Basic Physical Properties of PVOH Resin

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Kuraray Poval™

Basic Physical Properties of PVOH Resin

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1. Basic Physical Properties of PVOH Resin

1-1. DEFINITION OF PVOH

POVAL is the popular name for polyvinyl alcohol (PVOH) described as a organic polymer-based polymeric compound. Polyvinyl alcohol is a substance that was first created by German scientist W. Hermann. It is chemically classified as a polymeric polyhydric alcohol having a secondary hydroxyl group at every other carbon atom of a carbon chain and is expressed by the following general structure. There are several methods known for the manufacturing of PVOH. However, from an industrial point of view, the current mainstream method of production is as follows. Polyvinyl acetate is manufactured by radical polymerization using vinyl acetate as a raw material and then hydrolyzing it under an alkaline condition. Methanol is mainly used as a solvent in the polymerization process / hydrolysis process.

The basic properties of PVOH are typically governed by the degree of polymerization and the degree of hydrolysis. The degree of polymerization of PVOH is generally indicated by the viscosity-average degree of polymerization derived from the viscosity in water. Additionally, when expressing the degree of hydrolysis using the repeating units m and n in Figure 1, the degree of hydrolysis can be expressed as follows: Degree of hydrolysis (mol%) = m / (n + m) × 100. This is the value with which the proportion of the vinyl alcohol unit in all the repeating units is indicated in mol%. For details of these analysis methods, refer to JIS K 6726.

$$-(CH_2-CH)_m-(CH_2-CH)_n-$$
$$\quad\quad\; |\quad\quad\quad\quad\quad |$$
$$\quad\quad OH\quad\quad\quad\quad O$$
$$\quad\quad\quad\quad\quad\quad\quad\quad |$$
$$\quad\quad\quad\quad\quad\quad\quad C=O$$
$$\quad\quad\quad\quad\quad\quad\quad\quad |$$
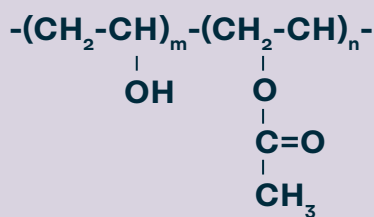$$\quad\quad\quad\quad\quad\quad\quad CH_3$$

Figure 1. General structure of PVOH

References
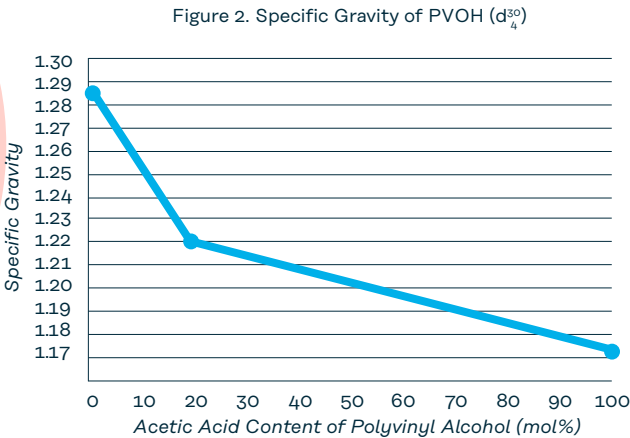*1) Sone et al., Polymer Chemistry, 14, 149 (1970)*

1-2. SPECIFIC GRAVITY

Although the apparent specific gravity of commercially available "PVOH" is approximately 0.6 to 0.7 g/cc, the values in Table 1 are described in the Encyclopedia of Chemical Technology (1970) by Kirk Othmer as the true specific gravities.

According to this table, the specific gravity of PVOH decreases as the amount of residual acetate group increases, and the values for partially hydrolyzed products of PVOH by Sone, et al. shown in Figure 2 also show the same tendency.

Additionally, Sone reported that the specific gravity of fully hydrolyzed PVOH was correlated with crystallinity regardless of the degree of polymerization, heat treatment

temperature, etc. and the extrapolated specific gravities of PVOH with crystallinities of 0 and 1 were 1.269 and 1.345, respectively. On the other hand, there is a published report that the extrapolated specific gravity for 100% PVOH concentration was about 1.27 when it was obtained from the actual measurement of the specific gravity of PVOH aqueous solution at 30°C and thus the result that agreed well with the specific gravity of 100% amorphous PVOH described above was obtained. In short, the specific gravity of PVOH can be considered as a value slightly exceeding 1.27 for fully hydrolyzed material.

Figure 2. Specific Gravity of PVOH (d_4^{30})

Source: Sone et al., Polymer Chemistry, 10, 277 (1953)

1-3. REFRACTIVE INDEX

In the Encyclopedia of Chemical Technology (1970) by Kirk Othmer, the values in Table 2 are described. Additionally, values such as $n_D^{20} = 1.51$[3], $n_D^{20} = 1.50\text{-}1.52$[4] are listed.

Table 1. Specific Gravity of PVOH

Residual acetate group (%)	d_D^{20}
0	1.329
5	1.322
10	1.316
20	1.301
30	1.288
40	1.274
50	1.260
60	1.246
70	1.232

Source: Kirk Othmer, Encyclopedia of Chemical Technology (1970)

Table 2. Refractive Index of PVOH

Residual acetate group (%)	n_D^{20}
0	1.557
5	1.553
10	1.548
20	1.539
30	1.530
40	1.521
50	1.512
60	1.503
70	1.494

Source: Kirk Othmer, Encyclopedia of Chemical Technology (1970)

References
2) Kawakami et al., Report of POVAL Conference, 33, 113 (1953)
3) R. H. Wiley, Ind. Eng. Cham., 38, 959 (1946)
4) Ullmanns, Encyklopadie der technishen Chemie, 239 (1963)
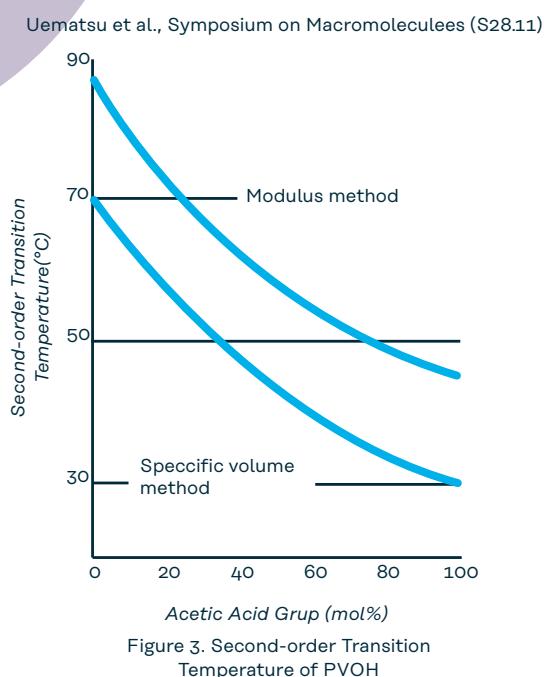
1-4. SECOND-ORDER TRANSITION TEMPERATURE

Although there is much literature on the second-order transition temperature of PVOH, major measured values can be summarized by the measurement method as shown in Table 3.

These are the results measured for individual samples using individual methods; however, there are the results of Uematsu et al. shown in Figure 3 that reveal the difference owing to measurement methods for a series of samples. Although the value varies depending on the measurement method, it can be said that the second-order transition temperature of fully hydrolyzed PVOH is 70 to 85°C regardless of the difference in the degree of polymerization, molecular structure, etc.

Second-order transition temperature (°C)	Measurement method	Sample used	Literature
71±2	Specific volume	Powder after vacuum drying at 100°C for 8 hr	Yano, Chemical Society of Japan, 73, 708 (1952)
65±3	Specific volume	Powder, stretched film	Futaba et al., Bussei-ron Kenkyu (Study on Physical Properties Theory), 71, 51 (1954)
70±5	Specific volume	Powder, stretched film	Futaba et al., Bussei-ron Kenkyu, 71, 51(1954)
70-80	Specific heat	Powder with a degree of polymerization of 550, 1550 after vacuum drying at 65–70°C for 8 hr	Nitta et al., Annual Report of Fiber Science, Vol. 7, 31(1953)
70	Dielectric loss angle		Hayashi et al., PVOH (by Hirabayashi)
70	Dynamic viscoelasticity	Film	Tokita et al., J. Phys. Soc. Japan, 6, 367, (1951)
87	Static viscoelasticity		Ofuka et al., Lecture at Chemical Society of Japan, S30.4
60-70	NMR	Fiber	Nohara et al., Polymer Chemistry, 15, 105 (1958)
70-	Moisture absorption	Fiber	Yano et al., Polymer Chemistry 11, 459 (1954)

Table 3. Second-order Transition Temperature of PVOH

Uematsu et al., Symposium on Macromoleculees (S28.11)

Figure 3. Second-order Transition Temperature of PVOH

Various effects such as the degree of hydrolysis, water content, plasticizer content ratio, etc. have been investigated as the factors influencing the second-order transition temperature of PVOH. The effect of the degree of hydrolysis is shown in Figure 3. Additionally, as for the effects of water content and plasticizer, the results of actual measurements using a film of PVOH (Kuraray Poval™ 25-100) with a degree of polymerization of 1720 and a degree of hydrolysis of 99.85 mol% are shown in Figures 4 to 6. To obtain these values,

samples were prepared using a film after heat treatment at 140°C for 10 minutes and changing the water content by humidity conditioning (films containing plasticizer were also prepared using a similar method for various additive rates), and then the values were obtained from the temperature characteristics of the dynamic torsional rigidity modulus and logarithmic damping rate that were measured using these samples.
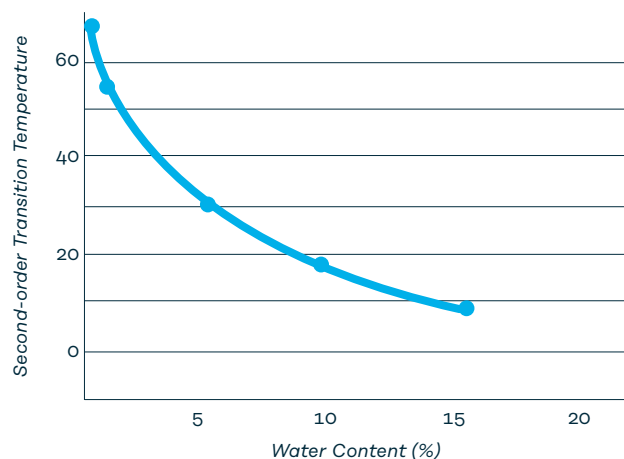
Figure 4. Influence of Water Content on Second-order Transition Temperature of PVOH
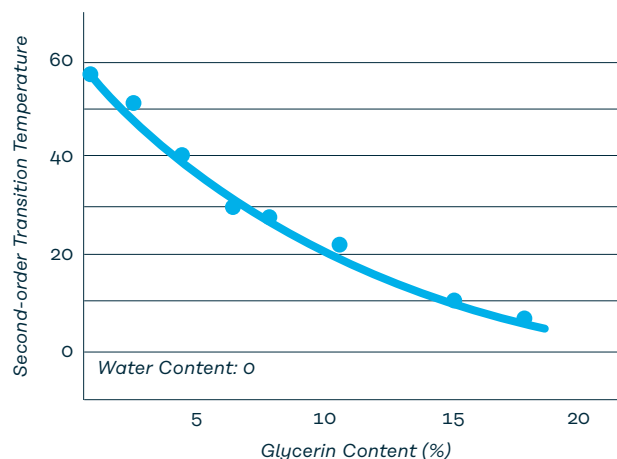
Figure 5. Influence of Glycerin Content on Second-order Transition Temperature of PVOH

(1) Glycerin content   0%
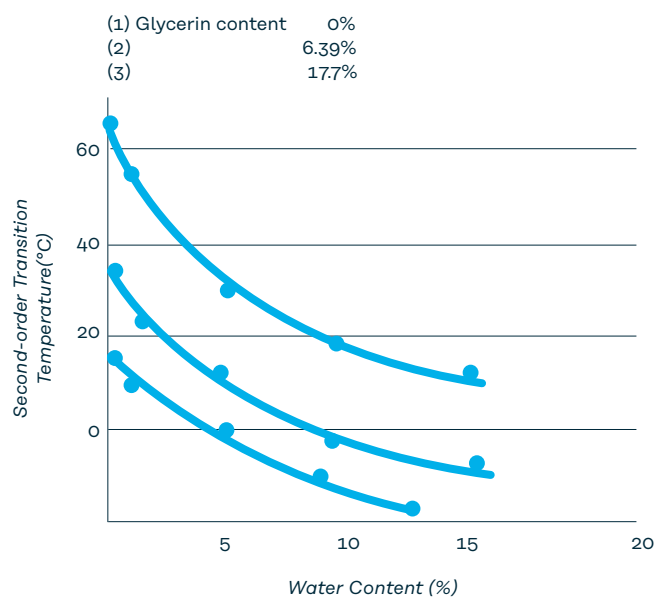(2)   6.39%
(3)   17.7%

Figure 6. Synergistic Effect of Water Content and Glycerin Content on Second-order Transition Temperature of PVOH

References
3) R. H. Wiley, Ind. Eng. Cham., 38, 959 (1946)
4) Ullmanns, Encyklopadie der technishen Chemie, 239 (1963)

1-5. CRYSTALLINITY

PVOH is widely recognized as a crystalline water-soluble polymer. It is known that the degree of crystallinity varies depending on the degree of hydrolysis and the degree of polymerization. In particular, the influence of the degree of hydrolysis is large, and the higher the degree of hydrolysis, the higher the crystallinity tends to be. Additionally, it is known that the degree of crystallinity changes with external factors, and it is particularly susceptible to the influence of heat treatment. As for the crystallinity of a fully hydrolyzed PVOH, the relationship between the heat treatment temperature (heat treatment time: 10 minutes) and the crystallinity of the film is shown in Figure 7[5]. The crystallinity varies depending on the degree of polymerization and, for PVOH with a low degree of polymerization in particular, the crystallinity is low in the region where the heat treatment temperature is low. However, the crystallinity of PVOH with any degree of polymerization also rises with a rise in the heat treatment temperature; for heat treatment at 200°C, the crystallinity of PVOH with any degree of polymerization are about the same (0.50−0.55).

Since PVOH is a crystalline water-soluble polymer, physical properties are greatly affected by its crystallinity. As an example, the swelling volume of the film when it is immersed in water (at 30°C for 48 hours) is shown in Figure 8[5]. The swelling volume of the film is correlated to the crystallinity of the film, and it can be seen that whatever degree of polymerization sample is used, the swelling volume closely correlates with the crystallinity.

It is difficult to obtain the true crystallinity of PVOH. Typical crystallinity measurement methods are introduced here. For details, please refer to the references.

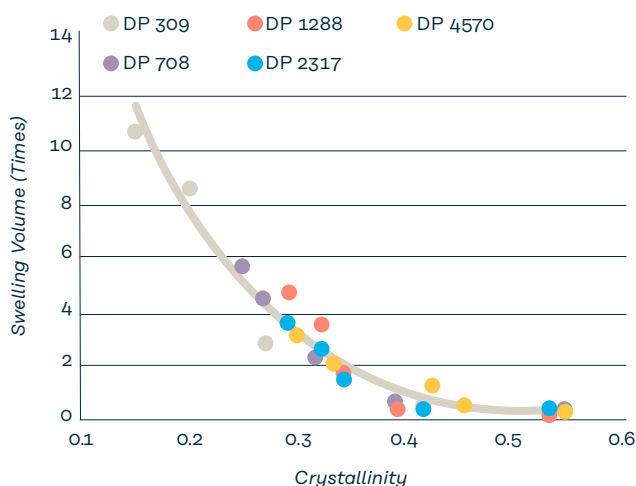Figure 7. PVOH Film Heat Treatment Temperature (10 min) and Crystallinity

Figure 8. Crystallinity and Swelling Volume (30°C for 48 hr)

References
5) Ichiro Sakurada, Yasuhiko Nukushina, Yasuo Sone, Polymer Chemistry, 12, 506 (1955)

Wide-angle X-ray: This is the most common measurement method and an absolute value can be measured directly. If the total scattering intensity curve of X-ray can be separated into the scattering contribution of the crystalline region and the scattering contribution of the amorphous region, the crystallinity can be obtained from the ratios of the respective areas to the total area. Separation of the crystalline and amorphous scatterings is done by waveform separation by the least squares method[6-8]. However, in the case of PVOH, since this waveform separation is difficult, a method of logically separating the crystalline and amorphous scatterings is performed [9].

Differential scanning calorimetry (DSC): This is a method for measuring the endothermic amount associated with melting (melting enthalpy: ▲H). ▲H is proportional to the amount of crystallinity and the relative value can be obtained. The advantages of the DSC are the speed of measurement and that accurate measurement is possible even with a very small amount of sample. Note that ▲H measured by the DSC is the relative value of crystallinity. Therefore, in order to obtain the absolute value, it cannot be determined unless ▲H is at a crystallinity of 100%, that is, the crystal melting enthalpy (▲Hm) is known. It is not easy to determine ▲Hm and the value varies depending on the measurement method. The most appropriate method is to calibrate from the precisely measured X-ray crystallinity (Xc). Additionally, for the measurement of ▲H by the DSC measurement, there is a problem of the influence of the temperature rising process. The temperature rising process corresponds to heat treatment and there is a possibility that ▲H is measured to be larger than the actual value.

Infrared/Raman measurement: Measurement of crystallinity by infrared or the Raman measurement is a method for obtaining crystallinity from the intensity of the crystallization band. In the case of PVOH, the crystallization band is observed around 1144 cm^{-1} in the infrared measurement and it is also observed in the Raman measurement [10]. There is a qualitative proportional relationship between the intensity of the crystallization band and the crystallinity. However, there is a critical point in the appearance of the infrared band and the band does not appear in an ordered structure below a certain size. For this reason, there is no proportional relationship between the crystallization band intensity and the X-ray crystallinity in the infrared measurement in a precise sense. This problem also applies to the Raman measurement.

Density measurement: This is a classical method for crystallinity measurement. Since the density of the crystalline part is higher than that of the amorphous part, the sample with higher crystallinity has a higher density. This relationship is used to obtain the crystallinity. However, it is necessary to know the values of the crystalline density and the amorphous density in advance. This is a classic but less arbitrary method. Since this method is based on a crystal-amorphous two-phase model, it is a problem that the amorphous density is assumed to be constant. Actually, the part considered as the amorphous phase contains the intermediate phase, and therefore the amorphous density is not constant.

References
6) Yasuhiko Nukushina, Kobunshi Jikken Gaku Koza 2, Edited by The Society of Polymer Science, Japan, Kyoritsu Shuppan (1957)
7) S. L. Aggarwal and G. P. Tilley, J. Polymer Sci., 18, 17 (1955)
8) A. M. Handeleh and D. J. Johnson, Polymer, 13, 27 (1972)
9) Y. Fu, W. R .Busing, Y. Jim, K. A. Affholter, and B. Wunderlich, Macromolecules, 26, 2187 (1993)
10) H. Tadokoro, The Structure of Macromolecule, Chapter5, P.187-351 (1976)

1-6. MELTING POINT

The melting point of PVOH is obtained exclusively from the endothermic peak temperature by the differential scanning calorimetry. As typical differential thermal analysis curves of fully hydrolyzed PVOH, actual measurement results are shown in Figure 9. To obtain these results, Kuraray Poval™ 28-98 in the powder state was re-saponified (fully hydrolyzed) and then it was extracted with methanol sufficiently to prepare samples for the measurement. In these curves,

sharp endothermic peaks can be seen around 235°C. As for the PVOH samples used for the measurement, pyrolysis may occur before reaching the melting point of PVOH in the temperature rising process if impurities such as sodium acetate are mixed, and thus the accurate melting point may not be measured. Therefore, it is necessary to sufficiently refine the samples in advance.
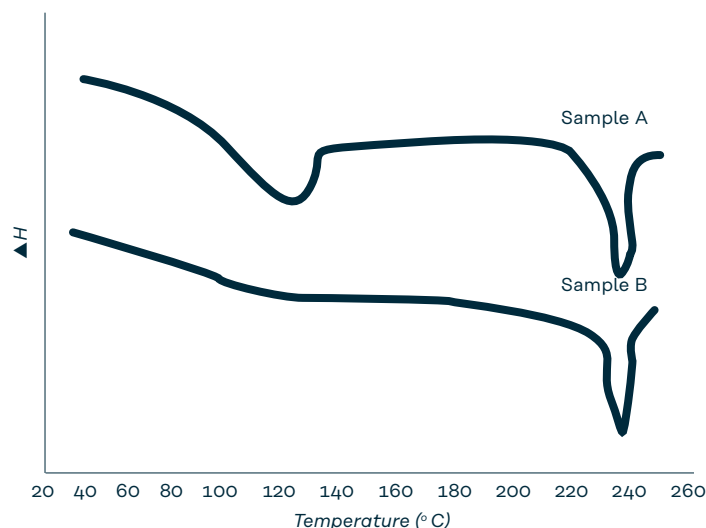

Sample A: Kuraray Poval™ 28-98 with re-saponifying and methanol extraction by Soxhlet
Sample B: Sample A with hot-air drying at 115°C for 60 min.
Measurement condition: Atmosphere - Air
Heating rate: 5°C/min

Figure 9. Differential Thermal Analysis Curves of Re-saponified Kuraray Poval™ 28-98

Although the melting point of PVOH decreases as the amount of residual acetate group increases, the degree of decrease depends on the distribution state of the residual acetate group in the molecule. As shown in Figure 10, in the case in which the residual acetate group is almost completely distributed blockwise (a), the melting point of PVOH hardly decreases. Conversely, in the case in which the residual

acetate group is distributed almost randomly (c), the melting point of PVOH linearly decreases in proportion to the amount of the residual acetate group. Commonly marketed PVOH is saponified under an alkaline condition in a methanol solvent and shows a melting point decrease as shown in (b). Therefore, it is known that the distribution state of the residual acetate group is intermediate between block and random.
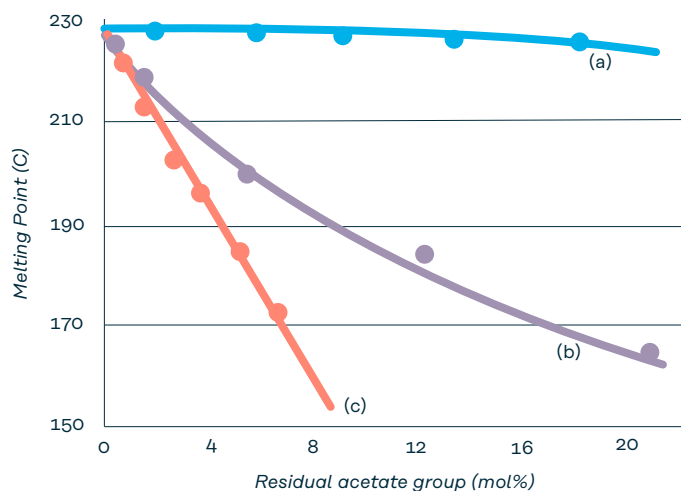

Sample:
a: Saponified with alkaline aqueous solution
b: Saponified with alkaline/ methanol solution
c: Reacetylated PVOH

Figure 10. Influence of Residual acetate Group Amount and Its Distribution State on Melting Point of PVOH

It is known that the melting point of PVOH also varies with other factors influencing the crystallinity. One of them is stereoregularity. While ordinary PVOH is atactic PVOH, it is possible to synthesize isotactic PVOH and syndiotactic PVOH by changing the polymerization mode and the raw material monomer [11]. The melting points of these stereoregular PVOH are shown in Figure 11 [12].
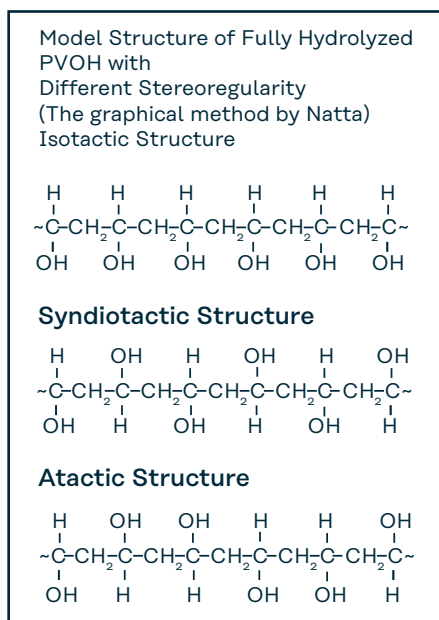
PVOH crystallizes and has melting points in all the stereoregularities. As the stereoregularity increases, the melting point increases in both isotactic PVOH and syndiotactic PVOH, with the melting point of atactic PVOH as a minimum.

