent of isocyanate are shown in Fig. 4.

[0055] In this embodiment, the amount of isocyanate (TAKENATE[®] D110N) is varied by keeping the amount of cross-linking agent (Guanidine carbonate salt) the same. Other conditions are same as the basic process as shown in Figs. 1 and 2. With this condition, the wall thickness can be tuned from 35 nm to 500 nm by using CITREPEL[®] as an active ingredient.

[0056] Mechanical strength (crushing strength) of these samples are carried out to check its strength. The tests are performed using a microparticle racking force measurement device, NS-A100 (Nano Seeds Corporation, Japan). The samples (polyurea microcapsule powder) are dispersed on a stage by free fall. The device applies a pressure to the microcapsule and increase the pressure. The applied pressure force is recorded until the microcapsule is finally collapsed by the pressure. The collapse pressure force $F[N]$ is obtained by comparing a peak value of the pressure force for the condition when the microcapsule is collapsed and a base line pressure force for the condition when no pressure force is applied to the microcapsule. The crushing strength $S[Pa]$ is calculated by the following equation:

$$S=2.8F/(\pi \cdot D^2) \quad (1)$$

F = collapse pressure force $[N]$

D = particle size $D [m]$

[0057] The particle size is measured by using an image analysis software, Leica EZ (Leica Microsystems). Particle size of each of the microcapsules is measured in the image. The longest diameter (a diameter of the major axis) of each microcapsule is used as the particle size.

[0058] From the results, it is concluded that the wall thickness is proportional to the amount of isocyanate and the mechanical strength is dependent on the wall thickness. When the amount of the isocyanate is increased, the wall thickness of the microcapsule is increased. When the amount of the isocyanate is decreased, the wall thickness of the microcapsule is decreased. When the wall thickness is decreased, the mechanical strength of the microcapsules is decreased.

[0059]

(Embodiment 2)

<Effect of Amount of Cross-linking Agent on Wall Thickness>

[0060] Polyurea microcapsules are prepared with five different weight percent of cross-linking agents. Polyurea microcapsules are prepared by the process shown in Fig. 2. 20 ml of 1 % poly(sodium 4-styrene sulfonate) (SIGMA-ALDRICH[®]) and 0.2 g (1.85 weight percent), 0.4 g (3.64 weight percent), 0.8 g (7.02 weight percent), 1.6 g (13.11 weight percent), or 3.2 g (23.19 weight percent) of guanidine carbonate salt (SIGMA-ALDRICH[®]), respectively in each sample, are mixed at room temperature in a first container to make a first mixture. In a second container, 6 g of glyceryl tributyrate (SIGMA-ALDRICH[®]), 3 g of CITREPEL[®] as an active ingredient, and 1.2 g of TAKENATE[®] D-110N are mixed to make a second mixture. The first mixture and the second mixture are combined to make a third mixture. The third mixture is emulsified by homogenizer (ULTRA TURRAX, T25 Basic, IKA) at 6,500 rpm for two minutes. The emulsified third mixture is stirred by magnetic stirrer at room temperature with 450 rpm for 10 minutes. The third mixture is cured under stirring at 55 °C for 2 hours. The cured third mixture becomes a polyurea microcapsule slurry. The polyurea microcapsule slurry is filtered by applying vacuum using a vacuum filtration device (*e.g.*, Buchner flask and Buchner funnel). The filtered polyurea microcapsule slurry is placed on a paper and dried at room temperature for 2 to 5 hours to get polyurea microcapsule powder.

[0061] The polyurea microcapsules prepared with different weight percent of cross-linking agent are sandwiched between two layers of Scotch Magic Tape[®] (3M). The resultant sandwiched tape is sliced to 5 to 10 microns by using Microtome (Nippon Microtome Laboratory). These slices are mounted on SEM sample holder for scanning the wall thickness. The results are shown in Fig. 5 for this condition. SEM images in 1,000x magnification and in 20,000x magnification of polyurea microcapsules prepared with different weight percent of cross-linking agent are shown in Fig. 6.

