

Studies on Synthetic Polymer Plates with High Surface Energy. I. Diallyl Phthalate-Unsaturated Carboxylic Acid System

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Synopsis

A new preparation technique of the polymer plate with high water wettability and sufficient mar resistance was proposed. The gel plate resulting from the prepolymerization of diallyl compound (M_1), diallyl phthalate (DAP), in a casting cell was immersed in an aqueous solution of unsaturated carboxylic acid (M_2), acrylic acid (AA), and methacrylic acid (MAA), at a specific temperature for a specific time. M_2 was copolymerized with the remaining M_1 in the region near the surface of the gel plate, and polymer plates with the following characteristics were obtained: for DAP-AA system, θ_i (contact angle of the alkali-treated plate) = 10.5° and mar resistance (for the alkali-treated plate at a dry state) = 70 g; for DAP-MAA system, θ_i = 8.3° , and mar resistance = 65 g.

INTRODUCTION

Most of the synthetic polymers for general purpose have nonpolar and hydrophobic characteristic on their surface. The following modifications have been carried out in order to alter physicochemical surface properties, such as wettability,¹ antifogging,² biocompatibility,³ dyefastness,⁴ and adhesion⁵: chemical reactions with hydrophilic reagents in liquid phase,⁶ oxidation by air, oxygen, or ozone,⁵ photoreactions with reactive gases,⁷ and photoinduced graft copolymerization.⁸⁻¹⁰

In this paper, a new preparation technique of the polymer plate with both high water wettability and sufficient mar resistance was reported.

EXPERIMENTAL

Materials

Diallyl phthalate (DAP), acrylic acid (AA), and methacrylic acid (MAA) were purified by distillation, boiling point $115^\circ\text{C}/0.4$ Torr for DAP, $43^\circ\text{C}/14$ Torr for AA, and $51^\circ\text{C}/6$ Torr for MAA. Benzoyl peroxide (BPO) was purified by recrystallization with chloroform and methanol. Methylene blue trihydrate purchased from Wako Pure Chemical Industries Ltd. was used without further purification.

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Preparation of Synthetic Polymer Plates

A casting cell was assembled with two glass plates and silicone tube (as a flexible gasket). DAP (M_1 monomer) containing 3 wt % of BPO was filled in a casting cell, then was heated at T_1 °C for t_1 min to obtain a prepolymer gel plate (PGP, with a size of $15 \times 50 \times 1.5$ mm). The PGP was fractionated into the following three parts by means of solvent extraction: methanol-soluble part, monomer remaining; methanol-insoluble and acetone-soluble part, oligomer and linear polymer; acetone-insoluble part, network polymer.

The resulting PGP taken apart from the casting cell was immersed in a glass tube containing 15 g of an aqueous C wt % M_2 solution at T_2 °C for t_2 hr. The resulting plate was designated as an original gel plate (OGP).

The value of weight increment (ΔW) as a measure of quantity of M_2 copolymerized with M_1 substrate was defined as

$$\Delta W = [(W/W_0) - 1] \times 100\%$$

where W_0 is the weight of the PGP and W is the weight of the resulting gel plate.

Measurement of Contact Angles

The equilibrium contact angles (θ) of distilled water drops on the gel plate (GP) were measured with an Erma Model G-I Contact Angle Meter at 20°C and 65% relative humidity. The specimens were treated as follows: (i) The GP was immersed in aqueous 0.1N NaOH solution for 2 hr in order to convert carboxylic group existing on the surface into ionizing form and washed with water and *n*-hexane, and followed by drying under reduced pressure (the contact angle measured is designated as θ_i); (ii) the above specimen was further immersed in aqueous 0.1N HCl solution for 2 hr to convert ionizing form into free form and followed by the same washing and drying process as in (i) (the contact angle measured is designated as θ_f).

Attenuated Total Reflection Infrared Absorption Spectra

Attenuated total reflection (ATR) infrared absorption spectra of the GP surfaces (with a size of $20 \times 50 \times 1.5$ mm) were examined with a Hitachi Model 225 Infrared Spectrophotometer. The absorption peak at 1715 cm^{-1} due to ester group of DAP monomer unit overlapped with the peak at 1720 cm^{-1} due to carboxylic group of AA or MAA monomer unit, therefore confirmation of carboxylic groups on the GP surface is quite difficult. On the other hand, carboxylic ion could be distinguished from ester band due to the absorption peak of the former (1580 cm^{-1} for acrylic ion and 1550 cm^{-1} for methacrylic ion unit). Hence, by examining the ATR absorption spectra of the alkali-treated GP, the existence of carboxylic groups on the GP surface could be confirmed easily. It was also estimated from the theoretical calculation that the penetrating depth of an incident light to the GP in the region of the examined wave numbers was about $1.6 \mu\text{m}$, using the refractive indices of both the GP ($n = 1.56$ for DAP homopolymer) and the KRS-5 prism ($n = 2.37$), and the incident angle of 45° .¹¹

