A Method Related to Adhesion of Glass / Primary Interface for Long-term Reliability

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ABSTRACT   A typical optical fiber is coated with UV curable resins in order to protect the glass. The coating consists of two layers, a soft inner primary layer and a hard outer secondary layer. The coatings are cured using ultraviolet irradiation. The polymerization reaction generates heat and because the coefficient of thermal expansion of the primary layer is greater than that of the secondary layer, a negative hydrostatic pressure is generated in the primary layer during the cooling process that has the potential to delaminate the primary layer from the glass. In order to ensure the long-term reliability of the optical fiber, it is important to accurately determine the adhesive force of the glass/primary interface. In this paper, we will report on a new glass/primary adhesion measurement method that has been developed for that purpose.

1. INTRODUCTION

Glass optical fibers are drawn with protective polymer coatings. In general, the protective polymer coating is a UV (ultraviolet light) curable resin. Most optical fibers have at least two coating layers. Each layer has a specific role to protect the glass. The first layer (in contact with the glass fiber), called the primary coating, works as a buffering layer against outside stresses that can cause bending loss. Therefore, the primary coating should be soft. The Young's modulus should be less than 1 MPa and the glass transition temperature (Tg) should be below the operating temperature range. The second layer, called the secondary coating, should be sufficiently hard to protect the glass from external mechanical stresses. The secondary coating should have a Young's modulus of more than 500 MPa and the Tg above 60°C.

In fiber drawing process, two coating layers of optical fiber are together heated by the curing exothermic reaction of the UV curable resin and the radiant heat from the UV lamp and the temperature of the coating layer is increased above Tg of the secondary layer. After that, the fiber is wound onto the spool while being naturally cooling to the room temperature. Therefore, whereas the phase of the secondary layer changes from a rubbery state to a glass state in the cooling process, the primary layer which Tg is lower than room temperature is present in a rubbery state. Since the coefficient of thermal expansion (CTE) of polymer materials changes greatly at the

boundary of Tg, it means that the heat shrinkage of the primary layer is larger than that of the secondary layer in the temperature range below Tg of the secondary layer. Such mismatch of the coefficient of thermal expansion generates a stress at the primary/secondary interface and a negative hydrostatic pressure in the primary layer. And also it leads to generate the force which delaminates off the primary layer from the glass at the primary/glass interface[1]-[4].

Therefore, it is estimated that the thermal stress of the secondary layer generated during the natural cooling process of the coating layer is accumulated due to the shrinkage of the outside diameter of the primary layer. While the secondary layer is cooled to the room temperature from around Tg, the outside diameter of the primary layer tends to become smaller than the inner diameter of the secondary layer. This is because the coefficient of thermal expansion of the primary layer is larger than the one of the secondary. Figure 1 illustrates a schematic diagram of the volume change occurring due to the mismatch in the coefficient of thermal expansion of the primary layer and the secondary layer. In Figure 1, β represents the coefficient of volume expansion, its subscripts represent the kind of coating material and ΔT represents the temperature difference between the room temperature and Tg of the secondary layer.

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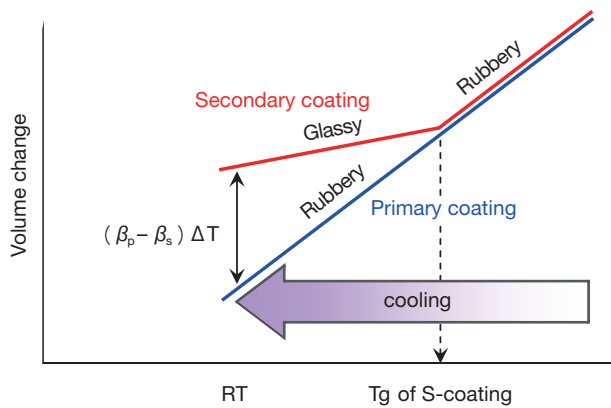   Polymer Materials R&D Laboratories

Figure 1 Schematic diagram of the volume change due to the CTE mismatch between the primary and the secondary layer.

