STUDY OF THE EFFECT OF CROSSLINKING AGENTS ON THE PHYSICAL PROPERTIES OF POLYMER FILMS BASED ON STARCH

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Abstract: *The effect of the chemical structure of crosslinking agents from the dicarboxylic acids class on the physical properties of polymer films based on starch is investigated in this article. As a result of complex studies it has been established that the best indexes of the polymer films stability are achieved with the use of malonic acid. An increase in the degree of crosslinking of the starch in the polymer film makes it possible to use this polymer composition to create special coatings on cotton textile materials.*

Keywords: *polymer films, starch, crosslinking agents, dicarboxylic acids, physical properties.*

1 INTRODUCTION

Today, there has been an increase in interest in textile materials with a set of special properties. The imparting special properties to textile materials are obtained by creation of polymer coatings for various purposes on the surface of fabrics.

The areas of use of materials with a polymer coating are various, because they have high mechanical strength, low gas, water, vapor permeability and resistance to aggressive media. A special place is occupied by textile materials with an antimicrobial coating containing stabilizers and biocides [1-4].

In terms of the peculiarities of creating a polymer coating, the main requirements for components of a polymer composition are high indices of their resistance to physical and chemical influences. This condition is ensured by a sufficient degree of crosslinking of the polymer components with each other to form a spatially crosslinked structure on the surface of the textile material.

Most often, precondensates of thermosetting resins are used to increase the density of polymer formation in the technology of the textile industry. As a result of the ability of thermosetting resins to release formaldehyde during the processing and use of products, these substances do not meet the requirements of Oeko-Tex Standard 100. This fact directly affects the competitiveness of products in the global and internal market.

The growing demand for high chemical stability and mechanical strength of polymer coatings, as well as limitations associated with the release of volatile organic compounds, led to the need to develop new polymer compositions for the textile industry. In this regard, studies aimed at creating environmentally friendly protective polymer systems are relevant. Promising is the use of polymer compositions based on natural polymers [5-11]. Polysaccharides, in particular starch, are widely used as natural film-forming substances. Starch is an affordable renewable environmentally friendly raw material. The disadvantage of individual starch polymer films is insufficient mechanical strength, rigidity and hydrolytic instability. Theoretically, the problem of improving the physical and mechanical properties of starch films is solved by increasing the content of the plasticizer in the composition. However, in practice, the use of a plasticizer in large quantities leads to instability in the mechanical properties of starch films. In this connection, into the polymer composition based on starch the crosslinking agents are added in addition to the plasticizer.

The crosslinking agents must provide a chemical interaction between the plasticizer and the starch via a covalent bond. Polycarboxylic acids and their derivatives are known as environmentally friendly crosslinking agents. The authors [12, 13] proposed the use of citric acid in polymer compositions based on starch for the purpose of forming spatially cross-linked three-dimensional structures. It should be noted that citric acid is a tribasic carboxylic hydroxyacid by its chemical structure. The presence of three carboxyl groups, as well as hydroxyl group, can cause less conformational mobility of citric acid during the formation of a spatially crosslinked structure with a plasticizer and starch.

In this connection, it was of interest to study the effectiveness of the use of crosslinking agents from the class of polycarboxylic acids of various chemical structures to improve the physical and mechanical properties of polymer films based on starch.

2 THE GOAL OF THE STUDY

The goal of present work was to study the effect of dicarboxylic acids with different lengths of the hydrocarbon chain on the physical properties of polymer films based on starch.

3 MATERIALS AND METHODS

3.1 Materials

Potato starch was used as a film-forming substance. Glycerine was used as a plasticizer. Succinic, malonic and oxalic acids were chosen as crosslinking agents. Citric acid was used to compare the experimental results obtained.

3.2 Methods

Polymer films are made from an aqueous solution. The crosslinking agent is added in an amount of 1% by weight of the composition. Boiling of the solution is carried out at 85-90°C for 30 min. The formed films are dried at 60°C with subsequent heat treatment at 150°C.

Hygroscopicity is determined as the mass part of moisture absorbed by the polymer film in 4 h at atmospheric moisture of 100%.

Water sorption is determined as the mass part of water absorbed by the polymer film in 24 h at 25°C.

Hydrolytic stability characterizes the degree of stability of a polymer film to the action of water and is determined by the weight method.

