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Research Article

SOLID PHASE DISSOLUTION FIBROIN OF NATURAL SILK

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ABSTRACT

Recycling of waste polymer raw materials is the most promising and actively developing method of recycling polymer waste. When recycling natural silk waste by obtaining structurally mixed fibers from joint solutions of any polymer and protein, the process of polymer dissolution plays an important role. The paper considers the process of solid-phase dissolution of natural silk fibrion as well as their mixtures with other polymers in the field of intense force impacts. The results of the study of the physicochemical properties and structure of the obtained materials showed that all the resulting mixtures of polymers have fiber-forming properties suitable for the formation of artificial or modified fibers based on them.

KEYWORDS

Processing, polymers, fibroin, natural silk, polymer solutions, polymer mixtures, fibers.

INTRODUCTION

The dissolution of polymers in order to obtain initial working solutions for molding products (fibers, films, etc.) is an important step in the technological process of processing polymers through solutions. The final

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concentration of the working solution depends on the type of polymer, its molecular weight, the chosen solvent, and the method of product molding [1–3].

Natural silk fibroin is insoluble in alcohol, petroleum ether, carbon disulfide and other organic solvents. In practice, it is also insoluble in water, but swells, and the swelling is limited: at a temperature of 18°C, the transverse size of the fiber increases by 16-18%, the weight of the fiber - by 30-35%.

Swelling is somewhat enhanced in acid solutions and especially in alkali solutions, in the latter case it can become irreversible. In concentrated solutions of some salts (chlorides, bromides, iodides, nitrates, calcium, strontium, barium and lithium thiocyanates, zinc chloride, etc.), fibroin swells indefinitely and forms a viscous solution, from which it can be regenerated in one way or another.

Fibroin is easily soluble in copper-ammonia solution, alkaline copper-glycerin solution, ethylenediamine solution of copper hydroxide, ammonia-nickel solution, in solutions of strong acids - phosphoric, sulfuric, hydrochloric, dichloroacetic and formic [4-6].

The solubility of fibroin is of practical importance and, in particular, the processing of the fibrillar protein of natural silk fibroin is of significant interest due to the possibilities:

- production of artificial fibroin fibers and creation of composite materials for special purposes on their basis;
- modification of chemical fibers by mixing their solutions in a common solvent in the process of preparing a spinning solution and improving the physico-chemical properties of the resulting materials based on them;
- -solutions to the problem of effective disposal of non-woven protein waste from the production of natural silk and the creation on this basis of a waste-free technology for processing this precious type of textile raw material.

The solubility of fibroin has been investigated by various researchers in their attempts to form artificial protein fibers from the waste products of natural silk production. In works [7-8], natural silk was dissolved at room temperature in a LiBr solution, purified in distilled water for 3-4 days. Silk isolated in this way is called LiBr-silk. The paper describes in detail the cleaning method. Drying the LiBr-silk solution at 100°C results in a water-soluble film, and drying the same solution at room temperature produces a film with a crystal structure called α-form. Such a crystal structure is metastable and gradually transforms into a stable crystal structure called the β - form. In works [9], a concentrated aqueous solution of lithium thiocyanate was used to dissolve the silk fiber. This solvent has a neutral reaction, dissolution is achieved within a few minutes at room temperature. In works [10-11], to dissolve silk fiber, a 63% aqueous solution of sodium thiocyanate containing 20-25% glacial acetic acid was used as a solvent. Known [12-13] are also works on the preparation of spinning solutions of silk fibroin in a 60% solution of sodium thiocyanate, where the concentration of fibroin was 12%, the dissolution time was 3 hours. In all cases, the content of fibroin was about 10-12% and a long dissolution time.

This necessitates the use of a number of additional ingredients. This circumstance, the duration of the dissolution process and the low maximum achievable concentrations of silk are the factors that make it difficult to obtain a solution even under laboratory conditions. As for large-scale industrial processes, they have not been mastered at all in our country so far.

Considering the above, we have made attempts to carry out the dissolution of silk, as well as the mixing of silk with other polymers in the field of intense shear stresses. To implement the dissolution of silk in the field of intense shear stresses, we used the processing of mixtures of natural silk fibroin (NSF) and their mixtures with other polymers with salts of some metals and water in a rotary disperser [12–15].

Even the first experiments convinced us that the process of fibroin processing from the crystalline to

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the plastic state is carried out quite effectively in the rotary disperser. Let us consider this process in more detail using the example of the following mixture (NSF:NaCNS:H2O), taken in the ratio of components (1:1:0.36), respectively.

The initial mixture was prepared in a glass desiccator by manual stirring. For this, fibroin, obtained from natural silk waste by washing sericin in hot water, was placed in a desiccator, then dried at a temperature of 60–80°C in a vacuum drying cabinet and cut to a size of 2–5 cm. Sodium thiocyanate, previously dehydrated by calcination at 150°C, and then the required amount of water was injected from above by spraying. Stirring continued for 10–20 min. When stirred, the general appearance of fibroin fibers and crystals of sodium thiocyanate did not change significantly.

The mixture prepared in this way was loaded into the hopper of a laboratory dispersant, from the hopper the mixture fell into a cylindrical chamber consisting of three zones: the loading zone (1), the compression zone (2) and the dispersion zone (3). The temperature was maintained in zones at the level of 20°C, 40°C and 50°C. Heaters, refrigerators, and recording thermocouples were used to maintain the required temperature regime. The heated and mixed material under pressure fell into the concentric transport gap of the dispersion chamber, where it was subjected to shear deformations.

As a result, a significant change in the structure of the processed material was observed, and after 10-15 minutes. a plastic mass with fiber-forming properties was separated from the rotary disperser. A more detailed study of this process was carried out in an installation in which the dispersion chamber was equipped with a special viewing window for visual control. At the same time, a heterogeneous material containing various inclusions of fibroin was observed in the dispersion chamber, and a more homogeneous material was observed on the right.

