

〈研究論文(學術)〉

개질 Polypropylene의 혼화성과 표백

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Miscibility and Bleaching of Modified Polypropylene

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요 약-이 연구는 염색성이 열악한 polypropylene(PP) 섬유의 염색성을 개선하기 위해 추진한 것이다. 연구목적에 따라서 PP 섬유를 개질하기 위해 1차 cellulosic 유도체를 추출하고 이 유도체와 PP를 9:1의 혼합비율로 섞어 master batch를 만든 다음 master batch 17%와 PP를 blending하여 개질 PP를 만들었다. 이렇게 제조된 개질 PP는 혼합된 변성 cellulosic polymer의 영향으로 착색이 심하게 되어 있으므로 이를 표백하는 것을 이 연구의 목적으로 하였다. 연구결과 blend한 개질 PP(Grand P)의 혼화성이 우수하였고, 아염소산나트륨에 표백적성을 가지며, 표백의 최적조건은 표백제의 농도가 0.1% NaClO₂, 표백온도 70°C, 표백시간 30분이었다.

1. Introduction

Polypropylene has good physical properties, and its mechanical properties are better than those of polyester. The main restrictions on the use of polypropylene fiber are its low thermal property, low hygroscopicity and poor dyeability. In spite of extensive research efforts of many researchers focused on the development of an dyeable polypropylene fiber, no truly commercial product is available on the market at present¹⁻⁴. Therefore, dope dyeing of polypropylene is still the most widely used. Pol-

ypropylene fibers are difficult to dye by conventional dyeing techniques due to either lack of dye receptor sites in their molecular structure or difficulty of penetration of certain types of dye molecules into the structure⁵.

The highly crystalline and oriented of polypropylene fibers make difficult in special dyeing method. In addition, modification of polymer before extrusion by introducing dye reactive groups(e.g., =O, SO₃H) also has a limited practical application⁶⁻¹¹. In spite of recent developments of synthetic dyes, no polypropylene dyeable dyes are develop-

ed due to compact structure of polypropylene fibers. Dope dyeing is widely used in plastic industry but is difficult to use in textile industry. The problem of dope dyeing is due to adequate colour yield and control of color matching.

Therefore, modified polypropylene(Grand P) was developed for this study. Grand P was made by mixing an natural additives such as the extracts of eulalia, reed, rice straw and leaves to the polypropylene prior to extrusion. It has both merits of polypropylene and cellulose fiber. Grand P has many attractive properties, such as low density combined with thermal stability, static resistance and biocompatibility. In addition, Grand P has a good dyeability.

1.2 deiner Grand P filaments was spun, the filament has grey color which originates from natural additive. The fabric knitted or weaved from Grand P filament which shows grey colour like flax. The purpose of this study was to standardization of bleaching process of the Grand P fabrics.

2. Experimental

2.1 Materials

Grand P and regular PP was supplied by Wooju Company. Grand P fiber was prepared by melt spinning. The fineness of obtained yarn was 80d/72 f. The drawn multifilaments were knitted to a fabric. After and before bleached, the fabric was weighed at RH 65% in order to calculate the amount of removed cellulosic materials(Table 1). Used Chemicals in this study were commercial grade.

Table 1. Amounts of removed impurities at 70°C, 60min.

Bleaching Conditions (% NaClO ₂)	0.4	0.6	0.8	1.0	1.2
Amount of removed cellulosic materials, % o.w.f	8.2	8.2	8.4	8.2	8.5
Amount of remained cellulosic materials, % o.w.f	8.8	8.8	8.6	8.8	8.5

2.2 Preparation of Grand P

Figure 1 shows Grand P preparation process.

