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

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The effect of the wettability of an injection nozzle on the size of oil droplets in water has been studied. Dodecane as an oil was dispersed into a continuous water phase through various polymers attached to the top of each single nozzle. The polymer filters used were polyethylene (PE), poly(vinyl chloride) (PVC), poly(vinyl alcohol) (PVA), cellophane (CP), and cotton (CT). The hydrophilic cotton filter is found to be more effective as the injection nozzle than any other hydrophobic polymer filter tested to disperse smaller oil droplets of dodecane into the continuous water phase. The droplet size is reduced with an increase in the hydrogen-bonding force of the polymer-filter surfaces. This may be attributed to the strong adhesion tension between the water molecules and hydrophilic groups of the polymer surface.

The technique for the 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 have been concerned with the effect of flow conditions, nozzle shapes and diameters, and the physical properties of the dispersed phase and/or continuous phase on the droplet formation. The sizes of the droplets formed are fairly large. However, few studies have been made of the influence of the chemical properties of the polymer filters attached to the nozzle top on the droplet formation.

The wettability of a polymer surface is of importance in various fields and is also of great theoretical interest. The contact angle is very useful in the evaluation of wettability. The magnitude of the contact angle is determined by the balance of forces at the boundary line between a liquid, a solid, and a second fluid, which is normally air. This balance of forces is described by Young's equation:

$$\gamma_S = \gamma_{SL} + \gamma_L \cos\theta \qquad (1)$$

where γ_{SL} is the interfacial tension between a solid and a liquid and where γ_S and γ_L are the surface tension of the solid and liquid phases.

Zisman[8,9] proposed the critical surface tension (γ_C) as a unifying concept, and it was found to be useful in correlating the wettability of many polymer surfaces. Since γ_L and θ are measured easily, we should then be able to obtain γ_L from Zisman plots.[8,9] Zisman and his co-workers observed that $\cos\theta$ is usually a monotonic function γ_C for a homogeneous series of liquids. Each line extrapolates to zero θ at a certain γ_L value, which Zisman[9] called the critical surface tension γ_C; since various series extrapolated to about the same value, he proposed that γ_C was a quantity characteristic of a given solid. The critical surface tension concept has provided a useful means of summarizing wetting behavior.

In recent years, many scientists, for example Fowkes,[10] Owens,[11] Kaeleble,[12] Wu,[13] and Kitazaki,[14] have developed equations for assuming the surface tension (γ_S) of a solid. Especially, Kitazaki et al.[14] reported that the surface free energy of an organic material was divided into three components: the dispersion force (non-polar γ^d), the interaction force of polar characters (γ^p), and the hydrogen-bonding force (γ^h). The surface tension of a solid and a liquid may, therefore, be described as follows:

$$\gamma_S = \gamma_S^d + \gamma_S^p + \gamma_S^h \qquad (2)$$

$$\gamma_L = \gamma_L^d + \gamma_L^p + \gamma_L^h \qquad (3)$$

The interfacial tension between solid and liquid phases (γ_{SL}) may be written by:

$$\gamma_{SL} = \gamma_S + \gamma_L - 2(\gamma_S^d \gamma_L^d)^{1/2} - 2(\gamma_S^p \gamma_L^p)^{1/2} - 2(\gamma_S^h \gamma_L^h)^{1/2} \qquad (4)$$

One interesting variation is obtained by combining Eqs. 1 and 4:

$$\gamma_L(1+\cos\theta) = 2(\gamma_S^d \gamma_L^d)^{1/2} + 2(\gamma_S^p \gamma_L^p)^{1/2} + 2(\gamma_S^h \gamma_L^h)^{1/2} \qquad (5)$$

When the critical surface tension can not be obtained from Zisman plots, the force components of a solid can be given from the contact angle measurements with Eq. 5.

In this study, we investigate the wetting behavior of polymers in terms of the force components. We discuss the effect of the wettability of the injection nozzle on the size of oil droplets in water.

Experimental

Material. Polymers: The polymer samples used are shown in Table 1. Films of PE and PVC were washed by the methods described by Tamai et al.,[15] while those of PVA and CP were washed by the method of Matsunaga et al.[16] Textile fibers of CT were purified by Soxhlet extraction with ethanol and diethyl ether; the fibers were dried by means of a through-flow of air and shaped into a sheet under pressure.