In order to ensure the reliability of the optical fiber, it is very important to know the thermal stress of the coating layer. In other words, it is to estimate the thermal stress and the residual stress generated in the coating layers by measuring the CTE of each coating layer from the actual optical fiber. Those studies were performed by Nakajima et al and the contents are summarized in Furukawa Review of No. 34 [5].

Nowadays optical fibers, which are widely used in a variety of fields and long term optical and mechanical reliability, are requiring special features, such as various aging conditions under extreme environments typically applied to ensure optical fiber properties such as strip force, pullout force, water or solvent resistance, are maintained. When an external stress is applied on an optical fiber, coating delamination can sometimes occur at the glass/primary interface that can cause microbending loss, a failure mode in optical fibers. If the adhesive force of the glass/primary interface becomes lower than the force to delaminate the primary layer from the glass, for example, by immersing the fiber in water, it may result in generating a micro-bending loss. Therefore, it is also important to accurately determine the adhesive force of the glass/primary interface, especially, if the fiber is immersed in water, in order to ensure the long term reliability.

A pullout force test is a useful methology to measure glass/primary coating adhesion strength. The pullout test is the only available method for measuring the adhesion at the glass/primary interface of an optical fiber in situ, but the pullout force is obtained as the one combining the mechanical properties such as the tightening force of the secondary coating, the shear strength of the primary coating and coating friction with other interactions at the glass/primary interface. In other words, the pullout force covers many non-adhesive interfaces in addition to the pure adhesion at the glass/primary interface. Moreover, the pullout force depends on the tensile speed of pulling the glass fiber out of the coating as described at Section 4.1.

In view of this, the development of a new measurement method was required in order to know the correct adhesive force of the glass/primary interface, in particular, when the fiber is immersed in water.

2. THE PULLOUT TESTING METHOD FOR OPTICAL FIBERS

2.1 Fiber Sample Preparation

The UV curable resins used for primary and secondary coatings were commercially available materials. We prepared the fiber samples with values for the glass/secondary coating O.D. of 125/245 μm, respectively.

2.2 Sample Preparation Method for the Pullout Test and the Measurements

1 cm length of coating is adhered to a rigid substrate. Figure 2 shows the schematic diagram. The coating is severed at the end of the substrate and by pulling the other end of the fiber sample at a constant rate using Tensilon Type tensile tester (A&D Company, Limited, RTC-1310A), the force needed to break the adhesive bond between the glass and the coating was measured. The measurement was performed under the ambient condition of 23°C/50% relative humidity based on the FOTP-105, 1993 draft.
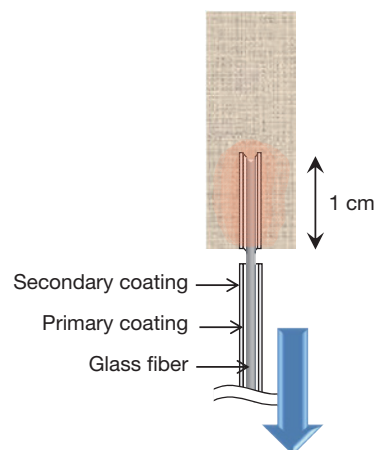

Figure 2 The schematic diagram of the sample for the pullout test.

2.3 Sample Preparation Method for the "Modified" Pullout and the Measurement Method

The "modified" pullout test sample is prepared in a similar way as the "standard" pullout test sample. For the modified pullout test we developed, a constant load is applied on the fiber, compared to the constant rate of force of the standard pullout test, and the time to pull out the glass fiber is measured. Therefore, hanging a various load to the samples, the time when the strip at the glass/primary interface begins was measured by the tags and the optical sensors. These samples are setup in the temperature/humidity chamber and the measurement was performed under a desired temperature/humidity ambient condition. The relationship between the time when the glass was pulled out from the coating and the load was determined

