Application and Characteristics of Lipophilic Gels

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Abstract

Equilibrium swelling curves of Octadecyl Acrylate (ODA) gels with various cross-linking densities in Benzene were measured as a function of temperature. The ODA gel with different five kinds of crosslink densities was prepared. Sample ODA gels were prepared by a free radical copolymerization in Benzene. At 20℃, ODA gel molar ratio 90:1 is swelling in about 30 times compared with the original volume. When ODA gels rises in temperature, the swelling ratio has grown, too. This change showed behavior opposite to Poly (N-isopropylacryamide) (PNIPA) gel of hydrogel. Moreover, the swelling degree of ODA gel has increased with the decrease in the cross-linking density. It is found that the cross-linking density of the networked structure play a key role in the swelling and collapsing of neutral polymer gels. From these results, a basic finding concerning the application development of the oil-water separator gel sheet was obtained.

Keywords : Octadecyl Acrylate (ODA) gels, cross-linking density, oil-water separator gel sheet, swelling ratio

1. Introduction

With the increasing awareness towards environmental preservation, pollution by the outflow of oil has becomes a serious problem in recent years. We live in a world encompassed by various environmental destructions, especially the pollution of rivers, lakes and marshes, the ocean, and soil caused by the outflow of oil from tankers, factories, homes and restaurants are becoming a serious problem. Recently, an oil spill which occurred in South Korea has ignited fear in us and thus, causing an increase towards environmental preservation. There are numerous lipophilic high polymer materials on the market for the purpose of disposal and for the treatment of the outflow of oil. However, most of these materials are disposable generating a lot of garbage, which results in a waste problem.

One of the causes of oceanic water pollution is the out flow of oil from the bilge of shipping vessels. As an effort to overcome such problems, a new standard for the processing of bilge (a compound liquid of oil and seawater) in the engine room was adopted by the IMO (International Maritime Organization) in July of 2003 and it was enforced in January of 2005.Morover, on January 1, of 2007, the standard density of oil emitted from the bilge in the engine room or any other un diluted oil was changed to 15ppm or less[1]. Most of the bilge in the engine room is treated by using a large-scale oil-water separation machine. The rest of the bilge is usually wiped off. The disposal of the cloth used for wiping the bilge results in a lot of garbage, which leads to a waste problem.

As a means to overcome said problem, there are many lipophilic high polymer materials other than the gels used from the disposal of cooking oil from homes and restaurants to treatment of oil spills in the ocean. However, due to the fact that most of these materials are disposable, it becomes a large amount of trash, which results in a waste problem. To overcome these problems, this research uses a lipophilic gels instead of a lipophilic high polymer material. At the present, lipophilic gels are hardly utilized due to the fact that they have inferior absorption and discharge rates when compared hydrogels. Regardless to the demand of lypophilic gels, because the characteristic is hardly understood as it is, application of said gel is not advanced. The reusability and physical properties of said lipophilic gel is researched. By combining this lipophilic gel and the water absorbent gel sheet, we hope to develop a reusable oil-water separator gel sheet, as shown in Fig. 1.

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Reusable absorbent gel sheet has up to now been studied in our laboratory[2-4]. From the results, it was found the absorption and the discharge properties of water absorbent gel sheet were the same as the SAP sheet on the market. And the sheet discharges the water rapidly in the transition temperature. Therefore, it is the best for the gel sheet repeatedly. It was thought that the oil-water separator was possible if lipophilic gel was used together with this hydrogel.

