

Estimation of Long-Term Change in Physical Property of Optical Fiber Coating Considering Effect of Humidity

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Our team has developed a degradation model considering the effect of humidity on Young's modulus of primary coating in the optical fiber, i.e. in situ modulus (ISM), and also established an estimation method for the long-term change in ISM based on the model. This method allows the estimation of ISM degradation at arbitrary conditions of temperature, relative humidity and duration. The derived contour profile of standard degradation duration, which is the duration estimated for ISM to reach a specific retention value by the degradation, and the equation of equivalent conditions are useful tools for the estimation of long-term change in ISM.

Keywords: optical fiber, primary coating, humidity, degradation, estimation

1. Introduction

The data communication traffic is increasing rapidly year by year in Japan because of the diffusion of the Internet.⁽¹⁾ Optical networks are supporting the increase, and those include core, metro, access and submarine networks. For these networks, various optical fiber cables are utilized, and communications are conducted by optical fibers inside the cables.

A standard optical fiber has a glass fiber composed mainly of silica glass transmitting optical signals, and protective optical fiber coatings having the composition of urethane acrylate ultraviolet curable resins (abbreviated as "UV curable resin" in this paper). While UV curable resins have a tendency to be degraded by humidity over time, optical cables are installed in various places, and inside of the cables where optical fibers are placed, it can sometimes become humid. Optical fibers are sometimes used for decades. Hence, it is critical for optical fiber development to estimate long-term effects of humidity on their coatings.

Although the effect of humidity on the physical property of optical fiber coatings has been presented in some papers,^{(2),(3)} they explained few details about assumptions of the utilized models and methods of the estimation. These make it difficult to conduct valid confirmation of their results and practically apply them for estimation.

We have established a method to estimate changes in an optical fiber coating's physical property at arbitrary conditions of temperature, humidity and duration, analyzing the accelerated aging test results with a degradation model.

At first, the primary coating, which is one part of optical fiber coating and focused on in this paper, and its Young's modulus are explained. Then, a degradation model, its assumptions and an analysis method are shown. Next, a way of accelerated aging tests with optical fibers and a measurement principle of Young's

modulus are described. We will conclude after their results are shown.

2. Primary Coating and ISM

Details of the optical fiber evaluated in this paper are summarized in **Figure 1** and **Table 1**. Primary, secondary and colored coatings are composed of UV curable resins, as explained above.

Young's modulus of primary coating is sometimes called "in situ modulus" (abbreviated as "ISM" in this paper), and it is typically less than 1 MPa because optical fibers are required to have a good microbending resistance. The primary coating has a low glass transition temperature of about -50°C and is normally in a rubbery state. It also has relatively lower cross-linking density than secondary and colored coatings.^{(4),(5)} Humidity causes a decrease in the primary coating's cross-linking density. It follows ISM decrease, and there are some concerns about the degradation of physical and/or optical properties of optical fibers over time. The purpose of this paper is to construct a degradation model considering humidity for ISM, and estimate its long-term changes at arbitrary conditions of temperature and humidity based on the model.

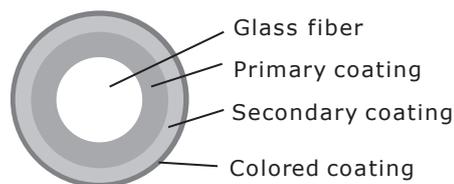


Fig. 1. Structure of optical fiber

Table 1. Details of each part of optical fiber

Part	Diameter (typ.)	Young's Modulus	Composition
Glass fiber	125 μm	-	Silica glass
Optical Fiber Coating	Primary coating	Less than 1 MPa	UV curable resin
	Secondary coating	About 1000 MPa	UV curable resin
	Colored coating	About 1000 MPa	UV curable resin Pigments

3. Model and Analysis Method

3-1 Degradation model

The degradation model considering humidity for ISM has four assumptions as below.

1. UV curable resins are degraded only by a hydrolysis reaction of urethane group caused by water vapor shown as **Equation 1** at the temperature of less than 120°C, ignoring other reactions such as pyrolysis, oxidation.



