

## STRUCTURAL ANALYSIS OF PAN FIBER BY X-RAY DIFFRACTION

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**Abstract:** Polyacrylonitrile (PAN) fibers are used on a large scale in textile industry but, some sorts of PAN fibers are valuable precursors for specific carbon fiber (CF) due to their best fitness to the purpose e.g. for high strength CF or for active CF. The application of PAN as precursors of CF is based on its specific structure and texture. Thus, the properties of PAN base CF strongly depend on PAN structure, texture and fiber morphology. In this respect, the paper addresses the modeling of PAN fiber structure and texture and, subsequently, estimation of structure and texture parameters based mainly on Wide Angle X-ray Diffraction (WAXD) technique and other data. The PAN fiber structure and texture parameters were calculated on the basis of classical X-ray diffraction theory applied to paracrystals. The preferred orientation parameters were calculated on a wide accepted model.

**Keywords:** WAXD, SEM, structure, preferred orientation, polyacrylonitrile fibers.

### 1. INTRODUCTION

Polyacrylonitrile (PAN) fibers are extensively used in textile industry. Since, 1961 some sorts of PAN fibers are used as carbon fibers (CF) precursors [1-4]. The PAN base CF are over 85% of world CF production due to their relative low cost and the ability to be adapted to the designed CF characteristics. Thus, about all high strength CF for aircraft applications have PAN precursors. It has already been established that PAN fibers not only serve as the most suitable precursor, but also the properties of the ultimate carbon fibers depend largely on the characteristics of the precursor [5-9]

In the last years, the active CF (ACF) became an attractive solution for specific environmental applications due to their high performance as adsorbents and absorbents [10]. The ACF has the advantage of a controlled porosity comparing with biomass or coal active carbon [11, 12]. The team used various techniques for PAN fiber characterization and for resulting CF as: optical microscopy, SEM, tensile test and two **WAXD** techniques i.e. diffractometry and Debye-Scherrer camera. Each investigation technique had provided useful information but WAXD have provided critical data that help us to establish and control some critical parameters of the PAN CF manufacture in the manner of published data [13, 14]. Some of significant WAXD data are the issue of this paper.

### 2. EXPERIMENTAL

#### 2.1. PAN FIBER STRUCTURE AND PREFERRED ORIENTATION MODEL

The chemical formula of PAN is:



where is the n number monomers known as the degree of polymerization.

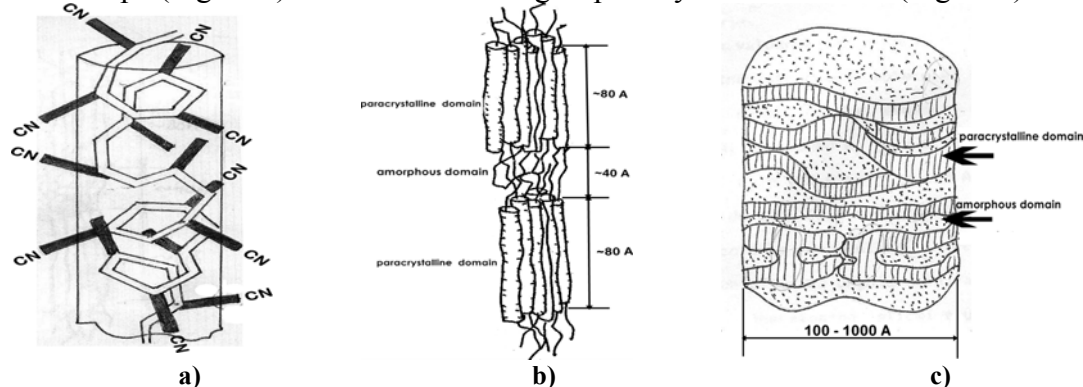
The most industrial PAN fibers are of copolymer nature containing 2-10% comonomers, as methyl acrylate or methyl metacrylate. PAN also contains a small quantity of catalytic comonomers, for stabilizing reactions at low temperatures as, especially, itaconic acid. The compositions of the investigated PAN fibers are specified in Table 1.