Dispersed and Continuous Phases: Dodecane as an oil was purchased from the Tokyo Kasei Co., Ltd. It was purified by conventional distillation and was chromatographi-

Table 1. Sample Polymer

Polymer		Manufacturer	Shape	Thickness /mm	Degree of polymerization
Polyethylene	(PE)	Sumitomo Chemical Co., Ltd.	Film	0.1	3000
Poly(vinyl chloride)	(PVC)	Shin-etsu Chemical Co., Ltd.	Film	0.1	1000
Poly(vinyl alcohol)	(PVA)	Mitsubishi Monsanto Chemical Co., Ltd.	Film	0.1	1800
Cellophane	(CP)	Tokyo Cellophane Co., Ltd.	Film	0.1	400
Cotton	(CT)	The Japan Oil Chemists' Society	Textile	—	—

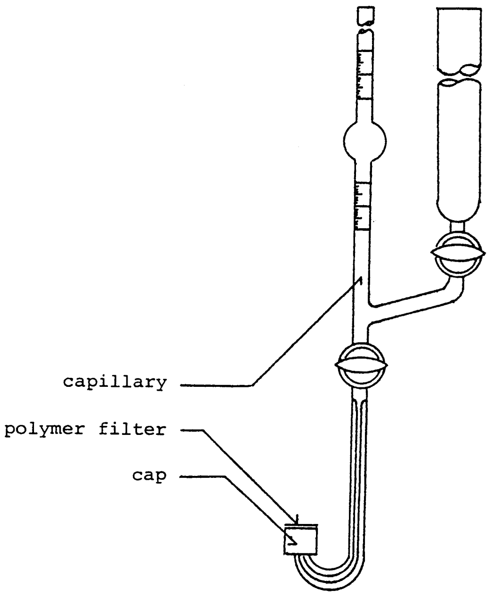


Fig. 1. Experimental instrument.

Table 2. Surface Tension[a] of Standard Liquids

	γ_L	γ_L^d	γ_L^p	γ_L^h
A-series(non-polar) liquid				
Octane	21.0	21.0	0	0
Decane	23.2	23.2	0	0
Dodecane	25.0	25.0	0	0
Tetradecane	26.5	26.5	0	0
Hexadecane	27.4	27.4	0	0
B-series(polar) liquid				
1,1,2,2-Tetrachloroethane	34.4	31.5	2.9	0
1,1,2,3,4,4-Hexachloro-1,3-butadiene	35.5	35.3	0.2	0
Tritolyl phosphate	41.0	37.5	3.5	0
1-Bromonaphthalene	43.3	43.1	0.2	0
1,1,2,2-Tetrabromoethane	47.1	43.9	3.2	0
Diiodomethane	48.9	45.0	3.9	0
C-series(hydrogen bonding) liquid				
Diethylene glycol	44.4	31.7	0.0	12.7
Ethylene glycol	50.5	31.9	0.0	18.6
Thiodiglycol	53.3	38.7	1.4	13.2
Formamide	58.8	35.5	1.6	21.7
Glycerol	64.4	37.4	0.1	26.9
Water	71.2	27.5	1.5	42.2

a) Units in dyn cm^{-1}.

cally pure. The water employed for the continuous phase was twice-distilled water.

Standard Liquids: The series of standard liquids used here for measurements of the contact angle were chosen on the basis of the classification (three series of liquids; non-polar, polar, or hydrogen bonding liquids) proposed by Kitazaki et al.[14] The classification is as follows: **A** series (non-polar) liquids, $\gamma_L=\gamma_L^d$; **B** series(polar) liquids, $\gamma_L=\gamma_L^d+\gamma_L^p$;**C** series(hydrogen bonding) liquids, $\gamma_L=\gamma_L^d+\gamma_L^p+\gamma_L^h$. The standard liquids used here were obtained from the Tokyo Kasei Co., Ltd. Their purification by conventional distillation was found to be chromatographically satisfactory.

Apparatus and Procedure. Measurements of the Droplet Size: All the polymer filters were holed with glass rods of given diameters. The hole size of the polymer filters was changed by using glass rods with various diameters. The polymer filter was attached to the top of the single nozzle. The instrument, with each polymer filter, is depicted in Fig. 1. The single droplets were formed statically (velocity of the dispersed phase=0) through the polymer filter after the instrument has been immersed in water at 30 °C. Their diameters were determined from photographs.

