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Measurement of interfacial tension by a deformed drop retraction method

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Abstract

This paper describes a technique, which enable one to overcome several difficulties encountered in a conventional deformed drop retraction method. The technique consists of forming deformed drops by the disintegration of a polymer thread and measuring the shape evolution of the drop. It is found that the technique enables one to overcome the difficulties encountered in the conventional deformed drop retraction method. By the optical microscope observation, it was confirmed that the disintegrated drop maintains the axisymmetrical ellipsoidal shape during the retraction process and was parallel to the observation plane. The interfacial tension obtained by the technique was found to be lower than the data from the breaking thread method. This variation was discussed in terms of the interfacial contact time.

Keywords: Deformed drop retraction method; Polyamide-6; Poly(styrene-*co*-acrylonitrile)

1. Introduction

The final properties of polymer blend depend critically on the morphology of the immiscible polymer blends that develop during blending and processing [1–3]. The final size and shape of the dispersed phase in a polymer blend depend on the properties of the blend components as well as processing conditions [4,5]. Several parameters influence the final morphology of polymer blends such as viscosity ratio, composition, processing method, and type of flow. In addition to the above, the role of interfacial properties is critical. The basic parameter, which characterizes the interface, is the interfacial tension. Until now, many attempts have been made to develop accurate and convenient techniques to measure the interfacial tension for polymers [6].

Earlier attempts were to adopt the conventional methods such as a pendant drop [7–9], sessile drop [10], and spinning drop methods [11,12], which are known to be proper for non-polymeric materials. In these methods, the interfacial tension is obtained by measuring the shape of the liquid–liquid interface when interfacial force is equilibrated by external forces like the gravitational force and the centrifugal force. They all require the accurate measurement of the density difference between two liquids. In many cases, the density difference between two polymers is very small, which limits the accurate measurement of the interfacial tension. Additionally, due to the high viscosity of polymeric materials, the equilibrium time is quite long, which gives a risk of the thermal degradation.

Dynamic methods can overcome those limitations. In these methods, the interfacial tension is obtained by observing the shape evolution of the interface. Main approaches in these methods are breaking thread method [13–16], imbedded fiber retraction method [17–19] and deformed drop retraction method [20]. The breaking thread method is based on the Tomotika's equation [21] that describes the capillary instability and disintegration of a long liquid cylinder surrounded by another fluid. In order to have a good experimental result, this method requires a perfect symmetrical and sinusoidal distortion of the interface. Additionally, this method requires that experimental dimensionless wave number and theoretical dimensionless wave number should be close. Both requirements are not easy to be attained in a practical experiment [14]. Imbedded fiber retraction method was first developed by Carriere et al. [17]. They modeled a short fiber as a cylinder capped with two hemispheres and expressed a governing equation from a macroscopic force balance between viscous dissipation and decrease in free energy of the interface. This method could overcomes two limitations encountered in the breaking thread method, but it requires empirical parameters of the mathematical model estimated by best fitting to experimental data for a system of known interfacial tension. Imbedded fiber retraction method often encounters a difficulty to

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remove the residual stress formed during a preparation of the short fibers, especially for the system that has a long relaxation time. In all dynamic methods, the driving force to the equilibrium shape is assumed to be a pure interfacial force. Therefore, the residual stress in the fiber causes an experimental error and generally gives higher value [6].

Recently, Luciani et al. [20] introduced a new technique which can overcome the limitations described above. They measured the interfacial tension by observing the shape evolution of a drop initially deformed by external shear force. From a general equation derived by Rallison [22], they derived the following theoretical equation describing the shape evolution of deformed drop at the cessation of the flow.

$$D = D_0 \exp\left\{-\frac{40(p+1)}{(2p+3)(19p+16)}\frac{\sigma}{\eta_m R_0}t\right\}, \quad (1)$$

Where D is the drop deformability parameter defined as $D = (L - B)/(L + B)$, L and B are the major and minor axis of the ellipsoidal drop respectively. D_0 is an initial deformability parameter, σ is interfacial tension, μ_m is viscosity of the matrix phase, R_0 is a radius of the drop at an equilibrium, p is viscosity ratio, and t is time. This equation is valid only for a small deformation of the drop of which shape is the axisymmetrical ellipsoid ($B = W$, W is the other minor axis.). Luciani et al. applied the shear stress to deform a drop. In this case, the B and W of a drop in viscoelastic fluid are generally not same due to the normal stress [23]. Though W and B approach same values before the drop becomes an equilibrium spherical shape, one cannot avoid large errors because of the relative error in determining the L and B of almost spherical drop. Additionally, the major axis of the ellipsoid has a non-zero angle with the observation plane, and consequently L cannot be measured directly. They measured B and calculated L, assuming axisymmetry of the ellipsoid and volume conservation ($L = 8R_0^3/B^2$). In this report, a experimental technique is introduced to overcome these two difficulties. Basically, the method shown in this study is based on the deformed drop retraction method, but the experimental technique in this study makes it possible to deform the drop axisymmetrically ($B = W$) and to orient the drop parallel to the observation plane so that L can be directly measured.

