Manufacture of Hygroscopic Nylon-6 Fabric by Radiation-grafting of Acrylamide

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Abstract: It was found, under the preirradiation of an electron beam on the nylon-6 fabric, that experimental parameters, such as dose, monomer concentration, immersion time, grafting temperature, and interval time, could have an effect on the grafting yield. Of which, the irradiated dose and the monomer concentration were major parameters for increase of the grafting yield. The radicals produced by irradiation of the electron beam onto the fabric were decayed slowly in the air for 60 min. The grafting reaction of the radicals with acrylamide were found to proceed in aqueous solution during more than several ten minutes. Irradiation of around 20 kGy controlled the grafting yield of the nylon-6 fabric by less than 10%, preserving its original softness. The moisture absorption of the nylon-6 fabric becomes nearly same as a natural cotton. It was found that fixation-ability of the monomer grafted onto nylon-6 fabric was excellent under the washing process with 70°C hot soapy water of 5000 ppm. Also the fixation of dyestuffs dyed onto the fabric could be considerably improved by radiation grafting.

Keywords: Nylon-6 fabric, electron beam, grafting, acrylamide, hydrophilic, dye, fastness

Introduction

Water soluble monomers such as acrylic acid and acrylamide have been grafted onto several kinds of polymers, such as starch, polyethylene, nylon, polyester, polypropylene, cotton, and cellulose, to modify its surface properties to be hydrophilic, resulting in the improvement of moisture absorption, water regain, and anti-electric charge [1-8]. Wherein, the energy sources for grafting monomers onto fabric were ultraviolet rays, gamma rays, plasma, and electron beams. Hydrophilic monomer grafted onto polymer by radiation-technology can also make superabsorbent polymers that are capable of absorbing and holding large amounts of water [1,5].

Electron beam technology has been most recently developed and tested for modification of several kinds of fabrics. Grafting and curing initiated by either ionizing (gamma or electron beam) or non-ionizing (UV) radiation are mechanically similar processes [9,10]. Even though penetration depth of the electron beam is much less than gamma rays, its dose rate is usually several hundred to several thousand times higher than gamma rays, leading to a high production capacity in application fields. UV- and EB-grafting processes are similar except that with UV, in order to achieve satisfactory rates of reaction in reasonable periods of time, photo initiators and/or photosensitisers are required, especially to modify inner properties of fibers.

In modification of fibers or fabrics, the absorbed energy from electron beams or gamma rays should be controlled by as low a value as possible, because they can degrade polymers due to their high beam energy. Especially, even under an exclusion of homopolymerization, the electron beam radiation can initiate preferentially excess grafting yield with high doses through grafting of both the surface and interior of the fabric. The excess grafting yield causes a loss of softness of fabrics. To prevent such excess homopolymerization of monomers onto fabrics, a pre-irradiation method was found to be superior to a post-irradiation one (or direct radiation), but the post-irradiation is particularly attractive for applications [13].

In commercial application of modified fabrics, the most important factor is that the monomers grafted onto the fabrics should not be broken away even after several washing processes, eventually preserving their peculiar
properties for a long time. Unfortunately, studies on the fastness of monomers grafted onto fabrics or fibers are very rare. Several researchers studied the hydrophilic properties for the nylon-6 fabric grafted with acrylic acid [14] or acrylamide [15], wherein Co^{60} rays have been used as an energy source.

In the present work, experimental parameters that give an effect on the grafting yield of acrylamide onto nylon-6 fabric were studied, to eventually minutely control the grafting yield. The morphological structure of acrylamide grafted onto the fabric was investigated. Also, several physical properties, such as moisture absorption, water regain and fixation of the dye, were tested on the grafted fabric.

**Experimental**

**Materials**

Undyed nylon-6 fabric with white color, which was supplied from Dongyang Dyeing Co., Ltd., was washed with 1% aqueous sodium hydroxide for five hours to clean possible contaminants in the fabric and dried under a vacuum atmosphere. The cleaned nylon-6 fabric was stored in a desiccator with silica absorbent. Acrylamide with reagent grade (Junsei Co., Ltd.) was used without further purification. Neutral-soap powder was used to test the fastness of the monomer grafted onto the fabric.

**Experimental Apparatus and Procedure**

The energy source for grafting of acrylamide onto the nylon-6 fabric was an electron beam that was generated from a high voltage accelerator (ELV-0.5, BINP) with maximum power and beam current of 25 kW and 40 mA, respectively. Irradiated doses were controlled by varying both conveyer speed and the beam current. Nylon-6 fabric for irradiation was mounted on an aluminum plate that was transported by the conveyer with speeds of 1 to 6 cm/s. For dose measurement according to ISO/ASTM 51650, CTA film with 15% triphenylphosphate as additive and UV spectrophotometer (UV-1201, Shimadzu Co., Ltd.) were used.

