

## Fine Structure of Cellophane-Acrylamide Graft Copolymer by the Ceric Ion Method

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### Synopsis

The relationship between the grafting yield and the structure of graft copolymer is studied by measuring the branched chain lengths, the number of branches, the crystallinities, and the diffraction intensities of the (101) and (10 $\bar{1}$ ) + (002) planes determined by x-ray diffraction, and the distribution of branched polymers, observed by interferometry. Over a relatively wide range of grafting yield the number of initiating sites is almost constant and about 1-2 per 2 moles of cellulose chain. Therefore, the increase of grafting yield seems to be due mainly to the propagation of branched polymers. Branched polymers are assumed to be formed in cellulose crystallites both on the normal (101) planes and in the amorphous regions of cellulose. It is found that branched polymers grow from the outer layer into the inner part of the film as the grafting yield increases. At more than 250% of grafting yield, however, branched polymers are uniformly formed throughout the layer of film in which the crystalline regions of cellulose are gradually destroyed. This result agrees with the dimensional change of gel film during the reaction. The temperature dependence of tensile strength and elongation and the wet strength of graft copolymer are also investigated. At higher grafting yields, such as 250%, the crystalline structure of cellulose is disturbed by the formation of branched polymer, and no improvement in waterproofness can be expected from grafting; the secondary bonding between branched polymers may be presumed to be same as those among cellulose. In addition, the fine cracking of the film in the burst state is found to appear more easily as the grafting yield increases, in which the aggregating state of cellulose is recognized to be changed by the formation of branched polymer.

### INTRODUCTION

Since Mino and Kaizerman<sup>1</sup> studied vinyl polymerization initiated by ceric salt, the grafting of vinyl monomers onto cellulose by the ceric ion method has been studied by many investigators. They mainly investigated the initiation mechanism of graft copolymerization, on which the writers have reported with respect to the ceric-salt-induced polymerization of acrylamide onto gel cellophane.<sup>2</sup> The relation between the mechanism of grafting and the structure of the graft copolymers, however, has not yet been elucidated.

The present work concerns an effort at getting a clear picture of the fine structure of graft copolymer by measuring the branched chain lengths, the

number of branches, the crystallinities, and the diffraction intensities of the (101) and (10 $\bar{1}$ ) + (002) planes, determined by x-ray, the distribution of branched polymers, observed by interferometry, the dimensional change of gel film during reaction, and the tensile strength and elongation properties in wet and dry state.

## EXPERIMENTAL

### Materials Used

Ceric ammonium nitrate, reagent grade, was used without further purification, and its purity was determined volumetrically with ferrous sulfate as 99.0%.

Commercial acrylamide was twice recrystallized with benzene-acetone, and its purity was determined bromometrically as 99.8%.

The cellulose samples used, free from commercial detergent, are the gel film made by an industrial casting machine of cellophane. The degree of polymerization of the cellulose was determined by viscometry to be  $320 \pm 10$ ,<sup>3</sup> the crystallinity of the film by x-ray to be 30-32%,<sup>4</sup> the water content to be 380-400%, and the thickness of the film to be  $100 \pm 10 \mu$ .

### Grafting Procedure

An aqueous mixture of ceric salt (Ce<sup>IV</sup>), acrylamide monomer (AM), and nitric acid is kept at 20°C. in air for a given time (0-300 min.). Gel cellophane (0.16-3.7 g./l.) is then introduced into the aqueous solution mentioned above and is treated for a given time (1.5-300 min.). The concentrations of Ce<sup>IV</sup>, AM monomer, and nitric acid are kept at  $6.0 \times 10^{-3}$ ,  $4.2-7.0 \times 10^{-1}$ , and  $3.75-15.0 \times 10^{-3}$  mole/liter, respectively. Grafted films in the grafting yield range of 5-450% are thus prepared.

Homopolymer is removed by Soxhlet extraction with hot water for 24 hr. After drying in vacuum the grafting yield is determined by the Kjeldahl method of nitrogen analysis.