Model Structure of Fully Hydrolyzed PVOH with
Different Stereoregularity
(The graphical method by Natta)
Isotactic Structure

$$\sim\!\overset{H}{\underset{OH}{C}}\!-\!CH_2\!-\!\overset{H}{\underset{OH}{C}}\!-\!CH_2\!-\!\overset{H}{\underset{OH}{C}}\!-\!CH_2\!-\!\overset{H}{\underset{OH}{C}}\!-\!CH_2\!-\!\overset{H}{\underset{OH}{C}}\!-\!CH_2\!-\!\overset{H}{\underset{OH}{C}}\!\sim$$

Syndiotactic Structure

$$\sim\!\overset{H}{\underset{OH}{C}}\!-\!CH_2\!-\!\overset{OH}{\underset{H}{C}}\!-\!CH_2\!-\!\overset{H}{\underset{OH}{C}}\!-\!CH_2\!-\!\overset{OH}{\underset{H}{C}}\!-\!CH_2\!-\!\overset{H}{\underset{OH}{C}}\!-\!CH_2\!-\!\overset{OH}{\underset{H}{C}}\!\sim$$

Atactic Structure

$$\sim\!\overset{H}{\underset{OH}{C}}\!-\!CH_2\!-\!\overset{OH}{\underset{H}{C}}\!-\!CH_2\!-\!\overset{OH}{\underset{H}{C}}\!-\!CH_2\!-\!\overset{H}{\underset{OH}{C}}\!-\!CH_2\!-\!\overset{H}{\underset{OH}{C}}\!-\!CH_2\!-\!\overset{OH}{\underset{H}{C}}\!\sim$$
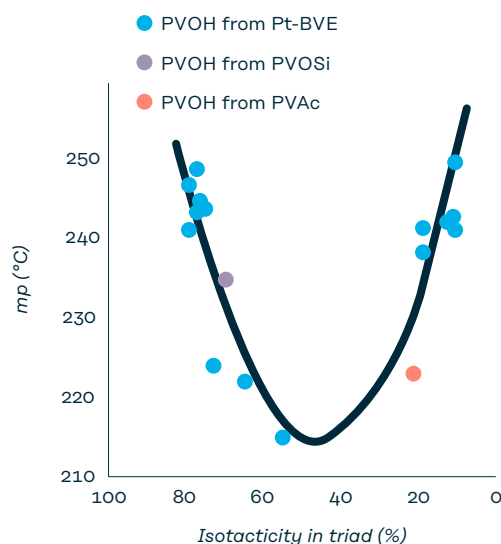
Figure 11. Relationship between Melting Point and Tacticity

Additionally, 1,2-glycol bond is a factor influencing the crystallinity of PVOH. The 1,2-glycol bond in PVOH is a result of heterophilic bond during the polymerization of vinyl acetate as a raw material. That is, the polymerization of vinyl acetate usually grows with head-to-tail addition, but trace amounts of the head-to-tail — tail-to-head addition is produced, which becomes 1,2-glycol bond. The amount of 1,2-glycol bond is uniquely determined by the polymerization temperature [13], and it increases as the polymerization temperature increases and decreases as the polymerization temperature decreases. The melting points of PVOH with various 1,2-glycol bond amounts are shown in Figure 12. As the amount of 1,2-glycol bond, which is a heterophilic bond, increases, the crystallinity decreases and the melting point also decreases.
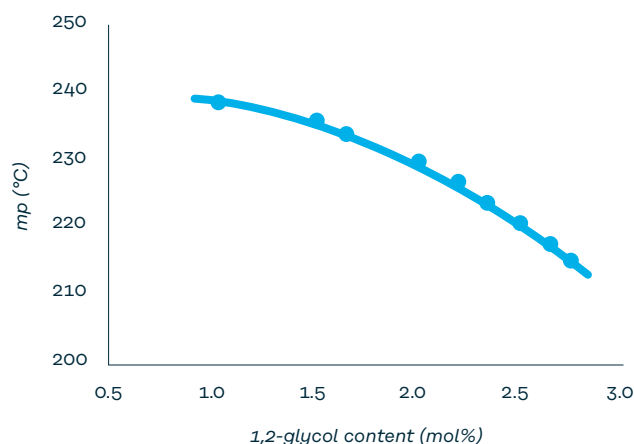
Figure 12. Relationship between Melting Point and 1,2-glycol Bond Amount

References
11) Toshiaki Sato, "PVOH no Sekai (The World of PVOH)", Kobunshi Kankokai, 1 (1992)
12) Masao Sumi, Keiji Matsumura, Ryotaro Ohno, Shunichi Nazakura, Shunsuke Murahasi, Polymer Chemistry, 24, 606 (1967)
13) Naoki Fujiwara, Toshiaki Sato, Hitoshi Maruyama, Kazutoshi Terada, Takuji Okaya, Report of 104th POVAL Conference, 114, (1994)

1-7. SPECIFIC HEAT

As for the specific heat of PVOH, there are only two measured values reported in the literature and there are considerable differences between them. These values are shown in Table 4.

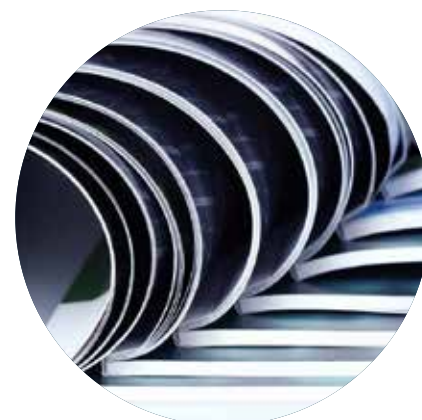| Measured Value	Literature
0.4 cal/(deg)(g)	Encyc. of Polymer Science and Technology, Vol. 14, 159 (1971)
0.00105 Kcal/(deg)(g) R	R. W. Warfield, Kolloid Z., 185, 63 (1962)

Table 4. Specific Heat of PVOH

1-8. LATENT HEAT OF MELTING

The latent heat of melting of PVOH can be obtained by two methods. That is, a method of indirectly calculating from that of the copolymer using Flory equation or the Baur's theory, and a method of measuring the melting heat in a two-component system containing an appropriate diluent and calculating the melting point of PVOH using Flory's equation. These values are shown in Table 5.

Measured Value (Kcal/mol) and Measurement Method	Literature
0.56, copolymer (Flory's equation)	J.P.S.A-1, 4, 623 (1966)
1.67, copolymer (Flory's equation)	Kikukawa et al., Polymer Chemistry, 25, 19 (1968)
1.57, copolymer (Flory's equation)	R. K. Tubbs, Monograph No.30, Society of Chemical Industry, London, 88 (1968)
1.64, dilution method (Glycerin)	J.P.S.[A]3, 4181(1965)
1.67, copoly 2.47, dilution method (Water) 2.00, dilution method (Ethylene glycol) 1.43, dilution method (Dimethylformamide) 1.47, dilution method (Acetamide) mer (Flory's equation)	Hamada et al., Polymer Chemistry 23, 395 (1966)

Table 5. Latent Heat of Melting of PVOH

1-9. ENTROPY, ENTHALPY

The melting entropies of PVOH are shown in Table 6.
The melting enthalpies of PVOH are shown in Table 7.

Described Value	Literature
0.2655 cal/(deg)(g) at 245°C	Kirk Othmer, Encyc. of Chem. Tech., Vol21 (1970)
3.3 cal/(deg)(mole)	Encyc. of Polymer Science and Technology, Vol14 (1971)
3.27 (e.u.)	R. K. Tubbs, J.P.S.(A)3, 4181(1965)

Table 6. Melting Entropy of PVOH

Described Value	Literature
32.45 cal/g at 245°C	Kirk Othmer, Encyc. of Chem. Tech., Vol21 (1970)

Table 7. Melting Enthalpy of PVOH

1-10. HEAT OF DISSOLUTION

The amount of heat diffused or absorbed when PVOH is dissolved in water, that is, the heat of dissolution with respect to water, is the energy generated when the hydrogen bond between PVOH molecules and/or water molecules is destroyed and new hydrogen bonds are formed between polymers and water molecules. According to a report by Meerson et al., when PVOH is dissolved in water, it generates heat at a water temperature of 55°C or lower and absorbs heat at a water temperature of 55°C or higher, as shown in Figure 13. They reported that the relationship as shown in the following formula was established between the dissolution heat ▲Hd (T) and the dissolution temperature T (°C) in the temperature range from 25°C to 80°C, and the heat of dissolution ▲Hd (Tg) of PVOH at its second-order transition temperature Tg (°C) was 6.25 cal/g.
$$\blacktriangle Hd(T) = \blacktriangle Hd(Tg) - 0.25\ (Tg\text{-}T)\ [14]$$

As for the heat of dissolution of PVOH with different degree of hydrolysis, there is a report by Oya [15]. As shown in Figure 14, the heat of dissolution of PVOH with respect to water at 30°C decreases linearly as the acetate group content increases when the degree of polymerization is 1400 or 165

(in this case, heat generation is observed and the amount of heat generation increases linearly). Additionally, the heat of dissolution is almost constant when the amount of acetate group is around 20 mol%, about -9.8 cal/g for the degree of polymerization of 1400 and about -8.1 cal/g for the degree of polymerization of 165, and the heat of dissolution shows almost no change when the amount is more than 20 mol%. The tendency of the heat of dissolution to decrease in accordance with increase of acetate group well supports the general fact that PVOH with a low degree of hydrolysis dissolves well at low temperature. In the report, Oya described that there was a bending point around the acetate group amount of 20 mol% and this showed good agreement with the case of the specific gravity of PVOH according to the research by Sone et al. [3], and it could be thought that it was a result of the difference in the aggregation state of PVOH molecules. However, as for the influence of the degree of polymerization, Oya concluded that although the difference in the heat of dissolution owing to the degree of polymerization was supposedly recognized, it was difficult to make a detailed discussion based on the experimental result of such extent.

References
14) Meerson, Kolloid-Z, 18, 447 (1956)
15) Oya et al., Polymer Journal, 12, 122 (1956)
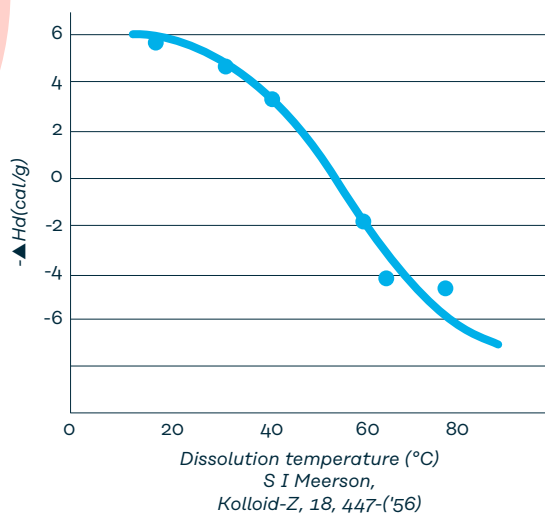16) Sone et al., Polymer Journal, 10, 277 (1953)
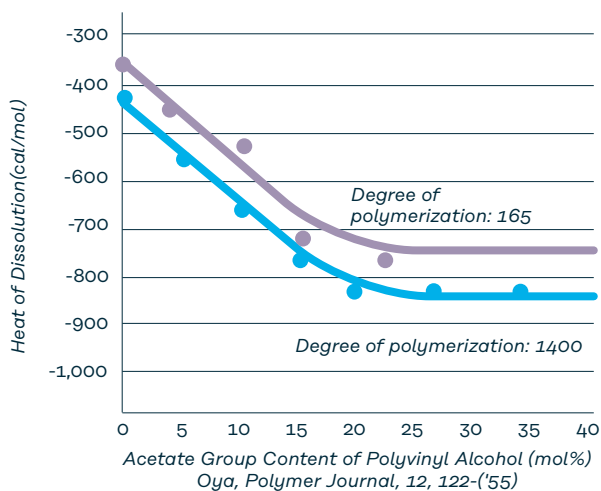
Figure 13. Heat of Dissolution of PVOH

Figure 14. Heat of Dissolution of Partially
Hydrolyzed PVOH (Dissolution Temperature: 30°C)

1-11. HEAT OF COMBUSTION

In the Encyclopedia of Chemical Technology (Vol. 21, (1970)), the heat of combustion of PVOH is described as 5902 cal/g [17]. In B.C.S.J (Vol.40, 2700−), there is a report that the heat of combustion per monomer unit is 263.2 Kcal. This value is converted to about 5980 cal/g and shows good agreement with the value of the former.

1-12. THERMAL CONDUCTIVITY, LINEAR EXPANSION COEFFICIENT

There is little data on the physical properties of PVOH such as thermal conductivity and linear expansion coefficient. This is probably because PVOH is not relatively used as a so-called molded product.

As for the values of thermal conductivity, 5×10^{-4} cal/(sec)(cm²) (°C/cm) for extruded products and 5×10^{-4} cal/(sec)(cm²) (°C/cm) for casted products are reported in Mod. Plastics, 18, 6, 53 (1941).

1-13. THERMAL DECOMPOSITION, THERMAL DECOMPOSITION PRODUCT

PVOH colors gradually and becomes difficult to dissolve in water when it is heated in air. In particular, coloring occurs remarkably at a temperature of 130°C or higher, and thermal decomposition progresses gradually when the temperature exceeds 200°C. The thermal decomposition mechanism of PVOH was researched by Yamaguchi et al. [18], [19] and Tsuchiya et al. [20]. An example of the thermal decomposition mechanism is shown in Figure 15.

It is assumed that the coloring of PVOH during heat treatment is caused by the formation of the enone structure in the initial reaction of thermal decomposition of PVOH. In this reaction, the hydroxyl group is oxidized to a ketone group and then the hydroxyl group adjacent to the formed ketone group is dehydrated. It is observed in UV absorption spectrum that absorptions of PVOH around 230 nm, 280 nm and 330 nm increase by heating in air. These absorptions correspond to the repeating unit n = 1 to 3 of the carbon-carbon double bonding in the enone structure. In Figure 15 it is thought that the coloring occurs by absorbing light in the visible light region owing to an increase in their chain length .
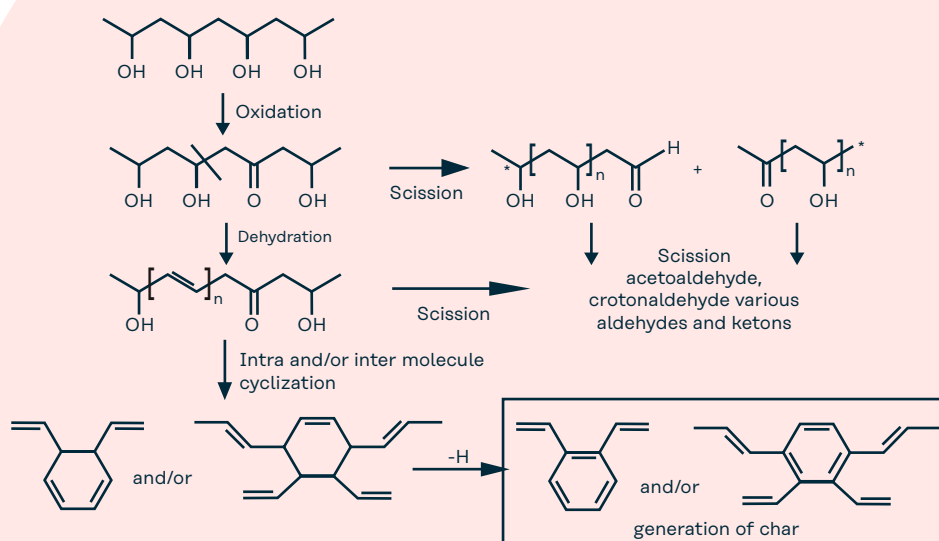

Figure 15. Thermal Decomposition Mechanism of PVOH

In the temperature range of 200°C or higher, a decrease in weight occurs because volatilization of thermally decomposed components starts to occur. Figures 16 and 17 show the rates of decrease in weight when Kuraray Poval™ 28-98 and Kuraray Poval™ 5-88 are heated (10°C/min) in air or in nitrogen.
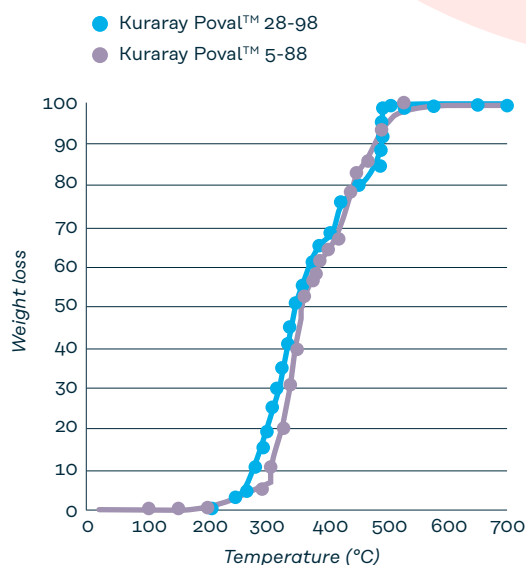

Figure 16. Thermal Decomposition of PVOH
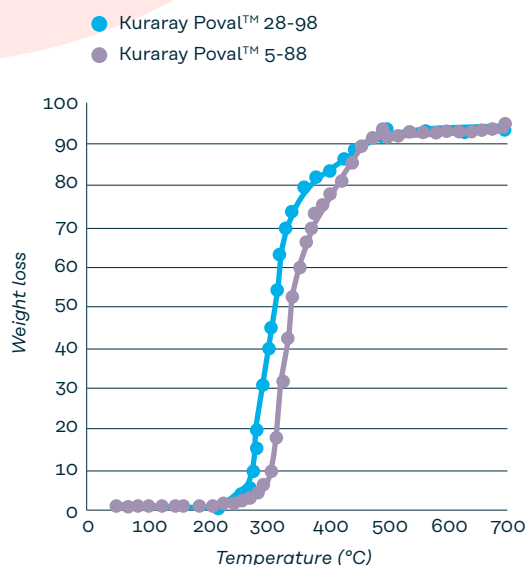(Rate of Temperature Rise: 10°C/min, in air)

Figure 17. Thermal Decomposition of PVOH
(Rate of Temperature Rise: 10°C/min, in nitrogen)

References
17) Texas. Rept. Miol. Med. 23(2), 432(1965)

In the heating test in air, it is considered that PVOH is almost completely decomposed thermally around 450 to 500°C and the decomposition products are volatilized. Meanwhile, in the heating test in nitrogen, the decrease in weight becomes gradual at around the same temperature and about 5% of nonvolatile components remain at the time when the temperature reaches 700°C. The residues are considered to correspond to so-called Char in the thermal decomposition mechanism, as shown in Figure 15. There are many reports on what is generated by the thermal decomposition and on the decomposition products. Some examples are shown in Tables 8 and 9.

Table 8. Thermal Decomposition Product of PVOH [20]

Thermal Decomposition Product	Weight % (based on the starting weight)
Water	33.4
Carbon monoxide	0.12
Carbon dioxide	0.18
Hydrocarbons (C1, C2)	0.01
Acetaldehyde	1.17
Acetone	0.38
Ethanol	0.29
Benzene	0.06
Crotonaldehyde	0.76
3-Penten-2-one	0.19
2,4-Hexadiene-1-ol	0.55
3,5-Heptadiene-2-one	0.099
Benzaldehyde	0.022
Acetophenone	0.021
2,4,6-Octatriene-1-ol	0.11
3.5.7-Nonatriene-2-one	0.020
Other	0.082

* Sample: Degree of polymerization = 3300, degree of hydrolysis = 99 mol% or higher
* Decomposition condition: Heating under vacuum at 240°C for 4 hr

Table 9. Thermal Decomposition Product of PVOH

Example	1	2	3
Decomposition temperature e (°C)	220–240	270–280	500
Atmosphere	Air	Air	Vacuum
Heating time (h)	10	10	Unknown
Residual acetate group of sample (mol%)	0.05	0.05	13-15
Rate of weight decrease (%)	36	41	95
Decomposition product (mol/PVOH basic mol)			
Water	0.62	0.635	0.670
Acetic acid			0.094
Acetaldehyde	0.0214	0.0117	0.378
Crotonaldehyde	0.0146	0.0118	0
2,4-Hexadiene-1-ol	0	0	0
2,4,6-Octatriene-1-ol	0	0	0
Benzaldehyde	0.0025	0.0035	0
Acetone	0	0	0
3-Penten-2-one	0	0	0
3,5-Pentadiene-2-one	0	0	0
3,5,7-Nonatriene-2-one	0	0	0
Acetophenone	0.0019	0.0051	0.0051
Ethanol	0	0	0.053
Carbon monoxide	0	0	0.070
Carbon dioxide	0	0	0.014
Benzene	0	0	0
Phenols	Trace	Trace	0

References
18) Yamaguchi et al., Polymer Chemistry, 18, 406 (1961)
19) Yamaguchi et al., Polymer Chemistry, 18, 653 (1961)
20) Tsuchiya et al., J.P.S., A-1, 7, 3151 (1969)
21) C.A., 68, 60189-g (1968)
22) Doklady Phys, Chem., 154, 125 (1964)

1-14. COMBUSTION CHARACTERISTICS (LIMITING OXYGEN INDEX)

The flammability of PVOH is generally said to be nearly that of paper. As one method to quantitatively compare the flammability of plastics, there is a report in which the limiting oxygen index was determined [23]. Considering air as a mixture of oxygen and nitrogen, the oxygen volume ratio in normal air is about 0.21. Limiting oxygen index (n) is the lowest oxygen concentration required for a specimen to keep burning stably even after removing the ignition source. This value was measured by burning long and narrow plastics such as a candle in an atmosphere in which the volume ratio of oxygen and nitrogen is changed. The value (n) of PVOH specimen with a degree of saponification of 98 mol% and a degree of polymerization of 550 was reported as 0.225 ± 0.004. This indicates that an atmosphere with a slightly higher oxygen concentration than ordinary air is necessary for the specimen to maintain a stable burn. Based on the value in this paper, PVOH is less flammable compared to polyethylene (n: 0.174 −), polystyrene (n: 0.181 −), etc., but is considered to be comparable to polyvinyl chloride (n: 0.45), polyvinylidene chloride (n: 0.60), Teflon (n: 0.95), etc.

1-15. DUST EXPLOSION

The ignition and explosion properties of PVOH powder are greatly affected by the natures of PVOH such as the average particle diameter and its distribution, the content of organic volatiles, moisture content, etc., fine particle size concentration, humidity conditions and the like. For this reason, it is basically impossible to obtain a measurement value common to all PVOH.

Although representative measured values are shown below, please understand that they are not common to all PVOH, as mentioned above.

Fine powder of Kuraray Poval™ 22-88 (passing a sieve with an opening of 63 μm, methanol content of 0.01%, methyl acetate of 0.04%) was used as a measurement sample. A minimum ignition energy measuring device (Type MIKE3) by A. Kühner manufactured in accordance with the international standard "IEC 61241-2-3 (1994-09), Section 3: Method for determining minimum ignition energy of dust / air mixtures" was used. This device can change the discharge energy by 7 steps of 1 mJ, 3 mJ, 10 mJ, 30 mJ, 100 mJ, 300 mJ and 1 J with the capacity discharge method. Additionally, a method in which sample powder was blown up by compressed air and dispersed in a 1.2 L explosive cylinder was adopted.

In the measurement, a test with a predetermined amount of sample and discharge energy was carried out 10 times to check wthether the sample ignites or not. When it ignited at least once, it was determined that there was ignition under that condition. Next, this operation was repeated by variously changing the sample amount and discharge energy to obtain ignition by the predetermined discharge energy for each sample amount. The ignition delay time was changed as necessary to obtain ignition. The results are shown in Table 10.

Figure 18 shows the relationship between the dust concentration and the discharge energy based on the data of Table 10. The minimum ignition energy (E_{min}) is in the range from the non-ignited maximum discharge energy (E_2) to the ignited minimum discharge energy (E_1) ($E_2 < E_{min} < E_1$). That is, the minimum ignition energy (E_{min}) of this sample is in the range from 30 mJ to 100 mJ ($30\ mJ < E_{min} < 100\ mJ$) and its statistical minimum ignition energy (Es) is 42 mJ. Note that the statistical minimum ignition energy was calculated based on the calculation formula described in European Standard EN 13 821: 2002.

Therefore, since PVOH has a risk of dust explosion with static electricity as an ignition source, it is necessary to securely ground the equipment, piping, etc. and to take measures such as using conductive materials.
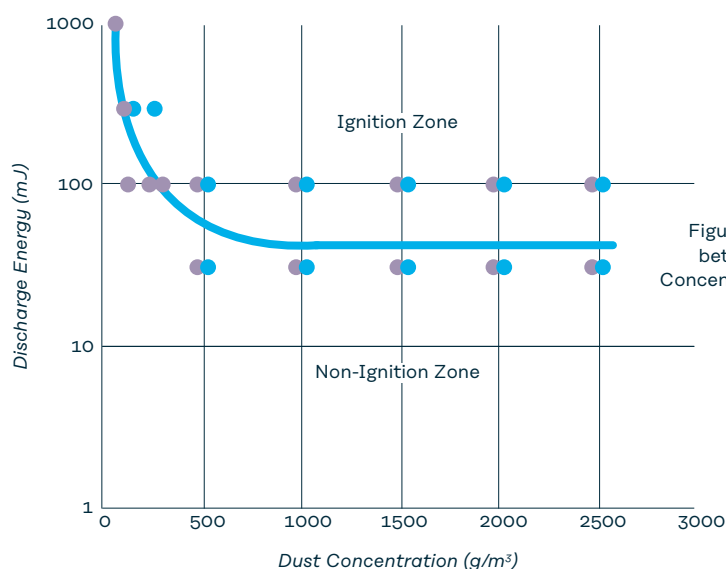

Figure 18. Relationship between PVOH Dust Concentration and Discharge Energy

References
23) C. P. Fenimore, Modern plastics, 43, 141 (1966)

Table 10. Minimum Ignition Energy of PVOH Floating Dust

Sample amount (g)	Dust concentration (g/m3)	Discharge energy (mJ)	Ignition delay time (min)	Ignition [1]
0.075	62.5	1000	60	×
0.15	125	300	90	×
		300	60	O5)
		1000	60	×
0.3	250	300	120	O(6)
		100	120	×
		100	90	×
		100	60	×
0.6	500	100	120	×
		100	150	O(3)
		30	150	×
		30	180	×
1.2	1000	100	120	×
		100	150	O(6)
		30	150	×
		30	180	×
1.8	1500	100	120	×
		100	150	O(6)
		30	150	×
		30	180	×
2.4	2000	100	120	×
		100	150	O(3)
		30	150	×
		30	180	×
2.4	2500	100	120	×
		100	150	O(3)
		30	150	×
		30	180	×

1) The test was conducted 10 times under the same condition, and the condition without ignition is marked with x. The condition with ignition is marked with O and the number of times required for ignition is shown in parentheses.

