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# Graft Copolymerization of Acrylonitrile onto Woodpulp\*

By

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木材パルプ紙葉へのアクリロニトリルの  
グラフト共重合\*

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## Introduction

Recently, the improvement of polymers by grafting side chains of another nature onto given backbone chains has widely been carried out in such industries as plastics, textiles and fibers including viscose.<sup>3,4,7,9,11,12,17,18,20~26)</sup> But in the paper industry this

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technique has not been applied yet, though a number of the effort had been done,<sup>5,14,18,19,28,29</sup> while wood-plastic complex (WPC) grafted by radiation has commercially been manufactured.<sup>1,6,10,14,16</sup>

Paper is now abundantly used in diverse areas on account of inexpensive. However, when wet, the paper has a fatal drawback on strength and dimensional stability. In order to modify these faults the addition of soluble synthetic polymer or dialdehyde starch<sup>2,8,27</sup> to pulps has often been introduced. It is obvious that the "true" chemical combination with the pulps opens up exciting new possibilities, for example, for the non-rotting (resistant to microorganisms), flame proofing, oil repellent and highly acid resistant uses. A new method for grafting onto cellulose has been disclosed by MINO and KAIZERMAN<sup>19</sup> that yields substantially pure copolymers. This method is the result of the finding that certain ceric salts form very effective redox systems with alcohols or amines. It proceeds by means of the reducing agents, which is able to initiate vinyl polymerization. If the oxidation happens on a cellulosic material like wood pulp in the presence of a monomer such as acrylonitrile, methyl methacrylate and styrene, it is apparent that the grafted paper can be formed.<sup>5,15,19,28,29</sup>

For the purpose of this application to the wood pulps, in the present study the pulps were prepared by sulfate, prehydrolysis sulfate and neutral sulfite semichemical processes, and bleached conventionally, and then beaten with a refiner. The hand-sheets prepared from them were graft-polymerized with acrylonitrile by the use of ceric ammonium nitrate in a nitric solution. The grafted sheets of different polymer pick-ups were examined on dry and wet strengths, dimensional stability and water-retention. For lack of the grafting know-how, the preliminary experiment was done in advance using filter paper under different conditions. With the resultant products, the determination of the concomitant homopolymer, IR spectral measurement and scanning electron microscope (SEM) observation were also carried out.

The authors are deeply indebted and would like to express their gratitude to Professor Dr. S. Ishida and Instructor Dr. J. Ohtani of the Laboratory of Wood Physics, Hokkaido University, for taking photographs of SEM and kind comments to them.

## 1. Materials

### 1.1 Wood Samples

The wood samples used for the study were birchwood (*Betula platyphylla* var. *japonica*) and larchwood (*Larix kaempferi*) obtained from Tomakomai Experiment Forest, Hokkaido University. The former felled in the natural forest had 40 annual rings and 18.0 cm in diameter at breast height, while the latter felled in the artificial forest was planted 36 years ago and had 15.5 cm. After these two kinds of wood were barked and cut with a laboratory chipper, the chips were screened, air-dried and then stored in a glass vessel. The proximate chemical analysis was carried out on 60 to 100-mesh fraction of the samples by standard procedures, and the analytical values are shown in Table 1.

**Table 1.** Chemical composition of samples (%)

Wood species	Ash	Extractives				Holocel- lulose	Alpha* cellulose	Total pentosan	Methyl pentosan	Lignin
		Cold water	Hot water	1% NaOH	Alcohol benzene					
Birch	0.80	1.6	2.4	11.8	2.2	81.7	48.0	26.3	1.7	19.0
Larch	0.51	8.0	9.3	18.0	2.1	66.8	43.1	14.2	4.8	27.9

\* Determined from holocellulose.

## 1.2 Reagents

Extra-pure acrylonitrile reagent was used by distillation at reduced pressure on the time of application. Guaranteed ceric ammonium nitrate ( $\text{Ce}(\text{NO}_3)_4 \cdot 2\text{NH}_4\text{NO}_3 \cdot 2\text{H}_2\text{O}$ ) reagent used as an initiator was applied with 0.1 M solution of 10 M nitric acid. The determination of the ceric salt was done by titration with ferrous sulfate using diphenyl amine as an indicator.

## 2. Experiments

### 2.1 Preparations of Pulp and their Handsheets

Air-dried birch- and larchwood chips corresponding to 500 g of oven-dried were cooked in a 4-1 laboratory stainless-steel digester by conventional sulfate, prehydrolysis sulfate and neutral sulfite semichemical processes. The cooking condition of the sulfate process was: addition of active alkali, 20%; sulfidity, 28%; liquor to chip ratio, 4; maximum temperature, 180°C; retention time, 1.5 hour. In the prehydrolysis sulfate process, the chips treated with water at 170°C for 1 hour, was cooked by the same sulfate condition. The condition of the semichemical process was: total chemicals, 8% as sodium carbonate; the ratio of sodium sulfite to the carbonate, 7; liquor to chip ratio, 4; maximum temperature, 170°C; retention time, 2.5 hours.

In order to obtain bleached pulp Roe number was measured, after the cooked had been passed through an 8-cut screen. A hundred grams of the prehydrolysis sulfate pulp (DKP), the sulfate pulp (KP) and the semichemical pulp (NSSCP) were bleached to about 70% in Hunter brightness by a sequence of following treatments: chlorination using chlorine solution of the same quantity as Roe No. of each pulp in 5% pulp consistency at room temperature for 1 hour; caustic alkali extraction with 1.2% addition of sodium hydroxide to pulp in 10% consistency at room temperature for 1 hour; finally chlorination with calcium hypochlorite leaching solution corresponding to 2% available chlorine to pulp in 5% consistency at 35°C for 2 hours. The second and third treatments were repeated, if necessary, to attain to the given brightness. After the yield and chemical components were determined, the pulps unbleached and bleached were beaten to 400 ml CSF in a Sprout Waldron laboratory refiner equipped with 12527 A disk blade at various clearances adjusted from 0.4 to 0.1 mm. The handsheets were made on a Tappi type sheet machine.

### 2.2 Grafting Procedures

Preliminary test was made using filter paper for the search of grafting condition

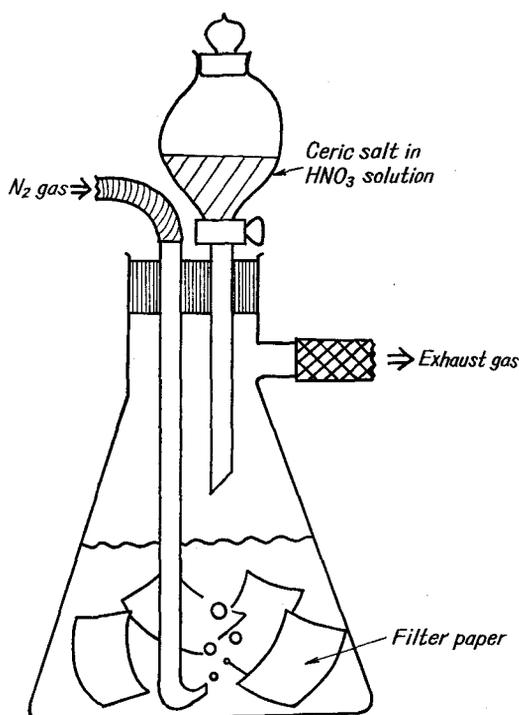


Fig. 1. Grafting apparatus used for preliminary test.

