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Changes of polyacrylonitrile fiber fine structure during thermal stabilization

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Abstract In this article regularities of length changes of polyacrylonitrile (PAN) fiber, as well as its structure transformation into the structure of thermally stabilized fiber, have been studied in detail. The fiber has been manufactured with the use of dimethyl sulfoxide (PAN^1) and dimethyl formamide (PAN^2), with methylacrilate content of 5% (mass). Thermal stabilization has been carried out under isothermal conditions at 245, 255 and 265, 275, 285 and 290 °C in atmospheric air at constant load of 0.6 g/tex. By X-ray structural analysis it has been shown that the structure of PAN fiber crystal component is depicted by two kinds of coherent-scattering regions (CSR), differing in the average size by an order of magnitude. Phase transition of PAN into the new highly dispersed phase is accompanied by dispersion of PAN larger CSR. Qualitative and quantitative regularities of fine structure evolution have been determined at thermal treatment in the indicated temperature range. It has been shown that the transition of PAN^1 fiber into the new two-phase state during thermal stabilization progressed more actively than the same process in PAN^2, by $\sim$25%. Increase of thermal treatment temperature leads to significant acceleration of PAN crystal phase dispersion and formation on the new highly dispersed phase. At that instance, average sizes of CSR of highly dispersed components of thermally stabilized fiber equal $\sim$1 nm at the end of the process, when aromatization index of the material amounts to 51–58%.

Introduction

Carbon fibers manufactured on the polyacrylonitrile (PAN) basis are among the principal kinds of reinforcing elements used for creation of composite materials with high elastic strength characteristics [1–4]. The transformation process of PAN fiber structure into the structure of high-strength or high-modular carbon fiber is multistage. According to [2, 4] it is usually carried out in three steps: through oxidation thermal stabilization, high-temperature (<1,600 °C) carbonization, and additional high-temperature (>2,000 °C) processing [5], with resulting high-modular fiber production.

Oxidation thermal stabilization of PAN fiber is one of the most important steps in structure formation of high-quality carbon fibers. The process is accompanied by chemical reactions of cyclization, dehydrogenation, aromatization, and oxidation, and degree of crystallinity and aromatization index of the material are changed [6–12]. In response to this interaction in the body of precursor PAN fiber at the temperature 200–300 °C, a new nanostructure of thermally stabilized fiber is formed.

A reasonably large number of published studies have been devoted to study of chemical transformation peculiarities of the material at the thermal stabilization stage, for example [4, 6, 10–19]. It has been shown that thermal stabilization conditions (temperature, gaseous medium, pulling load) have considerable effect on the properties of the resulting carbon fiber [12–15]. At such low-temperature

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processing, formation of a new nanostructure evolves within the original solid phase, accompanied by volumetric change. The process is controlled not only by the chemical stage, but also by mass transfer, formation of thermodynamically stable clusters of the new phase. Hence, one would expect appearance of intermediate states in the system under study, which can influence formation of the carbon fiber structure during high-temperature processing.

Regularities of PAN structure transformation into thermally stabilized fiber structure have been studied by diffraction methods [3, 6–10, 18, 19]. It has been demonstrated that in the process of thermal treatment the intensity of 010 maximum, peculiar to PAN structure, increases, while its width decreases, which points at increase of coherent-scattering regions (CSR) sizes. If thermal stabilization duration increases, then gradual decreasing of maximum intensity begins to the point of its complete disappearance, at that instance aromatization increases. Besides, displacement of center of gravity of the maximum has been observed, in lesser angles direction. Additional important data about PAN structure parameters at various stages of transition into thermally stabilized fiber structure can be secured by way of diffraction maximum profile analysis, which carries information about material fine structure.

In this article X-ray structure analysis method has been used for detailed investigation of the peculiarities of PAN fiber crystal structure transformation into the structure of thermally stabilized fiber, for the fiber manufactured with the use of dimethyl sulfoxide (PAN^1) and dimethyl formamide (PAN^2), during the process of isothermal treatment in atmospheric air at temperatures 245–290 °C.

