

(Received May 14, 1987)

EFFECT OF STRUCTURAL CHANGES ON THE SURFACE CHARACTERISTICS OF REGENERATED AND GRAFT COPOLYMERIZED SILK FIBROIN FILMS

By Wan Shik Ha*, Sang Kyun Oh*, Joon Ho Kim*
and Kea Yong Kim**

* (Department of Textile Engineering, College of Engineering, Seoul National University, San 56-1, Shinlim-dong, Kwanak-gu, Seoul 151, Korea)

** (Department of Industrial Chemistry, College of Engineering, Hanyang University, 17, Haengdang-dong, Seongdong-gu, Seoul 133, Korea)

Abstract

Silk fibroin (SF) and polyacrylic acid (PAA)-grafted silk fibroin were dissolved in calcium chloride/ethanol/water mixture (1/2/8 in mole ratio) at 70°C for 4 hrs. The dissolved silk fibroin and SF-g-PAA polymer were regenerated by casting the dialyzed solutions into the films, respectively. The freshly prepared silk fibroin film was soluble in water and mainly consisted of random coil structure. By treating with aqueous solutions of organic solvents, such as formic acid, trichloroacetic acid, and methanol, the silk fibroin was denatured into insoluble β -pleated sheet structure. The contact angles of silk fibroin and SF-g-PAA films were measured after treating the films with aqueous methanol solution. The surface tensions of the films were calculated in three dimensions consisting of dispersion, polar, and hydrogen bond components from the contact angle data by using determinant method. As IR crystallinity indices of silk fibroin films treated with solvents increased, the total surface tension, polar, and especially, hydrogen bond components increased linearly. However, the dispersion component was nearly independent of the IR crystallinity index of the film. On the other hand, in SF-g-PAA film, with increasing graft yield the total surface tension, polar and hydrogen bond components increased and the dispersion component decreased.

1. Introduction

Silk fibroin is a natural linear protein composed of seventeen kinds of amino acid residues¹⁾. Since silk fibroin, unlike wool keratin, has no disulfide linkage and most of amino acid residues have nonpolar side groups, molecular structure is maintained by the hydrogen bond between the peptide groups of adjacent molecular chains and by the hydrophobic bond between side groups. Therefore, silk fibroin is soluble in the solvents that can break these bonds.

However, no good organic solvent of silk fibroin is known yet, and silk fibroin is dissolved only in the aqueous solution of copper-alkaline complexes, or in the concentrated aqueous solution of inor-

ganic salts which can hydrate easily with a lot of water molecules.^{2,3)} Thus prepared silk fibroin solution can be cast into a regenerated film after removing inorganic salt by dialysis.

The protein molecules in general take three conformations⁴⁾ namely, random coil, α -helix and β -sheet. In the case of silk fibroin, it has been known that there are two types of crystalline structures^{1,4,5)} besides random coil and α -helix, that is, silk I type, crank shaft conformation and silk II type, anti-parallel β -pleated sheet conformation.

The real structure of silk fibroin molecule may be determined by the kind of side group and the condition of surroundings, and it was found that the molecular structure of silk fibroin is trans-

formed complicatedly by mechanical shear force, heat, and organic solvents.⁶⁻¹³⁾ For example, by the treatment of the silk fibroin of silk I type crystalline state or random coil structure with the mixture of alcohol and water, the molecular chains are extended under swollen condition and the concentrated intermolecular hydrogen bonds are formed, resulting in the transformation of silk I type into water-insoluble silk II type crystalline state.¹⁴⁾

The surface characteristics of polymeric materials determine the intermolecular interaction at the interface of the polymer and the other substance contacted with. In the case of medical polymeric material such as artificial blood vessel, the surface of the material interacts with the protein molecules of blood plasma and/or organisms, and from this point of view, the surface characteristics must be an important factor affecting the bio- and blood-compatibility of polymeric materials.^{15,16)}

In this paper, as the first step of the studies to examine the availability of silk fibroin as medical polymeric material, the effect of structural change of silk fibroin on the surface tension was investigated. The change in conformation was achieved by the treatment of silk fibroin films with the mixture of organic solvent and water and the alteration in chemical composition was made by the graft copolymerization of acrylic acid (AA) onto silk fibroin. In particular, for the calculation of three dimensional surface tensions, dispersion, polar, and hydrogen bond components, the three dimensional determinant method was derived from the Kaelble's computational method.¹⁷⁾

2. An Approach to the Determination of Three Dimensional Surface Tension

There have been known several ways to determine the surface energy of a solid from the contact angle data of liquids on the surface. Among them, the two dimensional determinant method proposed by Kaelble is one of the most widely used methods.