in a 1-l small apparatus shown in Fig. 1. While the factors affecting the reaction were considered the concentration of acrylonitrile, addition of the ceric salt, time and temperature, the weight of the filter paper was constantly 3 g in the shape of fragment ( $2 \times 3$  cm) and total volume of medium consisting of distilled water and the monomer was 500 ml. Before adding the initiator and during the reaction, nitrogen gas was flushed and bubbled so as to deaerate and stir in the reactor. Without expecting synergic action among the factors the experiment was done under following conditions :

- (1) The concentrations of acrylonitrile were 0.96, 1.44, 1.92 and 2.88 wt% on the medium basis, using 0.6 mM/l of the ceric salt at 25°C for 30 minutes.
- (2) The additions of ceric ammonium nitrate were 0.27, 0.34, 0.60 and 0.86 mM/l in the constant concentration of 1.44% monomer at 25°C for 30 minutes.
- (3) The reaction times were 15, 30, 60 and 120 minutes in the above concentration and 0.6 mM/l of the salt at 25°C.
- (4) The reaction temperature was chosen in the range from 15°C to 45°C by 10°C-step in the same concentration and addition as above for 30 minutes.

On the basis of the preliminary test, the grafting onto the different handsheets was carried out under the conditions described below in a 13-l glass box shown in Fig. 2. In each experiment thirteen specimens including a filter paper of 18.5 cm in diameter were inserted into a frame with rod-studded rack made of glass. The frame supporting the sheets was placed in the box, which was filled with a

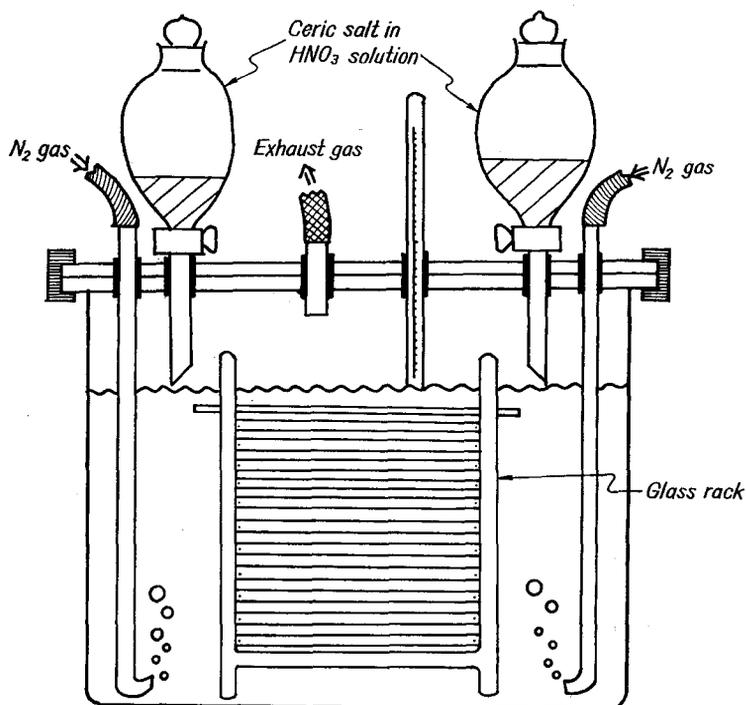


Fig. 2. Grafting apparatus.

9.5-1 aqueous solution containing different concentrations of the monomer, and the sheets were immersed into it. Being firmly closed with the lid, the resultant system was bubbled with nitrogen gas for 30 minutes in a thermostat bath at 35°C. Then the ceric salt solution corresponding to 0.6 mM/l was added into the system through two funnels. The reaction was maintained for 30 minutes at the same temperature. The concentrations of the monomer used for these grafting procedures were 0, 0.5, 0.7, 1.0 and 1.7% based on the reaction medium.

The grafted products prepared in this way covering different ranges of polyacrylonitrile pick-up (the increase in weight of the reaction products was termed pick-up, because a small amount of homopolymer was contained in the resultant sheets) were thoroughly washed with running water and dried to constant weight in a forced draft oven maintained at 50°C. The homopolymer stuck on them was removed with a brush.

In order to confirm whether the handsheets were uniformly grafted, the distribution of the weight increase was examined on the entire area of the products. The parts of the grafted of 47% and 41% pick-ups, obtained from birch KP sheet and filter paper, respectively, were precisely cut into a 2-cm square together with the non-grafted. Random ten pieces were weight with a chemical balance one by one, from which the variation was checked by F-test. Furthermore, to ascertain how much the homopolymer would exist in the grafted products, the 10, 37 and 48% pick-ups obtained from the filter paper were cut into pieces and extracted with hot dimethyl sulfoxide (DMSO) which was a most effective solvent to polyacrylonitrile.

The homopolymer determination was made by the weight difference between the product and the extracted residue.

### 2.3 Observations with SEM

The grafted filter papers were observed with a scanning electron microscope, Model JSM-2 made by Japan Electron Optics Laboratory Co., Ltd. Firstly, the small specimens were mounted and fixed on the stubs of an ion coater Model JEE-4B made by the above Co., LTD., with silver paste and coated with gold in a vacuum of  $5 \times 10^{-6}$  torr. Next, the coated specimens were placed in the SEM, inclined at  $45^\circ$  and observed under 25 kV accelerating voltage. At the same time the photographs were taken.

### 2.4 IR Spectral Measurements<sup>7,9</sup>

The specimens used in the infrared measurements were grafted products of 10, 37 and 48% pick-ups from the preliminary test, as well as filter paper (as pure cellulose), polyacrylonitrile and mixtures of cellulose and the homopolymer at the rate of 10, 20, 50 and 100%. After powdered, 5 mg of each specimen were mixed with 0.5 g of potassium bromide, then formed to a tablet. The spectra were recorded from  $4000 \text{ cm}^{-1}$  to  $600 \text{ cm}^{-1}$  by an IR Spectrophotometer, Type AR-275 made by Shimadzu Manufacturing Co., Ltd.

### 2.5 Physical Tests

All the tests were carried out under 70% relative humidity at  $20^\circ\text{C}$ . Thickness and thickness increase by grafting were measured with a dial micrometer thickness gauge. Thickness swelling was also shown by the percent thickness increase between before and after soaking the specimens into water at  $20 \pm 1^\circ\text{C}$  for 10 minutes, whose duration showed sufficient to gain the constant thickness swelling. Water retention was calculated from weight increase on soaking into it for the same duration. To evaluate dry and wet strengths (the same soaking condition as above), tensile, bursting, tearing and folding strengths were tested by Tappi Standard method, and expressed as breacking length, burst factor, tear factor and folding endurance, respectively, based on the weight of original untreated sheets.

## 3. Results and Discussion

### 3.1 Yield and Chemical Properties of the Pulps

Yield and chemical composition of unbleached and bleached DKP, KP and NSSCP from birch- and larchwood are shown in Table 2.

The yield of unbleached pulps was largely changed by the pulping process and wood species. The maximum was obtained from NSSCP of birchwood. As a whole, the pulping condition employed are a little severe so as to obtain the pulps of different chemical components. The yield of bleached pulps was naturally lowered on account of removal of lignin. Roe number of larchwood-NSSCP was 34.6, the highest among them.