Estimation of the Wettability of the Polymer Surface: The wettability of the polymer surface was estimated by measurements of the advancing contact angle (θ_a), using three series of liquids (**A**-series, **B**-series, and **C**-series liquids) as is shown in Table 2. The wettability was evaluated by means of the critical-surface tension and its components as obtained from a Zisman plot and Eq. 5. The advancing contact angles (θ_a) were measured by the sessile-drop (I) and inverted-bubble (II) methods, both shown in Fig. 2.[17] The measurements of the contact angles and the surface tension of standard liquids were performed with a Goniometer G-II (Erma Co., Ltd.) and a Wilhelmy-type Surface Tensiometer ST-1 (Shimadzu Co., Ltd.) at 30 °C.

Results and Discussion

Observation of Oil-Droplet Formation. Figure 3 shows the results of the observation of oil droplets formed through a polymer filter with a constant hole size at 30 °C. As can be seen in Fig. 3, the droplets formed with a polymer filter vary considerably in size.

In general, for a stationary continuous phase, drop-

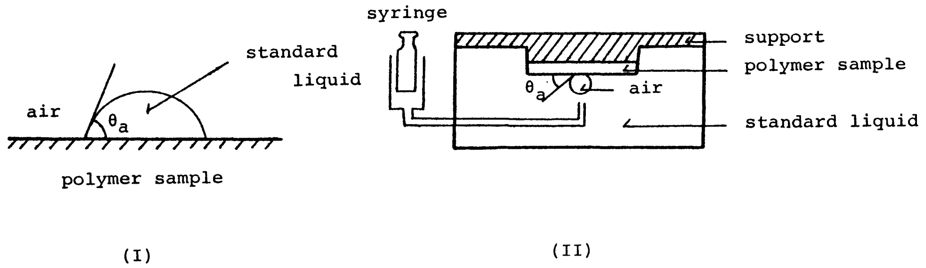


Fig. 2. Schematic diagram of an apparatus for measuring the contact angle by the sessile drop (I) and inverted bubble (II) methods.[17]

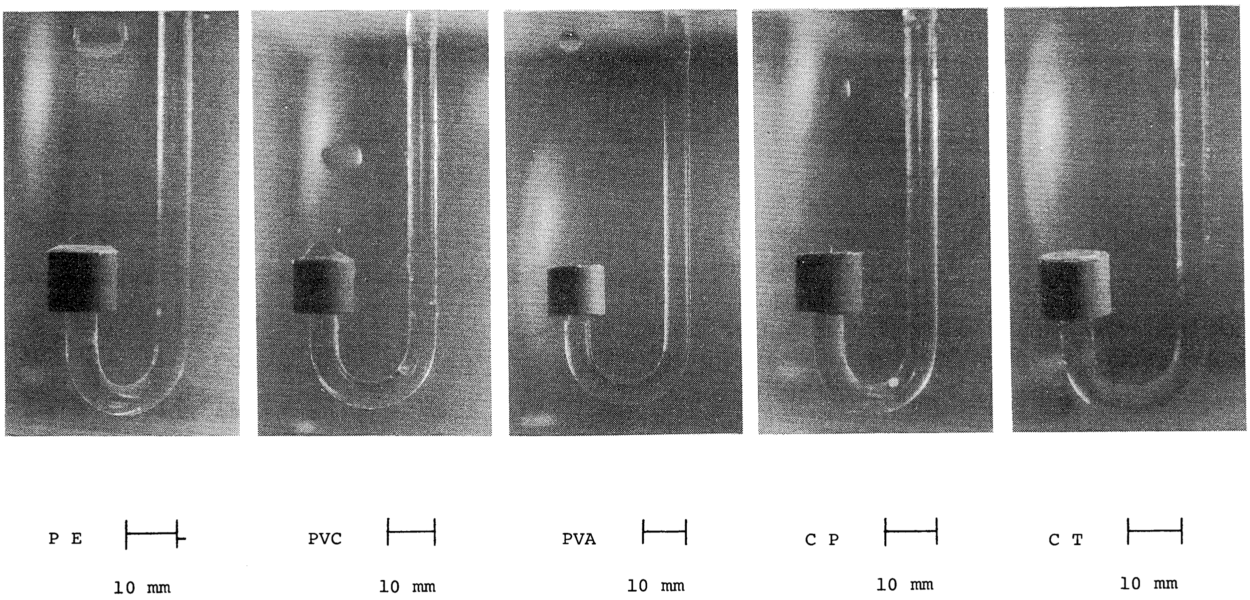


Fig. 3. Photographs of oil droplet formation.