[0062] In this embodiment, the amount of cross-linking agent is varied by keeping the amount of isocyanate constant. The wall thickness of the microcapsule is proportional to the amount of the cross-linking agent. At lower concentration, however, phase separation is noticed. Phase separation towards lower concentration of cross-linking agent may be caused due to the insufficient amount of the cross-linker in the third mixture as compared to the required amount of the cross-linker. Insufficient amount of cross-linker leads to poor encapsulation.

[0063]

(Embodiment 3)

<Effect of Amount of Isocyanate and Cross-linking Agent on Wall Thickness>

[0064] Polyurea microcapsules are prepared with nine different weight percent of isocyanate and cross-linking agent. The polyurea microcapsules are prepared by the process shown in Fig. 2. 20 ml of 1 % poly(sodium 4-styrene sulfonate) (SIGMA-ALDRICH[®]) and 0.12 g (× 0.33), 0.2 g (× 0.50), 0.26 g (× 0.67), 0.32 g (× 0.83), 0.4 g (× 1), 0.8 g (× 2), 1.2 g (× 3), or 1.6 g (× 4) of guanidine carbonate salt (SIGMA-ALDRICH[®]) are mixed at room temperature in a first container to make a first mixture. In a second container, 6 g of glyceryl tributyrate (SIGMA-ALDRICH[®]), 3 g of CITREPEL[®] as an active ingredient, and 0.4 g (× 0.33), 0.6 g (× 0.50), 0.8 g (× 0.67), 1 g (× 0.83), 1.2 g (× 1), 2.4 g (× 2), 3.6 g (× 3), or 4.8 g (× 4) of TAKENATE[®] D-110N, respectively in each sample, are mixed to make a second mixture. The first mixture and the second mixture are combined to make a third mixture. The third mixture is emulsified by homogenizer (ULTRA TURRAX, T25 Basic, IKA) at 6,500 rpm for two minutes. The emulsified third mixture is stirred by at room temperature with 450 rpm for 10 minutes. The stirred third mixture is cured under stirring at 55 °C for 2 hours. The cured third mixture becomes a polyurea microcapsule slurry. The polyurea microcapsule slurry is filtered by applying vacuum using a vacuum filtration device (*e.g.*, Buchner flask and Buchner funnel). The filtered polyurea microcapsule slurry is placed on a paper and dried at room temperature for 2 to 5 hours to get polyurea microcapsule powder.

[0065] The polyurea microcapsules prepared with different weight percent of isocyanate and cross-linking agent are sandwiched between two layers of Scotch Magic Tape[®] (3M). The resultant sandwiched tape is sliced to 5 to 10 microns by using Microtome (Nippon Microtome Laboratory). These slices are mounted on SEM sample holder for scanning the wall thickness. The results are shown in Fig. 7 for this condition. SEM images in 1,000x magnification and in 20,000x magnification of polyurea microcapsules prepared with different weight percent of isocyanate and cross-linking agent are shown in Fig. 8.

[0066] In this embodiment, the amount of isocyanate and cross-linking agent are varied by keeping the ratio of isocyanate /cross-linker weight percent 3 by using CITREPEL[®] as an active ingredient. This embodiment shows the same results as embodiments 1 and 2. An observed difference is no phase separation is noticed for the compositions of this embodiment and the increase in wall thickness is steady. Higher weight percent ratio of the isocyanate to the cross-linking agent does not result in larger or smaller wall thickness. Higher amount of both

isocyanate and cross-linking agent results in larger wall thickness of the microcapsules with the ratio of isocyanate /cross-linking agent weight percent 3.

(Embodiment 4)

<Effect of Amount of Solvent on Wall Thickness>

[0067] Polyurea microcapsules are prepared with three different weight percent of solvent. The polyurea microcapsules are prepared by the process shown in Fig. 2. 20 ml of 1 % poly(sodium 4-styrene sulfonate) (SIGMA-ALDRICH[®]) and 0.4 g of guanidine carbonate salt (SIGMA-ALDRICH[®]) are mixed at room temperature in a first container to make a first mixture. In a second container, 3 g (28.3 weight percent), 6 g (44.1 weight percent), or 9 g (54.2 weight percent), respectively in each sample, of glyceryl tributyrate (SIGMA-ALDRICH[®]), 3 g of CITREPEL[®] as an active ingredient, and 1.2 g of TAKENATE[®] D-110N are mixed to make a second mixture. The first mixture and the second mixture are combined to make a third mixture. The third mixture is emulsified by homogenizer (ULTRA TURRAX, T25 Basic, IKA) at 6,500 rpm for two minutes. The emulsified third mixture is stirred by at room temperature with 450 rpm for 10 minutes. The stirred third mixture is cured under stirring at 55 °C for 2 hours. The cured third mixture becomes a polyurea microcapsule slurry. The polyurea microcapsule slurry is filtered by applying vacuum using a vacuum filtration device (*e.g.*, Buchner flask and Buchner funnel). The filtered polyurea microcapsule slurry is placed on a paper and dried at room temperature for 2 to 5 hours to get polyurea microcapsule powder.

