ASIATRIB 2002International Conference
JEJU ISLAND, KOREA

Self-cleaning Surface Coating of Perfluorinated Additives with Resin and Their Surface Properties

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A series of alcohols with perfluorinated segments $F(CF_2)_m(CH_2)_n$-OH, with m=8, 10 and n=4, 6, 10, were synthesized. First, the alcohols were reacted with fatty acid to produce several esters ($F(CF_2)_m(CH_2)_n$-OOC-R with m=8, 10 and n=2, 4, 8) containing perfluoro group by a condensation reaction, and characterized by FT-IR, GC, and surface tension. The esters were soluble in ethyl ether, toluene, hexane, ethyl acetate, chloroform, and acetone, but insoluble in methyl alcohol, ethyl alcohol and isopropyl alcohol. Preliminary experiments on 1,2-dichloroethane solutions showed a remarkable decrease of surface tension upon addition of the esters. Also, the esters using urethane resin were coated onto glass substrate through spin-coating method. The contact angle of coated films ranged from 100 to 122°, depending on the structure of fatty acid esters. As the separate experiment, the water-repellency of coated paper and cotton was evaluated. As a result, the water droplet dropped in surface was not permeated for two weeks.

Keywords : *Perfluorinated Alcohol, Surface Tension, Contact Angle, Water-repellency*

1. INTRODUCTION

There are several ways to improve surface properties using physical treatments such as thermal treatment, plasma treatment, and electrolysis and chemical treatments such as film coating. Among chemical treatments, fluoro-resin is widely used as surface coating material with its water repellent and oil repellent properties due to low surface tension and low friction coefficient [1-5].

In this paper, we would like to describe the synthesis of a series of ***ω -perfluoroalkyl-1-alkanoyl alkanoates*** which have fluorine group in molecules for low friction coefficient and which also have fluorine unit and methylene unit in same molecules for solubilities against general hydrocarbon solvents. And water-repellent properties of urethane resin containing above mentioned ***ω -perfluoroalkyl-1-alkanoyl alkanoates*** were evaluated by measuring contact angle of water droplet onto coated films.

2. EXPERIMENTAL

All of ***ω -perfluoroalkyl-1-alkanoyl alkanoate*** esters (**FmHnEster-SA**, **-OA**, **-EA**, and **–LA** & **ZonylEster-SA**, **-OA**, **-EA**, and **–LA**) were prepared by esterification of fatty acid such as stearic acid (**SA**), oleic acid (**OA**), elaidic acid (**EA**), and linoleic acid (**LA**) and *ω -perfluoroalkyl-1-alkanols* (**FmHnOH** and **Zonyl-OH**) as shown in Scheme 1.

Scheme 1 : Synthesis of ***ω -perfluoroalkyl-1-alkanoyl alkanoates***

$$\underset{\textbf{FmHnOH}}{F(CF_2)_m(CH_2)_n\text{-OH}} + HOOC\text{-}R \rightarrow \underset{\textbf{FmHnEster}}{F(CF_2)_m(CH_2)_n\text{-OOC-}R}$$

$$\underset{\textbf{Zonyl-OH}}{F(CF_2)_{7,8}(CH_2)_2\text{-OH}} + HOOC\text{-}R \rightarrow \underset{\textbf{ZonylEster}}{F(CF_2)_{7,8}(CH_2)_2\text{-OOC-}R}$$

The ***ω -perfluoroalkyl-1-alkanoyl alkanoate*** esters were added into urethane resin (UT 2578-9000 : C.A 2598 = 2 : 1 vol ratio) at the weight ratio of 0 % ~ 20 % and the mixture was dissolved into toluene to become 20 % v/v ratio. The solution was spin-coated at the speed of 1500 rpm, and cured at the temperature of 80 °C for 2 hrs. And then, Contact angles of droplets of water were measured at 25 °C using a sessile drop method.