To graft acrylamide onto the nylon-6 fabric according to the preirradiation method, nylon-6 fabric pretreated with 1% aqueous sodium hydroxide, as mentioned above, was irradiated by an electron beam and then immersed in an aqueous acrylamide solution for a set period of time. Finally, the grafted fabric was washed with running water to remove an ungrafted monomer, and then dried by 50°C hot air. Control of the grafting yield was accomplished by varying several experimental parameters: absorbed dose, concentration of aqueous acrylamide, immersion time in solution, and interval time between irradiating and immersing. Wherein, representative immersion time and interval time were 30 min and 2 min, respectively.

**FT-IR Spectrophotometer**

Several kinds of chemical bonds of the monomer grafted onto the fabric were confirmed by the FT-IR spectrophotometer (FTS 3000MX, Bio-Rad Co., Ltd.) over the range of 500~4000 cm^{-1}. To prepare samples for observation of IR spectra, the nylon-6 fabric grafted with different acrylamide contents as well as an ungrafted sample were dissolved on the formic acid and then recrystallized from the solution by casting into films on aluminum foil.

**Grafting Yield, Moisture Absorption, and Water Regain**

Grafting yield for the grafted fabric, which was already washed by running water after being grafted during the preirradiation process, was determined by the percentage increase in weight using the following equation:

\[
\text{Grafting yield(\%)} = \frac{(M-M_o)}{M_o} \times 100
\]

where Mo and M represent the weights of the ungrafted- and grafted-fabrics, respectively.

The moisture absorption for the grafted nylon-6 fabric, which had been stored for 48 h in a desiccator containing a saturated sodium nitrous acid at room temperature (about 65% of relative humidity), was determined by the percentage increase in weight using the same equation as the grafting yield equation.

Water regain was determined by the percentage increase in weight using the same equation as the grafting yield equation in accordance with the following procedures: first, the dried fabric was immersed in distilled water for 12 h. Next, the sample was centrifuged for 5 min at a rate of 2000 rpm and the weight of the samples before and after the test were measured.

**Fixation Tests of Grafted Acrylamide and Dyed Dyestuff**

The fixation of the monomer grafted onto the nylon-6 fabric was determined by the percentage increase in weight using the following two tests. During the first test, the grafted fabric was washed in 70°C hot water for 30 min at a stirring rate of 120 rpm. Next, the fabric was dried by 50°C hot air and then the dried sample was weighed. During the second test, the fabric prepared during the first step was again washed in 70°C hot soapy water including 5000 ppm of neutral soap powder for 30 min at a stirring rate of 120 rpm. And then, the fabric was washed with cold water to remove all soap powder in the fabric and dried by 50°C hot air and then weighed.
Whether the fixation of the fabric dyed with acidic black stuff of metal complex type (Acid black 172, RIFA Co.,Ltd) could be improved or not was confirmed through grafting of acrylamide onto the dyed fabric. The test was accomplished by performing the following: the samples were washed in 70°C hot water including 5000 ppm neutral soap powder for 30 min at a stirring rate of 120 rpm, and then the chromaticities of the washed water was calculated from Adams-Nikesen's colour difference formula [16] after their transmittances in UV spectra were measured at several wave lengths.

**Colour Measurement of Dyed Fabrics and SEM Analysis of Grafted Fabrics**

The possible colour-changes of the dyed fabrics after electron beam irradiation were observed by use of the computer color matching (CCM, Mac Beth Color eye 3100).

The morphological structures of the grafted nylon-6 fabrics were examined by the SEM micrographs from FE-SEM (Field Emission Scanning Electron Microscope, Hitachi S-4100).

**Results and Discussion**

**Effects of Dose and Acrylamide (AAm) Concentration on Grafting Yield**

Nylon-6 fabric preirradiated by an electron beam was grafted by immersing it into 20% acrylamide solution for 30 min. In Figure 1, grafting yield of the acrylamide grafted onto the nylon-6 fabric increased linearly with the absorbed dose. This result would arise from such facts as the accelerated electron beam could produce radicals on the nylon fabric in proportion to the absorbed dose and eventually the radicals grafted preferentially with acrylamide in the solution. The figure also showed that the solution temperature could give a slightly effect on the grafting yield. Of 24, 40 and 60°C temperatures, 40°C of acrylamide solution gave the highest grafting yield: under 100 kGy dose, the grafting yields were 61, 55.7, and 48.6% at 40, 60, and 24°C, respectively. This result might arise from the fact that a higher temperature in the solution can accelerate a decay rate of radicals as well as the grafting rate of monomer with radicals on the fabric, resulting in the existence of an optimum temperature for maximum grafting yield [17].