Experimental

Materials

The investigation has been carried out for PAN fibers (with methylacrilate content of 5%), manufactured with the use of dimethyl sulfoxide (PAN^1) and dimethyl formamide (PAN^2).

Measurements

Thermal stabilization has been carried out under isothermal conditions at 245, 255 and 265, 275, 285 and 290 °C (complex fiber was moved into preheated oven within 2 s) in atmospheric air at constant load of 0.6 g/tex. Accuracy of temperature level maintenance comprises 1 degree. During the thermal treatment process the length changes of the complex fiber (ℓ/ℓ_0) have been controlled (where ℓ_0, ℓ are the initial and current values of fiber length).

X-ray structure analysis has been carried out with the use of D8 ADVANCE Bruker diffractometer (filtered CuKα radiation). CSR average sizes (L) and interplanar spacing (d) of crystallized PAN have been determined according to standard techniques. Degree of crystallinity $C = \mathrm{Cr}/(\mathrm{Cr} + A)$ has been calculated on the basis of the fiber amorphous crystalline structure (where Cr and A are the areas of diffraction maximums of crystalline and amorphous phases, respectively) [13]. Aromatization index of thermally stabilized fibers has been determined according to the formula: $\mathrm{AI} = I_a/(I_a + I_c)$, where I_a, I_c are maximum intensities of the newly formed aromatic structure and original crystalline PAN (20–25.5° and ~17°, respectively) [14]. In order to determine bulk density of fiber, γ, toluene–dichloroethane gradient column has been used.

Results and discussion

At the initial stage of PAN^1 fibers thermal stabilization (degree of crystallinity $C = 75.2\%$, bulk density $\gamma = 1.175$ g/cm^3) at the temperature 245 °C reasonably active increase of its length up to 2% is observed. However, the structural chemical transformations of PAN cause slowing-down of this process and shrinkage of length afterward (Fig. 1). Bulk density of the fiber achieves the value of 1.466 g/cm^3 during thermal stabilization process in 300 min. At that instance, aromatization index (AI) of the material is equal to 52.5% (Table 1), while decrease of length equals ~12%.

Increase of PAN^1 fiber isothermal treatment temperature to 255 °C somewhat accelerates the change of ℓ/ℓ_0 ratio, at that instance shrinkage value for 6 h after treatment stays within 12%. However, with such shrinkage the AI value increases to 58.2%.

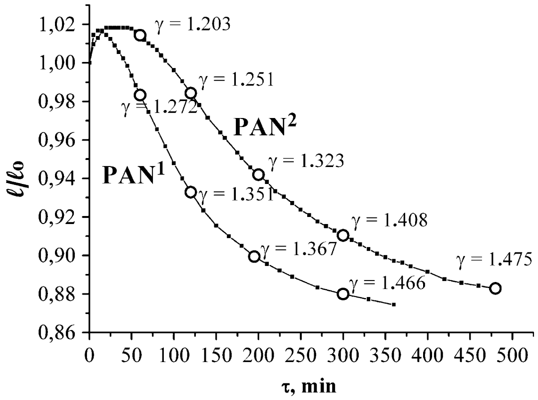

Fig. 1 Complex PAN fiber length (ℓ/ℓ_0) and bulk density (γ, g/cm^3) changes as the function of isothermal treatment duration in atmospheric air at 245 ± 1 °C. Density of precursor PAN^1 and PAN^2 fiber is 1.175 and 1.182 g/cm^3, respectively

Table 1 Change of aromatization index values (AI) of PAN fibers during thermal treatment

Temperature (°C)	Aromatization index (%) of the material after thermal treatment during					
	30 min	1 h	2 h	4 h	6 h	8 h
PAN^1						
245	–	–	19.1	40.0	52.5	–
255	–	–	26.3	47.6	58.2	–
265	–	17.6	46.2	55.8	–	–
275	–	30.5	53.0	–	–	–
285	26.1	51.3	–	–	–	–
290	36.8	53.9	–	–	–	–
PAN^2						
245	–	–	–	22.5	34.6	53.9
255	–	–	13.5	49.5	53.4	–
265	–	–	41.9	54.5	–	–
275	–	31.5	53.8	–	–	–
285	–	38.9	55.6	–	–	–
290	30.4	51.4	–	–	–	–