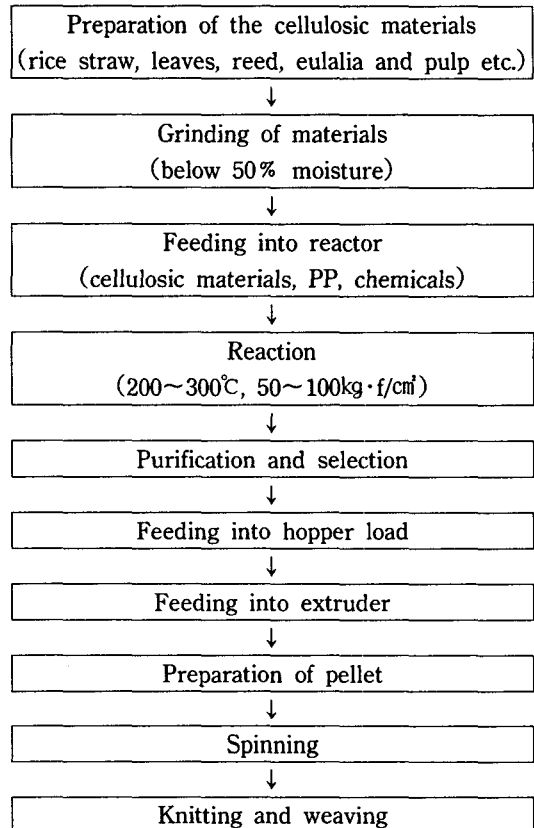


Fig. 1 Manufacture process of Grand P.

2.3 Miscibility

A polarizing optical microscopy(Carl Zeiss, Interphako JENAPOL, Germany) equipped with a hot stage was used to observe the miscibility of polypropylene with cellulosic extract. The polymer sample was observed at 160 and 278°C, and then held at 185°C for various times(5 sec., 25 min., 60min. and 120min.).

2.4 Morphology

The Morphology of Grand P filament was studied with a SEM(JSM-T330A, Jeol Co., Japan) equipped with a Plasma etcher. The cross sec-

tion and side face of filament was observed at the following conditons :

- Forward powe 400W
- Reflected power 12W
- Pressure 2mBar

2.5 Bleaching

In order to select the appropriate bleaching agent, Grand P was treated with various bleaching agents such as sodium hypochlorite, sodium chlorite, potassium permaganate, hydrogen oxide, sodium hydrosulfite and Rongalite C(NaHSO₂CH₂O). As a result of the treatment, sodium chlorite showed excellent bleaching effect than the others. Therefore, In this experiment we used sodium chlorite as bleaching agent.

Bleaching of fabrics were performed using shaking bath with bleaching solution as below and then treated with 0.2% H₂O₂ solution for dechlorination at room temperature for 20min.

The dechlorinated fabrics were rinsed throughly and dried.

The bleaching recipe used was :

- Sodium chlorite 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2 % o.w.f
- Acetic acid 0.3g/ℓ
- Penetration agent 0.3g/ℓ
- Bleaching time 10, 30, 60, 120 min.
- Bleaching temp. 50, 60, 70, 80, 90, 100°C
- Liquor ratio 30 : 1

2.6 Colour Measurement

Colour of bleached fabric was measured with Data Match Spectraflash 500(USA, Data Color International Co.,) equipped with data MASTER VI. O program. Colour Measurement gave L*, a*, b*, C*, H, X, Y, Z, x, y, and L* value used as a criterion of whiteness. The experimental condition was as below.

- Specular include

- Aperture small
- No. of flashes 5
- UV filter calibrator 70%

3. Result and Discussion

3.1 Mechanical properties of Grand P

Mechanical properties of Grand P filament and other synthetic fibers were shown in Table 2 for comparison. Tenacity of Grand P filament was lower than other fibers but elongation is higher. Moisture regain of Grand P was between regular PP and PET. This might be due to the pore generated during blending process and remained cellulosic material in the Grand P. The other mechanical properties of Grand P was similar to regular PP.