2. The rate constant of **Eq. 1** follows a modified Arrhenius formula*1 as below.⁽⁶⁾

$$\kappa \sim \exp(-\Delta E_{\text{act}} / RT) \times [\text{H}_2\text{O}] \quad (2)$$

ΔE_{act} , R , T and $[\text{H}_2\text{O}]$ are activation energy, gas constant, absolute temperature and molar concentration of water vapor, respectively (We express the molar concentration of material or functional group M as $[M]$, in this paper). κ is dependent on T and $[\text{H}_2\text{O}]$ (or humidity), and ΔE_{act} is independent of them.

3. Water vapor behaves as an ideal gas and follows the ideal gas equation⁽⁶⁾ written as

$$PV = nRT.$$

P , V and n show pressure, volume and molar number, respectively.

4. ISM is proportional to a molar concentration of urethane group of $R - \text{NHCOO} - R$, or $[U]$, based on the rubber elasticity theory.*2

The degradation model of ISM will be explained based on the assumptions. For simplicity, we will use ISM retention (expressed as “ R_{ISM} ”), instead of its absolute values.

At first, a standard R_{ISM} value has to be determined, and we express it as “ $R_{\text{ISM,st}}$.” Although the acceptable minimum value is often selected for $R_{\text{ISM,st}}$, we adopted the value of 20% referred from Tabaddor et al. (1996).⁽³⁾ We also defined a “standard degradation duration” (abbreviated here as “SDD,” and expressed as “ τ ”), which is the duration required for R_{ISM} to be degraded by $R_{\text{ISM,st}}$, and its relationship with κ as,

$$\tau = 1 / \kappa \quad (3)$$

The logarithms for both sides of **Equation 2** give,

$$\ln\{\kappa / [\text{H}_2\text{O}]\} = -(\Delta E_{\text{act}} / R) / T + C \quad (4)$$

C is a constant. When relative humidity (abbreviated as “RH” in this paper) is utilized for humidity, the molar concentration of water vapor $[\text{H}_2\text{O}]$ can be expressed as **Equation 5** under the third assumption.

$$[\text{H}_2\text{O}] = (\text{RH} / 100)\{P_0(T) / RT\} \quad (5)$$

RH and $P_0(T)$ refer to relative humidity in percent and saturated water vapor pressure at T , respectively. $P_0(T)$ is calculated from Tetens’ formula.*3,⁽⁷⁾

Next, a formula of duration dependence of R_{ISM} is derived. The change rate in molar concentration of urethane group $[U]$ can be written as below, based on chemical reaction kinetics.

$$d[U] / dt = -k[\text{H}_2\text{O}][U]$$

Here, t is duration (or time), and k is a rate constant defined as an inverse of duration needed for R_{ISM} to be degraded by $R_{\text{ISM,st}} = 1 / e$. Three points have to be considered in order to solve this differential equation. Firstly, although $[\text{H}_2\text{O}]$ could be a variable over time because water vapor is consumed by the reaction of **Eq. 1**, RH was controlled to be constant as will be explained later, and $[\text{H}_2\text{O}]$ can be considered as a constant. Secondly, R_{ISM} is equal to $[U] / [U]_0$ when $[U] = [U]_0$ at $t = 0$, under the forth assumption. Lastly, κ is defined as an inverse of SDD, which is the duration needed for R_{ISM} to reach an “arbitrary” $R_{\text{ISM,st}}$, while k is defined as one to be degraded by $R_{\text{ISM,st}} = 1 / e$. **Equation 6** can be derived, considering them.

$$R_{\text{ISM}} = (R_{\text{ISM,st}})^{\kappa t} \quad (6)$$

An equation of equivalent conditions, which is convenient to compare two or more conditions, will be explained. Here, “equivalent conditions” mean that they have the same R_{ISM} value after the degradation at each condition.

