

## Polyelectrolyte Complex Prepared from Carboxymethylated and Aminoacetalized Derivatives of Poly(vinyl Alcohol)

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### Synopsis

Some physical and chemical properties of an ionic complex made from the weak polyelectrolytes carboxymethylated poly(vinyl alcohol) (PA) and aminoacetalized poly(vinyl alcohol) (PC) are investigated in comparison with those of another ionic complex made from the strong polyelectrolytes sulfated poly(vinyl alcohol) (PSA) and poly(vinyl alcohol) acetalized with diethoxyethyltrimethylammonium (PTC). It was found that when the complex PC-PA was heated at high temperatures, covalent amide bonding took place, whereas no significant change occurred in the case of the PTC-PSA complex. As a result of these structural changes, the degree of swelling of the PC-PA complex in water was markedly decreased, but that of the PTC-PSA complex was not changed by the treatment. The PC-PA complex was insoluble in water and in 1N HCl and 1N NaOH aqueous solutions even if not heat treated, but the PTC-PSA complex was soluble in such acidic and basic aqueous solutions but not in water if heat treated. The PC-PA and PTC-PSA films exhibited good mechanical properties.

### INTRODUCTION

The complex formation between polyelectrolytes by ionic bonding has been extensively studied,<sup>1-12</sup> but the physical and chemical properties of the resultant complexes have not been investigated in the field of material science up to relatively recently.<sup>13,14</sup> Michaels and others prepared a polyelectrolyte complex from a pair of polyelectrolytes [poly(styrene sulfonate) and poly(vinylbenzyltrimethylammonium)] expecting specific properties because of the presence of ionic bonding in the structure;<sup>15-18</sup> its properties and practical applicability were demonstrated by Refojo,<sup>19</sup> Vogel et al.,<sup>20</sup> and Rembaum.<sup>21</sup>

We have synthesized a number of polyelectrolytes from poly(vinyl alcohol) (PVA) such as carboxymethylated PVA (PA), aminoacetalized PVA (PC), PVA acetalized with diethoxyethyltrimethylammonium (PTC), and sulfated PVA (PSA), and investigated the ionic bonding of different pairs of these polyelectrolytes with opposite charge.

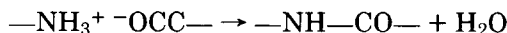
In the ionically bonded complex prepared from PC and PA, the amino groups in PC and the carboxyl groups in PA are at a very close distance because of ion

TABLE I  
Characterization of Polyelectrolyte Composite Films

Sample description	Sample no. <sup>a</sup>	Degree of acetalization for PC, mole-%	Degree of etherification for PA, mole-%	PC Content in films, mole-%
PC-PA	5	14.0	9.0	50.3
	8	14.0	9.0	50.6
	15	10.3	7.4	53.8
	17, 19	10.3	7.4	50.0
	Sample no.	Degree of acetalization for PTC, mole-%	Degree of sulfation for PSA, mole-%	PTC Content in films, mole-%
PTC-PSA	4	12.3	5.7	50.0
	10, 11	12.3	8.1	50.0

<sup>a</sup> Samples 5, 8, 4, 10, and 11 were prepared from fractionated PVA. The other samples were prepared from unfractionated whole PVA.

pairing. Consequently, it is expected that the ionic bonds are transformed to covalent amide bonds on heating:



If covalent amide crosslinks are formed, properties such as water swelling should be changed. On the other hand, such a covalent crosslink cannot be expected from ion pairing of the  $-\text{N}(\text{CH}_3)_3^+$  groups in PTC and the  $-\text{SO}_4^-$  groups in PSA. The purpose of this paper is mainly to compare the change in the physical and chemical properties produced by heating the complex made from PC and PA and the complex made from PTC and PSA.

## EXPERIMENTAL

**Materials.** A commercial PVA with a viscosity-average molecular weight and degree of saponification of 44,000 and 99.5 mole-%, respectively, was fractionated by a conventional liquid-liquid fractionation technique using isopropanol and water. The fractions with a molecular weight approximately equal to that of the original polymer were used together with the unfractionated polymer as starting materials in this work. The PC samples were prepared by reacting the PVA samples with aminoacetal in the presence of hydrochloric acid as catalyst at 70°C for 25 hr, and neutralizing and dialyzing with sodium bicarbonate and water. The PA samples were prepared by adding the PVA samples into caustic soda solution of sodium monochloroacetate at 0°C and heating at 60°C for 7 hr, and neutralizing and dialyzing with hydrochloric acid and water. The PTC and PSA samples were prepared from the PVA samples by a technique described previously.<sup>22</sup> The characterization of these polyelectrolytes is summarized in Table I together with the compositions of the composite films made by procedures described below.

