Formation of Silicone Coated Vesicle by Sol-Gel Method. TEM Observation

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The silane entrapped by a vesicle was polymerized by a base catalyst. A silicone membrane was formed around the vesicle. Most of the vesicular structure was maintained in the process. The vesicles coated by silicone were apt to aggregate with each other via the adhesion character of silicone.

Vesicles or liposomes have been studied in detail as media for drug delivery systems[1-4], artificial solar energy conversion[5,6], protection of metal colloids[7], and catalyses for various reactions[8-10], because the bilayer membrane of the vesicle can entrap various compounds on the outer and/or inner surfaces, in the internal water pool and in the membrane itself depending on the polarity of the reactants. However, even if the structure of the vesicle is static in contrast to the dynamic structure of the micelle, it slowly deaggregates with time. One of the well known methods to improve the mechanical stability of the vesicle is the polymerization of the surfactants in the vesicle[11]. The polymerization not only changes the mechanical strength but also changes the permeability of various substrate across the membrane and sometimes packing of the surfactant molecules in the vesicle. Another hopeful method to increase the strength of the vesicular membrane might be the coating of the membrane with an added polymer. One way to attain this is polymerization of the polymerizable organic counterions of the surfactant molecules[12-14]. Another method is the use of inorganic molecules for the vesicle coating. Kunitake et al.[15] reported the formation of a thin silicone polymer film between the bilayers. We then studied the formation of polysiloxane around a vesicle by the sol-gel method without destroying the surfactant aggregate.

The surfactant used for the preparation of the vesicle was dicetyldiallylammmonium bromide (DCAB). The DCAB was prepared by reacting diallylamine with cetyl bromide in two steps[16]. Diallylamine and cetyl bromide in THF were refluxed for two days. THF was removed using an evaporator, followed by solubilization of the product in chloroform. After the addition of aq. sodium cabonate solution, water soluble impurities were removed by extraction. This procedure was repeated several times. After removing the chloroform, the product was solubilized in chloroform/acetonitrile (v:v=1:1). Cetyl bromide was added to the solution, and the resulting solution was refluxed under nitrogen for three days. After concentrating the solution, n-hexane was added and the solution was allowed to stand overnight. The precipitate was collected, and the reprecipitation procedure was repeated several times. The structure of the DCAB was checked by H-nmr.

The vesicle was prepared by sonication of DCAB in water or various aqueous solutions.

The solution of the vesicle coated by silicone was prepared by cosonicating DCAB and ethyltriethoxysilane in NaOH solution (1.00 x 10^{-2} mol/l) for 5 min with a Ultrasonic Homogenizer (Nippon Seiki, US-150), and by subsequent heating at 50 °C for 6 hs.

Polymerization of the vesicle was conducted by the irradiation of light using a Wacom 500W Xe-lamp (KXL-500F) on the DCAB vesicle or the DCAB vesicle/silane solution in a quartz test tube under nitrogen. Glass lenses in the lamp house were removed for the ultraviolet light irradiation. The distance between the test tube and the lamp was fixed at 23 cm. The sample for the TEM obsevation was prepared by the negative staining of the vesicle solution on a Cu grid (200 mesh/inch x inch). The dye added was phosphotungstic acid. The grid was vacuum dried for more than 3 hs before the TEM obsevation. The TEM used was a JEOL TEM-2010.

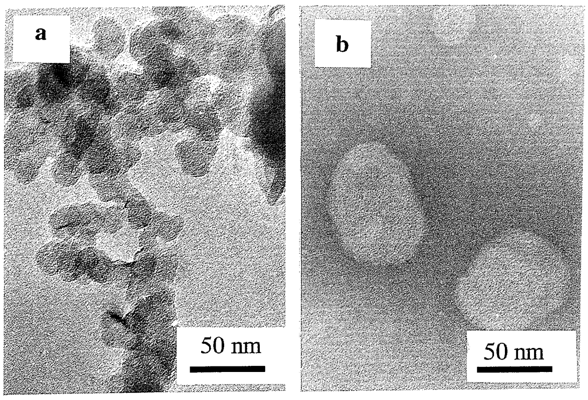

Figure 1. TEM micrographs of (a) silicone in the absence of vesicles and (b) nonpolymerized DCAB vesicle in the absence of silicone.