by changing the load gradually. In Figure 3, the typical measurement result is shown. As the load applied to the glass/primary interface decreases, the time when the glass is pulled out from the fiber increases, but when the load becomes below a certain value, the time when the fiber pullout increases rapidly and the slope becomes smooth. The load at the knee point where the slope becomes smooth is defined as the "limit adhesive force" and thereafter it is called the "static pullout force".
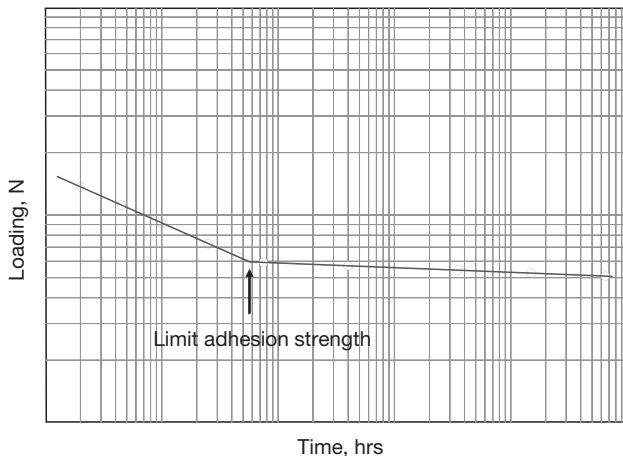
Figure 3   Typical measurement data of the static pullout force.

3.   OPTICAL FIBER PROPERTIES AFTER AGING UNDER EXTREME ENVIRONMENT

3.1   The Transmission Properties of the Ribbon After Hot Water Immersion for the Long Term

The trial fibers in section 2.1 were colored with a 5 μm thickness for identification and four fibers were arranged in parallel. The commercially available UV curable resin is applied to form 4-fiber ribbon. This 4-fiber ribbon was immersed in 60℃ hot water and the attenuation increase in the elapsed day was monitored in comparison to the initial value before water immersion.

Measurement was performed using optical pulse tester (Anritsu Corp. MW9060A). Attenuation for each fiber was measured at 1.55 μm by using optical time domain reflectometry (OTDR) method.

3.2   The Fiber Strength After Temperature and Humidity Aging

As the test sample, the trial fibers in section 2.1 were aged under zero stress in the condition of 85℃/85% relative humidity. The fibers which were cut to a length of 2 m were prepared. Both ends were fixed by wrapping onto the mandrel (ϕ100 mm). The distance between the mandrels is 500 mm. The test was based on TIA/EIA 455-28C and the fibers were pulled at a tensile speed of 2.5%/min. and the breaking strength was measured. The measurement was performed under the ambient condition of 23℃/50% relative humidity.

4.   THE RESULTS AND CONSIDERATIONS

4.1   The Relationship Between the Pullout Force and the Tensile Speed

In Figure 4, the measurement results of the pullout force when the fibers coated with two kinds of UV curable resins are pulled by changing the tensile speed are shown. As it is clear from Figure 4, the pullout force depends on the tensile speed when the glass is pulled out from the coating. And it can be seen that as the tensile speed decreases, it approaches to a certain saturated value. The measurement in Figure 4 was performed under the ambient condition of 23℃, but even when the temperature increased to 60℃, almost same result was obtained. In other words, although the tensile test is performed at the slowest speed which the tensile tester can control in order to minimize the influence of the tensile speed as less as possible, the pullout force still decreases so it is understood that there is a limit in the existing pullout test method.
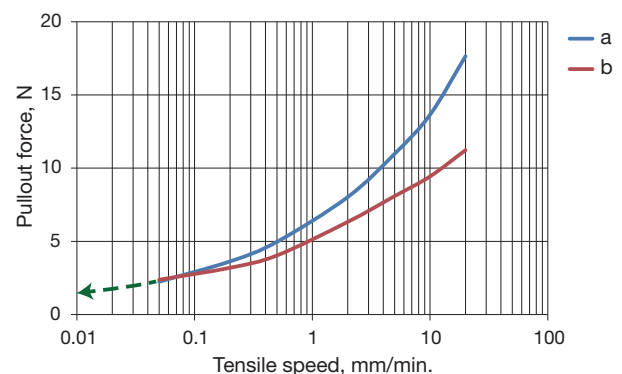
Figure 4   The pullout force vs. tensile speed.

