Research Report

Application of Optical Tweezers to Viscosity Measurements of Multi-layer Coatings

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ABSTRACT Viscoelastic properties are a key factor to control the appearance of automotive coatings. However, direct measurement of the viscosity of automotive coatings has not been achieved, because the automotive coating is a complex system consisting of multi-layers where solvent transfer occurs between each thin layer. A viscometer was developed using optical tweezers to realize non-destructive viscosity measurements of multi-layers. The viscosity of automotive coatings was estimated for (A) a clear coating alone, (B) a clear coating on a base coating, and (C) a clear coating on a base coating and primer coating. The results demonstrate an increase of viscosity in the order of (A) < (B) < (C), depending on the thickness of the lower layers. The viscosity increase suggests that the concentration of the clear coating should increase by transfer of the solvent into the lower layers.

KEYWORDS Optical Tweezers, Stokes' Law, Viscosity, Multi-layer, Coatings

1. Introduction

Automobile customers perceive quality when they look at the exterior finish of a car. A perfectly smooth surface with a mirror gloss would be an ideal appearance required for an automotive body. However, orange peel effects and slightly dull areas are still evident on actual coatings. Thus, many engineers have investigated the factors that determine the appearance of automotive coatings.(1)

The appearance of a coating surface is thought to be influenced by the viscoelastic properties of the paints, in addition to the decrease rate in the thickness of the film, the volume fraction of pigments in the paint, and the roughness of the substrate. To obtain a smooth surface, for example, a low viscosity paint can be used, whose thickness decreases slowly by evaporation of the solvent, although a paint with a viscosity that is too low sags by gravitation when applied to a vertically-placed body. Therefore, a high-performance paint has been designed to exhibit optimal viscosity change during the process of application and finishing.(2)

The appearance of coatings varies not only by the paint properties, but also according to the coating atmosphere. In particular, the finish of waterborne paint is sensitive to humidity, which affects the evaporation rate of the water in the paint. For example, as the humidity of the atmosphere increases and the evaporation rate decreases, the increase in the viscosity of the paint is suppressed and severe defects on the film, such as sagging, can be caused. However, elaborate techniques to control the viscoelastic behavior have resulted in the evolution of waterborne paints insensitive to the atmospheric conditions to reduce energy consumption and CO_2 emissions. Thus, the viscoelastic design of coatings is now one of the main areas for engineers to provide a fine finish, and the function of viscosity modifiers is an important research target for materials scientists.

Automotive coating systems consist of multi-layer films to realize various characteristics, such as anticorrosion, coloring, and weatherability. Generally, a base coating and clear coating are applied in a wet-on-wet manner and are simultaneously cured in a baking step, before which a primer coating is applied and baked on the vehicle body (2C1B process). However, in order to remove one baking step, a new process has been developed, where the three coatings are applied in a wet-on-wet-on-wet manner and are cured together in a single baking step (3-Wet process).(3,4)

To maintain a good finishing appearance, appropriate viscoelasticity of each of the three layers must be designed, even with the new 3-Wet process. However, it is much more difficult to control viscoelasticity in the 3-Wet process than in the conventional 2C1B process, due to solvent transfer between the multiple layers. The solvent in a clear coating is supposed to transfer into the primer coating through the base coating and induce a decrease in the viscosity of the primer coating and an increase in the viscosity of the clear coating. Thus, independent optimization in only one or two layers should not be a reasonable procedure for the development of multi-layer coatings prepared by the 3-Wet process.

Various types of viscometers have been developed and employed for process management, because such measurements are necessary to control the viscosity of a coating. For mono-layer coatings, the viscosity can be evaluated with coatings scrabbled from the substrate. However, as yet, there is no tool to measure the viscosity of multi-layer coatings.

In this report, we introduce a new viscometer that uses optical tweezers, which was developed to evaluate the viscosity of multi-layer coatings without damage to the structure of the layers. The measurement technique is firstly explained from the fundamental concept to the instrumental setup. Application of the measurement technique to multi-layer coatings is then provided to confirm the validity of the evaluated values.

2. Instrument for Viscosity Measurement Using Optical Tweezers

Multi-layer coatings prepared by the 3-Wet process are generally an open system where solvents transfer between each of the layers and even into the atmosphere. A sufficiently small object would not destroy the multi-layer structure when it moves slowly in a coating layer. Thus, the viscosity of multi-layer coatings can be evaluated if a small object is manipulated and the drag force is measured without touching the object, because the drag force acting on a moving object in a fluid is expressed by Stokes' law.(5) Therefore, optical tweezers are proposed as a promising tool for manipulation to realize this conceptual technique.

