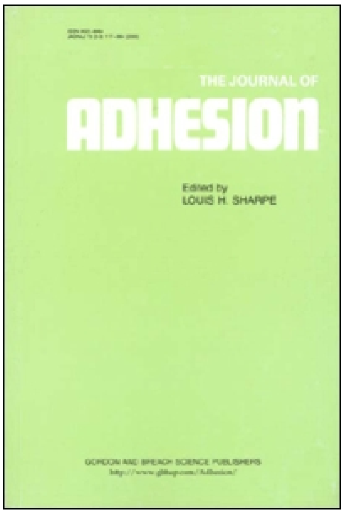

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T. Ogawa[a]; M. Ikeda[a]
[a] Laboratory for Material Design Engineering, Graduate School of Engineering, Kanazawa Institute of Technology, Ishikawa, Japan

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Determination of the Contact Angle of a Liquid Droplet on a Carbon Fiber

T. OGAWA and M. IKEDA

Laboratory for Material Design Engineering, Graduate School of Engineering, Kanazawa Institute of Technology, 7-1, Ohgigaoka Nonoichi, Ishikawa 921, Japan

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This paper describes an improved method for the accurate determination of the contact angle of a liquid droplet on a monofilament. Theoretically, in this improved method, contact angles do not depend on droplet size or the radius of the fiber. The accuracy of this method is thus expected to be higher than any other standard methods.

KEY WORDS contact angle; droplet shape; carbon fiber; ethylene glycol; n-hexadecane; surface free energy; improved method; droplet size.

1. INTRODUCTION

Interlaminar shear strength (ILSS) of fiber-reinforced plastic (FRP) is very important in composites, and is closely related to wetting of the fibers by the matrix polymer. Wettability can be principally estimated by the contact angle of liquid on a fiber. However, in the case of very fine monofilaments such as carbon fibers, it is very difficult to measure accurately the contact angle directly via the usual methods which are adopted from the plane surface method.

A tensiometric method is also known for determining contact angle of liquids on fibers.[1-3] However, a highly sensitive electromicrobalance is required. Moreover, Yamaki and Katayama[4] and Carroll[5] have developed a method in which the contact angle is indirectly determined by measuring the shape of a liquid droplet. Of the two methods, Carroll's is simpler. However, an accuracy better than ±5° can not be obtained using this method. This is due to the fact that an accurate measurement of the radius of monofilament is required. Large errors are introduced into calculated contact angles because it is usually difficult to measure the radius of fibers accurately. Another reason for error is that the measured contact angles vary depending upon the surface roughness of the fiber. Therefore, a new or improved method is required for accurate measurement of contact angles. Incidentally, a real droplet is deformed by the effect of gravity and by the roughness of the monofilament surface upon which it is placed. The former effect can be minimized by making a droplet as small as possible. However, the latter one always exists in fibers having a rough surface, such as carbon fiber. It should also be pointed out that it is not suitable to measure the contact angle at the point where the liquid contacts the monofilament surface. This method would lead to uncertain results, because the angle at this point is very ambiguous due to the effect of surface roughness. This phenomenon will be illustrated later in our study with experimental results.

In this study, we utilized Carroll's method and Wagner's interpolation technique.[6] The contact angles thus obtained were scattered because of the variation of the measured radii. Therefore, we undertook to improve Carroll's method for determining the contact angle of a liquid droplet on a carbon fiber. This paper describes in detail the improved method as well as the problems associated with the usual methods.

2. MATERIALS

PAN-based carbon fibres, High-carbollon 12000 produced by Asahi Chemical Co. Ltd. (Tokyo, Japan), were used in this study. These fibers had received no treatment. The surface of the carbon fiber was then oxidized by heating it for various periods of time at 350°C in an electric furnace. Ethylene glycol and n-hexadecane were used for determining the contact angle and surface energy of the carbon fibers. Other solvents or mixed solvents were not appropriate because either the droplets evaporated quickly or the solvents changed their composition during the measurement. Surface free energies of ethylene glycol and n-hexadecane are shown in Table I.[3]

3. DIRECT METHOD OF MEASURING CONTACT ANGLE

Photographs of liquid droplets were taken under an optical microscope. These measurements were done at 25°C. Contact angles were directly read from the photographs with a protractor.

