Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Effects of oxygen on the structural evolution of polyacrylonitrile fibers during thermal-oxidative stabilization

Liang Chen [a], Zhigang Shen [b], Jie Liu [a,c], Jieying Liang [a], Xiaoxu Wang [a,c]*

[a] Key Laboratory of Carbon Fiber and Functional Polymers, Ministry of Education, Beijing University of Chemical Technology, Chao-Yang District, Beijing 100029, China

[b] SINOPEC Shanghai Petrochemical Company Limited, 48 Jinyi Road, Jinshan District, Shanghai 200540, China

[c] Changzhou Institute of Advanced Materials, Beijing University of Chemical Technology, Changzhou, Jiangsu 213164, China.

Correspondence to:

Xiaoxu Wang (E-mail: *wangxiaoxu@mail.buct.edu.cn*)

Table S1 Various bulk densities of s PAN fibers thermally treated from 80 °C to 260 °C at air and nitrogen atmosphere.

Sample code	Density/g·cm^{-3}	Sample code	Density/g·cm^{-3}
N_2-SFs (80)	1.1812	Air-SFs (80)	1.1811
N_2-SFs (100)	1.1817	Air-SFs (100)	1.1821
N_2-SFs (120)	1.1809	Air-SFs (120)	1.1807
N_2-SFs (140)	1.1825	Air-SFs (140)	1.1827
N_2-SFs (160)	1.1965	Air-SFs (160)	1.1978
N_2-SFs (180)	1.1955	Air-SFs (180)	1.1943
N_2-SFs (200)	1.1964	Air-SFs (200)	1.1955
N_2-SFs (220)	1.1968	Air-SFs (220)	1.1967
N_2-SFs (240)	1.2007	Air-SFs (240)	1.2311
N_2-SFs (260)	1.2085	Air-SFs (260)	1.2622

Table S2 Various oxygen contents of PAN fibers thermally treated from 160 °C to 260 °C at air and nitrogen atmosphere.

Sample code	Oxygen content (%)	Sample code	Oxygen content (%)
Air-SFs (160)	3.307	N_2-SFs (160)	3.275
Air-SFs (180)	3.282	N_2-SFs (180)	3.277
Air-SFs (200)	3.228	N_2-SFs (200)	3.353
Air-SFs (220)	3.289	N_2-SFs (220)	3.388
Air-SFs (240)	3.997	N_2-SFs (240)	3.341
Air-SFs (260)	5.068	N_2-SFs (260)	3.413