Kaelble¹⁷⁾ expressed the work of adhesion as eq. (1) extending the Fowkes' geometric mean theory¹⁸⁾, on the assumption that the interaction between the solid and the liquid at their interface is attributed to the dispersive and the non-dispersive forces,

$$W_a/2 = \sqrt{\gamma_L^d \gamma_s^d} + \sqrt{\gamma_L^n \gamma_s^n} \quad (1)$$

where W_a is the work of adhesion, γ_L and γ_s are the surface tensions of liquid and solid, respectively, and superscripts d and n denote the dispersion and non-dispersion components, respectively. Since the work of adhesion is calculated from the contact angle, θ by the Young-Dupré eq.,

$$W_a = \gamma_L (1 + \cos \theta) \quad (2)$$

We can obtain the two components of surface tension of a solid by using the two dimensional determinant.

On the other hand, Yamaishi et al.¹⁹⁾ assumed that the surface tension is composed of three components, namely, dispersion, polar, and hydrogen bond components, and expressed the work of adhesion as eq. (3),

$$W_a/2 = \sqrt{\gamma_L^d \gamma_s^d} + \sqrt{\gamma_L^p \gamma_s^p} + \sqrt{\gamma_L^h \gamma_s^h} \quad (3)$$

where the superscripts p and h denote the polar and hydrogen bond components, respectively. In addition, they divided liquids into non-polar series ($\gamma_L = \gamma_L^d$), polar series ($\gamma_L = \gamma_L^d + \gamma_L^p$), hydrogen bond series ($\gamma_L = \gamma_L^d + \gamma_L^p + \gamma_L^h$), and EG series ($\gamma_L = \gamma_L^d + \gamma_L^h$) according to the classification of Kitazaki and Hata.²⁰⁾ Thus, the three components of surface tension of a solid are derived from eq. (3) by using the liquids of each series successively. In this method, however, the most difficult problem is that the selection of reference liquids is limited in the case of the solid having large surface tension. In fact, if the surface tension of a solid is larger than that of a liquid, the contact angle cannot be measured according to the critical surface tension theory of Zisman.²¹⁾

In this study, we tried to find a determining method of the three dimensional surface tension components for a solid by applying the Kaelble's computation method to eq. (3). The works of adhesion of the three liquids, i , j , and k , to a solid surface are expressed as eq. (4).

$$\begin{aligned} W_{ai}/2 &= \sqrt{\gamma_{Li}^d \gamma_s^d} + \sqrt{\gamma_{Li}^p \gamma_s^p} + \sqrt{\gamma_{Li}^h \gamma_s^h} \\ W_{aj}/2 &= \sqrt{\gamma_{Lj}^d \gamma_s^d} + \sqrt{\gamma_{Lj}^p \gamma_s^p} + \sqrt{\gamma_{Lj}^h \gamma_s^h} \\ W_{ak}/2 &= \sqrt{\gamma_{Lk}^d \gamma_s^d} + \sqrt{\gamma_{Lk}^p \gamma_s^p} + \sqrt{\gamma_{Lk}^h \gamma_s^h} \end{aligned} \quad (4)$$

Eq. (4) can be solved by using the three dimensional determinant, with inserting the works of

adhesion of the three reference liquids calculated from the contact angles measured and the components of the surface tension of each liquid. The standard determinant (D) and the components of surface tension of a solid are given in eqs. (5), (6), (7), and (8), respectively.

