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Rheological perspectives of industrial coating process

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Abstract

Coating process plays an important role in information technology such as display, battery, chip manufacturing and so on. However, due to complexity of coating material and fast deformation of the coating flow, the process is hard to control and it is difficult to maintain the desired quality of the products. Moreover, it is hard to measure the coating process because of severe processing conditions such as high drying temperature, high deformation coating flow, and sensitivity to the processing variables *etc*. In this article, the coating process is to be re-illuminated from the rheological perspectives. The practical approach to analyze and quantify the coating process is discussed with respect to coating materials, coating flow and drying process. The ideas on the rheology control of coating materials, pressure and wet thickness control in patch coating process, and stress measurement during drying process will be discussed.

Keywords **:** rheology, patch coating, drying, stress development

1. Introduction

Coating is to apply liquid, polymer solution or suspension in particular, on the surface to form thin liquid layer and then to transform into a solid film structure via drying, curing *etc*. in order to achieve protection, optical purpose and so forth. Traditionally, coating process has been employed in many industries that manufacture a large number of different products including paper, painting, and architecture, packaging and so on (Cohen and Gutoff, 1992). Recently, with the fast growth of information technology, the coating processes are applied to more diverse emerging industries to produce battery (Kosta and Pomper, 1974; Watanabe *et al.*, 1998; Kaido *et al.*, 2001; Hong, 2006), magnetic tape (Tanaka and Noda, 1984; Chino *et al.*, 1988; Feng, 1998), color filter (de Gans and Schubert, 2004) and optical film (Lin *et al.*, 2007) for the fabrication of display, optical storage media such as compact disk and digital video disk as well as electronic devices such as capacitor, electrode and printable circuit board (Choinski, 1990) to list a few.

As the coating material consists of many components like binder, pigment, solvent, additives, for example, the material is a kind of complex fluid. More often than not, manufacturing engineers encounter the variation of material properties due to sedimentation, phase separation and viscosity change before manufacturing process even though they are formulated with the same recipe and passed the quality test. Since the material experiences high shear flow due to the small gap of tens of micrometers and the dispersion of pigment is critical to the coating performance, it is important to precisely control the flow behavior, which is dependent upon the rheology of the material. However, this process has been depended heavily on the engineer's experience or the exclusive know-how that the company has accumulated for a long time. Therefore, it is a challenge to establish a systematic protocol to characterize the coating material and maintain the uniform quality of coating material during manufacturing at all times.

Various kinds of coating methods are employed in order to fulfill the requirement of specific manufacturing process; slot coating, roll coating, slide coating as well as pattern printing such as inkjet printing, screen printing and gravure printing. The most important point for the successful coating is to understand the flow characteristics when the coating liquid is fed, distributed and applied to the substrate because most coating defects originate from the irregularity of flow at this moment. The most persuasive measurement method is to visualize the flow, led by Scriven and his coworkers (Coyle, 1984; Sartor, 1990; Gates, 1999) at the University of Minnesota who began visualizing coating flows in order to verify their theoretical predictions. Recently, Chu *et al.* (2006) demonstrated the effect of inorganic particles on the flow behavior in slot coating process. With flow visualization technique, they investigated the effect of pH, degree of hydrolysis and molecular weight of poly(vinyl alcohol) on slot coating flow (Chu *et al.*, 2007). However, controlling the coating process has been regarded as a black box and there exist

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few pragmatic methods to measure the process.

In conjunction with coating process, drying is another complex process that we need to consider together. Even though the large majority of coatings are applied in liquid state, they are used in the solid state after drying. Therefore, drying is as important as coating and moreover, the quality of coating can be either deteriorated or enhanced through drying process. Drying itself has a long history back to BC 3000 as in drying of papyrus by Egyptians. However, it has mostly been regarded as a black box, and little is known what really happens during drying process. Consequently there's little established protocol that allows quantitative measurement of any variables or control of the process, partly due to unfavorable measuring condition such as fast volume shrinkage of thin film layer, high temperature drying environment and so on.

Therefore, precise control of the process, high shear rheology, flow control of the particles, quantitative description of coating and drying performance will be the challenges of this area. In this article, the current state of the art of the quantitative approaches for coating and drying process will be introduced. First, we will introduce some ideas on the characterization of the flow properties of the coating material, and point out the shortcoming of the conventional measurement that is widely employed in this industry. Secondly, we will discuss some ideas and experimental results that enable us to quantify the coating process, particularly in the patch slot coating process that is widely used in secondary battery manufacturing. Finally, stress measurement technique during drying process will be introduced.