Optical tweezers are a tool used for the manipulation of small particles by a focused laser light, and were developed by Ashkin et al. in 1986.(6) Optical tweezers have been extensively applied in the field of biophysics to manipulate cells and biomolecules.(7,8) Although it is understood that a drag force acts on a moving particle, some innovations were required to develop a tool to measure the viscosity of coatings.

Stokes' law is a fundamental formula for the evaluation of viscosity using the proposed viscometer. A drag force f, acting on a particle with radius a, is expressed by Eq. 1, when it moves at a speed of v, in a fluid with viscosity, η.

$$f = 6\pi a\eta v \cdots\cdots\cdots \quad (1)$$

Note that Eq. 1 is an approximation in the case of a small Reynolds number (Re << 1), which is calculated from $\mathrm{Re} = \rho v a/\eta$ with a fluid density, ρ. Typical values in the system under investigation are $\rho = 1$ kg/m^3, $v = 1$ μm/s, $a = 1$ μm, and $\eta = 1$ Pa·s, so that the evaluated Reynolds number, $\mathrm{Re} = 10^{-12}$, is sufficiently small to adopt the approximation. Thus, η can be obtained from Eq. 1 when f, a, and v are measured experimentally.

The shear rate γ, is also an important parameter, because viscosity is a function of γ for non-Newtonian fluids, such as most paints. In a conventional rotational rheometer with cone-plate geometry, the shear rate is a constant value across the sample. However, in the case of parallel-plate geometry, the shear rate varies proportionally from the center to the edge of the plate. When a particle is moving in a fluid, it is supposed that the shear rate on a particle surface has a symmetrical distribution against the movement direction, and has a value that is proportional to the speed v, and inversely proportional to the radius, a. Therefore, the practical shear rate of a moving particle is defined by Eq. 2; the validity of this definition will be discussed later.

$$\gamma = v/a \cdots\cdots\cdots \quad (2)$$

A schematic representation of the optical tweezers is given in **Fig. 1**. A laser beam is focused through an

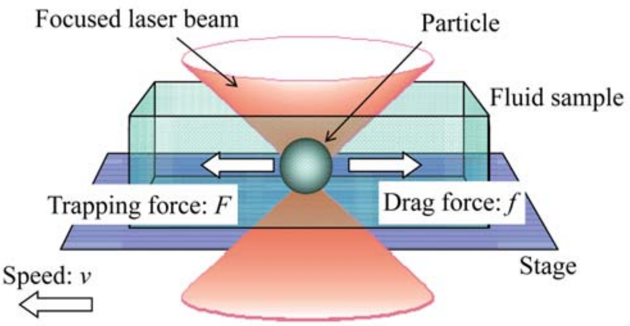

Fig. 1 Optical tweezers constructed with a focused laser beam. A trapping force is generated on a particle. When the stage is operated, the fluid moves at the same speed of the stage, while the particle remains trapped at the focus point. If the drag force acting on the particle exceeds the trapping force, then the particle is released.

objective lens and irradiates a particle in a fluid. The trapping force F, generated against the particle by the laser is dependent on the shape of the particle, the difference in the refractive index between the particle and the fluid, the focus shape and the power of the laser. F can be easily controlled by the power of the laser. On the other hand, the drag force f, increases as the speed v, increases. When f exceeds F, the particle no longer stays at the focus point, i.e., there is a maximum speed at which a particle can be manipulated with optical tweezers. The maximum speed is equal to $F/(6\pi a\eta)$, so that η can be evaluated from the observed value of the maximum speed if F and a are previously known.

The trapping force of the optical tweezers F, is obtained from measurement of the maximum speed for a reference sample with a calibrated fluid viscosity and particle radius. The viscosity of the reference sample can be estimated using a rotational rheometer. Note that the refractive index of the reference should be adjusted to the target sample. The radius of the particle a, can be measured using microscopy, while a certified value of a monodisperse particle would be reliable within an error of several percent of the radius.

Now the viscosity of coatings can be evaluated from measurements of the maximum speed for a particle trapped by optical tweezers. At first, a particle in a sample is trapped with the optical tweezers. The sample stage is then forced to oscillate with increasing speed. The maximum speed is determined by monitoring whether the particle is at the focus point. Although the influence of the focused laser on the sample is difficult to estimate, no bubbles induced by irradiation with the laser were observed in our experiments (presented below), which indicates that heat generation can be ignored for transparent samples.

