Influence of Batch and Continuous Stabilization Processes on Various Characteristics of Stabilized Rayon Fibers

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Introduction

Stabilization process prior to carbonization process is absolutely necessary to convert the precursor fiber into chemically, physically and structurally stable carbon fiber during heat-treatment [1-5]. Especially, it is more important for rayon precursor fibers that experience extremely severe weight loss and thermal shrinkage. The stabilization process is, in general, performed below 400°C depending on temperature and time used under dynamic or isothermal conditions. A greatest alteration of chemical, physical, and structural states takes place between 250°C-350°C [6]. Many properties of a stabilized rayon fiber strongly depend on a variety of processing parameters like heat-treatment temperature, heating rate, dwell time, flame retardant treatment, atmosphere gas, etc. [7]. Also, a batch process under dynamically or isothermally heating condition and a continuous process for stabilization also significantly influence the characteristics of stabilized rayon fibers to be explored.

Experimental

- Materials

Rayon precursor fibers (Acordis T-700 yarns) used in this work were supplied from Acordis Co., the Netherlands and were woven in 8 harness satin fabric in Korea. Stabilized processes were performed with the woven fabric form. Three different kinds of flame retardants were utilized to explore the effect of the presence and absence of the chemical treatment to 'as-received' precursor fiber prior to stabilization on various characteristics of stabilized rayon fabric. They are phosphoric acid (Yakuri Pure Chemicals Co., Japan), 3-(hydroxyl phenyl phosphynyl)propanoic acid (H-205, KOLON Co., Korea), and FR-SH (Tae

Hwa Co., Korea), all phosphorous-based. The fabrics were treated-with each retardant of 1.0 vol% conc. by a dip-coating method at ambient temperature for 1h and dried at 80°C.

- Batch-Type Stabilization Process

Each rayon precursor fabric of 50mmx60mm in size without and with a flame retardant treatment was isothermally stabilized using a batch-type heat-treatment furnace. A variety of processing conditions for stabilization were used to extensively examine the effects of temperature, time, atmosphere, and flame retardant, as summarized in the first column of Table 2.

- Continuous-Type Stabilization Process

Stabilization processes were conducted with commercial-scale 8H/S woven fabrics with 1022mm wide using a continuous-type heat-treatment furnace. The heat-treating dimensions of the furnace are about 400cm in length and 120cm in width. The process was performed continuously by conveying the fabric at variable processing conditions. Temperature, conveying speed, tension and atmosphere were controlled in the furnace. Table 1 summarizes the processing parameters used in the present work.

- Characterization

The changes of the weight loss and the thermal shrinkage occurred after batch and continuous stabilization processes were examined, respectively. The thermal stability of stabilized rayon fabrics was measured at a heating rate of 10°C/min in N_2 and also in air using a thermogravimetric analyzer (TGA 951). Their chemical compositions (C, H, N, S) were investigated using an elemental analyzer (Elemental Vario EL). X-ray diffraction measurements for the fabrics were performed using a high resolution XRD analyzer (X'pert PRO-MNR, Philips).

Results and Discussion

Fig. 1 shows the dimensional and weight changes from 'as-received' rayon precursor fabrics after each batch-type stabilization process at 350°C for different durations in air. The thermal shrinkage and weight loss of the precursor fabrics increase with increasing stabilization time. It is noted that at 3 min the weight loss and the dimensional loss seriously take place with about 84% and 33-40%, respectively.

Fig. 2 shows the dimensional and weight change occurred after batch-type stabilization process at 350°C for 3 min in air for the precursor fabric treated with each retardant of 1.0 vol% conc. Comparing with the result from the corresponding time of the untreated case in Fig. 1, the chemical treatment significantly reduces the thermal shrinkage and the weight loss. This is resulted from the less reduction of rayon fiber diameter during stabilization. Among three, phosphoric acid is relatively more effective on protecting the fabric from thermal shrinkage and weight reduction.

Table 2 summarizes the effects of temperature, time, processing atmosphere and flame

retardant type on the chemical compositions of the rayon fabrics obtained by a number of batch-type stabilization processes. The result indicates that variable processing parameters strongly influence the chemical characteristics. Upon stabilization, the carbon content greatly increases while the oxygen content decreases profoundly, due to a significant chemical transformation involved. After stabilization, the carbon and oxygen contents are in the range of 60-78% and 17-35%, respectively.

Table 3 represents the influence of various continuous-type stabilization processing parameters on the chemical composition of the fabrics. SP1, SP4, SP5 and SP6 have greater carbon contents than SP2, SP3 and SP7. This is because the stabilization processing conditions of the former are milder than the latter cases, in terms of temperature, conveying speed and/or tension.

