UV-LEDランプを用いた光ファイバ用UV硬化材料の硬化挙動検討

Investigation of Cure Behavior of UV Curable Coatings for Optical Fiber by UV-LED lamps

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光ファイバ用UV硬化材料のUV-LEDランプ適合性を検証するために，ランプ出力や波長が異なる種々のUV-LEDを用いて，硬化速度や機械的特性などのUV硬化材料の硬化特性をメタルハライドランプ対比で調査した．更にUV硬化材料の欠点の一つであるUV-LED使用時の表面硬化不良に関しても，材料の硬化度合い（重合度）に加えて，ファイバ実用特性である表面削れ耐性について調査した．一連の検討により，UV-LED使用時のUV硬化材料の欠点である低硬化速度，表面硬化不良に対する改善策として，高出力UV-LEDランプ適用，光重合開始剤の適正化が有用であることを見出した．

To demonstrate the applicability of UV-LED lamp to UV curable coatings for optical fiber, cure behavior of conventional secondary coatings such as curing speed and mechanical properties was investigated by using several UV-LED lamps with different lamp power and wavelength in comparison to conventional metal halide lamp. Addition to this, surface cure under UV-LED lamps, which is one of the drawbacks for UV curable coatings, was investigated not only by curing degree of UV curable coatings but abrasion resistance of fibers as a practical performance. We found promising countermeasures for two drawbacks for coatings under UV-LED such as low curing speed and poor surface cure, which were employing higher lamp power of UV-LED and adjustment of photo initiator package of coatings.

1 Introduction

UV-LED technology is drawing more and more interest from UV curing industry due to many benefits such as lower power consumption, longer lamp life, instant on-off function, total cost reduction of ownership and environmental preservation like ozone and mercury free. This technology has a large potential to save the cost and time for optical fiber manufacturing. However, since there are two concerns in UV-LED lamps for UV curing, namely lower power output than conventional UV lamps and monochromatic wavelength, performance of UV curable coatings could be affected in terms of curing speed and mechanical properties. Adjustment of UV curable coatings for optical fiber to UV-LED lamps might be indispensable to exploit the benefits of UV-LED technology at the maximum. As the first step, several UV-LED lamps with different lamp power and wavelength were evaluated by using UV conveyer based on the cure behavior of conventional secondary coatings such as curing speed and me-

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chanical properties in comparison to conventional metal halide lamp. The relationship between conveyer speed and Young's modulus of cured film can be regarded as the curing speed of coatings. As the second step, coatings were evaluated on our Draw Tower Simulator (DTS) equipped with UV-LED lamps to further clarify the applicability of UV-LED lamp to UV curable coatings for optical fiber. Details of these results are described in this paper.

2 Experimental sections

2.1 Material

All samples of secondary coatings consisting of polyurethane acrylate were prepared in our laboratories. Samples A, B and C have adjusted photo initiator packages.

2.2 Preparation of cured film

Liquid UV curable coatings were drawn on a glass plate with a certain thickness using an applicator bar. These liquid coatings were cured by using UV lamps of conveyor type at various conditions such as conveyer speed and curing atmosphere. The UV-LED lamps were put on the existing UV conveyer instead of metal halide lamp. Curing speed was evaluated by changes of Young's modulus at various conveyer speeds from 1.8 m/min to 30.9 m/min. The liquid coatings were cured with 130 μm thickness under nitrogen. The surface cure was evaluated by FT-IR using films of 200 μm thickness cured in 6 % oxygen at 30.9 m/min conveyer speed.

2.3 Measurement of Young's modulus

Young's modulus at 23 ℃ was measured by using a tensile machine (AG-X, SHIMAZU) at tensile speed of1mm/min. Young's modulus was defined by the secant modulus at 2.5 % elongation.

2.4 Measurement of surface cure of UV coatings

Surface cure of the film was measured by using a Nicolet 6700 FT-IR Spectrometer (THERMO ELECTRON Co., Ltd.). The area of the reference peak and the acrylate peak 810 cm^{-1} of the cured films were measured respectively. The conversion of acrylate (a.k.a. percent reacted acrylate unsaturation, %RAU) was calculated by changes of the acrylate peak area against the reference peak.