Measurement of the Thickness of the Copolymer Layers

A slice of the GP with about 100 to 200 μm thickness was prepared by cutting and grinding perpendicular to the GP surface. After alkali treatment the above slice was immersed in 0.01 mole/liter aqueous solution of methylene blue for 48 hr, and followed by washing with water and by drying under reduced pressure. The DAP homopolymer plate (HP, without immersion process of M_2 solution) was not entirely stained with methylene blue, but the surface layers of the GP were stained with it. The thickness of the stained layer measured from the micrograph of the slice was taken as that of the copolymer layer.

Observation of the GP Surfaces with Scanning Electron Microscope

The GP surfaces were observed by means of the scanning electron microscope (a JEOL Field Emission Scanning Electron Microscope Model JFSH-30) at a voltage of 30 kV. Pretreatment of a sample was carried out by the following method: the sample (thinned by grinding) cemented on a metal block was coated with Au-Pt by means of the ion sputter coater (a JEOL FINE COAT LFC-1100) for 4 min.

Antifogging Tests of the GP

Antifogging property was estimated by the following observation: fogging or no fogging after breathing at the sample at 20°C and 65% relative humidity (method A); fogging or dewing on the inner surface of the GP placed on an equipment as shown in Figure 1 (method B).²

Measurement of the Mar Resistance of the GP

The mar resistance of the GP was estimated by the scratching hardness test using a TYPE-HEIDON-14 Surface Tester at 25°C and 70% humidity. The values of the mar resistance were expressed as the vertical load against the sapphire needle point.

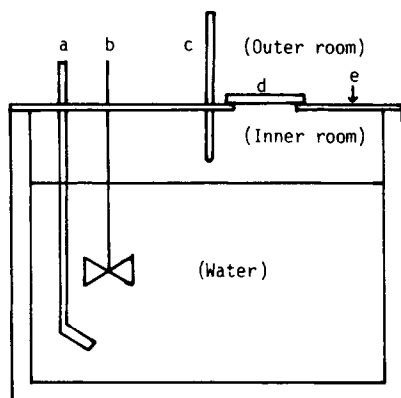


Fig. 1. Equipment for antifogging test (method B): condition; water 50°C, inner room 47.5°C, outer room 24.5°C: (a) heater and regulator; (b) stirrer; (c) thermometer; (d) sample; (e) lid.

RESULTS AND DISCUSSION

Confirmation of M_2 Monomer Unit Copolymerizing with DAP in the GP Surface

Most of the water-soluble component in the OGP surface was removed by the first alkali treatment. In order to remove the water-soluble part completely the cycle of alkali and acid treatment was repeated several times until the decrease in the weight of the GP was not recognized.

ATR absorption spectrum for the above GP after alkali treatment was of the peak at 1580 cm^{-1} for AA and 1550 cm^{-1} for MAA due to carboxylate ion, which disappeared by acid treatment. The proceeding alkali treatment brought again the same peak, from which the existence of M_2 monomer unit in the surface layer of the GP was confirmed.

It was also revealed by the micrograph of the stained slice of the GP (shown in Fig. 2) that M_2 diffused into the PGP and copolymerized with the remaining DAP monomer, and that the interior of the GP was DAP homopolymer.

Further, the surface structure of the GP was clarified from the observation by means of the scanning electron microscope. The surface structures of the HP and the GP for DAP-AA and DAP-MAA systems appeared to be almost flat from the observations under low magnification ($10,000\times$). On the other hand, as shown in Figure 3, the observations under higher magnification ($100,000\times$) revealed that the surface of the HP (a) was almost flat, but that of the GP for both DAP-AA (b) and DAP-MAA (c) systems exhibited orange-peel surfaces covered all over with the grains of about $0.01\text{ }\mu\text{m}$ size. These grains are presumably due to the aggregation of M_2 monomer unit existing in the GP surface.

Preparation Mechanism of the OGP

The preparation mechanism of the OGP is interpreted as follows: When a PGP is immersed in an aqueous solution of M_2 , M_2 diffuses into the PGP depending upon the partition coefficient (α) of M_2 between DAP monomer and water and upon diffusion constant (D) of M_2 into the PGP, and the diffusion of DAP monomer out of the PGP occurs simultaneously. M_2 in the PGP copolymerizes with allylic group in the PGP depending upon the monomer reactivity ratio of M_2 with DAP, and M_2 monomer unit is fixed in the GP. It should be noted that