## RESULTS AND DISCUSSION

### 1. Molecular Weight and Number of Branches

For the separation of branched polymer (polyacrylamide) from the cellulose backbone the hydrolysis of cellulose is carried out as follows. Graft copolymer (10 g.) is treated with 10 ml. of 2*N* sulfuric acid and 190 ml. of water at 85°C. for 5 hr. The concentration of polyacrylamide separated is kept in the range of 0.3-0.8 g./l., and then the average molecular weight in 1*N* NaNO<sub>3</sub> aqueous solution at 25°C. is determined by the viscometric method, the following equation being used:

$$[\eta] = 3.73 \times 10^{-4} M_w^{0.66}$$

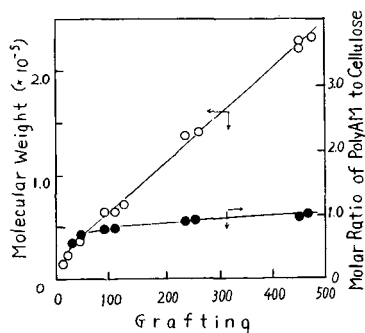


Fig. 1. Average molecular weight and number of branches of graft copolymer, versus grafting yield.

In a preliminary experiment the molecular weight of polyacrylamide (degree of polymerization 300, 3000) was recognized to be not affected by hydrolysis under the conditions mentioned above.

The number of branches is calculated on the assumption of a degree of polymerization of cellulose of 300 and is expressed as the molar ratio of branched polymer to cellulose.

The relationship between the molecular weight or the number of branches and the grafting yield is shown in Figure 1.

The molecular weight and the number of branches are found to increase in the range of  $1.1\text{--}23.1 \times 10^4$  and 0.4–1.0, respectively, as the grafting yield increases, when the grafting yield is kept within the range of 10–450%. However, since the increase of the number of branches is far smaller than that of the molecular weight, this result suggests that the grafting process means a growing of side chains rather than an increase in initiation, in the present system.

## 2. Crystallinities and Diffraction Intensities in Graft Copolymer

The fine structure of graft copolymer is studied by the x-ray diffraction method.

The degree of crystallinity of the graft copolymer in powder is determined as follows. The x-ray diffraction peaks of powdered specimens are measured by an automatic recording diffractometer with  $\text{CuK}\alpha$  radiation in the angular range of  $2\theta = 5\text{--}35^\circ$ . The powdered specimen, in the form of a board, is placed in a position perpendicular to the x-ray beams in which the field is rotated. No new peak corresponding to the deposited polyacrylamide is observed; therefore, on the basis of the diffraction peaks caused by the (101),  $(10\bar{1})$ , and (002) planes of the cellulose crystallites, the crystallinity as a percentage is estimated by calculating the peak area versus the total area, as shown in Figure 2.

The relationship between the crystallinity of the graft copolymer and the grafting yield is shown in Figure 3.

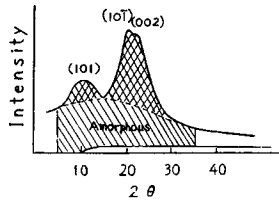


Fig. 2. X-ray diffraction diagram of powdered graft copolymer.

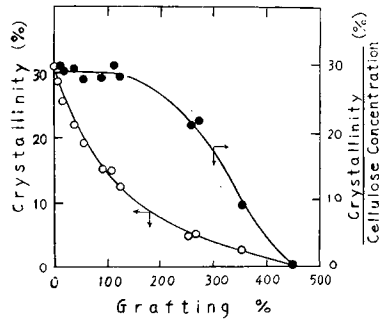


Fig. 3. Crystallinity of grafted film versus grafting yield.

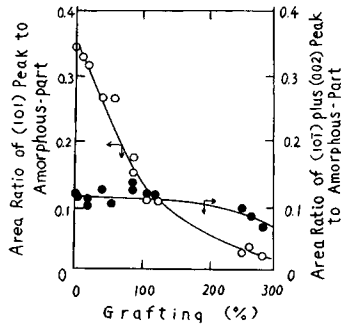


Fig. 4. Area ratio of (101) and  $(10\bar{1}) + (002)$  diffraction peaks to amorphous part, versus grafting yield.