4. CALCULATION OF CONTACT ANGLE

When the effect of gravity is negligible and a monofilament is regarded as a cylinder, the shape of a liquid droplet attached to a monofilament is symmetrical with respect to the X-axis, as shown in Figure 1. The condition for equilibrium of the droplet surface is that the Laplace excess pressure, ΔP, across the droplet surface is constant everywhere, *i.e.*,

$$\Delta P = P_L - P_V = \gamma_{LV} (R_1^{-1} + R_2^{-1}) = \text{constant} \tag{1}$$

where γ_{LV} is the surface tension between liquid and gas, and R_1 and R_2 are normal curvatures of the surface whose curves on the surface are perpendicular to each other. Based on this idea, Carroll[5] derived an equation for the shape of the droplet.

TABLE I
Surface free energies of liquids at 25°C[3]

Liquids	γ_{LV}* (mJ/m^2)	γ^D† (mJ/m^2)	γ^P‡ (mJ/m^2)
Ethylene glycol	47.5	31.6	15.9
n-Hexadecane	27.0	27.0	0

*total surface free energy
†dispersive component of surface free energy
‡polar component of surface free energy

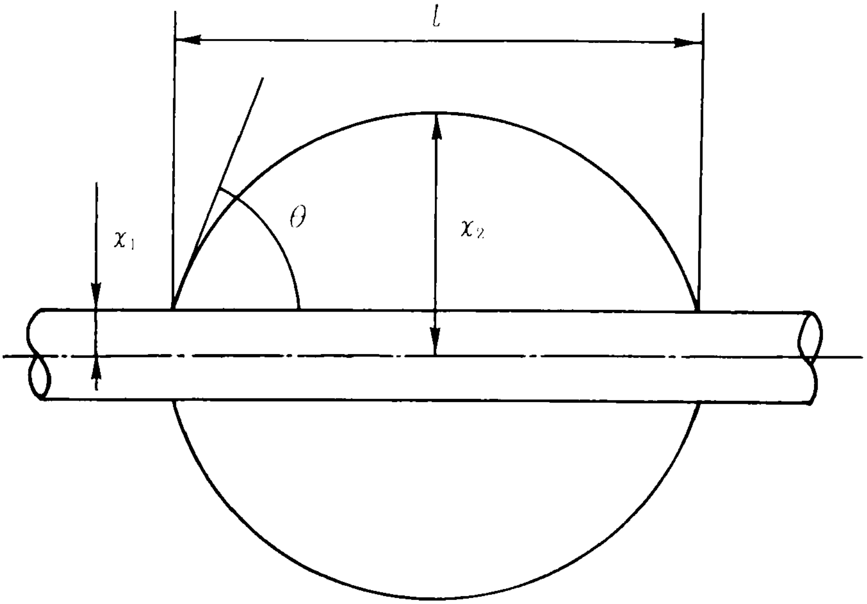

FIGURE 1 Geometry of a liquid droplet attached to a monofilament.

The shape can be defined by the following equation:

$$L = 2[\alpha F(\phi, \kappa) + nE(\phi, \kappa)] \qquad (2)$$

Where L is the ratio of the length of the droplet, *l*, to the radius of a monofilament, χ_1, *i.e.*, reduced droplet length, and n is the ratio of the radius of the droplet, χ_2, to that of the monofilament, χ_1, *i.e.*, reduced maximum radius of droplet as shown in Figure 1, and α is given by the following equation as a function of n and contact angle θ.

$$\alpha = (n \cos \theta - 1)/(n - \cos \theta) \qquad (3)$$

F (ϕ, κ) and E (ϕ, κ) are Legendre's incomplete elliptic integrals of the first and second kinds, respectively, and ϕ and κ are given by

$$\phi=\sin^{-1}[(1/\kappa^2)(1-1/n^2)]^{1/2} \tag{4}$$
$$\kappa=[1-(\alpha^2/n^2)]^{1/2}$$

It is desirable to obtain an expression for θ as a function of l and χ_2 by inverting Eq. 2, but this cannot be done due to the dependence of F, E, ϕ and κ on θ. Carroll presented the plot of L against n for values of θ ranging from 0° to 60° in intervals of 5°. However, contact angles of more than 60° can not be obtained from that plot. Furthermore, if L and n are larger than 18 and 8, respectively, the contact angle can not be obtained. Of course, we can obtain a similar plot for values of θ over 60° using the above equations. However, most investigators have difficulty using Carroll's method in practice. We prepared a plot of L against n for values of θ ranging from 0° to 85°. The range of L and n was also extended. As an example, Figure 2 shows the plot of L against n for values of θ ranging from 0° to 85°. A contact angle can be obtained using this plot. However, an error of about 5° is always present. This error is too large to discuss the surface conditions of treated fibers. Wanger[6] presented an interpolation technique for obtaining accurate contact