The chemical composition of the pulps sufficiently explains the difference of pulping. Unbleached DKP contained high alpha cellulose, as well as low pentosan

**Table 2.** Yield, Roe number and chemical composition of pulps

Pulps	Yield (%)	Roe No.	Components (%)				
			Holo-cellulose	Alpha cellulose	Total pentosan	Methyl pentosan	Lignin
Unbleached birch DKP	34	2.6	97.8	90.7	5.4	0.6	2.3
" " KP	49	2.3	98.0	82.2	16.8	0.7	2.0
" " NSSCP	72	17.1	85.5	68.7	20.0	0.8	13.7
Unbleached larch DKP	31	4.1	95.8	90.8	2.9	0.6	3.5
" " KP	40	2.9	96.6	85.2	7.9	0.6	3.0
" " NSSCP	62	34.6	74.0	56.9	8.1	2.6	25.8
Bleached birch DKP	31	—	99.2	90.6	6.0	0.9	0.9
" " KP	45	—	99.1	84.5	16.1	0.6	0.6
" " NSSCP	60	—	99.0	82.1	20.1	1.5	0.7
Bleached larch DKP	28	—	99.0	95.6	2.8	0.6	0.7
" " KP	35	—	99.0	88.9	9.0	0.7	0.7
" " NSSCP	45	—	98.5	81.0	8.6	1.8	1.3

due to the pretreatment with water, compared with the other pulps. Unbleached NSSCP showed extremely high lignin content, especially on cooking the larchwood. By bleaching, the lignin was almost perfectly removed.

### 3.2 Factors Affecting on Grafting

The influence of concentration of acrylonitrile, addition of ceric salt, reaction time, and temperature was investigated on grafting using filter paper as a preliminary experiment. The relations between polymer pick-up and each factor are shown in Fig. 3. With elevation of the monomer concentration the pick-up was increased to 48%, but the tendency became abated in the higher concentration. In a trial carried out with an extreme concentration as high as 5%, the precipitate of flaky homopolymer occurred in the medium and the resultant product amounted to 73% pick-up, which was so stiff that it was broken on folding test. The most suitable ceric salt addition was shown to be 0.6 mM/l. The pick-up was increased with duration of reaction time up to 30 minutes, after which the curve of the graph became gradually flat. The graph of reaction temperature shows that about 35°C was the best.

### 3.3 Characteristics of the Grafted Products

Graftization depends upon the chemical composition of the sheets. As shown in Table 3, the sheets obtained from unbleached pulps were hardly grafted even under the appropriate condition except birchwood DKP, on account of lignin contained in the sheets. Therefore, subsequent experiment was done using the bleached sheets.

Yields of grafted products prepared in different monomer concentrations are shown in Table 4, expressed as polymer pick-up. The highest pick-up, or 66% weight increase, was given by bleached KP and NSSCP of birchwood treated in

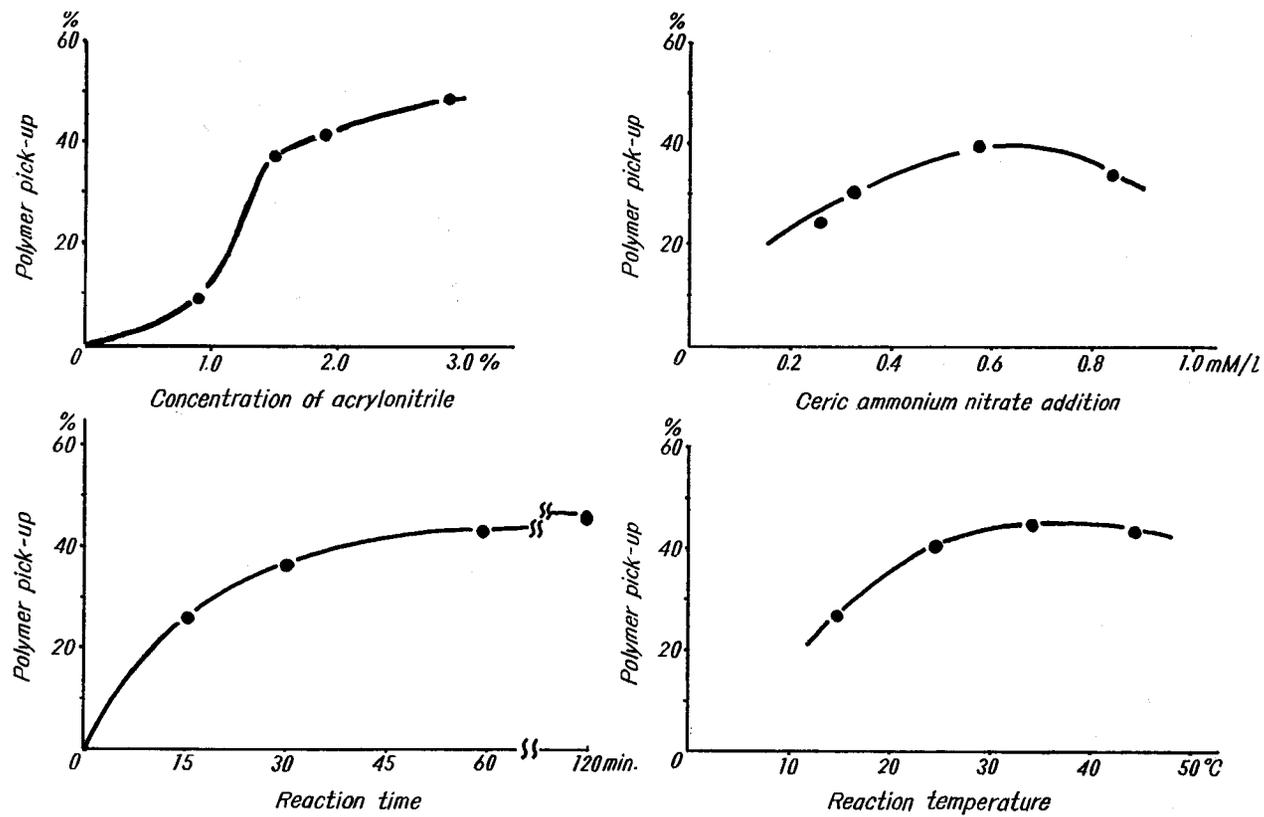


Fig. 3. Effect of condition factors on grafting.

**Table 3.** Polymer pick-ups onto sheets in 1% concentration of acrylonitrile

Sheet	Filter paper	Unbleached						Bleached							
		Birch			Larch			Birch			Larch				
		DKP	KP	NSSCP	DKP	KP	NSSCP	DKP	KP	NSSCP	DKP	KP	NSSCP		
Pick-up (%)	17	15	3	0	0	0	0	0	0	41	47	48	40	45	37

**Table 4.** Polymer pick-ups onto sheets of bleached pulps in different concentrations of acrylonitrile (%)

Sheet Concentration (%)	Filter paper	Birch			Larch		
		DKP	KP	NSSCP	DKP	KP	NSSCP
0.5	5	15	14	15	13	12	8
0.7	6	16	20	20	17	16	11
1.0	17	41	47	48	40	45	37
1.7	38	62	66	66	46	52	43

**Table 5.** Uniformity of grafted products

Sheet	Filter paper		Bleached KP (birch)	
	Grafted* <sup>1</sup>	Untreated	Grafted* <sup>2</sup>	Untreated
Weight of fragments ( $\times 10^{-4}$ g)	604	598	407	452
	638	674	440	411
	641	639	414	433
	649	582	413	442
	626	588	426	437
Mean ( $\times 10^{-4}$ g)	623.9	427.5	373.4	254.8
Mean square ( $\times 10^{-8}$ g)	886.1	241.6	38.267	13.289
Standard deviation ( $\times 10^{-4}$ g)	29.767	15.543	6.186	3.645
Coefficient of variation	4.77%	3.64%	1.66%	1.21%

\*1. 24% polymer pick-up.