Figure 2 indicated that acrylamide concentration in the solution also produced a large effect on the grafting yield, wherein the grafting yield increased linearly up to 20% and, after, it more abruptly increased, resulting in a 56.5% grafting yield at 30% acrylamide. Since the number of radicals produced onto to nylon-6 fabric are constant at a given dose, such a large increase of grafting yield in the range of high concentration may be related to excess homopolymerization between acrylamide molecules [18-20].

**Effects of Immersion Time and Interval Time on Grafting Yield**

Figure 3 shows that the time-period during immersing irradiated fabric into a monomer solution can change the grafting yield. In the figure, the grafting yields increased along with the increase of the immersion time and then leveled off. The time took to reach ultimate grafting yield increased with the acrylamide concentration: for example, with 50 kGy irradiation, the ultimate grafting yields, 3.2, 9.4 and 26.1%, were reached at around 30 min and 60 min for 5-10% and 20% of concentrations, respectively.

Figure 4 showed that interval time, i.e., the period with immersing the irradiated fabric into an acrylamide solution after irradiation of nylon-6 fabric, could cause a significant effect on the grafting yield. As shown in the
figure, as the interval time increased, the grafting yield decreased gradually until 50 min and became negligible over that amount of time. From these results, the radicals generated onto the fabric by an electron beam irradiation were slowly deactivated in the air and could exist on the fabric for a long time.

**Fastness of Acrylamide Grafted onto the Nylon-6 Fabric**  
As mentioned in the experimental method, the grafting yields in Figures 1~4 were measured after the acrylamide grafted onto preirradiated fabric was washed by a cold running water and then dried by an hot air. Fastness of such grafted acrylamide was examined through the two steps of washing tests, which included washing in 70°C of hot water (first step) and then washing in 70°C of soapy water (second step). In Figure 5, acrylamide grafted onto nylon-6 at 50 kGy, where the grafting yield had been controlled by varying immersion times, broke away from the fabric with about 5% decrease in weight during the first-step of washing. But the second step of washing with 70°C of soapy water could not make the grafting yield further decrease. From these results, we can conclude that preliminary washing with only cold running water may be insufficient for removing weakly grafted or homopolymerized acrylamide, but acrylamide left on the fabric after washing with hot water had already bonded strongly with nylon fibers, resulting in a good fastness.

**FT-IR Spectra on the Grafted Fabric**  
To prepare film samples for measuring FT-IR spectra, ungrafted and grafted fabrics were dissolved in formic acid respectively, coated onto aluminum foil, and then dried in a 50°C vacuum oven for 24 h to remove all formic acid. Wherein, the ungrafted acrylamide was almost removed through the first and the second-washing steps. As shown in Figure 6, for the ungrafted fabric, C=O peak in CO-NH group existed at around 1640 cm⁻¹ and -NH peak existed at around 3300 cm⁻¹ and 1540 cm⁻¹.
Figure 7. SEM chromatographs on ungrafted and grafted nylon-6 fabrics (A: ungrafted ; B: 3.5% grafted ; C: 15.2% grafted ; D: 55.7% ; magnification: -1: x70, x50, -2: x3000).

Also, -CH peak in aliphatic group appeared between 3000 and 2800 cm⁻¹. The spectrum for nylon-6 fabric grafted by acrylamide showed nearly the same characteristic peaks as ungrafted fabric, since nylon-6 was made by polymerization of acrylamide monomers. However, the peaks in grafted nylon-6 were much bigger than in ungrafted nylon-6, especially, at around 1645 cm⁻¹(C=O) and 3300~3225 cm⁻¹(-NH₂). This means that acrylamide was grafted onto the nylon-6 fabric.

SEM Micrographs of Grafted Nylon-6 Fabric
As shown in Figure 7, the original nylon-6 fabric had some gaps between webs (A-1) and the surfaces were very smooth (A-2). At 3.6% grafting yield, the gaps between webs slightly decreased (B-1) and a group of polymerized acrylamide was found on the threads (B-2). At 16.2% grafting yield, the groups of polymerized acrylamide widely spread onto the threads (C-2) and the gaps between webs decreased much more (C-2).

Figure 8. Water regain and Moisture absorbance in grafted nylon-6 fabric.