The crystallinity of cellulose in graft copolymer seems to be closely related to the ratio of the crystallinity of the graft copolymer itself to the concentration of the cellulose in the graft copolymer. It may be concluded that the crystalline regions of cellulose are not influenced by the deposition of branched polymer at less than 150% of grafting yield. At more than 150% of grafting yield, however, the amount of crystalline region actually decreases with the increase of grafting yield, and at 450% no diffraction peak of cellulose crystallite is detected.

From the result obtained branched polymer is supposed to be deposited, not only in the amorphous regions, but also in the crystalline regions of the cellulose.

In addition, it should be noted that grafting is very difficult to obtain at more than 450% yield under our experimental conditions.

On the other hand, the ratio of the diffraction area of the (101) and  $(10\bar{1}) + (002)$  planes to that of amorphous parts on an equatorial plane is measured in the film state, to determine the location of deposited branched polymer in the crystalline regions of cellulose. The film is placed in a position perpendicular to the x-ray beams, and the field is rotated at a constant angle between the chain axis of the film and the x-ray beams.

For the ungrafted film, a much sharper and stronger diffraction peak of the (101) on an equatorial plane than that of the  $(10\bar{1}) + (002)$  is observed. For the grafted film, however, the diffraction intensity of the (101) shows a considerable decrease with increase of grafting yield, as shown in Figure 4.

Since the diffraction intensity of the chain axis is not measured at all angles between film and x-ray beams, the change in alignment of the crystallite caused by the (101) plane cannot be made clear. From the results obtained, however, the branched polymer seems to be formed mainly in the layer between cellulose crystallites on the normal (101) planes.

### 3. Distribution of Branched Polymer

The distribution of the branched polymers in the grafted film is studied by the interferometric method developed by Matsuo et al.<sup>5</sup>

A strip of grafted film, embedded in a block of high-melting paraffin wax, is cut in the direction perpendicular to the surface of the film with a microtome cutter. A cross-section, 10–25  $\mu$  in thickness, is used as a specimen. A schematic diagram of the microinterferometer of the Mach-Zehnder type (Leitz) used in this work is shown in Figure 5.

The experimental procedure is briefly described below.

Parallel beams of monochromatic light from a mercury lamp are divided by the prism into two parts, one of which passes through the sample and the other through the control part. The interference pattern is observed with a microscope. Since polyacrylamide has a higher refractive index than cellulose, their interference patterns appear at different locations, and therefore the refractive index of a sample is determined by comparison with a control material, and the interference fringe as a function of the depth from the surface will directly indicate the distribution pattern of the branched polymers in the cross section of the grafted film. The immersion liquid of the control material was usually methylsalicylate, but in some cases benzene, monochlorobenzene, benzyl alcohol, or monobromobenzene was used.

Figure 6a is a microinterferometric pattern of a sample of ungrafted film (cellophane) for comparison. Since the feature of the fringe in the sample is the same as that of the background, uniformity of the refractive index throughout the sample is indicated.

Figures 6b–6f show cross-sections of samples with various grafting yields. Obvious gradients of the refractive index from the surface to the

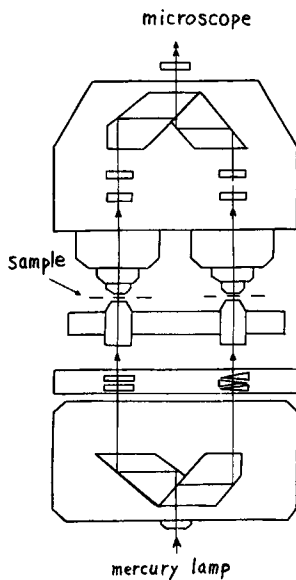


Fig. 5. Schematic diagram of microinterferometer.

center of the specimens are observed in the localized fringes. The distribution of branched polymer is found to change with grafting yield. The branched polymer is observed to be deposited mainly in the outer layer of the film in the case of low grafting yield (Fig. 6b) and in the inner layer, farther from the surface, as the grafting yield increases (Figs. 6c-6e). At more than 250% grafting yield it is found that the formation is distributed almost uniformly throughout the layer of the film (Fig. 6f).