\*2. 47% polymer pick-up.

the 1.7% concentration. Filter paper was less grafted than the pulp sheets. From this fact, hemicellulose seems to be favorable to grafting.

The homopolymer contained in the sheets was vigorously extracted with hot DMSO, in the quantity of 4.6, 9.2 and 4.5% on the basis of the grafted filter paper of 10, 37 and 48% pick-ups, respectively. It is indicated that the homopolymer content is as comparatively low as 5 to 10% ranges and that the sheet was surely grafted. The test of physical properties, however, were carried out without this extraction.

The uniformity of grafting is shown in Table 5. Coefficient of variation of the



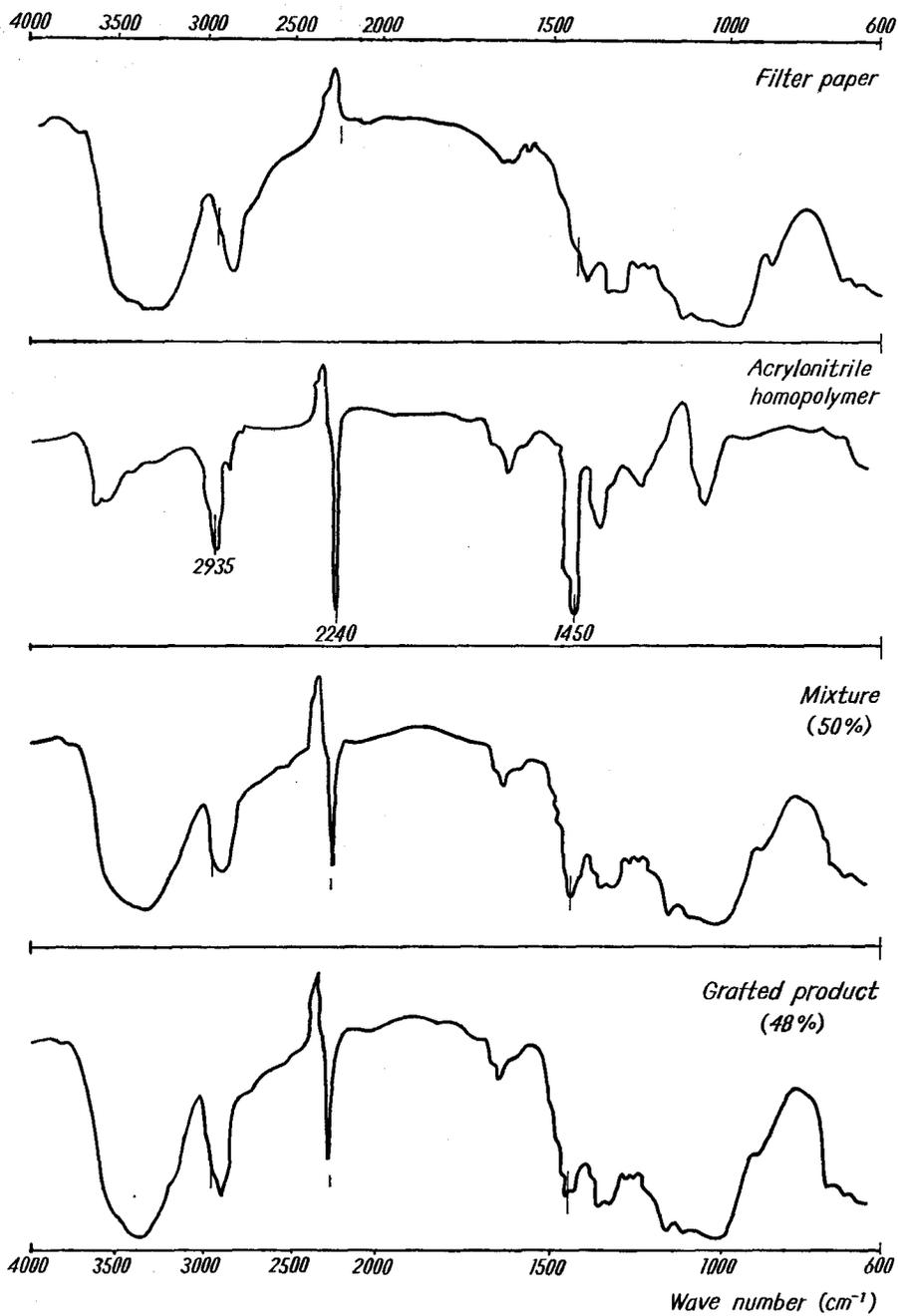


Fig. 4. Infrared spectra of several specimens.

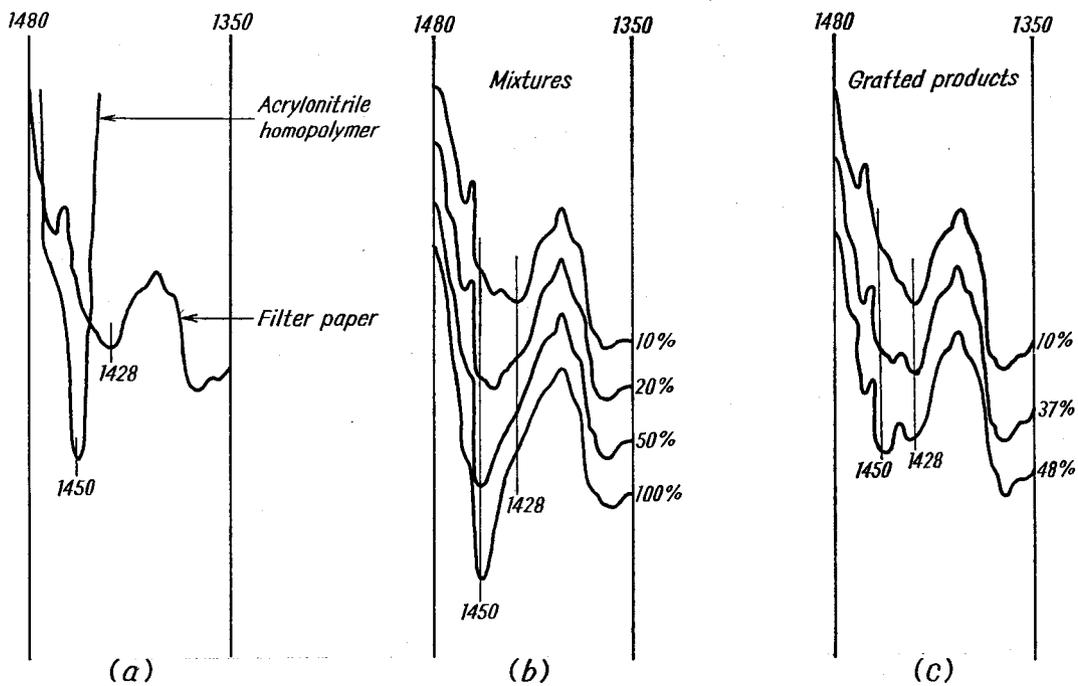


Fig. 5. Infrared spectra in the vicinities of 1450 cm<sup>-1</sup>.