**Preparation of Composite Films of Polyelectrolytes.** The composite films of PC and PA were made by casting the mixed alkali aqueous solution of PC and

PA in equivalent molar ratio at room temperature. The pH of the solution was controlled in a range of 9–10 by sodium hydroxide. In this pH range, ionic complex formation does not take place since the amino groups of PC are un-ionized and a uniform composite film made of PC and PA could be obtained. The films prepared by such a technique were soluble in water. The films were next washed with methanol to remove the sodium hydroxide. By this process, the films become insoluble in water. It is assumed that the removal of the sodium hydroxide results in ionization of amino groups in PC and ionic bonding between PC and PA. A composite film of PC and PA was also made from the mixed HCl-acidic aqueous solution of both components at a pH 2 in a similar manner.

Composite films of PTC and PSA were made using aqueous solutions of both polyelectrolytes. In this case, PTC and PSA were strongly basic and acidic, and ionization of either one could not be suppressed in any pH range. Therefore, when the solutions of PTC and PSA were mixed, a polyelectrolyte complex insoluble in water immediately was formed. However, by controlling the conditions for the mixing, a suspension of the polyelectrolyte complex in the form of oil-like sticky particles was obtained. The films of the PTC-PSA complex were obtained by collecting these particles and molding them into a film.

**Heat Treatment.** Heat treatment of the composite films was done in a temperature range of 120–200°C in air.

**Swelling and Weight Loss.** The degree of swelling (DS) of the samples was measured at room temperature after immersing in various media for three days. The weight loss (WL) of samples after immersion in water at room temperature was determined on film samples 0.1 mm thick.

**Moisture Regain.** The measurements were carried out in air of 65% relative humidity at 20°C. The water content was expressed in percent, based on the dried weight of the samples.

**Infrared Spectroscopy.** The spectroscopy was carried out by an infrared spectrometer, Type EPI-S2, from Hitachi Seisakusho Co.

**Tensile Properties.** Tensile strength, elongation at break, and Young's modulus of sample films were measured in air of 65% relative humidity and in water at 20°C by use of a Tensilon UTM-II from Toyo Baldwin Co.

## RESULTS AND DISCUSSION

### Swelling of Unheated Complexes

The degree of swelling (DS), the moisture regain (MR), and the weight loss (WL) of the PC-PA and PTC-PSA films are summarized in Table II. It is found that the DS of the PC-PA and PTC-PSA complexes is in a range of about 300%. The DS in this range is thought to be characteristic of ionically bonded complexes prepared from the PVA derivatives of which the degrees of acetalization, etherification, and sulfation are almost the same and roughly equal to 10 mole-%.

The WL of the PC-PA samples is considerably larger than that of the PTC-PSA samples. This larger WL of the former samples is due to imperfection of the ionic bonding. Although, as mentioned in the experimental section, these ionically bonded PC-PA films have been prepared by extracting the sodium hydroxide content of the cast films of the mixed PC and PA alkali solution, the

TABLE II  
Degree of Swelling, Moisture Regain, and Weight Loss

Sample description	Sample no. <sup>a</sup>	DS, %, in				MR, %	WL, %
		H <sub>2</sub> O	CH <sub>3</sub> OH	C <sub>2</sub> H <sub>5</sub> OH	<i>i</i> -C <sub>3</sub> H <sub>7</sub> OH		
PC-PA	8M	283	38.0	3.5	3.9	—	26.9
	5M	283	34.0	—	—	—	22.8
	15M	334	26.3	—	—	18.1	11.6
PTC-PSA	4	334	22.9	0.8	1.7	18.4	3.4
	10	314	22.7	4.6	8.2	—	2.8
	11	263	24.3	0.5	—	—	—
PVA	—	—	0.54	0.42	2.0	—	—

<sup>a</sup> M designates samples washed with methanol.

ionic bonding is believed to be incomplete because of the lesser degree of swelling in methanol as shown in Table II. By contrast, the WL of the PTC-PSA films is much smaller than that of the PC-PA films. This is due to the fact that the ionic bonding took place during the preparation of the films.