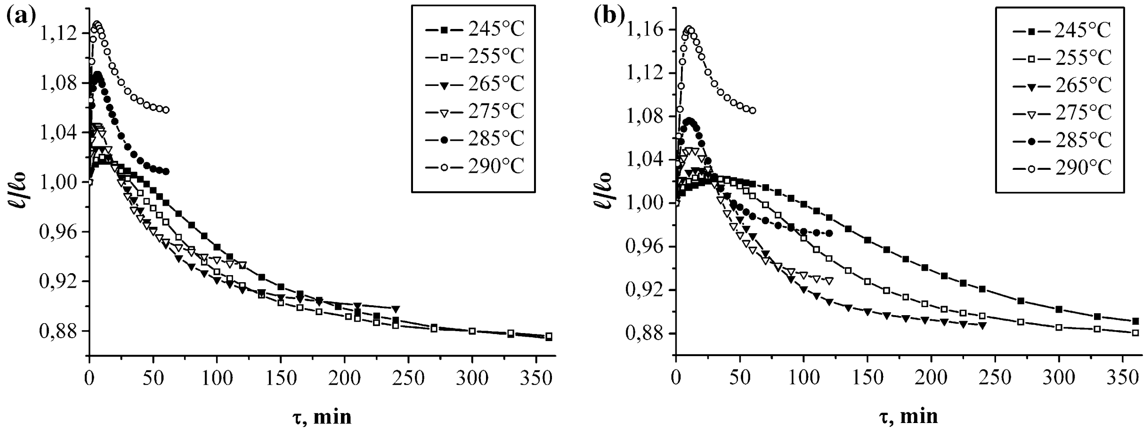

Fig. 2 Complex PAN^1 (**a**) and PAN^2 (**b**) fiber length (ℓ/ℓ_0) changes as the function of isothermal treatment duration in air

Significant (up to ~4.5%) increasing of drawing-out at the initial stage of thermal stabilization and decreasing of shrinkage value of complex fiber during isothermal treatment can be observed at 275 °C (Fig. 2a). At higher temperatures (285 and 290 °C) drawing-out at the initial stage of treatment increases steeply, achieves 9 and 13%, respectively, and is not compensated by the following shrinkage of the fiber, taking place at thermal treatment during 1 h. Aromatization indices of the materials manufactured at these temperature conditions for fibers equal 51.3 and 53.9%.

Degree of crystallinity and bulk density of the precursor PAN^2 fiber are higher: 78.6% and 1.185 g/cm^3. Kinetics of ℓ/ℓ_0 and γ changes for such fiber at 245 °C is different from the one described above (Fig. 1), the rate is significantly slower. In this case bulk density γ achieves the value of 1.466 g/cm^3 in 450 min, while length decrease measures ~11%. After thermal treatment during 8 h the value of ℓ/ℓ_0 is ~12%, at that instance AI = 53.9% and γ = 1.475 g/cm^3.

During thermal treatment at temperatures 255 °C (6 h) and 265 °C (4 h) fiber shrinkage achieves ~12% (Fig. 2b), at that instance AI values equal 53.4 and 54.5%, respectively (Table 1). When temperature is increased to 275 °C, drawing-out of complex fiber at the initial stage of thermal treatment achieves ~5%, and resulting fiber shrinkage is equal to 7% in 2 h. During thermal stabilization at 285 and 290 °C drawing-out of fiber at the initial stage of treatment increases up to 8 and 16%, which at 290 °C is not compensated by the following shrinkage, equaling 8%. It should be noted that time interval of PAN^2 fiber lengthening at all studied thermal treatment conditions is approximately twice longer, compared to PAN^1 at the same temperatures.