2. COATING MATERIAL

Coating materials such as ink, slurry and paste that are used for electronic materials show very complex flow behavior during processing. They sometimes lead to unexpected properties, resulting in coating failure. To prevent coating defects and to precisely control the coating process for high quality products, it is important to understand the flow behavior in the coating process. Rheological measurement is a useful tool to characterize the flow behavior of coating materials. Here we show an example on the characterization of the coating materials. There are two coating materials with the same formulation which are used in IT industry. According to the suppliers, sample A shows normal property in its performance in the final product while sample B does not. However, they exhibited the same viscosity when measured by a Brookfield viscometer which is a conventional measurement technique in the field. These two samples are now characterized and differentiated with rheological measurements.

2.1. Viscosity

The first step to setup the processing condition is to measure the viscosity of the coating liquid. According to Fig. 1, which shows the viscosity as a function of shear rate measured by a rheometer (RMS, Rheometrics, USA), they have almost the same viscosity at high shear rate. Probably this is the reason why they have the same viscosity when measured by a Brookfield viscometer because the Brookfield viscometer generally measures viscosity at medium and high shear rate. However, they have different viscosity by an order of magnitude at low shear rate. It means that they show totally different flow behavior in the real process where there are distributions of shear rate and processing environment. It implies that a simple measurement of viscosity at moderate and high shear may lead to false information to the field engineers, and they should consider the shear rate dependence of the viscosity, the viscosity at low shear rate in particular.

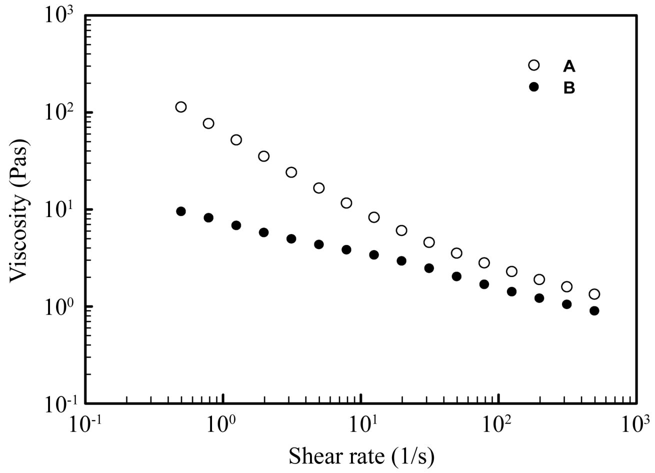

Fig. 1. Viscosity as a function of shear rate for coating materials A and B.

2.2. Flow history

The difficulty in controlling the complex fluid systems such as slurry and paste mainly comes from the fact that they memorize the deformation history in the past. The concentrated suspensions show diverse microstructures depending on flow history. The time-scales of these materials can range from micro-seconds to even hours. Because the change of microstructure can have a significant effect on the rheological properties such as viscosity or stress, the properties of these materials show time-dependent behavior as well as shear rate dependence. One of the methods to characterize time-effect is to perform a hysteresis loop test as shown in Fig. 2; to increase the shear rate from zero to a maximum value, and then to return at the same rate to zero shear rate.

Since the change of microstructure takes time and it cannot adjust itself fast enough to respond to the increasing or decreasing shear rate, the material has different stress state when increasing shear rate and decreasing shear rate.

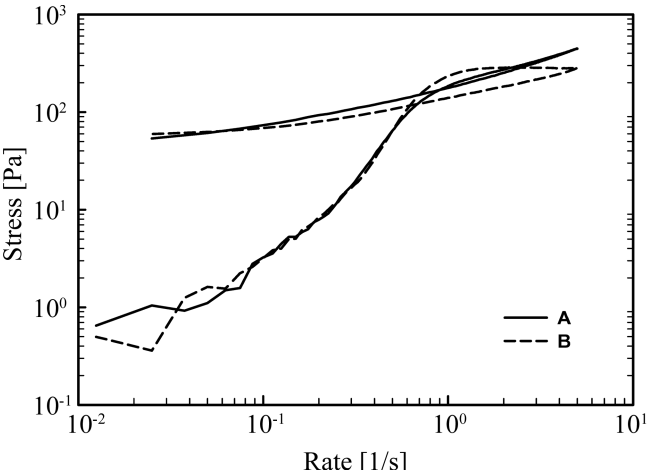

Fig. 2. Hysterisis loop of coating samples A and B.