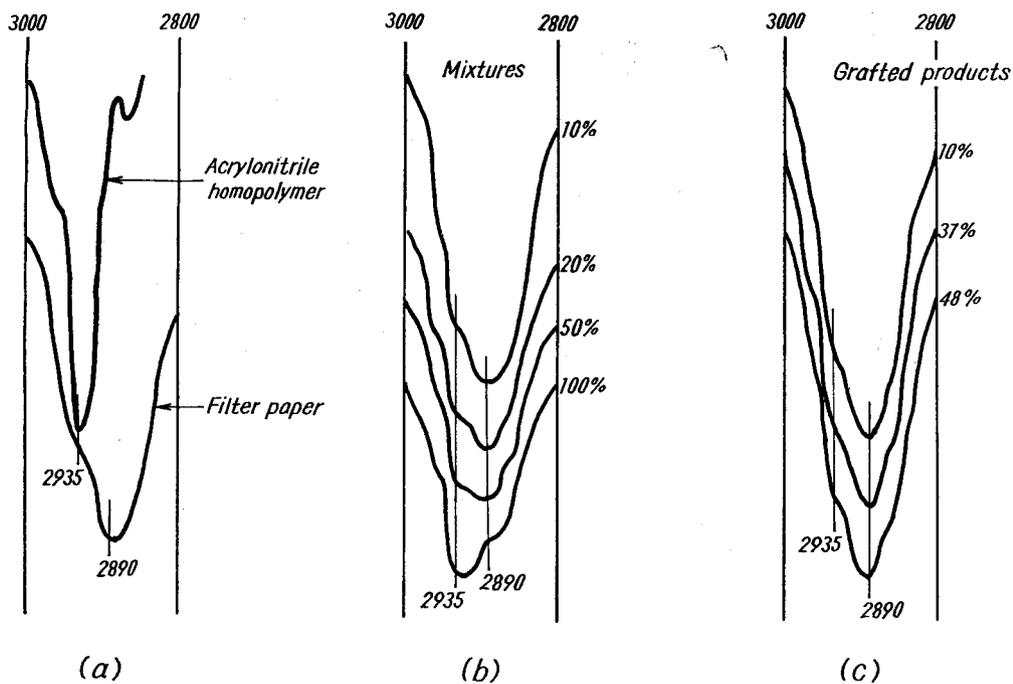


Fig. 6. Infrared spectra in the vicinities of 2935 cm<sup>-1</sup>.

polymer in the grafted. It might also be concluded that the products are the copolymer.

### 3.4 Physical Properties of the Grafted Sheets

The relation between thickness increase and polymer pick-up is shown in Fig. 7. The increase goes up nearly linearly with the pick-up. In the low pick-ups, however, the swelling appears to occur due to soaking into the aqueous medium on the preparation. The increase rate of the low pick-up is to some extent sharp.

In the meanwhile, the result of the thickness swelling in distilled water for 10 minutes at 20°C is shown in Fig. 8. It is extremely decreased to about 10% in the 50-60% pick ups. It is shown that the products grafted with polyacrylonitrile have a desired improvement in dimensional stability.

The relation between water retention and the pick-up indicated that with increase of pick-up the retention was decreased to nearly half of the untreated in any grafted sheets. It seems, however, to be a characteristic that these grafted

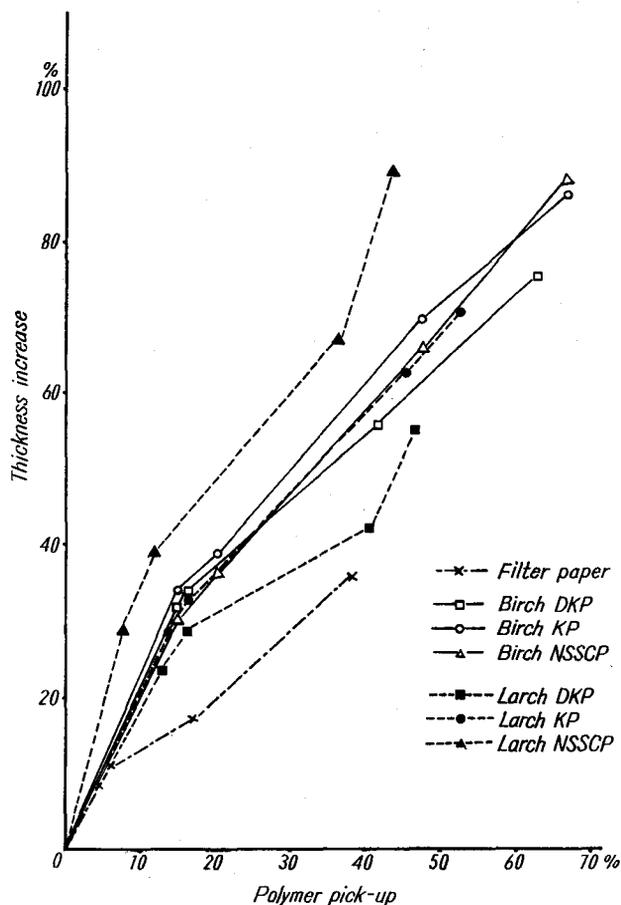


Fig. 7. Relation between thickness increase and polymer pick-up of bleached sheets.

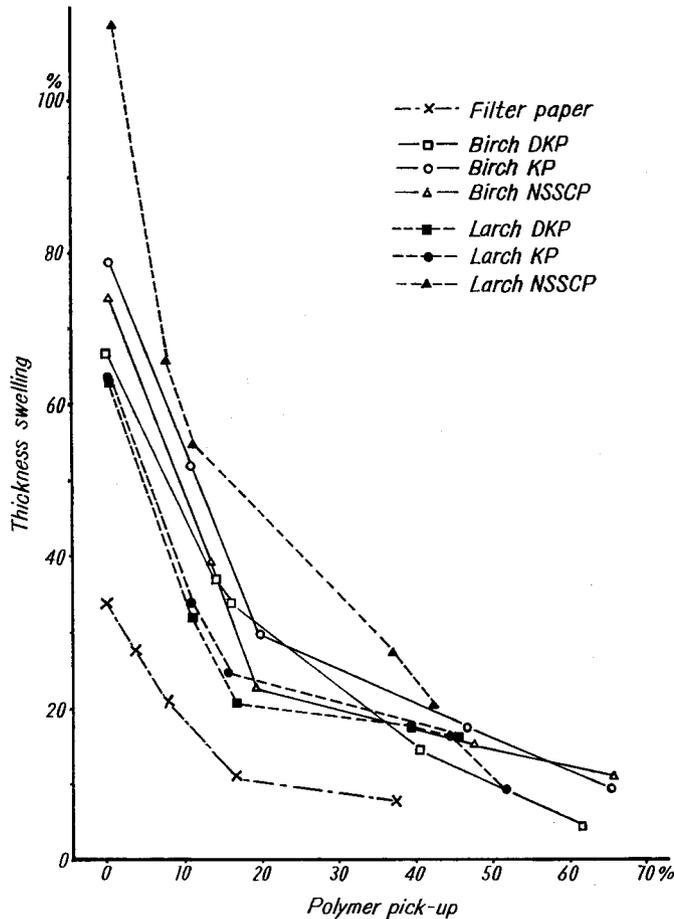


Fig. 8. Relation between thickness swelling in water and polymer pick-up of bleached sheets.

possess still a considerable water retention in spite of remarkably low swelling.