2. Experimental

2.1. Materials

The characteristics of the materials used are listed in Table 1. Polyamide-6 (PA-6) is a commercial product (trade name: Kolon KN171, Mn = 30,000). Three poly(styrene-*co*-acrylonitrile)s (SAN) having different AN content were used in this study. They were supplied by Cheil Industries.

2.2. Rheological measurement

The zero-shear viscosity is critical to get a correct interfacial tension in the dynamic method. They were obtained measuring the shear viscosity at different shear rate (10^{-2}–$5\ s^{-1}$) in the steady mode. All polymers used in this study show a newtonian regime at the shear rate 10^{-2}–$10^{-1}\ s^{-1}$. The rheometer used was a Rheometric Dynamic Spectroscopy, RMS-800. Parallel plate configuration (diameter = 25 mm) was used with a gap of about 1.5 mm. The temperature for measurement was 230°C.

2.3. Measurement of interfacial tension

Films of SAN of 1 mm thickness were pressed between two metal plates on a Carver laboratory press at 180°C. The PA-6 fibers were obtained by drawing on a capillary rheometer at 230°C. The fibers were cut with 20 mm length and annealed at 80°C for about 24 h. The interfacial tension between PA-6 and SAN at 230°C was measured by the deformed drop retraction method as well as the breaking thread method. A mettler hot-stage model FP82 HT connected to a FP 90 central processor and to an Olimphus transmission optical microscope was used. The breaking thread method consists of inserting a thread of PA-6 between two films of SAN. This sample is enclosed between two glass slides and then placed in the hot stage under the microscope. At first, the temperature of the hot stage was elevated and maintained at 200°C for 10 min in order to ensure the perfect imbedding without undesired deformation of PA-6 fiber ($T_m = 216$°C). The temperate was then increased to 230°C. To perform measurements, digital images from the microscope were captured periodically by a computer equipped with a Coreco Oculus image analysis system. After the thread was disintegrated into drops, the

Table 1
The characteristics of the materials used and interfacial tension obtained in this study

Materials	η_0 (Pa/s)	AN content (wt%)	σ[a] (mN/m)	Standard deviation[a] (mN/m)	σ[b] (mN/m)	Standard deviation[b] (mN/m)
SAN-24	450	24	3.40	0.15	4.38	0.40
SAN-32	2390	32.5	3.21	0.06	4.42	0.14
SAN-41	3150	41	3.32	0.21	4.55	0.13
PA-6	740	–	–	–	–	–

[a] Measured by the drop restraction method.
[b] Measured by the breaking thread method.

disintegrated drops were observed to follow a typical retraction process. Just after the disintegration, the shape of the drop did not look like an ellipsoid. However as time passed, the shape of the drop became ellipsoidal. When the ellipsoidal shapes appeared, the digital images from the microscope were captured periodically. Details about the calculation of interfacial tension and theoretical procedures for the breaking thread method and the deformed drop method are reported in other literatures [6,14,20].

3. Results and discussions

During the measurement of interfacial tension by the breaking thread method, it was observed that the disintegrated drops from a long thread are of ellipsoidal shape, followed by a typical retraction process. In this procedure, it is believed that the drops are the axisymmetrical ellipsoids because they are formed from an axisymmetrical cylinder under neither pressure nor external force. It is also expected that the major axis of the ellipsoid have zero angle with the observation plane since the axis of the original thread is parallel to the observation plane.

Fig. 1 is a sequence of four digital images for a typical retraction. Here, a PA-6 droplet was disintegrated from a thread originally immerged in SAN-24. As expected, the major axis of a drop was observed to be parallel to the observation plane, confirmed by the fact that both tips of the deformed drop are on a clear focus of the microscope. This was also confirmed by a plot of calculated volume ($V = \pi LB^2/6$) versus time as shown in Fig. 2. The calculated volumes are almost same regardless of elapsed time and equal to the volume of equilibrium drop ($4/3\pi R_0^3$). If the major axis was not parallel to the observation plane, the calculated volume would increase gradually and approach an equilibrium value. This plot also confirms that two minor axis (B, W) are same, which is necessary condition to apply the Eq. (1) to the deformed drop retraction method.