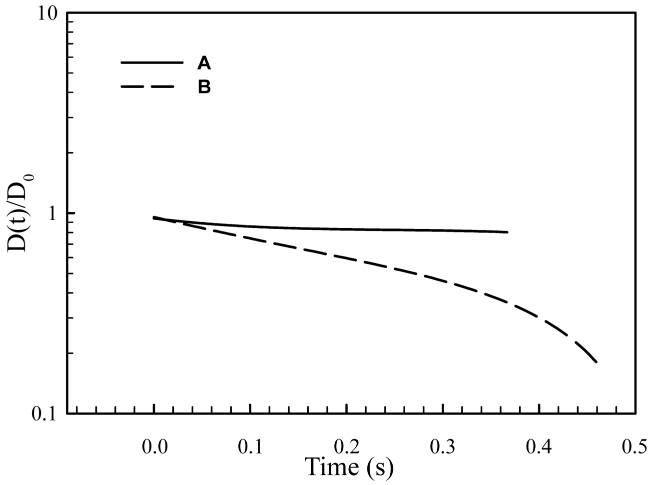

Fig. 3. Extensional properties of A and B.

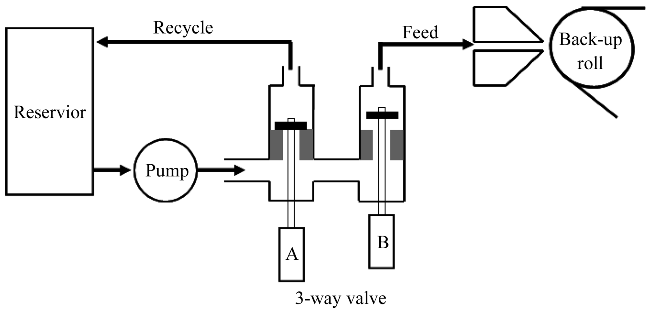

Fig. 4. Schematics of patch coating using 3-way valve.

Therefore, the complex fluid can have different material properties when the material experiences different flow history in the past due to time-effect of the micro-structural change, and it must be controlled during the coating process to reduce the failure.

2.3. Extensional property

Real coating processes consist of shear flow and extensional flow. Flow deformation by extension is much larger than that by shear. Moreover, the coating flow is significantly influenced by the extensional flow in almost all coating processes including roll coating, curtain coating, slot coating, even inkjet printing and dipping. Therefore, it is important to understand the extensional property of coating material and to tailor it to fulfill the requirement of specific coating process. The extensional properties of two coating materials illustrated above were measured with CaBER® (capillary breakup extensional rheometer) developed by McKinley and Tripathi (2000). It generates the liquid column between two cylindrical plates with sudden separation and measures the evolution of diameter at the midpoint of liquid column with time. Fig. 3 shows the result that measures the midpoint diameter of sample A and B. Sample A maintains the constant liquid column during the measured time interval. On the other hand, diameter of sample B decreases with time after separation of the plates. This result indicates that sample A and sample B exhibit totally different extensional behavior when subjected to manufacturing process.

3. Coating flow

Patch coating, sometimes called intermittent coating is a method to coat rectangular patterns regularly on a continuously passing web by comma, slot die or gravure roll. As a recently developed coating method, the patch coating process became quite important when applying the patterns in manufacturing of lithium-ion or lithium-polymer batteries. Patch coating has a short history and there exist only a few patents, which refer to flow rate control, die movement and relation between defect characteristics and operating parameters. Choinski (1990) invented the patch slot coater. In his invention, slot die moves up and down in order to create the patch formation. At the same time, displacement rod in the die also moves for releasing and stopping the coating flow. Sandock (1996) developed the device that can coat double side of substrate at one time. Milbourn and Barth (1994) employed the pneumatic three way valve in the patch slot coating. The valve controls fluid direction to either the slot die for patch formation or fluid reservoir for recycling. Yang *et al.* (2004) investigated the operating window of patch coating process. They found that the defect of patch coating at the commencement and termination is related to that of continuous slot coating, and the controlling factor that reduces defects is the time required for the flow to reach a critical value within the stable coating window. Fig. 4 shows the schematics for the patch coating process employing 3-way valve systems.

