Fibrillation Tendency of Cellulosic Fibers, Part 6: Effects of Treatments with Additive Polymers

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ABSTRACT: The influences of the treatments with various polymers on fibrillation and abrasion resistances of lyocell materials were investigated with respect to the type of polymer, the polymer concentration, and the drying temperature. Fibril number, generated with agitation using ball-bearings (FN_{ball}), was decreased with increasing the concentration of aminofunctional polysiloxane because of reduction in water retention capacity (WRV) in fibers. The never-dried lyocell fiber showed smaller decrease in FN_{ball} because of its higher WRV when compared to dried fibers. The treatment with aminofunctional polysiloxane enhanced not only the fibrillation resistance but also abrasion resistance, which was indicated as rotation number of abrasive bar in the abrasion test (RN_{abr}). No fibrillation was obtained in the fiber treated with 10 g/L aminofunctional polysiloxane at 120°C for 20 min, while the fibers treated at 60 and 170°C for 15 min were fibrillated in the agitation and abrasion tests. The addition of secondary polyethylene derivative also reduced the fibrillation tendency of lyocell; however, the extent of the reduction was lesser when compared with aminofunctional polysiloxane. The treatments with polyacrylate, polyurethane, and polyisocyanate derivatives improved the fibrillation resistance in lyocell fabrics, while fiber abrasion resistance was not significantly improved by the treatment with those additives, except in polyisocyanate. J Appl Polym Sci 101: 4140–4147, 2006

Key words: fibers; fibrillation; lyocell; silicones; swelling

INTRODUCTION

Lyocell is the first in a new generation of cellulosic fibers derived from sustainable pulpwood.[1] The development of lyocell was driven by the desire for a cellulosic fiber that cost performance was improved compared to viscose rayon. The other main reason was the continuing demands for industrial processes to become more environmentally responsible and utilize renewable resources as their raw materials. The lyocell was originally conceived as a textile fiber. It is fabricated into different fabric weights, and the fabrics can be engineered to produce a wide range of drapes, handles, and unique esthetic effects. Though the lyocell fiber has an excellent quality compared to other cellulosic fibers, it is easy for fibrillation to occur, which can be defined as the longitudinal splitting of a single fiber filament into microfibers. The fibrillation not only offers completely new possibilities to produce supersoft, voluminous peach-skin handle effects, but also makes unacceptable esthetic surface of fabrics. The control of the fibrillation behavior e.g., by new spinning technology,[2] a treatment with a crosslinking agent[3,4] or enzyme treatments,[5] both to increase and decrease fibrillation, is a major area of continuing research.

Many researches on controlling fibrillation discussed change in fiber structure. In wet-treatment processes, individual fibrils are split up from the fiber surface because of the fiber swelling and simultaneous mechanical strain.[6] We have investigated the effect of fiber swelling on fibrillation tendency of various cellulosic fibers in aqueous or ethanol solutions containing swelling agents e.g., alkali metal hydroxides or water.[7,8] The degree of fiber swelling increased with increase in concentration of the swelling agents, temperature, and size of the hydrated metal cation accompanying the increment in fibrillation tendency. The fibrillation tendency was evaluated with two specific parameters defined as fibrillation stability and fibrillation sensitivity to swelling agent. It was found that the lyocell fiber had the lowest fibrillation stability, and the highest fibrillation sensitivity to the swelling agents and heat, resulting in the highest fibrillation tendency.

An aqueous sodium hydroxide solution is the most frequently used activating agent for cellulose. Its effect on the structure, morphology, and reactivity of cellulose has been widely reviewed and has recently been

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TABLE I
Additive Polymers and Their Basic Components

Abbrev.	Component		Trade name
Polym1	Amino functional polysiloxane microemulsion	Softener	Siligen® SIN
Polym2	Amino functional polysiloxane microemulsion in water	Softener	Siligen® SID
Polym3	Amino functional polysiloxane in water/solvent	Softener	Siligen® SIA
Polym4	Amino functional polysiloxane emulsion in water	Softener	Siligen® SIO
Polym5	Secondary polyethylene dispersion	Smoothing ag.	Siligen® VN
Polym6	Polyacrylate dispersion	Binder	Helizarin® binder FWT 2003
Polym7	Anionic polyurethane dispersion	Binder	Perapret® PU neu
Polym8	Anionic polyacrylate dispersion	Binder	Perapret® HVN
Polym9	Modified aliphatic polyisocyanate	Hardener	Astacin® haerter CN

studied.[9] We formerly reported on fibrillation tendency of cellulosic fibers pretreated in different type of aqueous alkalis, at different concentrations.[10,11] The fibrillation of lyocell fiber was minimized by the pretreatment in 5 mol/L NaOH and KOH solutions, where the parameters indicating fiber properties, e.g., alkaline retention value, water retention value (WRV), and weight loss in fiber, were constant. These results and scanning electron microscopic images suggested the reorganization of macrofibrils.

