

## Graft Polymerization as the Method for Improvement of the Polyamide Fibers Features and Its Effects on the Structure of the Polymer

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### 1. Development of the consumer properties of synthetic fibers

Most of the synthetic fibers show a small attraction for water. We assume that the evaluation of clothing comfort is based on the determinations of the moisture absorption, moisture elimination, vapor permeability, and so on. Therefore, it is clear why the improvement of these features is so important. Clothes made from polyester and even more in the case of polyamide, despite valuable physicommechanical characteristics, often do not satisfy the requirements for comfort and hygienic properties due to pure absorption of moisture. However, as there are different types of modified molten fibers with improved consumer properties, polyamide fibers could be of interest due to a simpler and more direct method of fabrication.

The shortcoming of low moisture absorption could not be attributed only to the molecular composition of fibers, since polyamide contain some (C=O) hydrophilic groups. There is also a

very important role of geometrical arrangement of the molecules. Only a part of the fiber is accessible to water molecules. Regions in which the molecules have crystallized are not accessible. A molecular structure explicable by the "fringed micelle theory" occurs in most of fibers. This theory is based on X-ray diffraction studies and suggests that single long chain molecule spreads out and passes through several crystal regions and also on the edges of the crystal regions through the disordered regions [1]. The non-crystalline regions are most important in moisture absorption. It is predicted that in these regions molecules are linked together only at the few points and consequently most of the active groups are available to water molecules.

Hence, most of the directions in the improvement of the moisture sorption of the synthetic fibers had been based on the perturbations of the structure regularity, such as adding the alkali salts or oxides, a foaming agents which liberates the inert gas

into the polymer melt during the spinning in order to obtain the porous structure [2]. Other trends are the increase in the specific volume of the fibers (yarns) by such processes as the texturing of the filaments in order to increase transport of the moisture due to the increase of capillary activity [4]. In the case of polyamide fibers, the incorporation of the polar groups by addition of aliphatic hydroxy compounds like polyethylene glycol is also performed. In the last decade, the methods of concentrating sorption sites responsible for moisture sorption on the surface of the fiber prevail over other methods. This approach is implemented mainly by grafting the noncrystallizable carbochain polymers with hydrophilic groups to the fiber.

## 2. Advantages of the graft polymerization

If we compare the effects of various methods in increasing the hydrophilicity of the polyamide and other synthetic fibers, the advantages of grafting copolymerization are outstanding.

The above-mentioned methods based mainly on the perturbation of the structure assume that the absorption of moisture will increase with the increase in amorphous phase concentration. This is true, but this increase will be relatively small

because even if the concentration of the amorphous phase is 100%, the increase in moisture absorption will not be significant. Effect of this kind of modification could be seen from the extrapolation of the amorphous phase concentration plot via moisture sorption (wt%) shown at Fig. 1, for the copolyamide made from caprolactam and AG salt [2]. The explanation of this behavior could be based on the existence of the saturating cohesive forces that affect active (amide) groups even in the amorphous phase.

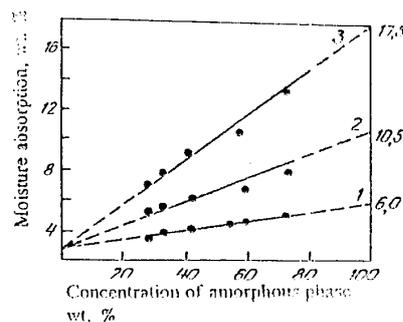


Fig. 1 Moisture sorption of copolyamide fibers vs. concentration of amorphous phase in the polymer for  $W_{rel}=65$  (1), 80 (2) and 95% (3).

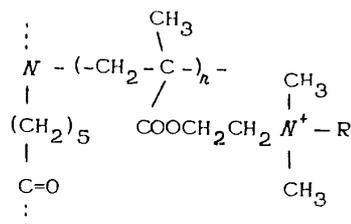
The addition of PEG increases the number of the polar groups in the matrix of polymer, but the effect is temporary (PEG is removed during washing for its solubility in water) and significantly worsens the mechanical properties of the fiber. Grafting polymerization allows the preservation of the fiber-forming polymer, since it concerns the concentration of sorption sites on the surface of the fiber with the possible regulation of

the amount of the noncrystallizable graft polymer. Therefore, the mechanical properties determined by main polymer can be maximally preserved [3].

