Long-term durability of Kuralon (PVA fiber) in alkaline condition

Masakazu Nishiyama, Ryo Yamamoto, *Hideki Hoshiro

Market Development Dept. Fibers and Textiles Company

Kuraray Co., Ltd,

Ote Center Bldg.1-1-3, Otemachi, Chiyoda-Ku Tokyo 100-8115, JAPAN

Abstract

The accelerated aging test of Kuralon (PVA fiber) was conducted in cement extracted solution (pH: 12.6, temperature range: 20˚C to 70˚C). That is, the effects of temperature and the soaking time on the structure, chemical properties and the tensile strength of the fiber were investigated. From the experimental results, we found that the tensile strength retention of the fiber is very sensitive to the amount of -CO-C=C- group generated by oxidation reaction of the molecules. We found that the amount of -CO-C=C- group increases markedly with soaking time and increasing temperature. Furthermore, we found that the generation rate of -CO-C=C- group in molecule differs a lot between below 40˚Cand above 50˚C. We found that there was a discontinuity boundary between 40˚C and 50˚C by arranging the data base on Arrhenius plot theory. From these relations, we obtained a relational equation between the tensile strength retention and the soaking time. Using this equation, we assessed the durability of Kuralon in the alkaline condition. The assessment proved that Kuralon is able to endure for satisfactory period in the alkaline solution derived from cement.

*Corresponding author. Tel.:+81-3-6701-1364; fax: +81-3-6701-1376

E-mail address: Hideki_Hoshiro@kuraray.co.jp

1. Introduction

It is apparent that the long-term durability under hostile environments is required for a reinforcement material used in roofing. PVA fiber have been used as a reinforcement material of cement for more than 25 years because they have high alkaline resistance

and high tensile strength. In fact, it was confirmed that the tensile strength of the fiber in cement sheet has kept their original levels after about 20 years outdoors exposure test. The durability assessment of the fiber should be established over a wide range of time. However, the change of tensile strength of the fiber with time is generally very small. Therefore, we need an accelerated aging test for the evaluation of the durability of PVA fiber.

The oxidation mechanism of PVA in an alkaline condition has been studied by Shiraishi [1] . He reported that the -CO-C=C- group is formed during the oxidation reaction of PVA molecules; discoloration is also accompanied with the formation (the oxidation process can be seen in Appendix I). As will be described later, we find that the tensile strength of PVA fiber is very sensitive to the amount of -CO-C=C- group generated during the oxidation process of PVA fiber, and that the amount of the generation increases largely with soaking time in alkaline solution. From these findings, we will obtain a relational equation between the retention of tensile strength of PVA fiber and the soaking time. Using this equation, we will estimate the durability of Kuralon (PVA fiber) in the cement environment.

2. Experimental

2.1 Sample

Kuralon 5501 (PVA filament yarn manufactured by Kuraray, JAPAN) was used as testing PVA fiber.

Yarn count and number of filament : 2000 dtex / 1000 filaments

Tensile strength : 196 N

Elongation at break : 6.7%

Elastic modulus : 4060 N(26.4 GPa)

Loss on boiling for 30 minutes : less than 1%

2.2 Preparation method of specimen

The filament yarn was twisted with a ring twister (ring size 3.5 inch). The twisting condition was 80 turns/meter. The twisted yarn was wound on a stainless frame with 0.09 cN/dtex load (see Appendix Ⅱ).

We prepared cement-extracted water solution as follows.

(i) One part of cement was put into five parts water and the mixture was stirred for

6 to 7 hours.

(ii) After the mixture being left at rest overnight, supernatant aqueous solution (pH = 12.6) was obtained by decantation.

The solution (10 L) was put into a plastic bottle with a lid, and then the yarn wound on a stainless frame was soaked into the solution at a given temperature. The yarn was taken out from the solution after a given time. The yarn was washed by water for 30 minutes. The yarn was neutralized with HCL (1 g/L) for 10minutes and then washed again with water for 6 hours. The yarn was dried at room temperature for 16 hours in wound state. Furthermore, the yarn was dried under vacuum for 8 hours at ordinary temperature. The dried yarn was re-wound on a paper bobbin. The yarn on a paper bobbin was kept in a desiccator at 20˚C, 65%RH for more than 5 days. The controlled yarn was made using the same procedure described above, but soaking into cement-extracted solution was not performed. These samples were used for the following measurements.