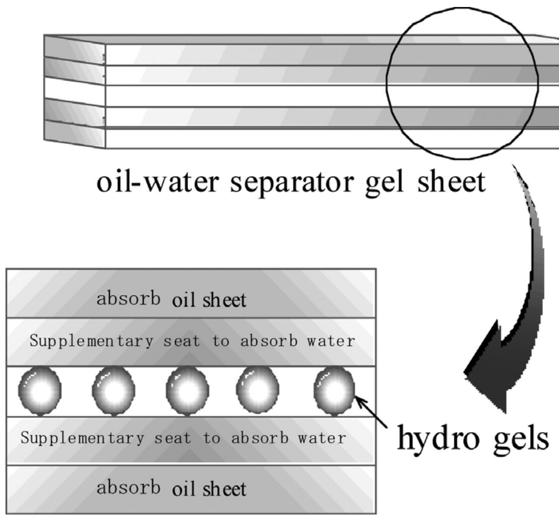

Fig. 1　Structure of oil-water separator gel sheet

2. Experiment

2-1 Preparation of Sample Gels

Sample ODA gels were prepared by a free radical copolymerization in Benzene. Five different kinds of gels were made by changing the ratio of the main constituent, Octadecyl Acrylate (ODA) and the cross-linker, Ethylene Glycol Dimethacrylate (EGDMA). The preparation method of a ODA:EGDMA=95:1 gel is as follows[5].

ODA monomer (9.863 g) was dissolved in 15.2 ml of benzene. After that cross-linker EGDMA (60.0 µl) was added. Followed by 0.099 g of Azobisisbutyronitrile (AIBN) as the initiator for polymerization. Gelation was carried out in 24 hours in 5.5 mm in diameter glass tubes at 60℃. ODA:EGDMA=90:1,85:1,80:1,75:1 gels were prepared using the same method.　The gels were removed from the glass tubes and cut into segments of approximately 1 cm in length and placed in a glass vial filled with benzene. The temperature of the bath could be controlled within a ±0.1℃ range. The temperature was decreased from 50 to 10℃ at 10℃ per interval. Measurements of the gels diameters were taken. The measurements were taken after the gels had reached the state of equilibrium, which takes more than 2 days (～48 hours).