Graft copolymers of the polyamide fibers containing polymeric quaternary salts (PQS) are of practical interest for fabrication of the modified textile fibers. Most extensively used PQS in this context are:

- Polyhydroxyethyl methacryl (PHEMA) QS
- Polyacrylic acid (PAA) QS
- Polymethacrylic acid (PMAA) QS
- Polymethylvinylpyridine (PMVP[N<sup>+</sup>]) QS
- Polydimethylaminoethyl methacrylate (PDMAEMA[N<sup>+</sup>]) QS

Druzhinina et al. had studied the Caprilon fiber, graft copolymer of polycaproamide (PCA) fiber and PDMAEMA [N<sup>+</sup>]. This fiber externally resembles cotton and finds a wide application as pure forms yarn or as the blends with cotton, in the production of tricot articles and clothes. Caprilon fiber in general has the following chemical structure:



### 3. Moisture sorption by grafted PCA/PQS copolymer

Originally, the graft polymerization hydrophilizing finishing was developed by using the PAA and PMAA. However, even more increase in hydrophilicity in the case of PAA and PMAA salts was observed. Therefore, radiation grafting of PAA and PMAA with subsequent conversion to Na salts has been developed, but chemical grafting became competitive to radiation method due to the absence of homopolymer formation [3]. The chemical copolymerization is performed in liquid phase and therefore, the concentration of the COOH groups can be determined gravimetrically and titrimetrically. When the moisture absorptions of PCA graft copolymer with PAA and PMAA before and after treatment with NaOH (in order to convert grafted PAA and PMAA in their sodium salts) are compared, the increase in moisture absorption after the conversion to Na salts is observed (Fig. 2).

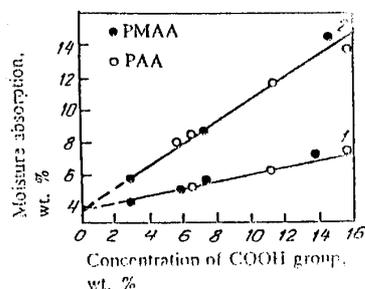


Fig. 2. Equilibrium moisture absorption of PCA fiber vs. concentration of graft PAA and PMAA for  $W_{rel} = 65\%$  before (1) and after treatment with NaOH (2).

Table 1 Specific electric resistance  $\rho_s$ , of tricot clothe made of PCA fiber, Caprilon and cotton-Caprilon blend as a function of relative humidity

Fiber used in fabrication of tricot	$W_{rel}=20\%$		$W_{rel}=65\%$		$W_{rel}=90\%$	
	$\varphi$ , %	$\rho$ , $\Omega$	$\varphi$ , %	$\rho$ , $\Omega$	$\varphi$ , %	$\rho$ , $\Omega$
PCA	0.8	$1.32 \times 10^{14}$	3.8	$4.05 \times 10^{12}$	7.5	$1 \times 10^{12}$
Caprilon	2.0	$1.97 \times 10^{12}$	7.8	$1.00 \times 10^9$	12.0	$1 \times 10^9$
Cotton	-	-	7.9	$1.00 \times 10^9$	16.0	$1 \times 10^9$
Cotton-Caprilon blend (55:45)	-	$0.97 \times 10^{12}$	7.8	$1.45 \times 10^9$	-	$1 \times 10^9$

Hence, for these copolymers, equilibrium moisture sorption can be successfully described by the analytical equation:

$$\varphi = 3.7 + 0.21[COOH] \quad (1)$$

After converting COOH groups into sodium salt form, the equation becomes:

$$\varphi = 3.7 + 0.64[COOH] \quad (2)$$

Measurements of the electrical resistance for tricot clothes made of different fibers, showed that Caprilon and cotton have approximately the same values over a wide range of relative humidity. Druzhinina et al. found that besides attributing formation of conductive layer to the increased moisture sorption due to the presence of grafted PQS, the ionic mechanism also plays an important role (Table1).

It is well known that polyamide staple fibers are extremely difficult to be processed at the conventional

equipment for spinning due to low cohesiveness and high electrifiability [4]. However, the above results confirm that only modified polyamide fibers could pass all technological operations in a pure form or in a blend with cotton due to their hydrophilicity, and the cotton-like appearance of the textiles will be obtained [2].

#### 4. Structure and morphology of the PA-6/PMAA copolymer

Main directives in the development of the grafting polymerization were turned more to the radiation grafting at the beginning. First detailed observations of the structure of the PA-6/PMAA graft copolymer were given by Smirnova et al. [3]. They performed scanning electron microscopy and electron probe X-ray spectra microanalysis on the polymer treated by  $AgNO_3$ . The results were given as the concentration profile, since the intensity of characteristic X-ray emission for  $Ag^+$  ions is dependent on their concentration in

the sample (concentration of the COOH groups of PMAA). The obtained concentration profile is given in Fig. 3.