The change of grafting layer thickness versus grafting yield is shown in Figure 7. The distributions of the grafting concentration in the cross-sections, however, could not be strictly calculated, because the difference in refractive index between polyacrylamide and cellulose is too small for calculation.

In all cases the interference pattern of the grafting parts shows a flat, straight line, and the boundary between the grafted and ungrafted parts is obvious. These results are rather noticeable.

If the monomer diffusion is the rate-determining step for this reaction, the grafting concentration from the surface to the center of the film should decrease gradually, as reported by Matsuo et al.<sup>5</sup> for the case of polypropylene-styrene graft copolymer.

Since the gradient of grafting concentration decreases remarkably in the region between grafted and ungrafted parts, and the cellulose film used here is fully swollen with water, so that the monomer diffusion into cellulose may be very fast, the propagation of branched polymers is assumed to be the rate-determining step for this reaction, rather than the monomer diffusion. This assumption is in accord with the result obtained from the esti-

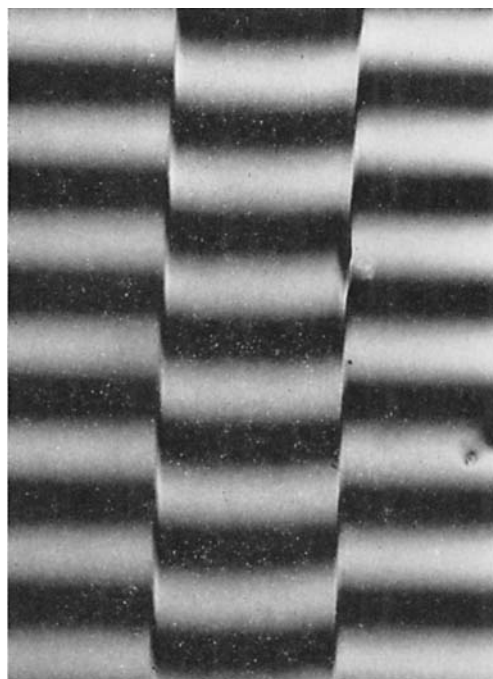
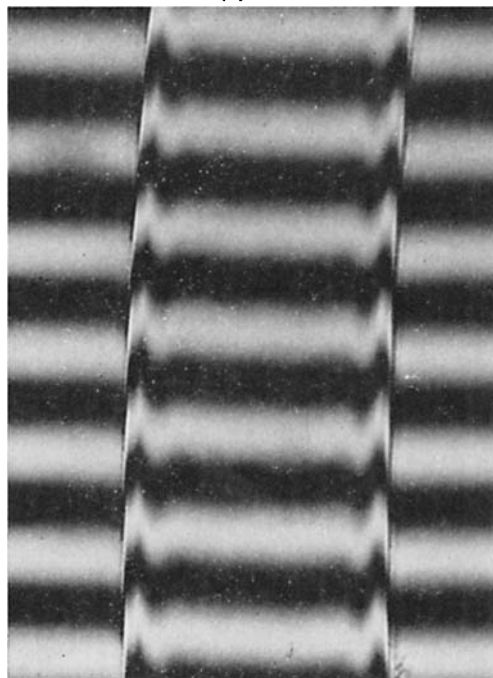
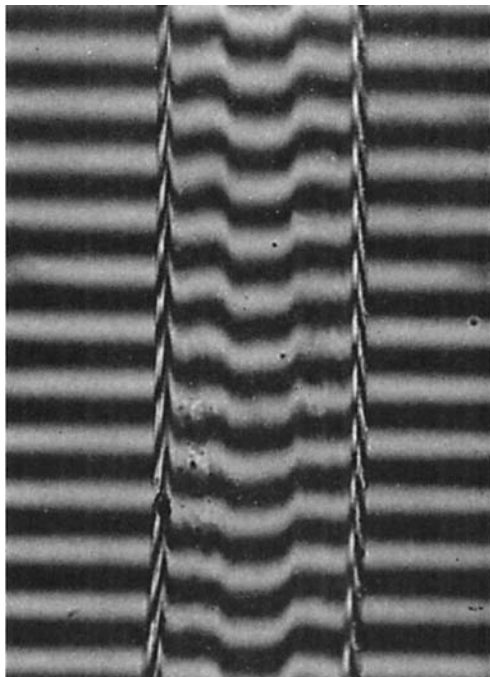
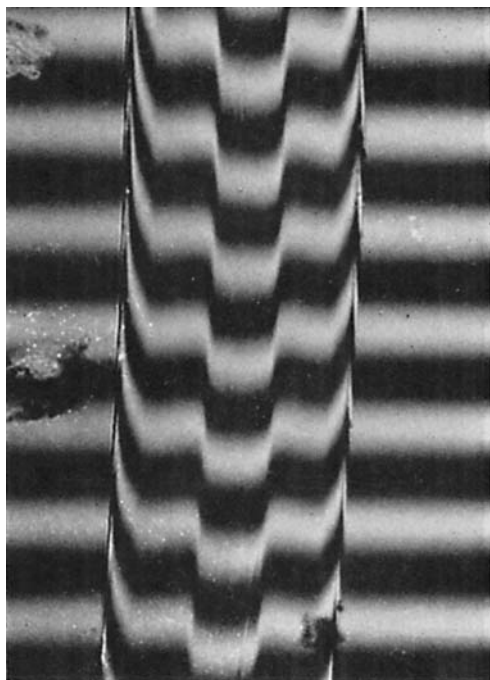
*(a)**(b)*