A photograph of the developed viscometer and an algorithm for the viscometry measurement are shown in **Fig. 2**. The viscometer is designed for the measurement of high viscosity samples (ca. 10 Pa·s). According to Eq. 1, high viscosity can be measured by increasing the trapping force F, of the optical tweezers and decreasing the movement speed v, of the particle. Therefore, a high power laser (JUNO5000, Showa Optronics Co., Ltd.) and a piezo stage (NPS-XY-100B, Queensgate Instruments Inc.) were employed. In Fig. 2(a), focused light from the laser on the left is introduced into a sample on the stage through an objective lens after reflection by the half mirror. The movement of a particle in the sample is monitored by a CCD camera at the top. Stage control software and image analysis software were developed for automatic measurement of the viscosity. The algorithm in Fig. 2(b) indicates that the oscillation speed of the stage is controlled after analyzing the particle image. If the image analysis software determines that the particle is in the trap, then the stage control software will increase the speed of the stage. The trap state of a particle is determined by monitoring the brightness at the focus point. A particle reflects much light when trapped, so that the brightness of the image remains at a high level. The brightness decreases when the particle is released from the focus point by a drag force at maximum speed. The speed of the stage is controlled with an exponential increase in speed until reaching the maximum speed.

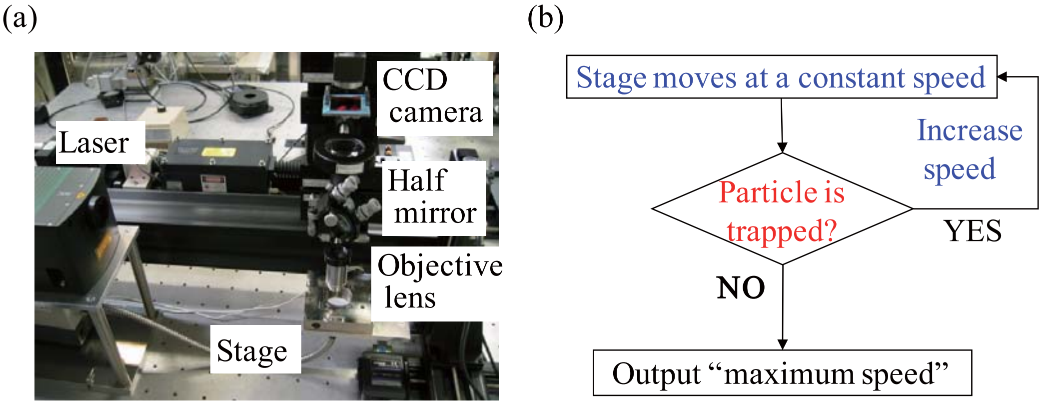

Fig. 2 (a) Photograph of the viscometer with optical tweezers. A beam irradiated from a laser is reflected by a half mirror and introduced into a sample on a stage through an objective lens. The trapped particle is monitored with a CCD camera. (b) Algorithm for the measurement software. The stage-control part maintains the increase in speed unless the image-analysis part recognizes the particle has been released.

3. Application of the Viscometer to Coatings

The viscometer was firstly applied for measurement of two types of monolayer coatings. The samples were glycerin solutions (Newtonian fluid) and a paint (non-Newtonian fluid). When a monolayer coating is sealed by covering its surface, the viscosity is identified as that of the bulk, which can be evaluated using a rotational rheometer (ARES, Rheometric Scientific Inc.). Thus, the performance of the developed viscometer can be examined by comparison. The new viscometer was then applied to the measurement of multi-layer coatings prepared by the 3-Wet process. This is the first experimental data for the viscosity measurement of multi-layer coatings.

Four glycerin solutions of various viscosity were prepared by mixing with different amounts of water. According to the rotational rheometer measurements, the viscosities were 0.04, 0.15, 0.32, and 0.73 Pa·s at 25°C. The solutions were held between two cover glasses with a gap of approximately 50 µm.

Figure 3 presents the maximum speed of a trapped particle as a function of the laser power of the optical tweezers. An increase in the maximum speed is observed for all samples as the laser power is increased. The maximum speeds of the various viscosity solutions have different values. **Figure 4** shows an alternative plot of the trapping forces, which are converted from the maximum speeds using Eq. 1. One master curve is evident, which indicates that the trapping force is dependent only on the laser power. Thus, it is confirmed that the viscosity is inversely proportional to the maximum speed when the laser power is constant.

