THE INFLUENCE OF COCON TREATMENT ON THE ELECTRIC PROPERTIES OF THE NATURAL SILK FIBROIN

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The influence of thermal treatment and treatment by the liquid nitrogen of cocons, on electric properties of the natural silk fibroin has been studied. It has been established, that the polarization (ε) and tangent of angle of dielectric losses ($tg\delta$) increase with the growth of amorphous sectors, that corresponds to the sample received from cocons, treated by the liquid nitrogen. Moreover the dielectric constant, tangent of the loss angle and the electroconductivity of the fibroin, received from cocons treated by the liquid nitrogen, are on 10 % more in comparison with the fibroin, received from cocons treated by the heated air and ultrahigh frequency (UHF) field.

It has been established [1] that in the fibroin received from cocons, treated by the liquid nitrogen, the improvement of physico-mechanical properties of natural silk is observed. We connected this improvement with the increase of amorphous portion of fibrion. [2,3].

We have studied in given article the influence of cocon treatment (thermal, by the liquid nitrogen and ultrahigh-frequency field) on the polarization (ε) and tangent of angle of dielectric losses $(tg\delta)$ of the natural silk fibroin. According to [4, 5] dependences of ε and $tg\delta$ on the temperature and the frequency of the electric field, authors connected with the structure of the polymer and the character of the heat motion of macromolecules.

The silk received from cocons was treated by different methods: by plunging into the liquid nitrogen during 2 minutes; by the thermal treatment at 350K during 60-90 minutes and by the UHF field (915 MHz) till 6 minutes. The samples of the silk fibroin were produced in the form of the pressed pills, on whose opposite surfaces silver layers of electrodes were sprayed. Measurements were made by means of P589 bridge in the closed volumes at temperature intervals 100-550 K.

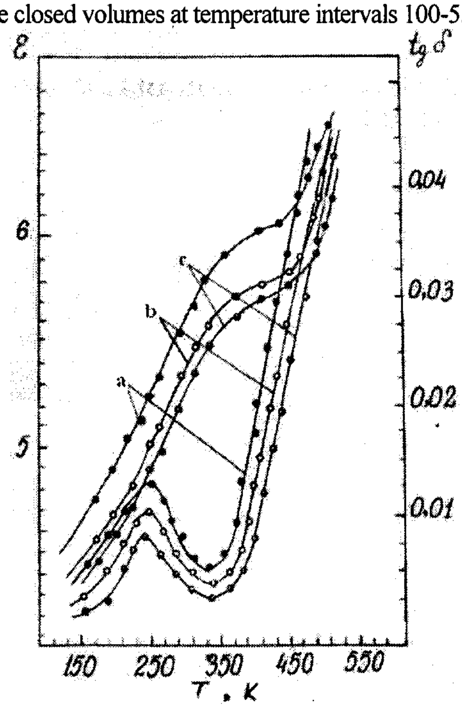

Fig.1. Temperature dependence of ε and $tg\ \delta$ of the fibroin at the frequency of the electric field 1KHz (the treatment: by the liquid nitrogen -a; by the heated air -b; by UHF field -c.

The dependences of ε and $tg\delta$ on the temperature are given on the fig.1 for the silk fibroin treated by the liquid nitrogen, heated by air and UHF field. As it is seen from the given fig.1, ε increases in steps with the increase of the temperature, and the dependences of $tg\delta$ on the temperature have maximum [6, 7], that is caused evidently by local motions of polar groups placed in the main and side chain of macromolecules, i.e. by the β - process in the silk fibroin.

The β -process at the frequency 1KHz takes place at temperatures which are lower than the vitrification temperature [4]. The transition from the glassy state to the high-elastic state takes place in temperature limits till 350K. High growth of $tg\delta$ is observed at further increase of the temperature and the second maximum is discovered before the material destruction caused by the process of dipole polarization

The last fact, apparently, is caused by the increase of leak currents, because at high temperature, thanks to the greater conductivity of the silk fibroin, dipole-segmental maximum is smoothed.

Values ε and $tg\delta$ for the fibroin received from cocons treated by the liquid nitrogen, at all temperature intervals are much more than for the fibroin, received from cocons, treated by the heated air and UHF field. Let us turn to some known considerations to explain this fact.

The silk fibroin is the partialy-crystallizing biopolymer, formed approximately from 60% of crystal and 40% of amorphous part. The crystal part mainly consists of rests of amino acids, glycin , alanin, serin and terozin. The amorphous part consists of numerous amino acid rests, containing polar groups. Moreover, intermolecular interactions in crystal region impose additional restrictions on polar group mobility. Hence it follows that the main contribution to ε and $tg\delta$ is made by amorphous parts of the silk fibroin. Consequently ε and $tg\delta$ will increase with the growth of part of amorphous sectors, that corresponds to the sample received from cocons treated by the liquid nitrogen (fig.1).