$$D = \begin{vmatrix} \sqrt{\gamma_{Li}^d} & \sqrt{\gamma_{Li}^p} & \sqrt{\gamma_{Li}^h} \\ \sqrt{\gamma_{Lj}^d} & \sqrt{\gamma_{Lj}^p} & \sqrt{\gamma_{Lj}^h} \\ \sqrt{\gamma_{Lk}^d} & \sqrt{\gamma_{Lk}^p} & \sqrt{\gamma_{Lk}^h} \end{vmatrix} \quad (5)$$

$$\sqrt{\gamma_s^d} = \frac{\begin{vmatrix} W_{ai}/2\sqrt{\gamma_{Li}^p} & \sqrt{\gamma_{Li}^h} \\ W_{aj}/2\sqrt{\gamma_{Lj}^p} & \sqrt{\gamma_{Lj}^h} \\ W_{ak}/2\sqrt{\gamma_{Lk}^p} & \sqrt{\gamma_{Lk}^h} \end{vmatrix}}{D} \quad (6)$$

$$\sqrt{\gamma_s^p} = \frac{\begin{vmatrix} \sqrt{\gamma_{Li}^d} & W_{ai}/2 & \sqrt{\gamma_{Li}^h} \\ \sqrt{\gamma_{Lj}^d} & W_{aj}/2 & \sqrt{\gamma_{Lj}^h} \\ \sqrt{\gamma_{Lk}^d} & W_{ak}/2 & \sqrt{\gamma_{Lk}^h} \end{vmatrix}}{D} \quad (7)$$

$$\sqrt{\gamma_s^h} = \frac{\begin{vmatrix} \sqrt{\gamma_{Li}^d} & \sqrt{\gamma_{Li}^p} & W_{ai}/2 \\ \sqrt{\gamma_{Lj}^d} & \sqrt{\gamma_{Lj}^p} & W_{aj}/2 \\ \sqrt{\gamma_{Lk}^d} & \sqrt{\gamma_{Lk}^p} & W_{ak}/2 \end{vmatrix}}{D} \quad (8)$$

The five reference liquids and their surface tension components are given in Table 1, and the standard determinants for the liquid triplets, $i-j-k$, are listed in Table 2. In Table 2, there is a liquid triplet, of which determinant is less than 10. In the two dimensional surface tension computation, according to Kaelble, the determinant of denominator was so small that the calculated components of surface tension of a solid showed too large meaningless values. In the three dimensional computation, however, it does not become large

Table 1. Dispersion, polar, and hydrogen bond components of surface tension (dyne/cm) of reference liquids at 20°C

No.	Liquid	γ_L^d	γ_L^p	γ_L^h	γ_L^{n*}	γ_L^{**}
1	Water	29.1	1.3	42.4	43.7	72.8
2	Glycerin	37.4	0.2	25.8	26.0	63.4
3	Formamide	35.1	1.6	21.5	23.1	58.2
4	Methyleneiodide	46.8	4.0	0.0	4.0	50.8
5	α -Bromonaphthalene	44.4	0.2	0.0	0.2	44.6

* $\gamma_L^n = \gamma_L^p + \gamma_L^h$

** $\gamma_L = \gamma_L^d + \gamma_L^p + \gamma_L^h$

Table 2. Determinant $|D|$ values for liquid triplets

Liquid triplet $i-j-k$	$ D $ (dyne/cm) ^{1/2}	Liquid triplet $i-j-k$	$ D $ (dyne/cm) ^{1/2}
1-2-3	11.6	1-4-5	66.9
1-2-4	44.6	2-3-4	26.3
1-2-5	24.7	2-3-5	28.2
1-3-4	695	2-4-5	52.2
1-3-5	13.6	3-4-5	47.6

simply, for the calculation is much more complicated. But the liquid triplet, of which determinant is less than 10, was omitted in the average calculation, because the result showed different tendency as compared with those of the other liquid triplets.

3. Experimental

3.1 Material

The commercial raw silk fibers (21 den.) were degummed by the following two bath method.²²⁾

The raw silk fibers were rinsed with warm water first, and were treated with 0.3% sodium oleate aqueous solution for 2hrs at 95°C. After washing with boiling water, the fibers were retreated with 0.1% sodium oleate aqueous solution for 1hr and washed with 0.05% sodium carbonate solution. After rinsing with water in several times, the fibers were dried in a vacuum at 50°C.

