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Analyses for Identification of Methacrylamide Graft-Polymerized Silk

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메타크릴아마이드 그라프트 重合絹의 分析 方法

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摘 要

絹에 대한 비닐單量體의 增量加工에 있어서 메타크릴아마이드(methacrylamide) 그라프트 加工絹의 判別 방법을 확립하기 위하여 加工絹에 대한 定性分析과 微細構造를 관찰한 결과 加工絹의 溶解性 및 窒素含有量은 未加工絹에 비하여 저하되었으며 IR-Spectra도 파장 1385cm^{-1}, 1210cm^{-1} 및 1125 cm^{-1}에서 未加工絹과 다른 吸收 peak를 보였고 加工絹의 pyrogram은 메타크릴아마이드의 熱分解로 未加工絹에서는 나타나지 않은 또 다른 peak를 보였다. 또한 加工絹의 表面微細構造는 未加工絹에 비하여 fibril이 膨大하여져 거친 面을 보였다.

Introduction

The vinyl monomers have been applied onto silk since the beginning of last decade for weighting of raw material silk yarn especially in some kinds of yarn dyed fabrics, neckties and so on.

The various vinyl monomers have been in industrial use, for instances, styrene, methylmethacrylate, hydroxyethylmethacrylate and methacrylamide. Among these monomers, methacrylamide has been lately introduced as a most favorable one which brought about less problems in the quality of grafted silk than the others. In addition, it has been known that the methacrylamide grafted silk makes the weaving efficiency increased to an extent even though the high degree of grafting-on might deteriorate the hand-touch of silk fabric. Therefore, this monomer is expected to be used continuously for neckties and the other yarn dyed fabrics. However, this monomer contains the same functional group (amide) as fibroin. So it is difficult to identify the silk grafted with the monomer. Concerning to this subject, two papers have been recently published (Shiozaki, H., 1983; Bianchi, S. & Massafra, M. 1986).

The results in this paper were obtained by analysing the methacrylamide grafted silk using the methods adapted by Stazione Sperimentale Per La Seta (Bianchi, S. & Massafra, M.).

Experimental

Materials

The sample silk was used as the degummed yarn (19.4d×2plies, 454 t.p.m.). Methacrylamide for grafting and the other reagents were used as extra pure grade.

Grafting Method

The sample of degummed silk yarn was immersed in the solution of metharylamide (50% o.w.f.) cont-

aining potassium persulfate (1% o.w.f.) as an initiator to pH 3.8 and the treatment was conducted from 40°C to 80°C for one hour at the end of the treatment, the samples were rinsed and left to dry at room temperature. The sample was weighed after conditioning at 20±2°C and R.H 65 ±2%.

The graft-on of sample silk was 28wt.%.

Tests of Solubility

Sodium hypochlorite : 0.2 grams of sample silk was dissolved in 20ml sodium hypochlorite solution (60% v/v) with shaking at room temperature for 30 minutes.

The dissolved solution was filtered by glass filter (No. 1) weighed in advance and then the residual amount with the glass filter was weighed.

Lithium Bromide : The sample silk of 0.2 gram was immersed in saturated lithium bromide solution and then kept at 63°C for 3 hours for dissolving. The dissolved solution after adding distilled water was filtered by the glass filter. The filtration with replications of washing was continued until no bromide in the filtrate was detected by drops of 0.1N $AgNO_3$ solution, the residuals of filtrate with glass filter were weighed.

Lithium thiocyanate : The sample was put into 3.5 ml of 60% LiSCN solution and heated for 10 minutes in order to prevent the solution from crystalizing.

The dissolved solution after adding distilled water filtered by the glass filter (No. 1) and the filtration with replications of washing was continued until no thiocyanate was detected by a few drops of 1% $FeCl_3$ solution. The residuals of filtrate were measured.

Formation of Polymethacrylic acid : The sample was dissolved into 8ml of 5% NaOH solution for 10 minutes with heating on the condenser.

Then the dissolution was neutralized with conc. hydrochloric acid and it was left for one hour for making precipitation.

The centrifugation of precipitated solution was carried out with replications of distilled water at 3,000r.p.m. until no chloride in the filtrate was convinced by drops of conc. nitric acid and 0.1N $AgNO_3$ solution. Finally, the amount of precipitation was weighed.

Determination of nitrogen

According to the microkjeldahl method, each sample silk of 0.1 gram was oxidized with 7ml of conc. sulfuric acid by adding cupric oxide as a catalyst for 2 hours and the oxidized sample was distilled until the ammonia gas developing from the sample was completely taken into 20ml of 0.1N HCl solution including methyl orange as an indicator.

The titration was done with 0.1N NaOH solution until the orange tint of distilled solution disappeared.

Infra-Red Spectra

The sample silks, both original and grafted, were cut about 2mm length and tableted with potassium bromide under the pressure of 10 tons/cm^2. The I.R. spectra of sample silks were run in the range of wavelength from 4,000cm^{-1} to 400cm^{-1} by Fourier Transform I.R. Spectrometer (Perkin-Elmer, 1710).