### Swelling of Heat-Treated Complexes

The degree of swelling (DS), the moisture regain (MR), and the weight loss (WL) of the PC-PA complexes after heat treatment under different conditions are shown in Table III. The DS in water is sharply decreased by the heat treatment. However, the effects of the heat treatment depend on the nature of the samples (8M, 5M, 15M), for which the WL before heat treatment varies over a wide range (see Table II). This is related to the difference in the degree of ionic bonding in the samples before heat treatment. It is found from Tables II and III that a smaller WL before heat treatment is associated with smaller DS in water after heat treatment. In order to further promote the ionic bonding in the PC-PA film and obtain higher heat treatment effects, sample 8M was dipped in water with higher swelling ability than methanol after washing with methanol for two weeks at room temperature. After drying in air, the sample (8MW) was heat treated and the swelling properties were examined. As expected, the effects of the heat treatment are much accelerated by this pretreatment, and a very small DS is observed.

On the other hand, no appreciable change in the DS in various media is observed for the PTC-PSA complexes as shown in Table IV.

These facts suggest that the character of the ionic bonding for the PC-PA complexes may be altered, but for PTC-PSA complexes, it remains substantially unchanged by heat treatment.

### Structural Analysis by Infrared Spectroscopy

**PC-PA (Unheated).** The spectra for the PC-PA composite films made either from the basic or acidic solutions are shown in Figures 1(a) and 1(b); each sample is designated either PC-PA-NaOH or PC-PA-HCl since the samples contain NaOH or HCl. For the PC-PA-NaOH, a strong absorption is observed at 1600 cm<sup>-1</sup>. This band is composed of superposed contributions of the ab-

TABLE III  
Degree of Swelling, Moisture Regain, and Weight Loss of Heat-Treated PC-PA

Sample no.	Heat Treatment		DS, %, in			
	Temp., °C	Time, min	H <sub>2</sub> O	CH <sub>3</sub> OH	MR, %	WL, %
8M <sup>a</sup>	120	60	288	—	—	—
	140	60	246	—	—	—
	160	60	183	28.9	—	0.7
	180	60	97.7	29.5	—	0.8
	200	10	95.7	30.1	—	1.6
5M <sup>a</sup>	140	60	105	29.8	14.8	0.2
	160	60	80.1	18.1	15.0	0.6
	200	30	65.7	15.8	15.4	0.3
15M <sup>a</sup>	200	10	79.5	29.7	—	0.0
	200	30	45.1	25.1	12.8	0.0
8MW <sup>b</sup>	no	—	276	32.0	13.1	—
	160	10	126	12.6	14.9	0.0
	160	30	80.1	3.9	13.7	0.2
	160	60	53.8	2.6	14.5	0.0
	160	120	48.1	4.9	14.1	0.4
	160	180	46.5	3.2	14.0	0.0

<sup>a</sup> M designates samples washed with methanol.

<sup>b</sup> This sample was immersed in water after washing with methanol and tested. M and W designate a sample washed with methanol and immersed in water.

sorptions at 1600 cm<sup>-1</sup> due to COO<sup>-</sup> stretching in PA Na salt (PA-Na) and 1590 cm<sup>-1</sup> due to NH<sub>2</sub> bending in basic PC. For PC-PA-HCl, three absorptions are observed at 1515, 1620, and 1740 cm<sup>-1</sup>, and can be assigned to NH<sub>3</sub><sup>+</sup> bendings in the PC HCl salt (PC-HCl) and C=O stretching in the acidic PA. Since all of these absorptions can be considered to be characteristic of each component, both the PC-PA-NaOH and PC-PA-HCl absorptions are the sums of absorptions by the two components, i.e., basic PC and PA-Na or PC-HCl and acidic PA.

