Effect of Wettability of Injection Nozzle on the Size of Oil Droplets in Water

Keizo OGINO, * Hiroshi OHKI, and Masahiko ABE
Faculty of Science and Technology, Science University of Tokyo,
2641, Yamazaki, Noda, Chiba 278

The hydrophilic cotton filter was found to be more effective as an injection nozzle than any other hydrophobic polymer filters tested to make smaller oil droplets of n-dodecane dispersed in continuum water phase. The droplet size is reduced with an increase in the hydrophilic property (especialy, the hydrogen bonding force) of the polymer surfaces.

The technique for dispersion of one liquid into another immiscible liquid is of importance in various fields. Droplet formation in the dispersion (from single nozzles and/or orifices) of one liquid into another immiscible liquid will assure the homogeneous size of the droplets. Many studies have been carried out: 1-7) most are concerned with the physical properties and flow conditions of the system. The sizes of droplets formed are fairly large. But few studies have been made on the influence of the chemical properties of the polymer filters attached to the nozzle top on the droplet formation.

In this work, n-dodecane as an oil was dispersed into water through synthetic polymers (vinyl polymers) and/or natural polymers (carbohydrate polymers) attached to the top of each single nozzle. We have studied the effect of wettability of polymer filters on the homogeneous size of the droplets.

The polymer samples used were polyethylene (PE, Sumitomo Chemical Co. Ltd.), poly(vinyl chloride) (PVC, Shin-etsu Chemical Co. Ltd.), poly(vinyl alcohol) (PVA, Mitsubishi Monsanto Chemical Co. Ltd.), cellophane (CP, Tokyo Cellophane Co. Ltd.) and cotton (CT, standard cotton of the Japan Oil Chemists' Society). Films of PE and PVC were washed by the methods described by Tamai et al.; 8) those of PVA and CP were washed by Matsunaga' methods. 9) Textile fibers of CT were purified by Soxhlet extraction with ethanol and diethyl ether; the fibers were dried with through-flow of air and shaped into a sheet under pressure. The n-dodecane was purified by conventional distillation. A series of standard liquid for measurements of contact angle used here were chosen on the basis of the classification (three series of liquids: non-polar, polar, or hydrogen bonding liquids) by Kitazaki et al. 10) They were purified by conventional distillation and were chromatographically pure.

All polymer filters were holed with glass-rods of given diameters. The instrument with each polymer filter was described in Fig. 1. The single droplets were formed statically (velocity of the dispersed phase = 0) after the instrument

2144 Chemistry Letters, 1987

was immersed into water. For estimation of the wetting of polymer surfaces, the measurements of contact angles land the surface tension of standard liquids were performed with a Goniometer G-II (Erma Co. Ltd.) and a Wilhelmy-type Surface Tensometer ST-1 (Shimadzu Co. Ltd.) at 30 °C.

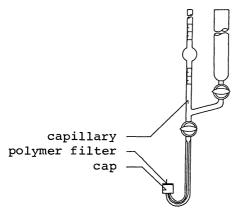


Fig. 1. Experimental instrument.

Table 1. The size of oil dropleta)

			Droplet size
(a)	Polyethylene	(P E)	10.11
(b)	Poly(vinyl chloride)	(PVC)	9.05
(c)	Poly(vinyl alcohol)	(PVA)	6.08
(a)	Cellophane	(C P)	3.21
	Cotton	(C T)	1.34

- a) Diameter of hole size = 0.566 mm, at 30 °C.
- b) Diameter of oil droplet.

First, we studied the effect of the kind of filter polymer (with a constant hole size) on the size of oil droplets. The results are shown in Table 1. size of oil droplets formed is strongly dependent on the kind of polymers. By the replacement of one hydrogen atom of ethylene group of polyethylene (PE) by a chlorine atom or a hydroxyl group, the size of oil droplets formed is reduced (PE, 10.11 mm; PVC, 9.05 mm; PVA, 6.08 mm). One should note that the size of droplets formed through a cotton filter (1.34 mm) is about 1/8 of that through a PE filter. The hole size of the polymer filters is changed by using glass-rods having various diameters. The size of oil droplet formed through PE and/or PVC filters did not change much with a decrease in the hole size of the filters. However, for the PVA, CP and CT filters, the sizes of oil droplet formed decreased with decreasing hole size of polymers. For the CT filter, when the low pressure exerted on the oil, the size of the oil droplets obtained was smaller than the hole size of the filters. It can be postulated that the size of oil droplets is closely related to the wettability of the polymer filter surfaces by the oil. The observed phenomena suggest that the oil did not spread out over the filter surfaces of PVA, CP and CT, while it did spread out over those of PE and PVC. So, a poor wettability of the surface of a polymer filter would make the size of droplet smaller.