2. Primary structure of PVOH

2-1. PRIMARY STRUCTURE

A PVOH polymer chain is schematically shown in Figure 19. PVOH is a copolymer of vinyl alcohol and vinyl acetate, and it contains most of the items that are problematic in the primary structure of a polymer, such as stereoregularity, short chain branching, heterophilic bond (1,2-glycol bond), double bond, end group, as well as sequence distribution of vinyl alcohol and vinyl acetate.
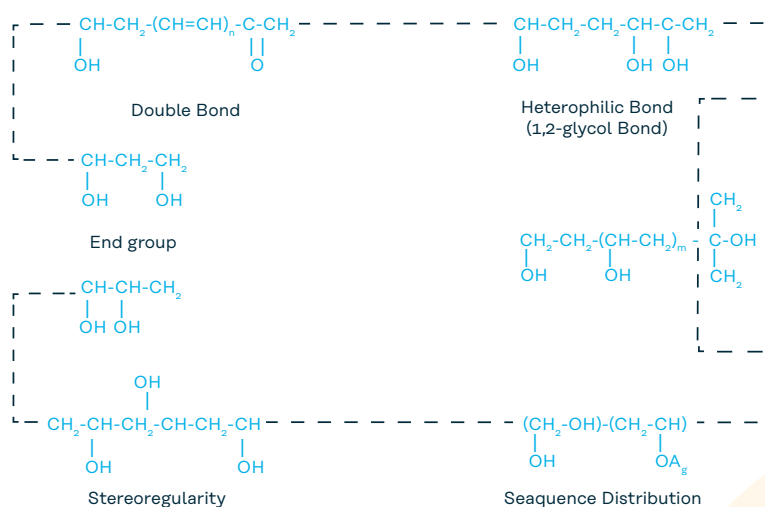

Figure 19. Primary structure of PVOH

2-2. STEREOREGULARITY

The stereoregularity of PVOH, can be measured by several methods such as infrared absorption spectrometry [24,25] and the NMR measurement [25] have been proposed. As a method that can determine the stereoregularity with the highest accuracy, there is the ^{1}H-NMR [26-28] or ^{13}C-NMR [29-31] measurement with the DMSO-d6 solution of PVOH. The chart of the hydroxyl group part of 1H-NMR is shown in Figure 20.

With respect to ^{1}H-NMR, it is split into isotactic, atactic and syndiotactic from the low magnetic field side, and the triad tacticity is determined based on the integral ratio. On the other hand, with respect to ^{13}C-NMR, the higher-order stereoregularity up to heptad can be evaluated based on the splitting of methine carbon of PVOH.

As for the effects of stereoregularity on PVOH physical properties, the melting point has already described in the previous chapter. In addition to this, there is the aqueous solution stability. Figure 21 shows the solution stabilitiy of concentrated aqueous solutions with different tacticity.

References
24) K. Fujii and J. Ukida, Makrmol. Chem., 65, 74 (1963)
25) Shunsuke Murahasi, Shunichi Nazakura, Masao Sumi, Heimei Yuki, Koishi Hatada, Polymer Chemistry, 23, 605 (1966)
26) J. R. DeMember, H. C. Haas et al, J. Polym. Sci., Polym. Lett. Ed., 10, 385 (1972)
27) T. Moritani, I. Kuruma, K. Shibatani, Y. Fujiwara, Macromolecules, 5, 577 (1972)
28) T. K. wu and D. W. Ovenall, Macromolecules, 6 (No.4), 240 (1973)
29) Y. Inoue, R. Cyujo, and A. Nishioka, Polymer J., 4 (No.3), 244 (1973)
30) T. K. Wu and M. L. Sheer, Macromolecules, 10 (No. 3), 529 (1977)
31) D. W. Ovenall, Macromolecules, 17, 1458 (1984)
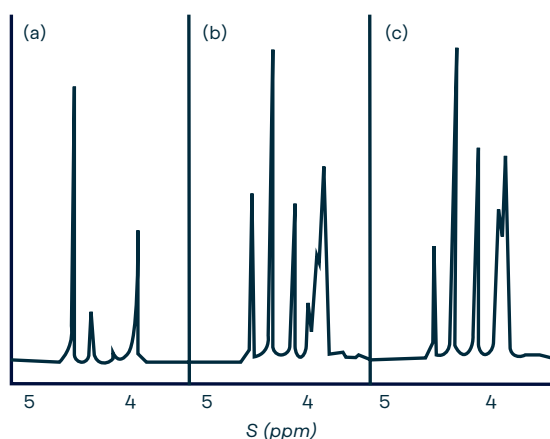
(d$_6$-DMSO, 500Mz)
(a) it-PVOH (mm/mr/rr=79.1/18.9/2.0
(b) at-PVOH (mm/,mr/rr=22.0/48.8/29.2)
(c) st-PVOH (mm/mr/rr= 14.1/48.9/37.0)

Figure 20. ^{1}H-NMR Spectrum of Stereoregular PVOH

Figure 21. Temporal Change of Viscosity of PVOH Aqueous Solution with Different Stereoregularity

Generally PVOH is basically atactic, it contains a slightly more racemo diad (syndiotactic structure). Normally, when the concentrated aqueous solution of general PVOH is left at low temperature, this solution thickens with time and turns into a gel (Figure 21: Racemo diad: 53.0 mol%). In contrast, the solution of PVOH, in which the meso diad increased by 2—3 mol% only, is not changed into gel even if the solution is left for a long time [32] (Figure 21: Racemo diad: 50.5 mol%). This is thought to be a r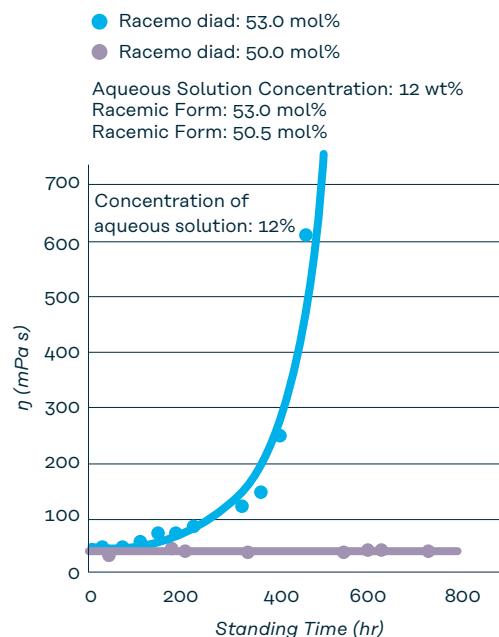esult of the decrease in the racemo diad that can form intermolecular hydrogen bonds and the increase in the meso diad form that cannot form the bonds. As described above, the tacticity of PVOH influences greatly on the physical properties.On the other hand, it is essential to change the polymerization method and the raw material monomer in order to change the tacticity. For this reason, PVOH having a special tacticity is not industrially produced at the present time.

2-3. HETEROPHILIC BOND (1,2-GLYCOL BOND)

A considerable amount of 1,2-glycol bond exists in the heterophilic bond of PVOH [33]. The quantitative determination method of 1,2-glycol bond by ^{1}H-NMR [34] and ^{13}C-NMR[35] has been studied [35].
As for the amount of 1,2-glycol bond and the melting point of PVOH, they were already described in "Melting Point" of the previous chapter. Here, the correlation between the amount of 1,2-glycol bond and the viscosity stability of the concentrated aqueous solution is shown in Figure 22 [36].

Figure 22 shows the temporal changes in the viscosity of 12% aqueous solutions of samples with a nearly identical degree of polymerization, containing 1,2-glycol bond of about 1.6 mol% and containing no 1,2-glycol bonding. Although the viscosity of the solution containing no 1,2-glycol bonding started to thicken quickly after 200 hours had elapsed , the solution turned into a gel. The viscosity of the ordinary PVOH solution (the amout of 1,2-glycol bond: 1.6 mol%) hardly changes under the same condition. This is interpreted to mean that the intermolecular interaction of PVOH is inhibited by 1,2-glycol bond. Additionally, it is known that 1,2-glycol bond becomes a factor disturbing the structure, such as decreasing the iodine coloring ability to PVOH [37], and existing in the amorphous part, not in the crystalline region [38].
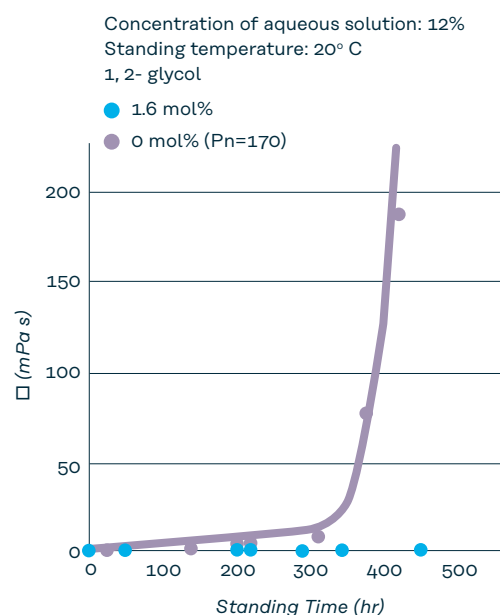

Figure 22. Temporal Change of Viscosity of PVOH Aqueous Solution with Different 1,2-glycol bond Content

References
32) Kiyokazu Imai et al, Content of 31st Symposium on Macromolecules, p. 1309 (1982)
33) P. J. Flory and F. S. Leutner, J. Polymer Sci., 3, 880 (1948)
34) S. Amiya and M. Uetsuki, Analytical Science, 1, 91 (1983)
35) S. Amiya and M. Uetsuki, Macromolecules, 15, 166 (1982)
36) Shigetoshi Amiya, Report of 92nd PVOH Meeting, (1988)
37) K. Imai and M. Matsumoto, J. Polymer Sci., 55, 335 (1961)
38) Imoto, Polymer Chemistry 16, 125 (1959)

2-4. END STRUCTURE

PVOH is obtained mainly from vinyl acetate as a raw material through a radical polymerization process and a saponification process. However, in the radical polymerization process in particular, the growing end radical of vinyl acetate has extremely high reactivity and the chain transfer reaction occurs easily. Therefore, PVOH is characterized by the end structure being changed depending on the type and concentration of the solvent, monomer concentration and initiator to be used, the conversion of polymerization, the polymerization temperature and the additives. The end structure of general PVOH is mostly of the methylol group formed by the chain transfer to the solvent (methanol) and the methylol group and methyl group terminated by the chain transfer [39]. Additionally, there is a sodium carboxylate or γ-lactone structure where molecules that are chain-transferred to a methyl proton of the acetate group of vinyl acetate or polyvinyl acetate produced in the reaction system are produced by hydrolysis of the acetate group in the saponification process. Although a small amount of the end derived from the initiator can be observed, the amount is extremely small compared with those of other end structures. It is considered that this is a result of the fact that, in the radical polymerization system of vinyl acetate, the rate of chain transfer is larger than that of termination.

2-5. BRANCHING

In the state of polyvinyl acetate before saponification, long chain branching exists in the side chain owing to the chain transfer to the methyl proton of an acetate group as described above. However, it is considered that such long chain branching does not exist in the PVOH state because it is eliminated by the saponification reaction. As the branching observed in PVOH, there is short-chain branching generated by back-biting reaction. The formation mechanism of short-chain branching by back-biting reaction is shown in Figure 23. The end methylol group of the butyl short-chain branching can be quantified by the ^{13}C-NMR measurement. However, these short-chain branches are not detected in general PVOH.
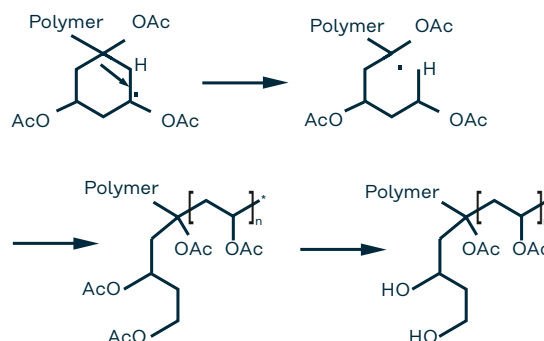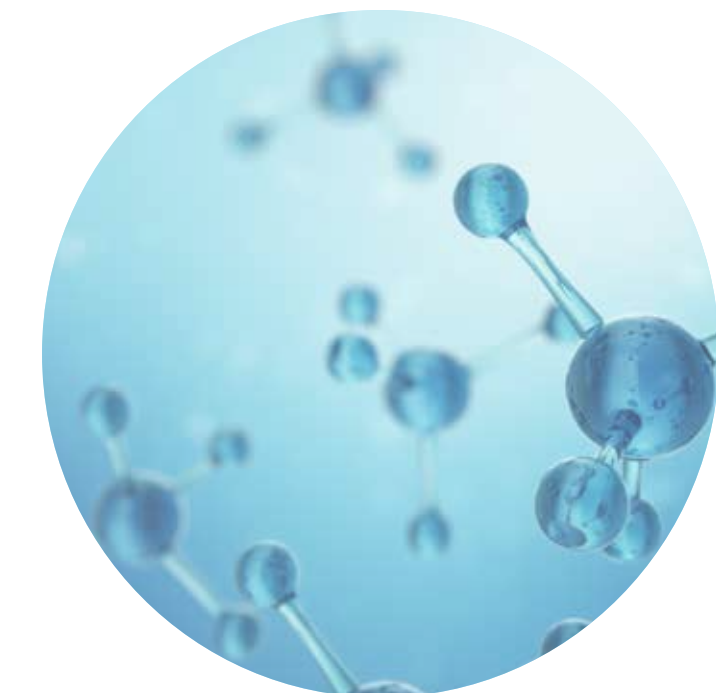

Figure 23. Formation Mechanism of Short-chain Branching by Back-biting reaction

References
39) Shigetoshi Amiya, Report of 86th PVOH Meeting, 37 (1985)

2-6. DOUBLE BOND

Coloring occurs when PVOH is heated. This is considered to be caused by conjugated double bonds of a certain length existing in the main chain. For the formation mechanism of double bonds etc., refer to the "Thermal Decomposition Product" in the previous chapter. Although the carbonyl group produced by oxidation of the hydroxyl group of PVOH is thought to be the base point for double bond formation in heat treatment, there is a method using chain transfer polymerization as a method for introducing the carbonyl group other than oxidation of the hydroxyl group. In the

coexistence of aliphatic aldehydes such as acetaldehyde, it is possible to introduce the carbonyl group to the polymer end by radical polymerization of vinyl acetate.

An example of the introduction is shown in Figure 24. The polyene structure is produced by saponifying the obtained polymer and heat-treating it. The obtained PVOH exhibits UV absorption peaks at aroud 230 nm, 280 nm, 330 nm which depend on the length of the conjugated polyene (n = 1, 2 and 3) [40-41].

$$CH_3C\text{-}(CH_2CH)\text{-}H$$
$$\underset{O}{\|}\quad\underset{OAc}{|}$$

Saponification →

Heat Treatment →

$$CH_3C\text{-}(CH=CH)_n\text{-}(CH_2CH)\text{-}H \quad (n=2\sim3)$$
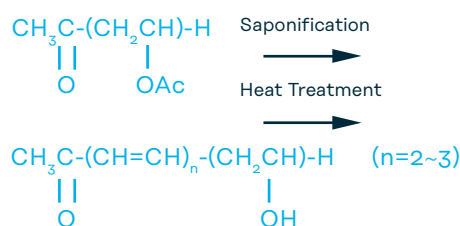$$\underset{O}{\|}\qquad\qquad\underset{OH}{|}$$

Figure 24. Double bond structure contained in PVOH

2-7. CHAIN DISTRIBUTION OF RESIDUAL ACETATE GROUPS

Partially hydrolyzed PVOH shows significant differences of physical properties such as surface activity depending on the amount of residual acetate groups and the sequence distribution of residual acetate groups. Measurements of Iodine absorbance [42] and melting point [41] are known as the indirect methods for estimating the distribution of

residual acetate groups. For the melting point and the chain distribution, refer to "Melting Point" in the previous chapter. Meanwhile, as for direct measurement methods, there is a report using a block character η by the ^{13}C-NMR measurement [44] and a composition analysis using a liquid chromatogram by Dawkins et al. [45]

References
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42) Hayashi, Nakano, Motoyama, Kobunshi Kagaku, 20, 303 (1963)
43) R. K. Tubbs, J. Polymer Sci., A-1, 4, 304 (1966)
44) T. Moritani and Y. Fujiwara, Makromol. Chem., 10, 532 (1977)
45) J. V. Dawkins et al., Polymer, 40, 7331 (1999)

3. Behavior of PVOH Aqueous Solution

3-1. SOLUBILITY IN WATER

PVOH is used mainly in aqueous solution. Its solubility in water depends on its degree of hydrolysis, degree of polymerization and degree of heat treatment received during the manufacturing process. The effect of the degree of hydrolysis is especially significant. PVOH has many hydroxyl groups with extremely high affinity for water. These hydroxyl groups act to induce strong inter and intramoleculare hydrogen bonding, which significantly inhibit the solubility in water. On the other hand, the residual acetate groups in partially hydrolyzed PVOH are essentially hydrophobic. As the number of acetate groups increases, steric hindrance increases, and disturbs the arrangement of the intermolecular chains and inhibits the formation of hydrogen bonds between the molecular chains. The presence of an adequate number of these acetate groups improves the solubility in water. As the amount of the residual acetate groups increases, the amount of heat generation increases

when PVOH dissolves in water, and the solubility at a constant temperature improves. However, the critical temperature at which phase separation occurs decreases, and the solubility at high-temperatures tends to decrease gradually. Figure 25 shows the relation between the degree of hydrolysis and the solubility of PVOH with a degree of polymerization of 1700. The sample was dissolved at a concentration of 4 % under constant stirring conditions. As is clear from this figure, the presence of only 2-3 mol% of residual acetate groups causes a significant difference in the solubility at 40-60°C. The PVOH with a degree of saponification of 97 mol% is almost completely dissolved. However, the fully hydrolyzed grade is only slightly soluble and heating to ≥80°C is necessary for complete dissolution. At around 20°C PVOH at 88 mol% hydrolysis dissolves well, but the solubility sharply decreases as the degree of hydrolysis increases further.

Dissolution condition
(Concentration 4%)
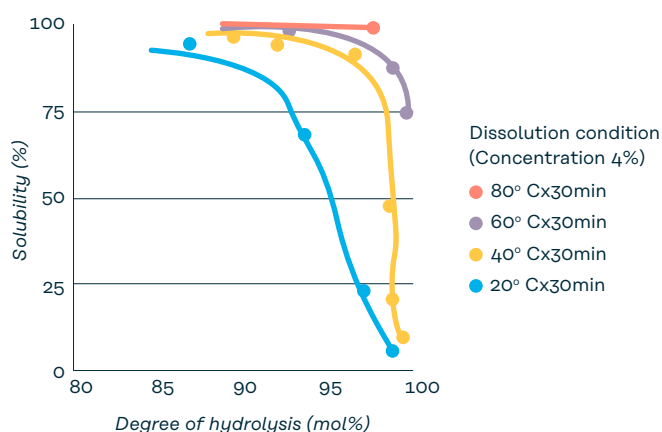● 80° Cx30min
● 60° Cx30min
● 40° Cx30min
● 20° Cx30min

Figure 25. Influence of degree of hydrolysis on solubility of PVOH

Figure 26 and Figure 27 show the results of dissolving a number of PVOH grades with varying temperature for 30 minutes with a solution concentrations of 4% and 10% under a constant stirring condition. The solubility of a so-called fully hydrolyzed grade of PVOH with a degree of hydrolysis of about 98 mol% decreases considerably as the degree of polymerization increases. However, the solubility of a so-called partially hydrolyzed grade of PVOH with a degree of hydrolysis of 88 mol% shows very little dependence on the degree of polymerization. Although PVOH with a degree of hydrolysis of 80 mol% dissolves better than PVOH with a degree of hydrolysis of 88 mol% in the low-temperature range, it shows unusual behavior that the solubility decreases extremely at a temperature of 30–35°C or higher and eventually coagulates.

As described above, as the amount of residual acetate groups increase, the mutual hydrogen bonding between the hydroxyl groups in and between the PVOH molecules becomes less and the bonding between the molecular chains is weakened, thus improving the solubility of PVOH. When the degree of hydrolysis becomes 80 mol% or less and the amount of residual acetate group exceeds 20 mol%, the solubility at low temperature still tends to increase. The critical temperature at which phase separation occurs decreases and the solubility at high temperature decreases. The degree of hydrolysis of the general grades sold as partially hydrolyzed products is mostly centered at 88 mol%. It can be thought that this value is set as the degree of hydrolysis that is relatively soluble at both low and high temperatures, and is stable without coagulation at the boiling point of water. When PVOH is used as a warp sizing agent it is dried in the process and is required to be able to be easily removed even after heat treatment. It is often desired to also improve water resistance and moisture resistance as an adhesive. Therefore, the change in the solubility of PVOH owing to the heat treatment received in the process is an important issue.
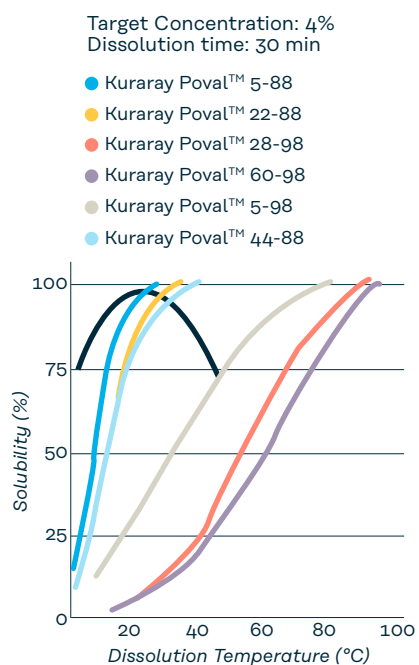
Target Concentration: 4%
Dissolution time: 30 min

● Kuraray Poval™ 5-88
● Kuraray Poval™ 22-88
● Kuraray Poval™ 28-98
● Kuraray Poval™ 60-98
● Kuraray Poval™ 5-98
● Kuraray Poval™ 44-88

Figure 26. Solubility of Major PVOH (Influence of Dissolution Temperature)

● Kuraray Poval™ 5-88
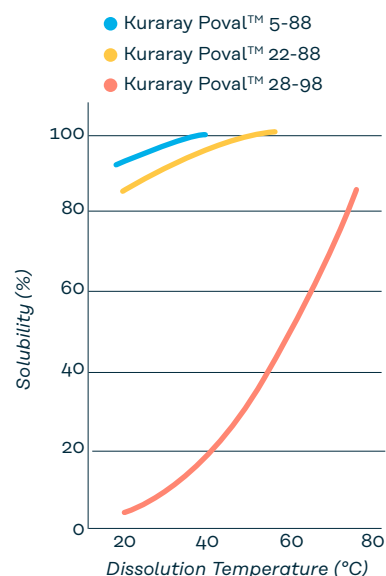● Kuraray Poval™ 22-88
● Kuraray Poval™ 28-98

Figure 27. Solubility of Major PVOH (Influence of Dissolution Temperature)

Figure 28 shows the results of investigating how heat treatment influences a slight difference in the degree of hydrolysis using PVOH with a degree of polymerization of 1750.

Partially hydrolyzed PVOH with a degree of hydrolysis of 88 mol% shows little influence on the solubility at a water temperature of 40 °C or higher unless it undergoes extreme heat treatment such as that at 180°C for 1 hour. Meanwhile, PVOH of the fully hydrolyzed type shows a decrease in the solubility owing to increase of crystallization when it is subjected to heat treatment at 100°C or more, particularly at 130°C or more. However, this tendency is considerably different below and over the residual acetate groups amount of around 2–4 mol% PVOH.

When considering which PVOH grade to use, solution concentration and viscosity are very important. In general, the practically usable concentration range is 35–40% when the degree of polymerization is around 500 and is 15–20% for a high polymerization degree grade with a degree of polymerization of around 2400.
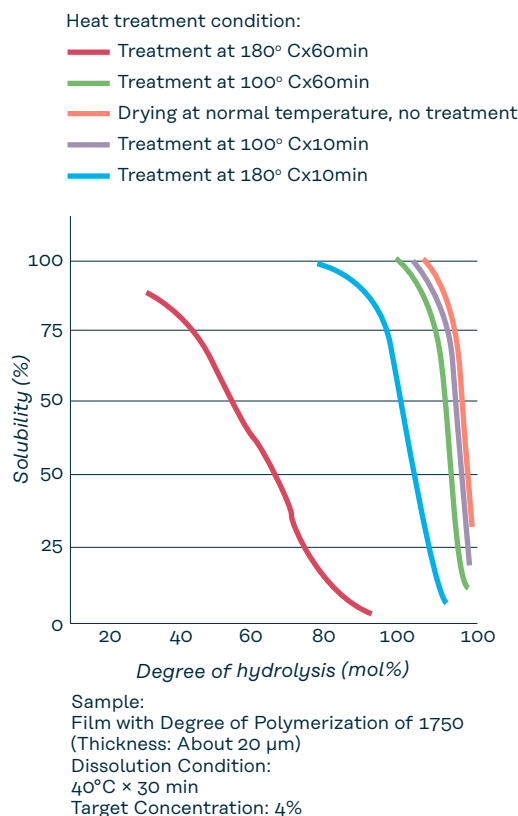
Heat treatment condition:
- Treatment at 180° Cx60min
- Treatment at 100° Cx60min
- Drying at normal temperature, no treatment
- Treatment at 100° Cx10min
- Treatment at 180° Cx10min

Sample:
Film with Degree of Polymerization of 1750
(Thickness: About 20 μm)
Dissolution Condition:
40°C × 30 min
Target Concentration: 4%

Figure 28. Influence of heat treatment on solubility of PVOH.

3-2. SOLUBILITY IN OTHER SOLVENTS

Although water is the most commonly used solvent for PVOH, can also be dissolved in a mixture of water and a lower alcohol if the concentration is low. The lower the degree of hydrolysis and the lower the degree of polymerization, the more soluble it is in a system with a higher alcohol concentration, and the more soluble it is at 50°C over 30°C. Figure 29 and Figure 30 show the solubility of major PVOH in a water-methanol mixture.