3.2 Reagents

Calcium chloride was dihydrate of GR grade and water used for the contact angle measurement was high purity grade for HPLC. AA monomer was purified by vacuum distillation with addition of cuprous chloride (1g/l) as stabilizer, and the other reagents were of GR grade and were used without further purification.

3.3 Dissolving and Film Casting of Silk Fibroin

The degummed silk fibers were dissolved in the mixed solution of calcium chloride, ethanol, and water for 4hrs at 70°C with stirring, and the 10% (w/v) silk fibroin solution was prepared. The mixed solution of calcium chloride, ethanol, and water in mole ratio of 1:2:8 was provided by dissolving calcium chloride dihydrate in distilled water and by adding ethanol.²⁾

The silk fibroin solution was dialyzed against water for 3days at 25°C using cylindrical cellulose dialysis sack (Sigma, 250-7u). After removing a small amount of undissolved or precipitated part

by centrifuging at 12,000r.p.m. for 20 min, the dialyzed silk fibroin solution was cast onto commercial acryl plate, of which thickness was 10mm, and dried under reduced pressure for 2days at 25°C. The films just after dried were soluble in water. By weighing the films cast with identical volume/area ratio, it was found that the silk fibroin solution was diluted to about 5% concentration during the dialysis.

3.4 Solvent Treatment and Analysis of Structural Change

The silk fibroin films were fixed between two rectangular acryl frames, and treated with various organic solvents at 25°C. The treated films were washed with water thoroughly and dried in air. The used organic solvent systems were 10% (v/v) formic and 10% (w/v) trichloroacetic acid aqueous solutions, and 10–100% (v/v) methanolic aqueous solution. The structural change of the silk fibroin films treated with 50% methanolic aqueous solution for from 15min to 12hrs was detected with IR spectrophotometer (JASCO, A 102 type) and X-ray diffractometer (Rigaku Denki, DMAX III type).

3.5 Contact Angle Measurement

The contact angles of the five reference liquids, listed in Table 1, on the silk fibroin films were measured with contact anglemeter (Erma, G-I type) at 20°C. The volume of liquid drop was regulated to about 0.6 μ l by using microsyringe. The averaged value of the angles of the left and right sides of each drop was counted as one measurement, and more than ten measurements for each film were averaged.

3.6 Preparation of Silk Fibroin-g-PAA Film

AA monomer was graft copolymerized onto silk fiber in water by using ammonium peroxydisulfate (APS) and sodium sulfite (SS) as redox initiators for 2hrs at 30°C. The amount of APS used was 0.09 mole % of monomer added and SS was 2.34 times of APS in mole ratio. The liquor ratio was 1:100.²³⁾ Graft yield was determined by weight increase, and was controlled by the alteration of monomer concentration from 0.85 mole/l to 2.00 mole/l.

The graft copolymerized silk fibers were dissolved and cast into films by the same procedure as described in 3.3, and the cast films were treated with 50% methanolic aqueous solution for 2hrs

at 25°C.

4. Results and Discussion

4.1 Structural Change of Silk Fibroin

The IR adsorption spectra of the silk fibroin films treated with 50% methanolic aqueous solution at 25°C are shown in Fig. 1, comparing with that of the untreated film. Amides I, II, and III bands, the characteristic infrared ones of proteins, appear at 1,700–1,600 cm^{-1} , 1,570–1,500 cm^{-1} , and 1,300–1,200 cm^{-1} , respectively. However, it can be seen from Fig. 1 that each amide band is overlapped complicatedly with three or four peaks which are seemed to be the characteristic ones corresponding to the random coil, α -helix, and β -pleated sheet conformations of silk fibroin molecular chains.