2.3 Measurement method of mechanical properties of the yarn

Tensile tests of the yarn were performed with Instron 4301 in accordance with JIS L-1013 standard (Japanese industrial standard).

The conditions are as follows.

Temperature and humidity: 20˚C, 65% RH

Grip head speed and air pressure: 100 mm/min, 4.0 N/cm^2

Specimen length: 200 mm

Number of specimens: n = 10.

The tensile strength retention was calculated by the following equation:

Tensile strength retention = (Tensile strength of the yarn treated by alkaline solution / Tensile strength of the untreated yarn)×100(%) (1)

2.4 Measurement method of UV absorption

The yarn (0.1 g) and ion-exchanged water (99.9 g) were put into a sealing type glass tube (Taiatsu Glass Industry Co. TEM-V300). We heated the tube to 115˚C at the heating rate 20˚C/min. to obtain PVA aqueous solution. Reaching to the temperature, the tube was cooled down to ordinary temperature, and the solution was filtrated using a filtration paper 5A, and the solution was provided for UV test. The UV absorption (235nm) of the solution was measured with a Hitachi Spectrophotometer (U-3210); light path length in quartz cell was 10mm; the amount of -CO-C=C- group is monitored by the

intensity of UV absorption at wave length 235 nm.
Measured values of UV absorption were all normalized to 0.1% of concentration by using calibration line, which was approximated from 3 different points of concentration near 0.1% (around 0.09, 0.10, 0.11%), because it was hard to prepare just 0.1% of concentration. As UV absorption changes depending on testing conditions etc, we recorded the average value for each testing.

2.5 Measurement method of other physical parameters

The molecular weight M_w was evaluated using a viscometry measurement , the degree of crystallinity X_c was evaluated using a wide angle x-ray diffraction method, the degree of molecular orientation f_c, was evaluated form the measurement of sonic velocity, and the degree of swelling *DSw* of yarn was evaluated using a gravimetric method; the details can be seen in Appendix Ⅲ.
The molecular weight retention was estimated by the following equation:
Molecular weight retention = (the molecular weight of the yarn treated by alkaline solution/ the molecular weight of the untreated yarn) ×100(%) (2)

3. Results and Discussion

Figure 1 shows the effect of alkaline soaking time on the tensile strength retention of PVA fiber. The tensile strength keeps original level below 40˚C. On the other hand, the retention value above 50˚C depends strongly on the soaking time and decreases rapidly by increasing temperature. For the evaluation for durability of PVA fiber used as reinforcement of cement, the tensile strength retention of the fiber which were kept in alkaline solution at ordinary temperature (around 20˚C) for long years would be important. However, the value cannot be exactly predicted from the data in Figure1 because the tensile strength does not change.
Figure 2 shows the effect of the soaking time on the appearance of the yarn. It can be seen that the discoloration takes place markedly at higher temperature. The change of discoloration is monitored using UV spectrometry. Table 1 shows the effect of soaking time and temperature on physical parameters of the yarn. It can be seen that the degree of crystallinity X_c, the degree of molecular orientation f_c, are not influenced by the soaking time and temperature. This result means that the PVA crystal regions are not deteriorated by the alkaline treatment. The degree of swelling is not influenced by the soaking time and temperature. This means that a large structural change does not take

place in the amorphous region.

It is noted that UV absorption and the value of the retention of M_w are dependent on the soaking time and temperature. This means that UV absorption and M_w values are sensitive to the deterioration of the tensile strength of yarn.

Figure 3 shows the relation between the tensile strength retention and the molecular weight retention.

Figure 4 shows the tensile strength retention and the UV absorption. It can be seen that the UV absorption has better correlation with the tensile strength retention than the molecular weight retention does. The tensile strength retention is almost constant up to the UV absorption value 0.085. Above this value, the tensile strength retention decreases linearly with increasing UV absorption. This linear relation can be approximated by the following equation:

Tensile strength retention = -505(UV abs.) + 143 (%) (UV abs.> 0.085) (3)

= 100 (%) (UV abs.≦0.085) (4)

The mechanism that the formation of -CO-C=C- group affects the tensile strength is not clear in this work. Such chemical reaction in amorphous region may affect the tensile strength of PVA fiber. It should be noted that the deterioration of tensile strength in alkaline condition is influenced markedly by the UV absorption.