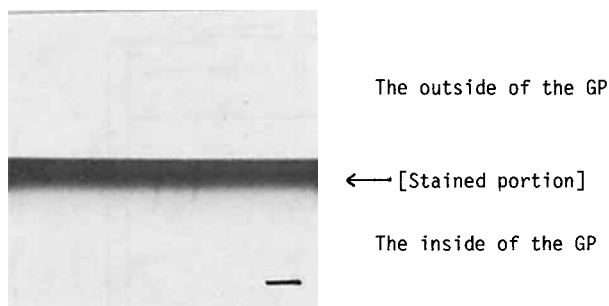
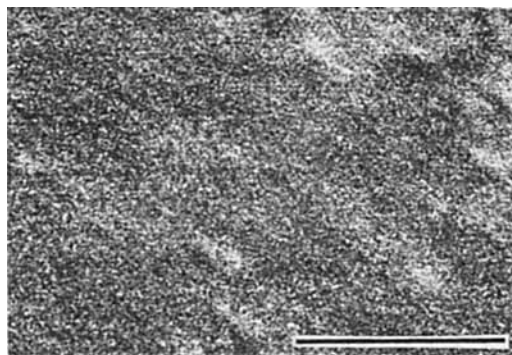
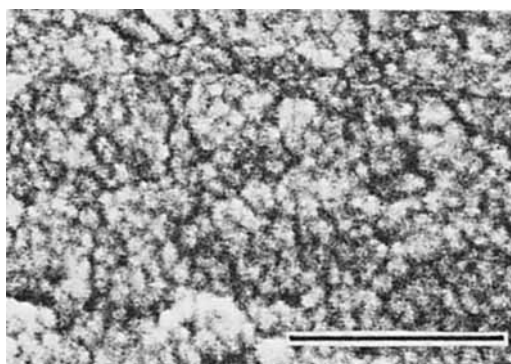


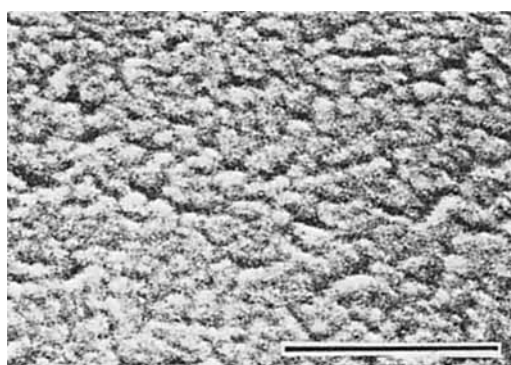
Fig. 2. Micrograph of the methylene-blue-stained slice of the gel place for DAP-MAA system prepared under the condition of $T_1 = T_2 = 90^\circ\text{C}$, $t_1 = 120\text{ min}$, $t_2 = 6\text{ h}$, and $C = 2\text{ wt } \%$. The bar represents $100\text{ }\mu\text{m}$.



(a)



(b)



(c)

Fig. 3. Scanning electron micrographs of the surface structure of the gel plates under the condition of $100,000\times$ magnifications: (a) DAP homopolymer plate; (b) DAP-AA plate prepared under the condition of $T_1 = T_2 = 90^\circ\text{C}$, $t_1 = 100$ min, $t_2 = 6$ h, and $C = 5$ wt %; (c) DAP-MAA plate prepared under the condition of $T_1 = T_2 = 90^\circ\text{C}$, $t_1 = 120$ min, $t_2 = 6$ h, and $C = 2$ wt %. The bar represents $0.1\ \mu\text{m}$.

TABLE I
Physical Properties of AA and MAA Monomer

Monomers	Molecular weight	Solubility parameter (cal/cm ³) ^{1/2}	Partition coefficient ^a	Reactivity ratios ^b	
				r_1	r_2
AA	72	12.0	0.52	0.044	19.06
MAA	86	11.2	2.57	0.021	44.05

^a $\alpha = [M_2]_{\text{DAP}}/[M_2]_{\text{water}}$ at room temperature.

^b M_1 monomer, DAP; M_2 monomer, AA or MAA.

the diffusion of M_2 into the PGP and the copolymerization of M_2 with allylic group in the PGP occur simultaneously. AA and MAA were used as M_2 in this paper. The observed values of α and the monomer reactivity ratios (calculated from Q and e values) of DAP- M_2 are shown in Table I along with a few other data. Because of the low reactivity of allylic group of DAP monomer, it can be presumed that M_2 -rich random copolymer by the continuous addition of M_2 is obtained, especially on the plate surface.

Properties of the HP

The HP were prepared by a similar process of the OGP except that the immersion solution was a total amount of 15 g of distilled water. The solubility of DAP monomer in water at ambient temperature is less than 0.01 g/100 g water,¹² but a significant amount of DAP monomer will dissolve in water at 90°C (immersion temperature T_1). As shown in Figure 4, the weight of the HP was reduced due to the above solubility of DAP monomer, but the reduction decreased with an increase in reaction time (t_1) due to the composition change in the PGP shown in Figure 5. Such the negative value of ΔW should correspond to the amount of DAP monomer diffusing out of the PGP. It should be noted that the amount (W_{in}) of M_2 diffusing into the PGP of 1 g in the preparation of the OGP is the sum of the observed ΔW and the amount (W_{out}) of DAP monomer diffusing out of the PGP of 1 g.