[0068] The polyurea microcapsules prepared with different weight percent of solvent are sandwiched between two layers of Scotch Magic Tape[®] (3M). The resultant sandwiched tape is sliced to 5 to 10 microns by using Microtome (Nippon Microtome Laboratory). These slices are mounted on SEM sample holder for scanning the wall thickness. The results are shown in Fig. 9 for this condition. SEM images in 1,000x magnification and in 20,000x magnification of polyurea microcapsules prepared with different weight percent of solvent are shown in Fig. 10.

[0069] In this embodiment, the solvent used in the process of encapsulation is an oil, which makes oil droplets of certain size. The effect of size of oil droplets on wall thickness is tested by varying the amount of oil, the oil used in this embodiment is glyceryl tributyrate. Significant difference in the wall thickness by changing the amount of glyceryl tributyrate is not observed. The results are shown in Figs. 9 and 10. The test results indicate that the amount of

solvent does not play a significant role on the size of droplets formed during homogenization. In other words, the solvent may have small or no effect on wall thickness of microcapsule.

(Embodiment 5)

<Effect of Homogenization Speed on Wall Thickness>

[0070] Polyurea microcapsules are prepared with five different homogenization speeds in emulsifying. The polyurea microcapsules are prepared by the process shown in Fig. 2 except the homogenization speed in emulsifying is varied. 20 ml of 1 % poly(sodium 4-styrene sulfonate) (SIGMA-ALDRICH[®]) and 0.4 g of guanidine carbonate salt (SIGMA-ALDRICH[®]) are mixed at room temperature in a first container to make a first mixture. In a second container, 6 g of glyceryl tributyrate (SIGMA-ALDRICH[®]), 3 g of CITREPEL[®] as an active ingredient, and 1.2 g of TAKENATE[®] D-110N are mixed to make a second mixture. The first mixture and the second mixture are combined to make a third mixture. The third mixture is emulsified by a homogenizer (ULTRA TURRAX, T25 Basic, IKA) at 5,500 rpm, 6,500 rpm, 7,500 rpm, 8,500 rpm, or 9,500 rpm, respectively for each sample, for two minutes. The emulsified third mixture is stirred by at room temperature with 450 rpm for 10 minutes. The stirred third mixture is cured under stirring at 55 °C for 2 hours. The cured third mixture becomes a polyurea microcapsule slurry. The polyurea microcapsule slurry is filtered by applying vacuum using a vacuum filtration device (*e.g.*, Buchner flask and Buchner funnel). The filtered polyurea microcapsule slurry is placed on a paper and dried at room temperature for 2 to 5 hours to get polyurea microcapsule powder.

[0071] The polyurea microcapsules prepared with different homogenization speeds in emulsifying are sandwiched between two layers of Scotch Magic Tape[®] (3M). The resultant sandwiched tape is sliced to 5 to 10 microns by using Microtome (Nippon Microtome Laboratory). These slices are mounted on SEM sample holder for scanning the wall thickness. The results are shown in Fig. 11 for this condition. SEM images in 1,000x magnification and in 20,000x magnification of polyurea microcapsules prepared with different homogenization speeds in emulsifying are shown in Fig. 12.

[0072] In this embodiment, an effect of processing conditions on the microcapsule is tested by changing the homogenization speed in emulsifying to the five different homogenization speeds. Other conditions are the same as other embodiments. Homogenization speed during polymerization shows a great influence on the size of microcapsule. When the homogenization

speed is higher, the microcapsule size becomes smaller, and the wall thickness becomes smaller, *i.e.*, thinner. In other words, when the droplets are smaller, the amount of isocyanate in the droplets become smaller, which results in thin wall thickness.

