TURBOSTRATIC STRUCTURE OF CARBON FIBERS BASED ON RIGID-CHAIN POLYMERS

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It is well known that high performance rigid-chain polymer fibers exhibit excellent thermal, mechanical and other properties. The temperature of degradation of such fibers (T = 400 – 600 °C) coincides with the temperature of the turbostratic carbon structure formation during carbonization. So, they are of interest as promising materials for forming of the turbostratic carbon structure providing high physico-mechanical properties.

In this work, a combined WAXD/SAXS study of structure and testing of mechanical properties were carried out for various fibers on the base of hydrate cellulose (HC), polyacrylonitrile (PAN), polyarilen-1,3,4-oxadiazole (POD), poly-amido-benzimidazole (PABI) and pyromellitic dianhydride-4,4'-oxydianiline (PMDA-ODA) polyimide before and after pyrolysis and carbonization. Much attention was given to the supermolecular structure of carbonization's intermediators.

It was shown that the long period in pyrolyzed HC fibers corresponded to the regular alternation of the initial HC crystalline and partly-pyrolyzed amorphous regions.

Upon pyrolysis at T = 320 ºC (Fig.1-2), a small-angle X-ray reflection arised whereas it was absent in the initial fiber (Fig.1-1). When the temperature of pyrolysis was growing up to T = 335 ºC, the intensity of the reflection was increasing also (Fig. 2).

But, its intensity dramatically decreased on pyrolysis at 340 – 350 ºC. Increasing in SAXS reflection intensity was accompanied by the decrease of fiber strength, significant weight loss and reduction of density. Herewith, the main parameters of structure - fibrils

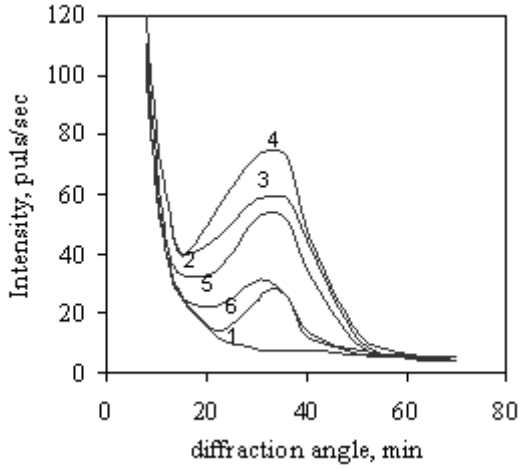

Fig. 1. Small angle X-ray diffraction profiles of HC fibers: as prepared (1), pyrolyzed at 320 (2), 330 (3), 335 (4), 340 (5) and 350º C (6).

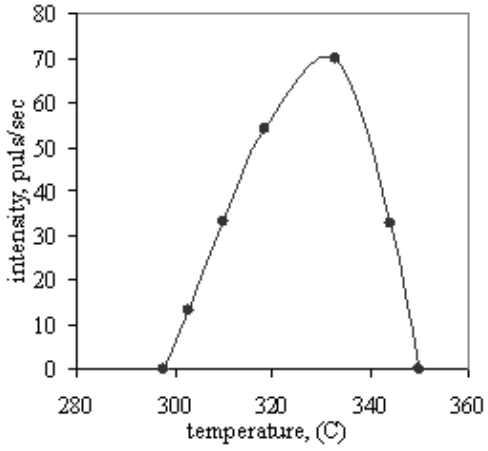

Fig. 2. Dependence of the intensity of HC fibers SAXS maximum on the temperature of pyrolysis.

diameter, a long period and sizes of crystallites were invariable. The destruction of crystalline structure caused the reduction of SAXS reflection intensity up to its disappearance at T = 355 ºC.

Under thermo-oxidation of PAN fibres, SAXS reflection (which was absent in initial fibers) arised at T = 210 ºC. Its behaviour was similarly to that of the pyrolyzed HC fibres. However, during this process, intramolecular and interchain cyclization occured, and, herewith, the density of fiber was growing up. Analysis of structure of oxidized PAN fibres allowed to conclude that contrary, the SAXS reflection in oxidized PAN was due to the alternation of more dense oxidized amorphous regions and less dense PAN crystallites.

The third type of density heterogeneity has been found in pyrolysed POD fibers. POD is famous as one of the most thermostable polymer on the base of polyheteroarilenes. Temperature of thermodestruction of POD (T = 500 – 575 ºC) is close to the beginning of polycyclic aromatization - formation of the turbostratic carbon structure. Reflection (002) of carbon on WAXD patterns was observed distinctly. At the same time, SAXS reflection arised in the beginning of pyrolysis of POD fibers as well as in the case of HC and oxidation of PAN. The intensity of SAXS reflection grows with increase of temperature of pyrolysis POD (T = 500 – 550 º) and then falls (T = 550 – 600 ºC).

Analysis of main parameters of supermolecular structure which affect upon value of intensities of SAXR, as well as change of density, strength, elasticity modulus etc. of specimen, allowed to conclude that the long period in pyrolyzed POD fiber is a regular alternation of more dense regions with the turbostratic carbon structure and less dense POD regions. Carbon fibers on the base of this polymer with anisotropic high-ordered turbostratic structure (Fig.3), exhibit high mechanical properties (σ = 1.8 GPa, E = 100 GPa) up to 900 °C.

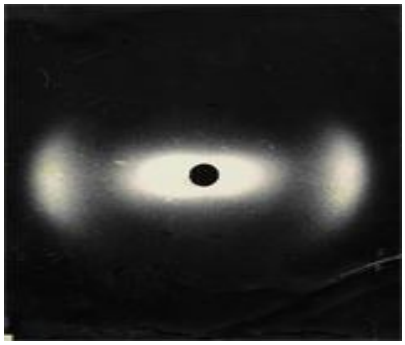

Fig.3. WAXD pattern of carbonized POD fibers at T = 900º C.

Conformational polymorphism of PABI macromolecules prevented the formation of the ordered turbostratic structure that was responsible for comparatively low mechanical properties (σ = 0.5 GPa, E = 32 GPa) of carbon fibers made from this polymer.

A particular feature of the PMDA-ODA fibers pyrolysis is very high thermal stability of their crystalline structure (up toT = 600 °C). As a result, low ordered turbostratic structure was revealed in PMDA-ODA based carbon fibers which corresponds to poor mechanical properties like in the PABI based carbon fibers.

References

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