let formation from a single nozzle is classified into several types in terms of the velocity (v) of the dispersed phase: (1) when the v is equal to zero, droplets are formed separately: (2) when the v is low, droplets are formed in a chainlike manner, and (3) when the v is high, droplets are sprayed out. If the velocity of the dispersed phase is markedly low (if, that is, the effect of the velocity is negligible), single droplets are formed "statically." Harkins and Brown[2] have reported that the droplet size is proportional to the interfacial tension between immiscible liquids, the radius of the nozzle, etc. At the same time the droplet size is inversely proportional to the local acceleration of gravity and the density difference between immiscible liquids. When the radii of nozzles with installed polymer filters are the same, droplets of the same size must be formed. It is, however, clear that the size of the oil droplets formed is greatly dependent on the chemical properties of the polymers (Fig. 3). The oil does not spread out over the filter surfaces of PVA, CP, and CT, while it does spread out over those of PE and PVC. It can, then, be postulated that the droplet size is closely related to the wettability of the polymer-filter surfaces.

Table 3. The Size of Oil Droplets[a]

		Droplet size[b] /mm
(a) Polyethylene	(PE)	10.11
(b) Poly(vinyl chloride)	(PVC)	9.05
(c) Poly(vinyl alcohol)	(PVA)	6.08
(d) Cellophane	(CP)	3.21
(e) Cotton	(CT)	1.34

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

The Size of Oil Droplets. Table 3 lists the size of the oil droplets obtained from a study of photographs (Fig. 3). By the replacement of one hydrogen atom of the ethylene group of polyethylene (PE) by a chlorine atom or a hydroxyl group, the size of the oil droplets formed is reduced (PE, 10.11 mm; PVC, 9.05 mm; PVA, 6.08 mm). It seems that a poor wettability of the polymer surface (the hydrophilic surface) by the oil would make the size of the droplet smaller. One should note that the size of the droplets formed through a cotton filter (1.34 mm) is the smallest, being about 1/8 of that of those formed through a PE filter.

Figure 4 exhibits the sizes of droplets against the change in the inner diameters of polymer filters (outer

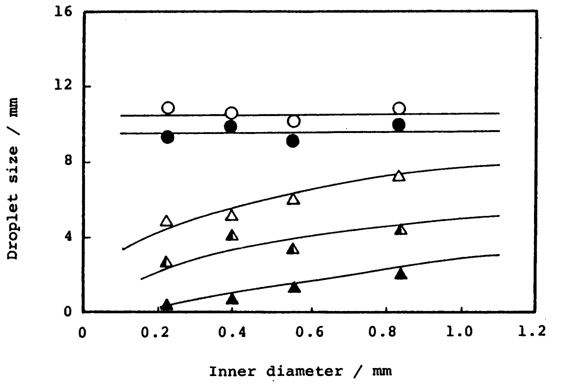
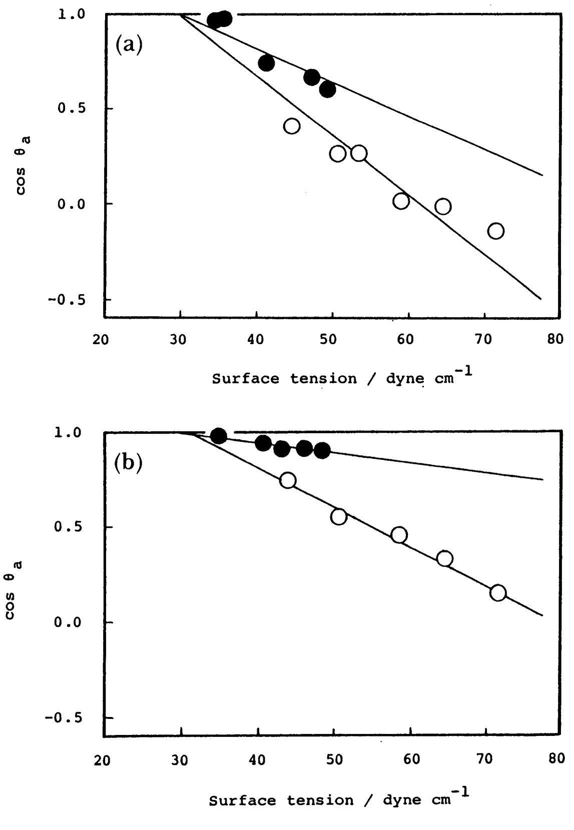