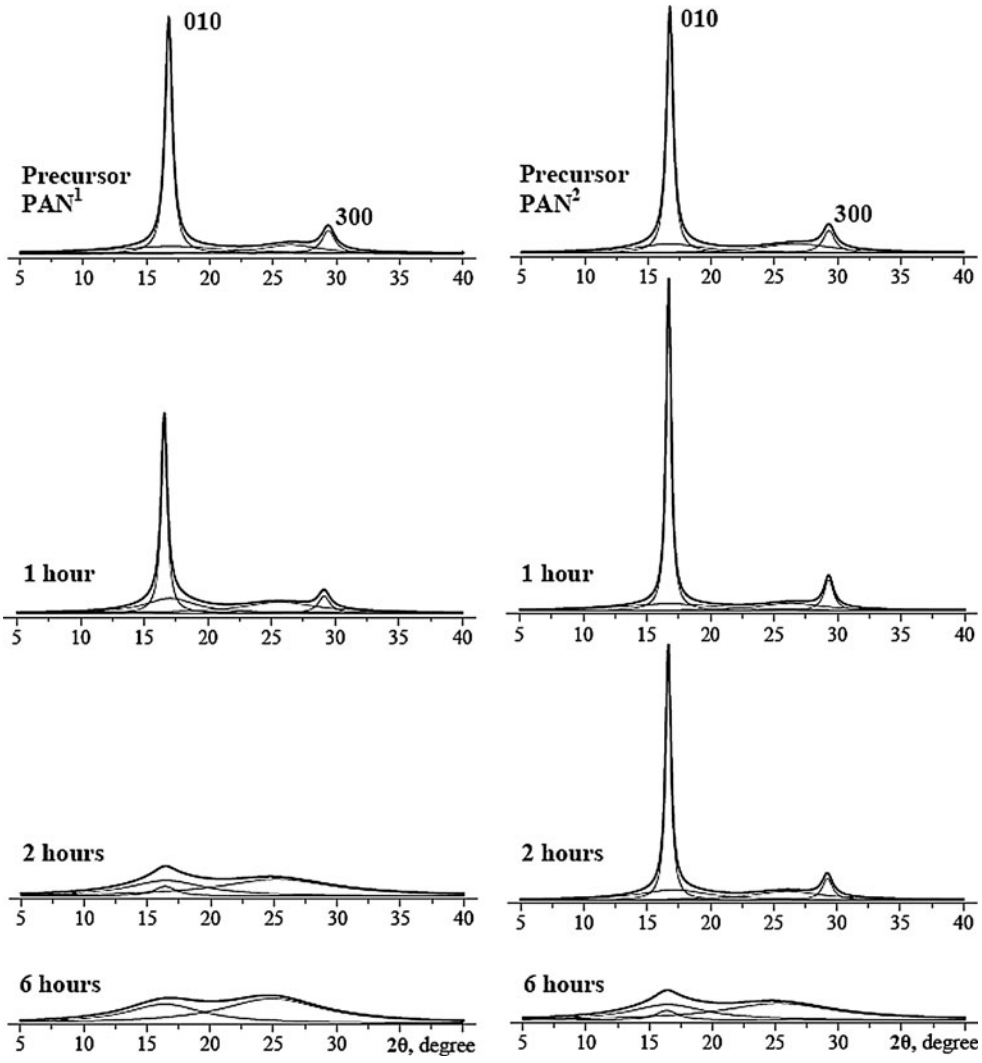

Fig. 3 Separation of experimentally observed diffraction peak into minimal number of peaks described by Lorentzian function. PAN isothermal stabilization at 245 ± 1 °C

Let us consider transformation of PAN fiber material structure into thermally stabilized fiber structure in more detail. On the X-ray diffraction pattern of PAN fiber maximums at the values $2\theta \sim 17$ and ~ 29 degrees have been observed, characteristic for crystalline structure of PAN, corresponding to diffraction from planes (010) and (300). Simultaneously a wide maximum in the region $2\theta \sim 26°$ is present, caused by nanodispersed phase scattering, for which the interplanar spacing is sufficiently near to turbo-strated carbon structure, it amounts to ~ 0.340 nm (Fig. 3). During isothermal treatment change of intensity and integral width of 010 maximum, as well as displacement of its centroid toward smaller angles, take place.

