Prediction of Physical Properties of Optical Fiber Coatings

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The long-term reliability of optical fibers heavily depends on the durability of the protective coating layers surrounding the glass fiber. The physical properties of the inner layer coating, such as Young's modulus and gel fraction are crucial to the durability. Ultraviolet light (UV) curable resins are commonly used for coating, and accurate prediction of the physical properties under different irradiation condition is essential for optimizing the manufacturing process. However, the complex reaction mechanism involved in UV irradiation-induced radical polymerization poses challenges in accurately modeling these properties. In this study, we presents an analytical formula based on chemical reaction kinetics to determine the concentration of photoinitiators. Moreover, we successfully predict coating properties by utilizing a calibration curve that compares the photoinitiator consumption rate with the coating properties after the curing process.

Keywords: optical fiber, UV-curable resin, chemical kinetics, long-term reliability

1. Introduction

The recent spread of cloud services and generative AI have resulted in the construction of data centers worldwide, leading to a subsequent increase in data traffic. Data communication relies on optical fiber cables, which are assumed to be used for more than a decade after installation, therefore, long-term reliability is crucial for the optical fibers within these cables.

Figure 1 illustrates the structure of an optical fiber, which consists of a transmitting glass fiber and two protective coating layers. The primary layer serves to disperse external forces applied to the glass fiber and reduce the increase in microbending attenuation. The secondary layer protects the glass fiber from external damage.

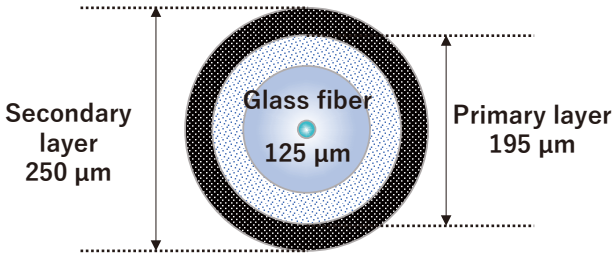

Fig. 1. Structure of a typical optical fiber

UV-curable resin*1 (UV resin) is a widely used coating material for optical fibers. In the manufacturing process, two layers of liquid UV resin are applied onto the surface of a glass fiber that is drawn to an outer diameter of 125 µm through heating and stretching of the optical fiber preform. These resin layers are then cured by ultraviolet light (UV) irradiation. In the curing reaction, the photoinitiator (PI) in the UV resin generates radicals upon exposure to UV, initiating the polymerization reaction. Coating properties, such as Young's modulus (E_p) and gel fraction (R_{Gel}) of the primary layer, are closely related to long-term reliability, and they can be influenced by various UV irradiation conditions, including intensity and time of UV irradiation. It is important to determine appropriate UV irradiation conditions for maintaining the coating properties within a controlled range at the optical fiber production, as well as to compare and evaluate the performance of coating resins. In order to achieve this quickly and accurately, it is desirable to establish a method to estimate the E_P and R_{Gel} obtained under arbitrary UV irradiation conditions in advance.

In the field of optical fibers, limited studies have been conducted on coating curing reactions[1],[2] with no attempts made to estimate coating properties. UV resins consist of a wide range of components, including monomers and oligomers, in addition to PI. Analyzing the curing reaction mechanism involving these components is complex and challenging, making it difficult to solely rely on chemical reaction kinetics.*2

In this paper, we present a newly derived PI concentration equation based on chemical reaction kinetics. Our approach focuses especially on PI-related reactions, rather than all the components in UV resins. By using this equation, it becomes possible to predict the PI concentration under arbitrary UV irradiation conditions. Additionally, we demonstrate the application of this equation to a calibration curve relating PI consumption rate after curing to the resulting coating properties, thereby enabling the prediction of these properties.

First, we derive the PI concentration equation. Then we present the correlation between the predicted and measured PI concentrations, as well as the predicted and measured curing properties. Finally, we conclude with our findings.