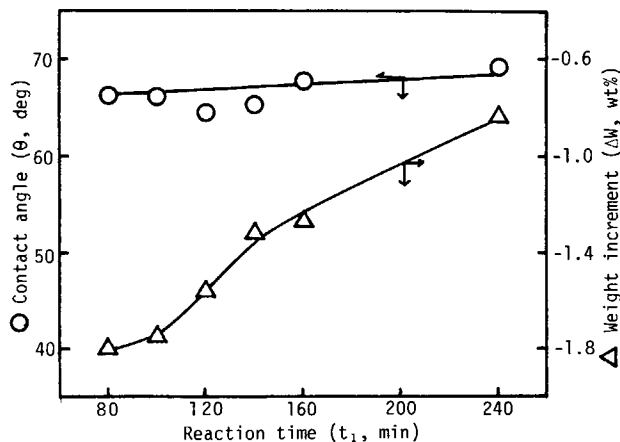


Fig. 4. Effects of reaction time (t_1) on contact angle (θ , \circ) and weight increment (ΔW , Δ) for DAP homopolymer plate prepared under the condition of $T_1 = T_2 = 90^\circ\text{C}$ and $t_2 = 6$ h.

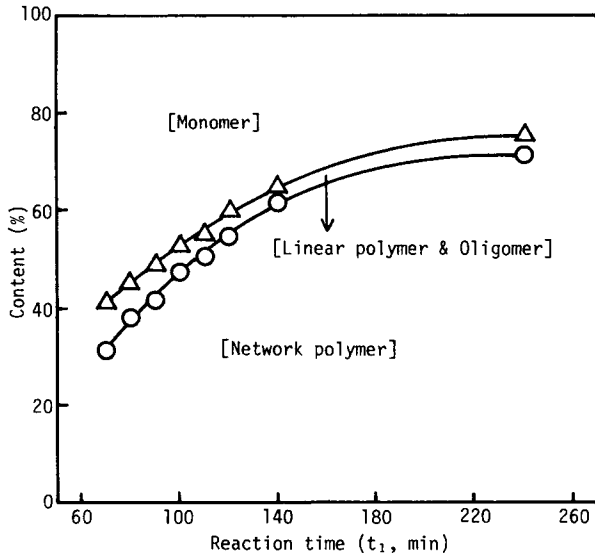


Fig. 5. Change of composition of DAP prepolymer gel plate with reaction time (t_1) at 90°C.

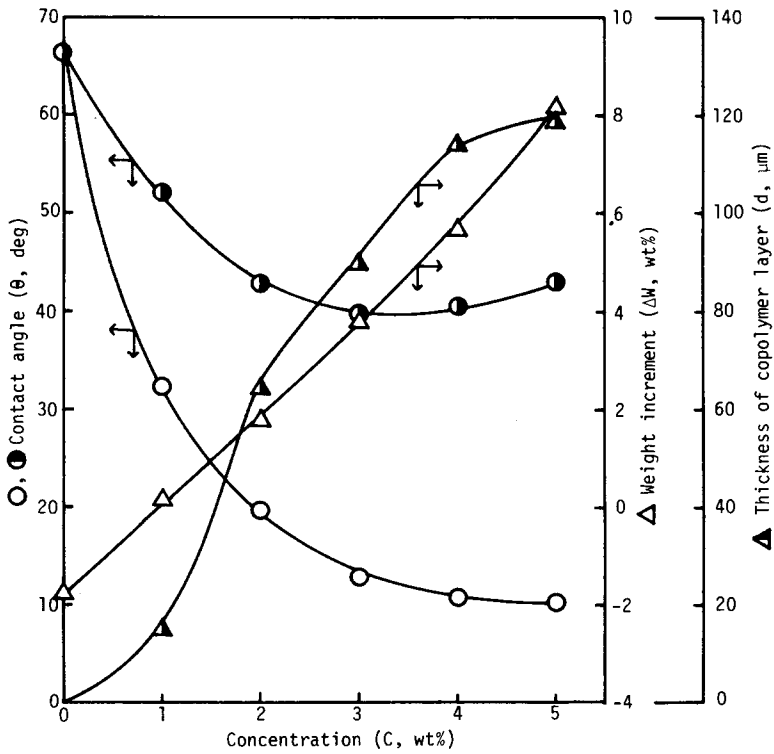


Fig. 6. Effects of concentration (C) of immersion solution on contact angle after alkali treatment (θ_i , O) and after acid treatment (θ_f , ●), weight increment (ΔW , Δ), and thickness of copolymer layer (d , ▲) for DAP-AA plates prepared under the condition of $T_1 = T_2 = 90^\circ\text{C}$, $t_1 = 100$ min, and $T_2 = 6$ h.