As pointed out in section 1, it has been known that there are four conformations of silk fibroin, namely, random coil, α -helix, and silk I and silk II type crystals. But among them silk I type crystal is so unstable that the crystal lattices have not been determined yet. In fact, silk I type crystal is transformed easily into silk II type one by solvent treatment. Furthermore, from the experimental conditions in this study, for examples, the concentration of silk fibroin solution and the drying

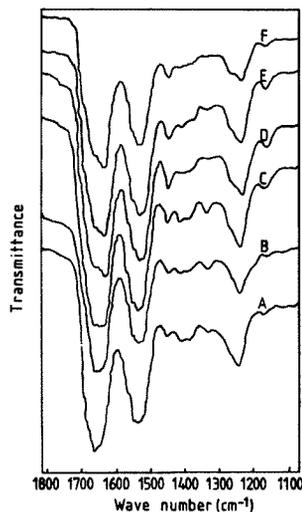


Fig. 1. IR spectra of silk fibroin films. Curve A: freshly prepared; curves B, C, D, E, and F: treated with 50% methanolic aqueous solution at 25°C for 15min, 30min, 1hr, 2hrs, and 4hrs, respectively.

condition of the films, the fraction of silk I type crystal seems to be negligible, and we consider only the other three conformations of silk fibroin.

The IR spectra of silk fibroin have been investigated earlier.^{4,8,9)} The characteristic bands assigned to each conformation were different from investigator to investigator and in accordance with the kind of silk fibroin. For *Bombyx mori* the bands at 1,655, 1,535, and 650 cm^{-1} were assigned to random coil conformation corresponding to amides I, II, and V, respectively, and those at 1,650, 1,545, and 620 cm^{-1} and those at 1,630, 1,530, and 690 cm^{-1} were assigned to α -helix and β -sheet conformations, respectively, by Miyazawa and Blout.⁴⁾ Magoshi et al.⁸⁾ indicated the bands at 1,630, 1,530, 1,265, and 700 cm^{-1} as amides I, II, III, and V assigned to β -sheet conformation of Mulberry silk and those at 1,660, 1,540, 1,235, and 650 cm^{-1} as the ones assigned to random coil conformation. In the case of Tussah silk, Magoshi and Nakamura⁹⁾ found that the amorphous part showed characteristic bands at 1,660, 1,550, 1,310, 1,270, 1,107, 890, and 650 cm^{-1} and on heating it was converted to β form showing characteristic bands at 1,630, 1,530, 1,240, 970, and 700 cm^{-1} .

The silk fibroin films regenerated from the mixed solution of calcium chloride/ethanol/water in this study show characteristic amide I, II, and III bands assigned to random coil conformation at 1,667, 1,554, and 1,235 cm^{-1} , respectively, and assigned to α -helix conformation at 1,645, 1,540, and 1,250 cm^{-1} and assigned to β -sheet conformation at 1,635, 1,535 and 1,265 cm^{-1} , respectively (Fig. 1). However, as the solvent treating time is prolonged, the absorption decreases rapidly at 1,667 cm^{-1} and increases gradually at 1,635 cm^{-1} in amide I bands. Similarly in amide II bands the absorption at 1,554 cm^{-1} decreases, but at 1,535 cm^{-1} increases. In amide III bands the peak at 1,265 cm^{-1} develops. However, the bands at 1,645, 1,540, and 1,250 cm^{-1} do not change largely. From these observations we can conclude that random coil conformation is transformed into β -sheet one by the solvent treatment, but α -helix portion remains. The remaining of α -helix conformation, which has been found by Tsukada and Hirabayashi,¹²⁾ Nagura et al.¹³⁾, and Scott and Scheraga²⁴⁾, is the result that α -helix conformation

would be stable and would seldom interact with adjacent chains, but only interact intramolecularly, even if it exists in isolated form between random coil or β -sheet chains.

On the other hand, Bhat et al.^{3,10,11)} pointed out the amide III bands at 1,265 and 1,235 cm^{-1} as the proper ones to calculate the crystallinity of silk fibroin quantitatively. In practice we calculated the IR crystallinity index by using the ratio of optical density at 1,265 cm^{-1} to optical density at 1,235 cm^{-1} . IR crystallinity indices of the silk fibroin films prepared freshly and treated with various solvents are listed in Table 3. The effect of the solvents on IR crystallinity index increases in order of trichloroacetic acid, formic acid, and methanol at the same concentration. In the case of methanol, it shows maximum at the concentration of 25% and decreases as the concentration increases. It is expected that IR crystallinity index shall increase in the more concentrated aqueous solution of trichloroacetic acid and formic acid as well as methanol, but the crystallization induced by these organic acids is accompanied with the degradation of silk fibroin. The effect of the treating time was also examined. The IR crystallinity indices of the silk fibroin films treated with the methanol/water mixture (50/50) for from 15min to 4hrs at 25°C are represented in Fig. 2. As the treating time increases, the IR crystallinity index increases rapidly in the beginning and slowly after 1 hr.