2.5 Fiber drawing simulation

We have been evaluating our coatings on DTS to simulate actual optical fiber drawing conditions[1]. DTS uses metallic wire of 125 μm in diameter instead of glass so that changes of draw speed do not affect the temperature of the substrate on which coatings are applied. Figure 1 shows our DTS. The wire is coated with a secondary coating by single coating die. The coated wire is cured with a single UV-LED lamp or conventional metal halide lamp. The coating was cured under 3 % oxygen flow. The wire drawing speeds were 200 to 1200 m/min. The diameter of coated metallic wire was 230 μm. The thickness of coatings was 52.5 μm. Young's modulus of the coating was evaluated by tubular sample obtained by removal of the metallic wire. Surface cure of the coating was evaluated by FT-IR as the same method as that for film.

2.6 Evaluation of abrasion resistance of fibers

The coated wire ran on DTS being rubbed against stainless steel rod as abrasion device. Accumulated debris or shavings on the rod were compared[2].

3 Results and Discussion

3.1 Influence of UV-LED lamp power on curing speed of coatings

There is no common ground to compare irradiance and energy illuminated by UV-LED and metal halide lamp. This is because an irradiance meter has its own sensitivity dependence on wavelength so

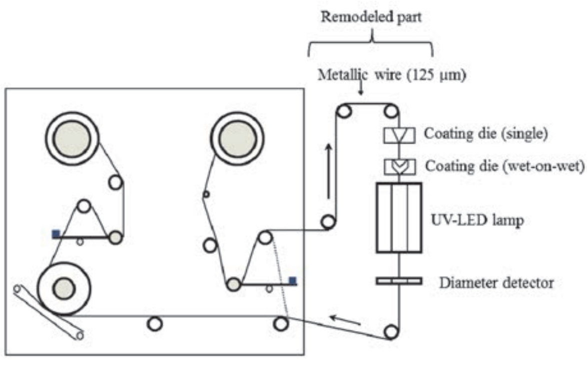


Figure 1 Schematic diagram of Draw tower simulator (DTS) with UV-LED lamps for optical fiber coatings.

that monochromic UV-LED and multi-chromic metal halide lamp cannot be compared evenly. As a practical comparison, we put UV-LED lamps on the existing UV conveyer and compare them how they cure the coatings at the same conveyer speeds. UV-LED lamps of 365 nm with high and low power were used to investigate the influence of lamp power on curing speed. UV irradiance and UV doses at various conveyer speeds were measured by the same irradiance meter (UVPF-A1, EYE GRAPHICS Co., Ltd.) as a reference, although the values are not consistent between UV-LED and metal halide lamp. The UV irradiances of 365 nm UV-LED with two types of lamp power were around 1,050 mW/cm^2 and 3,600 mW/cm^2 at any conveyer speed, respectively (Figure 2). Figure 3 shows relationship between conveyer speed and UV dose. When you compare Figures 2 and 3, it is clear that UV-LED and metal halide lamp are not fairly compared, since the metal halide lamp indicated the lowest irradiance showed higher UV dose than UV-LED of 365 nm with lower power. If you look at two UV-LED lamps, there is also an inconsistency. Namely, since the irradiance of UV-LED with higher power has about three times higher irradiance, it should show three times higher UV dose at every lamp speed. However it is not the case indicating non-liner sensitivity of the irradiance meter. Due to the inconsistency mentioned above, Young's modulus of cured films can be a common indicator of UV lamp performance. Therefore Young's modulus is plotted against conveyer speed to evaluate curing ability of each UV lamp. Figure 4 plots Young's modulus against conveyer speed. In case of UV-LED of lower lamp power, Young's modulus decreased with an increase of conveyer speed. On the other hand, Young's modulus of cured film obtained by UV-LED with higher lamp power kept almost the same level throughout the conveyer speeds. The metal halide lamp showed decline of the modulus as the conveyer speed went up. It was indicated that higher lamp power of UV-LED cures the secondary coating comparably or much better than the metal halide lamp. It seems that the performance of UV-LED lamp is highly dependent on the lamp power.