We have received the analogous conclusions by measuring of the biopolymer electroconductivity. For this we have measured the volume resistivity $\rho(T)$:

$$\rho = \frac{2\pi\cdot 1.8\cdot 10^{10}}{\omega\cdot\varepsilon\cdot tg\delta} ,$$

where ρ is the volume resistivity of the dielectric (om, m), ω is the circular frequency of the electric field. For samples, treated by different methods, the dependence $lg\rho$ (T) was determined at the same conditions. Obtained results are presented on the fig.2 from which follows that ρ for the fibroin, received from cocons treated by the liquid nitrogen, is considerably less than for samples, received by the heated air and UHF field. We have earlier established [1] that the electroconductivity reduces at the increase of the degree of polymer crystallinity, and the volume resistivity grows. The last fact has found the confirmation in experiments for samples received from cocons, treated by heated air and UHF field.

It is necessary to note that at the primary cocons treatment by the heated air and UHF field, the fraction of amorphous sections reduces and the quantity of submicrocracks in the fibroin will increase. The growth of submicrocracks leads to situation, when the increase of ion traps causes the decrease of mobility of latters. That is why the electroconductivity of the fibroin treated by the heated air and UHF field, reduces and the conductivity is the least at cocons treatment by the UHF field.

It has been established that the dielectric constant, tangent of the loss angle and electroconductivity of the fibroin, received from cocons treated by the liquid nitrogen, are on 10% more in comparison with the fibroin, received from cocons treated by the heated air and UHF field.

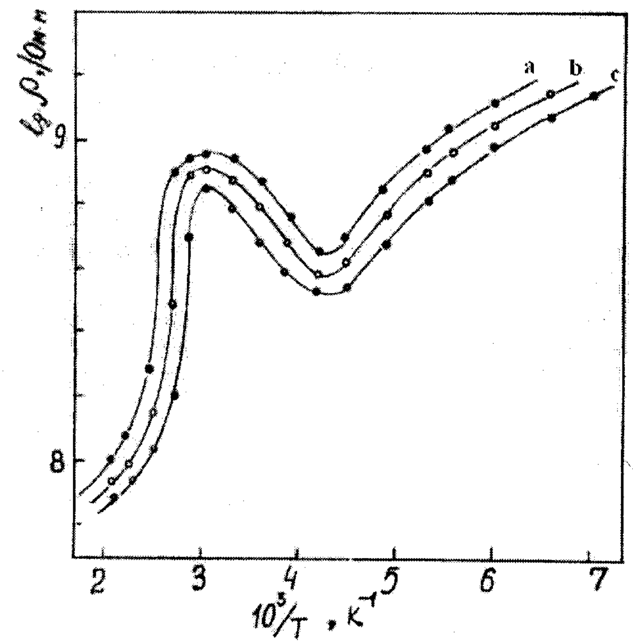

Fig.2. Temperature dependence of the fibroin specific resistance on the variable current (the treatment: by UHF field - a; by the heated air -b; by the liquid nitrogen -c).

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BARAMANIN İLKİN EMALININ TƏBİİ İPƏK FİBROİNİN ELEKTRİK XASSƏLƏRİNƏ TƏSİRİ

Baramanın ilkin emalının fibroinin elektrik xassələrinə təsiri öyrənilmişdir. Müəyyən edilmişdir ki, maye azotla emal edilən baramadan alınan fibroində amorf hissələr çox olduğundan, onların polyarizasiyası (ε) və tangens bucaq əmsalı $(tg\delta)$ da artır. Bundan başqa, maye azotla emal edilmiş baramadan alınan fibroinin dielektrik nüfuzluğu, tangens bucaq əmsalı və elektrik keçiriciliyi isti hava və yüksək tezlikli sahə ilə emal edilən baramadan alınan fibroindən 10% yüksək olur.

Р.С. Исмаилова

ВЛИЯНИЕ ОБРАБОТКИ КОКОНОВ НА ЭЛЕКТРИЧЕСКИЕ СВОЙСТВА ФИБРОИНА НАТУРАЛЬНОГО ШЕЛКА

Изучено влияние термической обработки и жидким азотом коконов на электрические свойства фиброина натурального шелка. Установлено, что поляризация (ε) и тангенс угла диэлектрических потерь $(tg\delta)$ увеличиваются с ростом аморфизации участков, а это соответствует образцу, полученному из коконов, обработанных жидким азотом. Кроме того, диэлектрическая проницаемость, тангенс угла потерь и электропроводность фиброина, полученного из коконов, обработанных жидким азотом на 10% больше по сравнению с фиброином, полученным из коконов, обработанных нагретым воздухом и СВЧ полем.

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