Figure 1(c) shows the spectrum for the PC-PA composite sample in which the NaOH content in PC-PA-NaOH was extracted by washing with methanol. The absorption band at 1600 cm<sup>-1</sup> is unaltered by the process. On the other hand, it was found that in the case of PA-Na, the absorption band at 1600 cm<sup>-1</sup> was shifted to 1740 cm<sup>-1</sup> by washing with methanol, and a major part of the carboxyl ions in Pa-Na was changed to acidic PA by hydrolysis. This fact suggests that the occurrence of hydrolysis in PA-Na is suppressed by the presence of an attractive force between PC and PA owing to ionic bonding. Accordingly, the absorption at 1600 cm<sup>-1</sup> can be considered to be characteristic of the PC-PA

TABLE IV  
Degree of Swelling and Weight Loss of Heat-Treated PTC-PSA

Sample no.	Heat Treatment		DS, %, in		
	Temp., °C	Time, min	H <sub>2</sub> O	CH <sub>3</sub> OH	WL, %
4	200	10	307	20.2	3.4
11	120	60	306	26.6	—
	160	60	246	27.8	5.8
	180	60	254	32.9	3.9
	200	10	300	31.8	4.9

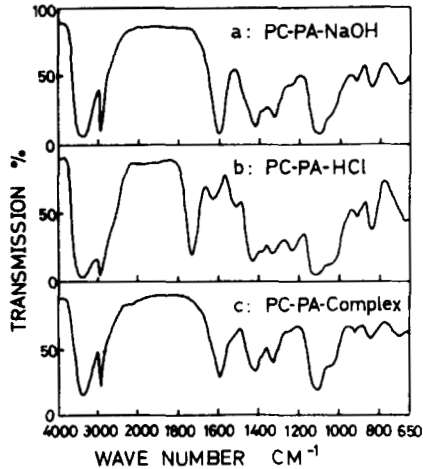


Fig. 1. Infrared spectra of PC-PA-NaOH (a), PC-PA-HCl (b), and PC-PA complex (c).

composite sample involving ionic bonding. Hereafter, this PC-PA composite sample is designated PC-PA complex.

**PC-PA (Heat Treated).** The spectra of the PC-PA-NaOH and PC-PA complex heat treated for different periods of time are shown in Figure 2. No appreciable change in the spectra for PC-PA-NaOH by the heat treatment in a range of  $1800\text{--}1400\text{ cm}^{-1}$  is recognized. In order to further characterize the structural change in this sample by the heat treatment, the sample was immersed after heat treatment in 0.02 mole/l. methanol solution of HCl. It was found that a new absorption band appeared at  $1660\text{--}1640\text{ cm}^{-1}$  by this process, in addition to the absorption bands due to COOH and  $\text{NH}_3^+$  groups. As mentioned previously, the PC-PA-NaOH films before heat treatment were soluble in water. By contrast, the PC-PA-NaOH films after heat treatment became insoluble in water, though the DS and WL were markedly higher than those of the heat-

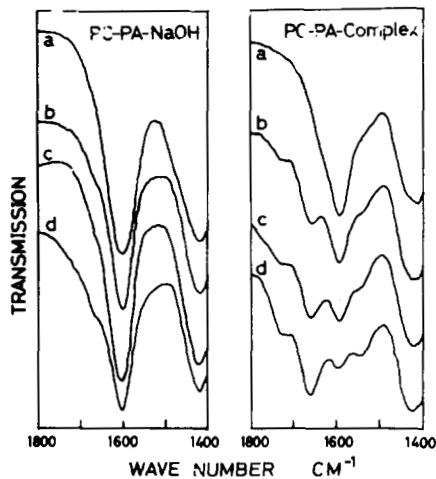
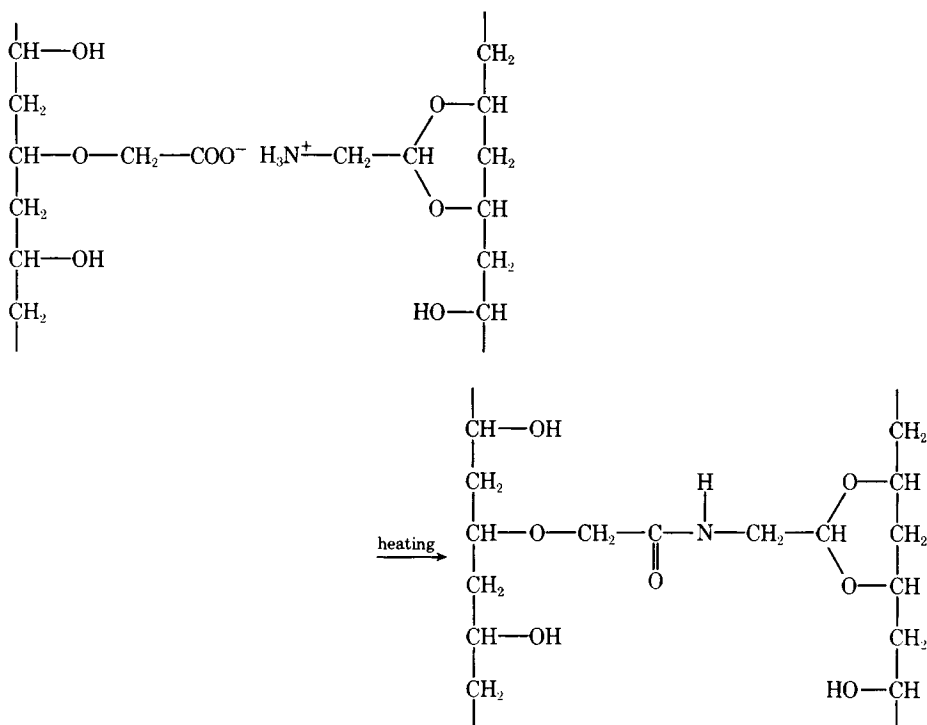


