A MATHEMATICAL MODEL OF META-ARAMID FIBRID FORMATION

by

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Meta-aramid fibrid is a key material for aramid paper preparation. Its formation mechanism is elucidated and a mathematical model is established to reveal the main effects of coagulation properties and shear stress on the properties of aramid paper.

Key words: *meta-aramid fibrid, coagulation, formation, mathematical model*

Introduction

Various kinds of fibrids are produced through two convenient methods, including beating. In beating, the liquid suspension of a shaped structure formed through an interfacial-forming procedure is beaten. In the interface of a two-liquid phase, a rapid reaction occurs between a polymer solution and a coagulant, and solidified intermediates are formed within a short period, which affects the shape and size of the prepared fibrids. This process was first described in the U. S. Patent 2708617 [1].

The properties of aramid fibers or aramid composites have been extensively investigated [2-7]. However, the preparation [8, 9] and formation mechanism of fibrids have been rarely explored. Meta-aramid fibrid and its properties have also been examined [10, 11]. In the current study, the formation of meta-aramid fibrid under turbulent conditions is described by using our homemade equipment.

Meta-aramid fibrid preparation

A coagulation bath composed of a H_2O/DMAc mixture was placed in a closed vessel. A needle was injected into the gap between a rotator and a stator from the side of the vessel. Rotating speed was set, and a polymer solution was fed through a feeding pump. A needle with an inner diameter of 0.5 mm was then used when the display speed reached the set value. Feeding speed was set to 5 ml per minute, and approximately 5-10 ml feed was generated at a time. After precipitation was completed, the fibrid suspension was filtered through an 80-mesh web, and wet fibrids were washed with tap water five times and dispersed in water until use. The fibrid suspension was then dropped onto the slide glass. Twenty samples were randomly examined, and their mean was calculated. The mean length of <1 mm fibrids was measured under a microscope.

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Discussion

In a high shearing fluid flow, a viscous droplet is elongated at x_1 direction by the shearing force and the thickness of the droplet is decreased at x_2 direction. The droplet solidifies when it is penetrated by the coagulant. Thus, deformation and coagulation simultaneously occur. Deformation stops when the coagulant concentration in the droplet reaches the critical value, and the fibrid is formed.

In fibrid formation, fig. 1, the spherical droplet in the coagulant at t_0 is elongated by shearing force, and deformation stops at t_2. The coagulant does not penetrate the center of the droplet when the fibrid is deformed. This phenomenon occurs because the droplet solidifies and deformation stops at a critical time.

Considering that a drop of aramid solution is suspended in the coagulant, fig. 2, we use a 2-D hyperbolic flow field to describe the drop deformation in a flow field far from the drop:

$$\mu_1 = kx_1 \tag{1}$$

$$\mu_2 = kx_2 \tag{2}$$

$$\mu_3 = kx_3 \tag{3}$$

$$\frac{x_1^2}{a^2} + \frac{x_2^2}{b^2} + \frac{x_3^2}{c^2} = 1 \tag{4}$$

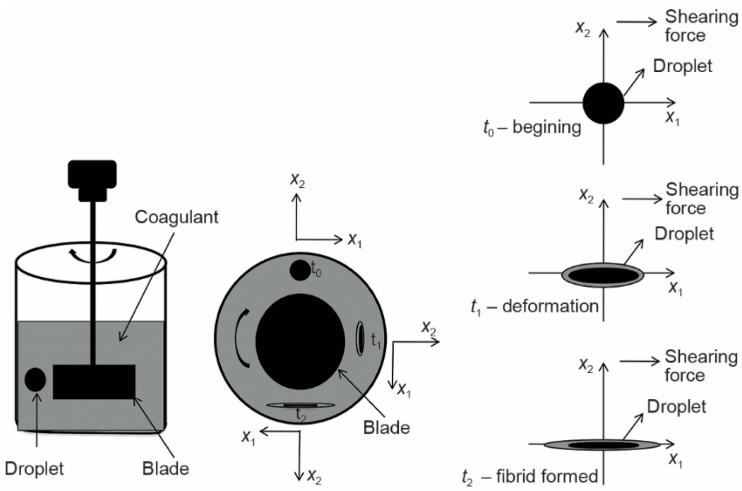

Figure 1. Deformation of meta-aramid droplet under shearing coagulant

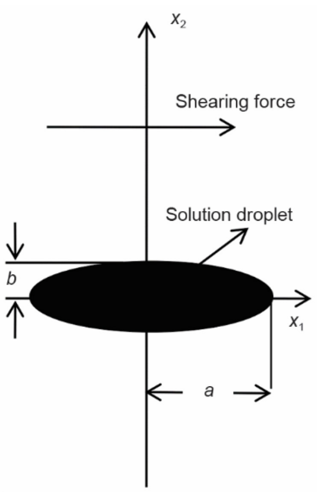

Figure 2. Fibrid in the x_1-x_2 plane

where μ_1, μ_2, and μ_3 are the velocity components in the x_1, x_2, and x_3 directions, respectively. Assuming that the fluids inside and outside the drop exhibit a Newtonian behavior, we demonstrate that an initial spherical drop is deformed into an ellipsoidal drop with semi-axes a, b, and c in the x_1, x_2, and x_3 directions, respectively. The distance of semi-axes c is also approximately constant during this deformation. The interfacial tension between the drop and the suspending medium is set to 0. This assumption corresponds to the practical condition observed in fibrid formation because the polymer solvent and the coagulant are miscible. An initial spherical drop is deformed into an ellipsoidal drop with semi-axes a, b, and c in the x_1, x_2, and x_3 directions, respectively. The diffusion coefficient of a viscous droplet is assumed negligible relative to that of the coagulant:

$$\frac{\partial C}{\partial t}+\mu_1\frac{\partial C}{\partial x_1}+\mu_2\frac{\partial C}{\partial x_2}+\mu_3\frac{\partial C}{\partial x_3}=D'\left(\frac{\partial^2 C}{\partial x_1^2}+\frac{\partial^2 C}{\partial x_2^2}+\frac{\partial^2 C}{\partial x_3^2}\right) \tag{5}$$

where t and C express the time and mass concentration of the coagulant, respectively. A smaller drop of dimensions in the x_1 and x_3 directions is formed because the effect of diffusion outside the drop is restricted to a thick boundary layer. Flow field is assumed the same as that inside the drop throughout this diffusion boundary layer because the boundary layer thickness is lower than any typical length scale of the low-Reynolds-number flow outside the drop:

$$\mu_1 = kx_1 \tag{6}$$

$$\mu_2 = -kx_2 \tag{7}$$

$$\mu_3 = 0 \tag{8}$$

where k changes over time, t. The velocity field inside the drop generates a flow outside the drop. The velocity field is far from the drop, whereas the velocity is continuous on the drop surface. Thus, eq. (5) governing coagulant concentration is expressed:

$$\frac{\partial C}{\partial t}+kx_1\frac{\partial C}{\partial x_1}-kx_2\frac{\partial C}{\partial x_2}=D'\left(\frac{\partial^2 C}{\partial x_1^2}+\frac{\partial^2 C}{\partial x_2^2}\right) \tag{9}$$

The diffusion constant, D', is the same inside and outside the drop, and no variation is observed in the concentration profile in the x_3 direction. The latter assumption is only valid when the drop is not too far from the central plane $x_3 = 0$, where the drop thickness is approximately constant and equal to b. According to Kalb's theory [12], the following equation is obtained when $i \geq 3$:

$$T(t)-T(t')=\frac{2D'}{Gd^2}\int_3^i\left[\frac{4\lambda}{i^{*3}}\left(\ln\frac{4i^{*2}}{i^*}-\frac{3}{2}\right)+1\right]i^*\mathrm{d}i^* \tag{10}$$

where $T(t)$ is the time function $T(t) - T(t') \approx T(t)$, which can be calculated for different polymer solutions, G – the shear rate, d – the original diameter of the droplet, D' – the diffusion coefficient of coagulant in the polymer solution, λ – the viscosity ratio of the polymer solution and the coagulation bath, and i – the dimensionless length of fibrid, which is the ratio of the length after deformation to the original diameter of droplet, and i^* – the dimensionless length of fibrid, which is the ratio of the length after deformation to diameter of droplet at deformation time. For example, $T(t) \approx 1.085$ for meta-aramid, the following expression is obtained to predict the length of meta-aramid fibrid:

$$\frac{i^2}{8\lambda}-\frac{1.89}{i}-\frac{1.125}{\lambda}+0.51\approx\frac{0.034Gd^2}{D'\lambda} \tag{11}$$

Equation (11) can be used to predict the effect of G, λ, D', and d on the final length of the fibrid. The influence of various parameters on the fibrid length is shown in fig. 3. Theoretical data show that fibrid length is directly related to G and the radius of the initial droplet d. By comparison, fibrid length is inversely related to D' and λ.