The sample of polymethacrylic acid was taken from the filtrate residuals in the above test of formation of polymethacrylic acid.

Pyrolysis Gas-Chromatography

3mg of each sample was used for analysis.

Pyrolysis was done at 550°C for 20 seconds under nitrogen gas (30ml/min) and with the column (3m long) containing 25% polyethyleneglycol (20M) at 80°C by using.

Gas chromatography (FRACTOVAP 4200, Carlo Erba) within 20 minutes, identification for methacrylamide could be made.

Surfacial Structures by SEM

The surfacial features of grafted silk fibres were observed in the magnification of about 11,000 times by Scanning Electron Microscope (Stereoscan 100, Cambridge).

Results and Discussion

1. Tests of Solubility and Nitrogen content

In the solubility tests against several chemical reagents, the insoluble residuals was the highest, 67.4% in lithium thiocyanate among three chemicals, next in order 56.0% in lithium bromide solution, but there was no significant difference in solubility between original and grafted silk which was completely dissolved in the sodium hypochlorite solution (see table 1).

The difference in nitrogen content between original and grafted silk was shown in Table 2. The nitrogen

Table 1. Comparisons of insoluble residuals between original and grafted silk against reagents.

Reagents	60% NaClO	Saturated LiBr	60% LiSCN
Original silk	trace	trace	trace
Grafted silk	trace	56.0%	67.4%

Table 2. Difference in nitrogen content between original and grafted silk.

Nitrogen content	Original silk	Grafted silk(28%)	deviation
Percent	18.76	15.26	−3.50
Index	100	81	19

content of grafted silk was 15.26%, this value was lower by 3.5% (19% index) than that of original silk.

This can be said that the nitrogen content of grafted silk is negatively related to the graft-on percent of silk.

2. FT.IR-Spectra

A little different spectra were obtained from original and grafted silk (Fig. 1). But, in the extended scale, a noticeable difference at the range of 1500cm^{-1} to 1100cm^{-1} could be found in both samples: 1385cm^{-1}, 1210 and 1125cm^{-1} (Fig. 2), where the existence of absorption was recognized in the methacrylamide grafted silk. The absorptions at 1385cm^{-1} and 1210 cm^{-1} of grafted silk were seemed to be influenced by the bond formation between methacrylamide and silk

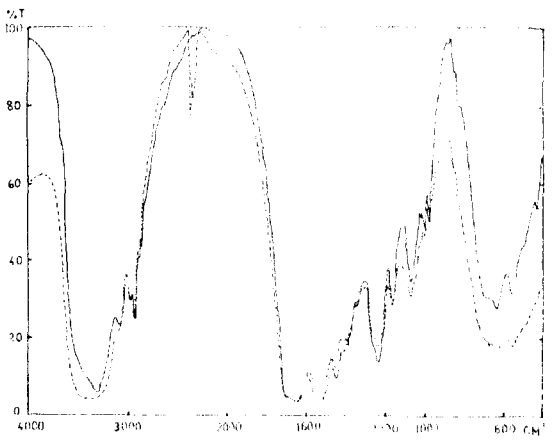

Fig. 1. IR-Spectrum of original and grafted silk at range of 4000 to 400^{-1}.
*—: original silk---: grafted silk (28%)

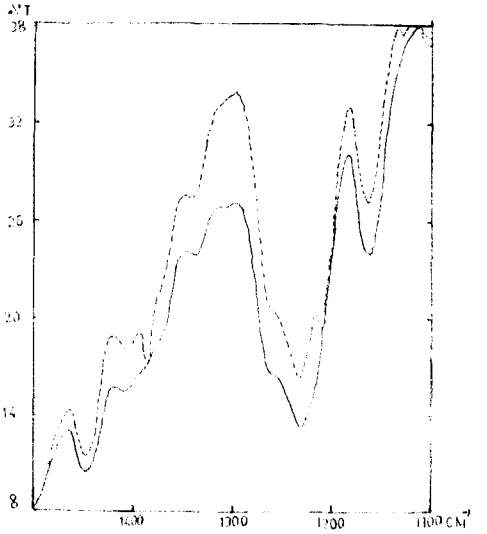

Fig. 2. IR-Spectrum of original and grafted silk at range of 1500 to 1100cm^{-1}.
*—: original silk ---: grafted silk (28%)

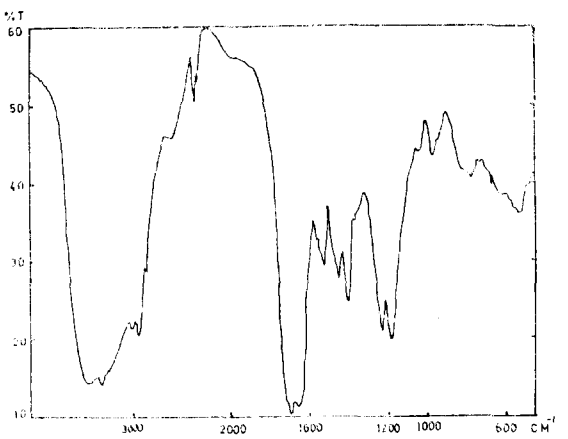

Fig. 3. IR-Spectrum of Polymethacrylic acid.

fibre. The polymethacrylic acid also showed the absorptions at 1385cm^{-1} and 1210cm^{-1}, respectively (Fig. 3).