4.2   The Measurement Condition for the Static Pullout Force

The purpose of this study is to measure the "pure" adhesive force by removing the non-adhesive factors as much as possible from the pullout force which includes many of them. By improving the dynamic pullout test where the force is measured at a constant tensile speed, and by measuring the time when the glass fiber is pulled out from the coating under the condition that a certain load is applied to the fibers, the static pullout force test method has been developed. It can be thought that the influence of the shear strength of the primary layer, the friction of the coating and etc. can be minimized as much as possible.

In order to remove the non-adhesive factors further, at first, the influence which the temperature affects the static pullout force was investigated. The testing equipment of the static pullout force is setup in the temperature/humidity chamber and the relative humidity was fixed at 50%. The temperature was set at 23℃, 45℃, 60℃ and 85℃.

The measurements were performed at each temperature. As the test results are shown in Figure 5, at any temperatures, the static pullout force was about 1.1 N so the temperature did not affect the values in this temperature range. However, it can be understood that concentrating on the time when the glass is pulled out from the coating, the time decreases as the temperature increases. In other words, it was found that the temperature does not affect the static pullout force, but it leads to shorten the measurement time. It is estimated that this time reduction is due to the reduction of the tightening force by the secondary layer. As for the test result of 60℃ and 85℃, around the static pullout force of one minute values for both temperatures were obtained. And also the subsequence values look same. Therefore, in consideration of operations, the 60℃/50% relative humidity is set as the provisional optimum ambient parameters for these conditions.
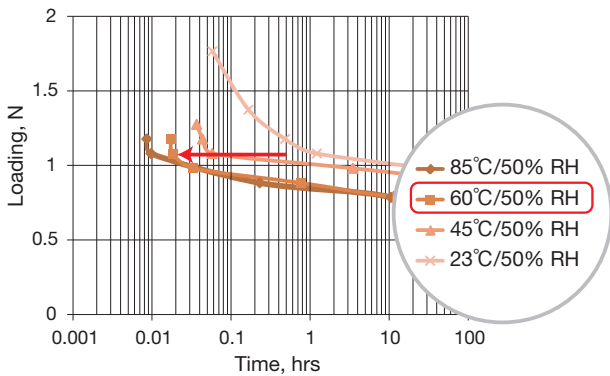

Figure 5 The relationship between the static pullout force and the temperature.

Next, in order to investigate the influence in which the humidity affects the static pullout force, on the basis of the provisional optimum condition (60℃/50% relative humidity) obtained in Figure 5, the relative humidity was changed to 30% and to 98% and further, the condition of the temperature of 85℃ that shows the highest saturated steam quantity within the controllable range of temperature/humidity chamber, 95% relative humidity was added and the measurement was performed. Figure 6 show the test results. As the humidity increases, the pullout force decreases and the pullout force at 60℃/98% relative humidity and 85℃/95% relative humidity was about 0.75 N. On the other hand, regarding the time when the glass is pulled out from the coating layer, no significant difference appeared. The time that static pullout force is obtained was only several minutes' difference in these conditions. It is estimated that the factor of the pullout force reduction at high humidity is due to the weakening of the hydrogen bond at the glass/primary interface. From the results of Figure 6, the test results for both the condition of 60℃/98% relative humidity and 85℃/95% relative humidity were around 6 minutes and also other values look same. Therefore, in

consideration of workability, the ambient condition of 60℃/98% relative humidity was set as the optimum measurement condition for static pullout force.
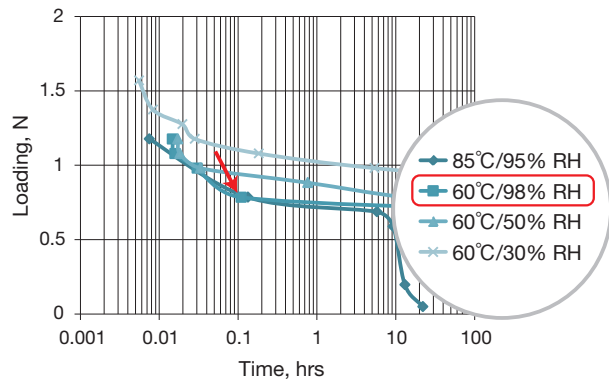

Figure 6 The relationship between the static pullout force and the humidity.