Table 2. Mechanical properties of Grand P

Fiber	Grand P	PP	PET	Nylon 6
Tenacity(g/d)				
dry	4.0~5.0	4.5~6.5	4.3~5.5	4.8~6.4
wet	4.0~5.0	4.5~6.5	4.3~5.5	4.2~5.9
Elongation(%)				
dry	25~80	25~60	20~32	28~42
wet	25~80	25~66	20~32	36~52
Modulus(g/d)	40~50	40~50	90~100	50~60
Specific gravity	0.98	0.94	1.38	1.13
Moisture regain(%)	0.25	0.0	0.5	4.5

3.2 Miscibility of Grand P

In order to investigate the dependence of miscibility of polypropylene and cellulosic extract upon time and temperature, polarizing optical microscopy is used. Their results were shown in Photo 1 and 2. Photo 1 showed the polarizing optical micrographs of Grand P at 160 and 278°C. As shown in Photo 1 (a), Grand P was almost solid phase which indicates miscibility of polypropylene and

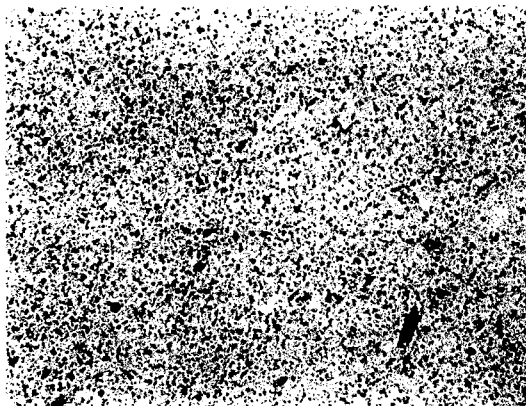
cellulosic extract at 160°C. Photo 1 (b) showed more homogeneous state which may induce miscible state on the spinning process of Grand P. The time dependence of miscibility of polypropylene and cellulosic extract was shown in Photo 2.

As seen in the Photo 2, Miscibility of Grand P was miscible state with time(5 sec., 25 min., 60 min. and 120 min. at 185°C). This meant that modified cellulose has high affinity with polypropylene.

Photo 3 showed the polarizing optical micrographs of Grand P filament. The upper Photo showed 750 multiple magnification and below one showed 1500 multiple magnification. As shown in two

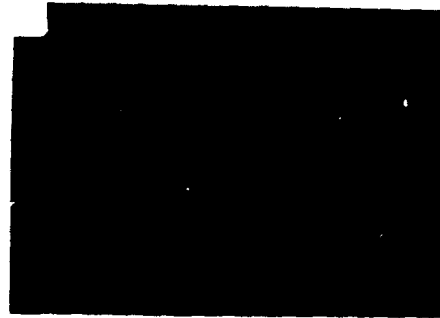


(A) at 160°C



(B) at 278°C

Photo 1. Polarizing optical micrographs of Grand P.



after 5 sec.



after 25 min.

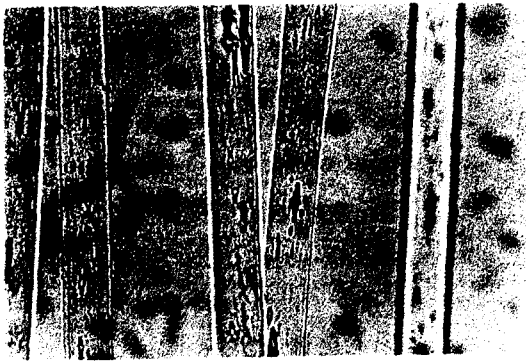


after 60 min

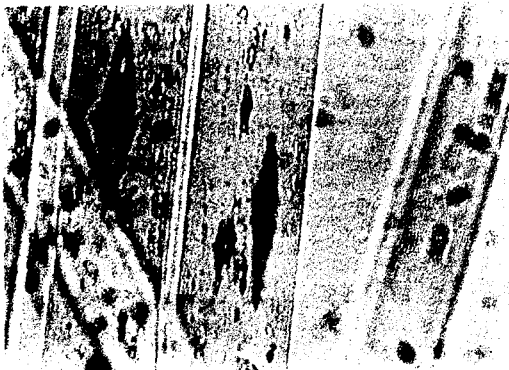


after 120 min

Photo 2. Polarizing optical micrographs of Grand P at 185°C.



(A) ×750



(B) ×1500

Photo 3. Polarizing optical micrographs of Grand P filament.