Table 3. IR crystallinity indices of silk fibroin films treated with various solvents at 25°C

Sample coad	Solvent treating condition	IR crystallinity index
A	Freshly prepared	0.570
B	50% methanol, 15 min	0.601
C	50% methanol, 30 min	0.619
D	50% methanol, 1 hr	0.637
E	50% methanol, 2 hr	0.649
F	50% methanol, 4 hr	0.675
G	50% methanol, 12 hr	0.678
H	10% formic acid, 2 hr	0.637
I	10% TCA* 2 hr	0.642
J	10% methanol, 2 hr	0.607
K	25% methanol, 2 hr	0.652
L	75% methanol, 2 hr	0.641
M	100% methanol, 2 hr	0.609

* trichloroacetic acid

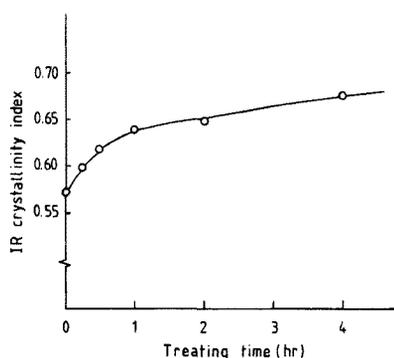


Fig. 2. Effect of treating time on IR crystallinity index of silk fibroin film treated with 50% methanolic aqueous solution at 25°C.

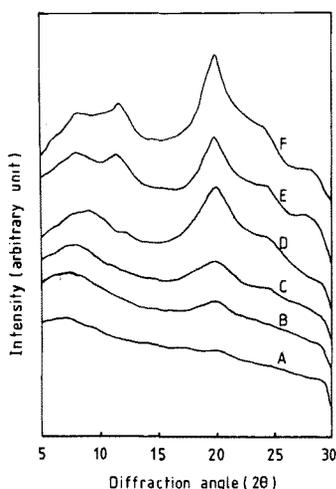


Fig. 3. X-ray diffraction patterns of silk fibroin films. Curve A: freshly prepared; curves B, C, D, E, and F: treated with 50% methanolic aqueous solution at 25°C for 15min, 30min, 1hr, 2hrs, and 4hrs, respectively.

In Fig. 3, which represents the X-ray diffraction patterns of the silk fibroin films treated under the same conditions as those in Fig. 1, the peak at 2θ of 20.2° develops well with the solvent treatment. This peak, according to Magoshi and Nakamura⁹⁾, corresponds to the $d(201)$ of silk II type crystal. Therefore, it is considered that the results from X-ray diffraction patterns support those from IR spectra.

4.2 Relation between Molecular Structure and Surface Characteristics of Silk Fibroin Film

The changes in surface characteristics of the silk

fibroin film were examined in connection with the structural change. Relations between the IR crystallinity index and the three dimensional surface tension components of the silk fibroin films treated with various solvents are represented in Fig. 4. Each component of the three dimensional surface tensions was calculated from eqs. (6), (7), and (8) by the method described in section 2. Total surface tension, γ_s , is the sum of all components.

It is obvious that the dispersion component of surface tension does not change with increasing IR crystallinity index. However, the polar and hydrogen bond components, and the total surface tension increased linearly. These results are consistent with those for nylon 6 and PET.²⁵⁾

The surface energy of polymeric material is subjected to the influences of the chemical composition and physical structure of polymer chain. From the theoretical point of view, the dispersion component of surface tension depends on the chemical composition only.²⁶⁾ Therefore, the change in surface tension caused by the change of physical structure, such as crystallization and transformation, may be mainly due to the change of the polar and/or hydrogen bond components. The above experimental results are coincident with this prospect. In particular, the increasing rate