As for other organic solvents, PVOH dissolves to a certain degree in glycols such as glycerin, ethylene glycol and diethylene glycol, amides such as formamide, ethanol formamide and ethanol acetamide, amines such as ethanol amine, diethylene triamine and triethylene tetramine, as well as dimethyl sulfoxide, phenol, etc. However, when it is dissolved in glycols such as glycerin, heating is necessary, and when the high temperature solution is cooled to room temperature, the whole liquid turns into a gel. Table 11 shows the dissolution temperature of Kuraray Poval™ 25-100 with a degree of polymerization of 1700 and a degree of hydrolysis of 99.5 mol% is dissolved in various glycols at a concentration of 1%. The cloud point is the temperature at which the solution becomes turbid. Although heating is also necessary when dissolving PVOH in dimethyl sulfoxide, the solution is stable even when cooled to room temperature. PVOH is soluble in diethylene triamine and triethylenetetramine even at room temperature.
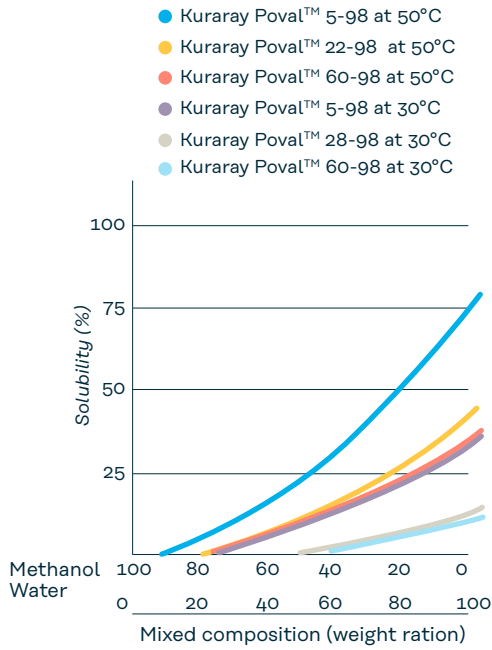
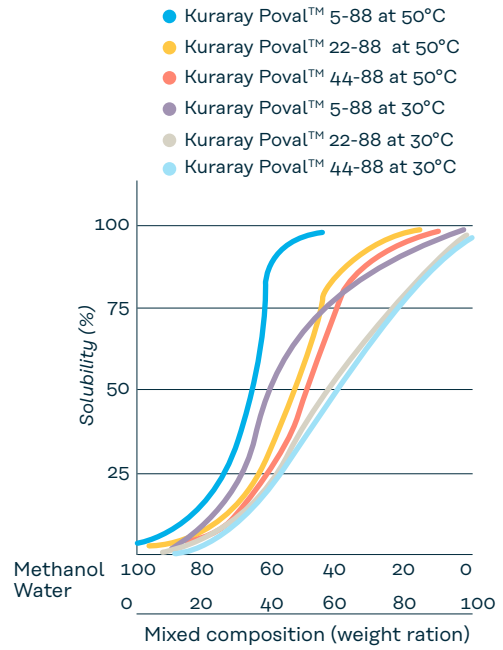Figure 29. Solubility of fully hydrolyzed grade in water-methanol mixture

Figure 30. Solubility of partially hydrolyzed grades in water-methanol mixture

* 96 weight parts of the mixture and 4 weight parts of PVOH were put in a predetermined solution and the solution was stirred at 2,000 rpm for 30 minutes. Then, the concentration of the solution part was measured, and the percentage with respect to the target concentration was taken as the solubility.

Plasticizer	Melting Point (°C)	Boiling Point (°C)	Dissolution Temperature of PVOH (°C)	Cloud Point of PVOH (°C)
Ethylene glycol	-12	197	140	110
Triethylene glycol	Liquid	214	160	130
Tetraethylene glycol	19.5	235	<200	150
Pentamethylene glycol	Liquid	239	190	175
Hexamethylene glycol	42	250	240	190
Propylene glycol	Liquid	187	190	150
Glycerin	19	290	160	120
2,3-Butanediol	34.4	184	240	175
1,3-Butanediol	Liquid	204	185	170
Diethylene glycol	-10.5	245	210	160
Triethylene glycol	Liquid	278	210	185

Table 11. Dissolution Behavior of Kuraray Poval™ 25-100 in Various Glycols (Concentration: 1%)

3-3. VISCOSITY OF AQUEOUS SOLUTION

The viscosity of aqueous solutions of PVOH depends on the grade, concentration and temperature. Figures 31 to 37 show the concentration-temperature-viscosity relationship (using a B-type viscometer) of some of our KURARAY POVAL™ grades. The viscosity of PVOH increases as the degree of polymerization increases. At the same degree of polymerization, the viscosity of the fully hydrolyzed grade is higher than that of the partially hydrolyzed grade. Additionally, the viscosity decreases as the temperature of the aqueous solution increases and this tendency is reduced for the partially hydrolyzed grade. In particular, the temperature dependence of PVOH with a degree of hydrolysis of 80 mol% is very small. Although the concentration range usually handled industrially seems to be in the range of 0.5−20%, the following can be understood when examining the aqueous viscosity in this area in detail. When plotting the relationship between the viscosity and concentration of fully hydrolyzed PVOH in detail, there is a bending point around concentration of 2−4%, as shown in Figure 38. It is understood that the concentration at this point agrees well with the bending point concentration observed in the relationship between the apparent activation energy of the flow of the PVOH aqueous solution and the concentration shown in Figure 39. There is another inflection point near a concentration of 10−12% in the relationship between the activation energy of flow and the concentration, and it is known that this concentration agrees well with the inflection point concentration of the melting point of PVOH gel [46]. Based on these facts, it is thought that the PVOH aqueous solution has different structures before and after the inflection point.

In a dilute aqueous solution of 2−4% or less, which is the first inflection point, the PVOH molecule becomes like a thread ball containing a large amount of water, and the molecules hardly interact with each other, being in a state of so-called molecular dispersion. However, with this concentration as a boundary, the thread ball-like molecules interact with each other, the degree of the interaction increases as the concentration increases, and a mesh structure is formed by entanglement of the PVOH molecules. The second inflection point is considered to be equivalent to the concentration at which the mesh structure owing to this entanglement is complete. There is a perspective that it is better to handle PVOH aqueous solution in the concentration range to be used industrially in general by regarding it as a melt of a gel. However, PVOH aqueous solutions are actually used in various conditions.
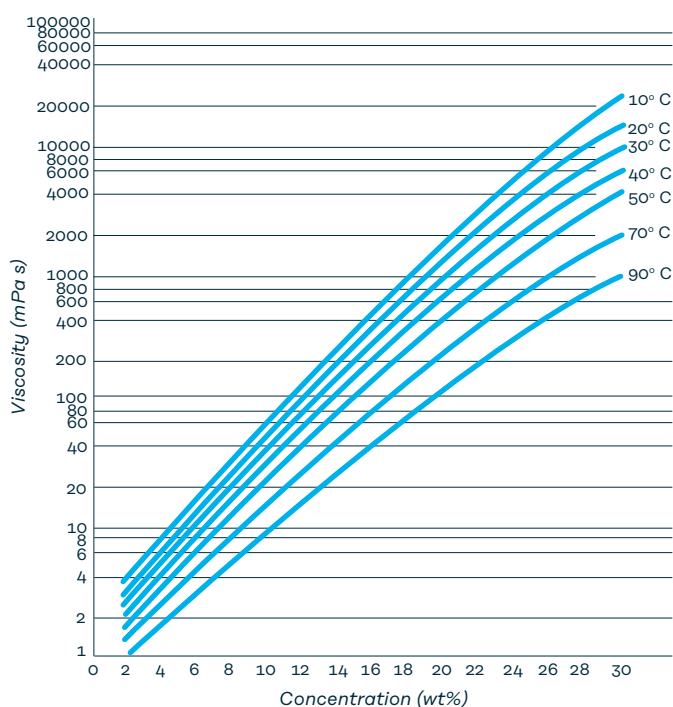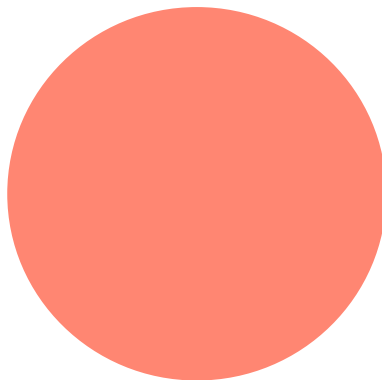

Figure 31.Relation between aqueous solution viscosity of Kuraray Poval™ 5-98 and concentration
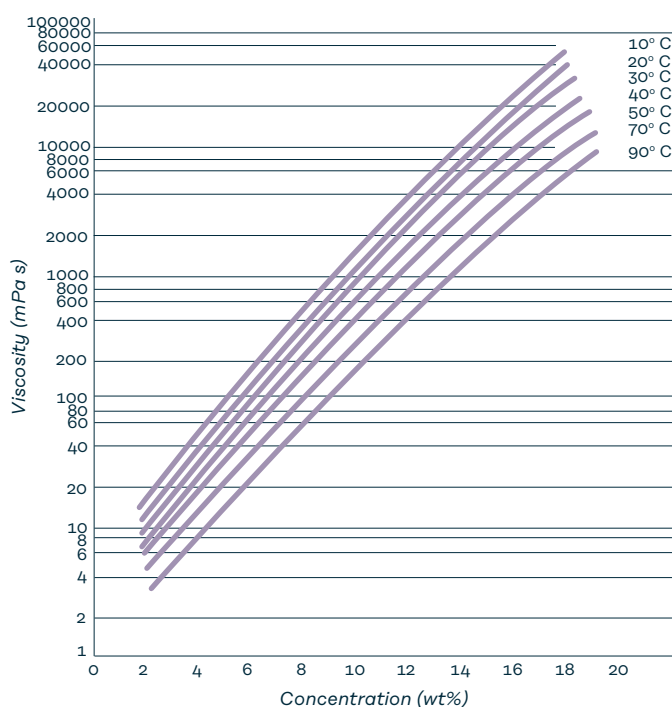
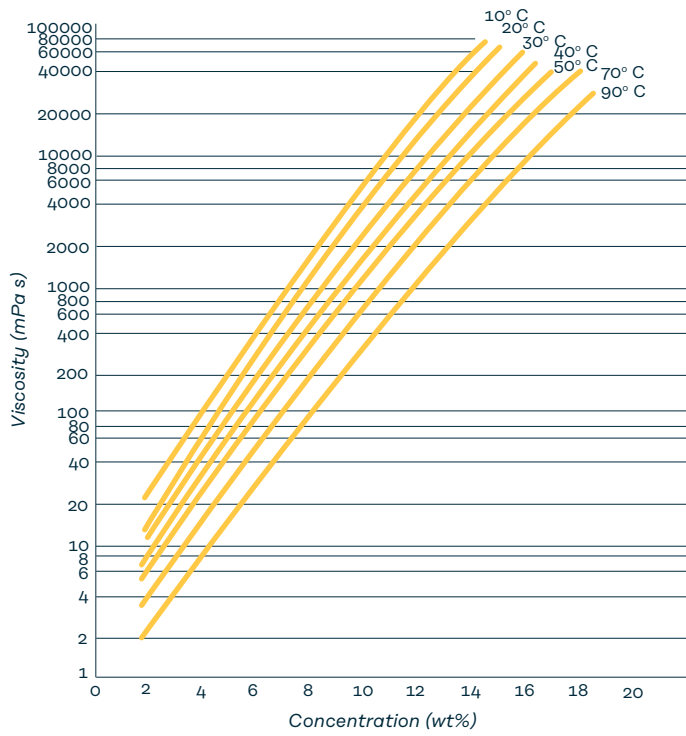Figure 32. Relation between aqueous solution viscosity of Kuraray Poval™ 28-98 and concentration

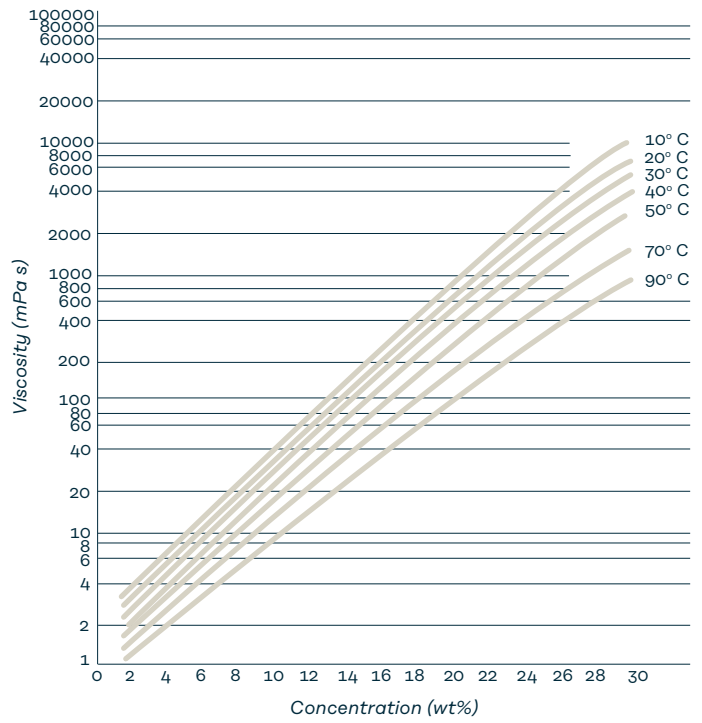Figure 33. Relation between aqueous solution viscosity of Kuraray Poval™ 60-98 and concentration

Figure 34. Relation between aqueous solution viscosity of Kuraray Poval™ 5-88 and concentration
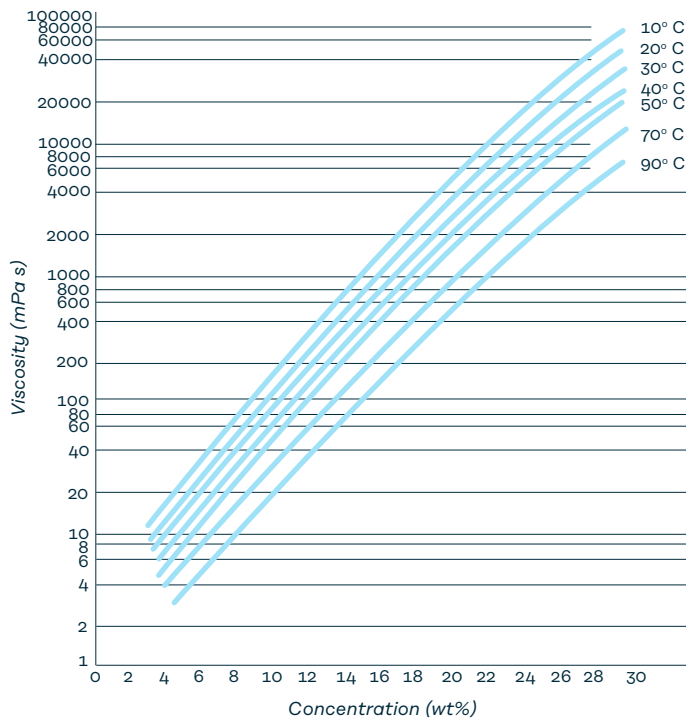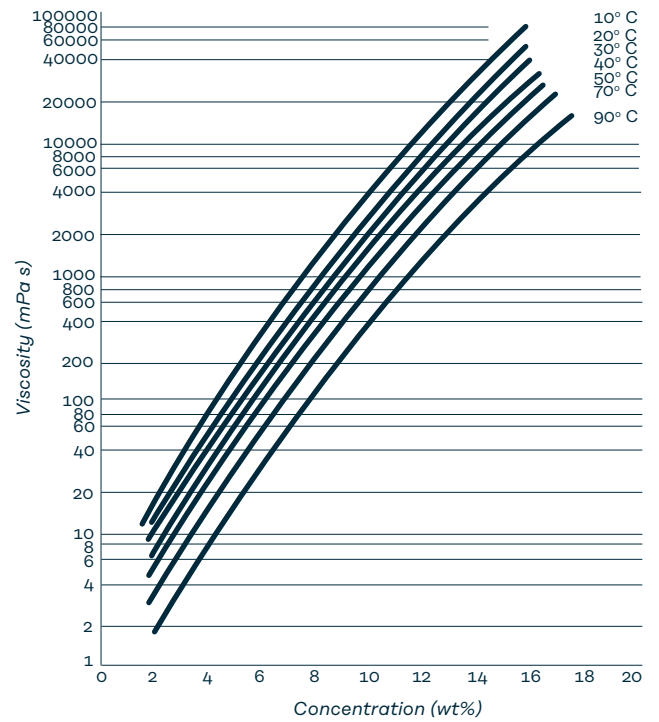

Figure 35. Relation between aqueous solution viscosity of Kuraray Poval™ 22-88 and concentration

Figure 36. Relation between aqueous solution viscosity of Kuraray Poval™ 44-88 and concentration
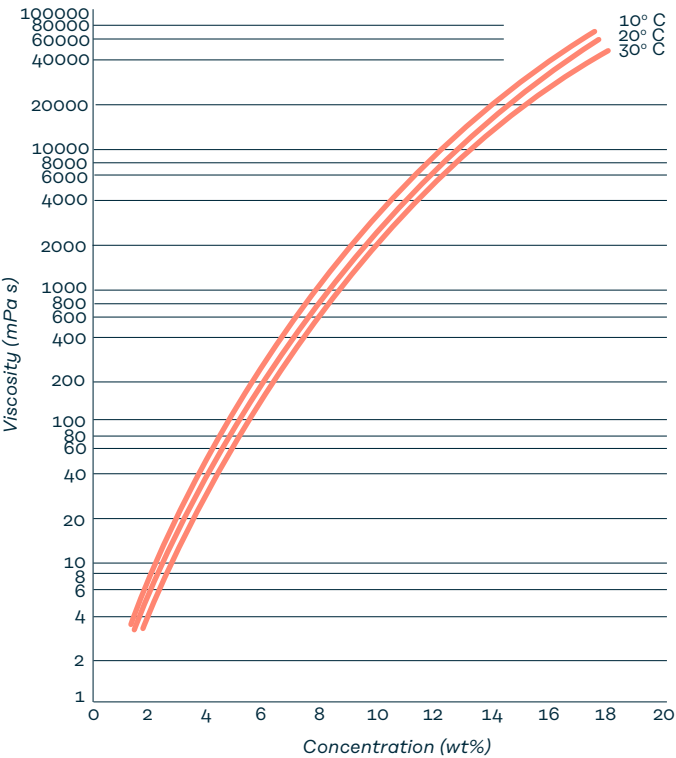
Figure 37. Relation between aqueous solution viscosity of
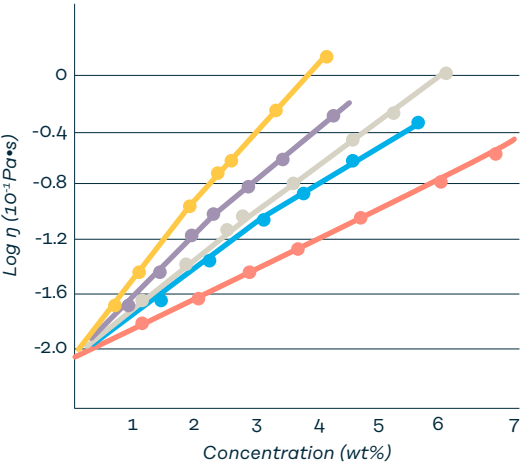Kuraray Poval™ 40-80 E and concentration

Figure 38. Relationship between concentration
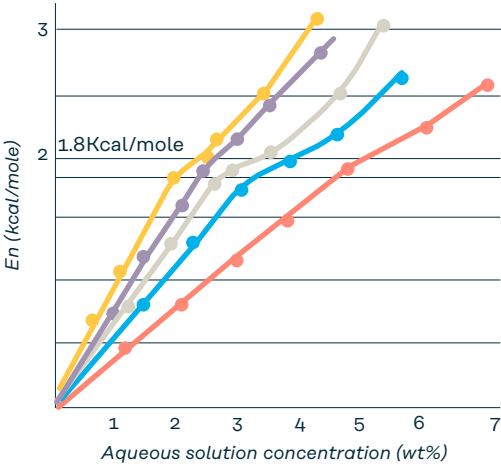and viscosity of various PVOH solution

Figure 39. Relation between concentration and
activation energy of apparent flow

Sample	Huggins coefficient	Degree Of polymerization
●	0.94	3115
●	0.70	2482
●	0.67	1906
●	0.96	1451
●	0.705	836

3-4. STABILITY OF AQUEOUS SOLUTION

When a PVOH aqueous solution with a high degree of hydrolysis is left for a long time in cold conditions < 50C the viscosity rises and the solution eventually turns into a gel. Figure 40 shows an example of Kuraray Poval™ 28-98, as an example of a fully hydrolyzed PVOH aqueous solution, the higher the concentration and the lower the temperature, the more unstable and the higher the viscosity increase. On the other hand, the partially hydrolyzed PVOH with a degree of hydrolysis of 88 mol% has a very small temporal change in viscosity, as shown in Figure 41. Therefore, the influence of the degree of hydrolysis of PVOH on the viscosity stability of the PVOH aqueous solution is recognized.

Assuming the aqueous solution viscosity immediately after dissolving PVOH as η_0 and the viscosity after t hours of the initial stage of storage as η_t, and then examining the relationship between them, η_t rises almost linearly with respect to time t at the initial stage. Expression of $\eta_t = \eta_0 * (1+Þt)$ is established approximately. We can then show an approximate relationship of $\eta_t = \eta_0 * (1+Þt)$. Therefore, Þ indicates the gradient of a straight line with respect to time t (Þ is referred to as a thickening coefficient). The relationship between this thickening coefficient Þ and the amount of residual acetate groups of PVOH, is shown in Figure 42, the thickening coefficient Þ decreases sharply as the residual acetate group increases, and the viscosity stability of the aqueous solution is improved when the amount of residual acetate group is 3 mol% or higher. As the amount of residual acetate groups increase, the network structure is hardly formed. It is thought that, owing to its steric hindrance, close entanglement of the molecules is hindered and and thus the increase in viscosity is decreased. Note that it has been confirmed that this thickening coefficient Þ is proportional to the 5.5^{th} to 6th power of the concentration, and the viscosity stability of the aqueous solution becomes worse as the concentration is higher and the degree of polymerization of PVOH is higher.
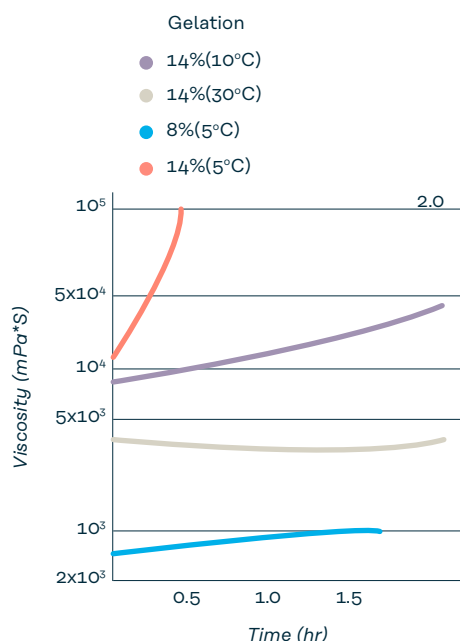

Figure 40 Viscosity Change of Kuraray Poval™ 28-98 Aquesous Solution
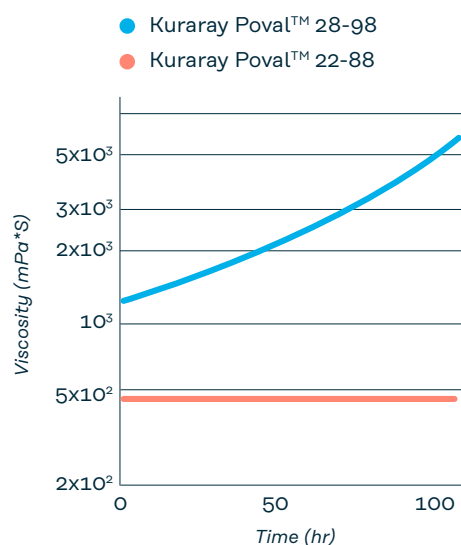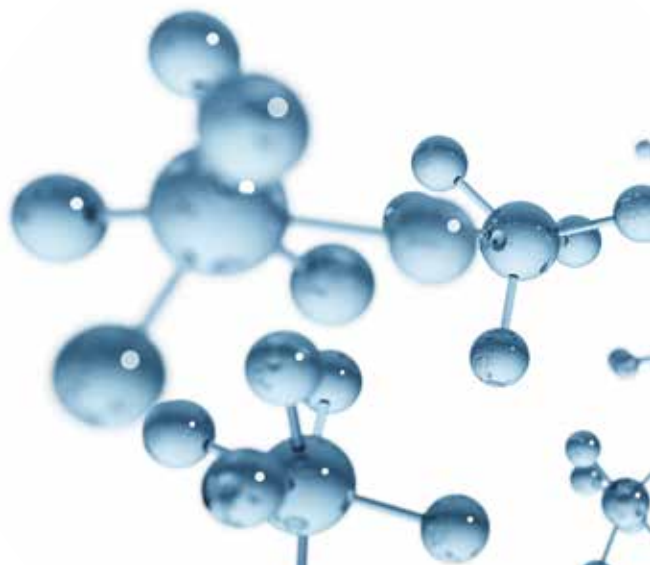

Figure 41 Viscosity Change of Kuraray Poval™ 28-98 and Kuraray Poval™ 22-88 with a Concentration of 8%

As shown in Figure 43 and Figure 44, the stability of the PVOH aqueous solution is also influenced by the preparation (dissolution) conditions and heat history of the PVOH aqueous solution. The higher the dissolution temperature, the longer the dissolution time, and the better stirring, the better the stability of the aqueous solution. Additionally, the stronger the heat treatment applied to PVOH before dissolution, the stability of its aqueous solution becomes worse. That is, the stability of the PVOH aqueous solution is also closely related to the crystallinity of PVOH itself and the dispersion state

of the molecules at the time of dissolution. It is difficult to completely release the hydrogen bonding between the PVOH molecules by dissolution. However, the stability improves as the dispersion state of the PVOH molecules is improved by enhancing the solubility condition. The stability becomes worse when the entanglement of molecules is insufficiently cleaved. Note that the thickening observed at the initial stage of storage is thought to be a result of very weak interaction between the molecules because the viscosity returns to the original one when stirring the aqueous solution.
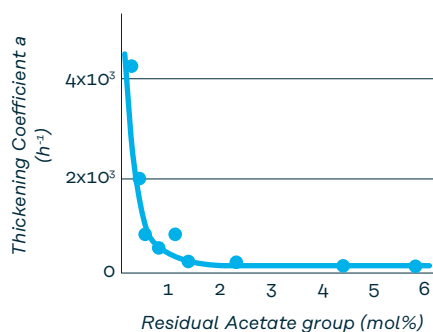