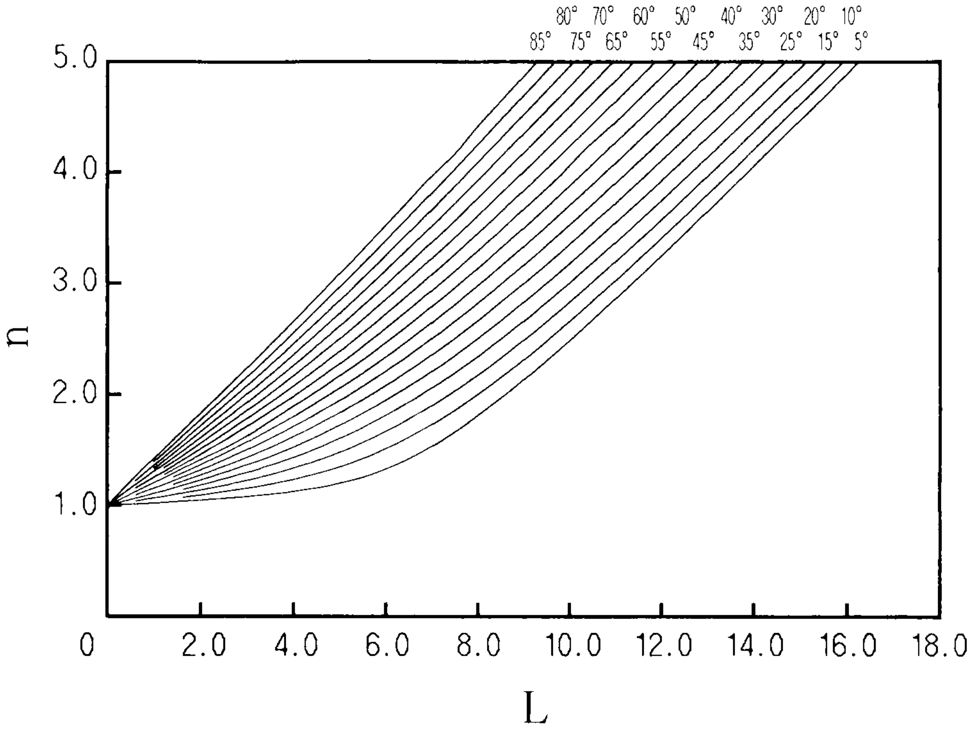

FIGURE 2 Reduced droplet length, L, as a function of n for values of θ up to 85°.

angle, θ, based on Carroll's method. In this case, the accurate contact angle is calculated from one measured value by an interpolation technique after an estimation of two θ values has been made using Carroll's plot. It is difficult to measure accurately the diameter, χ_2, of the carbon fiber, yet Carroll's method requires this. Obviously, the inaccuracy of χ_2 leads to a large error in the final contact angle. To avoid this problem, we propose the following algorithm based on Eq. 2 for calculating the contact angle.

(1) The values of ℓ and χ_1 are measured from a microphotograph of a droplet. The reduced droplet length, L, and reduced maximum radius of the droplet, n, are obtained from the observed ℓ and χ_1, using an appropriate radius, χ_2, of the fiber, for example $\chi_2 = 3.0$ μm, for which the measured value is not required.
(2) The range of θ for L and n is read from Figure 2. For example, if L and n are 10 and 4, respectively, it is seen from Figure 2 that the contact angle lies between 45° and 50°. Thus, the values 45° and 50° are assigned to θ_1 and θ_2, respectively.
(3) Reduced droplet length, L_M, is calculated using Eq. 2 for $\theta_M = (\theta_1 + \theta_2)/2$.
(4) L_M is then compared with the experimental value L. If the absolute value $|\epsilon| = |L - L_M|$ is smaller than a predetermined threshold value, then the value of θ_M is adopted as the contact angle.
(5) If $|\epsilon|$ is larger than a predetermined threshold value, the following process is conducted; the processes (3)–(5) are repeated until the difference reaches within $|\epsilon|$, where for $\epsilon<0$, the value of θ_1 is replaced by the value of θ_M, and for $\epsilon>0$, the value of θ_2 is replaced by the value of θ_M.