The schematic diagram of the patch coating apparatus we designed for this study is shown in Fig. 5. The apparatus consists of a backing roll with 300 mm outer diameter, slot

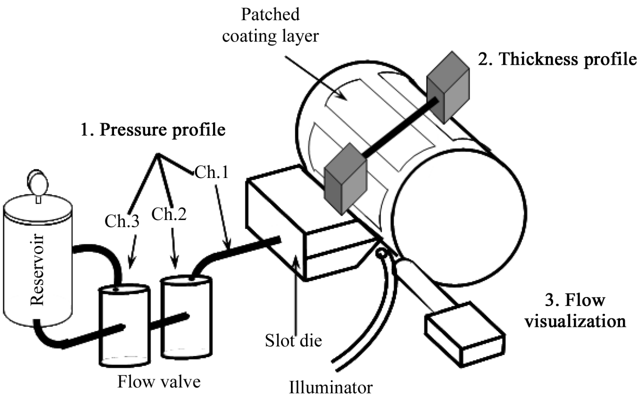

Fig. 5. Measurement technique of patch coating process.

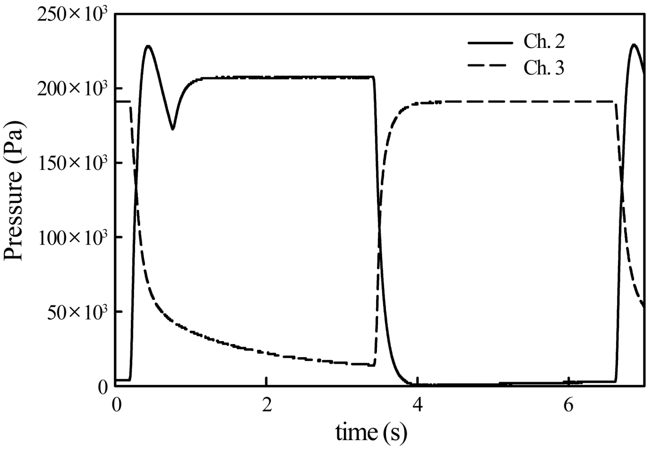

Fig. 6. Pressure profile during one-cycle valve motion.

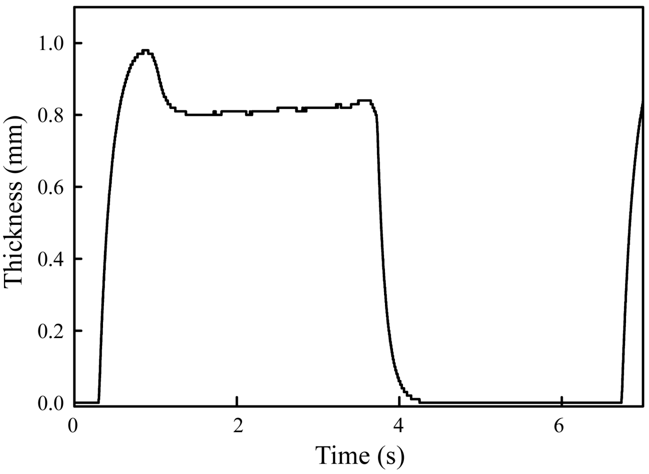

Fig. 7. Thickness profile of one-cycle valve motion.

die, pneumatic 3-way flow valve and feeding device. Coating liquid is supplied to horizontally fixed slot die and coated on the web intermittently by controlling 3-way valve.

The patch shape at the start and ending line is an important issue in manufacturing and quality control, and it is closely related with the pressure profile that depends on

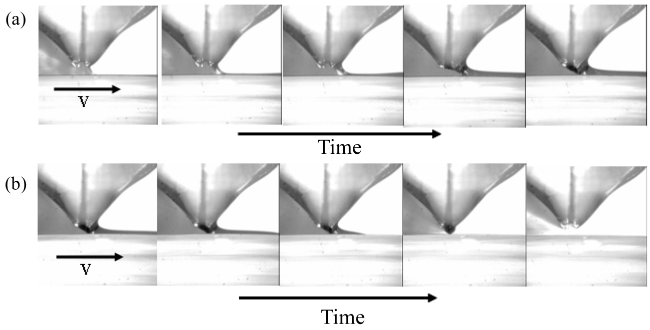

Fig. 8. Visualization of coating flow at the start and end of patch formation.

valve motion during supply of the coating solution to slot die. The in-situ pressure sensors were installed at each valve of the flow line to measure the pressure gradient when the 3-way pneumatic valve is in motion. It was observed that there exists a pressure overshoot at the start up of the patch as shown in Fig. 6.