3. RESULTS AND DISCUSSION

3.1 Synthesis and solubilities

The esterification was completed when a single peak was observed from fatty acid ester by using GC. In FT-IR spectra, after the esterification of **F10H10OH** and fatty acid, the strong absorption at 3400 cm^{-1} due to hydroxy group (-OH) of **F10H10OH**, at 3400-2600 cm^{-1} due to carboxylic acid group of fatty acid , and at 1712 cm^{-1} due to carbonyl groups of fatty acid disappeared because of the formation of ester linkage, whilst the absorption positions due to carbonyl group of ester newly appeared at 1736 cm^{-1}. The absorption bands at 1210 cm^{-1} due to C-F groups of **F10H10OH** and **F10H10Ester**, at 1150 cm^{-1} due to C-O groups of **F10H10OH** and **F10H10Ester** remained practically unchanged. These results were consistent with the structure as proposed. In the ^{1}H-NMR spectra of **F10H10OH** and **F10H10Ester-EA**, the peaks were appeared at 3.8 ppm (2H, OCH_2), at 2.1 ppm (2H, CH_2CF_2), 1.5 ~ 1.6 ppm (4H, $(CH_2)_2$), at 1.1 ~ 1.3 ppm (12H, $(CH_2)_6$).

All of the ***ω -perfluoroalkyl-1-alkanoyl alkanoate*** esters are soluble in such common solvents as $CHCl_3$, 1,2-dichloroethane, acetone, ethylacetate, ether, toluene, and hexane, but insoluble in methyl alcohol, ethyl alcohol. However, the **FmHnEster-SA** and **ZonylEster-SA** synthesized from stearic acid appeared to be less soluble than the other esters. The esters except **FmHnEster-SA** and **ZonylEster-SA** are also soluble in isopropyl alcohol.

3.2 Solution properties and surface tension

The curves of the surface tension versus the concentration for *ω -perfluoroalkyl-1-alkanoyl alkanoate* esters show a declining surface tension with increasing ester concentration. At the same concentration, the higher the fraction of fluorine the esters contain, the more quickly the surface tension decreases. That is, surface tension decreased from 32.0 to 20.0 dynes/cm when 1 weight percent of them was added. Also, surface tension critically depended on their structure

such that **F10H10Ester-OA** and **F10H10Ester-EA** synthesized from oleic acid and elaidic acid, respectively, showed a similar dependence of surface tension on concentration of the corresponding fatty acid esters, respectively, (i.e., both showed surface tension of 20 dynes/cm when 1 weight percent was added) whereas **F10H10Ester-LA** synthesized from linoleic acid showed that surface tension was 17 dyn/cm when 1 weight percent was added. By fixing structure of fatty acid with linoleic acid, **ZonylEster-LA**, **F8H10Ester-LA**, and **F10H10Ester-LA** synthesized from **Zonyl-OH**, **F8H10OH**, and **F10H10OH**, respectively, showed surface tension of 29.1, 20.9, and 16.8 dyn/cm, respectively with 1 weight percent. That is, decrease of surface tenstion was in the order of F10H10>F8H10>Zonyl.

The cmc and γ_{cmc} also depended on the structure of esters. The cmc of **ZonylEster-LA**, **ZonylEster-OA**, and **ZonylEster-EA** showed 39.6, 43.9 and 34.8 mmol/dm^3, respectively. The cmc of **F8H10Ester-LA**, **F10H10Ester-LA**, **F10H10Ester-OA**, and **F10H10Ester-EA** showed 2.70, 1.34, 45.3 and 48.6 mmol/dm^3, respectively. From the cmc results, the cmc value of esters with oleic acid and elaidic acid moiety showed higher than that of esters with linoleic acid moiety. And the cmc value of esters with high fluorine number was lower than that of esters with low fluorine number. The more fluorine unit the esters contained, the higher cmc value showed because of the easy allignment of fluorine group. The reason for showing a dependence of surface tension on structure of fatty acid ester is that linoleic acid has two double bonds whereas both oleic acid and elaidic acid have one double bond. Also, since two double bonds of linoleic acid are cis-cis forms, linoleic acid can occupy a larger space than either oleic acid or elidic acid which have one cis and one trans double bonds.