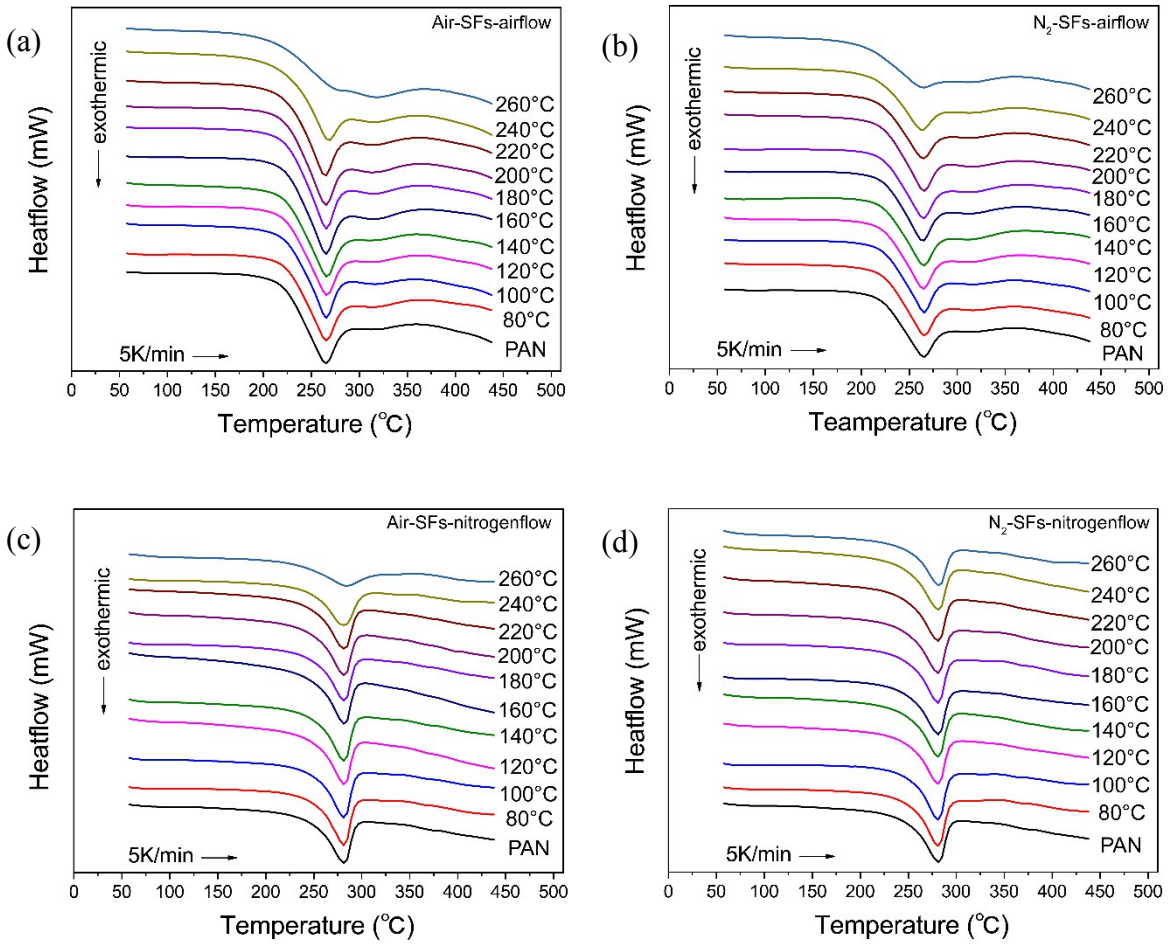

Figure S1 Various DSC curves of treated PAN fibers ranged from 80 °C to 260 °C at air and nitrogen atmosphere. (a) Air-SFs at measurement of airflow. (b) N_2-SFs at measurement of airflow. (c) Air-SFs at measurement of nitrogen-flow. (d) N_2-SFs at measurement of nitrogen-flow.

Table S3 Quantification from various DSC curves of untreated/treated PAN fibers under measurements of air-flow and nitrogen-flow.

Name	Airflow				Nitrogen-flow		
	Q_p/ $J \cdot g^{-1}$	T_{peak1}, T_{peak2}/ °C		T_{onset}/ °C	Q_p/ $J \cdot g^{-1}$	T_{peak1}/ °C	T_{onset}/ °C
PAN	2271.72	266.41	318.18	220.04	491.00	283.27	250.33
N_2-SFs (80)	2250.88	267.43	317.17	227.71	498.48	282.49	254.10
N_2-SFs (100)	2262.21	266.74	317.89	229.17	518.49	282.84	254.22
N_2-SFs (120)	2476.26	264.73	315.17	223.78	517.68	282.96	252.07
N_2-SFs (140)	2437.42	266.50	31467	222.92	513.21	283.04	252.52
N_2-SFs (160)	2480.66	265.58	315.37	228.24	513.44	282.39	250.41
N_2-SFs (180)	2505.63	264.07	317.69	227.09	517.06	282.49	252.22
N_2-SFs (200)	2573.09	266.93	316.83	226.00	533.61	282.38	250.18
N_2-SFs (220)	2333.66	265.44	317.86	220.35	514.35	282.86	249.37
N_2-SFs (240)	2226.52	264.26	316.66	220.32	504.91	282.78	248.57
N_2-SFs (260)	2078.38	265.04	316.54	201.25	443.70	283.10	252.51
Air-SFs (80)	2234.13	266.72	318.38	224.89	503.69	283.04	253.16
Air-SFs (100)	2210.76	266.83	317.05	229.49	501.46	283.38	254.27
Air-SFs (120)	2272.58	267.35	316.39	224.18	481.06	283.07	253.06
Air-SFs (140)	2215.34	267.72	317.37	222.38	496.43	283.41	252.36
Air-SFs (160)	2296.73	266.66	316.42	228.20	472.89	283.64	254.64
Air-SFs (180)	2354.72	266.02	316.53	228.36	480.32	283.54	254.14
Air-SFs (200)	2458.34	266.15	316.52	228.43	494.23	283.53	253.52
Air-SFs (220)	2053.53	266.34	316.74	228.60	471.62	283.51	252.78
Air-SFs (240)	1943.36	268.89	321.71	228.31	464.33	282.42	251.62
Air-SFs (260)	1578.21	276.91	321.44	206.71	362.17	284.69	235.02