Figure 5 shows the relation between the UV absorption and the soaking time. In this figure, the slope can not be observed below 40˚C, however it becomes steeper with increasing temperature (above 50˚C). We have no observation datum in the range that UV absorption is above 0.19. So, in this report, we can only discuss the durability in the area below 0.18 of UV absorption and above 45% of the tensile strength retention. Considering the usage of PVA fiber as reinforcement of cement, we must assess precisely the UV absorption measured below 40˚C.

Figure 6, in which the ordinate of Figure 5 is enlarged, shows that there is a linear relationship between the soaking time and UV absorption. Using the linear least-squares method, we calculate the relation at 20˚C. The calculated relation is given by the following equations:

UV abs. = 2.55E-8 x + 6.3E-2 (5)

where x is the soaking time (hrs)

Combining equations (3) and (5), we obtain the following equation (6):

Tensile strength retention = -1.3E-05x + 111.2 (%) (x : hrs, x ≧8.58E 5) (6)

$$= 100 \quad (\%) \quad (x : \text{hrs}, x < 8.58E5) \qquad (7)$$

Using the above equation, we calculate the estimated tensile strength retention after 60, 100 and 120 years. The results are as follows:

a. After 60 years at 20˚C

x = 60 years = 5.26E5 hours

Tensile strength retention = 100 (%) from equation (7)

b. After 100 years

x =100 years = 8.76E5 hours

Tensile strength retention = -11.4 + 111.2 = 99.8 (%) from equation (6)

c. After 120 years at 20˚C

x = 120 years = 1.05E6 hours

Tensile strength retention = -13.7 + 111.2 = 97.5 (%) from equation (6)

From these examples, we conclude that Kuralon (PVA fiber) would be able to endure for satisfactory period in the alkaline solution derived from cement.

Figure 7 shows Arrhenius plot of the generation rate of -CO-C=C- group. The plots below 40˚C and above 50˚C are divided into two different lines. The slope measured above 50˚C is almost same as that below 40˚C. This means that the activation energy for generation of the chemical group does not depend on temperature. The reason for this discontinuity is currently uncertain, however we assume that this phenomenon concerns with several factors such as molecule mobility, diffusion rate of oxygen and radical under the relevant condition.

4. Conclusion

The accelerated aging test of Kuralon (PVA fiber) was conducted in cement extracted solution (pH: 12.6, temperature range: 20˚C to 70˚C). The generation of -CO-C=C- group causes discoloration as well as decomposition which can be measured by UV absorption at 235 nm [2]. It can be seen that the UV absorption has better correlation with the tensile strength retention.

The main results obtained are shown below.

4.1 The tensile strength retention of PVA fiber can be expressed by the following

equation:

Tensile strength retention = -1.3E-05x + 111.2 (%) (x : hrs, x ≧ 8.58E5)

= 100 (%) (x : hrs, x < 8.58E5)

4.2 The values of tensile strength retention evaluated from the above equation after 60, 100 and 120 years soaking in cement extract are 100%, 99.8% and 97.5% respectively.

4.3 We conclude that Kuralon (PVA fiber) has enough long-term durability in alkaline solution derived from cement.

References

[1] Shiraishi et al ; Kobunshi Kagaku, 19, 722 (1962).

[2] Yamaguchi et al ; Kobunshi Kagaku, 16, 571 (1959).

Tables & Figures

Table 1. Effects of temperature and soaking time on the structual and physical parameters of PVA fiber