Fig. 2. Infrared spectra of PC-PA-NaOH and PC-PA complex not heated (a), and heated at a temperature of  $160^\circ\text{C}$  for 30 min (b), 60 min (c), and 180 min (d).

treated PC-PA complex. This finding suggests hydrogen bonding in the PC-PA-NaOH by the heat treatment.

In the spectra of the PC-PA complex, new absorption bands appear after heat treatment at  $1740\text{--}1730\text{ cm}^{-1}$ ,  $1670\text{--}1660\text{ cm}^{-1}$ , and  $1550\text{--}1540\text{ cm}^{-1}$ . In order to assign these bands, the heat-treated sample was immersed in 0.02 mole/l. NaOH methanol solution and 0.02 mole/l. HCl methanol solution at room temperature. The spectra for the samples are shown in Figure 3. It is first observed that the absorption bands at  $1670\text{--}1660\text{ cm}^{-1}$  and  $1550\text{--}1540\text{ cm}^{-1}$  stay unaltered by these treatments. The former band at  $1670\text{--}1660\text{ cm}^{-1}$  can be assigned to C=O stretching in amide I, and the latter  $1550\text{--}1540\text{ cm}^{-1}$  to NH bending and CN stretching in amide II. These results suggest that the following chemical reaction takes place in the PC-PA complex on heat treatment:



Secondly, it is observed that the band at  $1740\text{--}1730\text{ cm}^{-1}$  in Figure 3(a) is shifted to  $1600\text{ cm}^{-1}$  under basic conditions [Fig. 3(b)]. Hence, this band is assigned to C=O stretching of COOH groups. The presence of COOH groups in the complex is caused either by the separation of a part of the  $\text{NH}_3^+\text{--COO}^-$  ion pairs and their conversion to  $\text{NH}_2$  and COOH groups owing to mechanical strain in the structure resulting from the formation of amide bonds, or by the decomposition of acetal bonds in the PC component to COOH due to the heat treatment. However, when isolated PC was heated, the IR spectrum gave no evidence for such thermal decomposition.

**PTC-PSA.** For these compounds, absorptions in the range of  $2000\text{--}1400\text{ cm}^{-1}$  contained only bands at  $1650\text{--}1640\text{ cm}^{-1}$ ,  $1480\text{--}1470\text{ cm}^{-1}$ , and  $1440\text{--}1420\text{ cm}^{-1}$  due to  $\text{H}_2\text{O}$ ,  $\text{CH}_3$  groups, and  $\text{CH}_2$  groups, respectively. These could not be used for structural analysis by the IR spectroscopy.

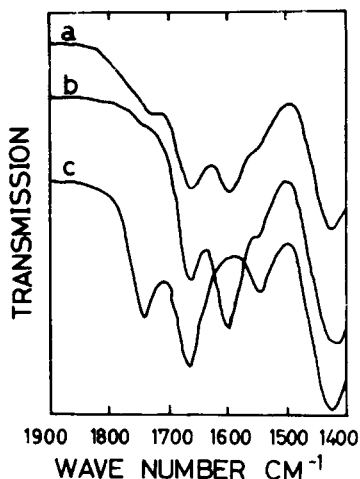


Fig. 3. Effects of immersion in NaOH and HCl methanol solutions for heat-treated PC-PA complex: (a) nonimmersed, heat treatment carried out at 160°C for 1 hr; (b) heat treated and immersed in NaOH-methanol 0.02 mole/l. solution; (c) heat treated and immersed in HCl-methanol 0.02 mole/l. solution.