**Table 1. The chemical compositions of the investigated PAN fibers**

Sample code	PAN Sv 41	PAN Sv 61
Acrylonitrile	94.6	95
Methyl Acrylate	4.0	5.0
Itaconic Acid	1.4	1.0

## 2.2. PARACRYSTALLINE MODEL OF PAN FIBER STRUCTURE

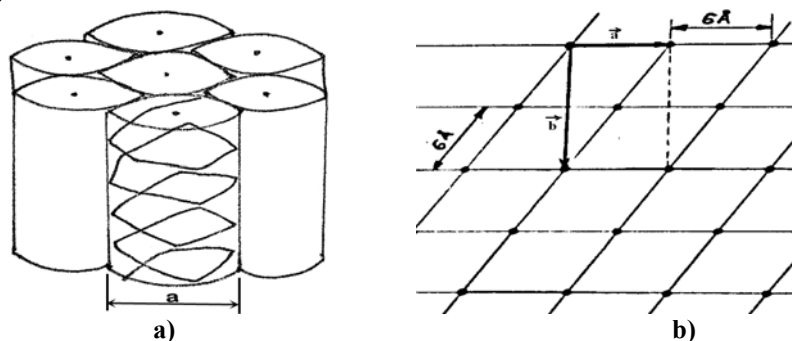
The most accepted molecular model of PAN fiber is schematically shown in Fig. 1. [3, 5, 6, 15]. The structural model of PAN fiber precursor could be structured on three levels: helical macromolecule (Fig. 1.a), *paracrystal* consisting of close packed macromolecule of cylindrical shape (Fig. 1. b) and fibril consisting of paracrystalline domains (Fig. 1. c).



**Fig. 1. Schematic illustration of the PAN structural levels: a) macromolecule helical structure; b) macromolecular orientation; c) fibril.**

The rod-shape (“wand”) macromolecule has a significant stiffness due to van der Waals bonds between the comonomer on the consecutive coil of helices (Fig. 1a). The aligned macromolecules bond each other by atomic links and became entrapped each-other into a bundle of close-packed macromolecules that form a so called paracrystal having two-dimensional order in the fibril cross-section of hexagonal type (Figs. 2a and 2b). The most convenient unit cell of PAN paracrystal is an orthogonal one with a parameter equal to macromolecule diameter ranging in 0.5-0.6 nm.

In the frame of orthogonal symmetry the b axis is perpendicular to a axis and is about  $1.73/a$  in length (Fig. 2b). The c axis is conventionally normal to (a, b) plane and has an arbitrary length.



**Fig. 2. The PAN paracrystalline structural model; a) close packed macromolecule; b) 2D lattice associated to the paracrystalline structure**

It makes sense to consider that at the end of a paracrystal the packed order diminishes due to different macromolecule length and other factors. Thus, the fibril consists of interlinked ordered and disordered domains.

The paper addresses two Romanian PAN precursor sorts e.g. PAN Sv 41 and PAN Sv 61. Also, the paper addresses mainly WAXD investigations of PAN precursor and subsidiary the SEM and optical microscopically investigations. The WAXD investigations were done with a DRON 3 diffractometer for structural parameter estimation while for preferred parameter estimation was used a Debye-Scherrer camera, with the diameter  $\phi = 57.3$  mm and Ni filtered  $\text{CuK}_\alpha$  radiation. The diffractometric data were corrected according classical procedure [23, 24]

The distances between (hkl) planes were calculated on the base of well-known Bragg relation:

$$2 \cdot d \cdot \sin(\theta) = n\lambda \quad (1)$$

where  $d$  is the inter-planar distance;  $\theta$  is the Bragg angle;  $\lambda$  is the wavelength of X-ray beam.