Temp.(.C)	Structure and physical Parameters	Time(hrs)										
		100	500	1000	1500	2000	3000	4000	10000	20000	26280	30000
20	*TSR* (%)	100	100	100	100	100	100	100	-	100	100	100
	MWR (%)	100	-	-	-	-	-	100	-	100	100	-
	Xc (%)	60	60	60	60	60	60	-	-	-	-	-
	fc	0.9	0.9	0.9	0.9	0.9	-	-	-	-	-	-
	DSw (%)	13	13	13	13	13	-	-	-	-	-	-
	UV abs.	0.0630	0.0630	-	-	0.0630	0.0631	0.0631	-	0.0633	0.0642	0.0634
30	*TSR* (%)	100	100	100	100	100	100	100	-	-	-	-
	MWR (%)	-	-	-	-	-	-	-	-	-	-	-
	Xc (%)	60	60	60	60	60	60	-	-	-	-	-
	fc	0.9	0.9	0.9	0.9	0.9	-	-	-	-	-	-
	DSw (%)	13	13	13	13	13	-	-	-	-	-	-
	UV abs.	0.0630	0.0630	-	-	0.0631	0.0631	0.0632	-	-	-	-
40	*TSR* (%)	100	100	100	100	100	100	100	-	-	-	-
	MWR (%)	100	-	-	-	-	-	100	-	-	-	-
	Xc (%)	60	60	60	60	60	60	-	-	-	-	-
	fc	0.9	0.9	0.9	0.9	0.9	-	-	-	-	-	-
	DSw (%)	13	13	13	13	13	-	-	-	-	-	-
	UV abs.	0.0630	0.0630	-	-	0.0632	0.0632	0.0633	-	-	-	-
50	*TSR* (%)	100	100	100	100	100	100	100	57	-	-	-
	MWR (%)	100	-	-	-	-	-	100	90	-	-	-
	Xc (%)	60	60	60	60	60	60	-	-	-	-	-
	fc	0.9	0.9	0.9	0.9	0.9	-	-	-	-	-	-
	DSw (%)	13	13	13	13	13	-	-	-	-	-	-
	UV abs.	0.0632	0.0634	0.0637	0.0697	0.0821	0.1031	0.1121	0.1704	-	-	-
60	*TSR* (%)	100	100	100	100	95	84	67	-	-	-	-
	MWR (%)	86	-	-	-	80	78	75	-	-	-	-
	Xc (%)	60	60	60	60	60	60	-	-	-	-	-
	fc	0.9	0.9	0.9	0.9	0.9	-	-	-	-	-	-
	DSw (%)	13	13	13	13	13	-	-	-	-	-	-
	UV abs.	0.0700	0.0700	0.0710	0.0830	0.0993	0.1274	0.1722	-	-	-	-
70	*TSR* (%)	100	100	90	75	73	56	42	-	-	-	-
	MWR (%)	83	82	81	80	75	66	62	-	-	-	-
	Xc (%)	60	60	60	60	60	60	-	-	-	-	-
	fc	0.9	0.9	0.9	0.9	0.9	-	-	-	-	-	-
	DSw (%)	13	13	13	13	13	-	-	-	-	-	-
	UV abs.	0.0735	0.0840	0.1020	0.1220	0.1288	0.1605	0.1910	-	-	-	-

TSR ; Tensile strength retention
MWR ; Molecular weight retention
Xc ; Crystallinity
fc ; Degree of molecular orientation
DSw ; Degree of swelling
UV abs. ; UV absorption