3.3 Water repellent properties

In order to measure water repellent properties of ***ω -perfluoroalkyl-1-alkanoyl alkanoate*** esters containing perfluoro group, we added them into urethane curing agent (2958 CA, isocyanate) and base resin (UT 2578-9000, polyol ester). And then, films were coated onto glass surface by spin coating and were cured for 2 h at the temperature of 80 °C. contact angles of droplets of water were measured at 25 °C using a sessile drop method.

We observed that water repellent properties depended on structure of fatty acid such as stearic acid, oleic acid, elaidic acid and linoleic acid rather than structure and concentration of perfluoro group. That is, the contact angle increased from 80° for the commonly used resin to 122° for **FmHnEster-SA**, **FmHnEster-EA** and **FmHnEster-LA** added resins. However, in the case of **FmHnEster-OA** added resin, the contact angle increased to 105°. From these results, we can expect that the contact angle largely depend on structure of fatty acid. Also, in order to evaluate their long-term stabilities of water repellent property, we measured the contact angle after storage for 30 days in air and hexane. In case of contact angle of the films stored in air, we found that there was no decrease in contact angle compared with that of initial film. However, we found that the contact angle decreased with storage time when the film was dipped into hexane solvent and the long-term stabilities of contact angle depended on the structure of ***ω -perfluoroalkyl-1-alkanoyl alkanoates***. That is, contact angle of the coated urethane film adding **F8H10Ester-LA** and **F10H10Ester-LA** after 2 weeks storage showed 10% decrease compared with that of initial film. And contact angle of the coated urethane film adding **F10H10Ester-EA** and **F10H10Ester-OA** after 2 weeks storage showed 30% decrease compared with that of initial film. In the case of **F10H10Ester-SA** added urethane resin, the contact angle showed 80% decrease even though only a day had passed. That is, we think that if there are no double bonds in fatty acid, ***ω -perfluoroalkyl-1-alkanoyl alkanoate*** esters does not form a bond with urethane resin but exist as blend form. If there are double bonds in fatty acid, they form a bond with urethane resin and thus, show a good water repellent property for a long time.

4. CONCLUSION

We synthesized several ***ω -perfluoroalkyl-1-alkanoyl alkanoate*** esters with fluoro group and good solubilities to the commonly used solvents and studied their solution properties. Their solubility was good in ethyl ether, toluene, ethyl acetate, chloroform, hexane, and acetone except for alcohols such as methyl alcohol and ethyl alcohol. Surface tension remarkably decreased even if only a small amount of them was added and surface tension decrease depending on their structure. The water repellent properties depended on structure of fatty acid rather than structure and concentration of perfluoro group. And the contact angles were very stable in air state for long-term storage about 30 days. However, in case of the films stored in hexane solvent, the contact angle decreased with storage time depending on the their structure.

5. REFERENCES

[1] Yoshino, N., Tagaki, T., and Kondo, Y., "Synthesis of Trimethoxy-type Silane Coupling Agents Containing Two Fluorocarbon Chains and Surface Modification of Glass," 日本油化學會誌, Vol 46, No. 8, pp. 49, 1997

[2] Tadanaga, K., and Minami, T., "Preparation and Application of Super-Water-Repellent Surface," 機能材料, Vol. 19, No. 4, pp. 47, 1999

[3] Morimoto, T., Gunji, F., and Yoneda, T., "Water Repellent Coating on Glass by Sol-Gel Process," 機能材料, Vol. 19, No. 7, pp. 40, 1999

[4] Ramharack, R., and Nguyen, T. H., "Fluoropolymers of Very Low Surface Energies," J. Polymer Sci., Part C, Vol. 25, pp. 93, 1987

[5] Park, I. J., Lee, S. B., and Choi, C. K., "Surface Properties of the Fluorine-Containing Graft Copolymer of Poly((perfluoroalkyl)ethylmethacrylate)-g-ploy(methyl-methacrylate)," Macromolecules, Vol. 31, pp. 7555, 1998