Table S4 Quantification from various FTIR curves of untreated/treated PAN fibers.

Name	Fraction of reacted nitriles (%)	Dehydrogenation index (a.u.)
PAN	11.50	58.47
Air-SFs (80)	11.32	57.39
Air-SFs (100)	11.13	58.46
Air-SFs (120)	11.39	58.67
Air-SFs (140)	11.23	59.12
Air-SFs (160)	12.08	59.34
Air-SFs (180)	12.19	56.39
Air-SFs (200)	12.65	60.67
Air-SFs (220)	15.97	68.48
Air-SFs (240)	21.74	86.62
Air-SFs (260)	31.97	117.26
N_2-SFs (80)	11.49	58.22
N_2-SFs (100)	11.46	57.89
N_2-SFs (120)	11.42	57.98
N_2-SFs (140)	11.35	58.22
N_2-SFs (160)	11.55	58.48
N_2-SFs (180)	11.69	58.48
N_2-SFs (200)	12.07	60.97
N_2-SFs (220)	13.82	62.35
N_2-SFs (240)	16.76	68.86
N_2-SFs (260)	24.07	82.02

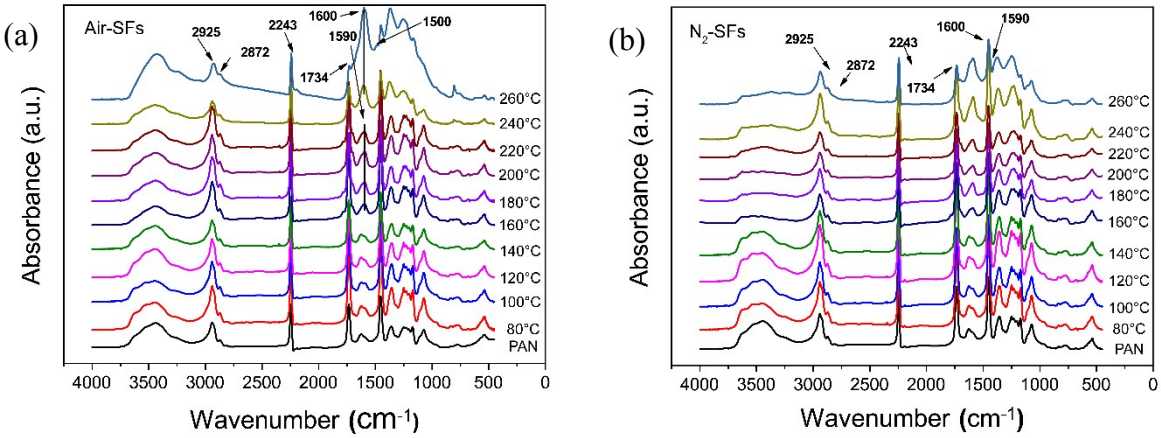

Fig. S2 Various FTIR curves of treated PAN fibers ranged from 80 °C to 260 °C. (a) Air-SFs and (b) N_2-SFs.