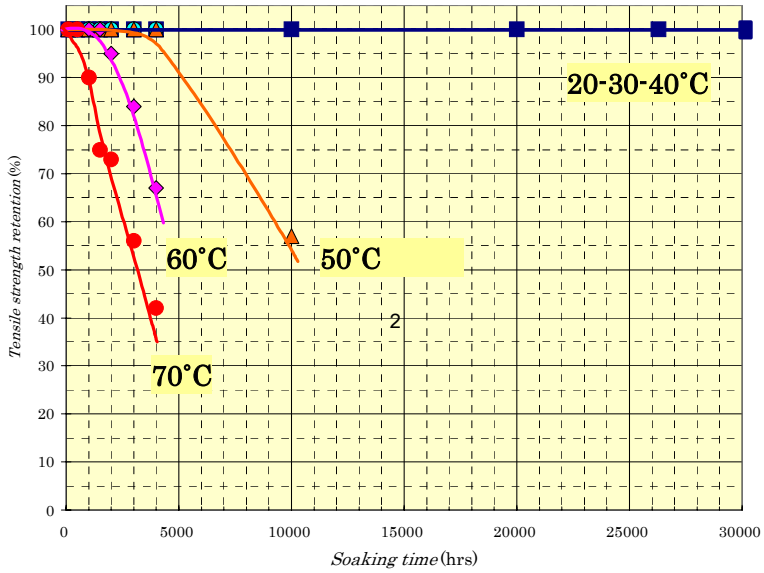


Figure 1. Effect of the soaking time on the tensile strength retention

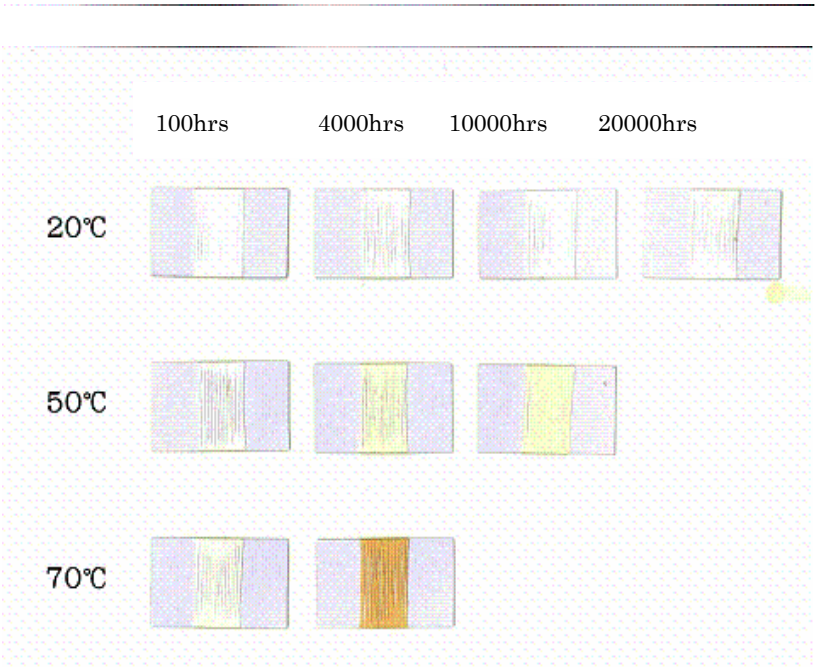


Figure 2. Fiber discoloration due to soaking in alkaline water

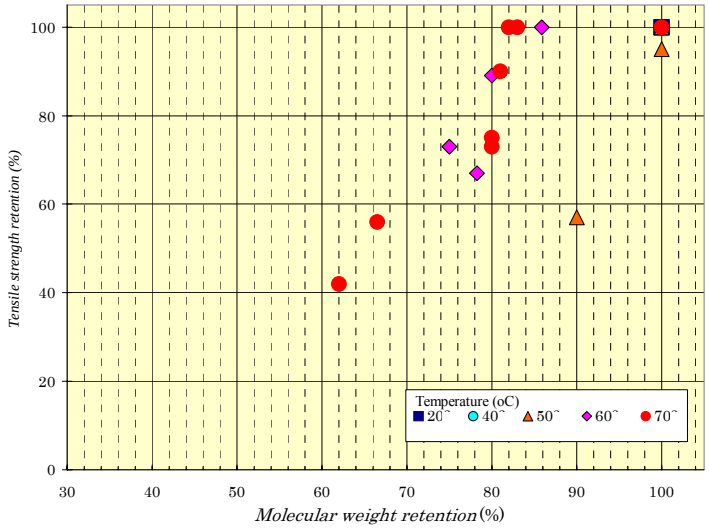


Figure 3. Relation between the tensile strength retention and the molecular weight retention