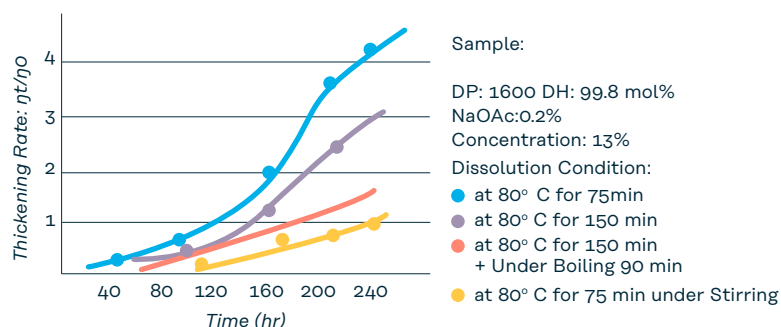Figure 42. Influence of Redisual acetate Group on Thickening Coefficient α

Figure 43. Influence of Dissolution Condition on Thickening of PVOH Aqueous Solution (30°C) (hr)
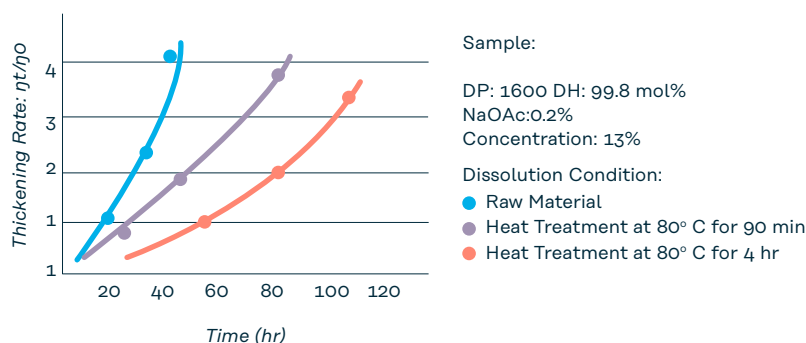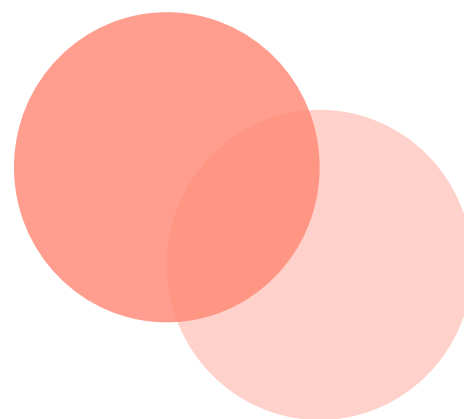
Sample:

DP: 1600 DH: 99.8 mol%
NaOAc:0.2%
Concentration: 13%
Dissolution Condition:
• at 80° C for 75min
• at 80° C for 150 min
• at 80° C for 150 min
  + Under Boiling 90 min
• at 80° C for 75 min under Stirring

Figure 44. Influence of Heat History before Dissolution on Thickening of PVOH Aqueous Solution (30°C)

Sample:

DP: 1600 DH: 99.8 mol%
NaOAc:0.2%
Concentration: 13%
Dissolution Condition:
• Raw Material
• Heat Treatment at 80° C for 90 min
• Heat Treatment at 80° C for 4 hr

3-5. SHEAR RATE DEPENDENCY OF AQUEOUS SOLUTION

It is well known that PVOH aqueous solutions exhibit non-Newtonian viscosity and the dependence of the aqueous solution on share rate has been clarified as follows. As for the PVOH aqueous solution, when it is a dilute aqueous solution with a degree of polymerization of 3000 or less and a concentration of 5 g/l (0.5%) or less, it can be regarded as a complete Newtonian fluid in a low-velocity gradient region where the share rate is 400—500 (1/sec) or less. However, as the concentration increases, the dependence on share rate increases, and when the concentration exceeds the critical concentration coinciding with the inflection point concentration obtained by the relationship between the viscosity and flow activation energy as described above, the share rate dependency increases sharply. Figure 45 shows the relationship between the m value [47], which is discussed

as a measure of share rate dependence, and the aqueous solution concentration. The critical concentration at which the sharp increase of the m value begins is around 2—3% and, in the case of PVOH with a higher degree of polymerization, the concentration is located on the lower concentration side.

Figure 46 shows the relationship between the degree of polymerization and the m value when the concentration is set to 20 g/l (2%) and Figure 47 shows the relationship between the residual acetate group and the m value of PVOH with a degree of polymerization of 1600 when concentration is set to 15 g/l (1.5%). The share rate dependence of the PVOH aqueous solution increases as the degree of polymerization of PVOH increases and the degree of hydrolysis increases.

References
46) Naito, Polymer Chemistry, 14, 117(1957)
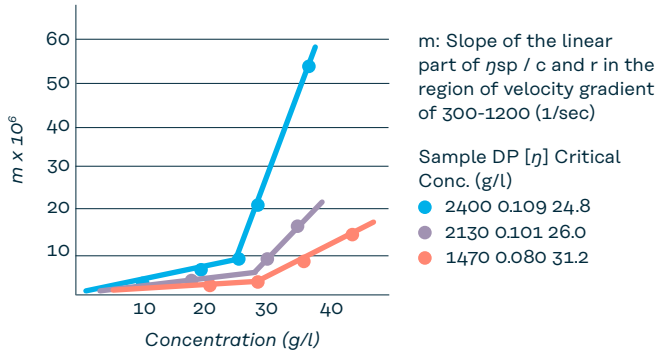*47) Naito, Polymer Chemistry, 16, 579 (1959)*

m: Slope of the linear part of ηsp / c and r in the region of velocity gradient of 300-1200 (1/sec)

Sample	DP	[η]	Critical Conc. (g/l)
●	2400	0.109	24.8
●	2130	0.101	26.0
●	1470	0.080	31.2

Figure 45. Relationship between m Value and Dissolution Concentration (30°C)

Sample:
● Before fractionation
● Sample (1) purified* once
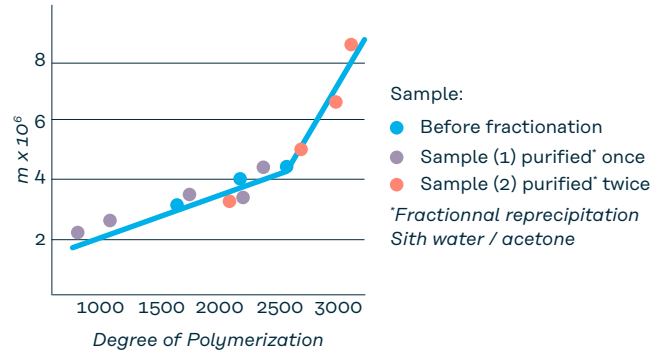● Sample (2) purified* twice

*Fractionnal repricipitation Sith water / acetone

Figure 46. Relationship between Degree of Polymerization and m of Various Samples (Concentration: 20 g/l, 30°C)

Sample:
● Before fractionation
● Sample (1) purified* once
● Sample (2) purified* twice
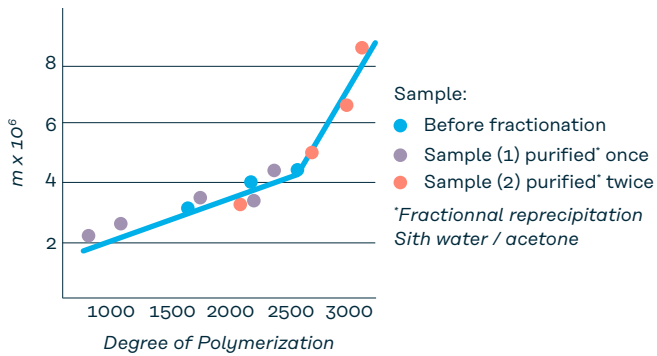
*Fractionnal repricipitation Sith water / acetone

Figure 47. Relationship between Residual Acetate Group Amount and m (Concentration: 15 g/l, 30°C)

3-6. SPECIFIC GRAVITY AND REFRACTIVE INDEX OF AQUEOUS SOLUTION

The actual measured specific gravity (Figure 48) and the refractive index (Figure 49) for the aqueous solution of Kuraray Poval™ 28-98 are shown here. The measurement of the refractive index of an aqueous solution has been put to practical use as a quick and qsimple method for investigating the concentration of a PVOH aqueous solution. For example in textile applications like fiber sizing.
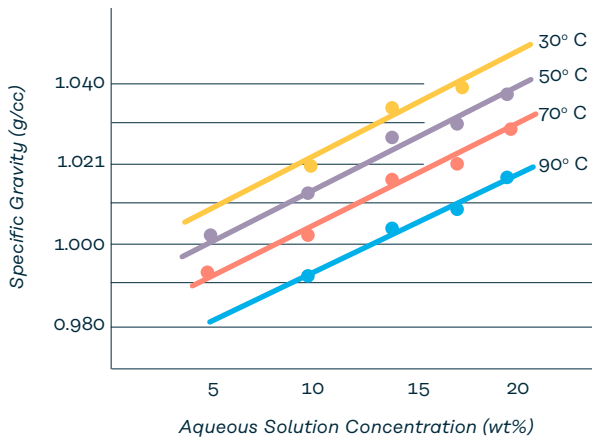

Figure 48-1. Specific Gravity of Kuraray Poval™ 28-98 Aqueous Solution
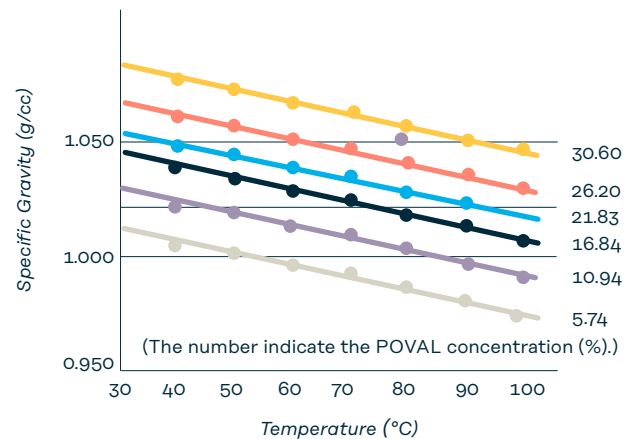

(The number indicate the POVAL concentration (%).)

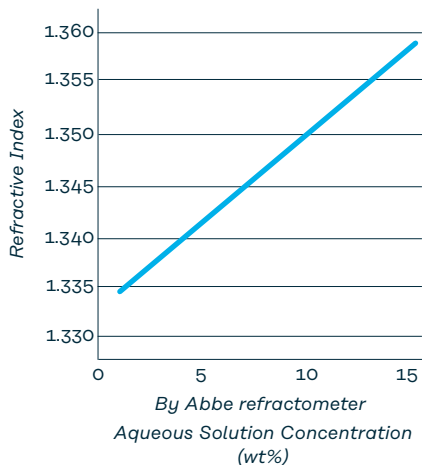Figure 48-2. Specific Gravity of Kuraray Poval™ 28-98 Aqueous Soltution

Figure 49. Refractive Index of
Kuraray Poval™ 28-98 Aqueous
Solution (20°C)

3-7. PH OF AQUEOUS SOLUTION

The pH of an aqueous solution of fully hydrolysed PVOH is slightly acidic and close to 7, but it decreases as the degree of hydrolysis decreases. The pH decreases to close to 5 in the case of the partially hydrolyzed product with a degree of hydrolysis of 88 mol%. When the aqueous solution of the partially hydrolyzed product is heated continuously at high temperature for a long time, the degree of hydrolysis increases and the pH tends to decrease. This change is not problematic under dissolution conditions which are usually carried out at the site of use. Figures 50 and 51 show examples of actual measurements of changes in the degree of hydrolysis and pH owing to prolonged heating.
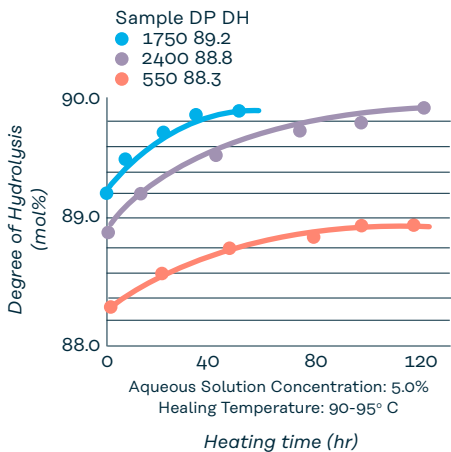

Figure 50. Change in Degree of
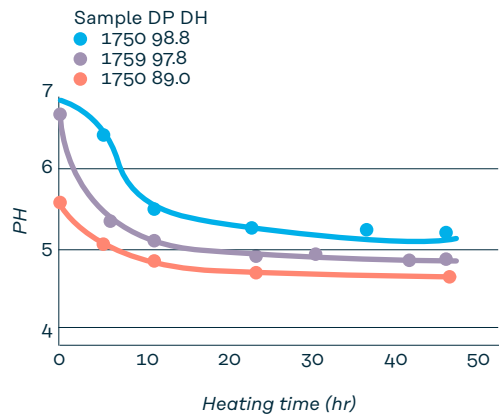Hydrolysis in PVOH Aqueous Solution
owing to Prolonged Heating

Figure 51. pH Change of PVOH Aqueous
Solution owing to Prolonged Heating

3-8. SURFACE ACTIVE PERFORMANCE OF AQUEOUS SOLUTION

PVOH is often used as a stabilizer for oil-in-water emulsions and suspensions. PVOH also has a function as a nonionic, surfactant and as a protective colloid. It is well known that the aqueous solution of a partially hydrolyzed PVOH having a hydrophobic acetate group and a hydrophilic hydroxyl group exhibits lower surface tension than the aqueous solution of a fully hydrolyzed PVOH. Figures 52 and 53 show the measured surface tensions of a few grades of PVOH. The ability to lower the surface tension of PVOH increases as the amount of residual acetate group increases, but almost no dependence of the degree of polymerization is observed. However, PVOH 5-88, which is a partially hydrolyzed product with a low degree of polymerization, shows a unique behavior and exhibits extremely low surface tension. Various investigations have been conducted on the surface activity of PVOH in association with the molecular structure of PVOH.

In terms of the molecular structure, partially hydrolyzed PVOH is well explained when considering it as a block polymer type polymeric surfactant composed of a hydrophobic acetate group and a hydrophilic hydroxyl group. It is generally observed that, as the residual acetate group increases and the distribution of the hydrophobic group and the hydrophilic group in the molecule becomes non uniform (blockwise), the surface activity increases and the protective colloid ability to the hydrophobic substances also increases.
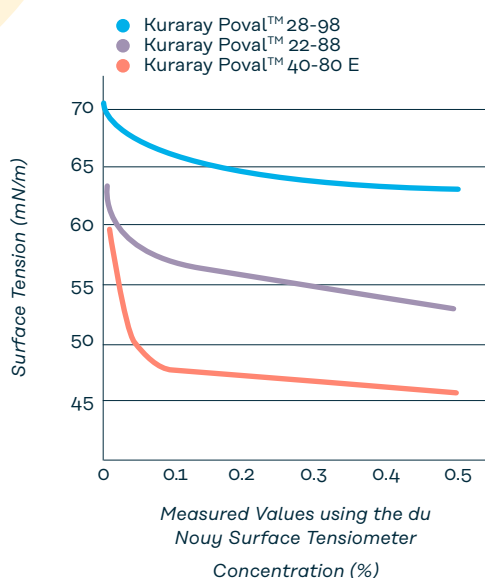

Measured Values using the du Nouy Surface Tensiometer

Concentration (%)

Figure 52. Surface Tension of PVOH Aqueous Solution (20°C)Influence of Degree of Hydrolysis

Measured Values using the du Nouy Surface Tensiometer
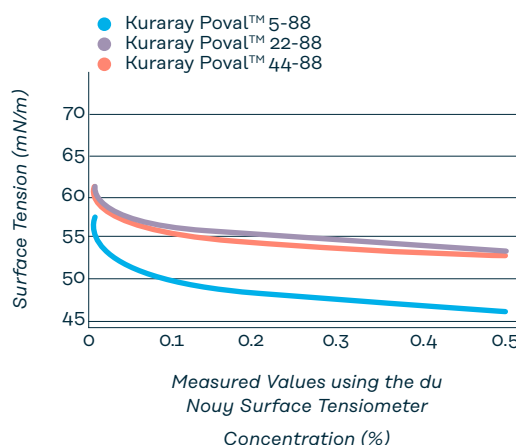
Concentration (%)

Figure 53. Surface Tension of PVOH Aqueous Solution (20°C) Influence of Degree of Polymerization

3-9. PERMEABILITY OF AQUEOUS SOLUTION

PVOH is used in large quantities as a surface sizing agent for both fiber and paper. In these cases, the permeability of aqueous solution to the fiber bundle is closely related to the warp conjugation force, the paper strength, etc. If the permeability of PVOH is too good and the yield to the surface layer of fibers and paper is small, fluff binding on the fiber bundle surface becomes poor and the surface strength of the paper does not increase. Conversely, if the permeability is bad, the enhancement of the physical properties inside the fiber or paper cannot be achieved. Regarding the size effect of a warp sizing agent for fiber as well as the performance required as a surface sizing agent for paper, it is not yet sufficiently understood how they are related to the permeability of PVOH. However, it is clear that the permeability is one important factor.

By using filter paper (Toyo Roshi No. 1) as a model of a porous material composed of fiber bundle, the height (h) of permeation of water by a method similar to paper chromatography was obtained with time. A linear relationship is established between the square value of the permeation height h (mm) and the time t (s), and this slope α is 0.129 cm²/sec. The α value of 0.5−4% PVOH aqueous solution was shown in Figures 54 and 55.

Permeation of a liquid into yarn and paper, which are considered to be porous materials, is caused by capillary force and it is known that the apparent permeation speed of a liquid is given by the following equation[48].

$$\frac{dh}{dt} = \frac{m}{k} \quad \frac{\gamma \times \cos\theta}{\mu} \quad \frac{1}{h}$$

References
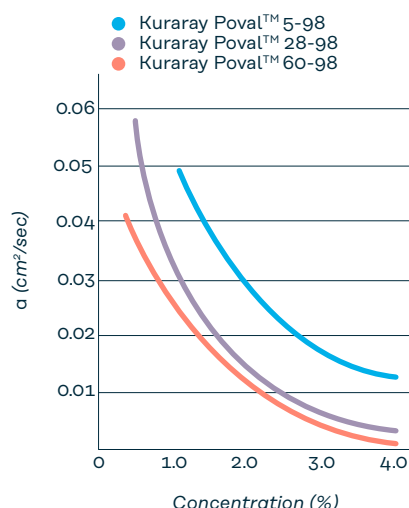*48) Shiozawa, Japan TAPPI Journal, 20, 668(1966)*

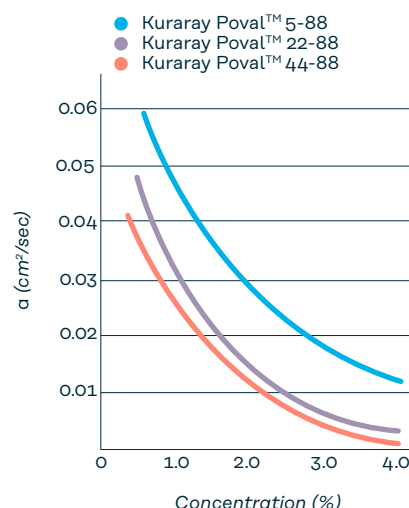Figure 54. a value of Fully Hydrolyzed PVOH Aqueous Solution (20°C)

Figure 55. a value of Partially hydrolyzed PVOH Aqueous Solution (20°C)

Where, h is the permeated distance of the liquid, γ is the surface tension of the liquid, Ø is the contact angle of the liquid, η is the viscosity of the liquid, and m/k is the constant determined by the porous structure. The m/k of the filter paper used in this test was 0.9325×10^{-5} (cm), the viscosity η of water was 0.01 (ps), the surface tension γ was 72.8 (dyne/cm) and the contact angle cosØ was 0.952. Using these values, the contact angle Ø of aqueous solution was calculated based on the a value of the PVOH aqueous solution obtained previously. Figures 56 and 57 show the results.
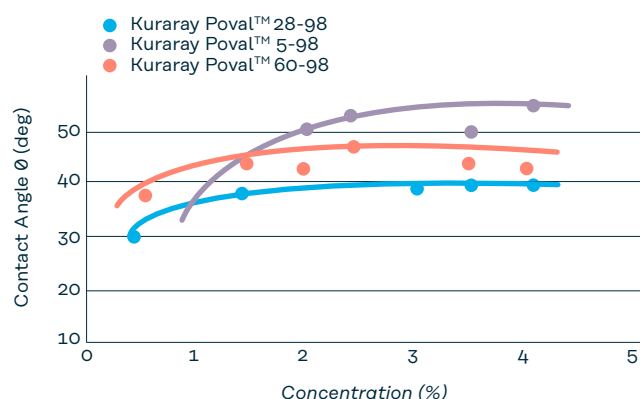

Figure 56. Contact Angle Ø of Fully hydrolyzed PVOH Aqueous Solution to Filter Paper (20°C)
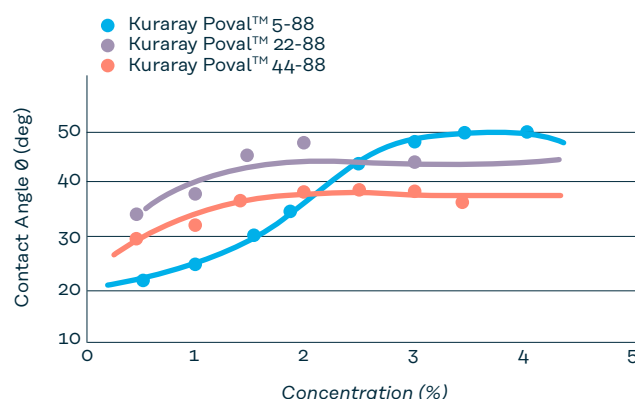

Figure 57. Contact Angle Ø of Partially hydrolyzed PVOH Aqueous Solution to Filter Paper (20°C)

From these results, the following can be seen. The apparent permeation speed of the PVOH aqueous solution decreases sharply as the concentration increases, but the degree becomes gentle when the concentration becomes 2–3% or more. Additionally, the higher the degree of polymerization, the slower the permeation speed, but there is almost no influence of the degree of hydrolysis within the range of this test. On the other hand, the contact angle of the PVOH aqueous solution with respect to the filter paper is almost constant when the concentration is 2–3% or more. As a result, it is clear that the permeation speed of the PVOH aqueous solution is governed by the viscosity, surface tension and contact angle of the aqueous solution. However, the concentration dependency of the surface tension also becomes extremely small at a concentration of 2–3% where the contact angle becomes a constant value; this means

that the viscosity has a large influence in this concentration region. Meanwhile, the wetting energy indicated by the product of the surface tension and the contact angle is calculated for the PVOH aqueous solution and the results are shown in Figure 58. The wetting energy decreases as the concentration increases. In the concentration region where the contact angle becomes nearly constant, this value also becomes nearly constant. As shown in Figure 59, the dependence of the degree of polymerization and the degree of hydrolysis can be observed for the equilibrium wetting energy in this concentration region. The equilibrium wetting energy increases linearly with the increase of the degree of polymerization and that with a higher degree of hydrolysis has a larger value. To summarize the above results, the PVOH aqueous solution with a higher degree of polymerization PVOH and a higher degree of hydrolysis PVOH has higher

wetting energy and the wettability to filter paper increases. Meanwhile, the apparent permeation speed is not so much related to the degree of hydrolysis within the range discussed so far, and the higher the degree of polymerization, the lower the penetration speed. The permeabilities of the aqueous solutions of the same concentration of Kuraray Poval™ 28-98 and Kuraray Poval™ 22-88, Kuraray Poval™ 5-98 and Kuraray Poval™ 5-88 to filter paper can be regarded as almost the same degree. This is because, although the partially hydrolyzed product has a considerably low wetting energy as compared with the fully hydrolyzed product, it has a low viscosity at the same degree of polymerization and same concentration. Therefore, it can be understood that it acts sufficiently for permeability and is a result of simply the offset of the difference between the wetting power and the viscosity effect.
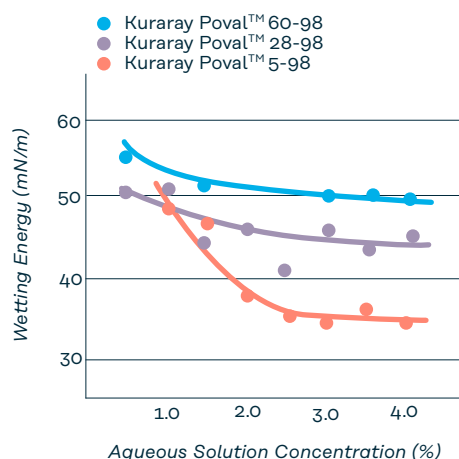

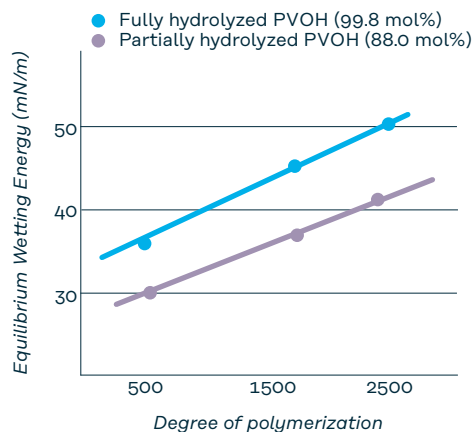Figure 58. Wetting Energy of Fully hydrolyzed PVOH Aqueous Solution

Figure 59. Equilibrium Wetting Energy of PVOH Aqueous Solution

3-10. CONTACT ANGLE FOR VARIOUS PLASTICS

When PVOH is used as an adhesive, or as a warp sizing agent or paper surface sizing agent, the compatibility and adhesion of PVOH to yarn and paper are important factors. The first step of adhesion is wetting of the adherend surface by adhesive. Table 12 shows the contact angles for various plastic films actually measured as an indication to understand how much compatibility and adhesion the PVOH aqueous solutions have for various plastics, and the wetting energy values calculated based on them.