When **Eq. 2** is substituted into **Eq. 5**, and **Eqs. 3 and 6** are utilized, the next equation can be obtained.

$$t \sim (100 / \text{RH}) \times \{RT / P_0(T)\} \times \exp(\Delta E_{\text{act}} / RT)$$

Now, two sets of parameters for Condition 1 as (T_1 , RH_1 , t_1) and Condition 2 as (T_2 , RH_2 , t_2) are assumed. Expressing the equation for Conditions 1 and 2, dividing the one for Condition 1 by Condition 2 gives,

$$t_2 = t_1 \times (\text{RH}_1 / \text{RH}_2) \times \{P_0(T_1) / P_0(T_2)\} \times (T_2 / T_1) \times \exp\{(\Delta E_{\text{act}} / R) \times (T_2^{-1} - T_1^{-1})\} \quad (7)$$

3-2 Analysis method

Two parameters of κ and ΔE_{act} in **Eq. 2** have to be known in order to estimate R_{ISM} at arbitrary conditions. The analytical procedure to obtain them will be shown as below.

1. An ISM degradation data over time at an accelerated aging condition of high T and high RH is measured, and a single logarithm graph is

described with the data because logarithm of R_{ISM} is proportional to t from **Eq. 6**.

2. The data is fitted with the least square line, and τ is estimated by extrapolating or interpolating the line to be $R_{ISM,st}$. κ can be calculated from **Eq. 3**.
3. κ is obtained at several accelerated conditions, according to the steps from 1 to 2.
4. Values of $\ln\{\kappa / [H_2O]\}$ are plotted against $1/T$. The slope of the least square line for the plot is equal to $-(\Delta E_{act} / R)$, according to **Equation 4**, and ΔE_{act} can be calculated. Its intercept is the parameter C .
5. Once ΔE_{act} and C are obtained, κ at an arbitrary condition of T and RH can be estimated from **Eq. 4**, and τ from **Eq. 3**.

R_{ISM} at arbitrary duration can be calculated from **Eq. 6** with κ for an arbitrary condition of T and RH .

SDD contour profile is described, when τ values at various T and RH conditions are calculated.

Utilizing **Equation 7**, if all of the parameters for Condition 1 (T_1 , RH_1 and t_1) and two for Condition 2 (for example, T_2 and RH_2) are given, the rest of one parameter (for example, t_2) can be calculated with the value of ΔE_{act} , and equivalent conditions can be obtained.

4. Experiments

4-1 Accelerated aging test

Optical fiber samples were degraded in four different ovens which were kept at high T and high RH conditions of 70°C 85% RH, 85°C 85% RH, 110°C 85% RH, 120°C 85% RH for each. After the specified number of degradation days of 0 (control), 30, 60, 90, 120 days passed, the samples were removed from the ovens and we measured their ISM, explained in the next section.

Table 2 shows $P_0(T)$ obtained from Tetens' formula and $[H_2O]$ calculated by **Eq. 5** for the test conditions.

Table 2. Calculated $P_0(T)$ and $[H_2O]$ at four accelerated aging test conditions

Temperature	[°C]	70	85	110	120
Temperature (T)	[K]	343	358	383	393
Relative humidity (RH)	[% RH]	85	85	85	85
Saturated water vapor pressure ($P_0(T)$)	10^5 [Pa]	0.312	0.580	1.45	2.02
Molar concentration of water vapor ($[H_2O]$)	[mol/m ³]	9.30	16.6	38.7	52.4

4-2 ISM measurement

A measurement principle of ISM is shown in **Figure 2**. An optical fiber was inserted in a metal tube, and fixed with an adhesive which has much larger Young's modulus than ISM, followed by removing the optical fiber coatings outside of the metal tube, as shown in the figure. At the measurement, while the metal tube was fixed, the bare glass fiber was moved at

a constant speed of $v = 3.5 \mu\text{m} / \text{min}$, and a load expressed as W was measured against the displacement of glass fiber expressed as Z . When the secondary, colored coatings, and an adhesive layer are assumed as a rigid body, ISM can be expressed as below.⁽⁸⁾

$$ISM = \{(1 + m)W / \pi LZ\} \times \ln(D_p / D_f)$$

Here, m , L , D_p and D_f are Poisson's ratio of primary coating, length of metal tube, diameters of primary coating and glass fiber, respectively. Although a shear modulus of primary coating can be obtained by the measurement, it is converted to Young's modulus, under an assumption of isotropic material for the primary coating.*4

