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Analysis of glass fabric impregnation using a resin drop method †

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Abstract

Wettability of a glass fabric was studied by use of a resin drop method. The mixing ratios of epoxy resin and anhydride hardener were adopted as 1:0.5, 1:1 and 1:1.2. A catalyst of 2-ethyl-4-methylimidazole added as much as 0.1wt% of the mixed resin. A curing analysis by differential scanning calorimeter (DSC) showed that the mixed resin could be infiltrative at room temperature. An effective contact angle and the height of the resin drop onto the glass fabric preset on a flat glass plate were measured as a function of time. The wet area of the resin drop was also measured. Behaviors of the contact angle, the drop height, the net wet area and the coefficient of wettability were analyzed in the glass fabric impregnation. The resin drop method was shown to be quite effective in evaluating the capillary-mode resin penetration into the fabric.

Keywords: Epoxy resin drop; Glass fabric; Contact angle; Wettability; Impregnation

1. Introduction

Fiber or fabric impregnation is an essential process usually used in the manufacturing of fiber reinforced composites. The space between the fibers is filled by molten polymers or liquid metals. Interfacial behaviors at the fiber/liquid/air interface play a key role in the infiltration process. The interplay between the surface tension of the infiltrating liquid, the wettability of the fibers by the surrounding liquid and the morphological details of the preform fabric directly affects the integrity of the manufactured composites [1-5]. Saunder et al. [6] investigated the compressor behaviors of fabric reinforcement and voidage structures during the polymer composite processing according to the fabric type, compressor speed, viscosity and wettability. Under the inadequate interplay conditions, voids can be formed in the composite microstructure, which causes a decrease in the modulus, the strength and the fatigue resistance [7-11]. In particular, void formation in the flexible transparent composite display films often used in the display industry can be detrimental to the display quality.

Saihi et al. [12] estimated the surface free energies of PET fibers grafted with different percent grafting by using the dynamic contact angle measurement and thus determined the surface fiber wettability by probe liquids. Lee et al. [13] studied wettability of the paper surface by using the dual measurement of contact angles at the two left and right tips of a resin drop to compensate for the roughness of the paper surface. Employing the dynamic contact angle measurement with a liquid drop, Simoncic and Rozman [14] investigated influences of surfactant structure on the wettability of woven cotton fabric and on the penetration rate of the resin into the cotton fabric and thus evaluated cotton surface properties. However, those measurements of contact angle using a liquid drop are conducted on the premise of a liquid drop resting at equilibrium on a flat surface of solid. Thus, for fabric having quite rough waviness and small space between fibers for resin infiltration, the conventional contact angle tests could not measure behaviors of the exact contact angle [15].

In this paper, an advanced resin drop method for measuring the wettability of the fabric is proposed. The capillary-mode resin penetration into the fabric is experimentally analyzed. Contact angles and heights of a resin drop measured as a function of time are used in search of the relation to the coefficient of wettability.

2. Materials and methods

2.1 Fabric and resin

The fabric reinforcement was type 1080 glass fabric supplied by Asahi Co. The product was a balanced biaxial, plain weave fabric made with approximately 400 μm wide and 50 μm thick glass fiber rovings (each fiber diameter 5.2 μm). Densities of the warp and the weft were 60 and 47 (g/m^3). The

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Table 1. Properties of the epoxy resin and hardener.

	Equivalent weight (g/eq)	Viscosity (cp at 25℃)	Specific gravity (20℃)
Epoxy (YD-127)	180-190	8,000-11,000	1.17
Hardener (MH-700G)	161-166	50-70	1.17

fiber content in this fabric varied locally from none to approximately 100 μm thickness.

An epoxy resin of diglycidyl ether of bisphenol-A (YD-127, Kookdo Chemical Co.) and a hardener of anhydride (MH-700G, New Japan Chemical Co.) were used for preparing the matrices in this study (see Table 1 for physical properties). The equivalent mixing ratios of the resin and the hardener were adopted as 1:0.5, 1:1, 1:1.2. A catalyst of 2-ethyl-4-methylimidazole was added equivalent to 0.1wt% of the mixed resins.