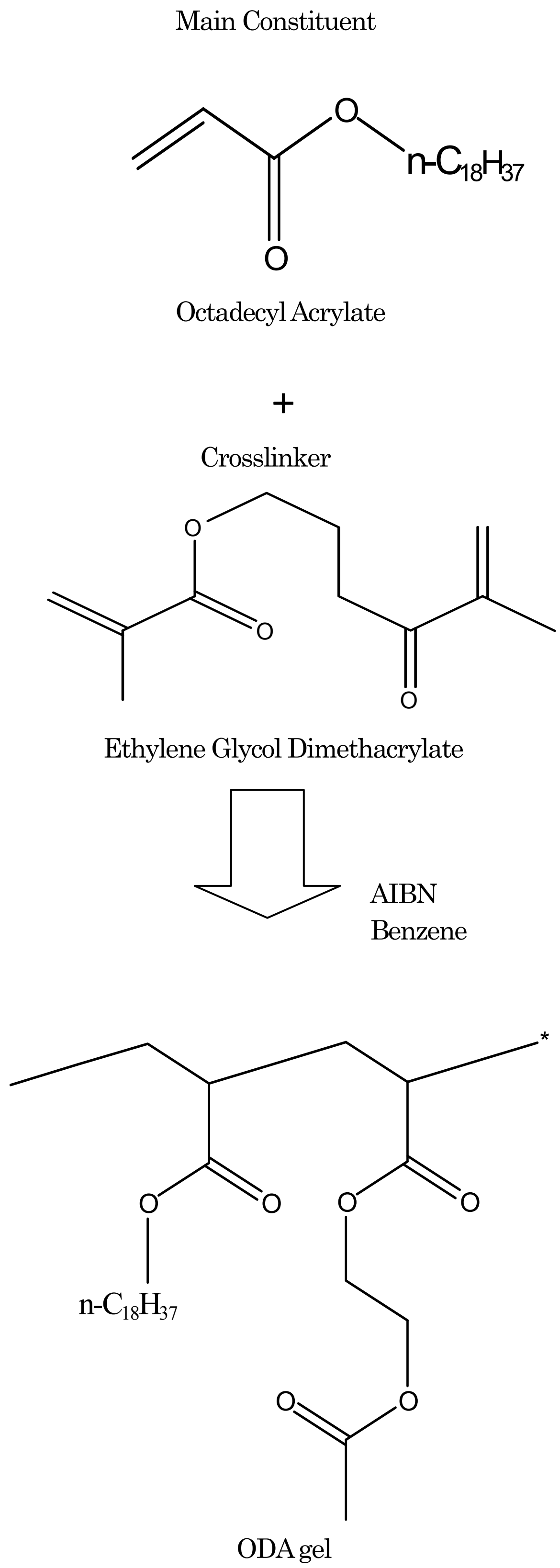

Fig. 2　Structural chart of ODA gel

The diameter of the gel, *d*, was measured by a microscope with calibrated scale. The swelling ratio of the gel, V/V_0, was calculated from the ratio of equilibrium gel diameter to the original diameter, (d/d_0), where d_0 was 5.5 mm. The temperature was controlled within 1℃ for more than a day by circulating water during the measurement.

The structural chart of ODA Gel is as shown in Fig. 2.

2-2 Swelling ratio of the gels

Fig. 3 shows the swelling ODA gel. The diameter (d_{wet}) of the gel is 11.9 mm and mass (W_{wet}) is 1.0890 g. It is very transparent, and looks like the PNIPA gel of hydrogel well. However, it is more elastic than the PNIPA gel. On the other hand, a dry ODA gel is shown in Fig. 4. The diameter (d_{dry}) of the gel is 4.5 mm and mass (W_{dry}) is 0.0685 g. All benzenes in the gel has not been exhausted, and some remains. The gel becomes cloudy transparently and pure white. A dry gel is elasticity, and is very hard. It easily returns to a transparent gel like Fig. 3 when this dry gel is soaked in benzene. Swelling degree *Q* of the gel is defined by as the following equation:

$$Q = (W_{wet} - W_{dry}) / W_{dry}$$

Where W_{dry} and W_{wet} are the weight of the dried gel and the wet gel, respectivity. The swelling degree of the gel was 15 times. The swelling degree of the gels in Benzene was about 20times. It is thought that the difference of the swelling degree is done by the benzene that remains in a dry gel as described in the above sentence.

The swelling ratio, V/V_0, was obtained from the relation, $V/V_0 = (d/d_0)^3$, where V_0 and d_0 are the volume and diameter of the when it was prepared, repectivity.

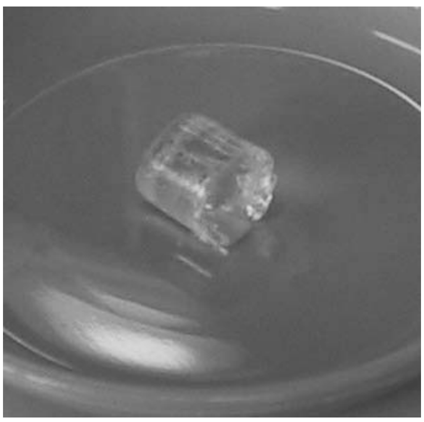

Fig. 3 Swollen ODA gel

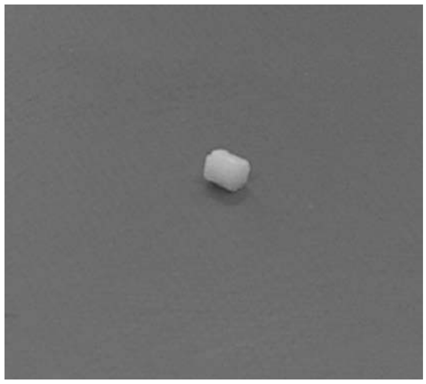

Fig. 4 Dry ODA gel

3. Conclusion and Discussion

3-1 Temperature Dependence of ODA Gels

Swelling curves measured on a series of gels in benzene are shown in Fig. 5. The degree of swelling of ODA gels of various cross-linking densities in Benzene is plotted as a function of temperature. When the ODA:EGDMA molar fraction is at 95:1, as the temperature decreases the volume ratio also decreases. Other molar fraction gels also show the same phenomenon. When the molar fraction is equal to 75:1, a greater decline in the gel's volume ratio is seen between temperatures 20℃ and 10℃. The decline of volume ratio for 95:1 and 85:1 gels are smaller when compared to the decline of volume ratio for the 80:1 and 75:1 gels. From these observations it is thought that ODA gels do have temperature dependence.