5. RESULTS AND DISCUSSION

The shape of a liquid droplet attached to a monofilament is generally different from Figure 1. Namely, the droplet surface changes steeply near the point where the liquid contacts the monofilament, as shown in Figure 3. In practice, two contact angles, θ_a and θ_b, can be measured. However, both values are very ambiguous, as shown in Figure 4. Therefore, the direct measurement of contact angle is very difficult and unreliable. Moreover, the length of a small droplet will become larger than its true length due to the effect of surface roughness. Thus, the calculated value of contact angle will become smaller than the true value. In the case of a large droplet, the effect due to the region of $(l_a - l_b)$ on the droplet length is small, although the calculated value of the contact angle will be smaller than its true value.

At any rate, l_b was adopted for calculation of L. For instance, Figure 5 shows the relationship between L and the contact angle, which was obtained for the ethylene glycol/carbon fiber system. The relationship seems to be influenced by gravity in the case of the larger droplets. Therefore, the range of L can be recommended experimentally to be 10–30, *i.e.* 30~90 μm in ℓ. Figure 6 shows the comparison between a theoretical curve and our experimental values. The curve was obtained using Eq. 2 under the condition of $\theta = 41.78°$ which is the average obtained by using processes (1) to (5) for the droplets shown in Figure 6. It is found that the

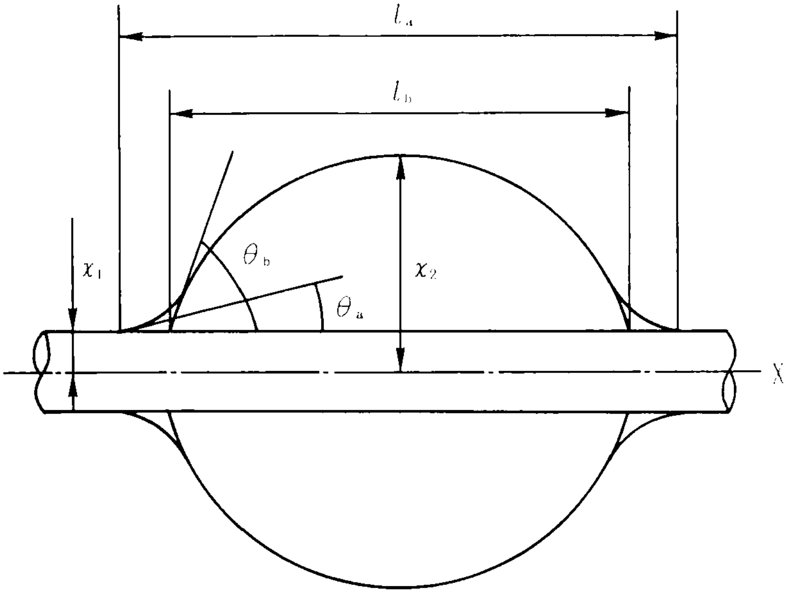

FIGURE 3 A real liquid droplet attached to a monofilament.

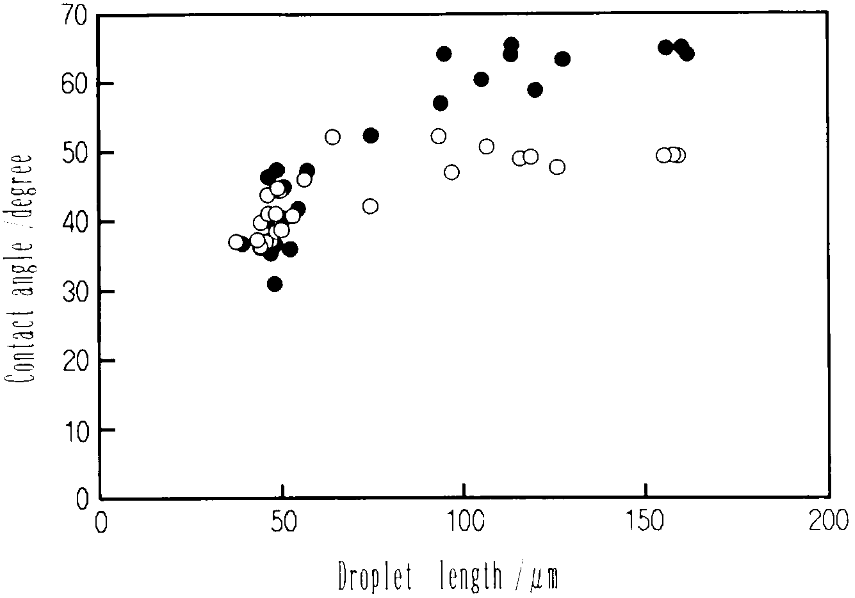

FIGURE 4 A plot of contact angle, θ, against droplet length by direct measurement for ethylene glycol/carbon fiber: ○ θ_a, ● θ_b.