Fig. 6. Distribution of branched polyacrylamide in grafted film. Grafting yield (%):  
(*a*) ungrafted; (*b*) 20; (*c*) 39; (*d*) 100; (*e*) 200; (*f*) 265.



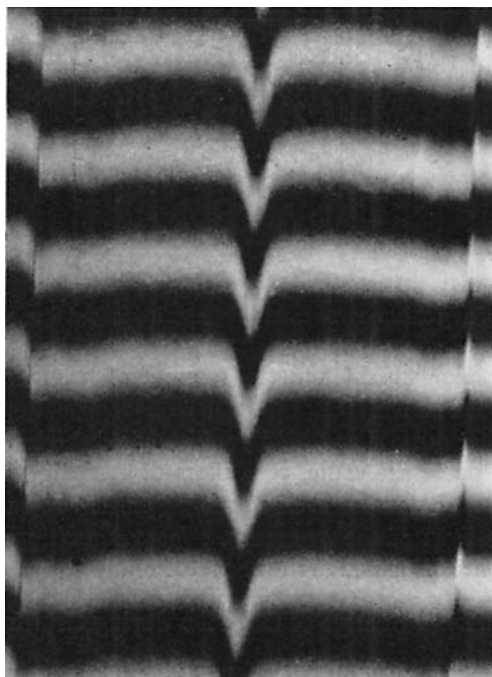
(c)



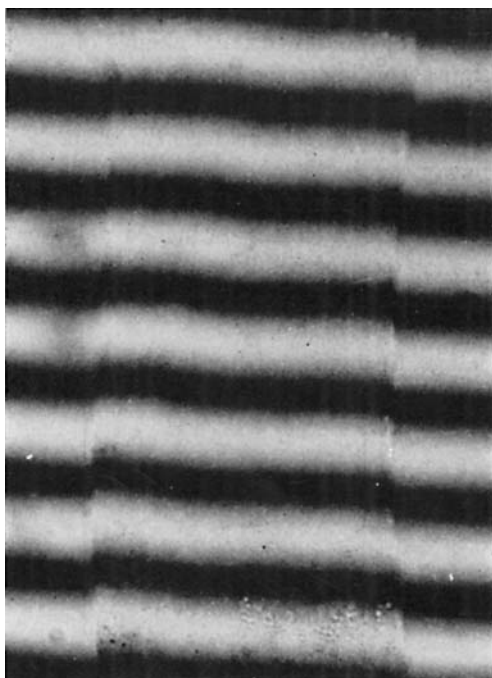
(d)

Figure 6 (continued).