(Embodiment 6)

<Effect of Amount of Surfactant on Wall Thickness>

[0073] Polyurea microcapsules are prepared with five different weight percent of surfactant. Polyurea microcapsules are prepared by the process shown in Fig. 2. 0.1g (0.5 weight percent), 0.2 g (1.0 weight percent), 0.4 g (2.0 weight percent), 0.6 g (3.0 weight percent), or 1 g (5.0 weight percent) of poly(sodium 4-styrene sulfonate) (SIGMA-ALDRICH[®]) in 20 ml, respectively in each sample, and 0.4 g of guanidine carbonate salt (SIGMA-ALDRICH[®]), are mixed at room temperature in a first container to make a first mixture. In a second container, 6 g of glyceryl tributyrate (SIGMA-ALDRICH[®]), 3 g of CITREPEL[®] as an active ingredient, and 1.2 g of TAKENATE[®] D-110N are mixed to make a second mixture. The first mixture and the second mixture are combined to make a third mixture. The third mixture is emulsified by homogenizer (ULTRA TURRAX, T25 Basic, IKA) at 6,500 rpm for two minutes. The emulsified third mixture is stirred by magnetic stirrer at room temperature with 450 rpm for 10 minutes. The third mixture is cured under stirring at 55 °C for 2 hours. The cured third mixture becomes a polyurea microcapsule slurry. The polyurea microcapsule slurry is filtered by applying vacuum using a vacuum filtration device (*e.g.*, Buchner flask and Buchner funnel). The filtered polyurea microcapsule slurry is placed on a paper and dried at room temperature for 2 to 5 hours to get polyurea microcapsule powder.

[0074] The polyurea microcapsules prepared with different weight percent of surfactant are sandwiched between two layers of Scotch Magic Tape[®] (3M). The resultant sandwiched tape is sliced to 5 to 10 microns by using Microtome (Nippon Microtome Laboratory). These slices are mounted on SEM sample holder for scanning the wall thickness. The results are shown in Fig. 13 for this condition. SEM images in 1,000x magnification and in 20,000x magnification of polyurea microcapsules prepared with different weight percent of surfactant are shown in Fig. 14.

[0075] The surfactant concentration affects the final size of the microcapsule, dispersion and other parameters such as wall thickness. High surfactant concentration decreases surface tension of the droplets and stabilizes newly developed surfaces during homogenization and

production of smaller particles. This can be seen from the results of the wall thickness with respective to the surfactant concentration. When the concentration of surfactant is increased, the size of the microcapsules is decreased, and the wall thickness of the microcapsules is decreased.

(Embodiment 7)

<Effect of Molecular Weight of Surfactant on Wall Thickness>

[0076] Polyurea microcapsules are prepared with three different surfactants with different molecular weights. The polyurea microcapsules are prepared by the process shown in Fig. 2. 20 ml of 1 % poly(sodium 4-styrene sulfonate) (SIGMA-ALDRICH[®]) with three different average molecular weight, 70,000, 200,000, or 1,000,000, respectively in each sample, and 0.4 g of guanidine carbonate salt (SIGMA-ALDRICH[®]) are mixed at room temperature in a first container to make a first mixture. In a second container, 6 g of glyceryl tributyrate (SIGMA-ALDRICH[®]), 3 g of CITREPEL[®] as an active ingredient, and 1.2 g of TAKENATE[®] D-110N, are mixed to make a second mixture. The first mixture and the second mixture are combined to make a third mixture. The third mixture is emulsified by homogenizer (ULTRA TURRAX, T25 Basic, IKA) at 6,500 rpm for two minutes. The emulsified third mixture is stirred by at room temperature with 450 rpm for 10 minutes. The stirred third mixture is cured under stirring at 55°C for 2 hours. The cured third mixture becomes a polyurea microcapsule slurry. The polyurea microcapsule slurry is filtered by applying vacuum using a vacuum filtration device (e.g., Buchner flask and Buchner funnel). The filtered polyurea microcapsule slurry is placed on a paper and dried at room temperature for 2 to 5 hours to get polyurea microcapsule powder.