The contact angles of the PVOH aqueous solutions were measured at a concentration of 3% as the contact angle with respect to the plastic film reaches an almost equilibrium around 3% concentration as shown in the example in Figure 60.

According to the data, for a plastic with a large contact angle, or a highly hydrophobic plastic that hardly gets wet with water, there is a tendency that the difference in the contact angles between the fully hydrolyzed PVOH and the partially hydrolyzed PVOH aqueous solution increases as the hydrophobicity increases. That is, it is found that the aqueous solution of the partially hydrolyzed PVOH is more easily wetted with respect to the hydrophobic polymer. In this test, the surface tensions of the 3% aqueous solution were 62.4 mN/m for Kuraray Poval™ 28-98 and 49.9 mN/m for Kuraray Poval™ 22-88. Figure 61 shows a plot of the correlation between the wetting energy calculated based on them and the contact angle of water, which is a rough indication of the hydrophobicity of the adherend.

As the hydrophobicity of the polymer increases, the wetting power decreases linearly in the case of both the fully hydrolyzed PVOH and the partially hydrolyzed PVOH. The fully hydrolyzed PVOH has larger inclination and exhibits higher wetting power than the partially hydrolyzed PVOH for polymers having large hydrophilicity. However, for strongly hydrophobic polymers, the partially hydrolyzed product with more hydrophobic acetategroups in the molecule has greater wetting power. That is, from the viewpoint of adhesion it can be said that it is better to use the partially hydrolyzed PVOH for polymers having high hydrophobicity.
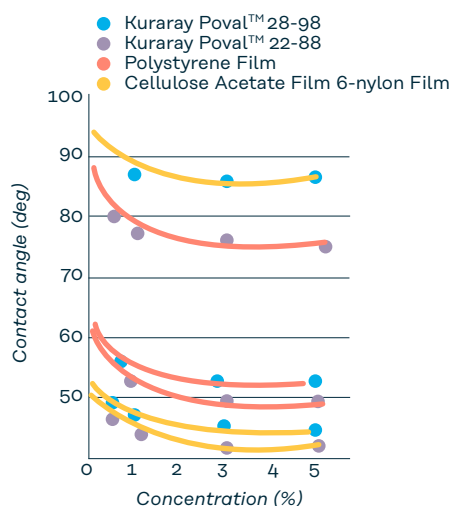
Figure 60. Contact Angle
of PVOH Aqueous Solution
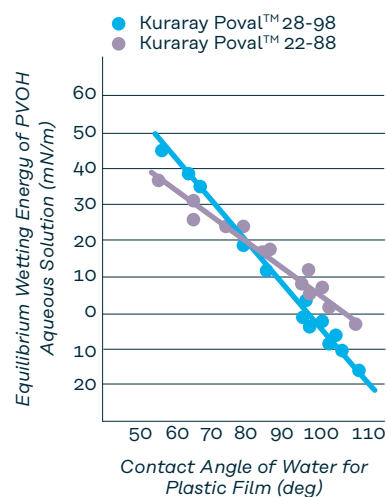for Various Plastic Films
(Influence of Concentration)

Figure 61. Correlation
between Equilibrium Wetting
Energy of PVOH Aqueous
Solutions for Various Plastic
Films and Contact Angle
of Water for Plastic Film
(PVOH Concentration: 3%,
Temperature: 20°C)

Film type	Contact angle			Equilibrium Wetting Energy (mN/m)	
	Water	Kuraray Poval™ 28-98 solution	Kuraray Poval™ 22-88 solution	Kuraray Poval™ 28-98 solution	Kuraray Poval™ 22-88 solution
Teflon	109.2	104	95	-15.1	-4.4
Polypropylene	102	95	89.5	-5.5	0.5
Delrin	99.9	91	82	-1.1	7
Polyethylene	96.8	93.2	84.8	-2.4	4.5
Polyester	96.1	86.5	76	3.8	12.1
ABS	94.7	91	81.2	-1.1	7.7
Polyvinyl chloride	84.6	78.8	69.9	12.1	17.2
Polyester	83.7	86.5	76	3.8	12.1
Phenolic resin	77.3	71	62.6	20.4	23
PMMA	74.2	68.6	62	22.8	23.5
Polyvinyl acetate	65.5	55.3	47	35.4	34
Melamine resin	65.3	60.8	58.2	30.5	26.2
Acetylcellulose	63.6	53.1	49	37.5	32.3
6-Nylon	54.6	44.3	42.4	44.5	37.4

Table 12. Contact angle and Equilibrium Wetting Energy of PVOH Aqueous Solution for Various Polymer Films (PVOH Concentration: 3%, Temperature: 20°C)

3-11. COMPATIBILITY WITH WATER-SOLUBLE POLYMERS

PVOH is often used in combination with other water-soluble polymers as a mixed aqueous solution. For application as a warp sizing agent for fibers, it is used in combination with corn starch, CMC (carboxy methyl cellulose), partially hydrolyzed products of polyacrylic acid ester, It is also used in combination with oxidized starch in the surface sizing of paper. When PVOH is used in combination with other water-soluble polymers like this, it is necessary to carefully consider the issue of the separation speed in the process from the occurrence of phase separation of the mixed solution to an equilibrium and the problem of the compatibility after reaching the equilibrium. In particular, the compatibility is a very large factor and an important problem not only for the stability of the mixed solution and workability together with the separation speed, but also for the physical properties of the film. As for the compatibility in the equilibrium state, the separation critical concentrations have been determined based on various mixing ratios of various combinations of polymers. As an example, the separation critical concentration curves obtained by combining three types of PVOH with different degrees of polymerization and dextrin are shown in Figure 62.
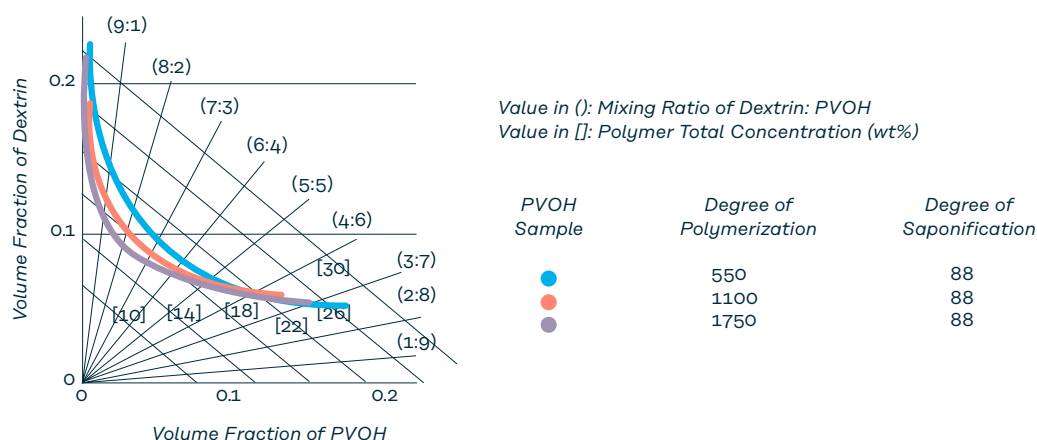

Figure 62. Separation Critical Concentration Curve of PVOH / Dextrin Mixture

In the case of a combination of PVOH and dextrin, although the influence of the degree of hydrolysis of PVOH on the separation critical concentration is hardly observed, the dependence on the degree of polymerization is large. As the degree of polymerization increases, the separation critical concentration decreases. Depending on the type of water-soluble polymer, the shape of the critical concentration curve is not alwaysuniform. However, as in the case of dextrin, the separation critical concentration of the mixed PVOH aqueous solution and another polymer tends to become higher as the degree of polymerization of PVOH and the degree of polymerization of the polymer to be fitted are lower or as the mixing ratio is extremely shifted to either side. For some polymers, general trends in the separation speed, compatibility, influence of the degree of hydrolysis of PVOH, etc. are summarized as follows.

Hydroxyethyl Cellulose (HEC)
The separation speed is fast. The higher the degree of hydrolysis of PVOH, the better the compatibility.

Carboxymethyl Cellulose (CMC)
Slight separation is observed at a mixing ratio of around 1:1, but the compatibility is very good at other mixing ratios. Almost no difference owing to the degree of hydrolysis of PVOH and the degree of etherification of CMC is observed.

Methyl Cellulose (MC)
The separation speed is relatively fast and the higher the degree of hydrolysis of PVOH, the better the compatibility.

Partially Hydrolyzed Product of Acrylic Ester
As the degree of hydrolysis of PVOH decreases, the compatibility improves considerably and no separation is observed in PVOH with a degree of hydrolysis of 88 mol%. The compatibility is better as the number of carbon atoms of the acrylic acid ester group decreases and the degree of hydrolysis of the ester increases. Sodium polyacrylate hardly separates when it is mixed with the fully hydrolyzed PVOH.

Polyethylene Glycol
It is not compatible with fully hydrolyzed PVOH. As the degree of hydrolysis of PVOH decreases, it becomes compatible.

Oxidized Starch
In general, the higher the degree of hydrolysis, the better the compatibility. In particular, the compatibility with the modified PVOH (K-series) having the anionic group (carboxyl groups) is excellent. Figure 63 shows an example of observing the phase separation state when a mixed solution of the PVOH aqueous solution and oxidized starch aqueous solution (Total concentration: 10%, mixing ratio: PVOH / oxidized starch = 2 / 8 (wt)) is left at 50°C.
The mixed solution was placed in a measuring cylinder and was left at 50°C to observe the rate of the supernatant phase appearing by phase separation as an indication of the compatibility. Figure 63 shows the result. When the mixed solution of a total concentration of 5% and PVOH / oxidized starch = 2 / 8 (wt) is left at 50°C, both Kuraray Poval™ 28-98 of normal fully hydrolyzed grade and the carboxyl group-modified Kuraray Poval™ K-series show no phase separation and exhibit good compatibility within the range of 100 hours or less. However, as shown in Figure 63, it is recognized that the compatibility of Kuraray Poval™ K-series is better than that of Kuraray Poval™ 28-98 at a total concentration of 10%.
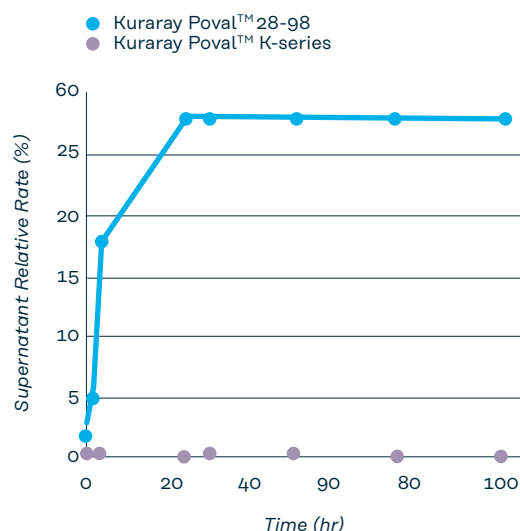
Figure 63. Compatibility of PVOH-starch Mixture (Left Stability at 50°C)

Other

PVOH is extremely compatible with casein and sodium alginate, and no apparent separation is observed. The separation speed from gelatin is very fast. Based on the experimental values of the separation critical concentration described above, an interaction parameter a_{23} [49] which is determined only by the type of the partner polymer to be mixed with PVOH has been calculated as a measure for uniquely expressing the compatibility between the two types of polymers.

This parameter a_{23}, which is a thermodynamic constant, is a universal constant between two polymers unrelated to the degree of polymerization of polymer, and the smaller the value, the better the compatibility between the two. These values are shown in Table 13. As described above, a_{23} of the partially saponified product of CMC and polyacrylic acid ester, which are easily compatible with PVOH, is clearly smaller than that of MC and HEC. Meanwhile, even if these mixed polymer aqueous solutions are in the phase equilibrium state or below the separation critical concentration as a solution, in the compatible state, when they are actually used in some application, the concentration gradually increases in the drying process; A dry film must be formed through the demixing region after exceeding the separation critical concentration. Therefore, even if the appearance varies depending on the drying speed and the separation speed, the dry film of the mixed polymer generally does not become a homogeneous phase and has a structure in which one takes the matrix structure and the other is dispersed as minute granular particles therein. Figure 64 shows the relationship between the mixing ratios of both polymers investigated based on the microscope photograph of a film dry-formed from the mixed solution of "PVOH" and cellulose derivative and the size of dispersed particles in the film. The mixing ratios at which the dispersed particle diameter becomes the maximum are HEC:PVOH = 3:7, MC: PVOH = 6:4, and CMC:PVOH = 5:5. These mixing ratios are in good agreement with the mixing ratios at which the mixed solutions show the lowest separation critical concentrations, respectively. Additionally, the maximum value of the dispersed particle diameter becomes smaller in the case of the combination of the polymers with smaller interaction parameters a_{23}.

Polymer	a_{23}
CMC	0.059
MC	0.128
HEC	0.177
Dextrin	0.29
Polymethyl Acrylate (Degree of Hydrolysis: 20%)	0.006
Polyethyl Acrylate (Degree of Hydrolysis: 20%)	0.074

Table 13. Interaction Parameter between PVOH and Various Water-soluble Polymers, a_{23} (ml^{-1})
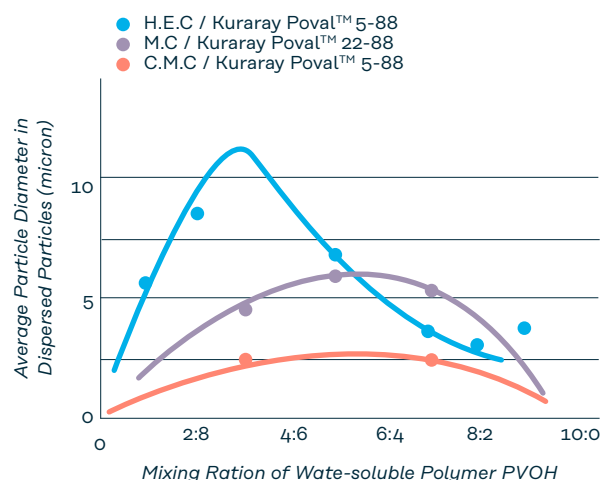
Figure 64. Size of Dispersed Particles Exist in PVOH / Cellulose Derivative Mixture Film

References
49) Poval (Nagano et al., Kobunshi Kankokai, 1970)

3-12. DISPERSIVE/AGGREGATING ACTION AGAINST CLAY PARTICLES

In PVOH, which is a non-electrolytic linear polymer, unique aggregating and dispersive actions from the electrolyte linear polymer are observed. As an example, the pH of the suspension system was changed in advance by processing Japanese Pharmacopoeia kaolin containing quartz and pyroferrite with a particle size of 20 µm or less as the main minerals with caustic soda; fully hydrolyzed PVOH with a degree of polymerization of about 1400 was added to this suspension up to 1%, and then the system was left for 2 hours. The relative turbidity in this case is shown in Figure 65.

In the high pH range where the mutual repulsion of clay particles is increased by the addition of caustic soda, the aggregating action of PVOH is weakened. However, in any system, the maximum aggregation is observed when the addition amount of PVOH is around 0.15%. In other words, PVOH exhibits the maximum aggregating action at a fixed amount ratio with respect to clay particles irrespective of the pH of the suspension system, and this phenomenon is essentially different from the case of electrolytic polymers such as sodium polyacrylate. The PVOH molecule is strongly adsorbed to the clay particle by the hydrogen bonding formed between the oxygen atom of the silicic acid layer on the surface of the clay and the hydroxyl group of the side chain. As a result, the surface of the clay particle is covered with the adsorbed hydrocarbon main chain of PVOH and rendered hydrophobic. This causes aggregation by the Van der Waals force in a form that minimizes the free surface energy in water. The major aggregation action by PVOH is the hydrophobization of the surface of the clay particle like this and the hydrophobic group interaction between some particles is considered to be involved. Furthermore, as for the state of redispersion observed when the amount of PVOH is increased, it is estimated that the secondary molecule of PVOH adsorbs to the primary molecular film of PVOH adsorbed to the clay surface by the Van der Waals force between the ethylene main chains. The surface of the particle becomes hydrophilic again owing to the hydroxyl group facing the aqueous phase, resulting in redispersion.

The maximum aggregation point exhibited by PVOH is not influenced by the pH of the system as described above, and it does not change even if salts such as aluminum sulfate are used in combination. The maximum aggregation point for the same type clay particles is closely related to the surface area of clay particle and irrespective of the clay particle concentration. Clay with stronger hydrophilicity will achieve maximum aggregation by adding a smaller amount of PVOH. The following order is observed for the aggregability of representative ones.

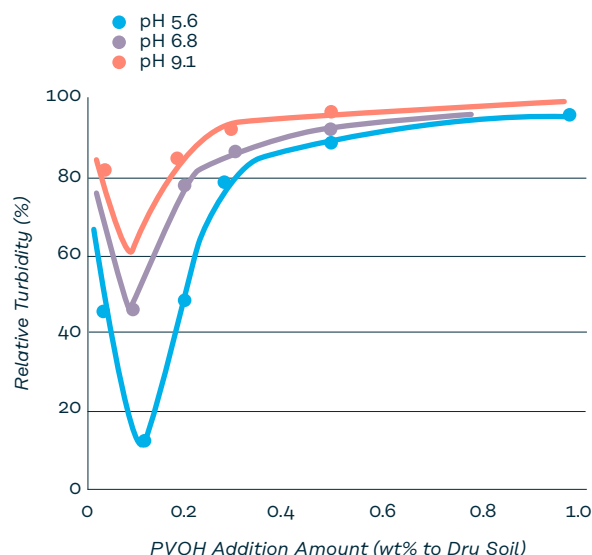Titanium oxide < Talc < Kaolin < Pyrophylite

Figure 65. Aggregating and Dispersive Actions of PVOH in Kaolin Suspension System (Kaolin Concentration: 1%)

Figure 66 shows an example indicating the influence of the degree of polymerization of PVOH on the aggregating action.

The aggregating power of PVOH weakens as the degree of polymerization decreases, but the concentration of PVOH that causes the maximum aggregation does not change. This also suggests that the mechanism of creating a bridge between the clay particles and forming a block also contributes to the aggregation action of PVOH. Meanwhile, Figure 67 shows the correlation between the additive amount and adsorption amount of PVOH for clay for PVOH with different degrees of hydrolysis.

Figure 67 shows that saturated adsorption is reached when more than a certain amount of PVOH is added, except for PVOH with a significantly lower degree of hydrolysis. However,

it has been confirmed that the PVOH molecules adsorb to the clay surface in a thin and considerably spread state and the amount decreases as the spread of the PVOH molecules in the aqueous solution widens. Note that when mixing the inorganic suspension system and PVOH, an aggregation phenomenon of inorganic substances may occur, which is co-called "clay shock". When mixing them, there is no problem if the suspension solution of inorganic substance is added and mixed into the PVOH aqueous solution. When this is not possible in practice, for example, when using PVOH as a pigment binder for paper, the "PVOH shock" can be prevented by adding PVOH with a low degree of polymerization to the clay suspension solution at first to minimize the aggregation and then adding PVOH with a high degree of polymerization after passing the aggregation region (concentration).
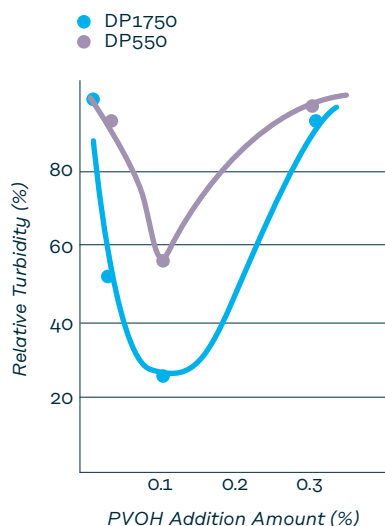
Figure 66. Influence of Degree of Polymerization of PVOH on Aggregation of Kaolin Suspension System
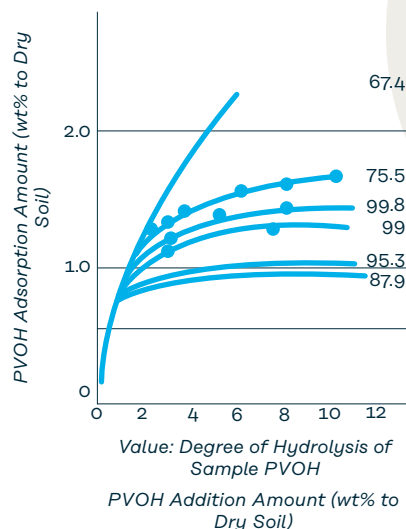

Figure 67. Adsorption Amount of PVOH to Clay* Particle (Influence of Degree of Hydrolysis)
* Shokozan Clay

3-13. INFLUENCE OF ELECTROLYTE

In general aqueous solutions of PVOH are considerably stable against strong acids and bases. Even when a large amount of ammonium hydroxide, acetic acid, hydrochloric acid, nitric acid, phosphoric acid or or similar is added, PVOH aqueous solution is stable.

Table 14 summarizes the minimum concentrations of salts required to coagulate and precipitate PVOH in solution. A 5% aqueous solution of Kuraray Poval™ 28-98 shows the influence and the precipitation/coagulation effects of salts for PVOH aqueous solution. The coagulation effect of salts for the PVOH aqueous solution is strong with sulphate ion, carbonate ion and phosphate ion the coagulation power for negative ions listed for example chlorine ion and nitric acid ion is extremely weak. As for positive ions, those with a large ionization tendency are more effective. Potassium, sodium, ammonium and the like are strong, and sodium sulfate, ammonium sulfate and the like have a particularly greater coagulation power. Note that the coagulation actions of these salts are a result of the dehydration action and are promoted as the temperature rises.

Table 14. Minimum Concentration of Various Salts Required to Coagulate PVOH from 5% Aqueous Solution of Kuraray Poval™ 28-98

Salt Type	Minimum Salt Concentration for Coagulation		Coagulation Effect Coagulation	Salt Type	Minimum Salt Concentration for Coagulation		Coagulation Effect Coagulation
	(N)	(g/1)	(1/N)		(N)	(g/1)	(1/N)
$(NH_4)_2SO_4$	1	66	1	$Al(NO_3)_3$	3.6	255	0.28
Na_2SO_4	0.7	50	1.43	HNO_3	-	-	0
K_2SO_4	0.7	61	1.43	NH_4Cl	-	-	0
$ZnSO_4$	1.4	113	0.71	$NaCl$	3.1	210	0.32
$CuSO_4$	1.4	112	0.71	KCl	2.6	194	0.38
$FeSO_4$	1.4	105	0.71	$MgCl_2$	-	-	0
$MgSO_4$	1	60	1	$CaCl_2$	-	-	0
$Al_2(SO_4)_3$	1	57	1	HCl	-	-	0
$KAL(SO_4)_2$	0.9	58	1.11	Na_2PO_4	1.4	77	0.71
H_2SO_4	-	-	0	K_2CrO_4	1.4	136	0.71
NH_4NO_3	6.1	490	0.16	Potassium	0.8	38	1.25
$NaNO_3$	3.6	324	0.28	Citrate			
KNO_3	2.6	264	0.38	H_3BO_3	0.8	165	1.25

* Condition: The minimum salt concentration at which cloudy precipitation of PVOH occurred was determined when 2 drops of a 5% aqueous solution of Kuraray Poval™ 28-98 was dropped into 10 cc of various salt aqueous solutions and it was shaken immediately. (Measurement temperature: 30°C)

3-14. GELLANT, PRECIPITANT

Besides coagulation by salts, it has long been known that aqueous solutions of PVOH thicken and gelate through chemical bonding with borax, boric acid, etc. An equal amount of an aqueous solution of borax or boric acid was mixed with a 3–10% aqueous solution of a fully hydrolyzed PVOH, the solution was stirred well and then left for 2 minutes to check the gelation. The results are shown in Table 15.

A small amount of Borax forms a gel compared with boric acid. Additionally, this gelation by chemical bonding shows a stronger tendency as the temperature becomes lower, and a so-called thermoreversible gel is produced. PVOH aqueous solution also forms a thermoreversible gel with certain types of organic compounds. Although an aqueous solution containing 8.5% of Kuraray Poval™ 28-98 and 1.5% of Congo red flows at a temperature of 40°C or higher, it turns into a red gel at room temperature. Direct dyes having the same molecular structure as Congo red, such as Benzopurpurine 4B and Japan violet extra, etc., have the same action. Resorcinol, catechol, phloroglucinol, vansan, gallic acid, etc. are known as those which produce a thermally reversible gel without color. Figure 68 shows the relation between temperature and elastic modulus of PVOH - Congo red gel. heck the gelation. The results are shown in Table 15.