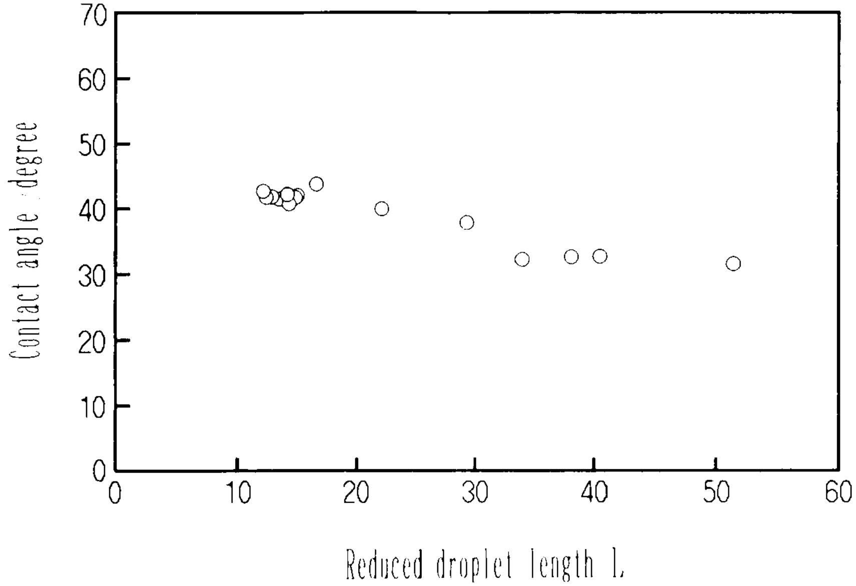

FIGURE 5 A plot of contact angle, θ, against reduced droplet length, L, of a droplet by the improved method for ethylene glycol/carbon fiber.

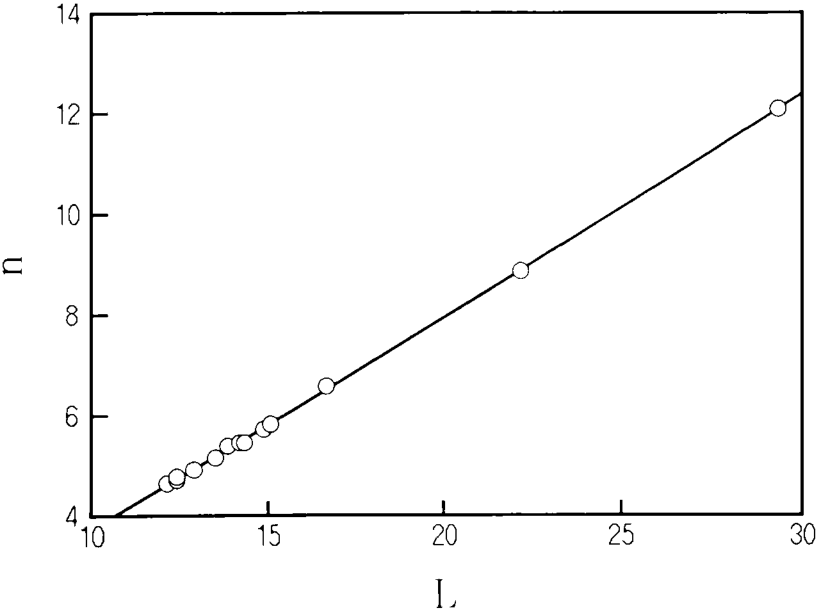

FIGURE 6 Comparison between theoretical and experimental values of L and n for ethylene glycol/carbon fiber: —theoretical curve for θ = 41.78, ○ experimental value.

experimental values agree well with the theoretical curve over a wide range of ℓ and χ_1.

We applied the new method for measuring the contact angle of organic liquids on carbon fiber. For example, Table II shows the contact angle of droplets of ethylene glycol on carbon fiber. The result reveals that the values calculated by this new method are more accurate than the values arrived at by other methods. Figure 7 shows the relationship between the surface treatment time and the contact angle, which was calculated by this method.