During thermal treatment for 20 min (at temperature of 245 °C) PAN^1 fiber degree of crystallinity increases by $\sim 10\%$, from 75.2% to 83%, then it begins to decrease. After isothermal treatment for 6 h maximum at $2\theta \sim 25.9°$ on the X-ray diffraction pattern is formed more distinctly, which points at formation of parallel-oriented fragments of carbon layers during thermal stabilization process. The following increase of thermal treatment interval causes increasing of its integral intensity and simultaneous decreasing of 010 maximum.

Polyacrylonitrile diffraction maximum 010 profile, during the transformation process from the initial stage into thermally stabilized fiber structure, cannot be described by Lorentzian or Gaussian functions. It might be due to simultaneous coexistence of CSR varying in size and interfacial distance. With the object of detailed analysis of material structural transformation during thermal stabilization process, separation of experimentally observed diffraction maximum into minimal number of maximums described by Lorentzian function has been carried out (Fig. 3), and structural parameters of the revealed CSR have been calculated. It has been found that the crystalline component of the precursor PAN^1 is represented by two kinds of CSR with average sizes ~ 13 and ~ 1 nm (for sizes calculations it has been adopted that physical

Table 2 Change of average value of interplanar spacing (*d*), coherent-scattering regions size (*L*), and degree of crystallinity (*C*) of PAN fiber

Temperature	Dwell time	CSR types	PAN^1			PAN^2		
			L (nm)	*d* (Å)	*C* (%)	*L* (nm)	*d* (Å)	*C* (%)
Precursor fiber		CSR1	13.2	5.289	75.5	14.4	5.297	78.6
		CSR2	0.9	5.235		1.3	5.304	
		CSR3	1.7	3.378		1.3	3.337	
245 °C	20 min	CSR1	17.3	5.309	83.0	17.3	5.297	85.1
		CSR2	1.0	5.178		0.8	5.101	
		CSR3	1.6	3.318		1.5	3.383	
	1 h	CSR1	15.4	5.346	71.6	19.3	5.298	84.6
		CSR2	1.8	5.200		1.0	5.280	
		CSR3	1.3	3.470		1.5	3.382	
	2 h	CSR1	9.8	5.354	52.6	17.5	5.314	78.5
		CSR2	1.4	5.297		1.4	5.171	
		CSR3	0.9	3.505		1.4	3.415	
	4 h	CSR1	9.3	5.369	42.7	9.1	5.349	48.6
		CSR2	1.4	5.405		1.3	5.314	
		CSR3	0.9	3.532		0.9	3.456	
	6 h	CSR1	–	–	–	4.2	5.405	–
		CSR2	1.2	5.401		1.2	5.375	
		CSR3	0.9	3.573		0.8	3.531	
	8 h	CSR2	–	–		1.8	5.538	–
		CSR3	–	–		0.7	3.633	
255 °C	20 min	CSR1	17.4	5.295	83.0	22.7	5.276	84.8
		CSR2	1.0	5.365		1.3	5.177	
		CSR3	1.5	3.425		1.4	3.376	
	1 h	CSR1	14.2	5.332	74.5	18.2	5.304	79.0
		CSR2	1.8	5.234		1.3	5.147	
		CSR3	1.4	3.514		1.4	3.377	
	2 h	CSR1	9.2	5.357	46.9	12.4	5.335	65.5
		CSR2	1.4	5.384		1.8	5.260	
		CSR3	0.9	3.499		1.3	3.556	
	4 h	CSR2	1.3	5.386	–	1.2	5.442	–
		CSR3	0.9	3.582		0.9	3.575	
	6 h	CSR2	1.1	5.544	–	1.0	5.444	–
		CSR3	0.9	3.566		1.0	3.562	
265 °C	20 min	CSR1	16.2	5.276	80.5	19.0	5.281	81.5
		CSR2	1.1	5.406		1.0	5.429	
		CSR3	1.4	3.407		1.2	3.433	
	1 h	CSR1	11.2	5.330	62.3	13.0	5.327	71.3
		CSR2	1.8	5.292		1.6	5.261	
		CSR3	1.2	3.518		1.4	3.514	
	2 h	CSR1	–	–	–	3.5	5.371	–
		CSR2	1.4	5.440		1.2	5.382	
		CSR3	0.9	3.583		1.9	3.519	
	4 h	CSR2	1.0	5.548	–	1.2	5.554	–
		CSR3	0.9	3.581		0.9	3.606	