4.3 The Comparison of the Pullout Force and the Static Pullout Force

In Figure 7, the measurement results of the static pullout force for the fiber coated with two kinds of UV curable resins are being superimposed to the measurement results of the pullout force shown in Figure 4 when changing the tensile speed. In Figure 7, it can be seen that the up and down relationship with pullout force is reversed in the static pullout force. This result suggests that the high pullout force does not always mean the high adhesive force.
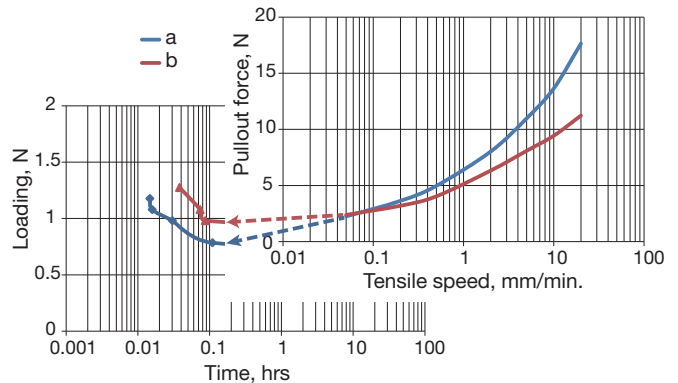

Figure 7 The comparison between the pullout force and the static pullout force.

Table 1 shows the difference between the pullout test and the static pullout test. The pullout test is shown by the "arrow" which means the dynamic tensile test and the static pullout test is shown by the "picture of the weight" which means the static load in a simplified manner. The pure adhesive force at the glass/primary interface is contained in both test results, but in contrast with the "dynamic" pullout test to measure the force at a constant tensile speed, the "static" pullout test is to measure the time when the glass is pulled out from the coating at a

certain load. By this modification of the testing method, the dynamic influence such as the shear strength of the primary layer, the coating friction and etc. can be minimized. Further, by performing the static pullout force test under the ambient condition of high temperature and humidity, in reality, 60℃/98% relative humidity, the tightening force of the secondary can be reduced and the hydrogen bonding strength can be weakened. In other words, by performing the static pullout test and removing the non-adhesive factors which, consequently included, as much as possible, the pure adhesive force can be obtained. Because the measurement is performed under the ambient condition of high temperature and humidity, it can be said that the adhesive force at the glass/primary interface, particularly when the optical fiber is immersed in water, can be obtained.

	5 mm/min.	60℃/98% RH
Pure adhesion at G/P	✔	✔
Hydrogen bonding strength	✔	✓
Tightening force of S coating	✔	✓
Shear strength of P coating	✔	✓
Coating friction etc.	✔	✓

Table 1　The comparison between the pullout test and the static pull out test.

4.4　The Relationship Between the Pullout Test and the Long-term Hot Water Immersion Test for Ribbon Fiber

The fibers which are coated with two kinds of UV curable resins (A, B) and have almost the same pullout force were prepared. Each fiber was colored and 4-fiber ribbon was fabricated.