2.2 Preparation of the plane glass fabric

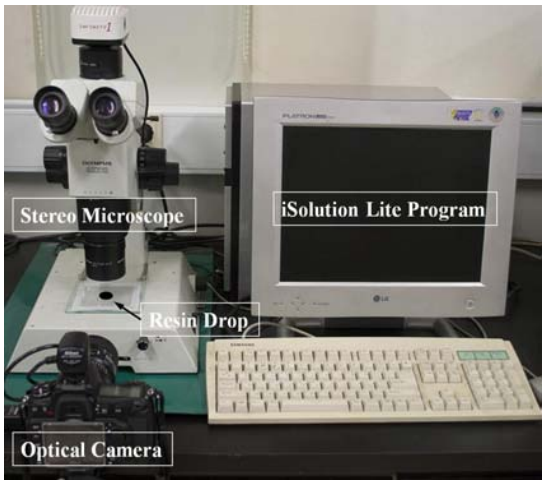
To make a plane of glass fabric, a square fabric was completely spread onto the glass plate. After that, the fabric was fixed onto the glass plate with adhesive tapes (Cat 810D, 3M) at the 4 corners of the fabric.

2.3 Differential scanning calorimetry

Curing characteristics of the mixture resin were studied with a differential scanning calorimeter (DSC 2910, TA Instrument). The test was conducted at a rate of 10°C/min from the room temperature to 250°C.

2.4 Goniometric measurement of a resin drop

As illustrated in Fig. 1, goniometric measurement of a liquid resin drop onto the fabric was conducted using a high resolution optical camera attached with proximity lens (Micro-Nikkor 60 mm f/2.8D, Nikon). When a resin drop was applied to a surface of the fabric using a goniometer micro-pipette drop technique, images of the drop in contact with the fabric surface were taken at specific time intervals. The initial image of the resin drop was taken just after confirming a complete settlement of the drop onto the fabric. The conventional contact angle measurement was based on the tangent line at the tip of the drop profile. The tangent line at the drop tip was highly variable due to the influence of the wavy profile of the fabric surface [16]. Thus, instead of the tangent line we drew a straight line from the tip point A to the point C on the drop profile illustrated in Fig. 2, where the horizontal coordinate of the point C was at 3% of the base diameter (d). An approximate contact angle θ_1 was measured between the straight line AC and the base line, as illustrated by the real image of the drop on the fabric in Fig. 3. The drop size just after dropping onto the fabric was 4.5~6.7 mm. By enlarging the captured image, the drop base diameter (d), the drop height (h), and the



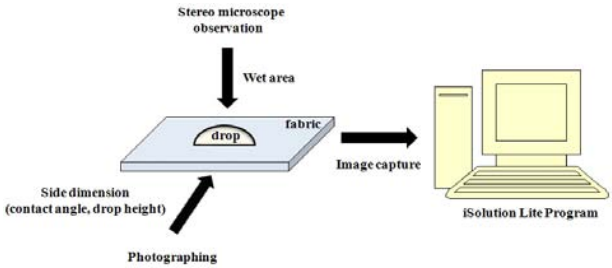


Fig. 1. An optical observation to measure contact angles, drop heights and wet areas of a resin drop on the flat fabric (actual photo and Schematic diagram).

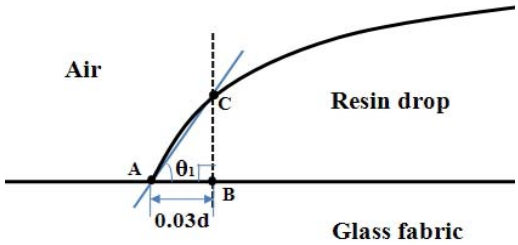


Fig. 2. Measurement of contact angle(θ_1) between the glass fabric and the resin drop.