In Fig. 3, the experimental contours of each drop are compared to the equivalent ellipse. In either plot, the equivalent ellipse is visibly coincident with the experimental contour, and the result is even more remarkable if one

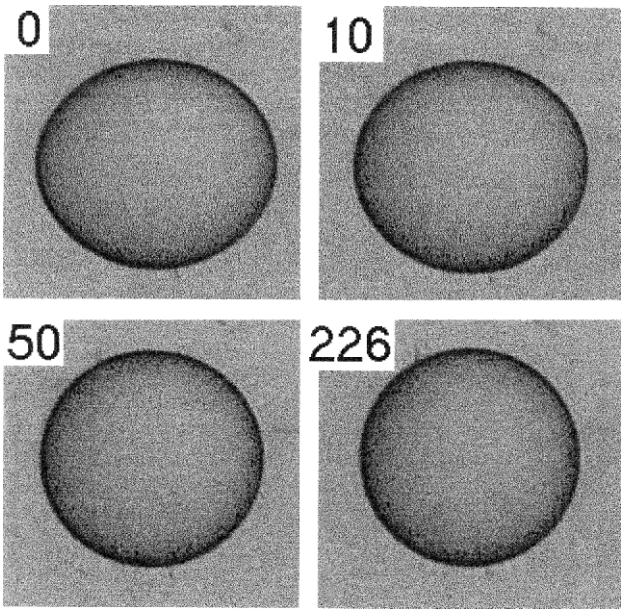

Fig. 1. Retraction of a PA-6 ellipsoidal drop immersed in SAN-24 at 230°C. Time for measurement is written on each micrograph by second. The spherical drop radius at equilibrium is $R_0 = 109$ μm.

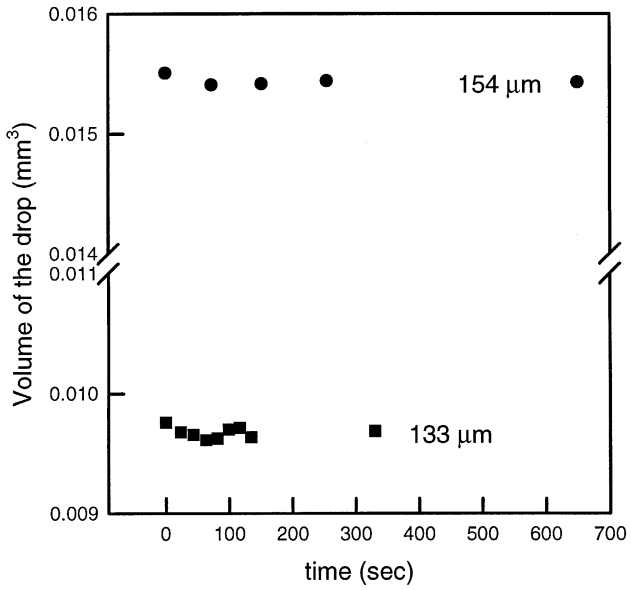

Fig. 2. Time evolution of the calculated volume ($=\pi LB^2/6$) for a PA-6 drop immersed in SAN-32. Numbers shown in the graph represent radius of the equilibrium drop.

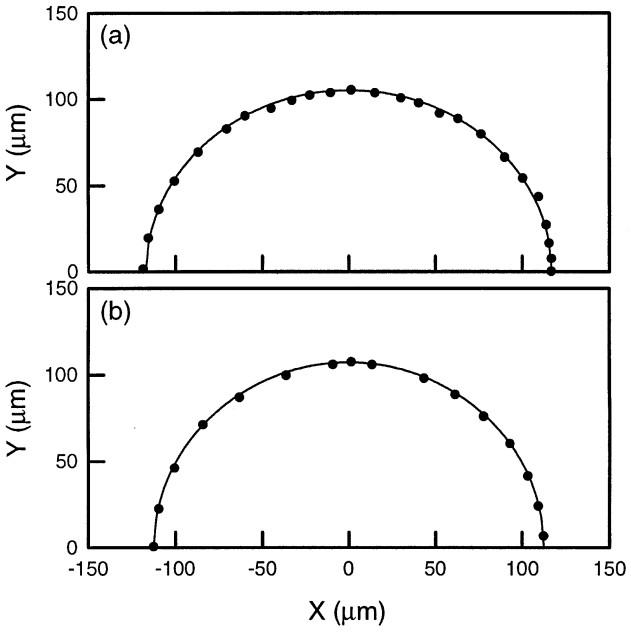

Fig. 3. Comparison of experimental contour and equivalent ellipse for PA-6/SAN-24 system. Experimental contours correspond to the first two photographs in Fig. 1; (a) 0 s and (b) 10 s.