Table 15. Gelation Tendency of Fully Hydrolyzed PVOH Aqueous Solution by Boric Acid and Borax

PVOH Conc.(%)		10		8		5		3	
DP	Temp. (°C)	Boric Acid	Borax	Boric Acid	Borax	Boric Acid	Borax	Boric Acid	Borax
2010	20	2.7	0.1	3.1	0.2	4	0.5	4	1.2
2010	20	>12	0.6	>12	3.1	>12	7.3	>12	18
1470	20	4	0.3	4.5	0.5	5	1	>5	1.5
1470	60	>12	4.6	>12	7.6	>12	15	>12	>20
980	20	4.5	0.8	4.5	0.9	5	1.2	>5	1.7
980	60	>12	1.3	>12	14	>12	18	>12	>20
300	20	5	1	5	1.3	5	1.5	>5	2
300	60	>12	1.5	>12	>20	>12	20	>12	>20

* Condition: An equal amount of a PVOH aqueous solution and boric acid (or borax) aqueous solution are mixed, and the concentration of the boric acid (or borax) aqueous solution is shown when the solution turns into a gel.
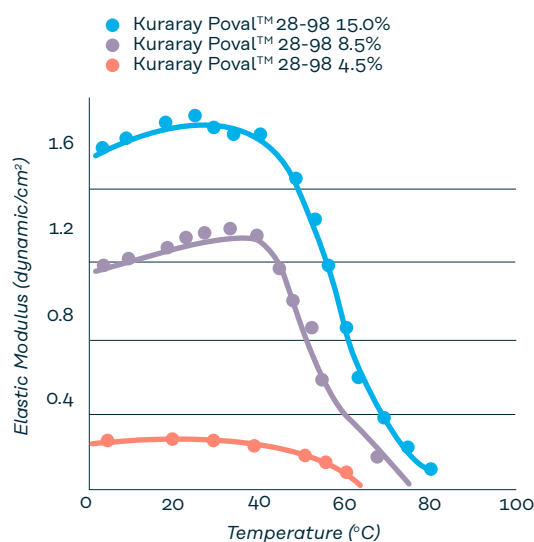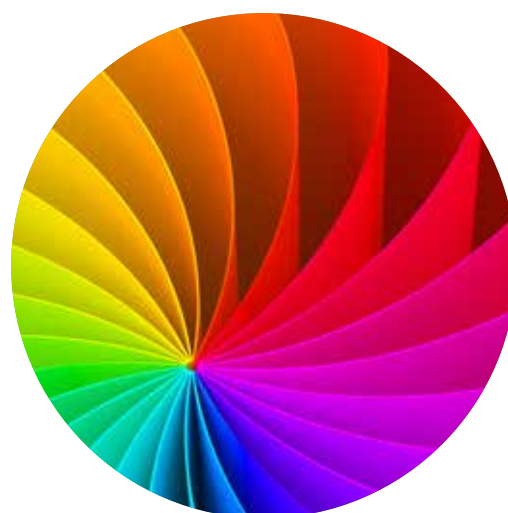

- ● Kuraray Poval™ 28-98 15.0%
- ● Kuraray Poval™ 28-98 8.5%
- ● Kuraray Poval™ 28-98 4.5%

Figure 68. Relation between Temperature and Elastic Modulus of PVOH − Congo Red Gel (Congo Red Concentration: 1.5%)

Additionally, if an appropriate amount of boric acid is used, it is effective as a thickener for the PVOH aqueous solution and there are many practical examples of its use. As other specific inorganic gellants, trivalent chromium is generated when the alkali metal salt of chromic acid or dichromic acid is reduced, vanadate or tetravalent titanium generated by oxidation of titanium trichloride, and their gelation abilities can often be adjusted by pH. As described in another chapter, the precipitants of PVOH include sodium sulfate, sodium carbonate and they are effective especially when PVOH is separated and removed from the aqueous solution. For the purpose of simply precipitating and removing PVOH from an aqueous solution, copper ion which forms a complex compound by coordination bonding can be used.

Note that the adsorption behavior of halogen, the thickening behavior of a special surfactant, etc. are known as the other adsorption phenomena to PVOH in the dissolved state. Halogen, especially iodine, adsorbs to PVOH and causes a unique color reaction and it is used for the quantitative concentration measurement etc. of the dilute PVOH aqueous solution. The color reaction of PVOH and iodine changes depending on the degree of polymerization and degree of hydrolysis of PVOH, the fully hydrolyzed PVOH exhibits blue and the partially hydrolyzed PVOH exhibits red. This discoloration point shifts to the range of a lower degree of hydrolysis as the degree of polymerization increases. These colorations are strengthened and stabilized in the presence of boric acid. For partially hydrolyzed PVOH, the degree of coloration varies depending on the distribution of the residual acetate group in the molecule even if the degree of polymerization and the degree of hydrolysis are the same. Additionally, there is a tendency that the degree of coloration tends to become larger as the residual acetate group is distributed nonuniformly in a block and this is used as a qualitative confirmation method of the block charactor. Meanwhile, as an example of a surfactant exhibiting a specific thickening effect, it is known that a significant increase in viscosity is observed when sodium dodecyl sulfate, sodium laurate, sodium dodecylbenzenesulfonate is added to a dilute PVOH aqueous solution.

3-15. CLOUD POINT

A PVOH aqueous solution is known as an aqueous solution exhibiting the lower critical solution temperature (LCST) or cloud point. The phase diagram of the LCST of an aqueous solution is schematically shown in Figure 69. The cloud point of an aqueous solution is the boundary between the uniformed-phase region and the separated-phase region, and is a temperature at which the aqueous solution becomes cloudy owing to the difference in the refractive indexes between the dense phase and the dilute phase when phase separation to the two phases occurs. In the case of PVOH, owing to various distributions such as the degree of polymerization and the degree of hydrolysis, it is difficult to determine the clear boundary. In general, however, the lower the degree of hydrolysis and the higher the degree of polymerization, the lower the temperature of the separated-phase region and the lower the cloud point.
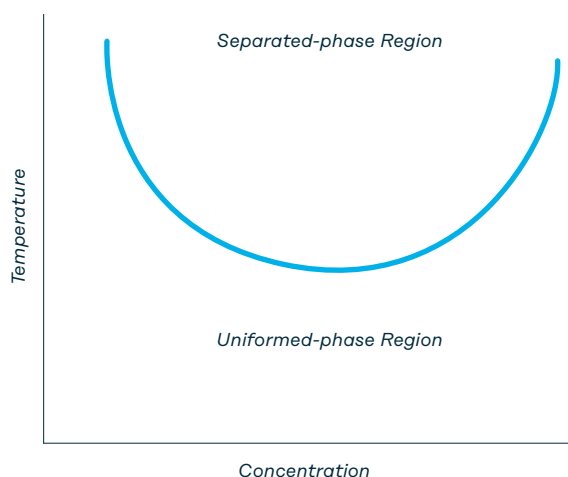
Figure 70 shows an example of the correlation between the concentration and the cloud point of a PVOH aqueous solution. In the case of the a PVOH aqueous solution, it generally exhibits a downward phase diagram with the apex at around an aqueous solution concentration of 0.5–2%. In the case of PVOH with a relatively high degree of hydrolysis of 88 mol% or more, since the separated-phase region becomes 100°C or higher, the phase diagram and cloud point shown in Figure 69 are not observed. However, in the case of PVOH with a low degree of hydrolysis 80 mol% or less, the cloud point can be seen. Additionally, as shown in Figure 71, when comparing at the same degree of hydrolysis, the cloud point decreases as the degree of polymerization of PVOH increases.
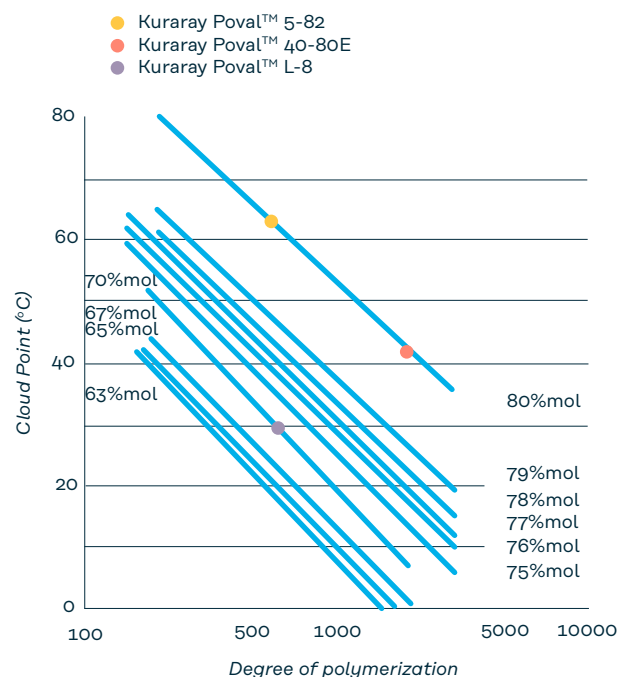

Figure 69. Phase Diagram of PVOH Aqueous Solution (Schematic Diagram)

Figure 71. Influence of Degree of Hydrolysis and Degree of Polymerization on Cloud Point of PVOH Aqueous Solution (4%)

Figure 70. Correlation Example between Cloud Point and Concentration of PVOH Aqueous Solution

3-16. BIODEGRADABILITY

It has been confirmed that PVOH is biodegradable using a biodegradability test method of plastics [50], and it is now practically used for industrial wastewater treatment containing PVOH using activated sludge. Many studies on the microbial degradation of PVOH have been made since the separation of PVOH degrading bacteria (Pseudomonaspace 0–3 strain) by Suzuki et al. in 1973 [51]. Sakai et al. [52], Shimao et al. [53] estimate that the 1,3-diol part in the PVOH chain is converted into 1,3-diketone by oxidase and then cleaved by hydrolase, the polymer chain is randomly cut into low molecules, and finally the PVOH is completely decomposed by being incorporated into the fungus body. Figure 72 shows the mechanism Tsuji et al. [54] investigated the relationship between the PVOH molecular structure and biodegradability using PVOH dehydrogenase (PVOHDH) isolated and purified from the degrading bacteria. Using commercially available representative PVOH with different degrees of polymerization and degrees of hydrolysis, the Michaelis constant Km (half of the substrate concentration at which the enzyme reaction rate becomes the maximum), which is a typical parameter of the enzyme reaction kinetics, and the maximum reaction rate Vmax, are determined. The results are shown in Table 16.

Where, Vmax / Km is an index showing the enzyme activity in the low concentration region. In commercially available PVOH, dependence of the enzymatic activity on the degree of hydrolysis is observed and the enzyme activity increases as the degree of hydrolysis decreases. This indicates the correlation with the content of the hydrophobic group in PVOH and it is thought that low degree of hydrolysis PVOH which has water solubility increases the enzyme activity (biodegradability) owing to the hydrophobic structure and affinity with the enzyme [55].

The influence of the degree of polymerization of commercial grades of PVOH biodegradeability is small. However, products with a degree of polymerization of about 20–100 are excellent in biodegradability. Furthermore, as for the influence of stereoregularity, PVOH with high isotacticity is excellent in biodegradability.

Activated sludge is usually used in waste water treatment for PVOH. Table 17 shows the examples of the BOD value and COD value of various polymer aqueous solutions with general activated sludge [56].

As shown in Table 17, since the PVOH aqueous solution is hardly decomposed in a general activated sludge, it is usual to cultivate PVOH assimilating bacteria to turn them into active sludge.
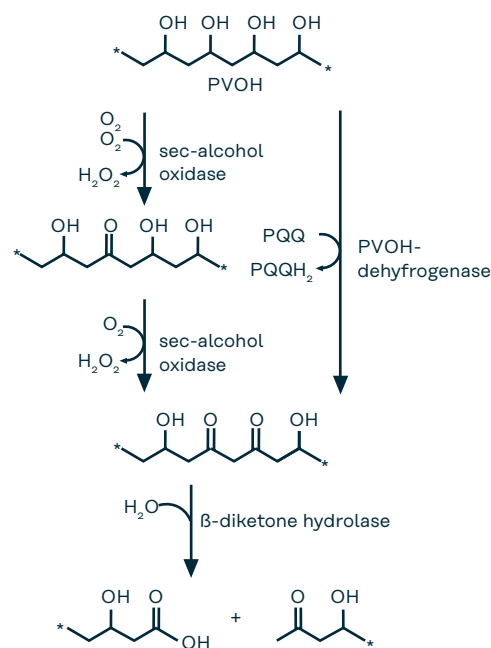
PVOH	DP	DH (mol1%)	Km (mg/l)	Vmax	Vmax/ Km
Kuraray Poval™ 28-98	1700	98.5	33.2	85.6	2.5
Kuraray Poval™ 3-98	330	98.5	24.2	73.6	3.0
Kuraray Poval™ 3-88	330	88.5	7.2	29.1	4.0
Kuraray Poval™ 3-80	330	81.0	4.8	31.4	6.5
Kuraray Poval™ 5-98	550	98.5	21.1	53.0	2.5
Kuraray Poval™ 5-88	550	88.5	8.1	30.5	3.8
Kuraray Poval™ 5-82	550	81.0	5.8	28.6	4.8

Table 16. Biodegradation Rate of PVOH

Figure 72. Biodegradation Mechanism of PVOH

Polymer	PVOH		Cornstarch	CMC
	Kuraray Poval™ 28-98	Kuraray Poval™ 22-88		
BOD	0.5	1.2	107	2.1
COD(Mn)	124	113	98.5	121

Table 17. BOD Value and COD Value of Various Polymer Aqueous Solutions (150 ppm)

References
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51) T. Suzuki, Y. Ichihara, M. Yamada, and K. Tonomura, Agric. Biol. Chem., 37, 743 (1973)
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55) Masao Tsuji, Yoshito Ikada, "Seibunkaisei Kobunshi No Kiso To Oyo (Basics and Applications of Biodegradable Polymers)", IPC, 323 (1999)
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4. Physical Properties of PVOH Film

4-1. PROPERTIES FOR WATER

When PVOH is used as a molded product, for example, as a film, or as an aqueous solution for fiber sizing, paper sizing, an adhesive, the properties of the PVOH film that is formed through the drying process for water, that is, solubility, swelling property and hygroscopicity are very important.

How the solubility of the film with water changes depending on the degree of heat treatment was also described in another chapter, "Solubility in Water". The solubility of the film hardly changes even when subjected to a heat treatment at a drying temperature of about 100°C for 60 minutes, and the film dissolves completely at 40°C in the case of a partially hydrolyzed PVOH with a degree of hydrolysis of 97 mol% or less. If the heat treatment temperature is raised to 180°C, the solubility decreases considerably even if the treatment is only for 10 minutes. If the treatment time is prolonged to 60 minutes, the partially hydrolyzed PVOH does not completely dissolve at 40°C. However, it is impossible to increase the water resistance against boiling water only by heat treatment even for the fully hydrolyzed PVOH which is susceptible to the effect of heat treatment. In practice, the temperature actually experienced by PVOH during the drying process in which a PVOH film is formed from the PVOH aqueous solution is estimated to be 100—130°C and it is considered that the solubility of PVOH does not change by the heat treatment received during this process. PVOH with a higher degree of hydrolysis as (and preferably with a high degree of polymerization) may be used to give a film of high water restance under a condition where heat treatment is performed at the highest temperature for a prolonged time. However, since thermal decomposition of PVOH occurs at 200°C or higher, it is desirable to set the heat treatment temperature around 180°C.

The water resistance required for PVOH film in practical use may be the water resistance in the sense of solubility in water as described above, but water absorption rate and swelling ratio are indicated as the water resistance. Figure 73 shows the results for various grades of PVOH with a various degree of hydrolysis and a degree of polymerization of 1750, the equilibrium moisture content of a film with a thickness of about 30 μm air-dried from a 10% aqueous solution and sufficiently dried at 50°C was obtained under each relative humidity. The results are shown in Figure 73.

In the low humidity range where the relative humidity is 50% or less, the equilibrium moisture content increases almost proportionally with the increase in the humidity, but the increase rate increases in the high humidity range exceeding 60%, and it increases considerably at 90% or more. In general, the equilibrium moisture content of the PVOH film does not differ when the temperature is in the range of 20—40°C. The influence of the degree of polymerization is hardly observed except for those with a low degree of polymerization.

However, the influence of the degree of hydrolysis of PVOH is relatively large and, as shown in Figure 73, the equilibrium moisture contents of those with a low degree of hydrolysis become high at a high humidity of 65% or higher.
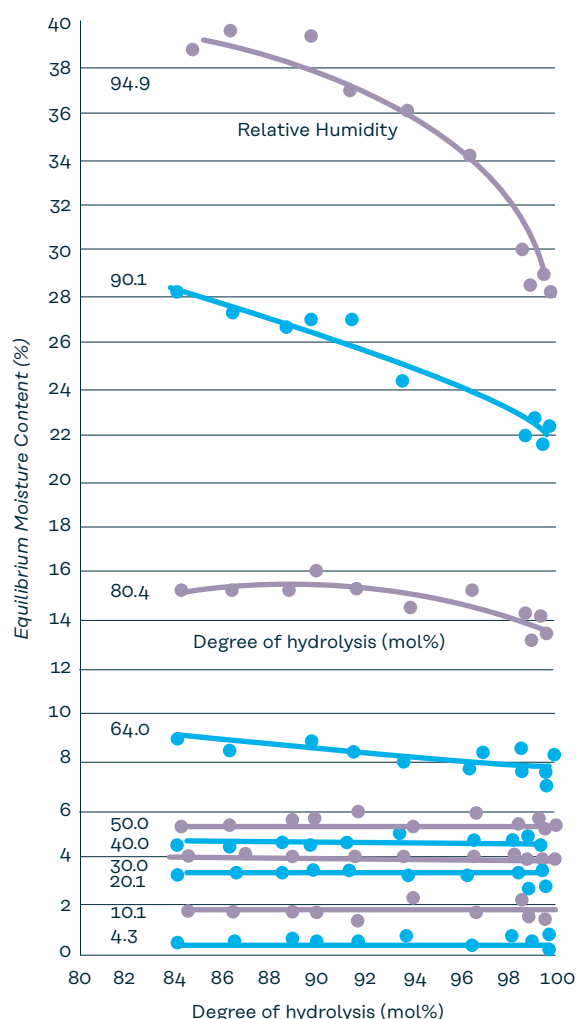
Figure 73. Equilibrium Moisture Content of PVOH Film

The equilibrium moisture content of the PVOH film also varies depending on the drying condition and heat treatment as with the solubility in water. As an example, the influence of heat treatment on the equilibrium moisture content is shown in Figure 74. It is considered that the decrease of the hygroscopic content by heat treatment is a result of the increase of crystallization of the film. When the PVOH film is immersed in water, the film absorbs a large amount of water and swells. Additionally, when the weight swelling degree (the ratio of the water absorption amount to the film weight before immersion) after immersion in water at 30°C for 48 hours is obtained, the influences of the degree of hydrolysis of PVOH and the heat treatment condition of the film are extremely noticeable as compared with the equilibrium moisture content of the film.

The films of Kuraray Poval™ 25-100 (degree of hydrolysis: >99.3mol%) and Kuraray Poval™ 28-98 (degree of hydrolysis: 98.8 mol%) were formed under the same condition and heat-treated a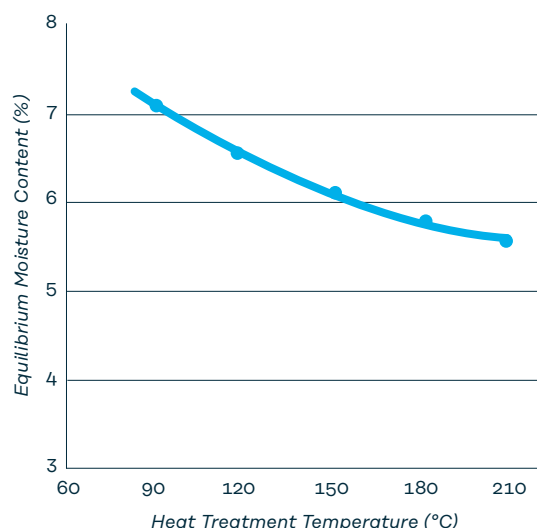t a predetermined temperature for 10 minutes to obtain the degrees of swelling. The results are shown in Figure 75. As is clear from this figure, when the heat treatment temperature is low, the difference owing to the degree of hydrolysis of 1 mol% is remarkably observed in the weight degrees of swelling of the PVOH films.

Although the degree of swelling of the PVOH film decreases significantly as the treatment temperature is raised, it is almost constant around 180°C and it is extremely difficult to achieve a lower level only with heat treatment even for Kuraray Poval™ 25-100. Figure 76 shows the moisture permeability measured at 35°C for the Kuraray Poval™ 25-100 film with a thickness of 20 μm containing 5% diethylene glycol and heat-treated at 130°C for 10 minutes as an example showing the moisture permeability of the PVOH film. Although the moisture permeability of the PVOH film tends to rapidly rise when the relative humidity of both surfaces of the film exceeds 60%, it can be considered in general that the moisture permeability of PVOH is roughly comparable to that of cellophane.
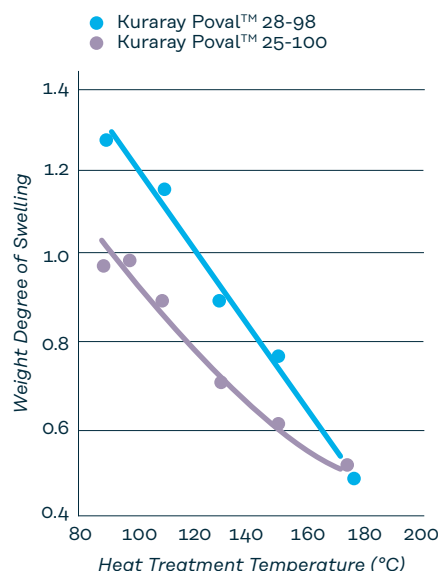

Figure 74. Influence of Heat Treatment on Equilibrium Moisture Content of PVOH Film*

The equilibrium moisture content at 20°C and 65%RH for the film of Kuraray Poval™ 25-100 which was dried at 50°C and then heat-treated at each temperature of 90—210°C for 10 minutes

Figure 75. Influence of Heat Treatment on Weight Degree of Swelling of Kuraray Poval™ 25-100 and Kuraray Poval™ 28-98
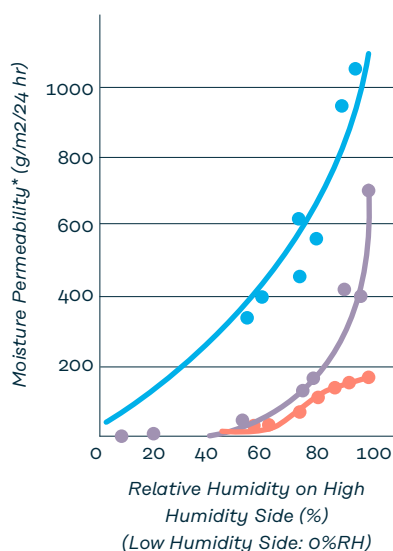

*According to JI S Z-0208 Sample Symbol

● Commercial Cellophone (Thickness: 20 μm) Kuraray Poval™ 25-100
● (Thickness: 20 μm, Containing 5 phr of diethylene glycol)
● Commercial biaxially streched 6-nylon (Thickness: 20 μm)

Figure 76. Moisture Permeability of Hydrophilic Polymer (35°C)

4-2. MECHANICAL PROPERTIES

PVOH aqueous solutions have good film forming properties and the film is tough and resistant to tearing and friction. In particular, the tensile strength belongs to the higher class when compared with plastic films widely available in the market as well as other water-soluble polymers. Although the physical properties of the PVOH film differ depending on the grades of PVOH, it greatly changes not only by the moisture content and the plasticizer addition but also by the degree of stretching and heat treatment related to the film forming condition. PVOH film used in general industrial applications is rarely subjected to stretching and heat treatment. Therefore, it can be considered as a film in a state dried at a temperature of 100°C at the highest. Figures 77 to 84 show the physical properties measured with films with a thickness of 0.03 mm, which were obtained by preparing aqueous solutions of around 10% concentration from general commercial grades, casting them on a glass plate, and drying them at 80°C for 2 hours after air-drying. The tensile strength and elongation of the PVOH film increase as the degree of polymerization increases. The partially hydrolyzed product has a slightly lower tensile strength than the fully hydrolyzed product, but the elongation increases somewhat under high humidity. Under high humidity, the tensile strength decreases for both the fully hydrolyzed product and partially hydrolyzed product, and the elongation tends to increase. However, unlike in the case of high degree of polymerization PVOH, a low degree of polymerization PVOH with a degree of polymerization of 550 exhibits a decrease in the elongation regardless of the degree of hydrolysis when the relative humidity is 60% or higher.

The tear strength of the PVOH film tends to increase as the moisture content of the film is higher, and the partially hydrolyzed PVOH with higher equilibrium moisture content has higher tear strength under the same humidity. The Young's modulus of the film decreases sharply as the humidity increases and the modulus of the partially hydrolyzed PVOH with higher equilibrium moisture content is lower than that of the fully hydrolyzed PVOH over the whole humidity range.

Overall, the mechanical properties of the PVOH film are at a higher level for the fully hydrolyzed PVOH with a high degree of polymerization and the film with a degree of polymerization of 550 is at a substantially low level. Additionally, it can be said that the dependence of the relative humidity, that is, the moisture content dependency on the physical properties of the partially hydrolyzed PVOH, is large. The properties of the PVOH film to water such as the hydroscopicity are improved after heat treatment, as described in another chapter, "Properties of PVOH Film in Water"; the mechanical properties can also be improved by heat treatment. Among the mechanical properties, the tensile strength, Young's modulus, etc. tend to increase almost linearly according to the degree of heat treatment.