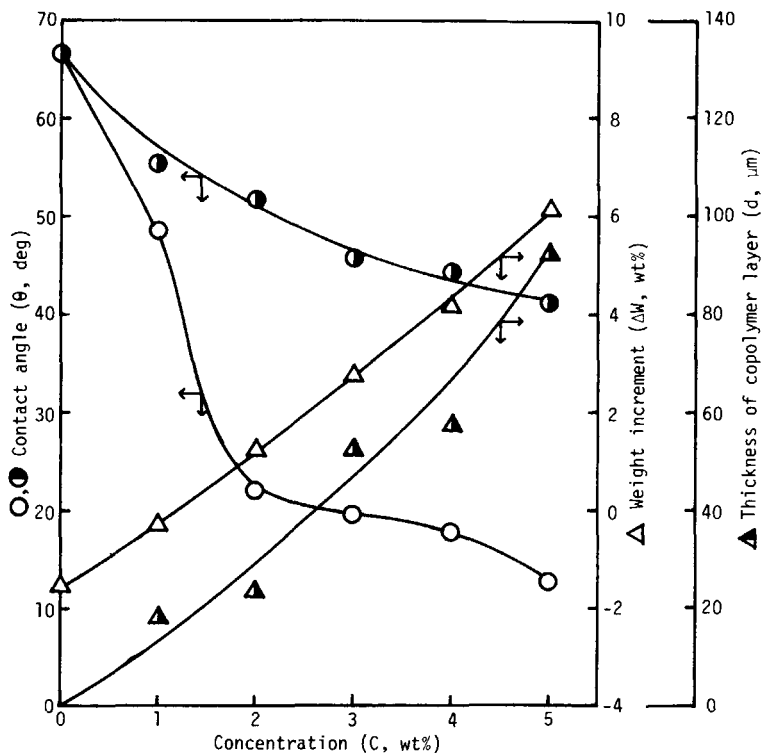


Fig. 7. Effects of concentration (C) of immersion solution on contact angle after alkali treatment (θ_i , O) and after acid treatment (θ_f , ●), weight increment (ΔW , Δ), and thickness of copolymer layer (d , \blacktriangle) for DAP-AA plates prepared under the condition of $T_1 = T_2 = 90^\circ\text{C}$, $t_1 = 120$ min, and $t_2 = 6$ h.

As shown in Figure 4, θ of the HP remained almost constant in the range of t_1 examined, and the mean value was 66.5° .

As shown in Table II, the HP had poor antifogging property, and the mar resistances of those were 20 to 25 g at a dry state, and 25 to 30 g at a wet state.

The plates in this system were transparent, but had a light yellow-green color, because of the absorption in the range from the ultraviolet region to about 450 nm (using air as a reference).

Properties of DAP-AA Plates

Effects of C on θ , ΔW , and the thickness of the copolymer layer (d) under the condition of $t_1 = 100$ min are shown in Figure 6, where the results for $C > 5$ wt % were omitted because there occurred a gelation in the immersion solution. ΔW varies from negative value to positive value due to an increase in W_{in} with an increase in C . θ_f decreased with an increase in C up to 3 wt %, afterwards increased slightly and on the whole much higher than θ_i . θ for water is influenced by the surface density and the orientation of carboxylic group locating in the GP surface and flatness of the GP surface. The above mode of variation in θ_f will be explained by the following terms: the low degree of dissociation of carboxylic group, the association of carboxylic group, and the uneven surface of the GP