3. Pyrolysis Gas Chromatography

The thermal decomposition of grafted silk was done by pyrolysis. Fig. 4 shows a result of Gas chromatography analysis.

There was a significant difference between Pyrograms of original (A) and grafted silk (B). Also, the pyrogram of methacrylamide monomer (C) shows the peak, which is produced by pyrolytic fragmentation

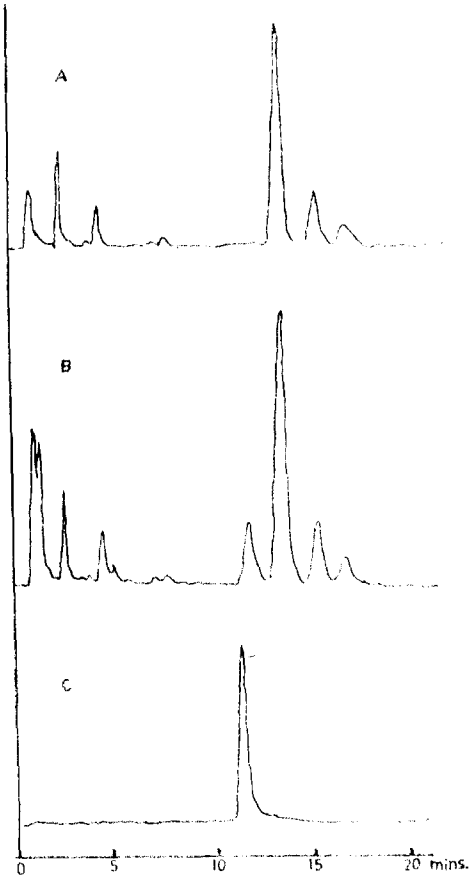

Fig. 4. Pyrograms of original and grafted silk.
A : Original silk B : grafted silk (28%)
C : methacrylamide (monomer)

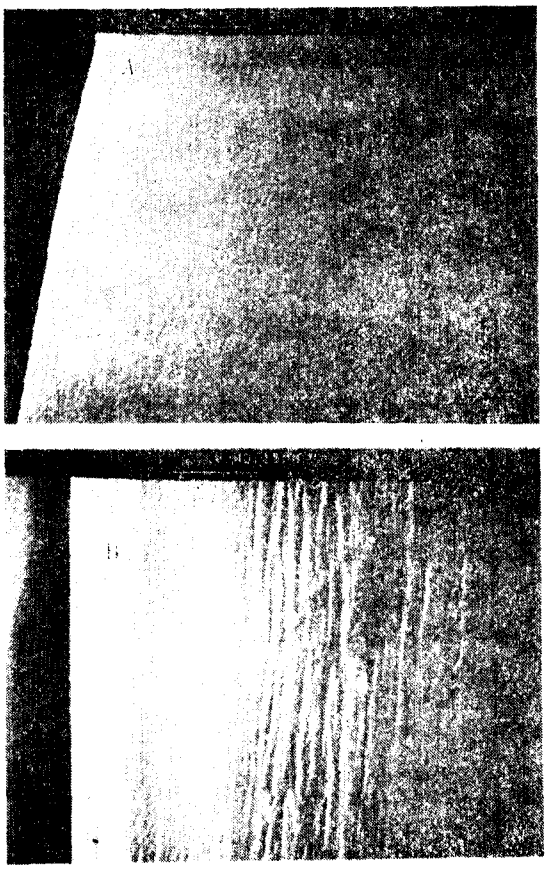

Fig. 5. Ultra-fine surfaces of original and grafted silk.
A : original silk
B : methacrylamide grafted silk (28%)

of methacrylamide.

4. Ultra fine surfaces of grafted silk

The surfacial features of grafted silk were observed in the magnification of about 11,000 times by Scanning Electron Microscopy (Fig. 5).

The grafted polymers were not visible on the surface of silk grafted with 28 percent of methacrylamide.

However, the ultra fine surface of grafted silk was longitudinally coarser than that of original silk, which seemed to be caused by diametrical expansion of microfibrils due to grafting-in of methacrylamide.

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Conclusions

The methacrylamide grafting finishing of silk should be continuously done on industrial scale for the time being. Therefore, the identification methods, such as the test of solubility against reagents, determination of nitrogen content, IR spectroscopy, and Pyrolysis gas chromatography, are to be studied widely. Especially, the Pyrolysis gas chromatography is the most promising method for the qualitative and perhaps

quantitative determinations.

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