TABLE II
Contact angles for droplets of ethylene glycol on carbon fiber

Reduced droplet length L	Reduced radius of droplet n	Contact angle θ (degree)* A	B	C
15.07	5.83	47.38	40–45	41.98
13.84	5.39	46.38	45–50	43.94
13.50	5.15	36.63	40–45	41.48
12.89	4.91	40.13	40–45	41.48
14.87	5.73	45.50	40–45	41.64
12.41	4.71	35.38	40–45	41.72
12.14	4.64	36.19	40–45	42.66
14.32	5.46	40.75	40–45	40.70

*

A: directly measured; the values correspond to open circles in Fig. 4.

B: determined from L and n according to Carroll's method (Fig. 2). In this case, constant radius of fiber was assumed. If we follow simply Carroll's procedure, very large error will be introduced into the contact angle.

C: determined with the interpolation by the new method, where $|\epsilon| = 0.005$. The effect of surface roughness was omitted.

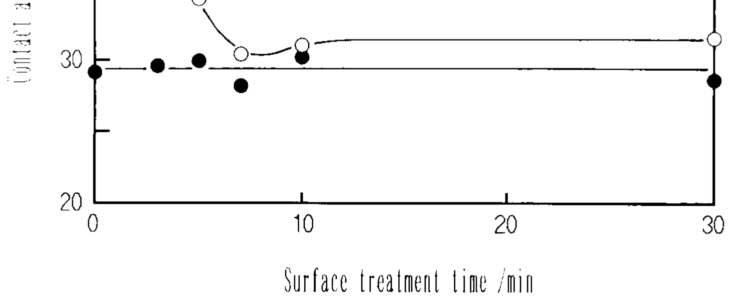

FIGURE 7 Dependence of contact angle on surface treatment time at 350°C: ○ Ethylene glycol, ● n-Hexadecane.

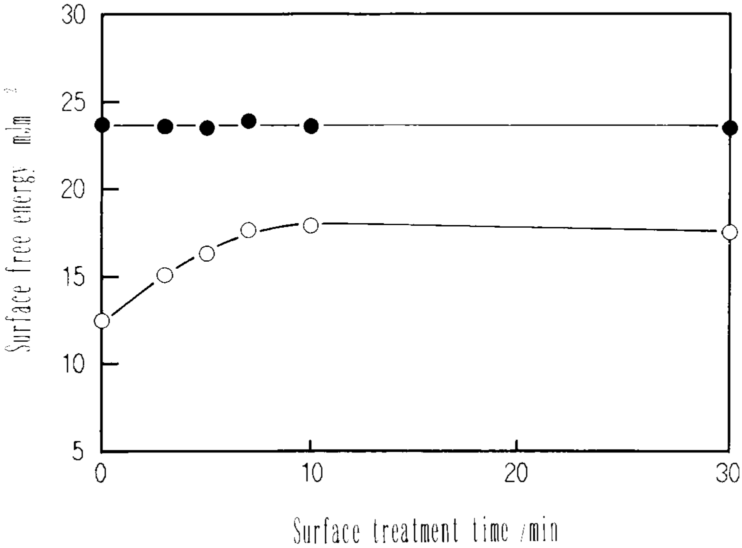

FIGURE 8 Dependence of surface free energy on surface treatment time at 350°C: ○ polar component, ● dispersive component.

Surface free energies of carbon fibers can be calculated by the contact angles of ethylene glycol and n-hexadecane, whose polar and dispersive components of their total surface energy are known. The contact angle, θ, is given as a function of surface tensions of solid and liquid as shown in Eq. 7,[4] where subscripts *S* and *L* mean solid and liquid, respectively, and superscripts *P* and *D* mean polar and dispersive components of surface energy.

$$\cos\theta = 2/\gamma_{LV}\,[(\gamma_S^D\,\gamma_L^D)^{1/2} + (\gamma_S^P\,\gamma_L^P)^{1/2}] - 1 \qquad (7)$$

Therefore, surface free energy of the carbon fiber was calculated from the contact angles for ethylene glycol and n-hexadecane. Figure 8 shows the relationship between surface treatment time and the surface free energy of the carbon fiber. The polar component of surface free energy increases with surface treatment time, and reaches a constant value around the treatment time of 5 min at 350°C. Thus, the accurate behavior of surface energy with surface treatment can be obtained by adopting the improved method.

6. CONCLUSIONS

We proposed an improved method for using Carroll's plot to obtain contact angle by plotting the reduced length of a droplet against the reduced radius of a droplet, using an appropriate radius of fiber. This method is not influenced by the radius of the fiber. Contact angles independent of the droplet size and the roughness of fibers can be obtained for systems such as ethylene glycol/carbon fibers.

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