(e)



(f)

Figure 6 (continued).

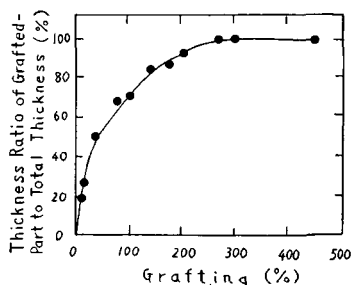


Fig. 7. Rate of grafting thickness to total thickness in grafted film, versus grafting yield.

mation of molecular weight and the number of branches versus grafting yield, as mentioned above.

Furthermore, at more than 250% grafting yield the interference patterns of the grafting parts are same, regardless of grafting yields, and it even seems to be inconsistent with the grafting yield. It can be understood, however, in the light of the expansion effect of grafting on a sample, the details of which are discussed in the next section.

#### 4. Dimensional Change of Gel Film during Grafting Reaction

The dimensional (and volume) change of the gel film during reaction is determined for the purpose of studying the reaction behavior in branched polymer formation.

As shown in Figure 8, the dimensional change of the gel film versus the grafting yield differs according to the thickness direction, the machine direction, and the cross direction of the film. The dimensional change decreases in the following order: thickness direction > cross direction > machine direction.

Since the thickness direction of the film is the vertical component of the (101) planes of cellulose crystallites, branched polymer is assumed to be formed easily in the layer of cellulose crystallites on the normal (101) planes. This conclusion is also consistent with the result obtained by x-ray analysis, as mentioned above.

No volume change through grafting is observed at less than 40% of

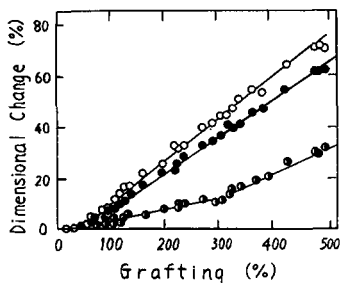


Fig. 8. Rate of increase of film dimension versus grafting yield in the wet state without drying process: (O) thickness direction; (●) cross direction; (◐) machine direction.

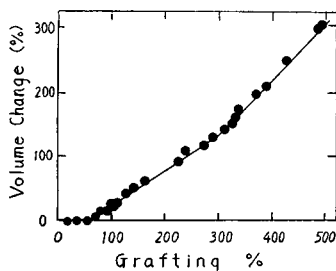


Fig. 9. Rate of volume increase of film versus grafting yield in the wet state without drying process.

grafting yield, but at more than 40% the volume increases in exact proportion to the grafting yield. The slope of the curve in the range of 40–300% is recognized to be about 0.7 and, at more than 300%, to be about 1.0, as shown in Figure 9.

The results obtained here seem to indicate that the behavior of the dimensional change of the gel film during the reaction is affected by the swelling of cellulose with water. There is enough space for branched polymers at less than 40% of grafting yield in which no volume change is detected.

On the other hand, at 40% and more the volume expansion of the amorphous regions, in which branched polymer is most easily formed, takes place slowly, and therefore the volume expansion of the gel film seems to be influenced by the yield of branched polymers formed in the layer between cellulose crystallites.

At more than 300% even the interlayer of the amorphous region seems almost unable to form branched polymers, and the volume of gel film is assumed to have expanded almost in linear proportion to the propagation of the branching chains. This result seems to suggest that branched polymer is formed through the whole layer of film at grafting yields of more than 300%.

The densities of the grafted films are measured by the density-gradient tube method.