2. PI Concentration Formula

2-1 Coating curing in the optical fiber drawing process

In the drawing process, there are various types of UV

irradiators available, including metal halide lamps, light-emitting diodes, and others. UV resins may also include different types of PIs that absorb specific UV wavelengths. Therefore, it is crucial to select the appropriate UV irradiator based on the specific type of PI used in the resin. However, for the purpose of simplifying calculations and analysis, we will assume the use of a single type of PI and a single type of UV irradiator.

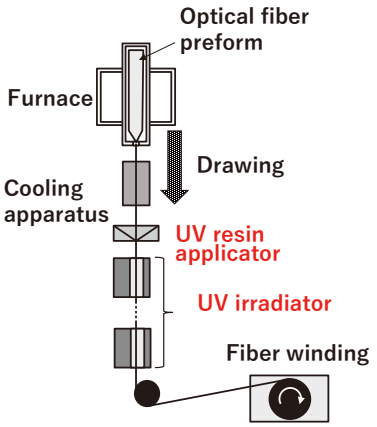

Fig. 2. Optical fiber drawing

2-2 Elementary reactions of PI

The general reaction formulas for curing reaction of UV resins can generally be written as follows.

Initiation reaction: $PI + hv \rightarrow 2R\cdot$
$R\cdot + M \rightarrow R\text{-}M\cdot\ (= P\cdot)$
Propagation reaction: $P\cdot + M \rightarrow P\text{-}M\cdot\ (= P\cdot)$
Termination reaction: $P\cdot + \cdot P \rightarrow P\text{-}P$

In this study, hv represents UV photons, R· refers to radical molecules, M denotes reactive components such as monomers or oligomers, P· represents polymer radicals, and P-P refers to resulting product polymers.

First, the PI absorbs UV photons and generates radicals that initiate the reaction. These radicals then interact with nearby reactive components (initiation reaction). Subsequently, the radicals propagate by moving to other reactive components and reacting with them. This process is repeated and leads to the growth of polymer radicals (propagation reaction). Conversely, when polymer radicals react with one another, bonds are formed and the radicals lose their activity (termination reaction). Considering all of these reactions to predict the physical properties is highly complex and challenging.

For simplicity of analysis, this study focuses solely on the reactions associated with the PI. Specifically, we consider the radical formation reaction, dark reaction, and recombination reaction. Each of these reactions can be described by the following elementary reaction formulas.

Radical formation reaction: $PI + hv \rightarrow 2R\cdot\ [\,k\,]$
Dark reaction: $PI + hv' \rightarrow 2R\cdot\ [\,k_D\,]$
Recombination reaction: $2R\cdot \rightarrow PI\ [\,k_R\,]$

For dark reactions, hypothetical UV irradiation is assumed and hv' represents its photons. k, k_D, k_R are the reaction rate constants for each reaction.

In the following, the reaction rate equations for each elementary reaction are derived and integrated to obtain the PI concentration equation after the curing reaction.

2-3 Radical formation reaction

The PI molecules undergo a radical formation reaction, producing two radical molecules upon UV absorption. The reaction rate equation for this radical formation reaction is expressed by Eq. (1).

$$dC_I(t)/dt = -k'\varphi BC_I(t) \quad \cdots\cdots (1)$$

Here, t represents time, k' is the reaction rate constant, φ denotes the nominal output ratio ($0 \leq \varphi \leq 1$), B [kW] represents the standard power of the UV irradiator, and C_I [wt%] denotes the PI concentration. Since the same UV irradiator is assumed for all units in the drawing process in this study, we can let B be a constant and write $k'B = k$. Considering the case where N units of UV irradiators are used for coating curing, the solution to the differential equation in Eq. (1) can be expressed as shown in Eq. (2).

$$C_I = C_0 exp(-k\varphi N t_I) \quad \cdots\cdots (2)$$

Here, C_0 [wt%] represents the initial concentration of the PI, and t_I [sec] shows the UV irradiation time per one unit of UV irradiator. Although it is understood that k can potentially vary as optical fiber passes from the first unit to the Nth unit of irradiator, for the purpose of simplifying the description, we treat k as a constant throughout the entire irradiation process.