Table 2 continued

Temperature	Dwell time	CSR types	PAN^1			PAN^2		
			L (nm)	*d* (Å)	*C* (%)	*L* (nm)	*d* (Å)	*C* (%)
275 °C	10 min	CSR1	18.1	5.269	84.4	18.4	5.309	83.4
		CSR2	1.0	5.367		1.4	5.434	
		CSR3	1.7	3.377		1.3	3.481	
	30 min	CSR1	13.2	5.320	65.6	19.5	5.303	81.9
		CSR2	1.7	5.282		1.2	5.227	
		CSR3	1.2	3.559		1.5	3.415	
	1 h	CSR1	10.1	5.313	49.3	7.6	5.315	46.1
		CSR2	1.2	5.384		1.3	5.376	
		CSR3	0.9	3.493		0.9	3.484	
	2 h	CSR2	1.0	5.470	–	1.0	5.645	–
		CSR3	1.0	3.555		0.9	3.592	
285 °C	10 min	CSR1	17.3	5.278	75.5	19.0	5.271	80.7
		CSR2	1.3	5.303		1.2	5.350	
		CSR3	1.2	3.401		1.0	3.416	
	30 min	CSR1	9.5	5.320	49.8	16.2	5.322	70.3
		CSR2	1.2	5.411		1.7	5.251	
		CSR3	0.9	3.460		1.4	3.556	
	1 h	CSR1	–	–	–	0.8	5.355	–
		CSR2	1.0	5.561		1.2	5.355	
		CSR3	0.9	3.569		0.9	3.565	
	2 h	CSR2	–	–	–	1.0	5.549	–
		CSR3	–	–		0.9	3.595	
290 °C	10 min	CSR1	16.2	5.283	75.1	19.7	5.271	80.5
		CSR2	1.0	5.285		1.4	5.356	
		CSR3	1.3	3.438		1.4	3.361	
	30 min	CSR1	10.8	5.342	46.0	9.5	5.305	47.3
		CSR2	1.3	5.402		1.3	5.434	
		CSR3	0.9	3.529		0.9	3.500	
	1 h	CSR2	1.0	5.598	–	1.0	5.639	–
		CSR3	0.9	3.574		0.9	3.578	

broadening of diffraction maximum is caused only by dispersion), Table 2. Interplanar spacings of CSR1 and CSR2 are 5.289 and 5.235 Å, respectively. At that instance ~56% of PAN^1 crystalline phase is formed by SCR of the first kind.

Average sizes of CSR1, after thermal treatment of fiber during 20 min (at temperature of 245 °C) increase by 31%; at that instance the CSR1 amount of matter increases by ~4%. Lengthening of thermal treatment causes gradual decrease in average sizes of CSR1. After treatment during 6 h dispersion of CSR1 is brought to a close, fiber material is transformed into two-phase highly dispersed condition with average sizes of CSR approximately 1 nm, Table 2. Average sizes of the most dispersed component of PAN crystalline phase (CSR2) during thermal stabilization process remain within 1.0–1.8 nm range. Intensity of maximum for the structure preceding the carbon fiber structure (CSR3) is increased; the amount of matter for this phase achieves 65% (Fig. 4).