Use of crosslinking agent during the fiber manufacturing process is a safe method for controlling and reducing the fibrillation of lyocell fibers. This is done by an additional step during the manufacturing process by means of chemical crosslinking in the spinning-moist fiber state.[12] This crosslinking prevents the fibrillation tendency, without having an impact neither on the following fall typical for lyocell or on the elegant handle of the fabric. However, the effectiveness of the crosslinking in the moist fiber cannot satisfy the consumer's request. In the previous studies, we reported that the fibrillation of lyocell was inhibited by crosslinking treatments of dried fibers with 2,4-dichloro-6-hydroxy-1,3,5-triazine.[13] Treatment with conventional crosslinking agent 1,3-dimethylol-4,5-dihydroxyethylene urea and 1,3-dimethyl-4,5-dihydroxyethylene urea, which are the most widely applied to cotton to obtain good durable press properties, also reduced fibrillation tendency, and addition of silicone softener caused no fibrillation in lyocell fabric.[14] The present work is a follow-up of the former work, to understand the effect of different additive polymer in treatments on the fibrillation tendency of lyocell materials.

EXPERIMENTAL

Materials

Nonspin-finished (NSF), spin-finished (SF), and never-dried (ND) lyocell staple fibers were supplied by Lenzing AG, Austria. The titer of the fibers was 1.3 dtex, and the length was 38 mm. Nine additive polymers and a wetting agent (Kieralon-TX1576) were provided by BASF in Germany and used for experiments. Chemical components of the polymers are given in Table I. Plane woven fabrics of lyocell fiber, treated with additive polymer polym6–polym9, were also offered by BASF. The woven fabrics were composed of SF fibers.

Treatments with additive polymers

The lyocell fibers were immersed in a solution containing a given amount of polym1–polym5 and 1 g/L acetic acid (60% w/w aq.). After excess solution was removed by using a vacuum filter or a centrifuge to obtain wet pickups of 100% w/w, the fibers were dried in the conditions shown in Table II. Methods Nos.1, 2, and 3 are control treatments in which lyocell fibers are untreated. The lyocell woven fabric was treated in a similar manner to the fibers. The fabric was immersed in a solution containing a given amount of polym6–9, wetting agent (2 g/L), and 0.5 g/L acetic acid (60% w/w aq.). After excess solution was removed by passing through squeeze rolls, the fabric was dried at 120°C and cured at 170°C (air temperature) for 40 s. The wet pickups were 75% w/w. The conditions in treatments are given in Table II.

Measurements

The fibers and fabrics treated with the additive polymers were agitated in water at ambient temperature using ball-bearings with tumbling, according to the previous work.[7] After the agitation, fibers were extracted from the fabrics and the degree of the fiber fibrillation was assessed by counting fibril numbers on 0.38 mm segments, using an optical microscope (FN_{ball}). Five fibers were used to obtain a mean value for each sample fiber.

The fibers were abraded by another method, using an abrasive metal bar with rotation.[13] After 50-cycle rotation of the bar, fibrils generated over 0.38 mm length of fiber were counted (FN_{abr}). The number of rotations of the bar was also recorded when the fiber was torn (RN_{abr}). Ten fibers were measured, to obtain

TABLE II
Various Conditions in Treatments of Lyocell Fibers with Additive Polymer

Method no.	Material[a]	Additive polymer (g/L)									Drying temperature (°C)	Drying time (min)	Curing temperature (°C)	Curing time (s)
		Polym1	Polym2	Polym3	Polym4	Polym5	Polym6	Polym7	Polym8	Polym9				
1	NSF													
2	SF													
3	ND													
4	NSF	1									60	240		
5	SF	1									60	240		
6	ND	1									60	240		
7	NSF	2									60	240		
8	SF	2									60	240		
9	ND	2									60	240		
10	NSF	5									60	240		
11	SF	5									60	240		
12	ND	5									60	240		
13	NSF	10									60	240		
14	SF	10									60	240		
15	ND	10									60	240		
16	NSF	10									120	20		
17	NSF		10								120	20		
18	NSF			10							120	20		
19	NSF				10						120	20		
20	NSF					10					120	20		
21	NSF	10									170	15		
22	NSF					10					170	15		
23	fabric													
24	fabric						25				120		170	40
25	fabric							25			120		170	40
26	fabric								25		120		170	40
27	fabric									3	120		170	40
28	fabric						50				120		170	40
29	fabric							50			120		170	40
30	fabric								50		120		170	40
31	fabric									5	120		170	40
32	fabric						25			3	120		170	40
33	fabric							25		3	120		170	40
34	fabric								25	3	120		170	40
35	fabric						50			5	120		170	40
36	fabric							50		5	120		170	40
37	fabric								50	5	120		170	40

[a] NSF, SF, and ND are nonspin-finished, spin-finished, and never-dried fibers.