The crystallite size ( $L_{(200)}$ ) was calculated from the Scherrer formula:

$$L_{(200)} = K \cdot \lambda / [B \cdot \cos(\theta)] \quad (2)$$

where  $K = 0.89$  is a constant,  $\lambda$  is the wavelength of the diffracted X-ray,  $B$  is the full width at half the maximum intensity (FWHM) of the (200) peak.

The crystallinity ( $X_c$ ) of fibers is measured by Hinrichen's method [25, 26]:

$$X_c = [I_c / (I_c + I_a)] \cdot 100\% \quad (3)$$

where  $I_c$  is the integral intensity of crystalline fraction which is the area under the diffraction peaks and background curve;  $I_a$  is the intensity scattered by the amorphous fraction which is the area of the diffractogram outside the peaks.

The uncertainties of crystalline and preferred orientation measurements are complicated to estimate thereof the crystallinity and preferred orientation of the candidate PAN precursors should be interpreted only by comparison with the reference materials (RM).

### 3. RESULTS AND DISCUSSION

The samples for WAXD investigation consists of aligned PAN bundles of the same volume. The bundles were aligned parallel to the diffractometer goniometer axis so that the diffracted intensities to be comparable from the irradiated volume point of view. The diffractogram given by the PAN Sv 41 and PAN Sv 61 samples are quite similar and comply to the reported patterns [15, 27, 28] as result from Figs. 3a and 3b.

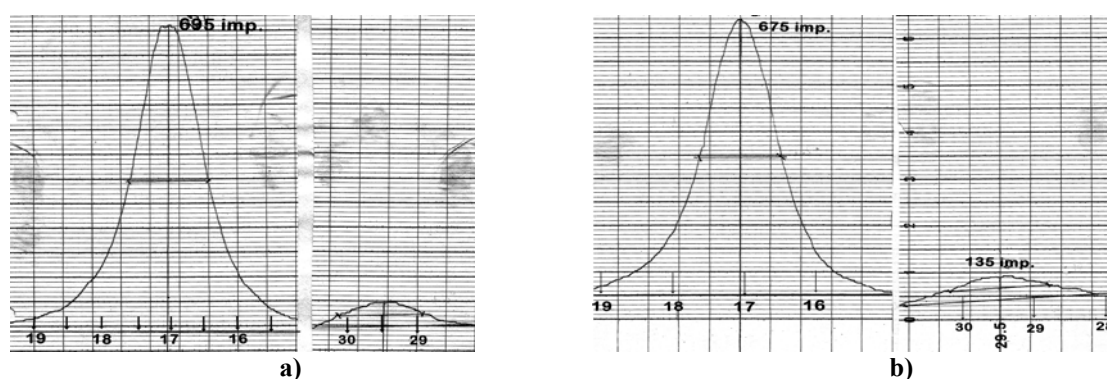


Fig. 3. Diffractograms of CF PAN precursors: a) PAN Sv 41, b) PAN Sv 61

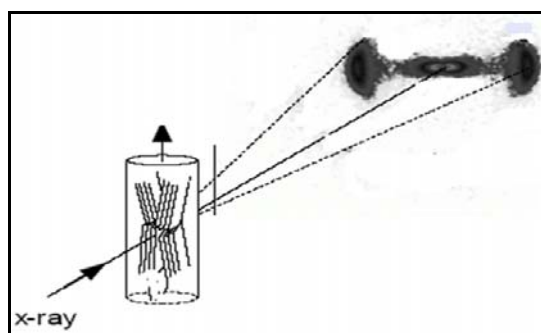
The peak positions in Figs. 3a and 3b were used to estimate the (200) ( $d_{200}$ ) and (310) ( $d_{310}$ ) interplanar distances while their FWHM for the apparent average diameters of the PAN paracrystals in the  $\langle 200 \rangle$  and  $\langle 310 \rangle$  directions ( $L_{200}$  and  $L_{310}$ , respectively). The integral

intensities of the (200) and (310) lines were considered as  $I_c$ . The uncertainties of the measurand given in Table 2 were calculated on the base of error propagation low i.e. in the hypothesis that the influence factors are of random nature and comply with normal density distribution [29]. The extended uncertainty factor was taken as 2 e.g. the significant degree is 0.05 or the degree of confidence is 95%.