2-4 Dark reaction

Dark reaction[3] refers to the phenomenon where radicals generated by previous UV irradiation continue the polymerization reaction even in the absence of UV irradiation. It is known that UV resin achieves a greater cure degree in intermittent irradiation with non-irradiated sections compared to continuous irradiation, and this is attributed to the effect of the dark reaction. In the non-irradiated sections, no new radicals are generated, and the propagation reaction proceeds at a lower radical concentration than during irradiation. This leads to a reduction in the termination reaction rate and the formation of higher molecular weight polymers.

To incorporate this phenomenon into the analytical equation for PI concentration, we introduce a hypothetical UV irradiation that is assumed to promote PI consumption. Assuming that the intensity of the hypothetical UV irradiation is proportional to the φ of the immediately preceding actual UV irradiation, the chemical reaction rate equation for the dark reaction is expressed as follows.

$$dC_I(t)/dt = -k_D C_I(t)\varphi \quad \cdots\cdots (3)$$

To take into account for the influence of the dark reaction on the PI concentration, we multiply the term derived from Eq. (3) with Eq. (2). In this case, if the PI concentration considering both the radical formation reaction and the dark reaction, is denoted as C_I' and the non-irradiation time as T, it can be expressed as follows.

$$C_I' = C_0\, exp(-k\varphi N t_I) \times exp(-k_D \varphi N T) \quad \cdots\cdots (4)$$

2-5 Recombination reaction

For this study, the PI concentration equation takes into account the recombination reaction, where two radicals generated from PI combine and deactivate before reacting with reactive components[4], is considered in the PI concentration equation. The reaction rate equation for this recombination reaction can be expressed as follows, based on the chemical reaction equation described in Section 2-2.

$$dC_R/dt = -k_R C_R(t)^2 \quad \cdots\cdots (5)$$

Here, C_R [wt%] represents the radical concentration. By solving Eq. (5) for the generated radical concentration C_R, we obtain the following expression.

$$C_R = C_{R0}/(1 + k_R t C_{R0}) \quad \cdots\cdots (6)$$

C_{R0} [wt%] represents the initial concentration of radicals. In order to establish a practical expression, determinting the initial concentration of radicals is necessary. However, due to the challenges in its determination, the initial value is assumed as in Eq. (7) in this study.

$$C_{R0} = 2C_0(1 - exp(-(kt_I + k_D T)\,\varphi) \quad \cdots\cdots (7)$$

This assumption considers the theoretical concentration of radicals produced by the radical formation reaction through one UV irradiator and the dark reaction occurring in one non-irradiated section. Based on this assumption, the PI concentration produced by the recombination reaction can be represented as C_I" according to the following expression of Eq. (8).

$$C_I'' = \frac{C_0(1 - \exp(-(kt_I + k_D T)\,\varphi))}{1 - 1/(1 + 2Nk_R t_I C_0(1 - \exp(-(kt_I + k_D T)\,\varphi)))} \quad \cdots (8)$$

2-6 PI concentration formula

The equation of C_{Net} for predicting PI concentration considering radical formation, dark and recombination reactions is obtained by summing Eqs. (4) and (8).

$$C_{Net} = C_I' + C_I'' \quad \cdots\cdots (9)$$

The variables in Eq. (9), namely k, k_D, and k_R, are unknown and can be determined based on experimental results. Once these values are determined, the PI concentration can be predicted using this equation.