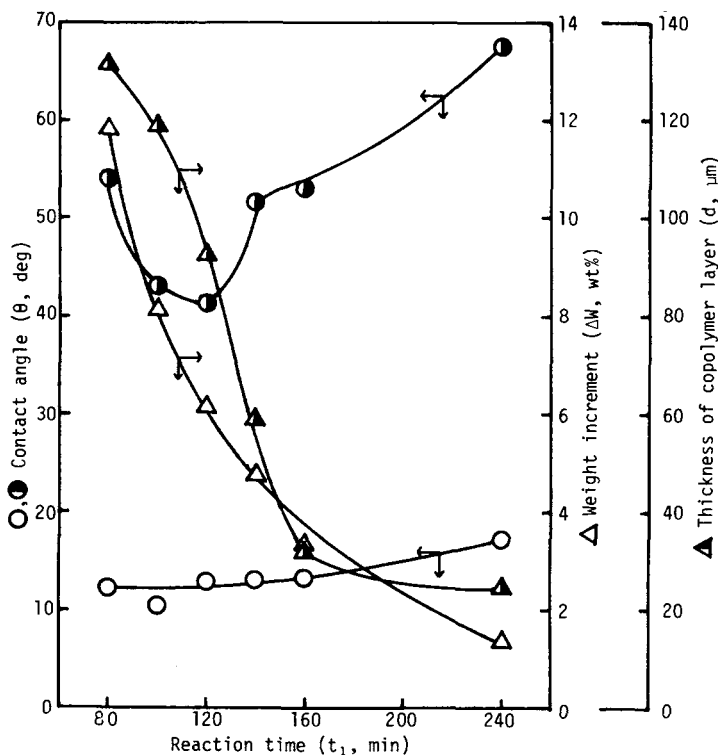


Fig. 8. Effects of reaction time (t_1) on contact angle after alkali treatment (θ_i , O) and after acid treatment (θ_f , ●), weight increment (ΔW , Δ), and thickness of copolymer layer (d , \blacktriangle) for DAP-AA plates prepared under the condition of $T_1 = T_2 = 90^\circ\text{C}$, $t_2 = 6$ h, and $C = 5$ wt %.

(observed by means of the scanning electron microscope) presumably due to a mutual aggregation of M_2 monomer unit chains on the GP surface. It is clear that θ_i decreased with an increase in C due to an increase in ΔW and was lower than θ_f due to the high degree of dissociation of carboxylic salt. The result for d indicates that AA penetrated up to $120\ \mu\text{m}$ depth at $C = 5$ wt % due to the appreciable high value of α for AA (for example, α for acrylamide is 0.09).

The results for $t_1 = 120$ min are shown in Figure 7. The trends of θ_i , ΔW , and d vs. C were similar to those in Figure 6. On the other hand, the variation of θ_f with C was slightly different from that in Figure 6, which is presumably due to difference in the amount of DAP monomer remaining in the PGP.

Effects of t_1 on θ , ΔW , and d under the condition of $C = 5$ wt % are shown in Figure 8. As can be seen from the change of θ_i , the surface density of carboxylic groups decrease with an increase in t_1 . θ_f , however, decreased in the range of $t_1 < 120$ min. It seems to be due to the change in surface flatness. ΔW and d decreased with an increase in t_1 due to reduction in the remaining DAP monomer in the PGP.

Taking account of the ease of handling the PGP, the optimum conditions for preparing the GP with high surface energy were as follows: $T_1 = T_2 = 90^\circ\text{C}$, $t_1 = 100$ or 120 min, $t_2 = 6$ h and $C = 5$ wt %. Here θ was reduced up to 10.5° from 65° for the HP. As listed in Table II, the alkali-treated GP had good antifogging property (a transparent dewing state), but the acid-treated GP had poor anti-

TABLE II
Properties of the DAP Homopolymer Plates and the Gel Plates for DAP-AA and DAP-MAA Systems

Systems	T ₁ (°C)	t ₁ (min)	T ₂ (°C)	t ₂ (h)	C (wt %)	ΔW (wt %)	θ _i (deg)	θ _f (deg)	d (μm)	Antifogging test				Mar resistance			Water content ^f (wt %)
										Method A I ^b	Method A II ^a	Method B I	Method B II	I (g)	II (g)	III ^e (g)	
HP	90	100	90	6	0	-1.75		(66.5) ^a		...	poor	...	poor	...	20	25	0.25
HP	90	120	90	6	0	-1.56				...	poor	...	poor	...	25	30	...
DAP-AA	90	100	90	6	2	1.80	19.9	43.0	64.7	poor	poor	Td	poor	0.50
DAP-AA	90	120	90	6	2	1.20	22.2	51.7	23.6	poor	poor	Td	poor	0.43
DAP-AA	90	100	90	6	5	8.13	10.5	43.0	119.1	Td ^c	poor	Td	poor	...	70	65	1.08
DAP-AA	90	120	90	6	5	6.13	12.8	41.2	92.6	Td	poor	Td	poor	...	80	70	0.87
DAP-MAA	90	100	90	6	2	9.36	13.1	58.7	137.5	Td	poor	Td	poor	...	65	55	1.33
DAP-MAA	90	120	90	6	2	7.13	8.3	61.5	101.7	Td	poor	Td	poor	...	65	50	1.18

^a Mean values for several HP.

^b Alkali-treated GP.

^c Transparent dewing state.

^d Acid-treated GP.

^e GP at a wet state.

^f Water content = $[(W_w/W) - 1] \times 100\%$, where W_w is the weight of the GP at a wet state.