When processing a mixture (NSF:ZnCl2:H2O), sufficiently homogeneous plastic materials were obtained when the ratio of the components of this mixture was (1:2:0.8) or (1:2:0.65). When processing a mixture with a lower water content, partial oxidation of fibroin was observed. The materials obtained in this case were colored red. At the same time, the presence of individual fibroin fibers was observed in them. A similar picture was observed during the processing of mixtures with a higher content of ZnCl2. When processing a mixture of composition (1:4:0.75), the load on the dispersant engine increased sharply. In this case, the resulting plastic material also acquired a color; it also showed isolated unresolved fibroin fibers.

Obtaining polymer-polymer mixtures is a common way to create composite materials with the desired set of properties. The chemical industry often uses the formation of fibers from mixtures of two or more polymers dissolved in a common solvent. In this case, a necessary condition is the use of a sufficiently homogeneous solution, since inhomogeneity leads to formation instability.

Considering the above, we tried to obtain a sufficiently homogeneous material by processing a mixture consisting of fibroin fibers, polyacrylonitrile (PAN) fibers, inorganic salt and water in a rotary disperser. Zinc chloride (ZnCl2) was used as the inorganic salt. The latter was determined by the fact that the solution of this salt is simultaneously a solvent for both PAN and NSF.

In the first experiments, we tried to process a mixture of NSF:PAN at a relatively low PAN content in the same temperature regime in which a homogeneous plastic material was obtained from fibroin alone. Before loading into the dispersant, the mixture of NSF fibers: PAN, taken in a ratio of 90:10 wt.%, was first well mixed. Then, placing a mixture of fibers in a glass vessel, water was introduced into this vessel in an amount of 80 ml per 10 g of fibers and the vessel was closed. The vessel was heated for 20 min at a temperature of 80-90°C. As a result of this procedure, water was absorbed by the fibers, then ZnCl2 was poured into the vessel in an amount of 200 g per 100 g of fibers and thoroughly mixed.

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In the same temperature regime, we managed to obtain homogeneous materials from NSF:PAN mixtures with a PAN content of 5, 10, 15, 20 wt%. When biopolymer mixtures of NSF:PAN:$ZnCl_2$ or NSF:PAN:NaCNS with a higher water content (see Table 1) were loaded into the rotary disperser, the solid components were squeezed out to one degree or another, i.e. part of the water was squeezed out of the processed mixture and gradually filled the cavity of the dispersant in the first zone. This made the true ratio of the components of the mixture under consideration, the processing of which was carried out in the compression and dispersion zones, very uncertain. At the same time, the material released from the rotary disperser lost its plastic properties to a large extent and contained undestroyed inclusions of fibers.

Table 1.

Processing in a rotary disperser of some NSF:PAN mixtures salt and water, processing mode and brief information about submissions received

№	The composition of the NSF:PAN mixture, wt.%.	Salt	Salt content relative to polymer	Water content relative to polymer	Temperature regime by dispersion zones		Time, process (min)	Note
					2 zone	3 zone		
1	90/10	$ZnCl_2$	1	0,8	40	50	15	Homogeneous material
2	80/20	$ZnCl_2$	1	0,8	40	50	15	
3	70/30	$ZnCl_2$	1	0,8	50	60	15	
4	50/50	$ZnCl_2$	1	0,8	50	60	15	
5	50/50	$ZnCl_2$	1,6	2	50	50	15	
6	50/50	$ZnCl_2$	2	0,8	50	60	15	
7	50/50	$ZnCl_2$	0,5	0,8	60	6	20	Undissolved PAN fibers are encountered
8	50/50	$ZnCl_2$	1,6	0,3	50	60	20	
9	50/50	NaCNS	0,66	0,2	50	60	18	
10	50/50	NaCNS	0,66	0,5	50	60	15	Homogeneous material
11	50/50	NaCNS	2	0,8	50	60	15	

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A characteristic feature of obtaining such materials in a rotary disperser is that this process is carried out at a very low water content (the water content in the mixture is from 6 to 25 wt.%, which is close to the maximum water content in fibroin during its swelling).

These results indicate that the processing in a rotary disperser of some compositions of fibroin, water and some salts allows to obtain sufficiently homogeneous materials. The most indicative results were achieved during the processing of mixtures (NSF:NaCNS:H2O) and (NSF:ZnCl2:H2O). It draws attention to the fact that mixtures processed in a rotary disperser and homogeneous materials obtained from them are characterized by a lower salt content, a significantly lower content of liquid components and a significantly higher content of fibroin compared to those fibroin solutions that are made according to standard technology, i.e. by dissolving fibroin in salt solutions with the addition of acetic acid.

We note once again that these materials obtained in a rotary disperser contain up to 30-50% fibroin and only 3-20% water. For comparison: solutions obtained by conventional technology contain 25-35% water and 12-16% acetic acid, i.e. the content of liquid components in the latter solutions is 2.5-6 times higher than in compositions efficiently processed in a rotary disperser.

Essentially, in a rotary disperser, we processed "dry" mixtures, for example, a mixture of dry fibroin with crystalline hydrates or a mixture of slightly swollen fibroin fibers with dehydrated salt crystals. It is under these conditions, i.e. when processing such solid mixtures, it is possible to realize those shear stresses that can be used with the used dispersant, and to carry out a fairly rapid dissolution of all processed fibers. With some reason, such a process can be called "solid-phase" dissolution, since the two outgoing solid components (fibroin and crystalline hydrate or slightly swollen fibroin and crystalline salt) pass into a highly viscous product that solidifies at temperatures below 40-70 ° C.

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