The experimental data are found to be in accord with the calculated data in the direct additivity of the densities of the polymer components. The structural change of the graft copolymer has not been elucidated by density measurements.

### 5. Tensile Strength and Elongation Properties of Graft Copolymer

The temperature dependence of tensile strength and elongation and the wet strength are evaluated for a consideration of the structural change of the graft copolymer with the grafting yield.

Tensile strength and elongation of grafted film are measured in the temperature range of 0–110°C. These results are shown in Figures 10 and 11.

At relatively low temperatures, such as 0–40°C., the elongation of grafted film decreases as the grafting yield increases, and a constant value is obtained at 100% and more of grafting yield. At higher temperatures the elongation increases with temperature elevation at more than 100% of grafting yield, especially above 265%. This result suggests that the crystalline structure of cellulose is diluted and discontinued by the formation of branched polyacrylamide at more than 265% of grafting yield.

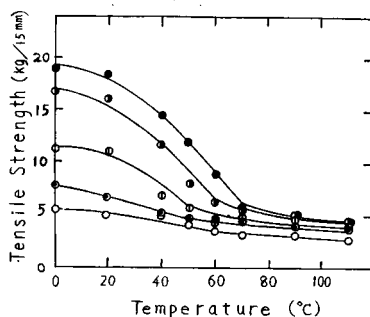


Fig. 10. Tensile strength of grafted film versus measuring temperature. Grafting yield (%): (○) 0; (◐) 55; (◑) 110; (◒) 265; (●) 450.

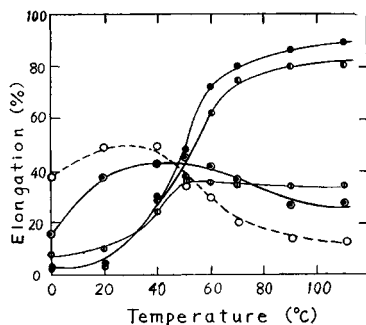


Fig. 11. Elongation of grafted film versus measuring temperature. Grafting yield (%): (○) 0; (◐) 55; (◑) 110; (◒) 265; (●) 450.

On the other hand, at less than 100% of grafting yield the elongation change is small, even at higher temperatures, and this fact shows that the branched polymer is not formed in the crystalline regions of cellulose below 100% of grafting yield and that elongation is subject to the degree of perfectness of the primary network structure of cellulose; that is, in this grafting yield range, the softening effect of polyacrylamide is saturated at 70°C., and then at higher temperatures the elongation decreases because the primary network becomes stronger.

Furthermore, the behavior of the wet strength of the grafted film is estimated for a consideration of the structural change of the graft copolymer with grafting yield.

The specimen is treated with water at 20°C. for 24 hr. and wiped out with a filter paper; then the tensile strength of the wet film (WS) is measured by an Instron Tester at 20°C. and 65% R.H. and the dry strength (DS) at 20°C. and 35% R.H.

As shown in Figure 12, the ratio of wet strength to dry strength decreases remarkably at low grafting yields. This suggests that the degree of cellulose chain penetration through crystallites is disturbed by the formation of branched polymer and also that no waterproof structure caused by the branched polyacrylamide can be expected.

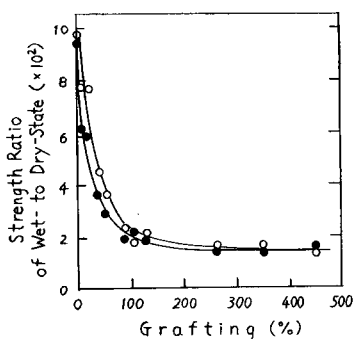


Fig. 12. Ratio of wet strength of grafted film to dry strength, versus grafting yield.