3. Experiment

3-1 Optical fiber drawing

Optical fibers were fabricated using the optical fiber drawing machine as shown in Fig. 2. The optical fiber preform was melted in a furnace and stretched to 125 μm in diameter to make a glass fiber. After cooling it rapidly, two layers of UV resin were applied on the glass fiber and cured using several UV irradiators with light-emitting diode modules, and the optical fiber was wound onto a bobbin. The diameter of the primary layer was about 195 μm and that of the secondary layer was about 250 μm.

A total of 48 different samples were obtained by changing the irradiation conditions, such as the number of UV irradiators, the nominal output ratio, irradiation time, and the length of the non-irradiated section. The non-irradiation time was adjusted by the installation distance between adjacent irradiators, and the irradiation time was adjusted by the line speed.

3-2 C_{Net} and PI consumption rate R_{PI}

Both the primary and secondary layers of the optical fiber coating contain the same PI. In this study, the combined PI concentration of the two layers is referred to as C_{Net} for further analysis.

To measure C_{Net}, the prototype optical fiber was initially immersed in an organic solvent to extract and remove the uncured components. Then, the coating was decomposed using acid. The concentration of specific elements obtained through ICP emission spectroscopy was used to calculate C_{Net}. Similarly, the initial PI concentration C_0 in the resin was measured using the optical fiber without solvent extraction following the same procedure.

In subsequent analyses, the PI consumption rate (R_{PI}) expressed in Eq. (10), is used instead of C_{Net}. R_{PI} represents the concentration of PI consumed under a given UV irradiation condition and is calculated as (C_0-C_{Net}) divided by the initial PI concentration, C_0. The value is expressed as a percentage.

$$R_{PI} = 100 \times (1 - C_{Net}/C_0) \quad \cdots\cdots (10)$$

3-3 Measurement of R_{Gel}

The optical fiber samples were immersed in an organic solvent to extract and remove uncured components. After extraction, the samples were dried, and the weight after drying w was measured. The gel fraction R_{Gel} is determined using the weight of optical fiber before extraction w_0 and that of glass fiber w_g, according to the following Eq. (11)

$$R_{Gel} = 100 \times (w - w_g)/(w_0 - w_g) \quad \cdots\cdots (11)$$

3-4 Measurement of E_P

The Young's modulus of primary layer E_P was measured using the method described in Reference (5).

4. Results

4-1 UV dose dependence of coating properties

The parameter $N\varphi t$ is considered to be proportional to the UV irradiation dose and is referred to hereafter as "UV dose". The PI consumption rate R_{PI}, the gel fraction R_{Gel}, and the Young's modulus of primary layer E_P can be influenced by the UV dose. It is important to note that these values are presented and analyzed as relative values, hereafter.

Figure 3 illustrates the dependence of R_{PI} on UV dose. As the UV intensity increases, R_{PI} also shows a monotonically increasing trend, stratified by φ. Additionally as φ increases, R_{PI} tends to decrease at the same UV dose with increasing φ, indicating an inverse relationship between φ and R_{PI}.

Figure 4 shows the UV dose dependence of R_{Gel} and E_P. Both R_{Gel} and E_P displays a logarithmic increase as the UV dose increases. On the other hand, similar to R_{PI}, E_P and R_{Gel} tend to decrease significantly with increasing φ even at the same UV dose.