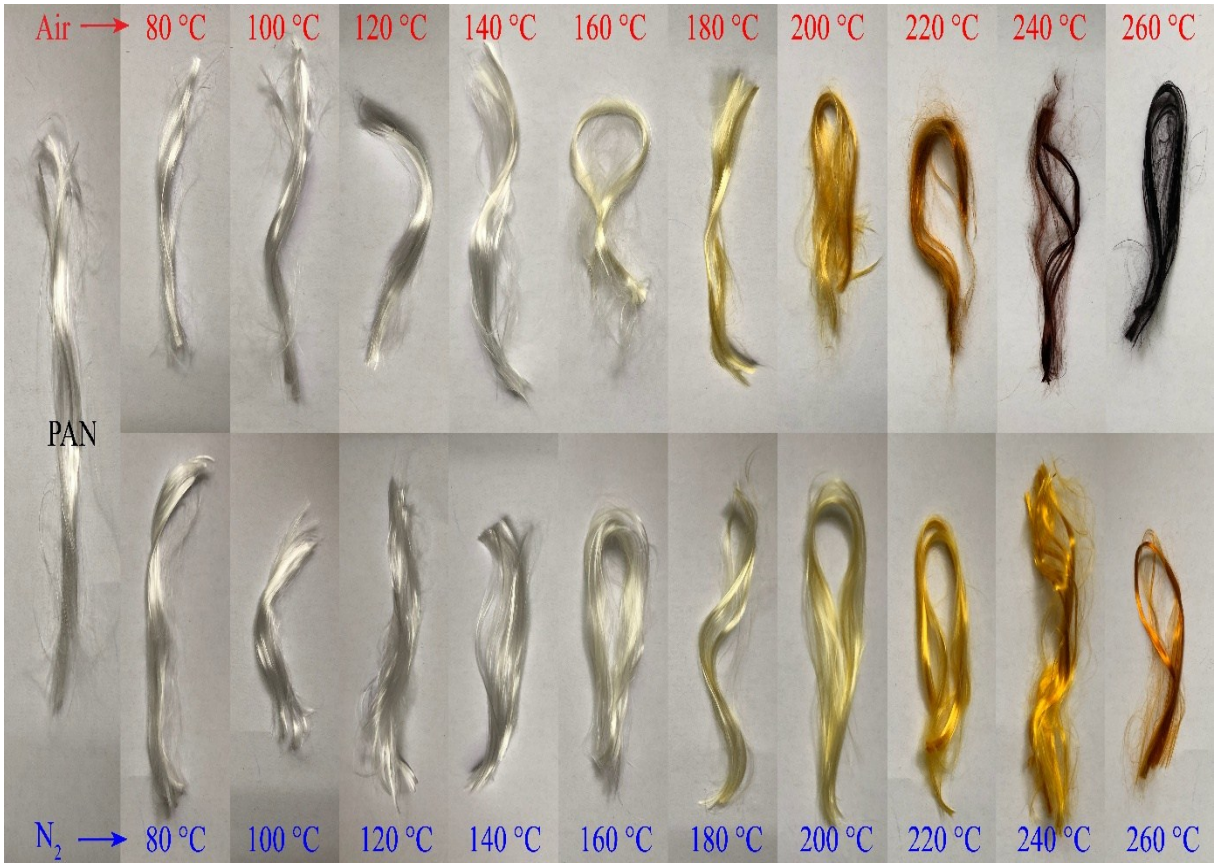

Figure S3 Color change images of treated PAN fibers ranged from 80 °C to 260 °C with illustration of structure evolutions of PAN fibers during thermal stabilization process.