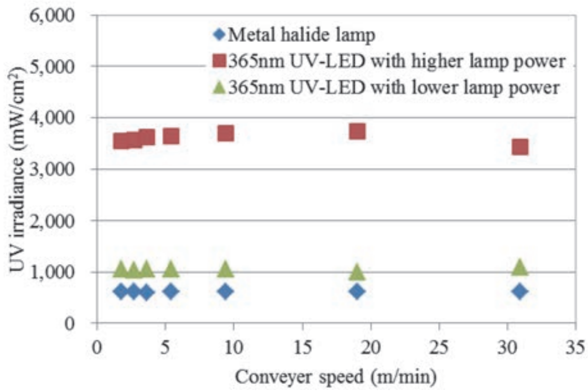


Figure 2 Relationship between conveyer speed and UV irradiance of 365 nm UV-LED and metal halide lamp.

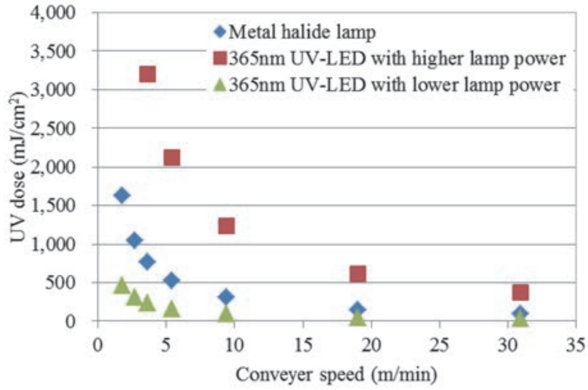


Figure 3 Relationship between conveyer speed and UV dose of 365 nm UV-LED and metal halide lamp.

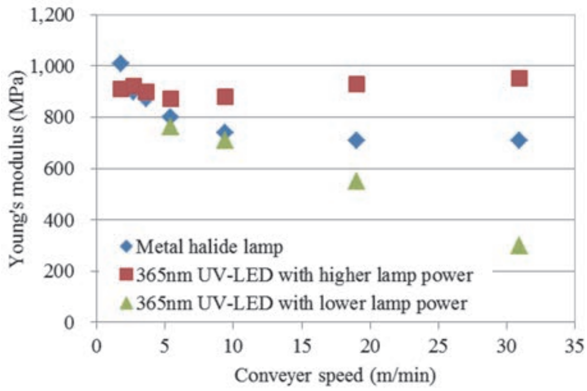


Figure 4 Relationship between conveyer speed and Young's modulus by using 365 nm UV-LED with high and low powers and metal halide lamp.

3.2 Influence of wavelength of UV-LED on curing speed of coatings

Cure speed of conventional secondary coating was investigated by using UV-LED lamps with different wavelength (365, 385 and 395nm). Results are plotted in Figure 5. UV-LED lamps with 385 and 395 nm behaved strangely. Namely, as the conveyer speed increases, Young's modulus goes up. The higher conveyer speed gives the smaller energy to the coating and usually it results in lower Young's modulus. It seems that this is not the case for these two UV-LED lamps. It is possible that the lack of heat irradiated from the UV-LED lamp might have an effect of Young's modulus build up. However, there is no clear explanation for this phenomenon at this moment.

3.3 Surface cure under UV-LED lamps for coatings

As the outer coating of optical fiber, surface cure of the secondary coating is important. If the surface cure is poor, handling of the optical fiber could be difficult because of the sticky surface. To evaluate surface cure, the liquid coatings were cured with 200 μm thickness under 6 % oxygen at 30.9 m/min conveyer speed by using UV-LED having higher lamp power with different wavelength. The results of surface cure by %RAU are shown in Figure 6. The conventional secondary coating showed poorer %RAU when it is cured with UV-LED regardless of the wavelength. In case of UV-LED lamp with 365 nm, it gave poorer surface cure than the metal halide lamp, although it gave higher Young's modulus at faster conveyor speed, 30.9 m/min than the metal halide lamp (Figure 5). It was indicated that conventional secondary coating gave poor surface cure under UV-LED lamps even if the UV-LED lamp has high enough lamp power to give comparable Young's modulus to the metal halide lamp.