[0077] The polyurea microcapsules prepared with different surfactant with three different molecular weights are sandwiched between two layers of Scotch Magic Tape[®] (3M). The resultant sandwiched tape is sliced to 5 to 10 microns by using Microtome (Nippon Microtome Laboratory). These slices are mounted on SEM sample holder for scanning the wall thickness. The results are shown in Fig. 15 for this condition. SEM images in 1,000x magnification and in 20,000x magnification of polyurea microcapsules prepared with different surfactant with three different molecular weights are shown in Fig. 16.

[0078] Poly(sodium 4-styrenesulfonate) surfactants with three different molecular weights are tested. The molecular weights of the tested poly(sodium 4-styrenesulfonate) surfactants are 70,000, 200,000 and 1,000,000. When the molecular weight is lower, the wall

thickness is larger. The sample prepared with the poly(sodium 4-styrenesulfonate) surfactants with the lower molecular weight shows many cracks in the wall. This results in fast release of active ingredients. These results can be applied to control the release of active ingredient by combining different molecular weights of surfactant.

(Embodiment 8)

<Effect of pH on Wall Thickness>

[0079] Polyurea microcapsules are prepared with four different pH levels. The pH is controlled by adding acetic acid. Polyurea microcapsules are prepared by the process shown in Fig. 2. 20 ml of 1 % poly(sodium 4-styrene sulfonate) (SIGMA-ALDRICH[®]) and 0.4 g of guanidine carbonate salt (SIGMA-ALDRICH[®]), are mixed at room temperature in a first container to make a first mixture. 2.5 ml (pH 7.5), 2 ml (pH 8.4), 1.5 ml (pH 9.9), or 0.25 ml (pH 11.5) of 1M acetic acid, respectively in each sample, is added to the first mixture. In a second container, 6 g of glyceryl tributyrates (SIGMA-ALDRICH[®]), 3 g of CITREPEL[®] as an active ingredient, and 1.2 g of TAKENATE[®] D-110N are mixed to make a second mixture. The first mixture and the second mixture are combined to make a third mixture. The third mixture is emulsified by homogenizer (ULTRA TURRAX, T25 Basic, IKA) at 6,500 rpm for two minutes. The emulsified third mixture is stirred by magnetic stirrer at room temperature with 450 rpm for 10 minutes. The third mixture is cured under stirring at 55 °C for 2 hours. The cured third mixture becomes a polyurea microcapsule slurry. The polyurea microcapsule slurry is filtered by applying vacuum using a vacuum filtration device (*e.g.*, Buchner flask and Buchner funnel). The filtered polyurea microcapsule slurry is placed on a paper and dried at room temperature for 2 to 5 hours to get polyurea microcapsule powder.

[0080] The polyurea microcapsules prepared with different pH levels are sandwiched between two layers of Scotch Magic Tape[®] (3M). The resultant sandwiched tape is sliced to 5 to 10 microns by using Microtome (Nippon Microtome Laboratory). These slices are mounted on SEM sample holder for scanning the wall thickness. The results are shown in Fig. 17 for this condition. SEM images in 1,000x magnification and in 20,000x magnification of polyurea microcapsules prepared with different pH levels are shown in Fig. 18.

[0081] For the standard condition, the first mixture containing surfactant and guanidine carbonate salt provides pH of 11.5. As this solution is quite alkaline, effect of lower pH is

studied. No obvious change in the wall thickness is noticed. In other words, this technology can be applied in neutral condition without losing its physical properties.

[0082] It should be evident that this disclosure is by way of example and that various changes can be made by adding, modifying or eliminating details without departing from the fair scope of the teaching contained in this disclosure. The disclosure is therefore not limited to particular details of this disclosure except to the extent that the following claims are necessarily so limited.