On the other hand, the elongation and tear strength are improved according to the degree of heat treatment up to a temperature of 140–150°C, but they decrease sharply when further subjected to an excessive heat treatment. That is, although the mechanical properties of the PVOH film

are improved by heat treatment, embrittlement of the film is also accelerated as the temperature becomes equal to or higher than 160°C. Note that when a plasticizer such as glycerin is added, the PVOH film becomes flexible and the elongation and tear strength increase significantly, but the tensile strength and Young's modulus decrease greatly.
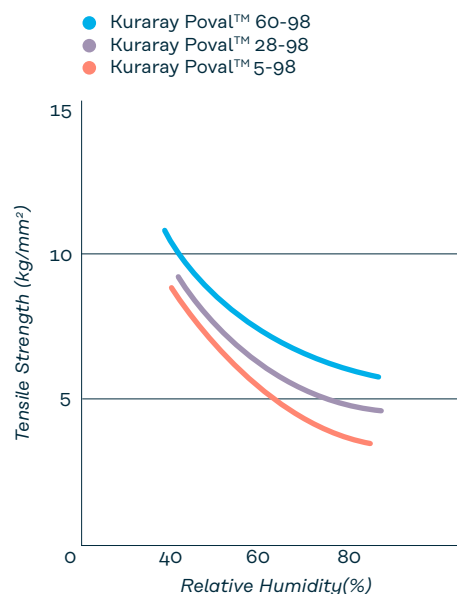

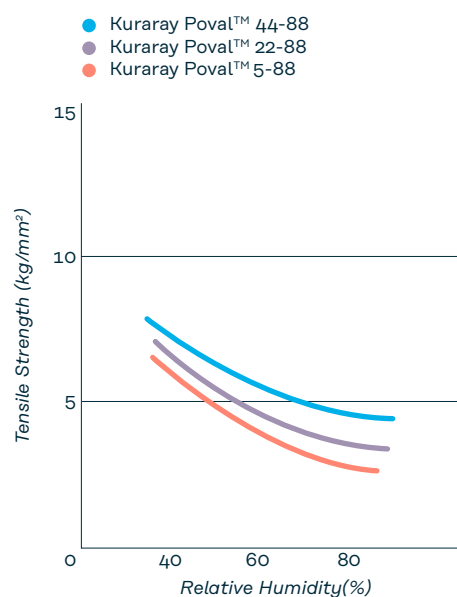Figure 77. Tensile Strength of Fully Hydrolyzed PVOH Film (20°C)

Figure 78. Tensile Strength of Partially Hydrolyzed PVOH Film (20°C) P. 31/36
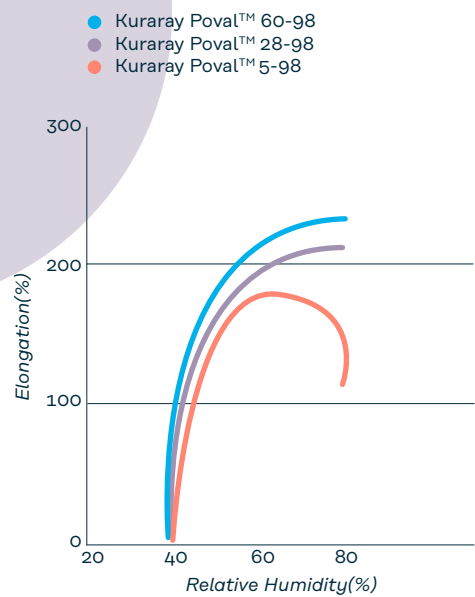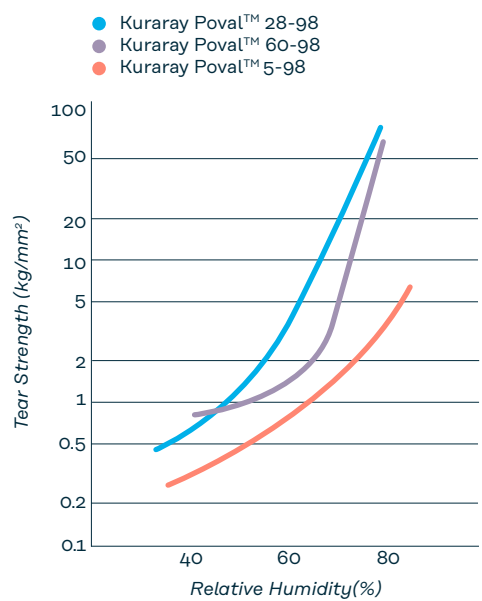
- Kuraray Poval™ 60-98
- Kuraray Poval™ 28-98
- Kuraray Poval™ 5-98

Figure 79. Elongation of Fully Hydrolyzed PVOH Film (20°C)

- Kuraray Poval™ 44-88
- Kuraray Poval™ 22-88
- Kuraray Poval™ 5-88
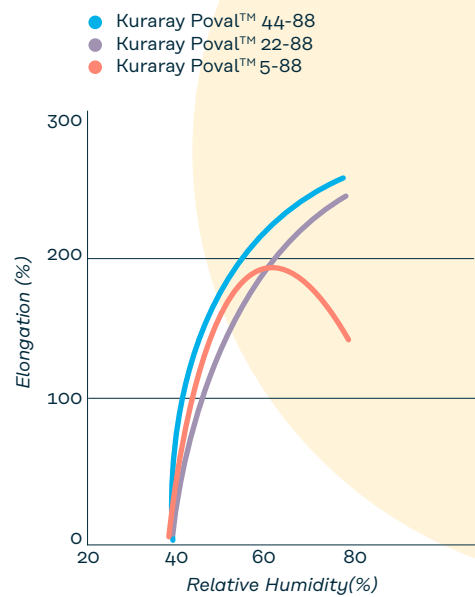
Figure 80. Elongation of Partially Hydrolyzed PVOH Film (20°C)

- Kuraray Poval™ 28-98
- Kuraray Poval™ 60-98
- Kuraray Poval™ 5-98

Figure 81. Tear Strength of Fully Hydrolyzed PVOH Film (20°C)

- Kuraray Poval™ 22-88
- Kuraray Poval™ 44-88
- Kuraray Poval™ 5-88
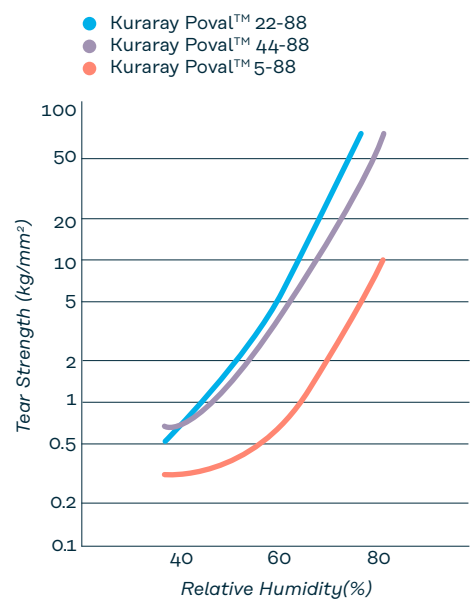
Figure 82. Tear Strength of Partially Hydrolyzed PVOH Film (20°C)

Kuraray Poval™ 5-98
Kuraray Poval™ 60-98
Kuraray Poval™ 28-98
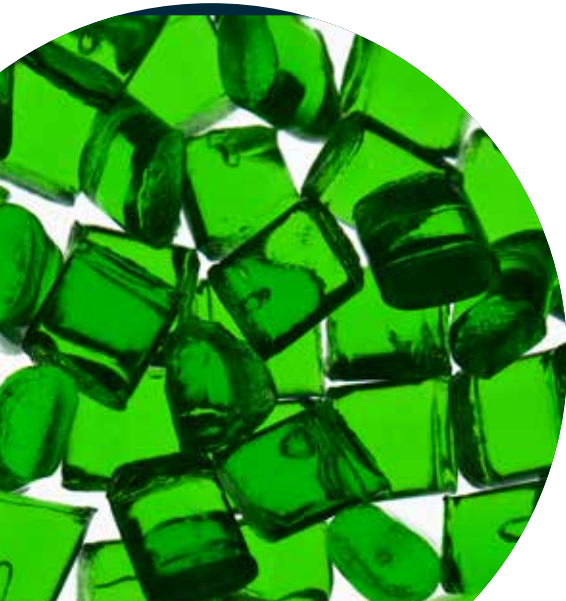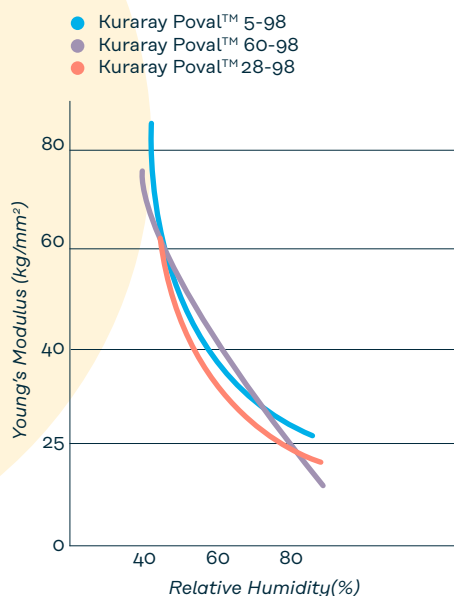
Figure 83. Young's Modulus of Fully Hydrolyzed PVOH Film (20°C)

Kuraray Poval™ 44-88
Kuraray Poval™ 5-88
Kuraray Poval™ 22-88

Figure 84. Young's Modulus of Partially Hydrolyzed PVOH Film (20°C)

4-3. GAS PERMEABILITY

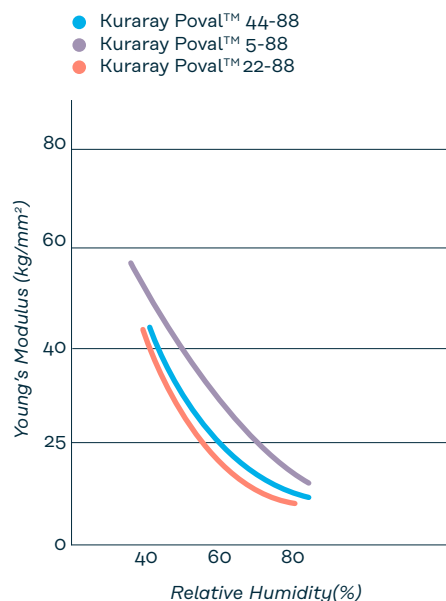It has long been known that it is difficult to pass various gases such as carbon dioxide, nitrogen, hydrogen, etc. through PVOH film, and many reports on the matter have been published. The gas barrier property of PVOH film is certainly remarkable. Table 18 shows the permeability coefficients of carbon dioxide gas and nitrogen gas measured by Ito [57]. All the values for PVOH are in the order of 10^{-13} (cc*cm/cm²/sec/cmHg) and they are extremely low even as a packaging material. However, since the PVOH film is strongly hydrophilic and is susceptible to humidity, the moisture content of the film increases and the permeability coefficient increases markedly under high humidity. Figure 85 shows how the permeability coefficient of oxygen changes depending on the moisture content of the film. When the PVOH film absorbs moisture, the adsorbed water first breaks the hydrogen bonding between the hydroxyl group of the PVOH molecules and then bonds with the hydroxyl group. As the moisture content increases, the water exists as free water between the

PVOH molecules. Therefore, it is considered that this free water plasticizes PVOH and activates the molecular motion, and the gas permeation increases. The gas permeability of the PVOH film also increases if there are other factors that activate the molecular motion of PVOH. In PVOH with a low degree of hydrolysis, the crystallinity of the film decreases and the mobility of the side chain owing to the acetate group increases, thus the gas permeability increases. Note that the gas permeability has a temperature dependency, and it generally tends to increase as the temperature rises, but the permeability coefficient increases sharply when the measurement temperature is above the second-order transition temperature of the polymer. It is thought that this is because the molecular motion of the polymer molecule becomes active when the temperature is above the second-order transition temperature and the diffusion and permeation of the gas increase rapidly.
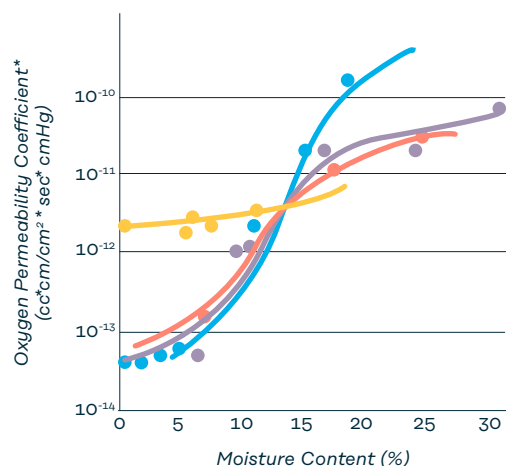
Figure 85. Influence of Moisture Content on Oxygen Permeability of Film (35°C)

*By vacuum pressure method sample:

● Kuraray Poval™ 25-100 (Unplasticized, Dreied at 80° C x 2hr
● Kuraray Poval™ 25-100 (Containing of DEG 5%, heat-treted at 130°C x 10min
● K cellophane (Vinylidene Chloride Applied)
● Commercial biaxially stretched 6-nylon

References
57) Ito, Polymer Chemistry, 18, 158 (1961)

Table 18. Gas Permeability of Various Polymer Films

Polymer	Gas	Temperature (°C)	Humidity (%RH)	Permeability Coefficient [1] $P \times 10^{11}$
PVOH	CO_2	23	0 44 94	0.01 0.52 119
	N_2	14	0 90	<0.01 3.3
Cellophane	CO_2	15	0 90	0.1 10.5
6-nylon	CO_2	30	0 44 95	1 1.7 2.9
Polyethylene (d=0.9203)	CO_2	15	0 43 95	61.4 57.8 85.3
	N_2	15	0 95	4.5 5
Vinyl Chloride	CO_2	20	0 86	4.2 3.5

1) Unit: cc*cm/cm²*sec*cmHg
Cited reference: Ito, Polymer Chemistry, 18, 158 (1961)

4-4. RESISTANCE TO OIL, RESISTANCE TO ORGANIC SOLVENT

PVOH has many hydrophilic hydroxyl groups and has strong resistance to many organic chemicals such as animal oils/ vegetable oils, mineral oils, aliphatic hydrocarbons, ethers, esters and ketones. Films with a thickness of 0.03 mm of Kuraray Poval™ 28-98 and Kuraray Poval™ 22-88 prepared by drying at 80°C for 2 hours were immersed in a chemical solution at 40°C for 70 hours and the weight swelling degree and the area expansion degree of the films were determined according to the method prescribed in JIS K-6301. The results are shown in Table 19. No swelling was observed in the PVOH films within the scope of this test, and a slight tendency of weight reduction and shrinkage was observed. However, this is thought to be a result of the fact that there is some moisture in the sample films and it is dehydrated during immersion in the chemical solution. In general, the oil resistance and organic solvent resistance of PVOH increase as the degree of hydrolysis increases, but the influence of the degree of polymerization has no effect. Resistance to lower alcohols such as methanol and ethanol has a relatively large dependency on the degree of hydrolysis and the partially hydrolyzed product tends to swell.

Table 19. Oil Resistance / Organic Solvent Resistance of PVOH Film, Weight and Area Change after Immersion at 40°C x 70 hr

Chemical Solution		Weight Degree of Swelling (%)		Area Degree of Swelling (%)	
		Kuraray Poval™ 28-98	Kuraray Poval™ 22-88	Kuraray Poval™ 28-98	Kuraray Poval™ 22-88
Hydrocarbon	Benzene	-0.6	-1.3	-1.6	-2.4
	Isooctane	-0.5	-1.1	-2.6	-2.3
	High-octane Gasoline	-0.6	-1.2	-2.6	-2.1
Halogenated Hydrocarbon	Monochlorobenzene	-0.8	-1.4	-2.4	-1.4
	Carbon Tetrachloride	-0.5	-1.1	-2	-0.9
Oil	Soybean Oil	-0.4	-0.6	-1.2	-1
	Castor Oil	-0.2	-0.9	-0.3	-1.3

According to JIS K-6301

4-5. OPTICAL TRANSMITTANCE

PVOH film allows good transmittance of light. The visible light transmittance of Kuraray Poval™ 25-100 film with a thickness of 0.025 mm containing 10 phr of glycerin is very high and, for example, the transmittance at 560 nm reaches 91%. The PVOH film also allows ultraviolet rays to pass through. An example of the measurement of Kuraray Poval™ 25-100 film is shown in Figure 86. Generally, ultraviolet absorption spectrum of PVOH is used for detection of the carbonyl group using the aqueous solution as a sample and PVOH with a low degree of polymerization tends to exhibit a stronger absorption than PVOH with a high degree of polymerization.

The infrared absorption spectrum of PVOH is measured using a casted and dried film. Figure 87 and Figure 88 show the examples of Kuraray Poval™ 25-100 and Kuraray Poval™ 22-88 as representative infrared absorption spectra of the fully hydrolyzed PVOH and partially hydrolyzed PVOH.
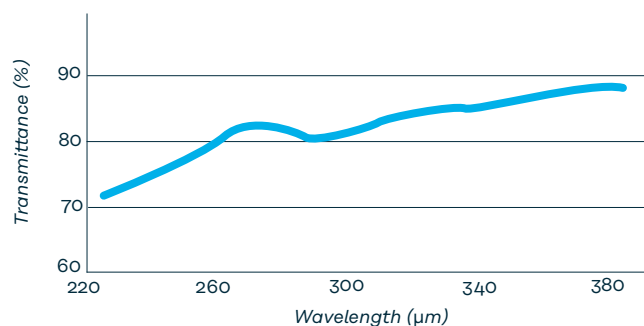
Kuraray Poval™ 25-100 film with a thickness of 0.025 mm containing 10 PHR of glycerin

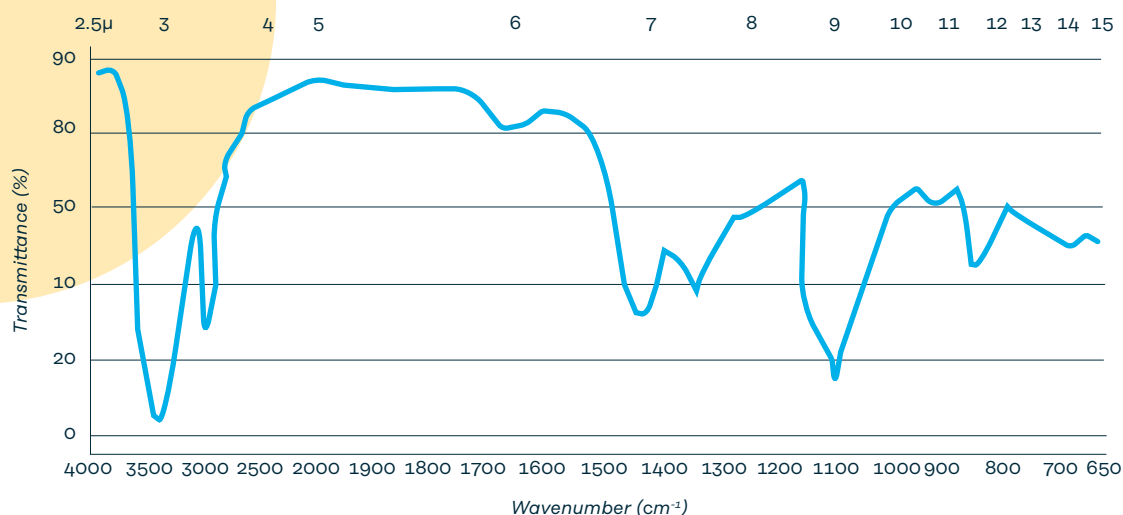Figure 86. Ultraviolet Ray Transmittance of PVOH Film*

Figure 87. Infrared Absorption Spectrum of Kuraray Poval™ 25-100 (Film)

In the infrared absorption spectrum, there is a characteristic absorption band owing to the existence of a specific atomic group in the molecule, called characteristic frequency. The major characteristic frequencies are shown in Table 20. Although the absorption at 1700–1800 cm^{-1} (1740 cm^{-1}) based on the carbonyl group belonging to the acetate group is hardly observed in the fully hydrolyzed PVOH, it is quite remarkable in the partially hydrolyzed PVOH. The intensity of the absorption at 1141 cm^{-11} in the infrared absorption spectrum is used for the quantitative analysis of the crystallinity of PVOH, and the absorptions at 916 cm^{-1} and 849 cm^{-1} are used for detailed investigation in the quantitative analysis of the stereoregularity. In this manner, the infrared absorption spectrum analysis is one of the effective methods for estimating the bonding state of PVOH. It was described that the PVOH film allows a ray to pass through well at the beginning of this section and the film certainly allows the visible ray and the ultraviolet ray well, but the infrared transmittance in the longer wavelength region is considerably lower than that of other transparent plastic films and it is substantially difficult for infrared rays to go through the film. Therefore, a heat retention effect can be expected.
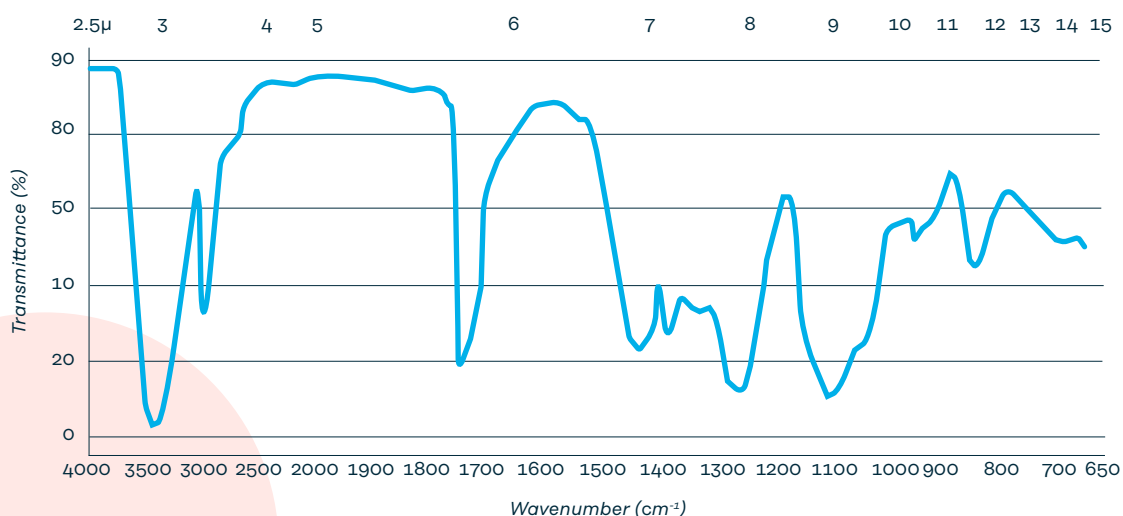

Figure 88. Infrared Absorption Spectrum of Kuraray Poval™ 22-88 (Film)

Table 20. Major Characteristic Frequencies on Infrared Absorption Spectrum

Characteristic Frequency Range	Atom Group	
3700-3500	H-O	Stretching Vibration
3500-3300	H-N	Stretching Vibration
3400-3300	H-C ≡ C	Stretching Vibration
3100-3000	H-C = C	Stretching Vibration
3100-3050	H-C (Aromatic Ring)	Stretching Vibration
3000-2800	H-C-	Stretching Vibration
2650-2550	H-S	Stretching Vibration
2300-2200	N ≡ C	Stretching Vibration
2270-2170	C ≡ C	Stretching Vibration
2160-2100	N ≡ N	Stretching Vibration
1800-1700	C = O	Stretching Vibration
1690-1630	C = N	Stretching Vibration
1650-1550	H-N	Bending Vibration
1650-1600	C = C	Stretching Vibration
1600-1500	S = C	Stretching Vibration
1460-1300	H-C	Bending Vibration
1400-1250	C-N	Stretching Vibration
1200-1050	C-OH	Stretching Vibration
1300-1100	F-C	Stretching Vibration
750-650	Cl-C	Stretching Vibration
650-550	Br-C	Stretching Vibration
550-400	I-C	Stretching Vibration

4-6. ELECTRIC PROPERTIES

The electrostatic propensity of PVOH film is very small. PVOH film with a strong hydrophilic property generates very little static electricity by friction and has antifouling property because dust, etc., in air do not electrodeposit on it. Table 21 shows the friction-charged electrostatic potential while comparing that of Kuraray Poval ™ 25-100 film containing 10 phr of glycerin with those of various packaging films. Although there is not much detailed data on the electric properties of PVOH, an example of how the electric properties change depending on the moisture content of the film is cited in Table 22. Additionally, Table 23 shows the dielectric constant and dielectric loss of Kuraray Poval™ 25-100 film in absolute dry condition.

Table 21. Electrostatic Propensity of Plastic Film

Type	Charged Voltage (Volt*)
Kuraray PovalTM 25-100	1
Cellophane	1
Vinyl Chloride	40
Polyethylene	50-90
Polystyrene	120-150

* The film after humidity conditioning at 30°C, 40% RH was rubbed with a rotary static tester at a speed of 800-1000 rpm and then the voltage was measured.

Table 22. Electric Properties of Fully Hydrolyzed PVOH*)

Moisture content of Film (%)	0.5	1	2	4	8	16	32
Specific Resistance (20°C), Ohm-cm	1011	1010	3×10^9	109	3×10^8	108	2×10^7
Dielectric Constant (20°C, 10^3 cycle)	3.5	4.5	6.5	13	>13	>13	>13
Surface Resistance (20°C), Ohm	1010	1010	1010	3×10^7	3×10^7	8×10^6	2×10^6

* Ullmanns Enzyklopädie der technischen Chemie (1963)

Table 23. Dielectric Constant & Dielectric Loss of Kuraray Poval™ 25-100 film in absolute dry condition

Frequency	Temperature	Dielectric Constant	Tan ∂ x 104
10^2	18	1.74	9.4
10^3	18	1.745	14
10^4	18	1.75	29
10^5	18	1.76	42
10^6	18	1.79	47.7

Precautions for Handling and Storage of PVOH

Please refer to our separate health and safety guidelines for handling our Handling:

1. Since this product contains fine powder and dust may stirred up when feeding it into a dissolution tank, wear rubber gloves and protective glasses etc. to protect your skin and eyes.

2. Install a dust collector when handling a large amount of this product. Additionally, since there is a risk of dust explosion with static electricity or spark as an ignition source, measures such as secure grounding and use of conductive materials are required.

Storage

1. Since this product dissolves in water, store it so that it will not be exposed to rain water or the like.

2. Since this product absorbs moisture and tends to become a block, store it away from hot and humid place.

3. When storing 3,000 kg or more of this product, it is subject to regulations as flammable material (combustible solids) specified by the Fire Service Act.

Safety

For detailed information on safety, refer to the Material Safety Data Sheet.

Although the description contents of this document are prepared based on the materials, information and data available at the time of preparation for accuracy, this does not guarantee the accuracy. The cautions and notes are intended for ordinary handling and do not necessarily conform to all situations and uses. Therefore, be sure to set and use safe management and use conditions at the responsibility of the user.

Adding value to your products — worldwide

KURARAY POVAL™, EXCEVAL™, ELVANOL™, and MOWIFLEX™ are the trademarks for polyvinyl alcohols (PVOH) made by Kuraray. Their key characteristics — outstanding film-forming properties and high binding strength — add real value to your products. Our polymers are water-soluble, highly reactive, crosslinkable and foamable. They have high pigment binding capacity, protective colloid characteristics and thickening effects. The physical and chemical properties of KURARAY POVAL™ make it ideal for a wide variety of applications, ranging from adhesives through paper and ceramics to packaging films. Many of our polymers are food contact-approved and thus suitable for food applications.

Kuraray produces its wide range of KURARAY POVAL™ grades in Japan, Singapore, Germany and the USA. Kuraray's global production and service network make us your partner of choice for innovative high-quality PVOH resins.

Kuraray Poval™

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