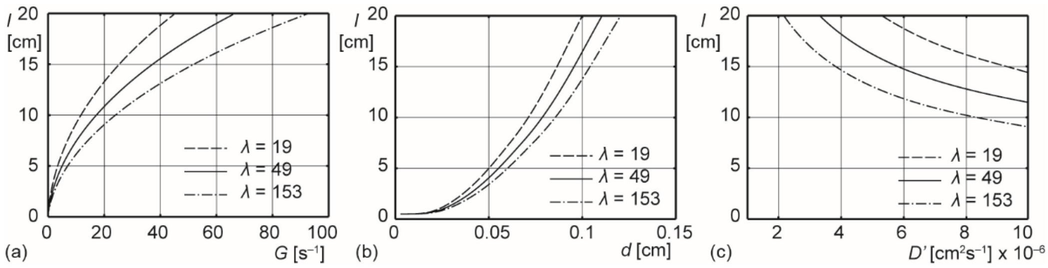

Figure 3. Relationship between (a) fibrid length and shear rate, *G*, (b) diameter of droplet, *d*, and (c) diffusion coefficient, *D'*

It was assumed that the solution droplet does not break during elongation in the shearing coagulation bath. However, the droplet may break when the shearing rate is sufficiently high. As such, a new fibrid model with a high-shearing coagulant should be established to describe fibrid formation accurately.

Conclusions

A mathematical model is used to describe the formation of meta-aramid fibrid at a low shear rate. The formation of meta-aramid fibrid usually involves a two-step process. A viscous polymer solution is initially dispersed as a droplet in the shearing coagulant. Droplet deformation occurs in the turbulent flow, where a polymer droplet is elongated by shearing force. Coagulation subsequently occurs when a sufficient amount of coagulant is diffused across the boundary between a deformed droplet and a coagulation medium. Thus, a solid fiber-like particle is fabricated. The length and morphological characteristics of fibrids are determined on the basis of shearing coagulants and polymer solutions.

Theoretical data reveal that fibrid length is directly related to G and the radius of the initial droplet d. However, fibrid length is inversely related to D' and λ.

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References

[1] Parrish, E., *et al.*, U. S. Patent 2988782, 1961
[2] Seretis, G. V., *et al.*, On the Strength and Failure Mechanism of Woven Para-Aramid Protection Fabrics, *Mechanics of Materials, 97* (2016), June, pp. 92-99
[3] Li, Z., *et al.*, Aramid Fibers Reinforced Silica Aerogel Composites with Low Thermal Conductivity and Improved Mechanical Performance, *Composites: Part A, 84* (2016), May, pp. 316-325
[4] Yahaya, R., *et al.*, Effect of Fibre Orientations on the Mechanical Properties of Kenaf-Aramid Hybrid Composites for Spall-Liner Application, *Defence Technology, 12* (2016), 1, pp. 52-58
[5] Wang, X., *et al.*, Low Velocity Impact Properties of 3D Woven Basalt/Aramid Hybrid Composites, *Composites Science and Technology, 68* (2008), 2, pp. 444-450
[6] Larin, B., *et al.*, Combined Effect of Shear and Fibrous Fillers on Orientation-Induced Crystallization in Discontinuous Aramid Fiber/Isotactic Polypropylene Composites, *Polymer, 49* (2008), 1, pp. 295-302
[7] Shabbir, S., *et al.*, Miscibility Studies of PVC/Aramid Blends, *Colloid Polym Sci., 286* (2008), 6-7, pp. 673-681

[8] Wawro, D., *et al.*, Chitosan Microfibrids: Preparation, Selected Properties and Application, *Fibers & Textils in Eastern Europe, 14* (2006), 3, pp. 97-101
[9] Kucharska, M., *et al.*, Potential Use of Chitosan-Based Material in Medicine, *Progress on Chemistry and Application of Chtin and Its Derivatives, 15* (2010), pp. 169-176
[10] Yao, L. R., *et al.*, Fabrication of Meta-Aramid Fibrid by Precipitation, *Fibers and Polymers, 13* (2012), 3, pp. 277-281
[11] Yao, L. R., *et al.*, Comparative Study on Fibrid Formation Models, *Fibers and Polymers, 14* (2013), 2, pp. 324-329
[12] Kalb, B., *et al.*, Hydrodynamically Induced Formation of Cellulose Fibers II. Fiber Formation by Deformation of Drops with Zero Interfacial Tension, *Journal and Colloid and Interface Science, 82* (1981), 2, pp. 286-297

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