The base catalyst was employed instead of the acid one for the preparation of silicone by the sol-gel method. During the use of the acid catalyst, the composition of the silicone can not be constant, because condensation occurs before the hydrolysis of the three ethoxy groups. Moreover, the reaction rate is too fast to maintain the vesicular structure, and the silicone precipitates during the early stage. If an alkaline catalyst is used, the condensation occurs after all the ethoxy groups are hydrolyzed, and the resulting silicone does not easily precipitate because the reaction rate is slow. In usual cases, ethanol is added to the aqueous solution to increase the solubility of silane in water. But, in our case, ethanol was not added, because ethanol may destroy the vesicular structure. However, there is a possibility that the vesicles are destroyed by the silane itself. This possibility may be experimentally checked. Figures 1(a) and (b) show the electron micrographs of silicone in the absence of vesicles and the unpolymerized DCAB vesicle in the absence of silicone, respectively. Many of the small silicone particles are not uniform, and growth by aggregation and fusion of the small particles is seen. This process corresponds to the sol-gel process. Figures 2(a) and (b) show interesting pictures of the nonpolymerized and polymerized vesicles in the presence of silane ([silane]/[DCAB]=5). It is seen that vesicles are coated by silicone, and the silicone is promoting the aggregation of the vesicle. In the latter case, some unfused extra small silicone particles exist outside the vesicle. The aggregated vesicles formed a open

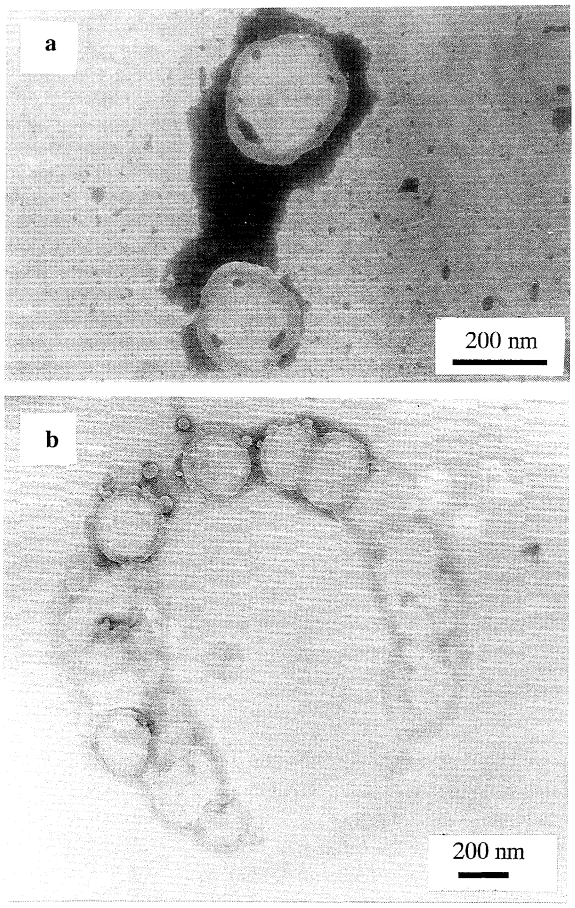

Figure 2. TEM micrographs of (a) nonpolymerized and (b) polymerized DCAB vesicles coated by silicone polymer. [silane] / [DCAB] = 5.

necklace type shape. From these results, it is apparent that (1) silane entrapped by the vesicles did not destroy most of the vesicular structure, (2) the entrapped silane polymerized by a base catalyst maintained the vesicle structure (some nonpolymerized vesicles were destroyed or punctured by either silicone formation or by the drying process to prepare the TEM samples; not shown), and (3) the vesicles coated by silicone aggregated with each other via the adhesion character of silicone. This characteristic resembles the adhesion of cells in biological tissues. The silicone-coated vesicle may be applicable to a strong spherical silicone shell containing various substrates.

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