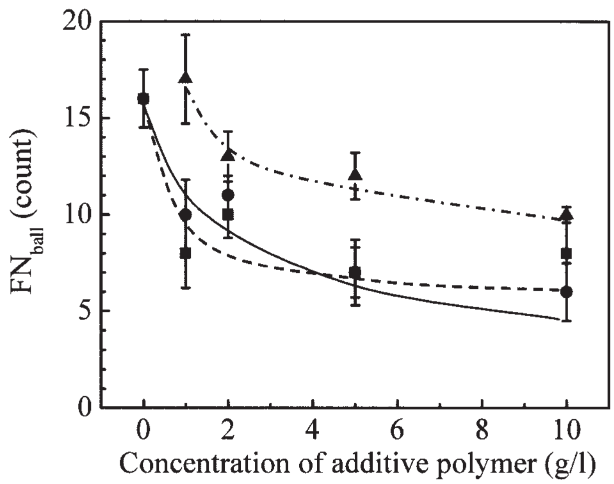

Figure 1 Plots of fibril number induced using ball-bearings of NSF (•), SF (■), and ND lyocell fibers (▲) treated with polym1 against the concentration of polym1. The fibers were treated according to method nos.1–15.

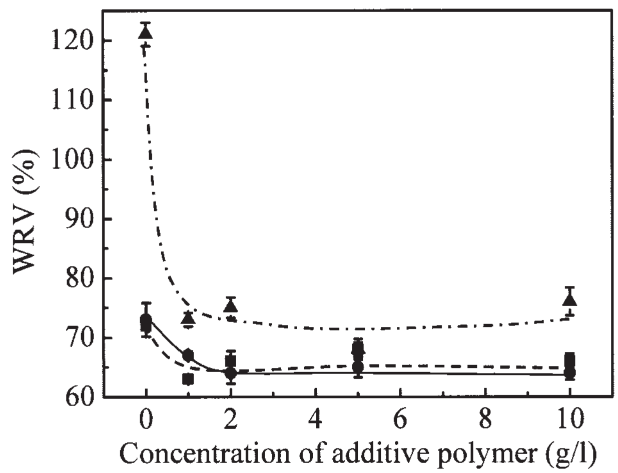

Figure 2 Plots of WRV of NSF (•), SF (■), and ND lyocell fibers (▲) treated with polym1 against the concentration of polym1. The fibers were treated according to method nos.1–15.

mean values of FN_{abr} and RN_{abr}. Statistical analyses of results were conduced at a 0.05 level of significance.

WRV in fibers and fabrics was measured by centrifugal method.[8] The measurement was conducted four times, to get a mean value.

RESULTS AND DISCUSSION

The fibrillation tendency of fibers was evaluated, by counting the number of fibrils generated owing to a mechanical abrasion, using metal balls in water. The fibril number of three different lyocell fibers treated with additive polymer, in which the main component is aminofunctional polysiloxane (polym1), is plotted against the concentration of polym1 in Figure 1.

FN_{ball} in NSF and SF are strikingly decreased from 16 to 8 counts by addition of 1 g/L or 2 g/L polym1, while FN_{ball} slightly decreases from 8 to 6 counts, when larger amount of polym1 than 2 g/L is added. The result indicates that the fibrillation resistance is enhanced by addition of aminofunctional polysiloxane, and the addition of small amount of polym1 decreases ~50% fibrillation. The reduction in fibrillation is caused by coverage of fiber surface with the polymer, resulting in the decrement in fiber/fiber friction. As compared to NSF and SF, the higher number of fibrils is induced in ND fiber treated with polym1.

For further discussion, WRV, which is an indicator of liquid water accessibility, was measured, and the relationship between concentration of the polym1 and WRV in the treated fibers is shown in Figure 2.