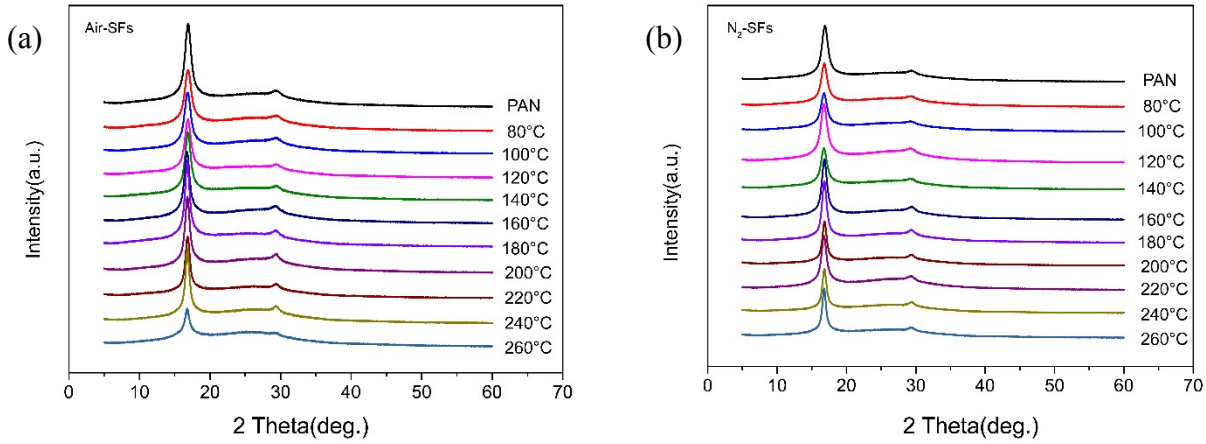

Figure S4 Various XRD curves of treated PAN fibers ranged from 80 °C to 260 °C. (a) Air-SFs and (b) N_2-SFs.

Table S5 Quantification from various XRD curves of untreated/treated PAN fibers.

Name	d_1/nm	d_2/nm	L_c/nm	L_a/nm	Crystallinity/%
PAN	5.2452	3.0377	7.4473	4.8320	66.62
Air-SFs (80)	5.2762	3.0479	7.0905	6.3435	65.46
Air-SFs (100)	5.2762	3.0530	7.3912	6.2699	66.06
Air-SFs (120)	5.2919	3.0581	7.7110	6.0773	66.41
Air-SFs (140)	5.2762	3.0327	7.6959	6.4855	67.64
Air-SFs (160)	5.2919	3.0479	7.9375	6.7501	56.39
Air-SFs (180)	5.2607	3.0377	9.8931	5.6184	43.65
Air-SFs (200)	5.2762	3.0428	8.8624	5.9919	38.48
Air-SFs (220)	5.2607	3.0377	9.9434	6.9408	38.13
Air-SFs (240)	5.2762	3.0377	10.0070	7.0927	37.42
Air-SFs (260)	5.2919	3.0428	6.1080	8.7182	24.18
N_2-SFs (80)	5.2607	3.0428	7.5477	6.0501	67.69
N_2-SFs (100)	5.3076	3.0530	7.1097	6.4443	65.78
N_2-SFs (120)	5.2273	3.0339	6.7605	5.0547	66.65
N_2-SFs (140)	5.2919	3.0530	7.5550	6.4036	65.86
N_2-SFs (160)	5.2607	3.0377	8.6854	7.2254	66.16
N_2-SFs (180)	5.2762	3.0377	9.3159	8.1399	65.56

N_2-SFs (200)	5.2919	3.0428	8.4970	7.2643	49.96
N_2-SFs (220)	5.2607	3.0428	10.3515	8.9297	48.55
N_2-SFs (240)	5.2762	3.0428	10.7207	9.8536	47.48
N_2-SFs (260)	5.2762	3.0428	10.5756	8.4191	47.53

Table S6 Mechanical properties of air-SFs and N2-SFs as a function of stabilization temperature, including tensile strength, modulus and elongation at break.

Name	T.S./MPa	T.S. Er ±	M./MPa	M. Er ±	ε/%	ε Er±
PAN	611.54	56.99	14162.97	2852.21	15.02	0.92
Air-SFs (80)	623.08	48.15	16075.38	3676.23	14.55	1.07
Air-SFs (100)	591.36	44.12	16345.91	3228.54	14.32	0.99
Air-SFs (120)	598.06	79.52	16219.56	2741.44	15.14	1.37
Air-SFs (140)	618.93	63.02	15204.68	2403.01	16.16	0.92
Air-SFs (160)	600.46	55.03	15301.09	2990.26	14.34	0.79
Air-SFs (180)	579.23	69.31	16249.78	2491.26	14.29	1.26
Air-SFs (200)	560.57	61.50	15353.18	2892.46	14.72	0.99623
Air-SFs (220)	541.74	61.26	14555.91	2284.03	14.76	1.17
Air-SFs (240)	491.92	53.20	14712.39	2456.64	17.75	1.64
Air-SFs (260)	351.70	20.39	11011.83	2796.01	27.39	1.67
N_2-SFs (80)	636.97	43.34	14469.84	2785.48	14.55	1.07
N_2-SFs (100)	634.54	50.07	15110.13	2872.37	14.32	0.99
N_2-SFs (120)	647.61	57.60	14750.61	2896.32	15.14	1.37
N_2-SFs (140)	631.44	63.30	15200.77	1721.16	16.16	0.92
N_2-SFs (160)	625.65	56.43	14362.03	2035.14	14.34	0.79
N_2-SFs (180)	624.36	68.27	15588.51	2852.77	14.29	1.26
N_2-SFs (200)	615.53	42.54	15344.61	2132.15	14.72	0.99
N_2-SFs (220)	614.94	34.07	15069.79	2577.09	14.76	1.17
N_2-SFs (240)	585.07	69.01	14797.09	2308.98	17.75	1.64
N_2-SFs (260)	544.74	28.83	13755.50	2559.85	27.39	1.67