Fig. 4. The change of droplet size as a function of varying inner diameter of filter at 30 °C (outer diameter=constant). (○): PE, (●): PVC, (△): PVA, (△): CP, (▲): CT.

diameter=constant). The sizes of the oil droplets formed through PE and/or PVC filters do not change much with a decrease in the hole size of the filters. However, for the PVA, CP, and CT filters, the sizes of the oil droplets formed decrease with a decrease in the hole size of the polymers. Furthermore, for the CT filter, when a low pressure is exerted on the oil, the size of the oil droplets obtained is smaller than the hole size of the filters.

Effect of the Wettability of the Polymer Filter Surface on the Sizes of Oil Droplets. Let us now consider the effect of the surface-tension components on the sizes of the oil droplets.



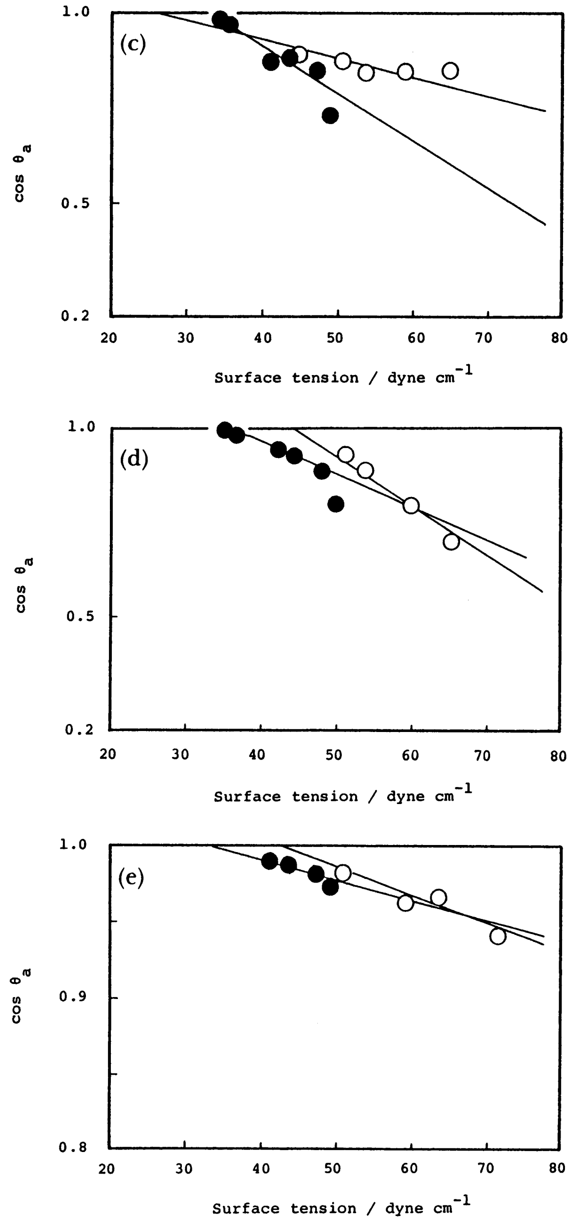


Fig. 5. Zisman plot for **B** series and **C** series liquids. (a) PE, (b) PVC, (c) PVA, (d) CP, (e) CT. (●): **B** series liquids, (○): **C** series liquids.

Figure 5(a—e) represent plots of cos $\theta_{\rm a}$ versus $\gamma_{\rm L}$ for various series (**B** series and **C** series) on polymers. As can be seen in these figures, each cos $\theta_{\rm a}$ is a monotonic function $\gamma_{\rm L}$ for **B**-series liquids and for **C**-series liquids. The value of $\gamma_{\rm L}$, extrapolated to zero $\theta_{\rm a}$ in these figures, corresponds to the $\gamma_{\rm C}$ obtained with **B**-series and **C**-series liquids, as has been mentioned above. The $\gamma_{\rm S}^{\rm h}$ was obtained from the difference between the two values of $\gamma_{\rm C}$. According to Kitazaki et al.,[14] the $\gamma_{\rm S}^{\rm d}$ is the value of $\gamma_{\rm L}$ extrapolated to zero $\theta_{\rm a}$ for **A**-series liquids, while the $\gamma_{\rm S}^{\rm p}$ is the $\gamma_{\rm C}$ difference between **A**-series and **B**-series liquids. All **A**-series liquids, however, spread out over the polymer-filter surfaces used here, so the plots could not be measured. Therefore, the $\gamma_{\rm S}^{\rm d}$ and $\gamma_{\rm S}^{\rm p}$ were obtained from measurements of the con-