WRV in ND treated with polym1 is larger than those in NSF and SF, at any concentration. The higher degree of fiber swelling in ND leads to the higher FN_{ball}. The ND lyocell fiber has high pore volume and large pore size when compared to dried fibers NSD and SF.[15] The porous structure in ND changes with drying treatment, resulting in collapse of pores, and ND loses its large accessibilities of water and chemical substances.[16] The NSF and SF are ND fiber-dried, without and with spin-finishing. This means that NSD and SF were dried totally twice when they were treated with polym1, while ND was dried once. The similar WRVs in ND treated with 1 g/L polym1 (73%), untreated NSF (73%), and untreated SF (72%) indicate that dry treatment also influences the water accessibility of lyocell fiber.

The influences of polymer type, used in the treatments on fibrillation tendency, evaluated using metal balls, abrasion resistance estimated using abrasive material, and WRV are given in Figures 3, 4, and 5.

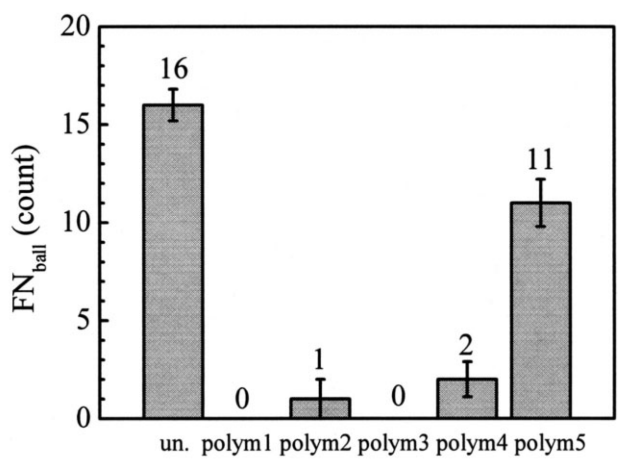

Figure 3 Effect of polymer type on fibril number induced using ball-bearings of NSF lyocell fiber, when treated with polym1–polym5. The abbreviation un. indicates untreated lyocell fiber. The fibers were treated according to method nos.16–20.

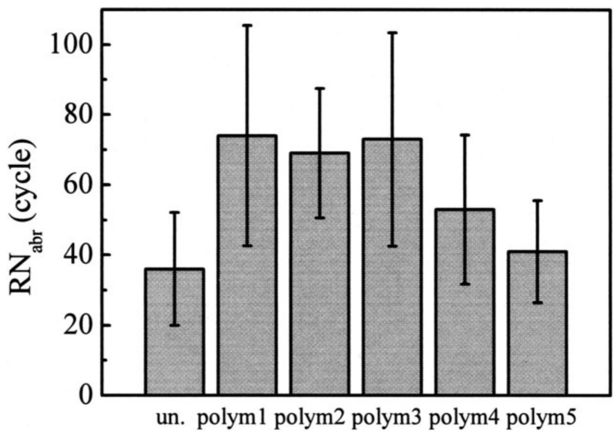

Figure 4 Effect of polymer type on RN_{abr} at break point of fiber for NSF lyocell fiber, when treated with polym1–polym5. The abbreviation un. indicates untreated lyocell fiber. The fibers were treated according to method nos.16–20.

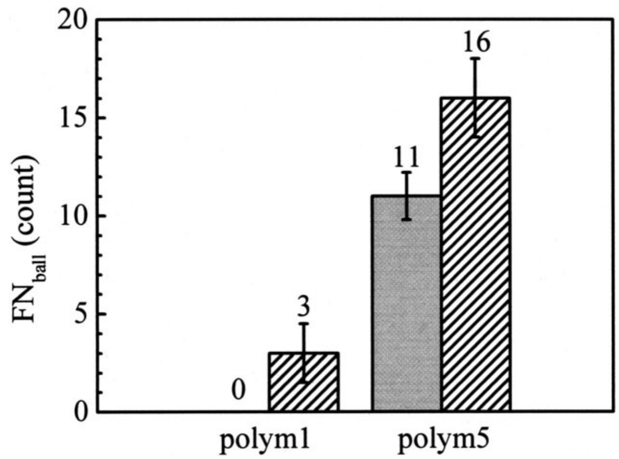

Figure 6 Effect of curing temperature on fibril number induced using ball-bearings of NSF lyocell fiber, when treated with polym1 or polym5. The fibers were cured at 120 (▭) and 170°C (▨), according to method nos.16, 20, 21, and 22.