3.4 Influence of photo initiator on surface cure under UV-LED lamps

As the countermeasure of surface cure improvement for UV curable coatings, influence of photo initiator on surface cure under UV-LED lamps was investigated. Figure 7 shows the surface cure of coatings with several photo initiator packages under UV-LED lamps with different wavelength. Samples A, B and C were prepared by the adjustment of photo initiator package based on the formulation of conventional secondary coating which was listed as "Reference" in Figure 7. Sample A, B and C showed better surface cure than that of the reference sample. It was found that the selection of photo initiator has a big effect on surface cure under UV-LED suggesting matching of wavelength from UV-LED and absorption of photo initiator is important. It was noted that by adjusting the photo initiator package to the appropriate composition, that is Sample B, surface cure under UV-LED became the same level as that of metal halide lamp.

3.5 Draw tower simulator (DTS) evaluation of conventional secondary coatings

Cure behavior of conventional secondary coating by using several UV-LED lamps with different wavelength in comparison to conventional 6 kW

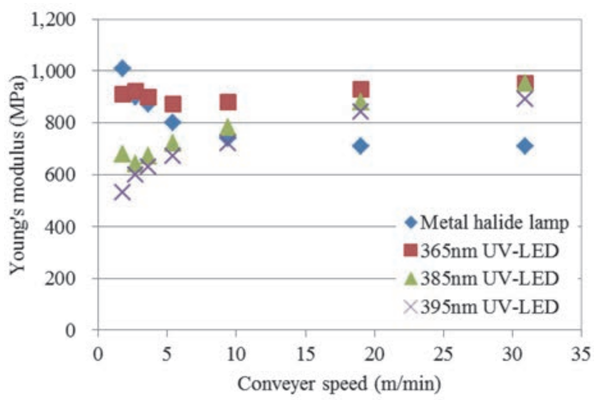


Figure 5 Relationship between conveyer speed and Young's modulus by using UV-LED and metal halide lamps with different wavelength.

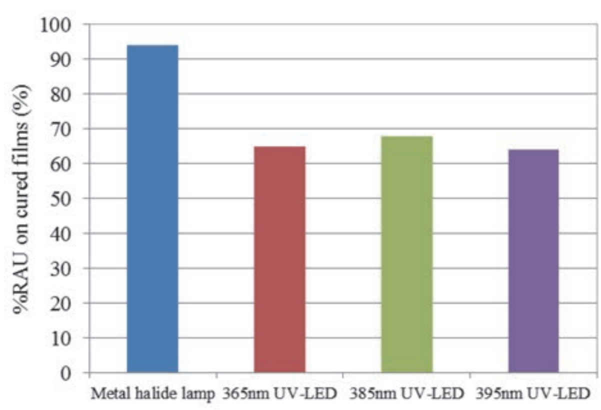


Figure 6 Surface cure of films under UV-LED and metal halide lamps with different wavelength.

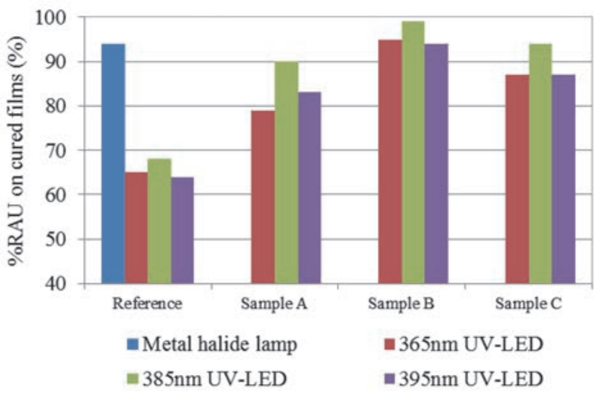


Figure 7 Surface cure of coatings with various photo initiator packages under UV-LED lamps with different wavelength.