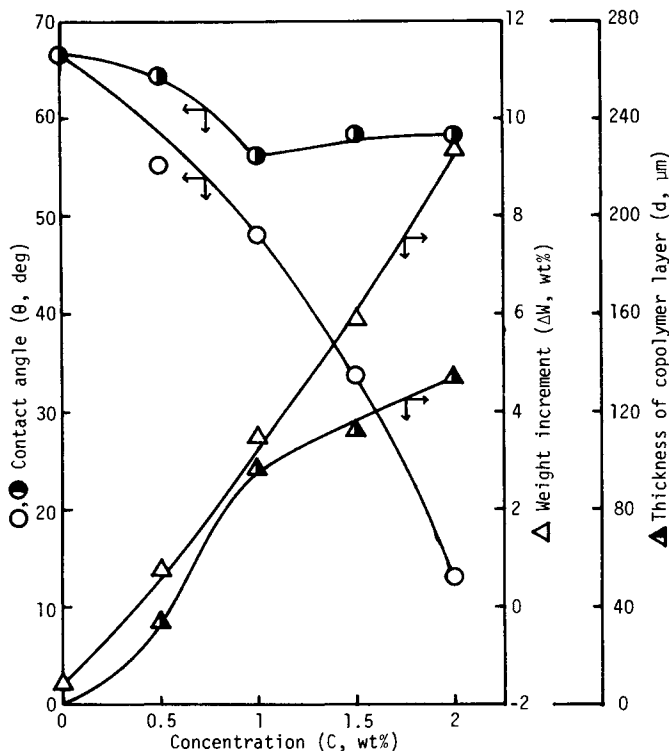


Fig. 9. Effects of concentration (C) of immersion solution on contact angle after alkali treatment (θ_i , \circ) and after acid treatment (θ_f , \bullet), weight increment (ΔW , Δ), and thickness of copolymer layer (d , \blacktriangle) for DAP-MAA plates prepared under the condition of $T_1 = T_2 = 90^\circ\text{C}$, $t_1 = 100$ min, and $t_2 = 6$ h.

fogging property due to the low degree of dissociation and the aggregation of carboxylic groups. The mar resistance of the GP at a dry state was two to three times larger than that of the HP due to introduction of AA monomer unit into the GP surface, whereas that of the GP at a wet state decreased by a half due to absorbing a large amount of water (listed in Table II as a water content).

Properties of DAP-MAA Plates

As shown in Figure 9, 10, and 11, the trends for DAP-MAA system are found to be similar to DAP-AA system. The results for $C > 2$ wt % were omitted because there occurred a gelation in the immersion solution. The optimum condition for preparing the GP with high surface energy was as follows: $T_1 = T_2 = 90^\circ\text{C}$, $t_1 = 120$ min, $t_2 = 6$ hr, and $C = 2$ wt %. As listed in Table II, θ could reduce less than 10° , and MAA penetrated up to $100\ \mu\text{m}$ depth. The alkali-treated GP had good antifogging property. The mar resistance at a dry state was two to three times larger than that of the HP, whereas that at a wet state decreased by a half.

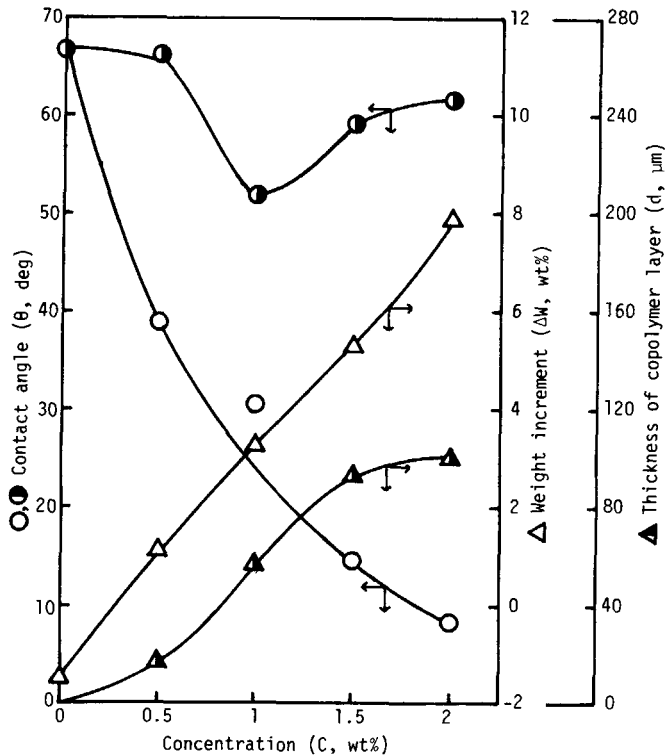


Fig. 10. Effects of concentration (C) of immersion solution on contact angle after alkali treatment (θ_i , O) and after acid treatment (θ_f , ●), weight increment (ΔW , Δ), and thickness of copolymer layer (d , \blacktriangle) for DAP-MAA plates prepared under the condition of $T_1 = T_2 = 90^\circ\text{C}$, $t_1 = 120$ min, and $t_2 = 6$ h.