FN_{ball} is decreased from 16 to 0 counts by treatment with 10 g/L polym1 and polym3. FN_{ball} is reduced from 16 to 1 or 2 counts, by treatment with polym2 or polym4, while the treatment with polym5 lowers FN_{ball} from 16 to 11 counts (Fig. 3). RN_{abr} is increased by treatments with polym1–polym3, while the influence of the treatment with polym5 is not significant (Fig. 4). The water accessibility in lyocell fiber is decreased by treatments with additive polymers though the difference of the decrement among five polymers is not meaningful (Fig. 5). Resultantly, the treatments with aminofunctional polysiloxane (polym1–polym4) heighten the fibrillation resistance of lyocell fiber to a greater extent than those with secondary polyethylene (polym5). The better performance of aminofunctional polysiloxane as a fibrillation-retardant may be due not only to reduction in WRV but also its chemical property, decreasing fiber/fiber friction when compared to polyethylene derivative.

The effects of drying temperature in treatment with polym1 and polym5 on fibrillation tendency and WRV in lyocell fiber are shown in Figures 6 and 7.

FN_{ball} of the fiber treated with polym1 and polym5 at 120°C is lower than that at 170°C, while WRV in the fiber treated at 120°C is higher than that at 170°C. The polymer might penetrate the inner site of the fiber at higher temperature or longer time, which reduces intermacrofibril friction force and increases the fibrillation tendency. The inner penetration might also lead to the decrease in water accessibility in fiber. Further experiments are required to clarify the effect of drying

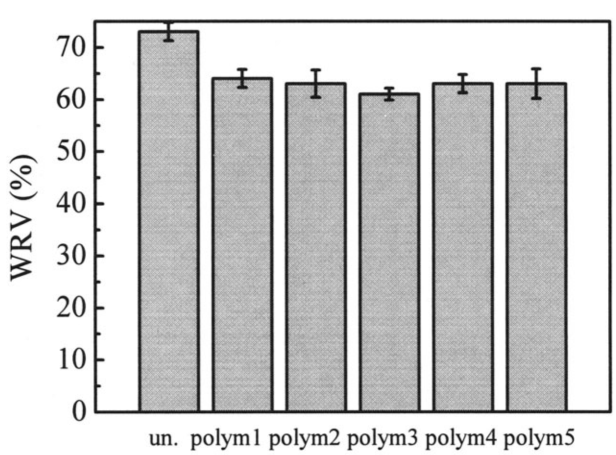

Figure 5 Effect of polymer type on WRV of NSF lyocell fiber, when treated with polym1–polym5. The abbreviation un. indicates untreated lyocell fiber. The fibers were treated according to method nos.16–20.

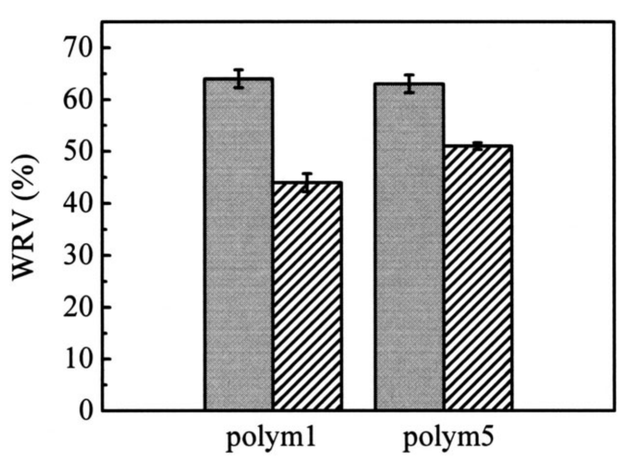

Figure 7 Effect of curing temperature on WRV of NSF lyocell fiber, when treated with polym1 or polym5. The fibers were cured at 120 (▭) and 170°C (▨), according to method nos.16, 20, 21, and 22.

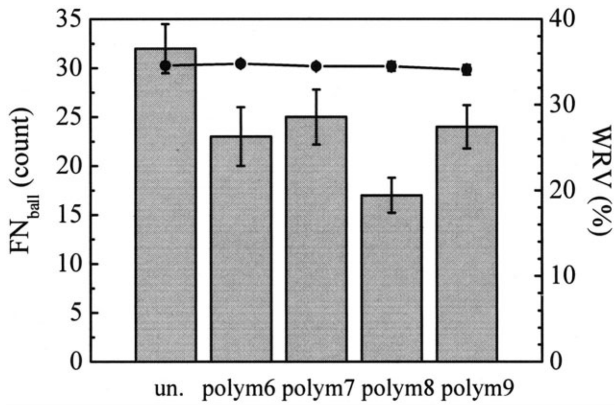

Figure 8 Effect of polymer type on fibril number induced using ball-bearings (▭) and WRV (•) of fabric, when treated with polym6–polym9. The concentrations of polym6–polym8 and polym9 were 25 and 3 g/L, respectively. The fibers were treated according to method nos.23–27.