The attenuation of those fibers after 60℃ hot water immersion was monitored periodically. Also, the static pullout forces for these two kinds of optical fibers were measured. These results are summarized in Figure 8. In the same way as Table 1, the pullout force and the static pullout force are shown by the "arrow" and the "picture of weight" respectively in a simplified manner.
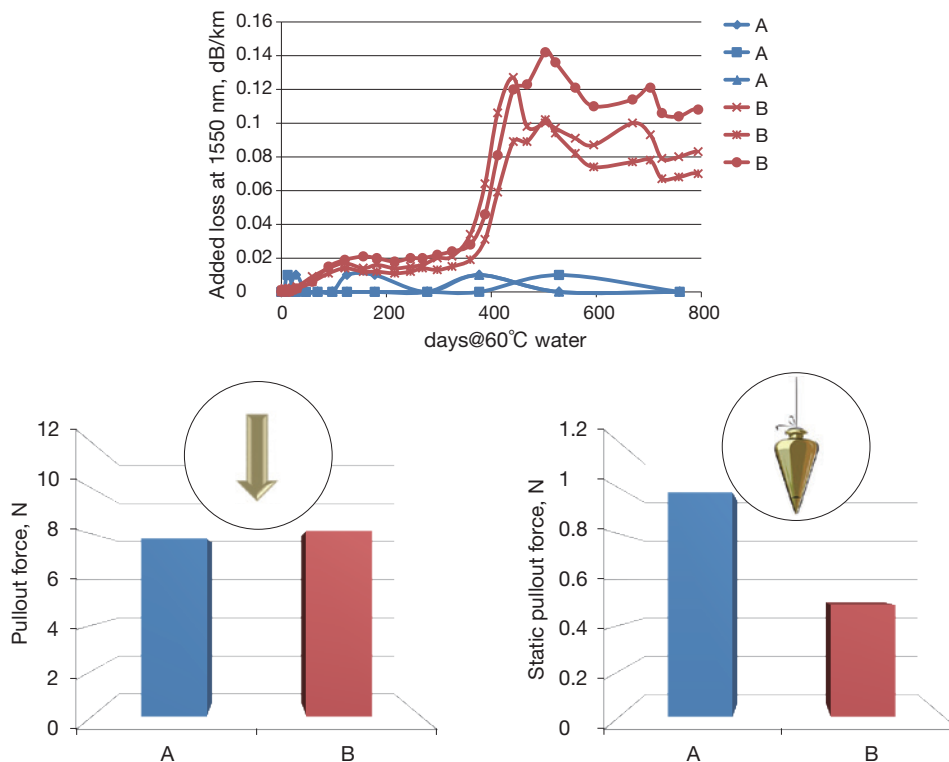

Figure 8　The relationship between the pullout test and the long term hot water immersion test for ribbon fiber.

Although the optical fibers which have almost the same pullout force are selected, the attenuation increase did not occur even after about 800 days hot water immersion in one of the ribbon fibers (A in the figure), but other fibers (B in the figure) attenuated after about 400 days of hot water immersion. In this experiment, the intent was that the difference between two kinds of samples is indicated clearly as the extreme environments. From these results, it is clear that the pullout force does not indicate the adhesive force at the glass/primary interface accurately when the optical fiber is immersed in water, but it can be seen that the static pullout force agrees well with the result of the optical fiber attenuation under the hot water immersion. In other words, these results are one of the results which support that there is a correlation between the static pullout force and the adhesive force at the glass/primary interface when the optical fiber is immersed in water.

4.5 The Relationship Between the Pullout Test and the Fiber Strength After Temperature and Humidity Aging

Another result which supports that there is a correlation between the static pullout force and the adhesive force at the glass/primary interface when the optical fiber is immersed in water is the fiber tensile strength after the temperature and humidity aging. In Figure 9, the result of the optical fiber coated with another different kind of UV curable resin (C in the figure) is added. The lower left graph shows the Weibull plots of the fiber strength measured after 30 days zero stress aging under the ambient condition of 85℃/85% relative humidity. If the distribution is wider, it means that there is a higher possibility of the weak fibers. However, it can be understood that the result of the fiber strength after temperature and humidity aging agrees well with the result of the static pullout force (right below graph).