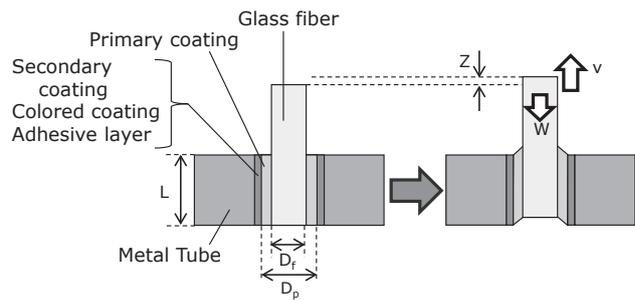


Fig. 2. Principle of ISM measurement

5. Results and Analysis

5-1 Results

The degradation duration dependence of R_{ISM} that is measured with the samples degraded at the four high T and high RH conditions explained in section 4-1 is shown in **Figure 3**.

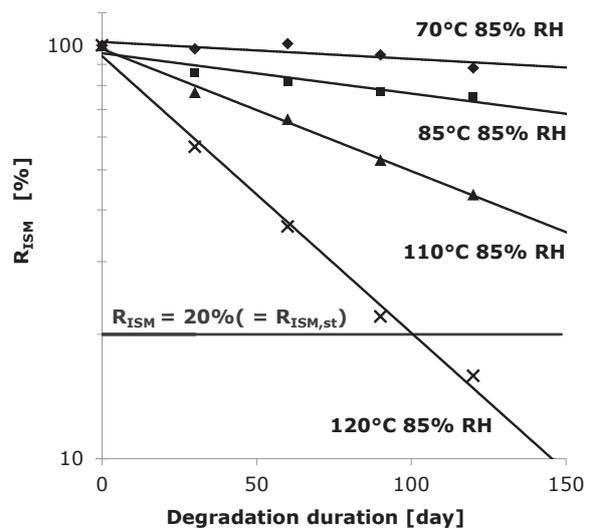


Fig. 3. Degradation duration dependence of R_{ISM}

5-2 ΔE_{act} and C

For each accelerated aging condition, τ was estimated, and values of κ and $\kappa / [\text{H}_2\text{O}]$ were calculated. The results are summarized in **Table 3**.

The values of $\ln\{\kappa / [\text{H}_2\text{O}]\}$ are plotted against $1/T$ from **Table 3**, and the result is shown in **Figure 4**. The least square line is also shown in the figure. Its slope ($-\Delta E_{act} / R$), intercept (C), and calculated ΔE_{act} are summarized in **Table 4**.

Table 3. τ , κ and $\kappa / [\text{H}_2\text{O}]$ at each accelerated aging condition

Condition	τ	κ	$\kappa / [\text{H}_2\text{O}]$
	[day]	$10^{-4}[\text{day}^{-1}]$	$10^{-5}[\text{day}^{-1}\text{m}^3 \text{mol}^{-1}]$
70°C 85 % RH	1700	5.8	6.3
85°C 85% RH	700	14	8.7
110°C 85% RH	230	43	11
120°C 85% RH	100	100	19

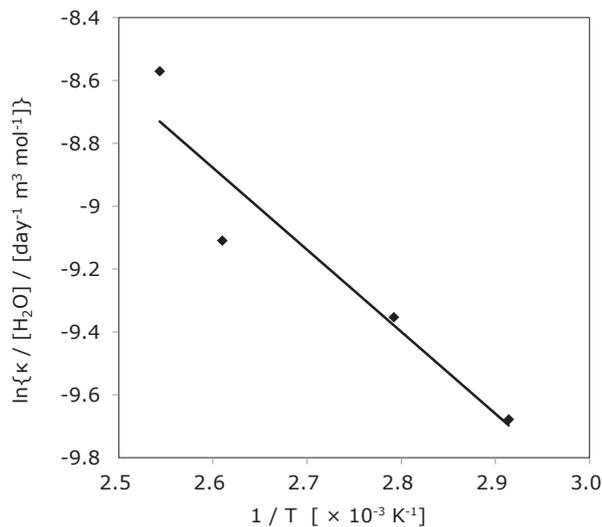


Fig. 4. $\ln\{\kappa / [\text{H}_2\text{O}]\}$ vs $1/T$ plot

Table 4. The slope, intercept of the least square line shown in Fig. 4, and calculated ΔE_{act}