The degree of swelling of polymer films is determined by the change in the samples mass depending on time of stay in water.

4 RESULTS AND DISCUSSION

The effect of the selected crosslinking agents on the change in the physical properties of starch films, such as thickness, surface density and appearance, was determined at the first stage of the work. The results are shown in Table 1.

Table 1 The effect of crosslinking agents on the physical properties of starch films

Crosslinking agent	Physical properties		
	Thickness [μm]	Surface density [g/m^2]	Appearance
Without a crosslinking agent	190	190	transparent, rigid
Citric acid	130	130	turbid, elastic
Succinic acid	120	158	whitish, elastic
Malonic acid	110	175	transparent, elastic
Oxalic acid	150	163	transparent, elastic

The data obtained (Table 1) show that addition of selected carboxylic acids into the composition helps to reduce the thickness of starch films by 21-42%. The surface density of all samples decreases compared to the individual starch film. The lowest value of this index is observed when citric acid is used. It should be noted that the starch film has the greatest surface density with the smallest film thickness when malonic acid is used. All the acids studied contribute to the rise of starch films elasticity. However, the use of succinic acid causes the whitish color of starch film, which can be explained by the formation of acid crystals on the film surface during drying and heat treatment.

An important characteristic of starch polymer coatings is attitude to the action of atmospheric moisture and resistance to wet treatments. In this connection, the effect of crosslinking agents on the hygroscopicity, water sorption and hydrolytic stability was determined at the next stage of the work. The results of the experiment are shown in Figures 1, 2.

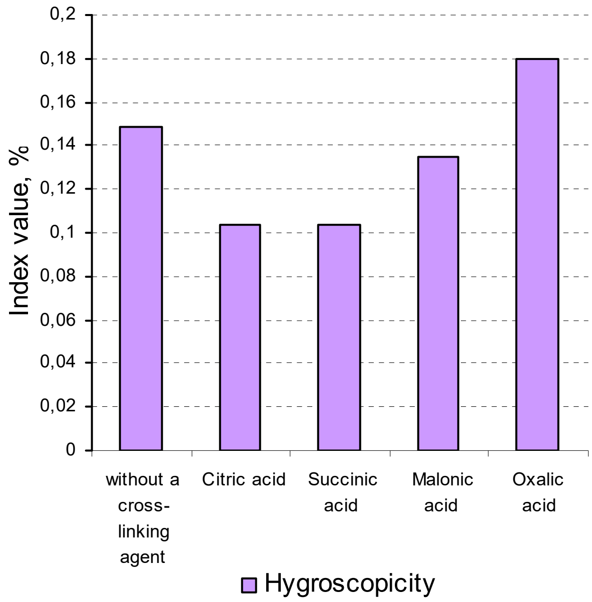

Figure 1 The effect of crosslinking agents on the hygroscopicity of starch films

Hygroscopicity is an important characteristic of starch polymer coatings, since changes in atmospheric moisture can lead to a change in moisture content in the films. This fact is reflected on the technological properties of starch films. The results of the study (Figure 1) show that at atmospheric moisture of 100% the hygroscopicity of films containing citric and succinic acids decreases by 30% compared to a starch film without a crosslinking agent. In the presence of malonic acid, this index is reduced by 9%. When oxalic acid is used, the hygroscopicity of the film is increased by 21%. Thus, as the length of the hydrocarbon chain of the polycarboxylic acids under study decreases, an increase in the hygroscopicity of the starch polymer films is observed.

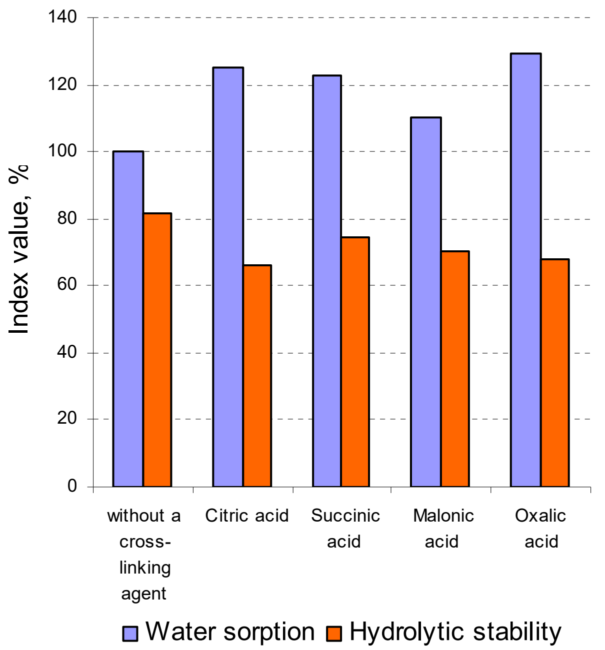

Figure 2 The effect of crosslinking agents on the attitude of starch films to wet treatments