Here, the worth noting further is the time required for the accelerated test. In IEC 60793-1-50, in order to measure the optical fiber strength after temperature and humidity aging, 30 days aging period under the ambient condition of 85℃/85% relative humidity was required. On the other hand, the required time to measure the static pullout force was only several minutes and even the time to confirm the knee point of the curve for the time when the fiber is pulled out from the coating vs. added load was considered, it can be thought that 30 minutes is enough. When compared to the typical accelerated aging period of 30 days for evaluation of the optical fiber properties, it is an overwhelming time reduction and the static pullout force is the one which can predict the optical fiber properties after the aging under these extreme environments in a very short evaluation period. In other words, the static pullout test can provide us a better screening method to select a reliable optical fiber than the conventional method.
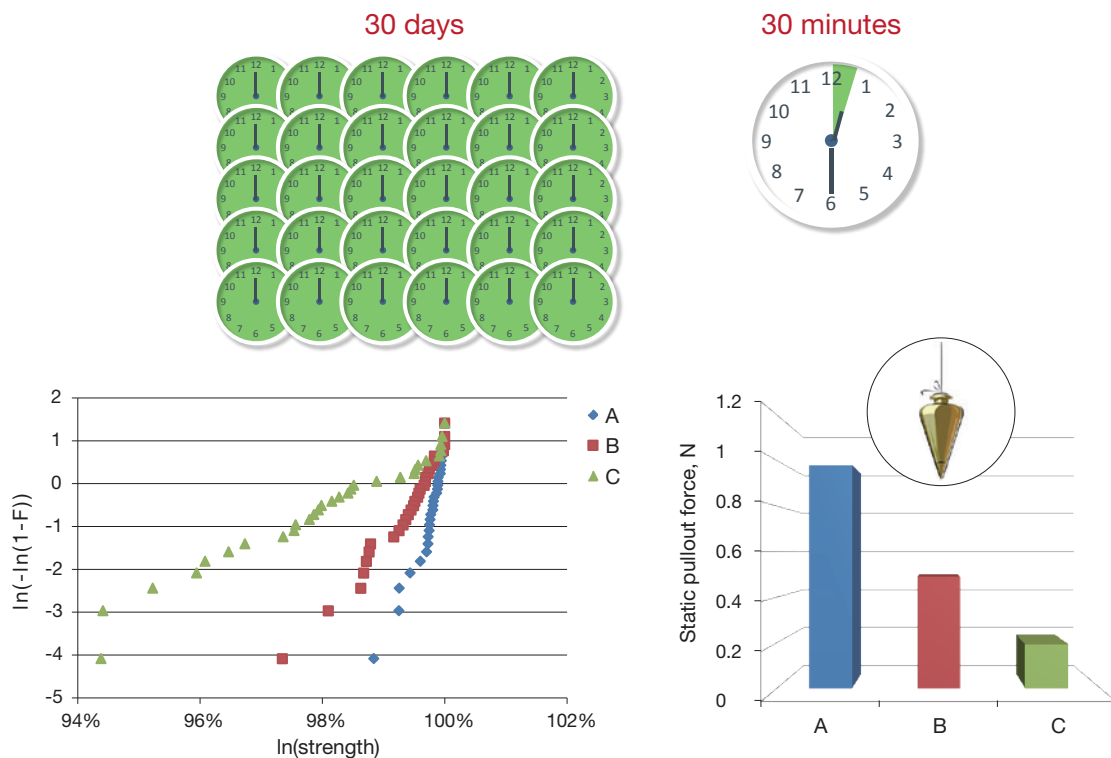

Figure 9 The relationship between the pullout test and the fiber strength after temperature and humidity aging test.

5. CONCLUSION

In order to accurately determine the adhesive force the glass/primary interface, in particular, when the optical fiber is immersed in water, the existing pullout test has been modified and a new measurement method has been developed. It is the second method which can measure the adhesive force at the glass/primary interface in situ. The adhesive force at the glass/primary interface called the static pullout force can be considered as the "pure" adhesive force from which the non-adhesive factors inherently included during the "dynamic" pullout test to measure at a constant tensile speed are removed as much as possible. This testing method not only shows the correlation between the static pullout force and the optical fiber properties, but also is very useful as the method which is able to select the reliable optical fiber because the evaluation period can be shortened.

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