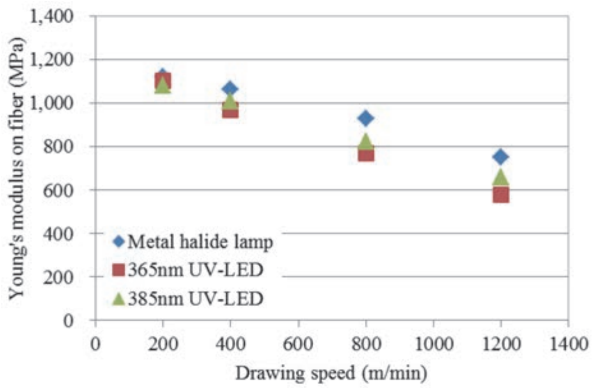


Figure 8 Relationship between drawing speed and Young's modulus on wire of conventional secondary coating by using UV-LED with different wavelength and metal halide lamp.

metal halide lamp was investigated by our DTS. Figure 8 shows the relationship between drawing speed and Young's modulus of conventional secondary coating on metallic wire. In case of metal halide lamp, the Young's modulus on fiber decreased as the drawing speed increased. In case of UV-LED lamp with 365and 385 nm, Young's modulus also decreased with an increase of drawing speed, but the decline of Young's modulus under UV-LED lamps was larger than that of 6 kW metal halide lamp, which means curing speed under UV-LED lamp of conventional secondary coating is lower than the metal halide lamp. Regarding the surface cure, the relationship between drawing speed and surface cure of conventional secondary coating on wire was investigated (Figure 9). Similar to the behavior of film evaluations mentioned above, the conventional secondary coating showed poorer %RAU at any drawing speeds when it was cured with UV-LED regardless of the wavelength. It was confirmed that conventional secondary coating also gave poorer surface cure under UV-LED lamps than the metal halide lamp by the DTS experiments.

3.6 DTS evaluation of secondary coatings with customized photo initiator package

Cure behavior of secondary coating, Sample B, with customized photo initiator package was investigated by our DTS. Figure 10 shows the relationship between drawing speed and Young's modulus of Sample B by using UV-LED lamps with different

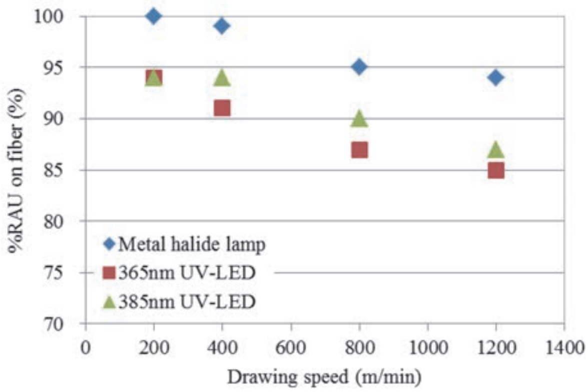


Figure 9 Relationship between drawing speed and surface cure on wire of conventional secondary coating by using UV-LED with different wavelength and metal halide lamp.

wavelength. Young's modulus of Sample B under UV-LED was slightly higher than that by metal halide lamp at any drawing speeds. Young's modulus decline of metal halide lamp using conventional secondary coating is steeper than those of UV-LED samples using Sample B. This indicates if the coating has appropriate photo initiator package, the UV-LED lamps can cure the coating with comparable ability to the metal halide lamp. Figure 11 shows relationship between drawing speed and surface cure on wire of Sample B by using UV-LED lamps with different wavelength. Sample B showed almost the same surface cure as the conventional secondary coating cured by metal halide lamp at any drawing speeds. Based on these results, it was indicated that Sample B showed comparable curing speed and sur-

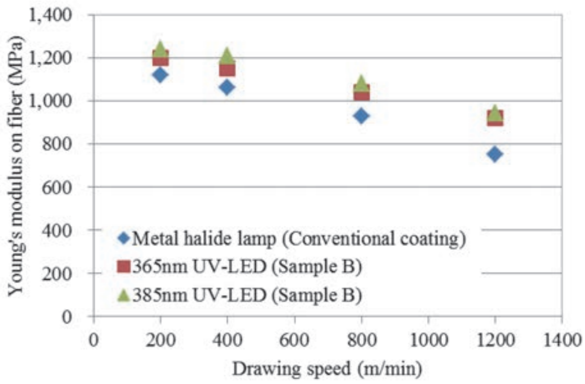


Figure 10 Relationship between drawing speed and Young's modulus on wire of customized secondary coating by using UV-LED lamps with different wavelength.