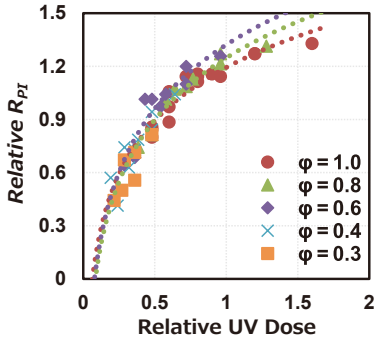

Fig. 3. UV dose dependence of R_P

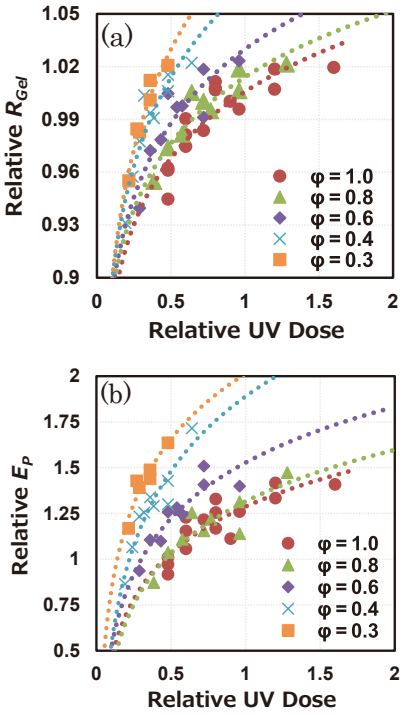

Fig. 4. (a) UV dose dependence of R_{Gel}
(b) UV dose dependence of E_P

4-2 Calibration curve of PI concentration and curing properties

The calibration curves for R_{Gel} and E_P plotted against R_{PI} are illustrated in Fig. 5.

Similar to Fig. 4, the calibration curves in Fig. 5 shows a startification based on φ. This implies that there are variations in the cured properties of the coating resin even when the same amount of PI is consumed.

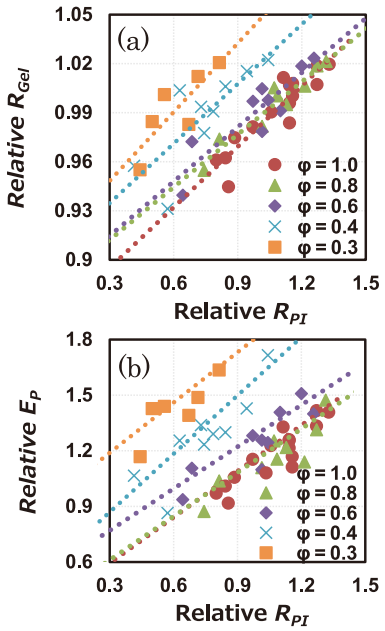

Fig. 5. (a) Calibration curve for R_{Gel} versus R_{PI}
(b) Calibration curve for E_P versus R_{PI}

5. Discussion

5-1 UV dose dependence of R_{Gel} and E_P

In Figs. 3 and 4, R_{PI}, R_{Gel}, and E_P demonstrate a dependence on the nominal output ratio φ, which is considered to be proportional to the UV intensity irradiated onto the optical fiber. These values decrease as φ increases, indicating the effect of the termination reaction.

The rate of the termination reaction increases as the concentration of radicals increases. When the termination reaction dominates the curing process, it suppresses the propagation reaction of polymer radicals, and the degree of curing for the UV resin is reduced. This effect is more prominent in UV resins with a lower modulus for similar resin compositions. In the case of optical fibers, the Young's modulus of the primary layer is typically less than 1 MPa, while the Young's modulus of the secondary layer is greater than 1,000 MPa. Consequently, the UV intensity dependence of the degree of curing appears to be more pronounced in the primary layer.

5-2 Determination of reaction rate constants

In the PI concentration equation, as shown in Eq. (8), the unknown reaction rate constants k, k_D and k_R are determined using the least squares method with the measured values of R_{PI}. The results of this determination are presented in Table 1.

Table 1. Calculation results of each reaction rate constant by fitting

	Initiation reaction	Dark reaction	Recombination reaction
Reaction rate constants	k	k_D	k_R
	66	0	0

However, it should be noted that the estimated values for both k_D and k_R are determined to be 0. This contradicts the trend observed in Fig. 3, which indicates that R_{PI} decreases with higher UV intensity, suggesting that k_R should be greater than 0. This discrepancy may be attributed to factors such as the potential influence of measurement error in R_{PI} on the PI concentration. Further investigation is needed to address this discrepancy and improve the accuracy of the rate constant estimation.