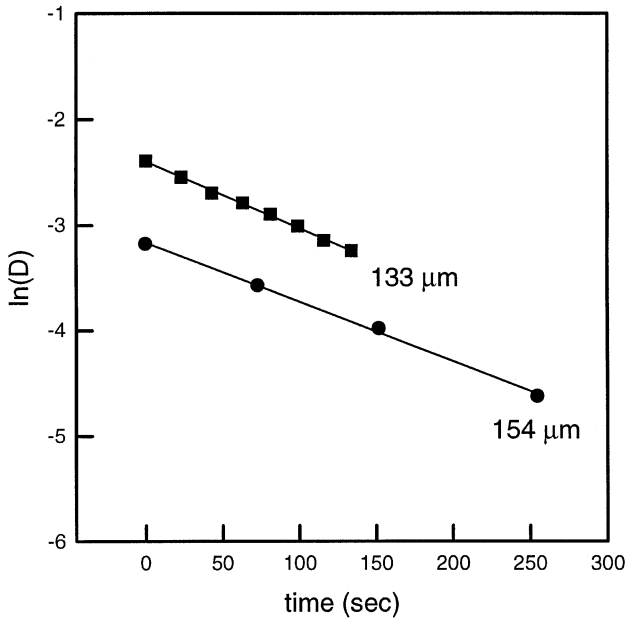

Fig. 4. Time evolution of deformability factor D for a PA-6 drop immersed in SAN-32. Numbers shown in the graph represent radius of the equilibrium drop.

takes into account that D is not small, which means that the experimental technique proposed in this study can be well applied to the deformed drop retraction method with Eq. (1).

Fig. 4 shows a plot of ln(D) vs. time at 230°C of a PA-6 drop surrounded by the SAN-32 matrix. The plot shows a straight line with the slope from which σ is estimated by Eq. (1).

Interfacial tension measured by the deformed drop retraction method and the comparison with the data by the breaking thread method are listed in Table 1. The variation of the interfacial tension with AN content in SAN (24–41 wt%) is within the experimental error regardless of the experimental methods (the deformed drop retraction and the breaking thread methods).

The interfacial tension values measured by the deformed drop retraction method were lower than those by the breaking thread method. The values are different, but the variation is acceptable considering the following fact. The elapsed time for the deformed drop retraction method used in this study is longer than that in the breaking thread method. This means that the polymer–polymer contact time during the measurements in the deformed drop retraction method used in this study is longer than that of the breaking thread method. As indicated by Luciani et al. [20], due to the migration of the low molecular weight species and impurities toward the interface, the interfacial tension decreases with the time and approaches the equilibrium value. Therefore, it is not surprising that experimental values by the deformed drop retraction method used in this study are lower than those by the breaking thread method. The argument is expected to be improved by comparing the experimental data with the similar polymer–polymer contact time.

The proposed technique enables us to use the interfacial force-driven shape recovery of a axisymmetric ellipsoidal drop disintegrated from a thread to measure the interfacial tension. The technique makes it possible to measure the interfacial tension of the polymer pair of which viscosity ratio is higher than a critical value. According to Grace's work [24], the viscous drop, having viscosity of 3.4 times higher than matrix phase, is hardly deformed by the shear force. Therefore, in such case, it is difficult to obtain a deformed drop by the conventional technique proposed by Luciani et al. This limitation may be circumvented using extensional stress. However, it is not easy to design a experimental technique using extensional force.

One advantage of the conventional method suggested by Luciani et al. is that the experiment can be repeated several times on one sample by deforming a spherical drop again after cessation of one run unless the thermal degradation is serious. The technique proposed in this study cannot be repeated with same sample because the deformed drop is formed by the disintegration of a thread. However, the method has capability to observe the retraction process of several drops simultaneously by changing the view area of the microscope because a thread produces several disintegrated droplets.

4. Conclusions

In this study, the dispersed polymer ellipsoid in another polymer matrix is obtained by the disintegration of a long thread. Then, the shape evolution of the drop was observed, and the interfacial tension was calculated by the deformed drop retraction method. It is demonstrated that the proposed experimental technique can overcome several limitations encountered in the conventional deformed drop retraction method. The interfacial tension values obtained for the SAN/PA-6 were found to be lower than those obtained by the breaking thread method. This is because the interfacial contact time for the method in this study is longer than that for the breaking thread method.

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