In order to figure out the effect of pressure on the coating shape, we measured the thickness profile of the wet film with digital micrometer (LS-7030, Keyence, Japan). In Fig. 7, the thickness profile shows an overshoot at the start of the patch.

It clearly indicates that the pressure directly affects patch shape. Flow visualization technique with high speed camera was also developed to analyze the coating bead and the flow behavior at the start up and end of the patch coating process, as shown in Fig. 8.

4. Drying process

During drying process, the coating layer shrinks because of solvent evaporation, coalescence, and cross-linking and so on. The tensile stress develops in the coating layer because of constrained shrinkage resulted from adhesion to a rigid substrate, therefore, the film deflects due to bending moment. The stress in the coating layer may result in defects such as peeling, cracking and deformation. Croll (1979) explained the coating stress of polymer solution in terms of free volume change. The free volume means the vacant region in the coating layer that is occupied by neither solvent nor polymer. When coating layer remains liquid state, the polymer can move freely and occupy the vacant place where solvent evaporates. The rate of polymer chain relaxation is equal to the rate of solvent evaporation. Therefore the coating layer has no free volume in the liquid state and the coating reaches stress-free state. However, when coating layer becomes solidifying as solvent evaporates and polymer cannot occupy the vacant space, the free volume is created. Thus the free volume generates strain, and the stress develops proportional to strain. However, solution coatings used in a wide variety of industries often contain large amount of pigments. Stress development of real coating material such as paste or slurry is influenced by particle migration, capillary pressure, dispersion of particle and binder, compatibility between particle and polymer and so on. Therefore, the mechanism of stress development is much more sophisticated than pure polymer solution.

The most popular stress measurement method is based on the beam deflection method. The first quantitative relation between stress and deflection was suggested by Stoney (1909) who related the curvature of a coated metal strip to the average coating stress by

$$P = \frac{Et^2}{6rc} \tag{1}$$

where P is the tension per unit cross-sectional area parallel to the substrate; E is the substrate modulus; t and c are the substrate and coating thickness, respectively, and r is the radius of curvature of an unconstrained strip. Stoney assumed that the coating and substrate moduli were similar and the coating thickness was much less than the substrate thickness. He also assumed that the coating stress was not significantly reduced by the bending of the substrate and coating, and this assumption is valid for stress measurement with rigid substrate.

For a rectangular beam held rigidly at one end like cantilever, the radius of curvature can be estimated by

$$r = \frac{L^2}{2d} \tag{2}$$

where L is the free length of the beam and d is the deflection at the free end. Combining Eqs. (1) and (2) gives a modified Stoney equation for cantilever beams:

$$\sigma = \frac{Et^2 d}{3cL} \tag{3}$$

where P was replaced by σ as the average coating stress. The modified Stoney equation was derived based on classical beam theory, which assumes a uniaxial stress along the length of a bending beam. However, because the stress state away from the edges of a coating is biaxial, Corcoran (1969) derived the following formula to relate deflection of a cantilever to stress in an adhered coating based on plate theory developed by Timoshenko and Gere (Timoshenko and Gere, 1961).

$$\sigma = \frac{dEt^3}{3cL^2(t+c)(l-v)} + \frac{dE_c(t+c)}{L^2(l-v_c)} \tag{4}$$

where d, E, t, l and v are deflection, elastic modulus, thickness, and Poisson ratio, respectively. Subscription s and c means substrate and coating film after drying, respectively. Second term of Eq. (4) accounts for stress relaxation in a coating because of bending of the cantilever. However, this second term can be ignored if modulus of coating is much less than that of substrate. Other assumptions such as spherical deflection, isotropic mechanical properties, good adhesion are introduced by Corcoran's analysis (1969).