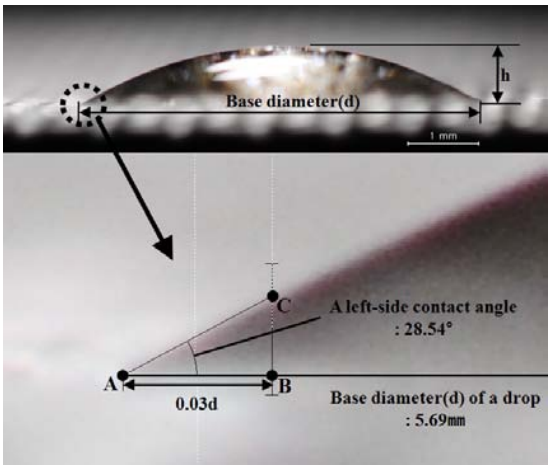


Fig. 3. Actual measurement of the contact angle between the glass fabric and the resin drop.

contact angle (θ_1) were measured through an image analysis program (iSolution Lite [17]). The measurements of the normalized contact angle and the normalized height were performed 5 times for each experimental condition.

2.5 Measurement of wet area on the fabric

The drop and its wet area were also observed by a stereo optical microscope (SZX12, Olympus) in the direction normal to the fabric plane simultaneously with the above side view measurement of the drop (see Fig. 1). Through the image analysis program, the wet area of the drop was calculated for a unit drop weight. The weight for a drop was measured as an average of 10 tested drops using a precision weight tester (GR-200, A&D Co.). The average weight was about 12.12 mg, 11.26 mg and 6.98 mg for the equivalent ratios of 1:0.5, 1:1 and 1:1.2, respectively.

2.6 Measurement of capillary pressure

The wettability of the liquid epoxy resin onto the glass fabric is strongly affected by the environmental pressure and the temperature. The total pressure P_t is expressed to be the sum of the process pressure P_p, the gravity pressure P_g and the capillary pressure P_c as given in the following equation [18].

$$P_t = P_p + P_g + P_c \tag{1}$$

Because this study performs an open wettability test, P_p is negligible. The gravity pressure P_g is ρgh, where ρ is the density of the resin, g is the gravity acceleration, and h is the height of the drop. The capillary pressure can be calculated from the fiber arrangement data in the fabric. Using the Young-Laplace equation [19-21], P_c may be given by the equation

$$P_c = \frac{4\sigma\cos\theta}{D_e} \tag{2}$$

where σ is the surface tension of the resin, θ the contact angle between the resin and the fiber, D_e the equivalent diameter of the vacant space in the fabric. D_e is calculated by the equation

$$\frac{\pi D_e^2}{4}\cdot n = A_0 - \sum_{i=1}^{n}\frac{\pi d_i^2}{4} \tag{3}$$

where A_0 is the cross-sectional area of the fabric, d_i the fiber diameter. The surface tension σ was measured using a contact angle and surface tension tester (Phoenix300, Surface Electro Optics). The contact angle θ was obtained using the E-glass plate similar to the E-glass fiber. All the data was measured through the analysis of the image by the iSolution Lite program.

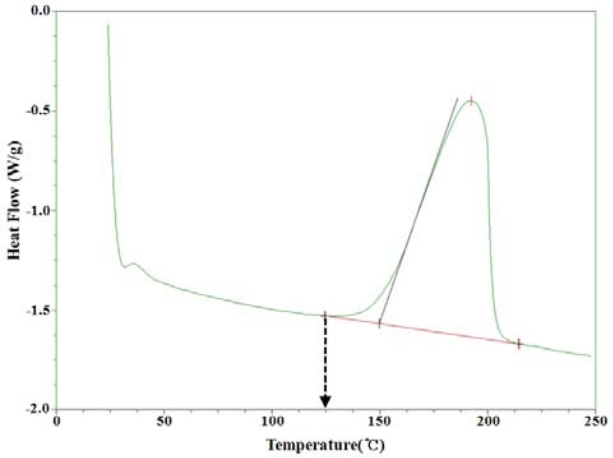


Fig. 4. DSC analysis curve during resin curing at equivalent ratio 1:0.5 of epoxy and hardener.