**Table 2. Structural parameters of PAN Sv 41 and of PAN Sv 61 estimated by WAXS.**

Sample	$d_{200}$	$U_d$ (95%)	$L_{200}$ (nm)	$U_L$ (95%)	$d_{310}$	$U_d$ (95%)	$L_{310}$ (nm)	$U_L$ (95%)	$X_c$	$U_x$ (95%)
PAN Sv 41	5,18	0,09	67	11	3,03	0.06	66	11	0.52	0.08
PAN Sv 61	5,40	0,10	80	16	3,06	0.06	41	8	0.49	0.08

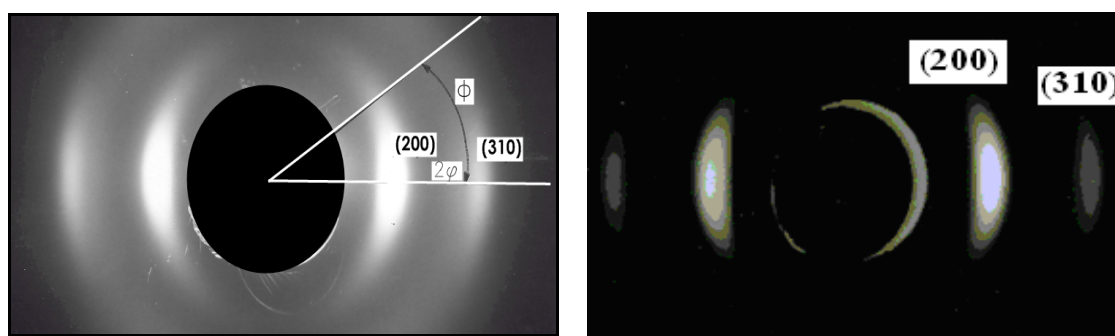
Unfortunately, the WAXD data are insufficient for technologists thus the PAN fiber preferred orientation was investigated by Debye-Scherrer technique. The geometry of the Debye-Scherrer experiment is given in Fig. 4.



**Fig. 4. The geometry of the Debye-Scherrer experiments.**

The diameter of the camera is  $\phi = 57,3\text{mm}$ . The  $\text{CuK}\alpha$  X-ray beam was Ni filtered. The PAN fiber bundle was aligned parallel to the camera axis. Two representative Debyeogram taken on PAN Sv 41 and PAN Sv 61 samples are shown in fig. 5 a),b).

The WAXS images of the PAN Sv 41 and of PAN Sv 61 sample (Fig 5 a), b) show that these fibers have similar preferred orientation.