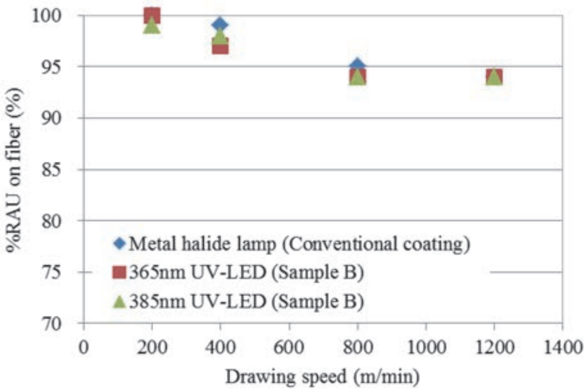


Figure 11 Relationship between drawing speed and c surface cure on wire of customized secondary coating by using UV-LED lamps with different wavelength.

face cure to that of metal halide lamp, and adjustment of photo initiator package of coating is important when you apply the UV-LED lamps to UV curable coatings for optical fiber.

3.7 Abrasion resistance of secondary coating cured by UV-LED

One of the issues which UV curable coating is facing is that tolerance to shaving, that is, abrasion resistance in actual usage for optical fibers. When optical fiber runs through drawing machine, the surface of the fiber touches and detaches to the various parts. The surface of the UV coating should not be shaved. If the surface cure of the secondary coating is poor, abrasion resistance could be a big problem. It was reported that model experiments using our DTS clearly showed the difference in the behavior from coating to coating[2]. This time, based on this procedure, the wire coated with Sample B was evaluated. It ran being rubbed against stainless steel rod equipped with our DTS as abrasion device at 400 m/min of drawing speed (Figure 12). Then, accumulated debris or shavings on the rod were compared with between fibers. Table 1 shows the comparison of accumulated debris of the coatings cured under several UV lamps. In the case of metal halide lamp, abrasion resistance depends on coatings, which means conventional coating A showed less debris (good abrasion resistance) and another conventional coating C showed much debris (poor abrasion resistance). As for customized secondary coating, Sample B, under UV-LED lamps, abrasion resistance gave moderate to tolerance giving a little shaving. It was indicated that even if UV-LED lamps was used, certain level of abrasion resistance can be realized by using the coating with customized photo initiator package.

4 Conclusions

To demonstrate the applicability of UV curable coatings for optical fiber to UV-LED lamps, cure behavior of conventional secondary coatings was investigated by using several UV-LED lamps with different lamp power and wavelength in comparison to conventional metal halide lamp. Regarding curing speed of UV-curable coatings under UV-LED, it was indicated that higher lamp power of UV-LED was effective to obtain comparable curing speed to that of metal halide lamp. As for surface cure under UV-LED, it was found that the selection of photo initiator has a big effect suggesting matching of wave-

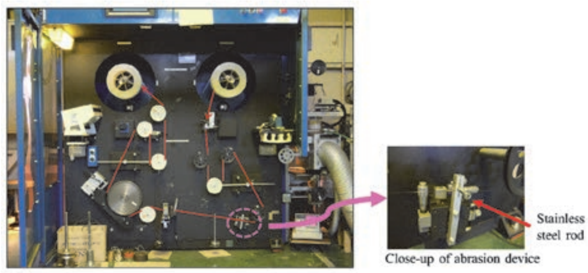
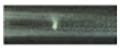


Figure 12 DTS for evaluation of abrasion resistance of coated wire.

Table 1 Comparison of accumulated debris of coatings cured under various UV lamps

Coatings	UV lamps	Abrasion resistance
Conventional coating A (exhibted as Reference in this paper)	Metal halide lamp	 Good
Conventional coating B	Metal halide lamp	 Poor
Sample B	365nm UV-LED	 Moderate
Sample B	385nm UV-LED	 Moderate

length from UV-LED and absorption of photo initiator is important, and also by adjusting the photo initiator package to the appropriate composition, surface cure under UV-LED became the same level as that of metal halide lamp. It should be noted that adjustment of photo initiator package of coatings is important to apply the UV-LED lamps to UV curable coatings for optical fiber especially for surface cure of coatings. As shown in this paper, the fact that the cure speed and surface cure can be satisfactory level if UV-LED has high enough irradiance and the coating has appropriate photo initiator package would accelerate the introduction of UV-LED lamps to optical fiber production.

Published conference

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