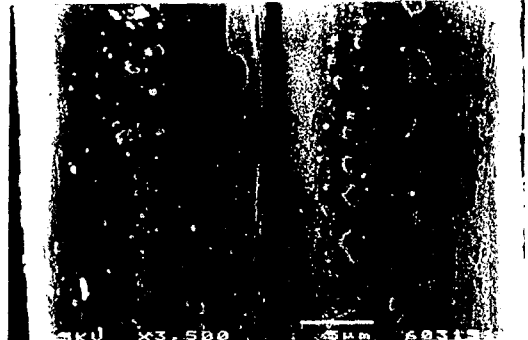
photos, Grand P was homogeneously mixed. Photo 4 showed the polarizing optical micrographs of Grand P filament with 1500 multiple magnification. The upper Photo showed side face and below one showed cross section of filament which etched by oxygen plasma. As shown in two photos, modified cellulose polymers were homogeneously dispersed as a shape of filler.

3.3 Bleaching of Grand P

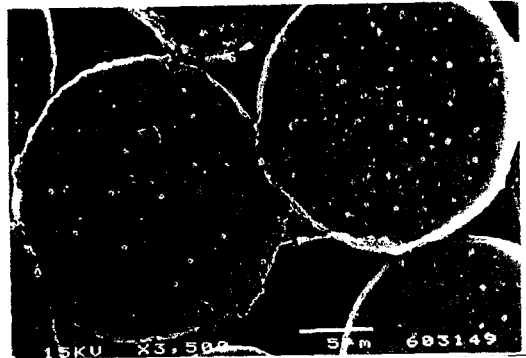
3.3.1 Time dependence of bleaching

Figures 2~7 showed the time dependence of bleaching of Grand P under various concentration of sodium chlorite and bleaching temperature. L^* values of bleached sample with 0.4~1.2% NaClO_2 at 50~100°C were plotted against time. As shown on the figures, L^* value increased with the time

of bleaching where L^* value of untreated sample was 63.



(A) ×3500



(B) ×3500

Photo 4. SEM photographs of Grand P.

Figures showed that bleaching was more effective at high temperature. The result demonstrated that the time required for bleaching was 120 min. at 50°C, 60 min. at 60°C, 30 min. at 70~90°C and 10 min at 100°C. From the result it is believed to be induced that it was effective to bleach Grand P at 100°C for 10 min. in a short time but 70°C for 30 min. was optimum in an economic point of view.

3.3.2 Dependence of bleaching temperature

It is general to bleach cotton fabric at about 90°C when using sodium chlorite. To investigate temperature dependence of bleaching of Grand P, Grand P was bleached in 1% NaClO_2 solution for va-

rious times, ie, 10, 30, 60, 120 min at each temperature. These results were shown in figure 8. L^* value showed a tendency to increase exponentially with temperature, increasing drastically upto 70°C and slowly increasing at above 70°C . It can be deduced that 70°C is optimum in economic point of view except 10 min. of bleaching time. This result indicated that 70°C was optimum temperature to activate NaClO_2 when bleaching Grand P.

3.3.3 Dependence of bleaching concentration

In order to find out optimum concentration of sodium chlorite, Grand P was bleached under the fixed temperature of 70°C and treatment time of 30 min.. Figure 9 showed L^* value with NaClO_2 concentration. As shown in figure 9, L^* value increased with NaClO_2 concentration, and then equilibrated above 0.1 % NaClO_2 concentration. According to these results, the optimum bleaching concentration was 0.1 % sodium chlorite.