The data presented in Figure 2 show that when all studied crosslinking agents are added into the polymer compositions, the water sorption of the samples is increased compared to the starch film without a crosslinking agent. The lowest increase of this index is observed when malonic acid is used.

Hydrolytic stability characterizes the degree of stability of the polymer film to the action of water. The results of the experiment (Figure 2) show that the addition of polycarboxylic acids in the polymer composition leads to a decrease in the stability of starch films to hydrolytic destruction by 9-19%. It should be noted that the lowest index of hydrolytic stability (66.2%) is observed when citric acid is used.

The degree of crosslinking of the starch in the polymer material can be assessed indirectly by the degree of swelling of the polymer film. In this connection, the effect of crosslinking agents on the process of swelling of starch films was investigated at the next stage of the work. The results of the experiment are shown in Figure 3.

The results obtained (Figure 3) show that the use of citric acid leads to the greatest swelling of the starch film. The sample mass increases by 65% after 72 h of treatment. The degree of swelling of a starch film without a crosslinking agent over the same period of time is 51%. A longer stay in the water of an individual starch film, as well as films containing citric and succinic acids, leads to a gradual loss of the mass of the samples. This fact can be explained by removal of non-crosslinked starch. A sample containing oxalic acid begins to lose weight after 120 h of treatment. It should be noted that the film with the content of malonic acid is characterized by the lowest degree of swelling and continues to swell after 120 h of treatment. This fact indicates a high degree of crosslinking of starch.

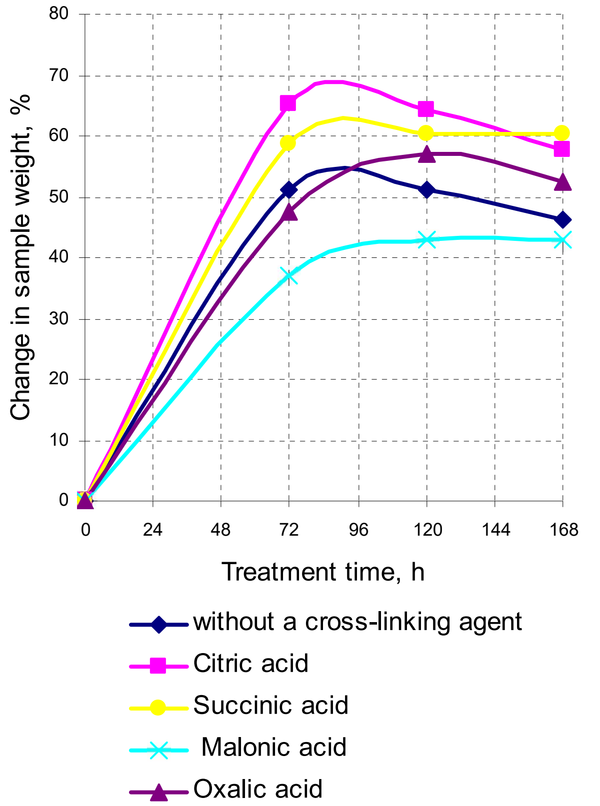

Figure 3 The effect of crosslinking agents on the degree of swelling of starch films

5 CONCLUSIONS

The effect of the chemical structure of dicarboxylic acids on the physical properties of polymer films based on starch was studied. It was determined that the use of malonic acid as a crosslinking agent makes it possible to obtain transparent elastic starch polymer films that are characterized by a lower thickness while maintaining a high surface density, as well as low hygroscopicity, water sorption and high resistance to hydrolytic destruction. This polymer composition can be used to create special coatings on cotton textile materials in order to improve the ecological character of finishing work.

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