2.7 Measurement of wettability coefficient

In the actual rheological situation, the infiltration of the liquid resin into the fiber bundles is largely hindered by the viscous phenomena. Accordingly, the wettability coefficient α may be expressed assuming the basic equation

$$\alpha = \frac{P_c}{\mu} \tag{4}$$

where μ is the viscosity of the liquid resin. This equation does not mean the resin transfer speed as a function of time.

3. Results and discussion

3.1 Curing behaviors of the epoxy resin

Fig. 4 shows the heat flow result obtained by the DSC measurement for an equivalent mixing ratio 1:0.5 of the epoxy resin and the hardener. The curing began to arise at approximately 124°C. The beginning temperatures of the curing for the equivalent ratios of 1:1 and 1:1.2 were measured to be 134°C and 145°C, respectively. With an increase in the content of the hardener, the curing happened at a higher temperature. Increasing the equivalent mixing ratio decreased the content of the catalyst for an equivalent weight of the hardener, which led to an increase in the curing temperature. For all the equivalent ratios adopted in this experiment, the curing phenomena hardly arose at room temperature.

3.2 Behaviors of the contact angle and the height of a drop on the fabric

Fig. 5 shows the typical behaviors of the height and the contact angle of a liquid resin drop with an equivalent mixing ratio of 1:1.2 as a function of time just after the contact of the drop onto the glass fabric. As time passed, the drop height

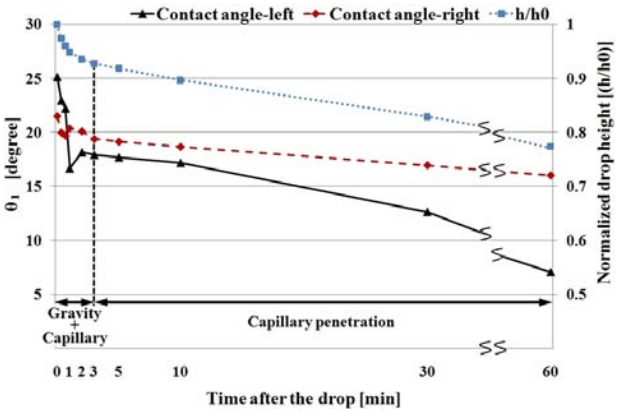


Fig. 5. Measurement data for left/right-side contact angle and normalized drop height with time at equivalent ratio 1:1.2 of epoxy and hardener.

became lower while the contact tip slowly spread outwards from the initial wet domain of the drop. The decreasing speed of the drop height was the highest just after the initial contact time with the fabric, and then slowed down to a constant speed around 3 min and maintained it until the test time of 30 min. The drop height behavior indicates a characteristic behavior of the penetration rate of the liquid resin into the fabric. On the other hand, the contact angles on the left side and the right side also changed from the initial state, and showed large fluctuations with some transient up and down behaviors. Such fluctuations of the contact angle might be caused by the contact tip location following the wavy profile of the fabric surface as well as the resin penetration speed around the contact tip depending on the direction of the warp and the weft of fiber bundles. When the resin penetration is parallel to the fiber bundle, the penetration speed can be high due to the continuously thin space and thus the high capillary pressure formation (see Eq. (2)). In the case perpendicular to the fiber bundle, the resin penetration can be very slow due to the contrary. The fluctuation vanished around 3 min, which corresponded to the start point of the constant speed for the decreasing behavior of the drop height decrease. During the initial fluctuation period of 3 min (1st stage penetration), the resin penetration into the fabric seemed to be affected by both the gravity and the capillary pressure. After that, however, the penetration became stable and kept a constant speed not only in the drop height decrease but also in the contact angle decrease (2nd stage penetration). This penetration might be proceeded along the outward directions mainly by the capillary pressure in the fabric.

Such resin penetration phenomena is described through a schematic drawing of the penetration of a resin drop into the fabric as illustrated in Fig. 6. The decreasing speed of normalized height (h/h_0) in the 2nd stage was the maximum at an equivalent ratio of 1:1.2, and the minimum at 1:0.5. This indicates that the resin penetration was more rapid with increasing content of the hardener.