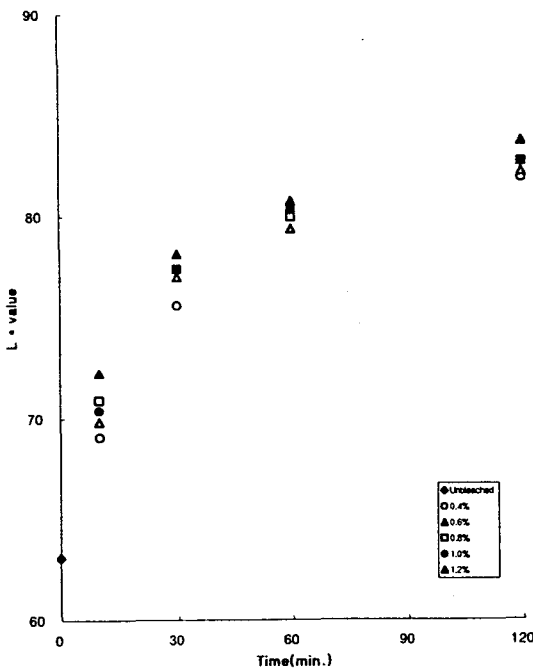


Fig. 2 L^* value of Grand P fabrics bleached at 50°C .

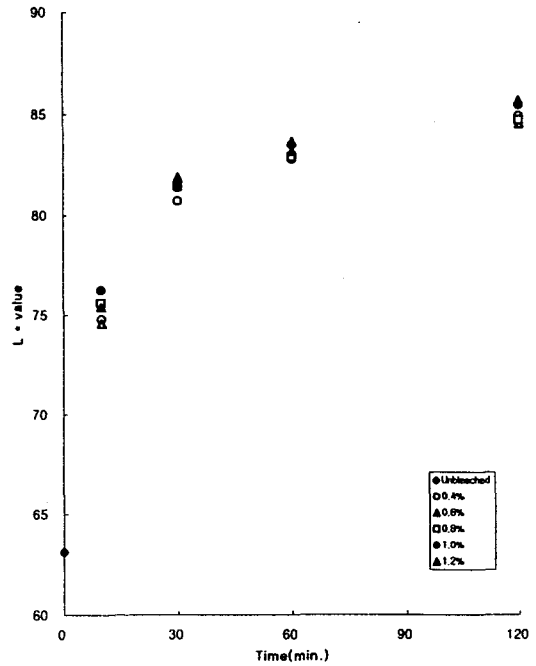


Fig. 3 L^* value of Grand P fabrics bleached at 60°C .

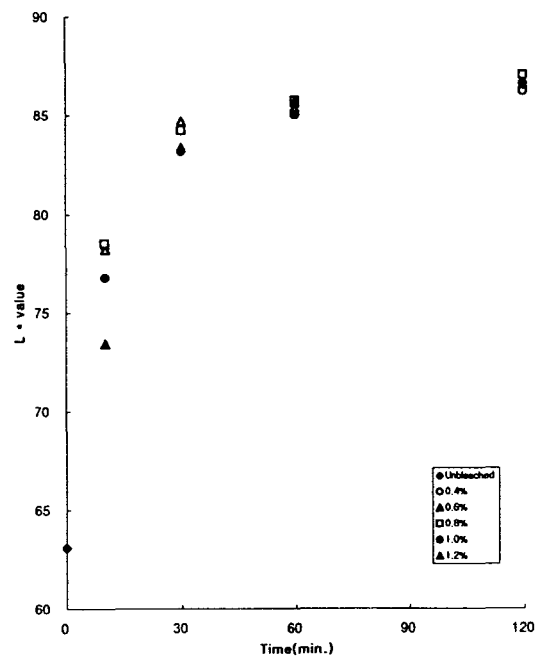


Fig. 4 L^* value of Grand P fabrics bleached at 70°C .

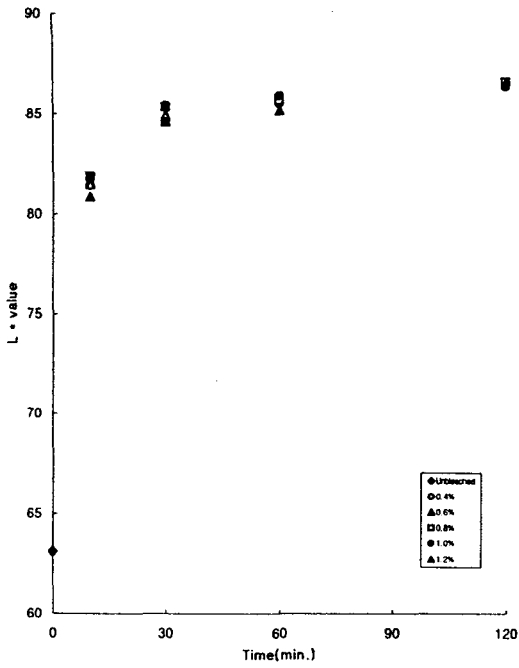


Fig. 5 L* value of Grand P fabrics bleached at 80°C.