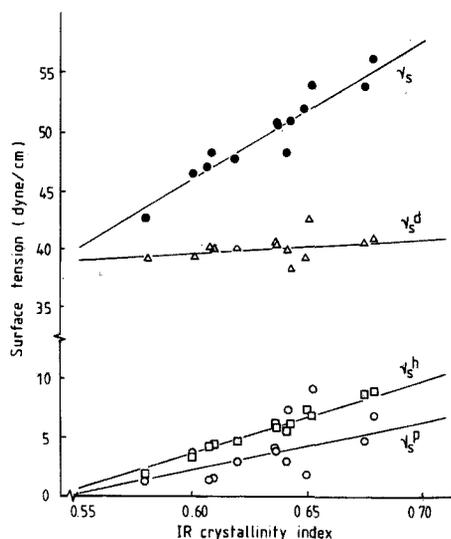


Fig. 4. Relation between IR crystallinity index and three dimensional surface tension components of silk fibroin films.

of hydrogen bond component is larger than that of polar component in Fig. 4. This is considered that the structural change of silk fibroin is closely concerned with hydrogen bond, that is, as pointed out in subsection 4.1, when random coil is transformed to β -sheet conformation, molecular chains are extended and the density of intermolecular hydrogen bond increases largely.

4.3 Effect of Graft Copolymerization on Surface Characteristics of Silk Fibroin Film

The surface characteristics of the silk fibroin film graft copolymerized with AA were investigated in connection with the graft yield. Under conditions described in subsection 3.6, the graft yield could be varied from 4.7% to 26.5% by the change of monomer concentration from 0.85 mole/l to 2.00 mole/l. The effect of the graft yield on the three dimensional surface tension components is illustrated in Fig. 5. As the graft yield increased, the dispersion component decreased, and the non-dispersion components, especially the polar contribution increased remarkably. As a result, the total surface tension increased a little, and the silk fibroin films, of which surface tension is similar but each component contributes in different extent, could be prepared.

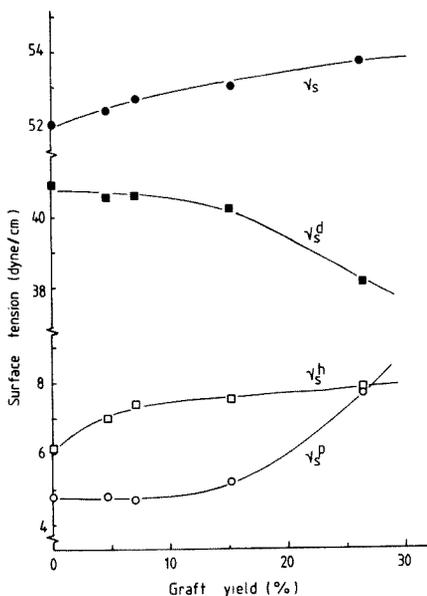


Fig. 5. Effect of graft yield on the three dimensional surface tension components of silk fibroin-g-PAA films.

5. Conclusions

The surface tensions of the silk fibroin films regenerated from the mixed solution of calcium chloride/ethanol/water and treated with various solvents were measured. As the crystallinity of the silk fibroin film treated with solvent increased, the total surface tension, polar, and especially, hydrogen bond components increased linearly. The silk fibroin films, of which surface tensions were 43–55 dyne/cm, consisted of 38 dyne/cm of dispersion, 2–5 dyne/cm of polar, and 2–8 dyne/cm of hydrogen bond components, were prepared.

The silk fibroin films graft copolymerized with AA were also prepared. As the graft yield increased, the dispersion component decreased from 41 dyne/cm to 38 dyne/cm, whereas polar and hydrogen bond components increased from 5 dyne/cm to 7.5 dyne/cm and from 6 dyne/cm to 7.5 dyne/cm, respectively.

Acknowledgment

The authors wish to thank the Korea Science and Engineering Foundation for the financial support of this research.