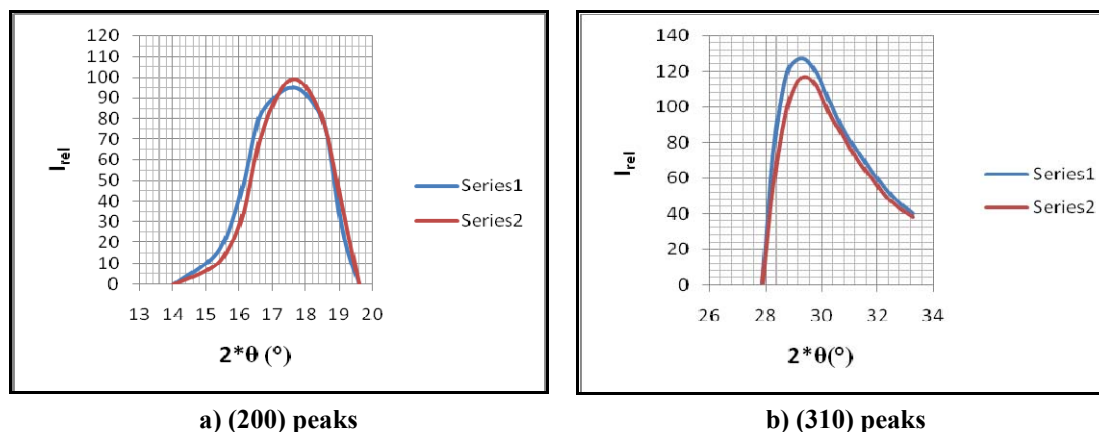


**a) PAN Sv 41**

**b) PAN Sv 61**

**Fig.5. Debyegrams for PAN Sv 41 and PAN Sv 61**

The Debyegrams show net (200) and (310) peaks. The densitometry curves of the diffraction maximum peaks (200) and (310) are shown in Figs. 6a and 6b. As it results from Fig. 6a, the positions of the main maximum peak (200) of PAN-Sv 41 and PAN Sv 61 fibers are closer and the FWHMs are very similar, as well.



a) (200) peaks  
b) (310) peaks  
Fig. 6. Densitometric curves for PAN-Sv 41 (red) and PAN Sv 61 (blue)

Fig. 6b shows that (310) line profiles are asymmetrical and have the same shape for PAN Sv 41 and PAN Sv 61 fibers. The structural parameters estimated based on densitometric curves are given in Table 3. The extended uncertainties with 95% degree of confidence show that the structural data obtained by Debye–Scherrer technique are consistent with the diffractometric ones.

Table 3. Structural parameters for PAN Sv 41 and PAN Sv 61 precursors

Sample	$d_{200}$ (Å)	$U_d$ (95%)	$L_{200}$ (nm)	$U_L$ (95%)	$d_{310}$ (Å)	$U_d$ (95%)	$L_{310}$ (nm)	$U_L$ (95%)
PAN Sv 41	5.14	0.09	3.08	0.041	3.03	0.06	3.01	0.043
PAN Sv 61	5.24	0.09	3.06	0.043	3.04	0.06	3.06	0.044

The structural data in Table 3 are significantly different from data in Table 2 especially for average diameters. These differences are caused by multiple factors as different technique for X-ray beam collimation, filtration and detection: different irradiation time etc. It is quite a matter of evidence, that the Debye–Scherrer technique could provide structural data as  $d_{200}$ ,  $d_{310}$ ,  $L_{200}$ , and  $L_{310}$  but at lower quality than WAXD technique. On the other hand, Debye–Scherrer technique is the best for PAN fiber preferred orientation investigation (see Fig. 5).

## 5. CONCLUSIONS

The paper shows why the WAXD techniques (diffractometry, Debye-Scherrer) are of great interest for PAN fiber testing. e.g. underlines the effectiveness of the classical WAXD technique for the PAN carbon fiber manufacture.

The paper argues that diffractometry is better fitted for PAN fiber structure characterization while Debye-Scherrer technique for preferred orientation characterization. Also, the paper proves the role of uncertainty in results quality assurance.

The WAXD results prove that the structure and texture of PAN Sv 41 and PAN Sv 61 are very similar to the ones that had been described by Chari and Bahl [27] and by Mathur and Bahl [28] for the same type of fiber.

The WAXD results made the main part of inference if a PAN fiber is proper to be considered as precursor for a specific type of carbon fiber. In this sense, the PAN Sv 41 and PAN Sv 61 are most fitted for medium strength carbon fiber. Also, they could be used as ACF precursor but from economical point of view this is not recommended.

The quality of WAXD results could be improved if there will be developed special equipment provided with texture goniometer and a hemispherical PPD detector but this means

at least one thousand cost then those for a routine Debye-Scherrer camera. Besides, the expected quality enhancement will not exceed 10 times which is unbearable.