Comparison between AA and MAA Using as M_2 Monomer

AA and MAA have miscibility with both water and DAP monomer. However, their partition coefficients between water and DAP monomer (listed in Table I) indicate that MAA is more hydrophobic than AA due to the existence of methyl group in α position. In addition, it is expected from the reactivity ratios for DAP- M_2 that concerning composition of DAP- M_2 copolymer at a fixed feed ratio, MAA content is always higher than AA content. From these factors fixation of MAA is predicted to be more easy than that of AA. In fact, a comparison of θ_i values of the respective system under the same conditions ($T_1 = T_2 = 90^\circ\text{C}$, $t_1 = 100$ and 120 min, $t_2 = 6$ h and $C = 2$ wt %) indicates pronouncedly that affinity of MAA with DAP is much higher than that of AA.

Utility of the New Technique for Preparing Synthetic Polymer Plate with High Surface Energy

The alkali-treated GP with both high water wettability and sufficient mar resistance at a dry state could be prepared by the procedure described here. However, θ of alkali-treated surface increased by acid treatment due to converting carboxylic salt into free form. Further, the mar resistance of the GP at a wet state reduced to a quarter of that at a dry state, but seems to remain in the level enough for practical use.

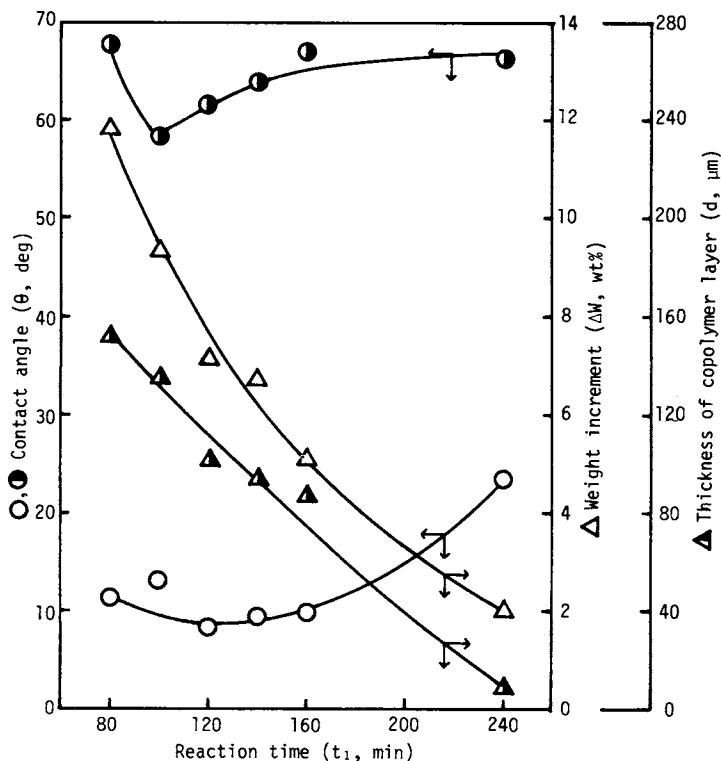


Fig. 11. Effects of reaction time (t_1) on contact angle after alkali treatment (θ_i , O) and after acid treatment (θ_f , ●), weight increment (ΔW , Δ), and thickness of copolymer layer (d , \blacktriangle) for DAP-MAA plates prepared under the condition of $T_1 = T_2 = 90^\circ\text{C}$, $t_2 = 6$ h, and $C = 2$ wt %.

In addition, there are the following advantages in the procedure; the facility in the preparation performance, the simplicity in the apparatus, the use of water as the medium, and achievement of the surface modification without variation of the characteristic of the substrate polymer.

CONCLUSION

Synthetic polymer plates with high surface energy could be prepared by the following procedure: the GP resulting from the prepolymerization of DAP in a casting cell at T_1 °C for t_1 min was immersed in an aqueous solution of AA or MAA at T_2 °C for t_2 hr.

(i) The existence of M_2 monomer unit in the surface layer of the GP could be confirmed from ATR absorption spectra for the GP completely removed the water-soluble component and from the observation of the methylene-blue-stained slices of the GP.

(ii) The observation by the scanning electron microscope indicated that the surface of the HP was almost flat under 100,000 \times magnifications, but that the surface of the GP for both DAP-AA and DAP-MAA systems was covered all over with the grains of 0.01 μm size presumably due to the aggregation of M_2 monomer unit chains.

(iii) The alkali-treated GP for both DAP-AA and DAP-MAA systems had

both water wettability and sufficient mar resistance at a dry state. However, θ of the alkali-treated GP increased by acid treatment, and the mar resistance of the GP at a wet state reduced to $1/3$ - $1/4$ of that at a dry state.

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