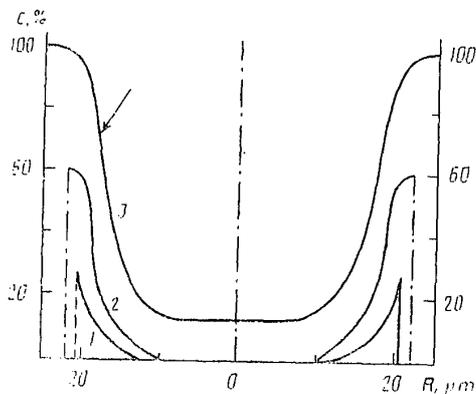


Fig.3 Change in the size of the concentration profile with the degree of grafting of PMAA ( $\omega$ ). Degree of grafting for PMAA was 9.7(1), 30.7(2) and 57.2%(3).  $R$  is the radius of the modified fiber;  $c$  is concentration.

Fig. 3 shows how fundamentally different is the concentration profile of the PMAA grafted in the PA-6, depending on the degree of the grafting  $\omega$ . For low degrees of grafting ( $\omega < 10\%$ ), it has the concave form, and therefore it is clear that grafted polymer gradually penetrates deep into the matrix. For  $\omega > 30\%$  the stepped profile points out that the concentration in the near-surface layer is nearly constant, which continues into the extended diffusion "tail" towards the fiber core. There is a small increase in the fiber diameter. The concentration of the grafted PMAA increases as the step moves deep into the polymer matrix for  $\omega > 50$ . Practically the core becomes filled up with PMAA and the significant

increase in diameter of the fiber is observed. Follows that the kinetics of the graft polymerization are characterized by

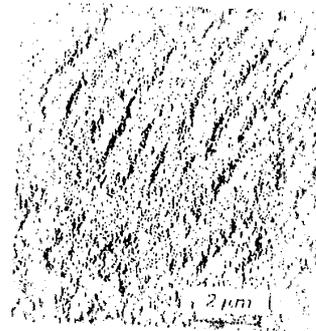


Fig.4 Photomicrographs of the PA-6 modified fibers cross-section. Degree of grafting PMAA: 30.7%.

simultaneous rise of the PMAA concentration in near-surface layers, penetration into the fiber and by increase of fiber diameter [3]. At the higher degrees of grafting  $\omega > 30\%$ , the phasic inclusions and the continuous layers of grafted PMAA are visible on the photomicrographs (Fig. 4), which indicates that the penetration of PMAA occurs deep into the polymer matrix. Evidently, this could lead to destruction of the fibrillar structure of PA-6 and formation of the heterogeneous destroyed paracrystalline PA-6/grafted PMAA systems.

Comparison of the structural and the concentration profiles (Fig.3) shows that PMAA chains in segregated the surface layers are represent the continuous phase ( $\sim 90\%$ ) while the PA-6 spherical particles can be considered for the occlusions. As the concentration profile moves towards

the core of the fiber, the size of PA-6 inclusions increases to 1-3  $\mu\text{m}$  and the concentration up to 70%, which causes phase inversion. Hence, the PA-6 becomes continuous phase and PMAA the phase inclusions. It is also observable that the diffusion of the PMAA in the near surface layers at the high concentration is hampered in the beginning. The observation can be attributed to the increase in density of the grafted layer. This may be the factor for creating the conditions for penetration of the growing PMAA chains over the interfibrillar space of the non-grafted regions in PA-6 fiber [3]. From all discussed it is obvious that the graft copolymers of polyamide with PAA, PMAA or PQS merit to take an important role in the production of textiles as the supplement for natural fibers or in blend with them. If the mechanism of grafting is well known, it is possible to preserve valuable mechanical properties given by PA-6, by gradual grafting to the appropriate degree of grafting. In other words, the concentration of grafted polymer in the near surface layer will be the factor for preserving the fibrillar structure of fiber-forming PA-6. The practical interest can be primarily found in regulating the moisture sorption of the modified fiber to values of 6.5-8.5%. This would bring them close to the properties of the cotton

fibers and make possible their application in the production of the textiles with high demands for hygienic properties, such as different tricot articles or even clothes for children.

## 5. References:

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