## REFERENCES

- [1] Shindo, A., *Rep. Govn. Md. Res. Osaka*, 317, 1961.
- [2] Johnson, W., Phillips, I., Watt, W., *Brit. Pat.*, 1,110,1964, 791.
- [3] Fitzer, E., *Carbon*, **27**, 621, 1989.
- [4] Eslami Farsani, R., Shokuhfar, A. and Sedghi, A., *World Academy of Science, Engineering and Technology*, **35**, 2007.
- [5] Chair, S. S., Bahl O.P., Mathur, R. B., *Fiber Sci. Technology*, **15**, 153, 1981.
- [6] Mathur, R. B., Bahl, O. P., Kundra, K. D., *J. of Mat. Sci. Letters*, **5**, 757, 1986.
- [7] Zussman, E., Chen, X., Ding, W., Calabri, L., Dikin, D.A., Quintana, J.P., Ruoff R.S., *Carbon*, **43**, 2175, 2005.
- [8] Meijie Y., Chengguo W., Yujun B., Yanxiang W., Yong X., *Polymer Bull.*, **57**, 757, 2006.
- [9] Vasiliu, F., Pencea, I., Popov, A.M., *Rev. Phys. Studies and Researches*, **43**, 3-4, 135, 1991.
- [10] Vasiliu, F., Pencea, I., *Rev. Phys. Studies and Researches*, **43**, 3-4, 156, 1991.
- [11] Konovalova, L.Ya., Negodyaeva, G.S., Kumok, I.L., Tikhomirova, M.V., Dorenskii, A.L., Iovleva, M.M., Azarova, M.T., *Fibre Chemistry*, **23**(3), 193-196, 1992.
- [12] Yoshinobu K., Shiro I., Hiroshi F., Isao M., *Fuel*, **63**(12), 1738, 1984.
- [13] Liu, X.D., Ruland, W., *Macromolecules*, **26**, 3030, 1993.
- [14] Belenkov, E. A., *Russian Journal of Applied Chemistry*, **72**(9), 1612, 1999.
- [15] Fitzer, E., Frohs, W., Heine, M., *Carbon*, **24**, 387, 1986.
- [16] Junga, B., Yoona, J.K., Kima, B., Rhee, H.W., *Journal of Membrane Science*, **246**, 67, 2005.
- [17] Tan, L., Chen, H., Pan, D., Pan, N., *European Polymer Journal*, **45**, 1617, 2009.
- [18] Pick, M., Lovell, R., Windle, A. H., *Polymer*, **21**(9), 1017, 1980.
- [19] \*\*\* [www.polymer.kth.se/grundutbildning/.../Chapter%207.pdf](http://www.polymer.kth.se/grundutbildning/.../Chapter%207.pdf)
- [20] Paris, O., Loidl, D. and Peterlik, H., *Carbon*, **40**(4), 551, 2002.
- [21] Zhi-Xian, X., Jing, X., Liang-Hua, X., Yong-Qiang, D., Li-Wei, J. and Ri-Guang, J., *Polymer (Korea)*, **32**(2), 150, 2008.
- [22] Pencea, I., *Elements of applied structural analysis*, Ed. PrintTech, Bucharest, 2001.
- [23] Pencea, I., *Basics of structural analysis*, Ed. Print Tech, Bucharest, 2001.
- [24] Drambei, P., Ciocoiu, M., Drambei, C., Craus, M.L., *Mat. Plast.* **46**(3), 2009.
- [25] Hinrichsen, G., *J Polym. Sci.* **38**, 303, 1972.
- [26] Lipatov, I.S., *Rentgenograficeshie metodi izucenia polimernish sistem*, Ed. Nauka Duma, 1982.
- [27] Chari S. S., Bahl O.P., *Fiber. Sci. Tech.* **15**, 153, 1981.
- [28] Mathur R. B., Bahl O.P et.all, *Fib. Sci. Technol.* **21**, 223, 1984.
- [29] \*\*\* SR EN 13005, 74, 2005.

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