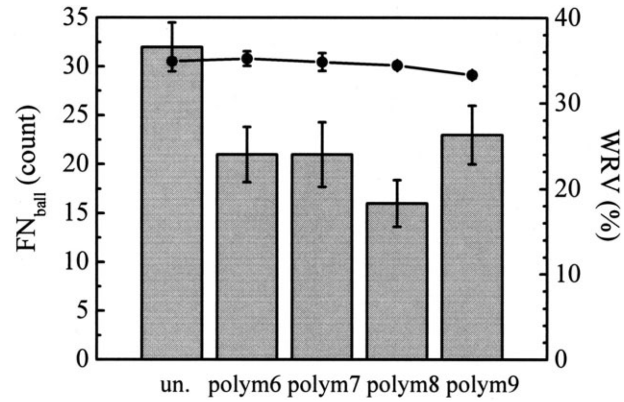

Figure 10 Effect of polymer type on fibril number induced using ball-bearings (▭) and WRV (•) of fabric, when treated with polym6–polym9. The concentrations of polym6–polym8 and polym9 were 50 and 5 g/L, respectively. The fibers were treated according to method no.23 and nos.28–31.

temperature in the treatment with additive polymer on the fibrillation tendency.

The polym1–polym5 are silicone and polyethylene derivatives, which are generally used as softener and as smoothing agent in textile finishing. To investigate the influence of other types of polymer on the fibrillation tendency, the lyocell woven fabric was treated with polyacrylate, polyurethane, and polyisocyanate derivatives, which are used as binders. FN_{ball}, WRV, FN_{abr}, and RN_{abr} in the fabrics were measured, and the results are shown in Figures 8 and 9.

FN_{ball} is decreased with the treatment using polym6–polym9. However, the treatments retard the fibrillation to a lesser extent in comparison to those with aminofunctional polysiloxanes though the higher concentration of polym6–polym9 is used in the treatments. The fibrillation tendency of lyocell is improved by treatments with binders to a less extent than those with softener and smoothing agent, in the experimental conditions used here. The differences between FN_{ball} and WRV among the polymers, except in FN_{ball} with polym8, are not significant. WRV in untreated lyocell fabric is not changed by the treatment with any additive polymers of binders and hardeners. WRV in untreated fabric is 34.6%, which is rather small as compared with that in the untreated fiber (73%); thus, the change in liquid water accessibility is not obvious and does not affect the fibrillation tendency significantly. Only the addition of polyisocyanate (polym9) enhanced RN_{abr}, while no significant change in FN_{abr} and RN_{abr} occurs among the fabric treated with and without polymers (Fig. 9). The polym9 that has reactive isocyanate groups can crosslink the cellulose, resulting in the increment in the abrasion resistance.

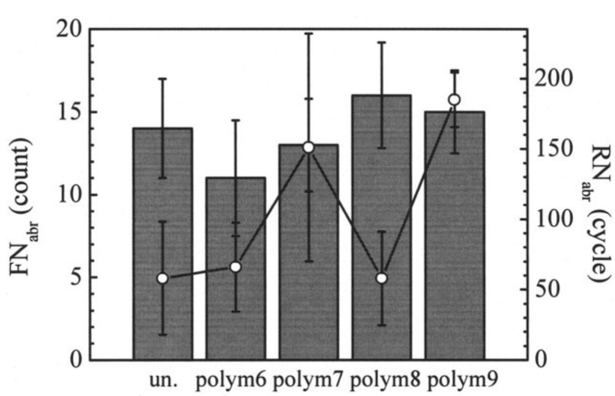

Figure 9 Effect of polymer type on fibril number induced using abrasive bar (▭) and rotation number (○) of fabric, when treated with polym6–polym9. The concentrations of polym6–polym8 and polym9 were 25 and 3 g/L, respectively. The fibers were treated according to method nos.23–27.

The influences of the polymer type used in the treatments on fibrillation tendency and abrasion resistance, when larger amount of the polymer (50 g/L) is used, are given in Figures 10 and 11.

There is no striking difference of FN_{ball} WRV and FN_{abr} between the treatments with 25 and 50 g/L polymers. RN_{abr} of the fiber treated with polym9 decreases with increasing the concentration of the polymers from 185 to 30 cycles. The decrease in RN_{abr} with polym9 may be owing to increase in the brittleness of fiber caused by over-reaction, at the higher concentration.