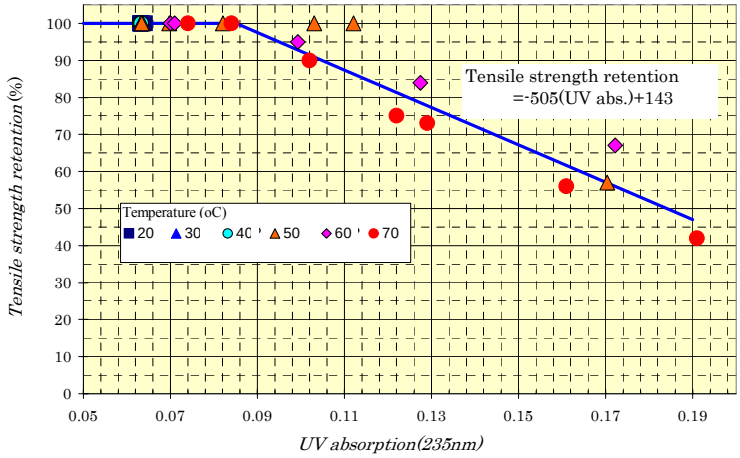


Figure 4. Relation between the tensile strength retention and UV absorption

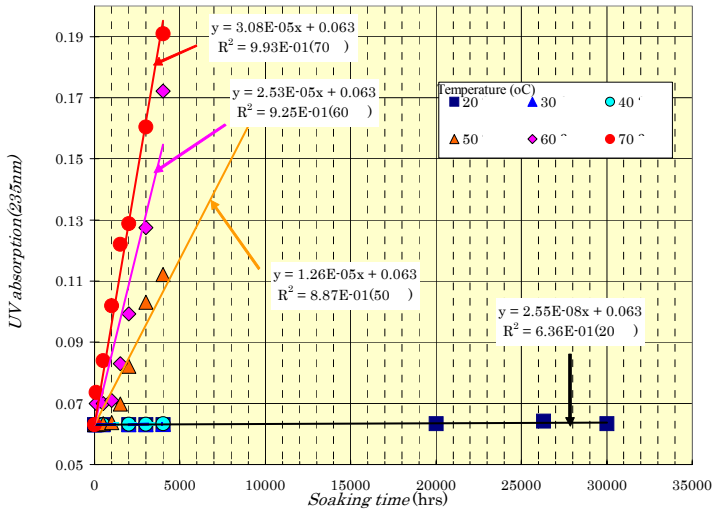


Figure 5 Relation between UV absorption and soaking time

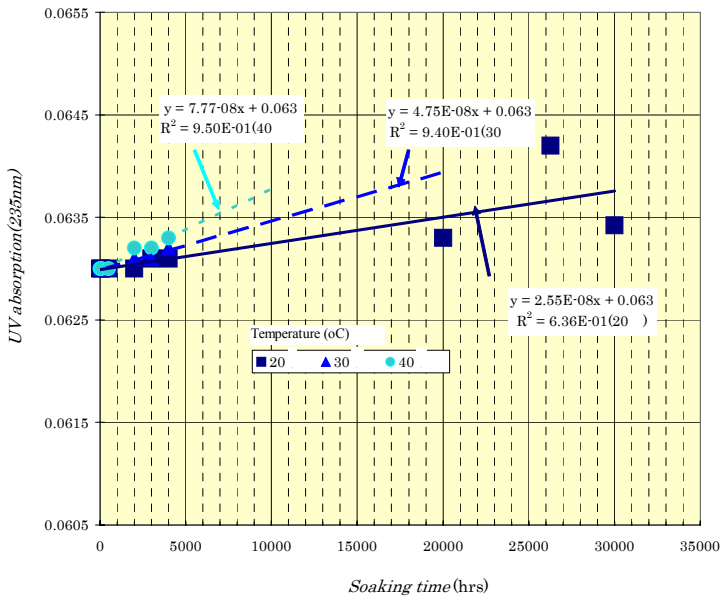


Figure 6. Relation between UV absorption and soaking time mesurured below 40

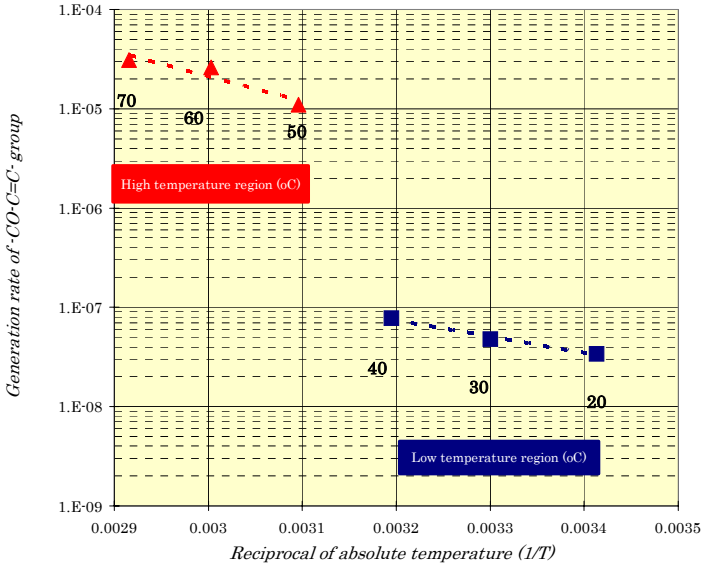


Figure 7. Dependence of the generation rate of -CO-C=C- group on temperature (Arrhenius plot)

Appendix I

The oxidation mechanism of PVA in alkaline condition

When we leave PVA alkaline aqueous solution in the air at relatively high temperature, it reduces the viscosity and is discolored. On the other hand, in the nitrogen, it does neither decrease the viscosity nor induce discoloration. About the viscosity depression and discoloration of PVA solution, Shiraishi et al [1] pointed out the following items:

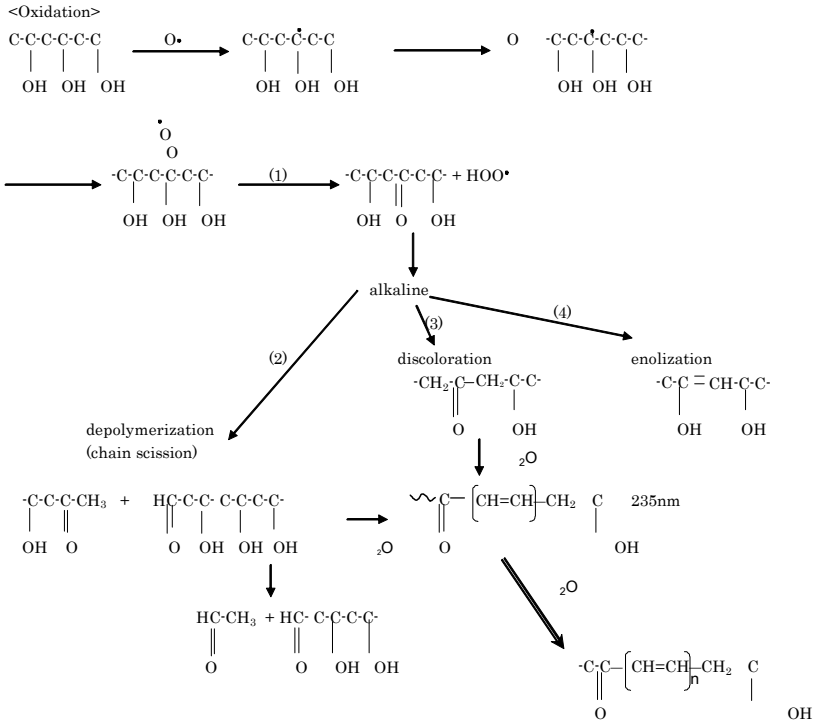
1) At first, carbonyl group is generated in the main chain of PVA molecule by oxidation in alkaline solution.

2) The formation of carbonyl group induces the chain scission (retro-aldole reaction: reducing molecular weight due to splitting) and/or enolization (does not induce chain scission). These reactions generate competitively, and which reaction would occur is depending on the temperature.

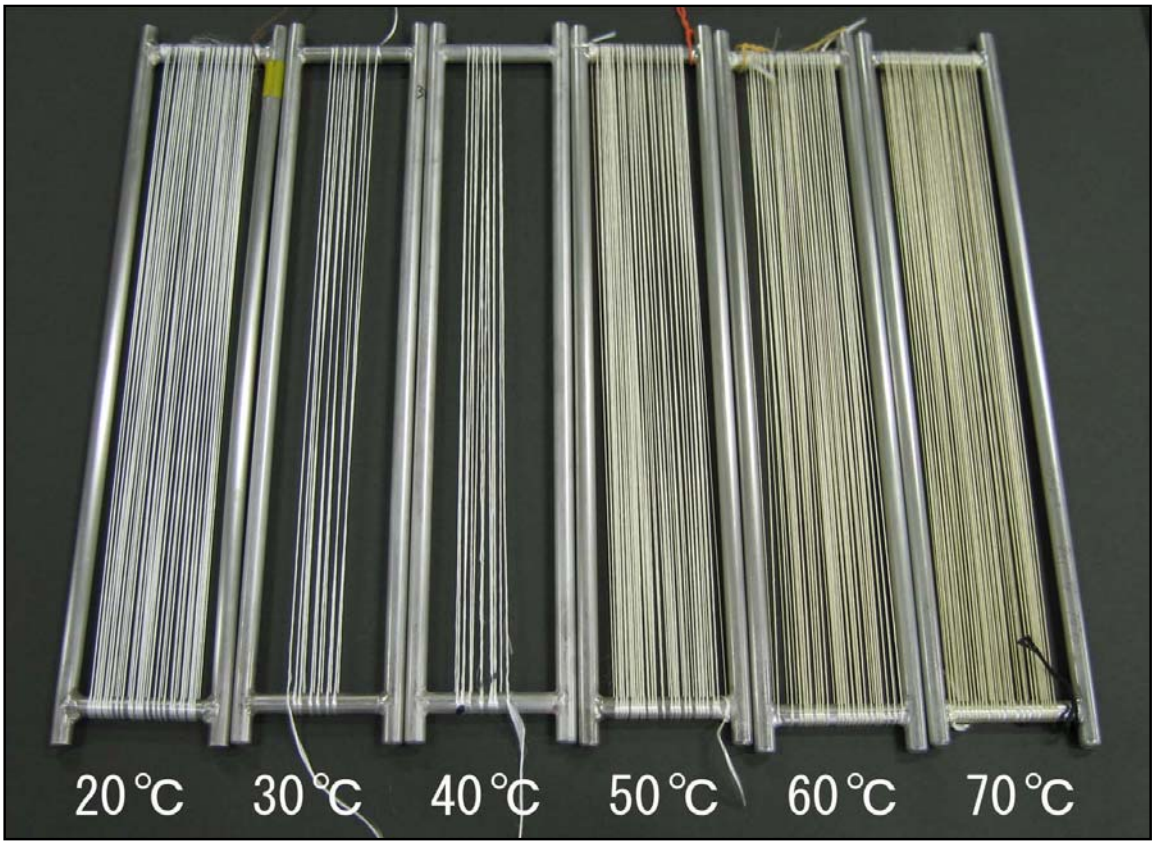
3) The generation of carbonyl group in the main chain of the polymer causes discoloration.