Fig. 3 depicts the XRD diffractogram measured for the 'as-received' rayon precursor fabric. The peak at $2\theta = 22^\circ$ is due to the (002) plane of monoclinic cell of cellulose. The shoulders near $2\theta = 16.5^\circ$ and 20° are from the (101) plane, indicating a typical crystal structure of cellulose II. The two peak intensities become more distinct with batch-type stabilization processes at 350°C for 30s and 1 min as seen in Fig 4. On the other hand, for a longer period of time such as 2 min and 3 min, the XRD result shows no characteristic peaks at $2\theta = 22^\circ$ and 16.5°. They all disappear upon the process. This is because the chemical structure with cellulose crystal form is degraded and changed into amorphous form under such the isothermal stabilization conditions.

Fig. 5 shows the thermal stability of the fabrics obtained by batch-type stabilization processes at 350°C for different durations in air. A short stabilization time (30s) does not much influence the thermogram of 'as-received' one. With increasing time, the thermal stability is obviously improved, especially at longer processing time. This is because the primary weight loss from volatile components has already been completed during the stabilization process in the furnace, leaving more thermally stable components of the fabric behind.

Fig. 6 compares the thermal stability of the fabrics obtained by various continuous-type stabilization processes. The result indicates that the thermal stability is greater in the order of SP2>SP7>SP3>SP1>SP4>SP5>SP6. This agrees with the EA result seen in the variation of the carbon contents in Table 3 and the XRD result in Fig. 4.

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Table 1. Processing parameters for continuous-type stabilization.

Stabilization Process	Temp (°C)	Speed (M/min)	Tension (kg_f/cm^2)	Atm
SP1	350	0.88	30	N_2
SP2	400	0.88	30	N_2
SP3	350	0.88	40	N_2
SP4	350	1.04	30	N_2
SP5	350	1.36	30	N_2
SP6	350	1.36	30	Air
SP7	350	0.59	30	N_2

Table 3. Results of chemical composition measured for the fabrics after continuous stabilization with different conditions.

Sample	N	C	H	S	O
SP1	0.185	54.790	5.568	0.543	38.913
SP2	0.168	71.732	4.340	0.510	23.248
SP3	0.171	70.377	4.026	0.451	24.973
SP4	0.066	53.602	7.189	0.481	38.660
SP5	0.045	48.595	7.435	0.526	43.397
SP6	0.014	45.572	8.381	0.412	45.619
SP7	0.050	71.379	4.673	0.544	23.338
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SP6	0.014	45.572	8.381	0.412	45.619
SP7	0.050	71.379	4.673	0.544	23.338

Table 2. Results of chemical compositions measured for the fabrics after batch stabilization with different processing conditions.

Sample	N	C	H	S	
As-received Rayon Fiber	0.247	38.853	6.389	0.334	54.509
No Treatment (350℃) ,30s	0.249	42.686	5.586	0.361	51.115
No Treatment (350℃), 1min	0.117	49.496	5.881	0.264	44.180
No Treatment (350℃), 2min	0.152	69.563	4.362	0.208	25.713
No Treatment (350℃), 3min	0.157	73.276	3.639	0.274	22.651
No Treatment (400℃), 30s	0.103	46.923	6.394	0.289	46.289
No Treatment (400℃), 1min	0.182	49.400	6.196	0.537	43.684
No Treatment (400℃), 2min	0.144	74.121	4.409	0.381	20.909
No Treatment (400℃), 3min	0.224	78.190	3.991	0.324	17.269
H_2SO_4, 1vol%, 350℃,3min, in air	0.091	62.690	3.598	0.235	33.310
H-2051vol%, 350℃, 3min, in air	0.091	74.383	3.281	0.492	21.756
FR-SH1vol%, 350℃, 3min, in air	0.608	73.846	3.148	0.526	21.871
H_2SO_4, 1vol%, 350℃, 3min, in air	0.138	60.570	3.464	0.349	35.477
H-2051vol%, 400℃, 3min, in air	0.110	72.403	3.383	0.162	23.607
FR-SH 1vol%, 400℃, 3min, in air	2.371	68.456	2.753	0.205	26.213
H_2SO_4, 1vol%, 350℃, 3min, in N_2	0.085	69.373	3.072	0.216	27.252
H-205 1vol%, 350℃, 3min, in N_2	0.097	69.850	3.611	0.325	26.117
FR-SH 1vol%, 350℃, 3min, in N_2	0.844	73.096	3.538	0.245	22.275
H_2SO_4, 1vol%, 400℃, 3min, in N_2	0.088	70.720	3.461	0.244	25.152
H-205 1vol%, 400℃, 3min, in N_2	0.108	75.383	3.506	0.258	20.746
FR-SH 1vol%, 400℃, 3min, in N_2	0.080	76.676	3.417	0.233	19.592

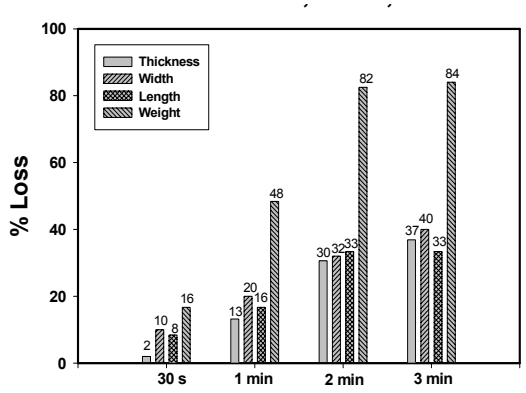

Fig. 1. Dimensional and weight changes of rayon precursor fabrics after batch stabilization at 350°C in air.