Increasing of isothermal treatment temperature causes significant decreasing of time during which the two-phase highly dispersed structure of thermally stabilized fiber is formed. Thus, for example, diffraction maximum 010 of CSR1 phase on the X-ray pattern is no longer observed after treatment of the fiber during 2 and 1 h at temperatures 265 and 290 °C, respectively, Table 2. However, despite the fact that formation of the new highly dispersed component of thermally stabilized fiber structure (CSR3) takes

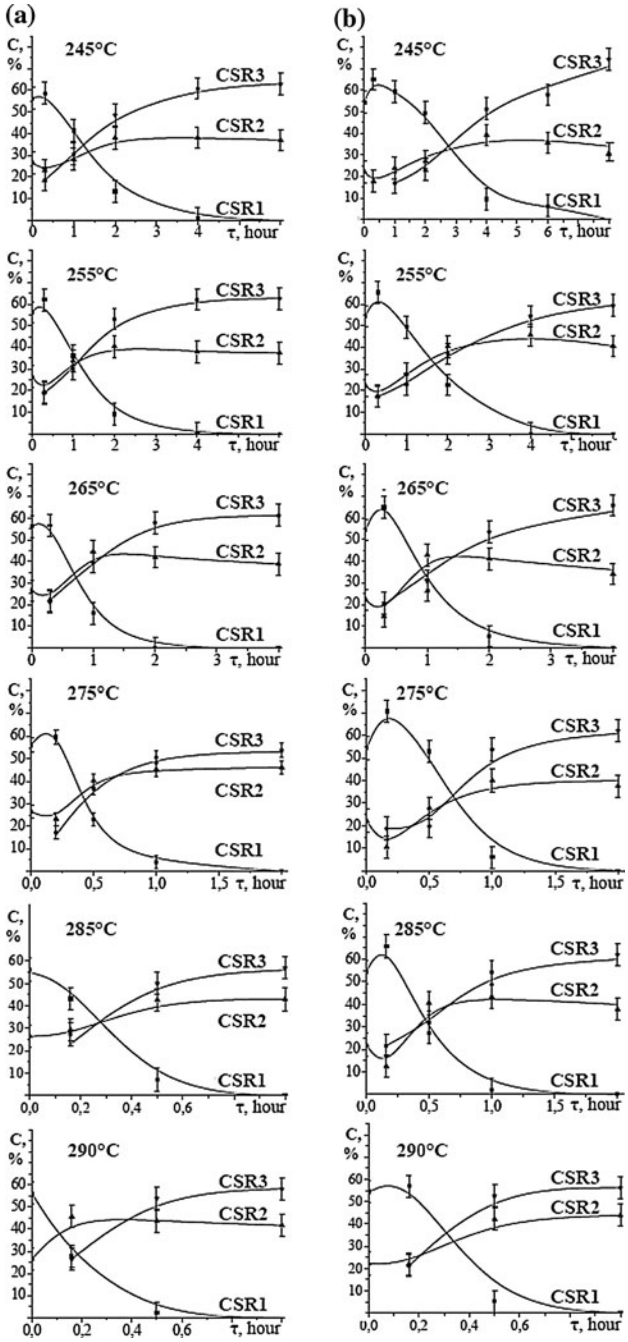

Fig. 4 Changes of PAN^1 (**a**) and PAN^2 (**b**) phase constitution during thermal stabilization

place at higher temperatures, average sizes of CSR2 and CSR3 have turned out of the order 1 nm at the end of the process for each studied temperature conditions.

Crystalline component of the precursor PAN^2 is also represented by two types of CSR, average sizes of which are 14.4 and 1.3 nm (interplanar spacing are 5.297 and 5.304 Å, respectively). PAN^2 fiber degree of crystallinity is higher, 78.6%, but, at that instance, CSR1 include only ~54% of crystalline phase (Fig. 4).