Both the compatibility of the polymer chain with the organic solvents and the cross-linking density of the networked structure play a key role in the swelling and collapsing of neutral polymer gels. As a result, the lipophilic gels swell using the same mechanism as that of the ionic gels.

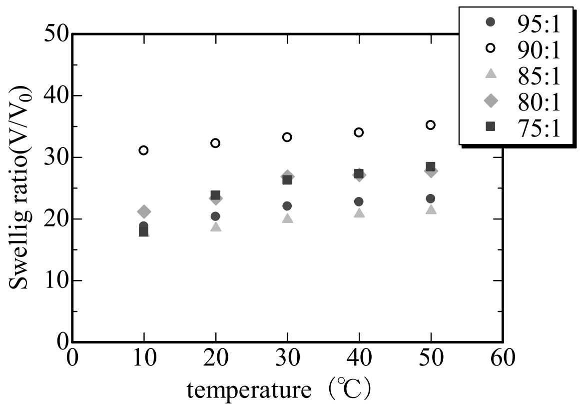

Fig. 5 The swelling degree of ODA gels with various concentration in the network in Benzene is plotted as a function of temperature.

3-2 Cross-linker concentration Dependence of ODA Gels

Fig. 6 shows the relationship between the swelling ratio and the cross-linker concentration of ODA gels from Fig. 5. The swelling ratio of the gel with molar fraction ODA:EGDMA = 90:1 is the largest of about 30 times. Theoretically, as the concentration of the cross-linker increases, the amount of oil absorbed should decrease, meaning that the swelling ratio should also decrease. On the other hand, reducing the amount of cross-linker increases the swelling ability, but stable network cannot from it density is too low. However, it was not seen as such a tendency was remarkable. Therefore, it will be necessary to do a more detailed experiment.

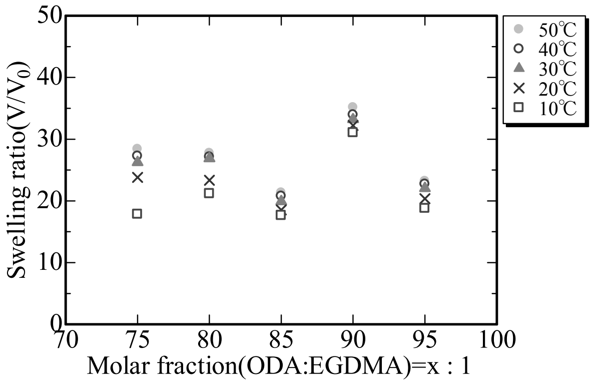

Fig. 6 Swelling ratio vs. concentration of cross-linker of ODA gels.

4. Summary

Equilibrium swelling curves of Octadecyl Acrylate (ODA) gel in Benzene were measured as a function of temperature. From these observations, it is found that when the temperature is decreased, ODA gel's volume ratio also decreases. This shows reverse temperature dependency when compared to PNIPA gels. The gel does not follow the theory that, when the cross-linker concentration increases, the volume ratio decreases. From these results, it is found that both the compatibility of the polymer chain with the organic solvents and the cross-linking density of the networked structure play a key role. And a basic finding concerning the application development of the oil-water separator gel sheet was obtained.

Finally, to be able to adopt this gel in the development of reusable oil-water separator sheets, more detailed experiments are necessary. In addition to its scientific importance, an understanding of the volume transition in lipophilic gels will hasten the application of gel technology to reusable oil-water separator sheets.

Acknowledgment

This work was supported by KAKENHI (19760581).

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