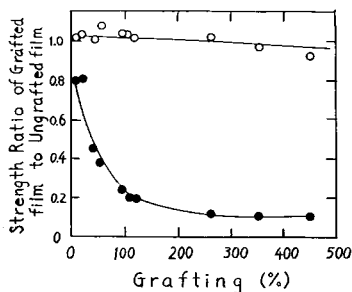
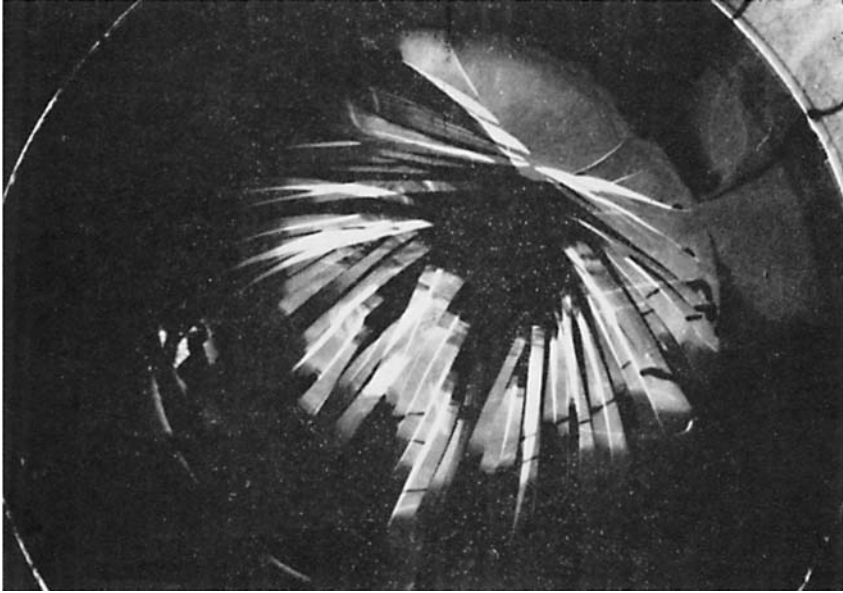


Fig. 13. Tensile strength ratio of grafted film to ungrafted film, versus grafting yield (%): (●) wet strength; (○) dry strength minus wet strength.

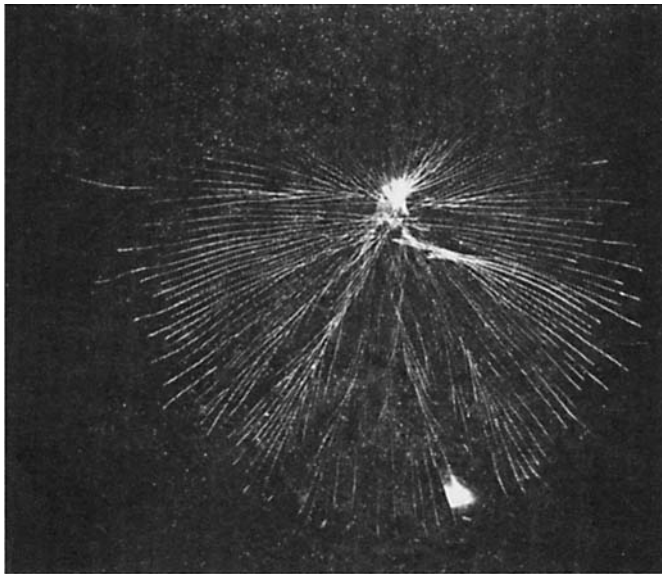
Since the secondary network structure, which is composed of the hydrogen bond, is liberated by water absorption, the wet strength is closely related to the degree of the primary network structure, and the difference between the wet and the dry strengths is an indication of the degree of the secondary network formation.

As shown in Figure 13, the ratio of grafted film to cellulose, expressed as DS/WS, is found to be nearly 1, and therefore it seems that the secondary network structure of the grafted film is similar to that of ungrafted cellulose.

In addition, the fine cracking of the film in the burst state is found to appear more easily as the grafting yield increases, as shown in Figure 14 and the aggregating state of the cellulose is assumed to be influenced by the formation of branched polymers.



(a)



(b)

Fig. 14. (a) Bursting behavior of ungrafted film; (b) bursting behavior of grafted film; grafting yield 55%.

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