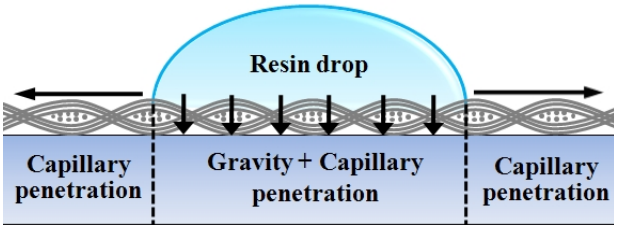


Fig. 6. A schematic penetration of a resin drop into the fabric.

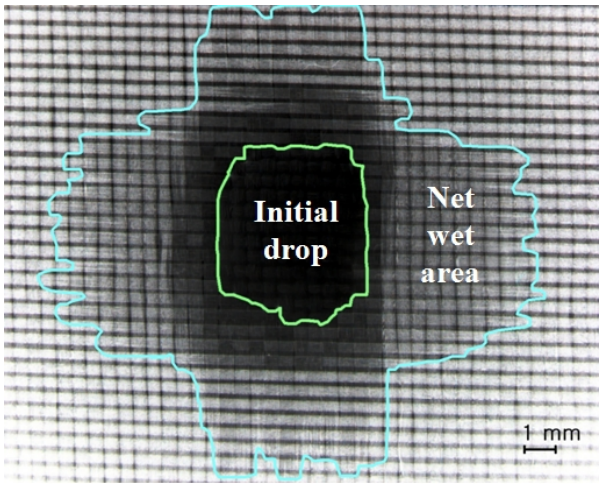


Fig. 7. Resin drop area into the fabric after 10 min.

3.3 Behaviors of the net wet area

Fig. 7 shows photographs of the wet area of the liquid resin drop of a ratio equivalent to 1:1.2 penetrated into the fabric, which was optically observed on the fabric plane just after the contact with the fabric as well as at the test time of 10 min. Through the image analysis program the wet area on the fabric was measured using an intaglio and homogenization filtering technique. The net wet area in the test time was calculated from the difference between the extended wet area and the initial drop area. The net wet area (ΔA_w) for a unit weight at 10 min was approximately 1.99, 4.40 and 6.36 mm^2/mg for equivalent ratios of 1:0.5, 1:1 and 1:1.2, respectively.

3.4 Behaviors of the capillary pressure and viscosity

For the calculation of the capillary pressure P_c by Eq. (2), surface tension σ and contact angle θ of the resin drop were measured as listed in Table 2 for the respective equivalent ratios. The equivalent diameter D_e of the vacant space in the fabric calculated by Eq. (3) was also measured to be approximately 3.42 μm through the image analysis on a scanning electron micrograph of the cross-section of the cured fabric/resin film. Values of the capillary pressure so obtained to be 6.11 ~ 8.44 kPa for the respective ratios are also listed in Table 2. These values were about 770 times as large as that of the gravity pressure of the resin drop (around 9.4 Pa). The capillary pressure for the ratio 1:1.2 was the lowest among the tested ratios and was expected

Table 2. Average value of surface tension, contact angle, capillary pressure, viscosity and wettability coefficient measured as a function of equivalent ratios(1:0.5, 1:1, 1:1.2) of epoxy and the hardener.

	Equivalent ratio 1:0.5	Equivalent ratio 1:1	Equivalent ratio 1:1.2
Surface tension (mN/m)	9.69	7.36	6.61
Contact angle (°)	41.90	38.88	37.76
Capillary pressure (kPa)	8.44	6.70	6.11
Viscosity (cp)	2008	882	750
Wettability coefficient (Pa/cp)	4.20	7.60	8.15