Dry and wet strengths of the grafted sheets are summarized in Tables 6 and 7, respectively. As the strength of the grafted sheets prepared in the 0.5% concentration showed the similar values to that in the 0.7%, the data were not offered. In dry strength, breaking length was somewhat improved by the increased pick-up, but burst and tear factors of the grafted were given similar values to those of the untreated. Folding endurance was rather decreased by grafting on account of their stiffness.

In wet strength of the sheets water-soaked for 10 minutes, considerable improvement was recognized by grafting treatment. The higher polymer pick-ups proved to gain almost the same wet strength as the dry one. As making an additional remark, the grafted sheets of the 3-day soaking showed the nearly equal strength to the above data.

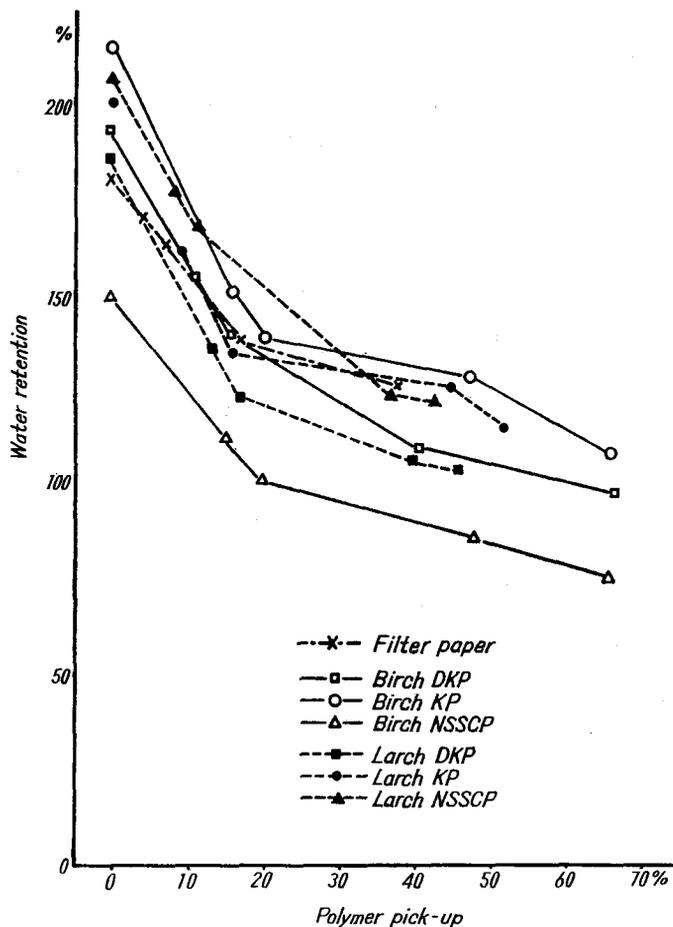


Fig. 9. Relation between water retention and polymer pick-up of bleached sheets.

Table 6. Dry strength of grafted handsheets

Strength Concentration (%) Sheet	Breaking length (km)				Burst factor				Tear factor				Folding endurance			
	0*	0.7*	1.0*	1.7*	0	0.7	1.0	1.7	0	0.7	1.0	1.7	0	0.7	1.0	1.7
Birch DKP	6.3	7.2	9.9	11.4	5.2	5.0	6.5	4.0	69	61	62	66	39	39	10	9
" KP	8.3	7.7	9.3	10.2	7.5	6.3	6.5	10.0	84	74	113	103	56	65	20	17
" NSSCP	7.9	7.9	9.5	11.4	11.0	8.3	9.5	10.0	94	80	144	105	140	131	33	11
Larch DKP	8.0	7.8	9.1	10.5	9.5	9.3	10.5	14.7	210	146	144	184	148	140	50	40
" KP	8.8	8.6	9.9	11.7	10.7	10.0	9.8	13.5	179	148	191	176	177	162	143	55
" NSSCP	9.0	7.0	6.0	9.3	10.7	9.3	8.8	10.0	124	135	117	127	545	226	264	190

\* Handsheets grafted in the concentration of 0, 0.7, 1.0, and 1.7% acrylonitrile.

Table 7. Wet strength of grafted handsheets

Sheet	Strength Concentration (%)	Breaking length (km)				Burst factor				Tear factor				Folding endurance			
		0*	0.7*	1.0*	1.7*	0	0.7	1.0	1.7	0	0.7	1.0	1.7	0	0.7	1.0	1.7
Birch DKP		0.1	1.1	4.4	7.0	0.2	1.0	4.5	6.2	20	25	75	106	0	0	22	22
" KP		0.1	1.0	2.9	7.1	0.3	0.7	2.7	7.5	19	27	66	119	0	0	23	29
" NSSCP		0.2	1.0	3.5	7.1	0.2	0.7	4.7	9.7	25	37	95	118	0	0	26	83
Larch DKP		0.2	1.5	4.4	7.2	0.3	2.2	6.0	9.2	20	77	135	156	0	0	50	250
" KP		0.1	1.0	3.4	6.5	0.3	1.0	5.0	11.0	20	56	115	203	0	0	117	157
" NSSCP		0.2	0.5	1.9	3.8	0.3	1.0	3.2	4.2	26	57	128	155	0	0	111	124

\* Handsheets grafted in the concentration 0, 0.7, 1.0 and 1.7% acrylonitrile.

### Conclusion

From these results, following conclusion was given :

(1) Under the grafting condition selected from preliminary test, the sheets of unbleached pulps were hardly grafted except that of DKP from birchwood on account of hinderance of lignin contained in the sheets. On the other hand, considerable polymer pick-ups were obtained from those of bleached pulps. Generally, higher pick-ups were shown in the sheets from birchwood than in those from larchwood under equal condition, probably due to the higher hemicellulose content of the former.

(2) The 5 to 10% homopolymer content was estimated in the grafted products by extraction with dimethyl sulfoxide. The uniformity of grafting was confirmed by weight distribution of equal area-fragments and by observation of the surface with a scanning electron microscope.

(3) The products were shown to be true copolymers in comparison with the mixture by the  $-CH_2$  group difference in infrared spectral measurements.

(4) By grafting of polyacrylonitrile the thickness and stiffness of the products were increased.

(5) Thickness swelling was decreased to 10% in the higher pick-up. It was, therefore, indicated that dimensional stability was given by grafting. Water retention was also decreased by nearly half of the untreated, but even the highest pick-up retained water as high as 100% on the basis of dry weight.

(6) Tensile strength was somewhat improved by grafting, while bursting and tearing strengths were not so much changed and folding strength was lowered on account of their stiffness.

(7) Wet strength was considerably raised by grafting. In the sheets of 50 to 60% pick-ups the values attained to be almost equal to those of dry strength.

(8) It is concluded that this grafting provides characteristics of both dimensional stability and comparatively high water retention as well as improvement of wet strength to the paper.