Meanwhile, when acrylamide was being grafted onto the fabric with 55.7% grafting yield, the polymerized acrylamide covered the whole surface of the threads completely. Some parts of the acrylamide layer became cracked (D-2), and the gaps between webs almost disappeared (D-1). This highly grafted fabric became considerably rigid, resulting in the loss of some softness in itself.

Moisture Absorption and Water Regain
To confirm the hydrophilic property on the nylon-6 fabric grafted by acrylamide, two testings, moisture absorption and water regain, were conducted upon the grafted fabric. As shown in Figure 8, the moisture absorption ability of grafted fabric increased linearly with the grafting yield, reaching 7.4% for 55.7% grafting yield from 1.4% of the original nylon-6 fabric. Moisture absorption for untreated cotton was measured by 2.6%, hence, the nylon-6 fabric grafted by about 10% grafting yield was found to be nearly the same ability of moisture absorption as natural cotton. Water regain also considerably increased with grafting yield, reaching 31.7% at 55.7% grafting yield.

Fixation-ability of Dyestuff onto Nylon-6
First, the nylon-6 fabric was dyed with acidic black dyestuff and then the dyed fabric was grafted with acrylamide by preirradiation method. Dyeing fastness of such treated fabric was compared with an ungrafted dyed fabric. In this procedure, the electron beam irradiation with 20 kGy was unlikely to change the chromaticity of the dyed fabrics as indicated in Table 1. Wherein, The $\Delta L^*, \Delta a^*$, and $\Delta b^*$ represent value differences between dyed nylon-6 fabric and undyed one in the light-dark axis, in the red-green axis, and in the blue-yellow axis, respectively. And, the $\Delta E'$ is calculated by the equation:

$$\Delta E' = \sqrt{\left(\Delta L^*\right)^2 + \left(\Delta a^*\right)^2 + \left(\Delta b^*\right)^2}.$$
Table 1. Effect of Electron Beam Irradiation on Colour Change of Dyestuff Dyeed onto Nylon-6 Fabric

<table>
<thead>
<tr>
<th>Nylon-6</th>
<th>Colour differences</th>
<th>ΔK*</th>
<th>ΔL*</th>
<th>Δa*</th>
<th>Δb*</th>
<th>ΔL*</th>
</tr>
</thead>
<tbody>
<tr>
<td>EB-untreated</td>
<td></td>
<td>72.96</td>
<td>0.95</td>
<td>-3.85</td>
<td>-72.857</td>
<td></td>
</tr>
<tr>
<td>EB-treated</td>
<td></td>
<td>72.61</td>
<td>0.98</td>
<td>-375</td>
<td>-72.509</td>
<td></td>
</tr>
</tbody>
</table>

Figure 9. Changes of chromaticities of soaping water after soaping the dyed nylon-6 fabrics grafted and ungrafted by acrylamide.

As shown in Figure 9, chromaticity of washing water for ungrafted fabric increased largely with soaping time due to dissolving the stuffs into washing water, whereas the chromaticity of washing water for grafted fabric increased much less during initial times and the stuffs onto the fabric was not nearly dissolved into the washing water after 30 min. These results showed that fixation of dyestuff onto nylon-6 fabric could be improved through grafting of acrylamide onto the dyed fabric with electron beam radiation technology.

Conclusions

1. Grafting yield can be controlled mainly by several experimental parameters such as: absorbed dose, monomer concentration, interval time, and immersion time. Of these, dose and monomer concentration can give a large effect on the grafting yield.
2. Radicals generated onto the nylon-6 fabric by an irradiated electron beam were found to accomplish grafting reaction with acrylamide in aqueous solution during more than several ten minutes.
3. Also, it appeared that the radicals on the fabric decayed slowly in the air and the grafting yield decreased along with an increase of interval time, accomplishing the grafting reaction even at more than 60 min after the fabric being irradiated by electron beam.
4. Acrylamide grafted onto the nylon-6 fabric could break away by around 5% through a washing process with 70°C hot water, but the acrylamide existing on the fabric after such washing process was strongly chemically combined with the nylon polymer, resulting in its excellent fixation.
5. The grafted acrylamide can change the hydrophobic nylon-6 fabric to a hydrophilic one, turning out a moisture absorbability for the nylon-6 fabric with 10% grafting yield that can could reach a natural cotton’s one, and also its water regain was largely improved.
6. Fixation of dyestuff can be considerably improved by grafting acrylamide onto the dyed nylon-6 fabric with no further change of fabric colour by irradiation of an electron beam.

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References

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