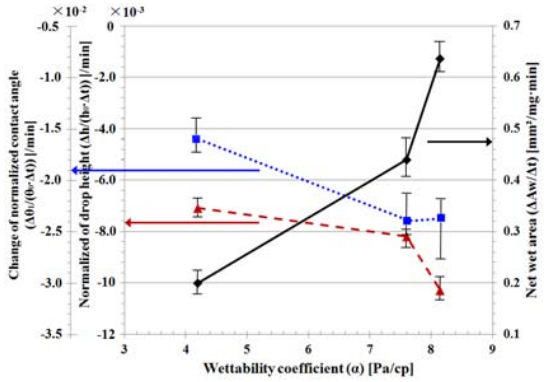


Fig. 8. Net wet area($\Delta A_w/\Delta t$), normalized drop height difference($\Delta h/(h_0 \cdot \Delta t)$) and normalized contact angle difference($\Delta\theta_1/(\theta_0 \cdot \Delta t)$) as a function of wettability coefficient(α).

to slow the resin penetration in the fabric. However, this behavior was contrary to the results of the net wet area. On the other hand, viscosity μ in Table 2 showed also the lowest value at the ratio of 1:1.2, which should assist easy and rather quick penetration of the resin due to a weak resistance against the fluidic infiltration between fibers [22].

3.5 Behaviors of the wettability coefficient

Values of the wettability coefficient α calculated by Eq. (4) considering the effects of P_c and μ are presented in Table 2. α was the highest at the ratio 1:1.2.

Fig. 8 shows the changing behaviors of the normalized contact angle ($\Delta\theta_1/\theta_0$), the normalized height ($\Delta h/h_0$) and the net wet area of the drop as a function of α. The change amount ($\Delta\theta_1$, Δh) was measured from 3 min to 10 min in the 2nd stage penetration period driven by mainly the capillary pressure indicating a constant decreasing speed in the drop height and the contact angle. With an increase of α, ΔA_w increased whereas $\Delta\theta_1/\theta_0$ and $\Delta h/h_0$ decreased significantly. The changing behavior of ΔA_w was very reverse to that of $\Delta\theta_1/\theta_0$ and $\Delta h/h_0$. It is confirmed that the resin of equivalent ratio 1:1.2 showed the best in the wettability and the penetration speed.

4. Conclusions

Wettability analysis of the epoxy resin onto the plain woven glass fabric has been performed. A contact angle measurement method was suggested for the goniometric measurement of the resin drop. The changing behaviors of the drop height and the net wet area as a function of test time were analyzed as well. The results are summarized as follows:

(1) The contact angle in the initial period showed large fluctuations due to the contact tip location following the fabric wavy profile and to the resin penetration speed depending on the warp and the weft direction of fiber bundles. During the initial fluctuation period of 3 min (1st stage penetration), the resin penetration into the fabric seemed to be affected by the gravity and the capillary pressure. After that, the penetration became stable and kept a constant speed (2nd stage penetration), mainly due to the capillary pressure in the fabric. The resin penetration got rapid with increasing the hardener.

(2) The net wet area for a unit weight was the largest at the equivalent ratio 1:1.2, which corresponded to the highest in the decreasing speed of the drop height and the contact angle.

(3) The wettability coefficient considering the capillary pressure and the viscosity increased with the increase of the net wet area and the decrease of the contact angle and the height. The 2nd stage penetration driven by mainly the capillary pressure could be a good indication for the wettability evaluation of a resin drop onto the fabric. The resin of equivalent ratio 1:1.2 showed the best in the wettability and the penetration speed.

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Nomenclature

α	: Wettability coefficient
μ	: Viscosity
θ	: Contact angle (onto the E-glass plate)
θ_0	: Initial contact angle (onto the fabric)
θ_1	: Approximate contact angle (onto the fabric)
$\Delta\theta_1$	: Contact angle difference for a period
ρ	: Density of the resin
σ	: Surface tension
A_0	: Cross-sectional area of the fabric
ΔA_W	: Net wet area
d	: Base diameter
d_i	: Fiber diameter
D_e	: Equivalent diameter of the vacant space (in the fabric)
h	: Resin drop height
h_0	: Initial of resin drop height
Δh	: Drop height difference for a period
P_c	: Capillary pressure

P_g : Gravity pressure
P_p : Process pressure
P_t : Total pressure
Δt : Time difference

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