We reported in a previous study[14] that the treatment using a mixture of crosslinking agent and silicone derivatives markedly enhanced fibrillation resistance. The application of crosslinking agent and some additive polymer is of great interest to control fibrillation. In Figures 12, 13, 14, and 15, the effect of the

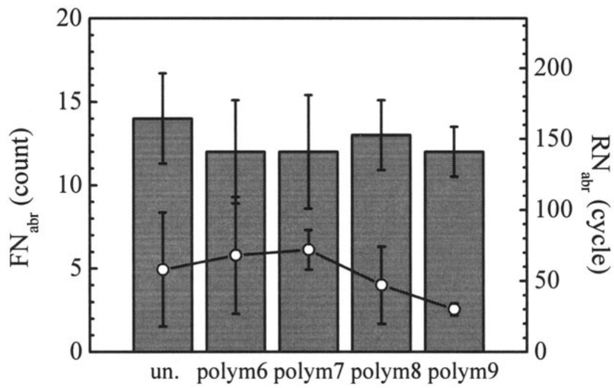

Figure 11 Effect of polymer type on fibril number induced using abrasive bar (▭) and rotation number (○) of fabric, when treated with polym6–polym9. The concentrations of polym6–polym8 and polym9 were 50 and 5 g/L, respectively. The fibers were treated according to method no.23 and nos.28–31.

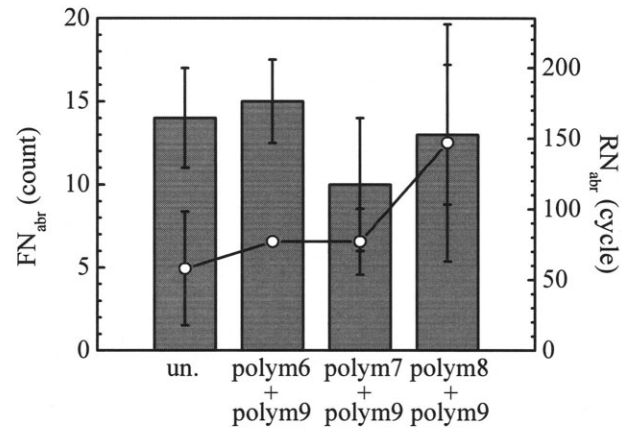

Figure 13 Effect of polymer type on fibril number induced using abrasive bar (▭) and rotation number (○) of fabric, when treated with a mixture of polym9 and polym6–polym8. The concentrations of polym6–polym8 and polym9 were 25 and 3 g/L, respectively. The fibers were treated according to method no.23 and nos.32–34.

treatment of lyocell fabric with a mixture of polym9, which has reactive isocyanate groups, and another polymer on the fibrillation resistance and the abrasion resistance are shown.

FN_{ball} in the fabric treated with 25 g/L polym8 and 3 g/L polym9 is 14, while that with only 25 g/L polym8 is 17. No substantial difference of FN_{ball}, WRV, and FN_{abr} is observed between the fibers treated using the polymer solutions, with and without polym9. The influence of the polymer concentration on the fibrillation and the abrasion resistances is also not significant. RN_{abr} is increased by the treatment with the mixture of polym8 and polym9 in comparison to that with polym8 alone.

CONCLUSIONS

In the present study, the fibrillation tendency of lyocell fiber and the fabric treated with various additive polymers was investigated, and the influences of the treatment conditions, such as the polymer type, the concentration, the curing temperature, the curing time and the mixture of two different polymers on the fibrillation resistance, and the abrasion resistance, were discussed. The fibrillation was retarded with the treatment, especially using small amount of aminofunctional polysiloxane, accompanied with the decrease of liquid water accessibility. The fibrillation tendency of ND fiber was improved to a lesser extent

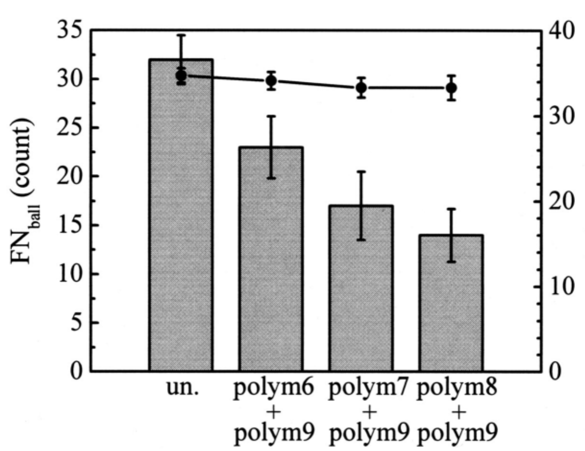

Figure 12 Effect of polymer type on fibril number induced using ball-bearings (▭) and WRV (•) of fabric, when treated with a mixture of polym9 and polym6–8. The concentrations of polym6–polym8 and polym9 were 25 and 3 g/L, respectively. The fibers were treated according to method no.23 and nos.32–34.