The result of the rotational rheometer viscosity measurement for the paint is shown in **Fig. 5** with the viscosity evaluated using optical tweezers. The viscosity of the paint in the bulk decreases as the shear rate increases (solid line), thus, exhibiting non-Newtonian fluid behavior. The maximum speed could be measured for the paint between cover glasses and was 2.6 µm s^{-1} when the laser power was 1.2 W. The maximum speed of glycerin (viscosity: 0.73 Pa·s, dashed line in Fig. 5) was 85 µm s^{-1} under the same condition; therefore, the viscosity was evaluated as 24 Pa·s. The shear rate was calculated as 1.3 s^{-1} using

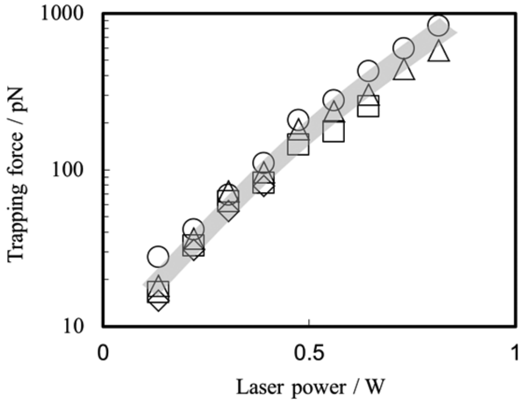

Fig. 4 Relationship between the trapping force and laser power for glycerin solutions of various viscosity. The trapping force is dependent only on the laser power, irrespective of the viscosity.

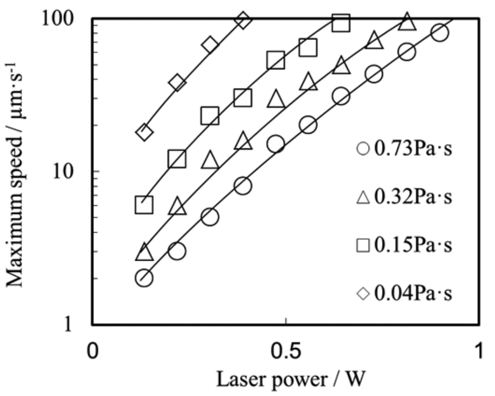

Fig. 3 Maximum speed vs. laser power for glycerin solutions of various viscosity. An increase of the maximum speed is evident as the laser power increases and the viscosity decreases.

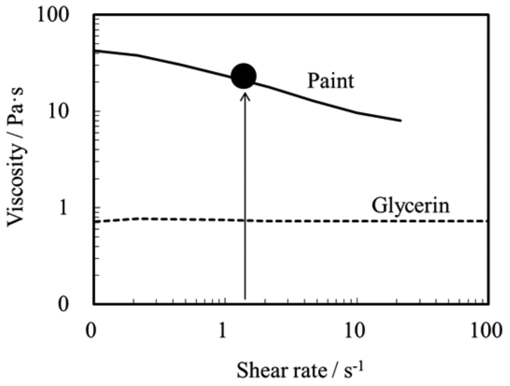

Fig. 5 Viscosity of a paint estimated using the viscometer with optical tweezers is plotted as a solid circle. The viscosities of glycerin and paint measured using a rotational rheometer are presented as lines.

Eq. 2. The solid circle in Fig. 5 indicates the viscosity against the shear rate for the paint obtained using the optical tweezers. The plot is almost on the line, which implies that the new viscometer is useful for viscosity measurements of coatings.

The viscometer with optical tweezers was then applied to evaluate the viscosity of a clear coating in a multi-layer prepared by the 3-Wet process. The multi-layer structure of the coatings is illustrated in **Fig. 6**. A waterborne primer (Primer), a waterborne base coating (Base), and a solvent-based clear coating (Clear) were employed for each coating. Two series of coatings (Series A and Series B) were examined. Primer and Base were specially prepared without pigments, because pigments would act as obstacles to the laser transmission. The Primer was coated on a cover glass followed by coating with the Base in a wet-on-wet manner. The Base and Primer bilayer was dried at 70°C for 3 min. The viscosity of the Clear coating was adjusted by collecting sprayed coating on an aluminum foil, into which trace amounts of borosilicate spheres (1.0 μm radius, Duke Inc.) were dispersed. The Clear coating was then coated on a cover glass and contacted with the dried Base/Primer bilayer (Clear on Base/Primer). The cured thicknesses of the Primer, Base, and Clear coatings were designed to be 20, 10, and 25 μm, respectively. For reference, the Clear coating was contacted with a Base coating without the Primer (Clear on Base) and also on a cover glass without the Base or Primer layers (Clear only).

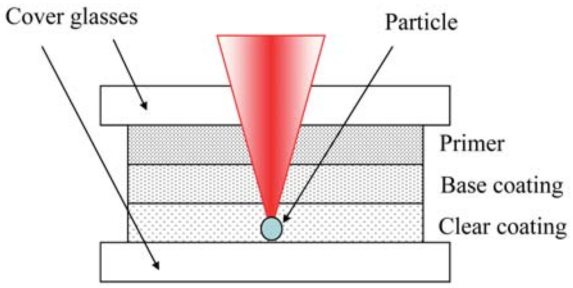

Fig. 6 Structure of multi-layer coatings. Three layers consisting of a primer, base coating, and a clear coating are stacked between two cover glasses. A particle is set in the clear coating layer.