### Summary

In order to investigate the properties of the products grafted onto woodpulp sheet, pulps were prepared from birchwood (*Betula platyphylla* var. *japonica*) and larchwood (*Larix kaempferi*) by conventional sulfate (KP), prehydrolysis sulfate (DKP) and neutral sulfite semichemical processes (NSSCP), and then by bleaching. The handsheets from bleached and unbleached were graft-polymerized with acrylonitrile by the use of ceric ammonium nitrate (ceric salt) in a nitric acid solution. The different polymer pick-up sheets were obtained with different monomer concentration of 0.5 to 1.7% using 0.6 mM/l ceric salt at 35°C for 30 minutes, selected by preliminary tests.

The investigation of the characteristics of grafted products was carried out: extraction of homopolymer contained in the grafted with hot dimethyl sulfoxide (DMSO), observation with a scanning electron microscope (SEM), and analysis of infrared absorption spectra to confirm the difference between the grafted and mixed with polyacrylonitrile. The grafted sheets obtained from bleached pulps were tested on thickness increase by grafting, on thickness swelling and water retention by soaking into water, as well as on dry and wet strengths.

The results are summarized as follows:

(1) The data carried out with 1.0% monomer concentration showed that the unbleached pulp sheets were hardly grafted except that of DKP from birchwood, while the bleached ones were considerably grafted. The maximum pick-up of 66% was obtained from both birch DKP and NSSCP sheets.

(2) The extraction of homopolymer contained in the grafted products with DMSO decreased their weight as low as 5 to 10%. This fact proved them to be graft-copolymers.

(3) The uniformity of grafting was also recognized by weight distribution of the grafted fragments of equal area, and by observation with SEM.

(4) A new information on grafting was given from the result by IR spectra of both filter paper grafted and mixed with polyacrylonitrile, showing the difference in the absorption of the  $-\text{CH}_3$  group, which was less in the former.

(5) The sheets were increased in thickness as well as stiffness by grafting, without a large change of the appearance.

(6) Thickness swelling by soaking into water was as extremely low as 10% on testing the higher polymer pick-ups, which showed that dimensional stability was given by grafting.

(7) Water retention of the same sheets as above was lowered by nearly half of that of untreated. But the fact that the retention of 60% pick-up amounted to about 100% with same swelling shows an excellent ability of the grafted products. Even the sheets soaked for 3 days revealed almost equal retention.

(8) As far as dry strength was concerned, bursting and tearing strengths of the grafted sheets were not so much changed, compared with non-grafted, but tensile strength was considerably increased, while folding strength was decreased

on account of stiffness of the sheets.

(9) Wet strength of the sheets water-soaked for 10 minutes were remarkably improved by grafting, namely the sheets grafted in the range from 50 to 60% showed almost the same as dry strength. Also wet strength did not change even in the case of soaking of 3-day duration.

(10) It is concluded from these results that the bleached woodpulp sheets grafted with polyacrylonitrile provide characteristics of both dimensional stability and comparatively high water retention as well as the improvement of wet strength.

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## 摘 要

木材パルプから調製した紙葉にグラフト共重合を行い、その性質を調べた。試料はシラカンバ (*Betula platyphylla* var. *japonica*) とカラマツ (*Larix kaempferi*) 材で、クラフト法 (KP)、前加水分解クラフト法 (DKP) および中性亜硫酸ソーダ法 (NSSCP) によって蒸解され、一部は漂白された。あらかじめ濾紙を用いて行われた予備実験で、グラフト条件を調査した後、それぞれの紙葉に硝酸第二セリウムアンモニウムを開始剤として、0.5~1.7% にわたる4段階の濃度のアクリロニトリル水溶液に浸漬し、35°C で30分間処理して、種々のグラフト添加率の生成物をえた。えられたグラフト紙葉に対して、ジメチルスルフォキシドによる、アクリロニトリルホモポリマー抽出試験、走査型電子顕微鏡による観察、赤外線スペクトルによるセルロースとポリアクリロニトリルの混合物との相違などを調べ、グラフト重合が成功した漂白パルプ紙葉について、乾燥および湿潤強度を含む2・3の物理的性質の測定を行った。

その結果は次の通りである。

1) 1% のモノマー濃度で実施されたグラフト重合の実験では、未晒しの紙葉はシラカンバ DKP から作成したもの以外は、ほとんど成功せず (Table 3)、漂白パルプは、すべて十分にグラフト化された。この条件内でのポリマー添加率の最高は66% で、シラカンバの DKP と NSSCP の紙葉からえられた (Table 4)。

2) グラフト生成物中に混入していると思われる、アクリロニトリルのホモポリマーは、2・3の紙葉の細片を熱ジメチルスルフォキシドで、徹底的に抽出して除いた。その結果は5ないし10%の重量減少をもたらしたのみで、本実験により、グラフト共重合体が調製されたものと判断した。

3) グラフト生成物の均一性を見るため、紙葉を正確に2 cm 角の細片として、その中から任意に10枚を秤量し、同様のグラフト処理前の試料の重量とのバラツキを比較した結果、有意の差はなかった (Table 5)。また走査型電子顕微鏡による観察でも、極端なポリマー添加率のものを除き、紙葉の全面に等しくポリマーが付着しており、その均一性が確かめられた (Photo 1~10)。

4) 赤外線スペクトルを、濾紙に対して行われたグラフト生成物、およびセルロースとアクリロニトリルホモポリマーの混合物について調べ、ほぼ同一ポリマー量で、グラフト生成物のメチル基に相当する波数の吸収が混合物より小さいことが認められ、このことから、グラフト化の成功が確認された (Fig. 4~6)。

5) グラフト紙葉は、その添加率の上昇とともに、厚さ (Fig. 7) と剛度を増したが、外観はほとんど変化していなかった。

6) 水中に浸漬することによる厚さの膨潤率は、高ポリマー添加率では、わずかに10%程度であり、グラフト化は寸度安定性を向上させることがわかった (Fig. 8)。

7) 水に浸漬した際の保水率の試験では、グラフト紙葉は無処理紙葉の約半分まで、その値いが低下したが、およそ60%添加率でも、100%に近い保水率の紙葉がえられたことは、アクリロニトリル共重合紙の特長といえよう (Fig. 9)。なお水中に3日間浸漬した場合でも、ほぼ同様の保水率を示した。

8) グラフト紙葉の乾燥強度について見ると、破裂および引裂強度は、無処理紙とほぼ同じであったが、引張り強度は向上し、一方耐折度は、剛性が増したためかなり低下した (Table 6)。

9) 水中に10分間浸漬したグラフト紙葉の湿潤強度は、著しい向上を示した。とくに50ないし60%のポリマー添加率の場合は、ほとんど乾燥強度と変りがなかった (Table 7)。この強度は、3日間という長期の浸漬でも、10分間の場合と大体同一の値いを示した。

10) 以上のことから、漂白木材パルプ紙葉に対し、アクリロニトリルを共重合することは、湿潤強度の向上ばかりでなく、寸度安定性と比較的高い保水率をもつ点で、極めて有効であることが結論された。

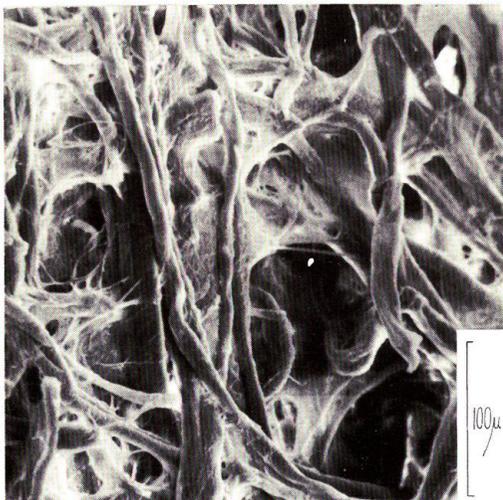


Photo 1. An original filter paper.