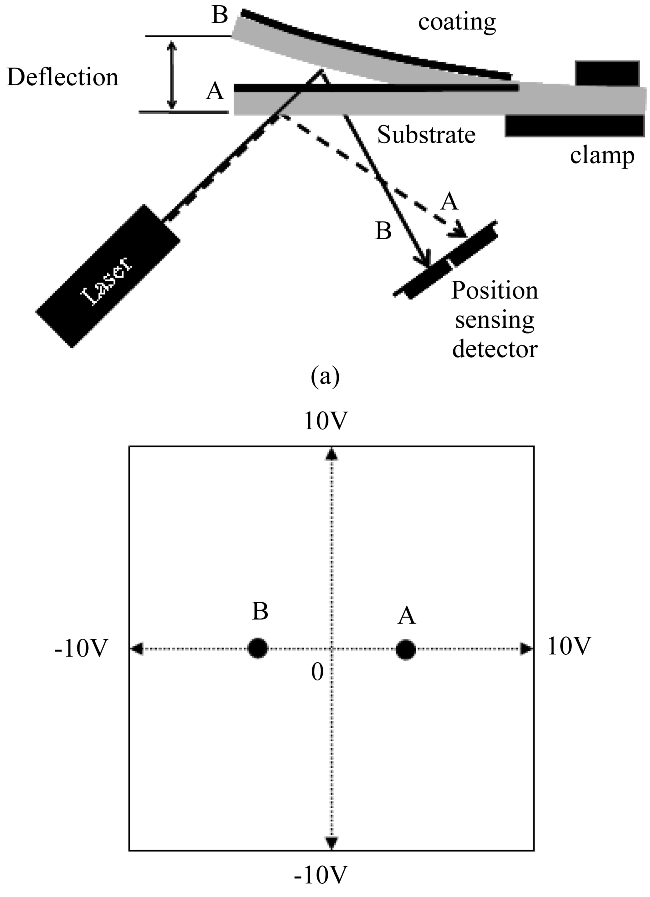

Fig. 9. Principle of stress measurement.

In order to monitor the stress evolution in-situ, a device that observes the deflection of substrates was designed based upon the works carried out by Payne *et al.*(1997), as shown in Fig. 9.

Once coated by blade coating on the silicon substrate, the film is drawn into the drying chamber with controlled environment such as relative humidity, airflow and temperature. Laser beam illuminates under the substrate and reaches position sensing detector (PSDM4, Thorlabs, USA). Because of shrinkage of coating layer during drying, the cantilever deflects. As a result, the position of the laser beam in detector moves due to the change of incident and reflective angle under the substrate. The voltage obtained by detector as drying time passes is transformed to deflection of the substrate. Stress is obtained from deflection using Corcoran's equation. Stress development of 15 wt% polystyrene in toluene coating was measured and compared to the previous result conducted by Lei *et al.*(2001). Fig. 10 shows a good agreement with the pre-

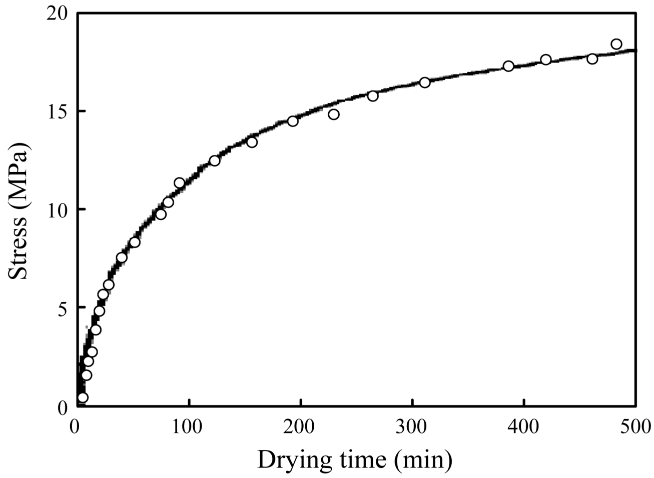

Fig. 10. Stress development during drying of polystyrene coating. Straight line is from our experiment and the symbols are reproduced from Lei *et al.*(2001).

vious result. To understand the stress development during drying process, the stress measurement technique will be useful in understanding various coating phenomena such as cracking (Tirumkudulu and Russel, 2004), glass transition temperature effect on film formation (Martinez and Lewis, 2002), wrinkle formation (Basu *et al.*, 2006) *etc.*

5. Conclusions

The practical approaches to analyze and quantify the coating process were discussed in this article. Rheological measurement of coating materials is a powerful tool to overcome many mistakes which often appear in the industrial measurement. In patch coating process, we suggested three measurement techniques in terms of pressure, wet thickness and flow behaviour at the start and termination of unit patch. We demonstrated that the pressure overshoot in patch valve affects the film thickness profile. As a final step of coating process, we introduced the stress measurement technique for the drying process measurement. It is expected that these concepts and measuring techniques will contribute to better control and performance of the coating process in relevant industries.

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