The critical surface tension (γ_c) was proposed as a unifying concept by Zisman^{12,13)} and has been found to be useful in correlating wettability of many polymer surfaces. So, we tried to study the relationship between γ_c and the size of the droplets formed. The critical surface tension and its components (dispersion force, γ_s^d ; polar force, γ_s^p ; hydrogen bonding force, γ_s^h) of the respective polymers were obtained from the Zisman plot.^{12,13)} The results are summarized in Table 2. The dispersion force (γ_s^d) of polymer surfaces, except for CT, is almost the same, while the non-dispersion forces of polymer surfaces are

Chemistry Letters, 1987 2145

Table 2. Critical surface tension and its components for polymer surfaces at 30 °C

•			Dispersion Non-dispersion				
			force	for	ce		
		Ϋ́c	γ ^đ	$\gamma_{\mathbf{s}}^{\mathbf{p}}$	γsh		
		dyne cm ⁻¹	dyne cm ⁻¹	dyne cm	l dyne cm ⁻¹		
(a) (b) (c) (d) (e)	P E PVC PVA C P C T	42.8 41.4 43.2	34.5 34.4 34.1 34.0 42.5	0.0 8.1 0.8 0.7 0.2	0.0 0.3 6.5 8.5 9.5		

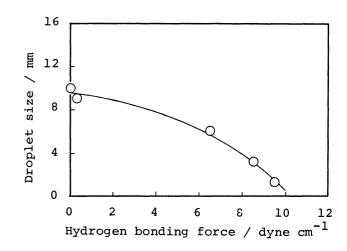


Fig. 2. Relation between droplet size and hydrogen bonding force.

dependent on the kind of polymers: the hydrogen bonding force (γ_s^h) increases with increasing hydrophilic property of polymers. Kitazaki et al. ¹⁴⁾ have mentioned that γ_s^h correlates with the wettability of solids by the liquids having hydrogen bonding like water, glycerol, and formamide. The values of γ_s^h at 30 °C are plotted against the size of oil droplets in Fig. 2. This shows that the size of oil droplets is reduced with an increase in γ_s^h .

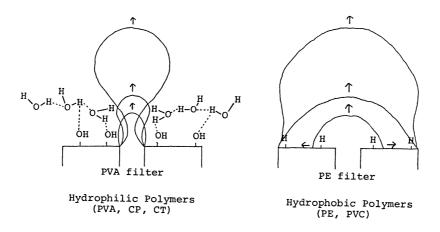


Fig. 3. Schematic model for formation process of oil droplets.

The above suggestion is illustrated by a schematic model for the formation process of oil droplets shown in Fig. 3. As the γ_s^h values of PE and PVC are small, the interaction between water molecules and polymer surface is weak; the oil which comes out from a hole is spread out over the surface of the polymer filter.

2146 Chemistry Letters, 1987

Necking occurs over the surface of polymer filters and results in the increase of the size of oil droplets. On the other hand, for the hydrophilic polymers (PVA, CP, CT), the interaction between water molecules and polymers is stronger because of hydrogen bonding. So the oil droplets which come out from a hole do not spread out over the surface of the polymer filter; as a result, the necking which occurs in the vicinity of a hole brings about the decrease of the size of the oil droplets.

We conclude that the size of oil droplet formed through a hole is dependent on the property of the polymer filter surface. The cotton filter which has a large hydrogen bonding force (γ_s^h) is most available for the formation of small-sized oil droplets.

References

- 1) F. Bashforth and J. C. Adams, "An Attempt to Test the Theory of Capillary Action," Univ. Press, Cambridge, England (1883).
- 2) W. D. Harkins and F. E. Brown, J. Am. Chem. Soc., 41, 999 (1919).
- 3) T. Otaka and S. Fujita, Chem. Eng. Jpn., 13, 199 (1949).
- 4) C. B. Harworth and R. E. Treybal, Ind. Eng. Chem., 42, 1174 (1950).
- 5) H. R. Null and H. F. Johnson, A. I. Ch. Journal, 4, 273 (1958).
- 6) J. F. Paddy, "Surface and Colloid Science," Wiley Interscience (1969), Vol. 1, p.38.
- 7) M. Hozawa, T. Tsukada, N. Imaishi, and K. Fujinawa, J. Chem. Eng. Jpn., <u>14</u>, 358 (1981).
- 8) Y. Tamai, K. Makuuchi, and M. Suzuki, J. Phys. Chem., 71, 4177 (1967).
- 9) T. Matsunaga and Y. Ikada, J. Colloid Interface Sci., 81, 9 (1981).
- 10) Y. Kitazaki and T. Hata, Nippon Settyaku Kyokaishi, 8, 133 (1972).
- 11) Y. Ikada, T. Matsunaga, and M. Suzuki, Nippon Kagaku Kaishi, 6, 1080 (1985).
- 12) W. A. Zisman, J. Phys. Chem., <u>58</u>, 260 (1954).
- 13) W. A. Zisman, "Contact Angle, Wettability and Adhesive," Adv. Chem. Ser., 43, American Chemical Soc., (1964).
- 14) Y. Kitazaki and T. Hata, Nippon Settyaku Kyokaishi, 8, 126 (1972).

(Received July 29, 1987)