Table 4. Critical Surface Tension and Its Components for Polymer Surfaces at 30 °C

	Dispersion force		Non-dispersion force	
	γ_c	γ_s^d	γ_s^p	γ_s^h
	dyn cm^{-1}	dyn cm^{-1}	dyn cm^{-1}	dyn cm^{-1}
(a) Polyethylene (PE)	34.5	34.5	0.0	0.0
(b) Poly(vinyl chloride) (PVC)	42.8	34.4	8.1	0.3
(c) Poly(vinyl alcohol) (PVA)	41.4	34.1	0.8	6.5
(d) Cellophane (CP)	43.2	34.0	0.7	8.5
(e) Cotton[a] (CT)	52.2	42.5	0.2	9.5

a) Inverted bubble method.

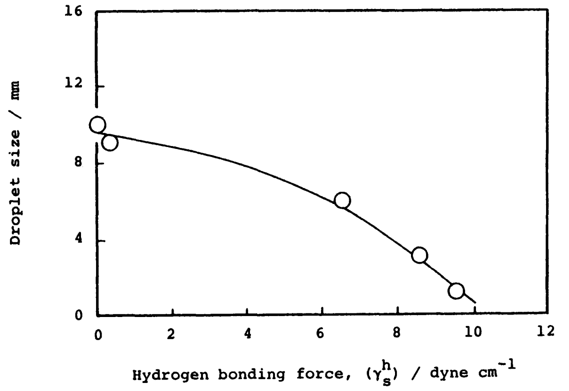


Fig. 6. Correlation between droplet size and hydrogen bonding force.

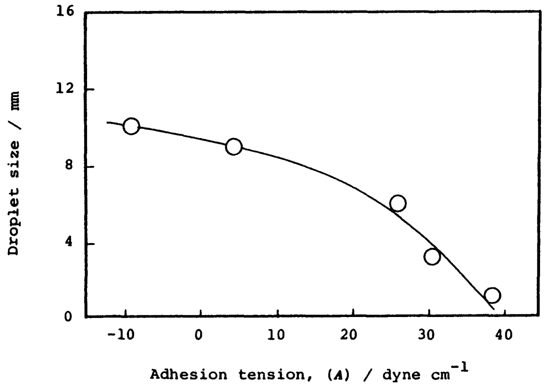


Fig. 7. Effect of adhesion tension on droplet size.

tact angles of two different liquids of the **B** series by using Eq. 5. The results of γ_S^d, γ_S^p, and γ_S^h are summarized in Table 4.

The dispersion force (γ_S^d) of the polymer surfaces, except for CT, are almost the same, while the non-dispersion forces (γ_S^p and γ_S^h) of polymer surfaces are dependent on the kind of polymer. Kitazaki et al.[19] have mentioned that γ_S^h correlates with the wettability of solids by liquids with hydrogen-bonding, like water, glycol, and formamide. The values of γ_S^h at 30 °C are plotted against the size of the oil droplets in Fig. 6. The size of the oil droplets is reduced with an increase in γ_S^h. This may indicate that the droplet size is reduced by using polymer filters, which are easily bonded to water molecules because of hydrogen bonding formation.