Average sizes PAN^2 fiber CSR1, unlike PAN^1 fiber, increase after 20 min and 1 h of thermal treatment at 245 °C by 20 and 34%, respectively. Then, as duration of treatment increases up to 6 h, average value L gradually decreases to 4.2 nm. After isothermal treatment during 8 h PAN^2 fiber material becomes highly dispersed two-phase, aromatization index increases to 53.9% (Tables 1, 2). Sizes of crystalline phase CSR2 during thermal stabilization process remain within 0.8–1.8 nm.

Quantitative changes of PAN^2 phase constitution also differ from those described above (Fig. 4). After 20 min of thermal treatment at 245 °C the area of maximum (phase CSR1 quantity) increases by ~19%, at that instance the quantity of highly dispersed phase (CSR2) decreases by ~20%. After 2 h of thermal treatment the CSR1 amount of matter, compared to the initial state, decreases only by 1.1 times and diffraction maximum is formed quite distinctly at ~26 degrees. As duration of thermal treatment increases up to 8 h the quantity of CSR3, preceding the carbon fiber structure, is increased, while the CSR1 amount of matter is decreased. Quantity of PAN highly dispersed phase (CSR2) achieves maximum value after thermal treatment during 4 h, and then it begins decreasing.

Rise of oven temperature to 255 and 265 °C causes increase of CSR1 average sizes after 20 min of thermal treatment, to ~58 and ~32%, respectively. At that instance, CSR1 amount of matter increases by ~20%. At further increasing of thermal treatment the process of CSR1 dispersion is developed, this phase quantity is decreased and CSR3 amount of matter gradually increases. PAN crystalline phase CSR2 average sizes remain within 1.0–1.8 nm during the thermal stabilization process at these temperatures.

At thermal stabilization temperature of 275 °C the structural transformation of PAN^2 material develops approximately four times faster compared to that at 245 °C. Fiber degree of crystallinity in the first case, after 1 h of thermal treatment, equals 46.1%; in the second case, after 4 h, it is somewhat greater, 48.6%. Thermal treatment at 290 °C during 30 min causes decrease of PAN^2 degree of crystallinity value to 47.3%.

Conclusion

Hence, increase of thermal stabilization temperature from 245 to 290 °C has caused decrease (from ~25 to ~6 min) of plastic flow time for PAN^1 material at the initial stage of thermal treatment, at that instance elongation has increased by ~6 times. The time interval, within which elongation of PAN^2 fiber is observed, with higher degree of crystallinity and bulk density, is enlarged by ~2.5 times compared to PAN^1 at all studied temperature conditions.

Abrupt decrease of shrinkage value of the investigated fibers is observed at thermal treatment temperature of 275 °C and higher.

Crystalline component structure of the precursor fiber is represented by two kinds of PAN CSR, differing by an order of magnitude in their average sizes. Accompanying reactions of cyclization, dehydrogenation, and oxidation stimulates phase transition of PAN into intermediate highly dispersed phase (CSR3 average size is approximately 1 nm)—newly formed structure of carbon fiber in local microvolumes of PAN fiber CSR1. This process appears to be followed by dispersion of CSR1 and increase of highly dispersed component of PAN (CSR2). Maximum (~70%) quantity of CSR3 is formed at 245 °C in PAN^2 material. At thermal stabilization, at temperatures of 255–285 °C the ratio CSR3:CSR2 is equal to 60:40%. In the fiber that has undergone thermal treatment at 290 °C the ratio CSR3:CSR2 equals 55:45%.

Transformation of PAN^1 fiber during thermal stabilization into two-phase state progresses more actively by 25% compared to the same process in PAN^2. At that instance, the ratio CSR3:CSR2 turns out to be somewhat less at all studied temperature conditions.

Increase of thermal treatment temperature causes acceleration of PAN crystalline phase (CSR1) dispersion and formation of the new phase (CSR3). However, average sizes of CSR2 and CSR3 (highly dispersed components of thermally stabilized fiber) prove identical, ~1 nm, at the end of the process, when material aromatization indices achieve value 51–58%.

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