Next, the correlation between the calculated and measured values of R_{PI} is shown in Fig. 6.

The regression line of the plot has a slope of 1.01, and the coefficient of determination (R^2) is 0.92. These values indicate a strong correlation between the calculated and measured values. Based on these results, it can be concluded that the newly developed equation of Eq. (9) can be used to accurately predict PI concentrations with high accuracy under arbitrary UV irradiation conditions.

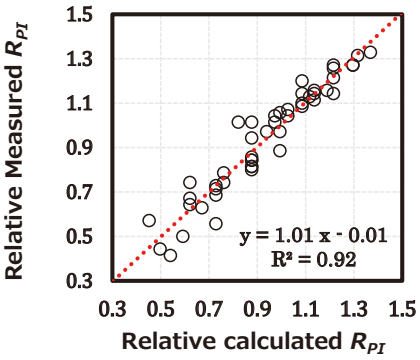

Fig. 6. Correlation between relative R_{PI} measured and calculated values

5-3 Prediction of curing properties

By using the reaction rate constants obtained in section 5-2, the PI concentration equation, and the calibration curves between PI concentration and curing properties, the predicted values of R_{Gel} and E_P can be calculated. The measured values as well as calculated values for each irradiation condition are then plotted in Fig. 7.

Both R_{Gel} and E_P demonstrate a strong correlation between calculated and measured values, as indicated by the regression line slopes of 1.01 and 1.02, respectively. Additionally, the coefficients of determination (R^2) of 0.78 and 0.79 further support this correlation.

These results validate the possibility of predicting coating properties by calculating PI concentrations under arbitrary UV irradiation conditions and establishing a calibration curve for coating properties.

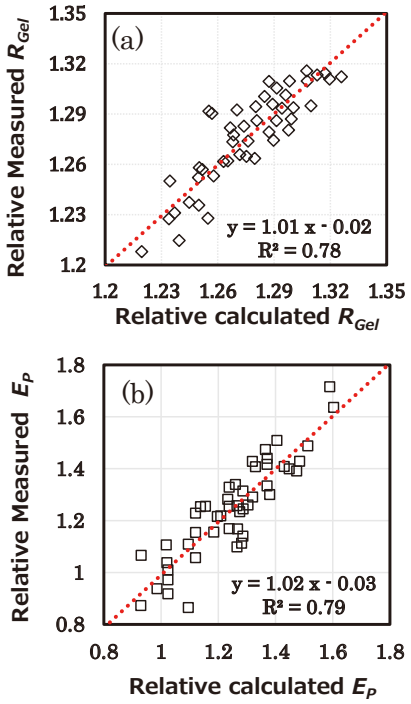

Fig. 7. (a) Correlation between relative R_{Gel} measured and calculated values
(b) Correlation between relative E_P measured and calculated values

6. Conclusion

A new PI concentration equation is developed based on chemical reaction kinetics. It enables the prediction of PI concentration under arbitrary conditions. Additionally, the establishment of a calibration curve relating PI concentration to important coating properties, such as gel fraction R_{Gel} and Young's modulus of primary layer E_P, which directly impact the reliability of optical fiber.

To further enhance the accuracy of predictions, improvements are required in accurately measuring PI concentration and coating properties. Additionally, further research is needed to clearly understand and account for the effects of dark reactions and recombination reactions.

Technical Terms

∗1 UV curable resin: A synthetic resin commonly used in various industries contains photoinitiators (PIs), monomers, and oligomers. PIs play a crucial role in the curing process of the resin when exposed to UV. Upon UV irradiation, PIs generate radicals, which in turn initiate the chain polymerization reaction.

∗2 Chemical reaction kinetics: The study of mathematical elucidation of changes in the amount of substances over time resulting from chemical reactions. It aims to analyze the underlying mechanisms of complex reactions by breaking them down into elementary reactions and simplifying them through steady-state approximations and collision models.

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