Parameter	Unit	Value
Slope ($-\Delta E_{act} / R$)	[K]	-2600
Intercept (C)	[-]	-2.1
ΔE_{act}	[kJ / mol]	22

5-3 R_{ISM} estimation at arbitrary conditions

Although the estimation of long-term change in R_{ISM} is available at arbitrary conditions of T and RH with the model, we set two specific conditions for convenience. One was the condition of 40°C 75% RH, which was used in Tabaddor et al. (1996),⁽³⁾ called "Condition A," here. The other was the condition of 4°C 50% RH, as a lower temperature example, called "Condition B." A

duration of 30 years for both of the conditions was assumed.

R_{ISM} values for Conditions A and B after 30 years were estimated. $[\text{H}_2\text{O}]$ values were $2.12 \text{ mol} / \text{m}^3$ for Condition A, $0.176 \text{ mol} / \text{m}^3$ for B, calculated from Tetens' formula and **Eq. 5**. κ values were calculated from **Table 4** and **Eq. 4**. The results were $6.3 \times 10^{-5} \text{ day}^{-1}$ and $1.8 \times 10^{-6} \text{ day}^{-1}$. Hence, R_{ISM} values calculated from **Eq. 6** are 33% and 97%, respectively.

R_{ISM} at arbitrary T, RH and duration can easily be estimated, as shown in the examples above.

5-4 SDD contour profile

A contour profile of SDD in the relationship of T and RH is described, utilizing the results of **Table 4**, and shown in **Figure 5**. Points for Conditions A and B are also plotted in the figure.

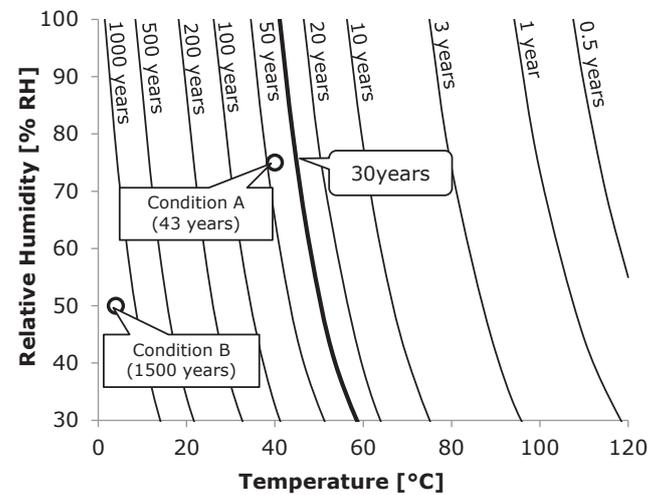


Fig. 5. Contour profile of SDD in the relationship between T and RH ($R_{ISM, st} = 20\%$)

We found that SDD became longer exponentially, when T became higher. The optical fiber which we evaluated had SDD of 43 years for Condition A and 1500 years for B, which were more than 30 years.

SDDs at arbitrary conditions of T and RH are easily determined with the profile and quick estimations of R_{ISM} at specific conditions of (T, RH, t) for various applications are available.

5-5 Equivalent conditions

Duration at Condition B which is equivalent to Condition A for 30 years was calculated from **Eq. 7**. The result was about 1100 years, and both conditions have the same R_{ISM} of 33%.

As we showed above, the equation of equivalent conditions can be used to compare two or more conditions of (T, RH, t). It can be used in order to find the relationship between accelerated aging test conditions conducted at a laboratory and an operating condition that optical fibers' performance has to be estimated, for example.

SDD contour profile is a visualizing tool of equivalent conditions at the specific value of R_{ISM} , i.e. $R_{ISM, st}$. The advantage of the equation of equivalent conditions is that equivalent conditions can be calculated without the limitation of R_{ISM} value.