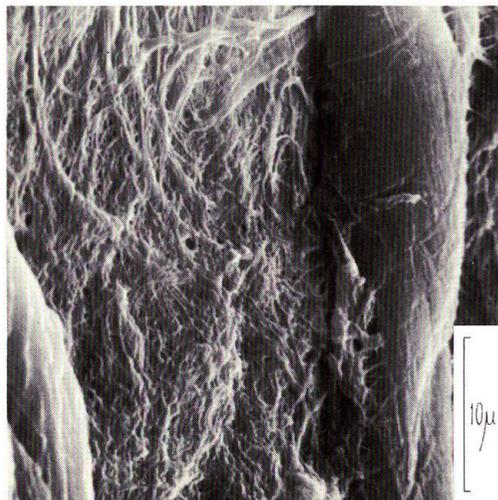


Photo 2. A higher magnified view in the center of Photo 1.

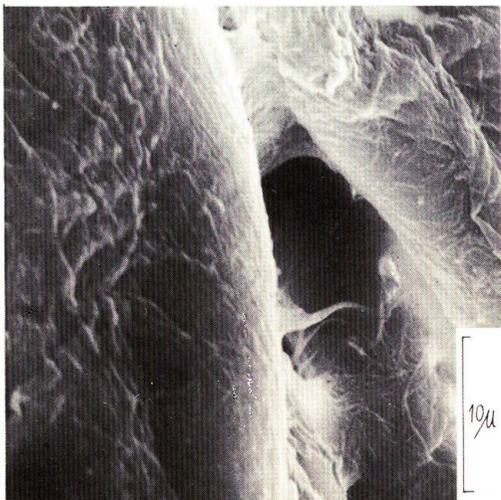


Photo 3. A view of 25% polymer pick-up.

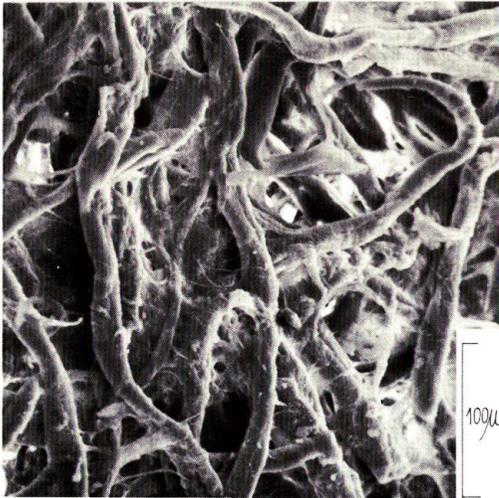


Photo 4. A view of 48% polymer pick-up.

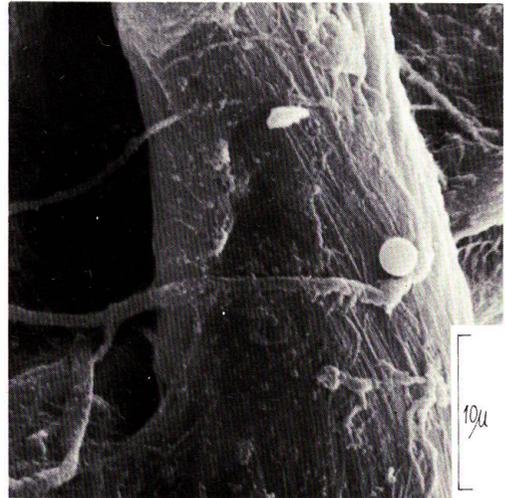


Photo 5. A higher magnified view of Photo 4.



Photo 6. A view of 73% polymer pick-up.

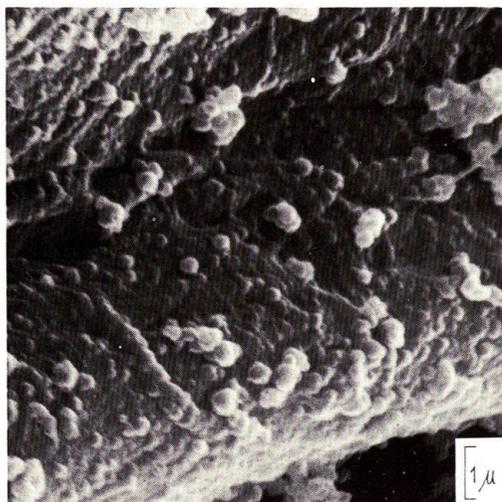


Photo 7. A higher magnified view of Photo 6.

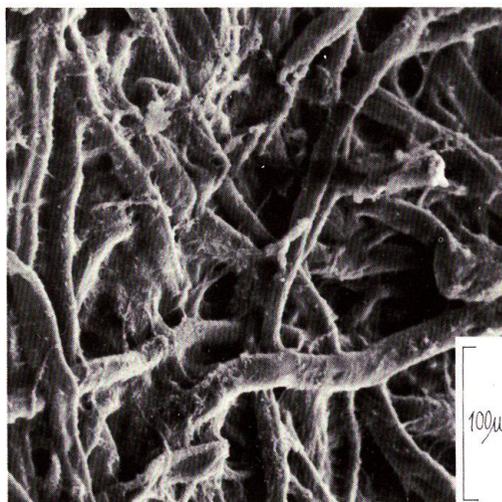


Photo 8. A view of DMSO-treated 73% polymer pick-up.

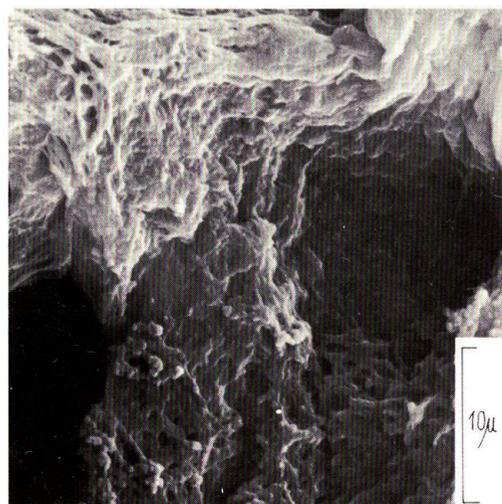


Photo 9. A higher magnified view in the center of Photo 8.

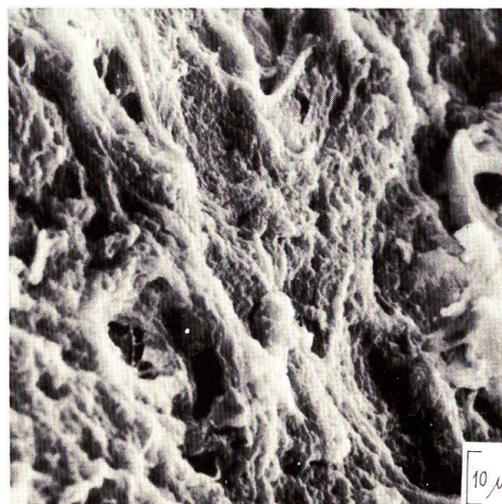


Photo 10. A view of conc.  $H_2SO_4$ -treated 48% polymer pick-up.