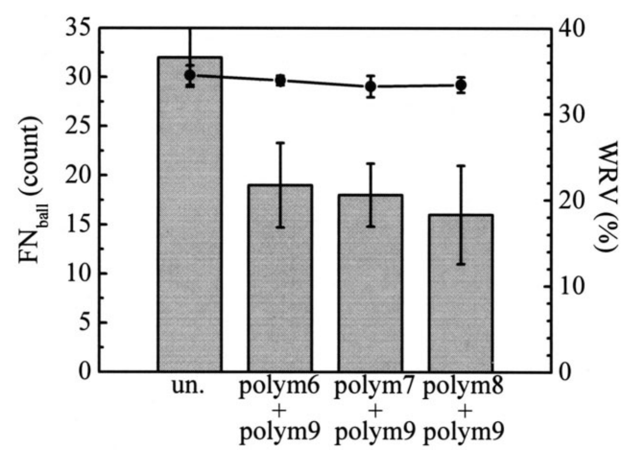

Figure 14 Effect of polymer type on fibril number induced using ball-bearings (▭) and WRV (•) of fabric, when treated with a mixture of polym9 and polym6–polym8. The concentrations of polym6–polym8 and polym9 were 50 and 5 g/L, respectively. The fibers were treated according to method no.23 and nos.35–37.

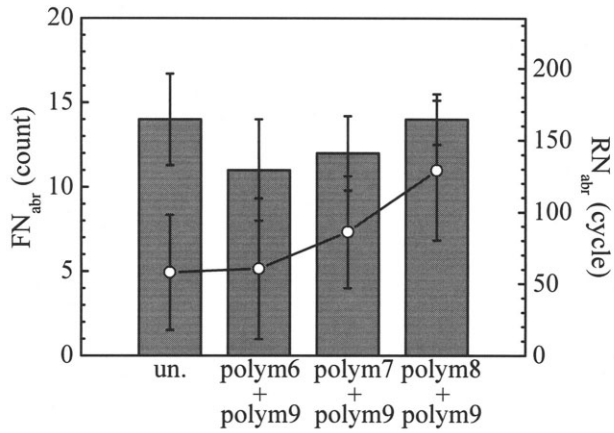

Figure 15 Effect of polymer type on fibril number induced using abrasive bar (▭) and rotation number (○) of fabric, when treated with a mixture of polym9 and polym6–polym8. The concentrations of polym6–polym8 and polym9 were 50 and 5 g/L, respectively. The fibers were treated according to method no.23 and nos.35–37.

than those of dried fibers, because of its higher water accessibility. The treatment with aminofunctional polysiloxane or secondary polyethylene at 120°C for 20 min provided the higher fibrillation resistance to lyocell fiber when compared to that at 170°C for 15 min. In comparison to secondary polyethylene derivative, aminofunctional polysiloxane performed better as a fibrillation-retardant.

The addition of other type of polymers, such as polyacrylate, polyurethane, and polyisocyanate derivatives in the treatments, also inhibited the fibrillation. However, the fibrillation was observed in the fabric treated with polyacrylate, polyurethane, or polyisocyanate in all conditions, while no fibrillation occurred in the fiber treated with polysiloxane in the condition used in the present study. The influences of the polymer type, the polymer concentration, and the use of mixture containing polyacrylate (or polyurethane) derivatives and polyisocyanate on the fibrillation resistance and the abrasion resistance were not significant, except anionic polyacrylate and polyisocyanate. The treatments with polyisocyanate alone and the mixture of polyisocyanate and anionic polyacrylate enhanced not only the fibrillation resistance, but also the abrasion resistance, except when higher amount (5 g/L) of polyisocyanate was used.

APPENDIX

Symbols; abbreviation; description

NSF	Nonspin-finished lyocell fiber
SF	Spin-finished lyocell fiber
ND	Never-dried lyocell fiber
FN_{ball}	Fibril number obtained using ball-bearings (count)
FN_{abr}	Fibril number obtained using abrasive bar (count)
WRV	Water retention value (%)
RN_{abr}	At break point of fiber (cycle)

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