The structural change in the samples during the heat treatment confirmed by the IR spectroscopy is thought to be related to the change in the swelling properties of the samples described in the foregoing section. For example, when the PC-PA complex is heated at high temperature, a large proportion of ionic bonds between  $\text{NH}_3^+$  and  $\text{COO}^-$  groups is transformed to amide bonds. This is reflected in decreased water swelling. By contrast, since such transformation does not take place in the PTC-PSA complex, the degree of swelling in water is not altered appreciably after heating.

#### Interaction of Polyelectrolyte Complexes with Salt, Acid, and Base

The PC-PA complexes before and after heat treatment were immersed in 1*N* aqueous solutions of NaCl, HCl, and NaOH for three days at room temperature, and the DS and WL are measured. Table V shows that these samples exhibit excellent resistance to NaCl, HCl, and NaOH solutions. It seems that such resistance of the PC-PA complex before heat treatment is caused by hydrogen

TABLE V  
Degree of Swelling and Weight Loss of PC-PA Complex in HCl, NaOH,  
and NaCl Aqueous Solutions

Sample no.	Medium	DS, %	WL, %
17M <sup>a</sup>	1 <i>N</i> HCl	2070	42.3
	1 <i>N</i> NaOH	1260	61.0
	1 <i>N</i> NaCl	970	45.1
Heat-treated <sup>b</sup> 17M	1 <i>N</i> HCl	83.0	0.0
	1 <i>N</i> NaOH	179.0	0.0
	1 <i>N</i> NaCl	74.1	0.6

<sup>a</sup> M designates sample washed with methanol.

<sup>b</sup> The heat treatment was carried out at 160°C for 30 min in air.



TABLE VI  
Mechanical Properties of PC-PA and PTC-PSA Composite Films

Sample description	Sample no.	Condition of heat treatment		In air atmosphere, 65% R.H., 20°C			In water, 20°C		
		Temp., °C	Time, min	Tenacity, psi	Elongation, %	Modulus, psi	Tenacity, psi	Elongation, %	Modulus, psi
PVA <sup>a</sup>	—	no	—	5,000	220	31,000	—	—	—
		200	10	6,700	140	72,000	—	—	—
PC-PA	19M <sup>b</sup>	no	—	3,000	201	12,000	20	179	4
		140	60	6,300	117	82,000	400	24.6	1,700
		160	10	4,400	125	41,000	340	26.0	1,600
		160	30	4,700	73.3	65,000	350	14.8	2,500
		160	60	4,800	17.0	118,000	670	16.3	4,200
PTC-PSA	4	160	180	4,600	12.0	118,000	560	8.3	6,000
		no	—	4,700	139	81,000	40	600	1
		200	10	5,800	192	117,000	80	250	43

<sup>a</sup> PVA fraction; the degree of polymerization was 1,120.

<sup>b</sup> M designates sample washed with methanol.

bonding of amino groups which is too small to be recognized in the IR spectrum. By contrast, the PTC-PSA complex, both before and after heat treatment, was soluble in these solutions, although it was insoluble in pure water.

### Tensile Properties of Polyelectrolyte Complexes

The mechanical tensile properties of the PC-PA and PTC-PSA complex films in air of 65% R.H. and in water at 20°C are shown in Table VI. The tensile strength at break of the PC-PA complex in air is comparable to that of the parent polymer PVA independent of the heat treatment. However, decreased elongation and increased Young's modulus are observed for the complex after heat treatment, due to the formation of amide bonds. Also, in the measurement in water, increased strength and decreased elongation are observed after heat treatment. However, the elongation in water is appreciably smaller than that in air. This is due to the fact that molecular chains in the structure are transformed into an extended form in water due to isolated NH<sub>2</sub> and COOH groups formed by the treatment, as mentioned above, in addition to amide bonding. However, with the PTC-PSA complex, excellent tensile strength is observed with high elongations, independent of the heat treatment, although sufficient strength in water was not obtained even if it was heated at high temperature.

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