6. Conclusions

A degradation model considering the effect of humidity on ISM and an estimation method of long-term change in R_{ISM} have been explained. The model is based on four assumptions; (1) adoption of single degradation mode of hydrolysis reaction for urethane group in UV curable resin by water vapor, (2) a modified Arrhenius equation for a rate constant of the reaction, (3) water vapor following the ideal gas equation, (4) ISM being proportional to a concentration of urethane group in the primary coating. An estimation method for the long-term change in R_{ISM} was also established utilizing the model. We introduced convenient tools, namely SDD contour profile and the equation of equivalent conditions.

However, this model has some limitations. There are some elements that were not taken into consideration in the conditions, but which might have impact on the method. For example, increase in estimation error is predicted when RH at operation or accelerated aging tests becomes lower because rates of other reactions like oxidation or pyrolysis would become relatively larger. These elements must be considered on applying this method.

Technical Terms

*1 Arrhenius' formula: Rate constant for many chemical reactions follows Arrhenius' formula given as $k = \exp(-\Delta E_{act} / RT)$.

A chemical reaction can be explained with a model that it has a specific energy barrier, called activation energy ΔE_{act} , and the reaction occurs when a system has higher energy than ΔE_{act} .

*2 Rubber elasticity theory: The primary coating is normally in a rubbery state, as explained in context. Rubber elasticity theory explains elasticity or modulus of rubbery materials including primary coating. From the theory, a shear modulus can be expressed as below.⁽⁵⁾

$$G = \rho RT / M_c$$

ρ and M_c are density and molecular weight between cross-linking points. Each unit chain consisting of a network of primary coatings has one or more urethane groups. When the urethane groups are decomposed by hydrolysis reaction, breakage of the chain occurs, and M_c is increased. That means the decrease in G , inversely. We assumed that $[U]$ is proportional to the inverse of M_c .

*3 Tetens' formula: This is a formula which expresses the temperature dependence of saturated water vapor pressure, and written as,

$$P_o(T) = P \times \exp\{b(T - T_1) / (T - T_2)\}.$$

Here, $P = 610.8$ Pa, $b = 17.2694$, $T_1 = 273.16$ K, $T_2 = 35.86$ K. Although there are some other formulas for saturated water vapor pressure, Tetens' formula is frequently used because it is simple and fitted well to the measurement data.⁽⁷⁾

*4 Conversion of modulus: Shear modulus (G) can be converted to Young's modulus (E), when a material is assumed to be isotropic, as following,

$$E = 2G(1 + \nu).$$

References

- (1) Lecture material for "Photonic network symposium 2014," National Institute of Information and Communication Technology in Japan, March, 25, 2014, pp. 1-10
- (2) H. C. Chandan et al., "Fiber Protective Coating Design for Evolving Telecommunication Applications," Proc. 41th IWCS, pp. 239-248 (1992)
- (3) P. L. Tabaddor et al., "An Evaluation of Protective Polymer Coatings for Optical Fiber Applications," Proc. 45th IWCS, pp. 302-311 (1996)
- (4) M. Koshiba et al., "Properties of Ultra-Violet Curable Polyurethane Acrylates," J. Mat. Sci. pp. 1447-1458 (1982)
- (5) S. Wu, "Chain Structure, Phase Morphology, and Toughness Relationships in Polymers and Blends," Polymer Eng. Sci. pp. 753-761 (1990)
- (6) G. L. Welch, "Estimating Service Life of Two Specific Potting Compounds Using Accelerated Hydrolytic Reversion at High Temperatures and Humidities," Proc. Nat'l. SAMPE Conf., Vol. 2, October, pp. 649-662 (1970)
- (7) H. Sugawara et al., "Errors in Calculation of Saturation Vapor Pressure," J. Japan Soc. Hydrol. & Water Resour., Vol. 7, No. 1, pp. 22-25 (1994)
- (8) H. Uchida et al., "Evaluation of Modulus of Inner Primary Coating of Dually Coated Optical Fiber by Using Novel Pull-Out-Modulus Technique," RadTech Japan Symposium, M14-9, pp. 112-115 (2000)

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