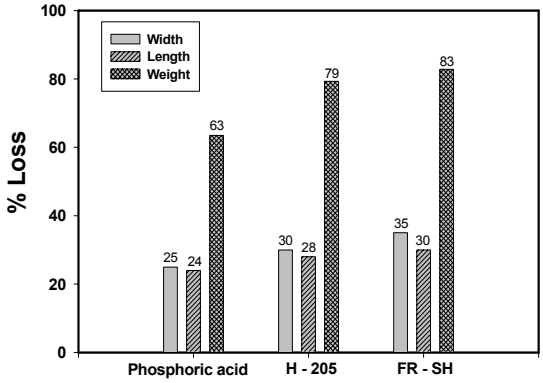

Fig. 2. Dimensional and weight changes of fabrics treated with 1 vol% flame retardant after stabilization at 350°C for 3 min in air.

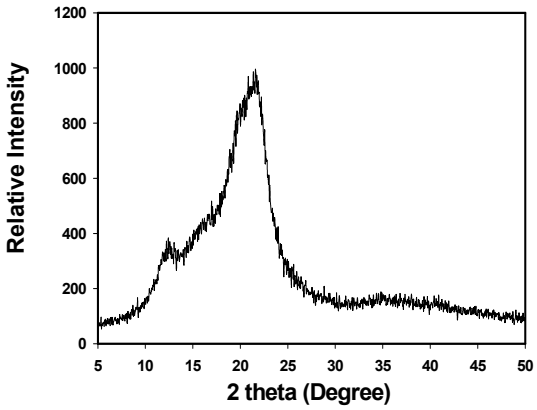

Fig. 3. XRD diffractogram of 'as-received' rayon precursor fabric.

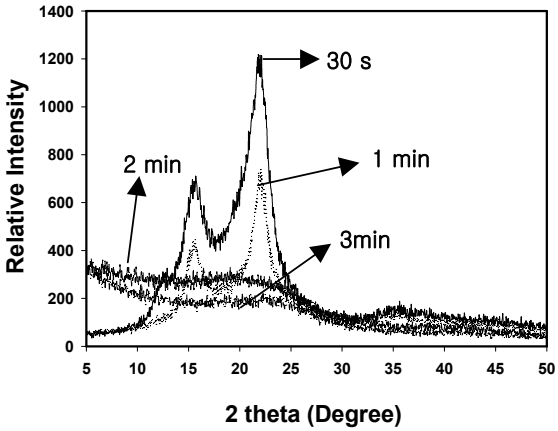

Fig. 4. XRD result from the untreated rayon produced by batch stabilization at 350°C for different durations in air.

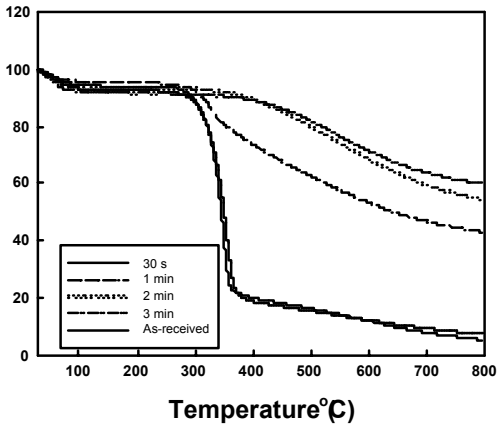

Fig. 5. TGA result of the untreated rayon fabrics batch-stabilized at 350°C for different times In air. Measurement was done in N_2.

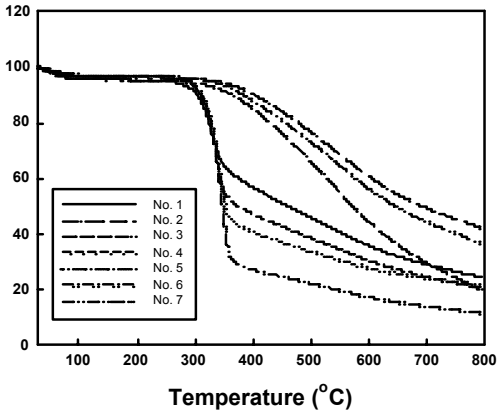

Fig. 6. TGA result measured in N_2 for the untreated rayon fabrics produced by continuous stabilization with different conditions.