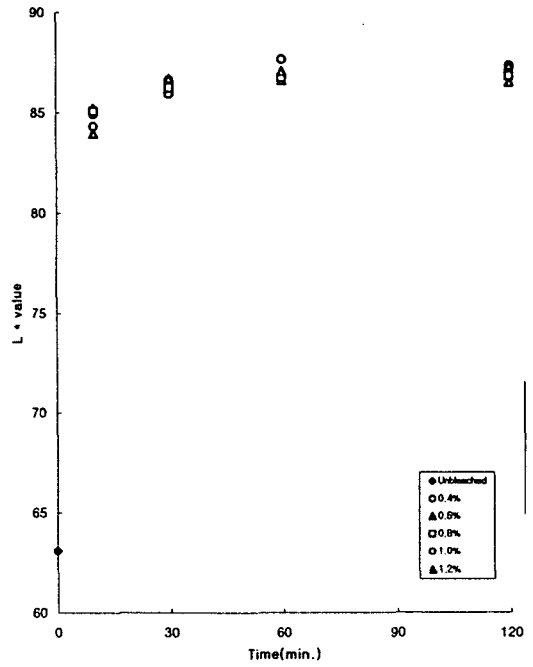


Fig. 7 L* value of Grand P fabrics bleached at 100°C.

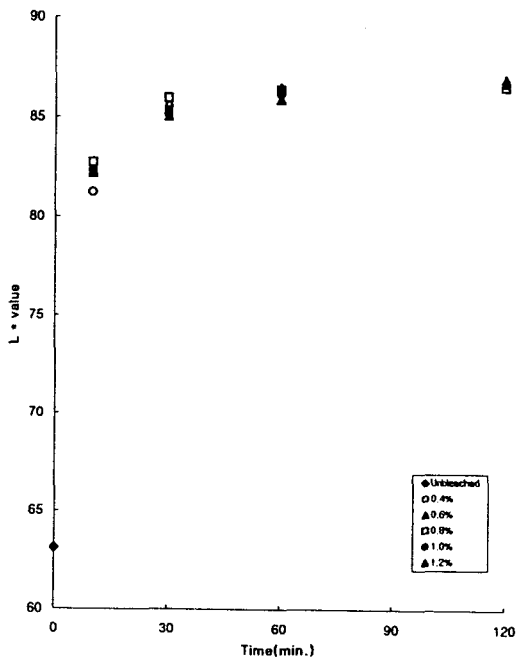


Fig. 6 L* value of Grand P fabrics bleached at 90°C.

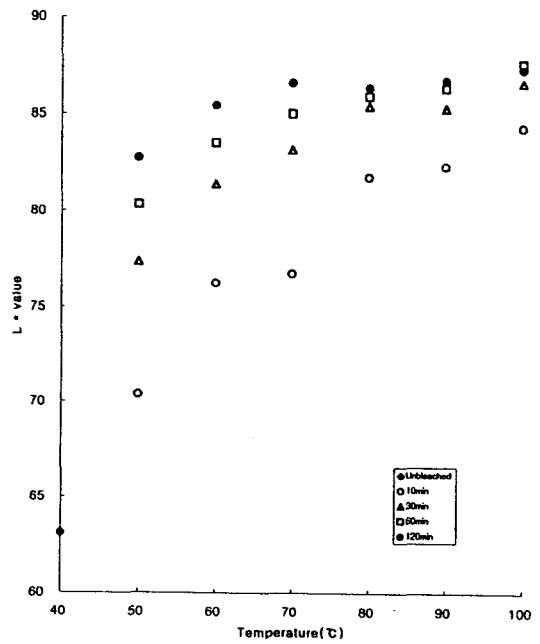


Fig. 8 L* value of Grand P fabrics bleached in 1%NaClO₂ solution.