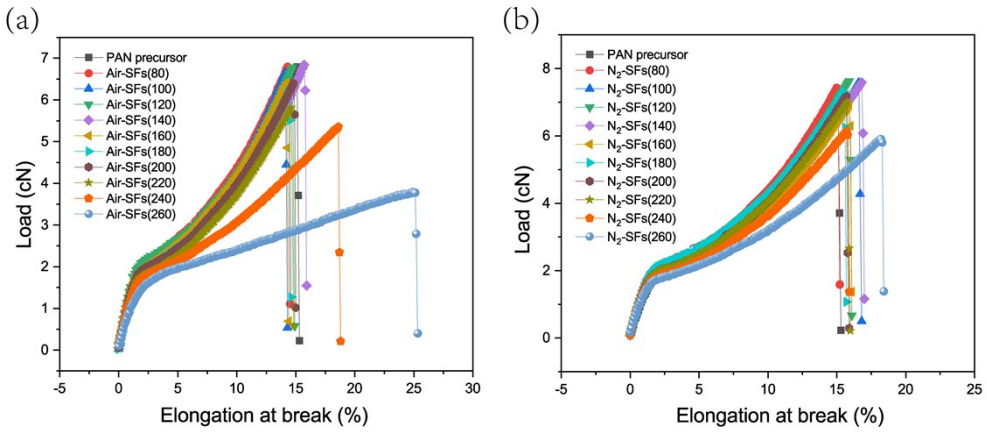

Figure S5 Load(stress)-elongation(strain) curves of stabilized fibers: (a)Air-SFs, (b)N_2-SFs.

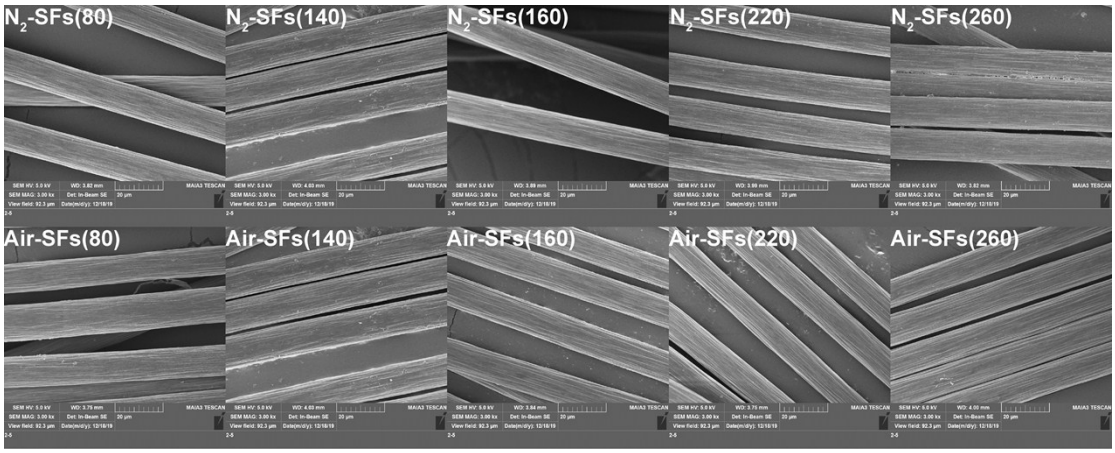

Figure S6 Scanning Electron Microscope images of PAN fibers treated by different atmospheres as a function of stabilization temperature.