The reaction process of oxidation can be written as:

Carbonyl group generation (1), and then, de-polymerization (2), -CO-C=C- group (3) and/or enolization (4) would occur depending on the condition. The generation of -CO-C=C- group causes discoloration and can be measured by UV absorption at 235nm [2].



Appendix II



Frames used for soaking yarn into alkaline solution

Appendix III

Measurement of molecular weight (M_w)

-1. Measurement of liquid plunge time

-1-1. Set a viscometer "Ubelode (SU)" (#0), proper volume of ion-exchange water and the 0.1% PVA solution (which is made for ultraviolet absorption measuring test) into bath kept at a constant-temperature of 30˚C, and keep it for 1 hour.

-1-2. Set 14ml of the water in the viscometer and leave it for 10 minutes

-1-3. Measure the water plunge time twice.

-1-4. Confirm the difference between the twice values is within 0.2% of the average value, and then proceed the calculation. Z0 (sec.)

-1-5. Measure the plunge time on the same protocol with PVA solution. Z (sec.)

-2. Identification of the concentration of the sample solution

-2-1. Weigh the drying evaporation dish (A)

-2-2. Set 10ml of 0.1% PVA solution on the evaporation dish and dry it out at 105℃for 4 hours.

-2-3. Cool it in the desiccator for 30 minutes and measure its weight (B)

-2-3. Calculate the solution concentration level using the following equation (2)

$C(g/l)=\{B(g)-A(g)\} \times 1000/10$ --- (2)

-3 . The way of calculation

-3-1. Measuring viscosity and calculating on the following Sakurada-Mark-Houwink equation

$〔\eta〕=KM^a \cdots (3)$

K and a are following constant number.
K:8.29 x 10^{-4}(cm_3/g)
M: molecular weight
A:0.62
〔η〕: Inherent viscosity is calculated from following equation(4) and (5)
Inherent viscosity: $[\eta]_r = Z/Z0 \cdots (4)$
〔η〕=2．303x$\log[\eta]_r/C \cdots (5)$
Z : specimen plunge time　Z0 : water plunge time　C : Liquid concentration level(g/l)

Measurement of crystallinity (*Xc*)

-1. Apparatus; Wide-angle X-ray diffraction of Rigakudenki: RINT-2400
-2. Set specimen on a rolling specimen support in order to avoid the orientation effect.
-Power: 40kV 100mA
-Target: Cu
-Wavelength (CuKα1)λ=1.5405
-Counter: SC
-Operation speeed:0.5°/min
-Step size:0.02°/Step
-Measurement range:2θ=5~35°

Measurement of degree of swelling (*DSw*)

-1. Pick up 2g specimen from the soaking alkaline water.
-2. Dehydrate the specimen with centrifugal dehydrator at 3000rpm for 10 min and weigh it.
-3. Bone-dry the specimen in weighing tube at 105˚C for 4 hours.
-4. Weigh the specimen (B) after cooling it in the desiccator for 30 min.
-5. Calculate degree of swelling using the following equation (6)
Degree of swelling = (A-B)/B x 100 (%) --- (6)
A (g): Weight after dehydration , B (g): Weight after drying

Measurement of the molecular orientation in fiber (*fc*)

-1. Measure by sonic velocity method with "Orientic Reovibron DDV-V-B type"
-2. Calculate degree of molecular orientation (α) by the following equation (7)
$\alpha = 1 - (Cu^2/C^2)$ --- (7)
C: sonic velocity through fiber (measured value)
Cu: measured sonic velocity of PVA non-oriented film: 2.2 (km/sec)