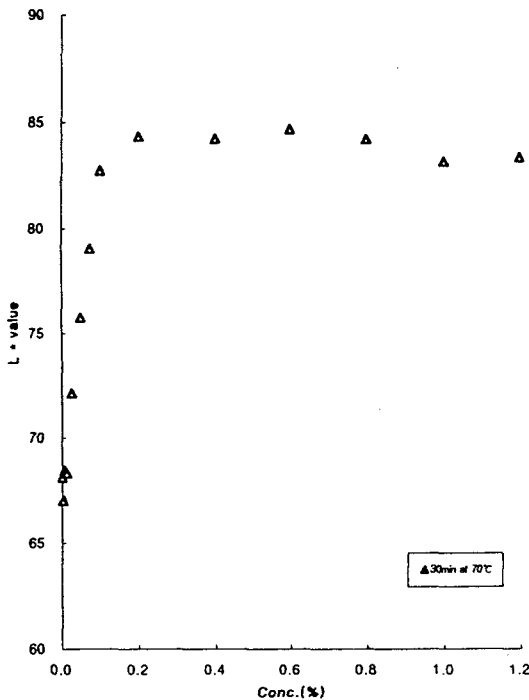


Fig. 9 L* value of Grand P fabrics bleached in a various concentration of NaClO_2 .

3.3.4 Photo of bleaching sample

Photo 5 showed photographs of bleached sample. The treatment condition of each sample was : (A) original sample, (B) treated with 0.1 % NaClO_2 solution (L. R. 1 : 30) at 100°C for 20 min., (C) treated with 0.1 % NaClO_2 solution (L. R. 1 : 30)

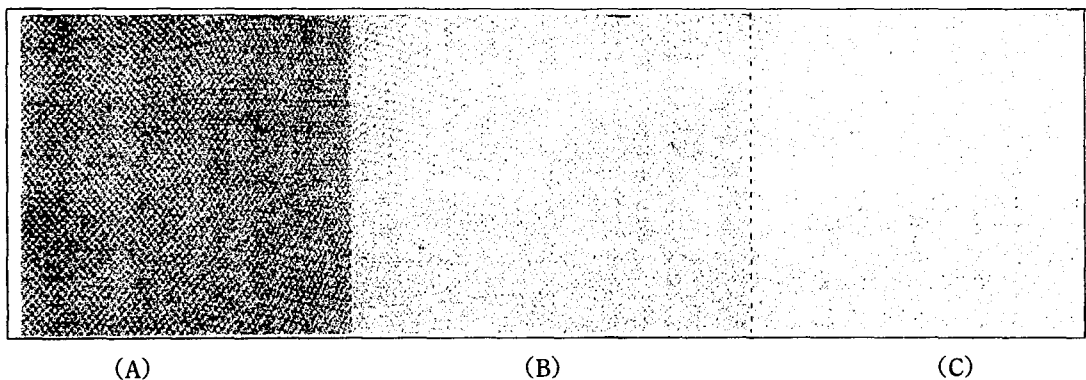


Photo 5. Photographs of Grand P treated with 0.1% NaClO_2 solution. : (A) untreated, (B) treated (30min. at 70°C), (C) treated(120min. at 100°C)

at 100°C for 120 min.. As shown in Photos, untreated sample (A) showed deep grey color, (B) showed light cream color and (C) showed white color. According to these results, samples (B) and (C) showed good result. Considering economic condition, sample (B) was good enough to be reached whiteness standard.

4. Conclusions

To improve dyeability of polypropylene, we prepared modified cellulose polymer as master batch (contain 90% of modified cellulose polymer) and then melt blended with polypropylene.

From results of the polarizing micrographs, the modified polypropylene showed a miscible state. The fabric knitted from Grand P was grey colored like flax. The present work aimed for the standardization of bleaching process of modified polypropylene filament, and from the experimental results, the optimum bleaching condition was 0.1 % NaClO_2 concentration, 70°C and 30 min.

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