Figure 7 shows the viscosity of the Clear on Base/Primer (○), Clear on Base (△), and the Clear only (□) for the two series of coatings. The measurements were performed at different laser powers to observe the effect of the shear rate on the viscosity. When the laser power is increased, the trapping force increases which results in an increase in the maximum speed and the shear rate. The solid lines in Fig. 7 indicate the viscosity curve for the sprayed Clear layer evaluated using the rotational viscometer. As a reference, viscosity curves of condensed Clear are presented as dashed lines. For both series of coatings, the viscosity of the Clear layer did not vary significantly with the shear rate. However, the Clear layer exhibited a significant change in viscosity when

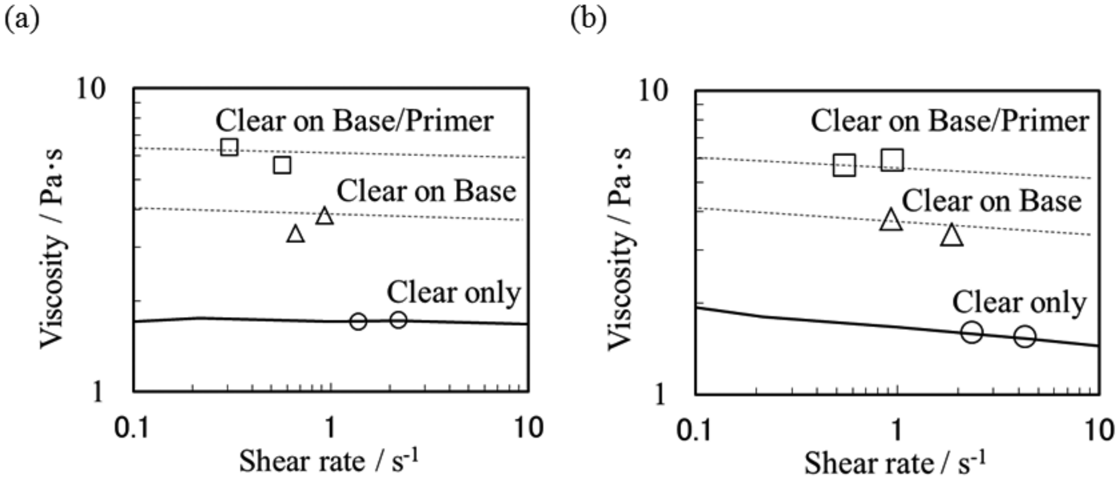

Fig. 7 Viscosity of multi-layer coatings estimated using the viscometer with optical tweezers for (a) Series A and (b) Series B. The two plots for each sample indicate the viscosities measured using different laser power intensity. Reference values measured using a rotational rheometer are presented as lines that were estimated using clear coatings prepared by solvent evaporation.

it was coated on a different substrate. The viscosities were 6, 4, and 2 Pa·s for Clear on Base/Primer, Clear on Base, and Clear only, respectively. It should be noted that the viscosity around a shear rate of 0.1 s^{-1} influences the smoothness of a coating.(1)

The viscosity of the Clear coating increased as the number of lower coating layers was increased from zero to two. The Base and the Primer layers can absorb solvent from the Clear layer; therefore, the solvent in the Clear layer should transfer into the Base and Primer layers more than that only into the Base layer. Thus, it is supposed that the Clear layer in contact with the Base and Primer layers has a higher concentration (and therefore viscosity) than the Clear layer on only a Base layer.

4. Conclusion

A viscometer was developed using optical tweezers for the non-destructive measurement of small samples, such as multi-layer coatings. The viscosity was measured up to 20 Pa·s for a paint using the newly developed viscometer. An increase in viscosity was observed for multi-layer coatings due to solvent transfer between layers.

In multi-layer coatings prepared by a Wet-on-Wet process, viscosity design based on the measurements of each monolayer is misleading, because the viscosity of a coating is changed by the other layers. This was the first observation of the quantitative change in viscosity for multi-layer coatings using the new viscometer. Comparing the viscosity of a Clear on Base/Primer coating with a Clear on Base only coating indicated that the viscosity of a clear coating prepared by the 3-Wet process could be too high. Therefore, some procedure would be required to suppress solvent transfer from a clear coating to prevent insufficient leveling on a surface.

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