CLAIMS

What is claimed is:

1. A method of controlling a wall thickness of a polyurea microcapsule comprising:
mixing a surfactant and a cross-linking agent to make a first mixture;
adding an isocyanate compound to a solvent to make a second mixture;
combining the first mixture with the second mixture to make a third mixture; and
emulsifying the third mixture to make the polyurea microcapsule,
wherein when making the wall thickness of the polyurea microcapsule larger, increasing
an amount of the isocyanate in the third mixture; and
when making the wall thickness of the polyurea microcapsule smaller, decreasing the
amount of the isocyanate in the third mixture.
2. The method of claim 1, wherein the amount of the isocyanate in the third mixture is 1
weight percent to 50 weight percent.
3. The method of claim 2, wherein the wall thickness of the polyurea microcapsule is 35 nm
to 500 nm.
4. A method of controlling a wall thickness of a polyurea microcapsule comprising:
mixing a surfactant and a cross-linking agent to make a first mixture;
adding an isocyanate compound to a solvent to make a second mixture;
combining the first mixture with the second mixture to make a third mixture; and
emulsifying the third mixture to make the polyurea microcapsule,
wherein when making the wall thickness of the polyurea microcapsule larger, increasing
an amount of the cross-linking agent in the third mixture; and
when making the wall thickness of the polyurea microcapsule smaller, decreasing the
amount of the cross-linking agent in the third mixture.
5. The method of claim 4, wherein the amount of the cross-linking agent in the third mixture
is 1.85 weight percent to 23.19 weight percent.

6. The method of claim 5, wherein the wall thickness of the polyurea microcapsule is 140 nm to 473 nm.
7. A method of controlling a wall thickness of a polyurea microcapsule comprising:
mixing a surfactant and a cross-linking agent to make a first mixture;
adding an isocyanate compound to a solvent to make a second mixture;
combining the first mixture with the second mixture to make a third mixture; and
emulsifying the third mixture to make the polyurea microcapsule,
wherein when making the wall thickness of the polyurea microcapsule larger, increasing an amount of the isocyanate and an amount of the cross-linking agent in the third mixture; and
when making the wall thickness of the polyurea microcapsule smaller, decreasing the amount of the isocyanate and the amount of the cross-linking agent in the third mixture.
8. The method of claim 7, wherein the amount of the isocyanate in the third mixture is 1.9 weight percent to 31.2 weight percent, and the amount of the cross-linking agent in the third mixture is 1.85 weight percent to 23.19 weight percent.
9. The method of claim 5, wherein the wall thickness of the polyurea microcapsule is 62 nm to 464 nm.
10. The method according to any one of claim 7, wherein a ratio of the weight percent of the isocyanate to the weight percent of the cross-linking agent in the third mixture is 3.
11. A method of controlling a wall thickness of a polyurea microcapsule comprising:
mixing a surfactant and a cross-linking agent to make a first mixture;
adding an isocyanate compound to a solvent to make a second mixture;
combining the first mixture with the second mixture to make a third mixture; and
emulsifying the third mixture by homogenizing the third mixture to make the polyurea microcapsule,
wherein when making the wall thickness of the polyurea microcapsule smaller, increasing a homogenization speed in the emulsifying within a range from 5,500 rpm to 9,500 rpm; and

when making the wall thickness of the polyurea microcapsule larger, decreasing the homogenization speed in the emulsifying within a range from 9,500 rpm to 5,500 rpm.

12. A method of controlling a wall thickness of a polyurea microcapsule comprising:
mixing a surfactant and a cross-linking agent to make a first mixture;
adding an isocyanate compound to a solvent to make a second mixture;
combining the first mixture with the second mixture to make a third mixture; and
emulsifying the third mixture to make the polyurea microcapsule,
wherein when making the wall thickness of the polyurea microcapsule smaller, increasing an amount of the surfactant within a range from 0.5 weight percent to 5 weight percent in the first mixture; and

when making the wall thickness of the polyurea microcapsule larger, decreasing the amount of the surfactant within a range from 5 weight percent to 0.5 weight percent in the first mixture.

13. A method of controlling a wall thickness of a polyurea microcapsule comprising:
mixing a surfactant and a cross-linking agent to make a first mixture;
adding an isocyanate compound to a solvent to make a second mixture;
combining the first mixture with the second mixture to make a third mixture; and
emulsifying the third mixture to make the polyurea microcapsule,
wherein when making the wall thickness of the polyurea microcapsule smaller, increasing a molecular weight of the surfactant within a range from 70,000 to 1,000,000; and
when making the wall thickness of the polyurea microcapsule larger, decreasing the molecular weight of the surfactant within a range from 1,000,000 to 70,000.