References

- 1) K. Hirabayashi, *Sen-i Gakkaishi*, **40**, P-119 (1984).
- 2) A. Ajisawa, *Sen-i Gakkaishi*, **24**, 61 (1968).
- 3) N. V. Bhat and S. M. Ahirras, *J. Polym. Sci.: Polym. Chem. Ed.*, **21**, 1273 (1983).
- 4) T. Miyazawa and E. R. Blout, *J. Am. Chem. Soc.*, **83**, 712 (1961).
- 5) Wan Shik Ha, "The Structure and Property of Fibers", Korean Soc. Text. Eng. Chem., Seoul, p.105 (1984).
- 6) J. Magoshi and S. Nakamura, *J. Appl. Polym. Sci.*, **19**, 1013 (1975).
- 7) J. Magoshi, *Polymer*, **18**, 643 (1977).
- 8) J. Magoshi, Y. Magoshi, and S. Nakamura, *J. Appl. Polym. Sci.*, **21**, 2405 (1977).
- 9) J. Magoshi and S. Nakamura, *Rept. Progr. Polym. Phys. Jpn.*, **19**, 661 (1976).
- 10) N. V. Bhat, G. S. Nadiger, K. M. Paraliker, and S. M. Betrabet, *J. Appl. Polym. Sci.*, **25**, 635 (1980).
- 11) N. V. Bhat and G. S. Nadiger, *J. Appl. Polym. Sci.*, **25**, 921 (1980).
- 12) M. Tsukada and K. Hirabayashi, *Sen-i Gakkaishi*, **39**, T-265 (1983).

- 13) M. Nagura, H. Ishikawa, and M. Tsukada, *Kobunshi Ronbunshu*, **41**, 139 (1984).
- 14) R. H. Peters, "Textile Chemistry", Vol. 1, Elsevier, London, p.309 (1963).
- 15) R. E. Baier, G. I. Loeb, and G. T. Wallage, *Federation Proceedings*, **30**, 1523 (1971).
- 16) K. Y. Kim and K. J. In, *Polymer (Korea)*, **5**, 459 (1981).
- 17) D. H. Kaelble, *J. Adhesion*, **2**, 66 (1970).
- 18) F. M. Fowkes, *Ind. Eng. Chem.*, **56**, 40 (1964).
- 19) K. Yamaishi, H. Kumazawa, and H. Sanuki, *Sen-i Gakkaishi*, **32**, T-154 (1976).
- 20) Y. Kitazaki and T. Hata, *J. Adhesion Soc. Jap.*, **8**, 129 (1972).
- 21) W. A. Zismann, "Encyclopedia of Polymer Science and Technology", Vol. 1 (H. F. Mark, N. G. Gaylord, and N. M. Bikales, Ed.), Interscience Publishers, New York, p.445 (1964).
- 22) N. S. Kim, "Introduction to Scouring and Bleaching", Moon Woon Dang, Seoul, p.184 (1982).
- 23) K. Matsumoto, H. Hoshiro, N. Inove, T. Kiyotsukuri, and N. Utsumi, *Kobunshi Ronbunshu*, **39**, 717 (1982).
- 24) R. A. Scott and H. A. Scheraga, *J. Chem. Phys.*, **45**, 2091 (1966).
- 25) Wan Shik Ha and Dong Soo Han, *J. Korean Soc. Text. Eng. Chem.*, **22**, 124 (1985).
- 26) J. H. Hildebrand and R. L. Scott, "Solubility of Nonelectrolytes", 3rd ed., Reinhold, New York (1955).

再生及びグラフト共重合絹フィブロン膜 の構造変化が表面特性に及ぼす影響

ソウル大学校工科大学 河完植, 吳相均, 金俊浩
漢陽大学校工科大学 金啓用

絹フィブロン(SF)及びポリアクリル酸(PAA)グラフト共重合絹フィブロン膜の有機溶剤処理及びグラフト率による表面特性の変化を膜の表面張力の変化の検討により解析した。

溶剤処理絹フィブロン膜のIR結晶化度指数の増加とともに、膜の全表面張力及び表面張力の極性、特に水

素結合成分が直線的に増加した。これに反して表面張力の分散成分は膜のIR結晶化度指数の影響をほとんど受けない事が明らかとなった。

一方、SF-g-PAA膜の場合はグラフト率の増加とともに膜の全表面張力、極性及び水素結合成分は増加し分散成分は減少した。