Interaction between Water Molecules and Polymer Surfaces. In general, the term "wetting" is taken to mean the phenomenon which occurs when a solid/air interface is replaced by a solid/liquid interface. In practice, we may distinguish three distinct types of wetting (adhesional, immersional, spreading) which are involved when a dry solid is placed into a liquid so that it is completely immersed within the liquid. Immersional wetting is the phenomenon whereby a unit area of surface is completely immersed in the liquid. In this phenomenon, a specific area of the solid/air interface is converted to a solid/liquid interface. The work involved, ***A***, per unit area of the surface is given by:

$$A = \gamma_S - \gamma_{SL} = -\Delta G \qquad (6)$$

From Eqs. 4 and 6, we obtain:

$$A = 2(\gamma_S^d \gamma_L^d)^{1/2} + 2(\gamma_S^p \gamma_L^p)^{1/2} + 2(\gamma_S^h + \gamma_L^h)^{1/2} - \gamma_L \qquad (7)$$

The relationship between the adhesion tension and the size of the oil droplets obtained is shown in Fig. 7. The size of the oil droplets becomes smaller with an increase in the adhesion tension. As can be seen from Eq. 6, the adhesion tension also means a change in the surface free energy. If the free energy (negative) of a liquid/polymer interface is large, in other words, the interface is thermodynamically stable. This is reasonable if the wetting of the liquid is carried out spontaneously. Since a water/hydrophilic polymer such as a water/cotton interface is thermodynamically stabilized, a decrease in the droplet size results from the prevention of oil spreading. That is, the droplet size is dependent on the interaction between water molecules and polymer surfaces.

Formation Process of Oil Droplets. The above suggestion is illustrated by the schematic model of the formation process of oil droplets shown in Fig. 8. Figures 8(A) and (B) exhibit typical examples of a hydrophilic-surface polymer (PVA) and of a hydrophobic-surface polymer (PE). In the case of Fig. 8(B), as the γ_S^h of polymer surface and adhesion tension of polymer-water are small, the interaction between the water molecules and the polymer surface is weak (no water/polymer interface is stabilized); the oil which comes out from a hole is spread out over the surface of

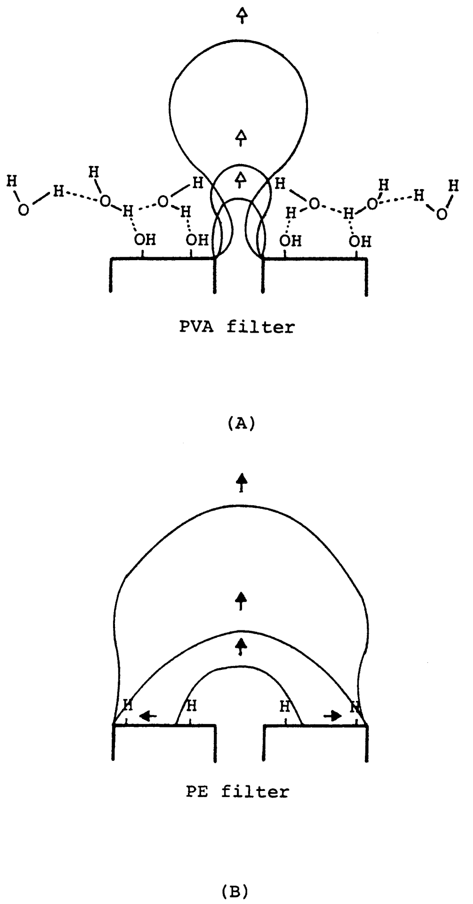


Fig. 8. Schematic model for formation process of oil droplets. (A) hydrophilic polymer (PVA, CP, CT), (B) hydrophobic polymer (PE, PVC).

the polymer filter (the arrow →), and then the droplet grows along the outer edge of the filter. Necking occurs over the surface of the polymer filters and results in the increase in the size of the oil droplets. In the case of Fig. 8(A), on the other hand, the interaction between the water molecules and the polymers is stronger because of hydrogen bonding (the water/polymer interface is stabilized by the large reduction in the surface free energy). As a result, water molecules are adsorbed strongly on the polymer surfaces. Therefore, the oil droplets which come out from a hole do not spread out over the surface of the polymer filter by the adsorption of water molecules (a droplet grows toward the arrow ⇾); as a result, the necking which occurs in the vicinity of a hole brings about the decrease in the size of the oil droplets.

Conclusion

We conclude that the size of an oil droplet formed through a hole is dependent on the chemical property (wettability) of the polymer-filter surface. A cotton filter is most suitable for the formation of small-sized oil droplets. This may be attributed to the fact that the interaction between the continuous phase (water) and the hydrophilic polymer-filter surface, which has a large hydrogen-bonding force (γ_s^h), becomes strong; in other words, the adhesion tension between water molecules as a continuous phase and the polymer-filter surface becomes large.

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