1. Introduction

There is at present a rapid growth in consumption (and, accordingly, in production) of packaging made from combined film materials. Such packaging fulfills its functional purpose—preserves quality and quantity of packaged goods, as well as contributes to their fast selling.

Combined film materials are divided into the following three groups:

1) multilayer films composed of polymers only;
2) metallized multilayer films and multilayer films made of aluminum foil;
3) films made on a textile, paper or cardboard base [1].

We should not mix up combined packaging and combined packaging materials. Combined material is a single, non-separable system with different nature of components. Combined packaging is made of two or more different materials, which represent a single structure [2].

A market of combined film materials is practically non-existent in Ukraine while materials produced with rubber and monomeric coating (mainly polyvinylchloride) do not meet modern requirements to product quality.

2. Literature review and problem statement

Aqueous dispersions of polymers are of great practical importance in technology of producing packaging textile materials due to a combination of valuable properties and compliance with modern environmental requirements [3–5].

The films based on aqueous dispersions are characterized by lower strength, higher resistance to water and organic substances.
solvents when compared to solvent-based polymeric films, due to the presence of hydrophilic groups in the molecular chain of a polymer.

There are known cases of the use of polymers in the form of non-crosslinked thermoplastic films [7], however, crosslinks are necessary for such functional groups as: aziridine [6], epoxy [8], isocyanate [9], oxazoline [10], keto-, acetoacetoxy and carbodiimide [11] to obtain materials with improved performance properties.

There are several methods to introduce additional functional groups to the dispersion system [12].

A method of autoxidizing of unsaturated functional groups is used most often to provide self-crosslinking of polymers. Carbonyl-amine crosslinking is also widely used for crosslinking of aqueous polymers and can provide a significant improvement in the strength properties of polyurethanes, but it is noted that hardened coatings show poor water resistance (Fig. 1).

Acetoacetoxy reactions proceed very quickly and are an effective crosslinking method, however the problem is concentrated in hydrolytic stability of an ester, premature crosslinking and production of an undesired color of the dispersion itself and of the formed coating.

Another method [13] is shown in Fig. 2, it consists of the synthesis of two different latexes, which contain mutually complementary functional groups and mixing of these latexes before use. Reactive groups are initially separated from each other, but, their particles are crosslinked after mutual diffusion of polymer chains during formation of a film.

The next method is the use of crosslinking agents (Fig. 3), in which additional groups are introduced into the aqueous phase where they remain unreacted until they approach reactive groups of a polymer particle during film formation.

Melamine-formaldehyde resins [14] are commonly used to structure aqueous dispersions of polymers, the crosslinking process is a trans-esterification of hydroxyl groups. Traditional crosslinking agents are dangerous because of their toxicity, since they release volatile substances, such as formaldehyde, during hardening and use of products.

Multifunctional epoxy resins such as glycidyl esters are commercially available and well known for their properties, including high mechanical strength, heat resistance, etc. The reaction between epoxide and amine shown in Fig. 4 was investigated by authors of a paper [15] in the temperature range from 40 to 150 °C. On the one hand, studies were aimed at catalysis, on the other hand, on selectivity of addition, since in addition to α-addition to the carbon atom of the CH group is also possible.
Epoxides are multi-hydroxide compounds and can introduce branch points into the polyurethane backbone to form a crosslinked structure [16, 17]. Glycidyl esters are used for the preliminary crosslinking of the aqueous dispersion of polyurethane. Its reaction is based on the interaction of epoxy groups with hydroxyl and secondary amino groups (Fig. 4).

Thus, the most promising way to develop a polymer coating composition for textile packaging materials is to use polymer components based on aqueous dispersions of polymers and formaldehyde cross-linking agents.

3. The aim and objectives of the study

The aim of present study was to develop styrene-acrylic polymeric compositions for coating the textile packaging material.

To achieve this objective, the following tasks were set:
– to investigate structural parameters (a number of acetone-insoluble fractions, characteristics of a spatial grid) of individual styrene-acrylic polymers and their compositions with crosslinking agents;
– to investigate hydrolytic stability of individual styrene-acrylic polymers and their compositions with crosslinking agents;
– to investigate physical and mechanical properties (nominal tensile strength, breaking length, Koenig hardness, stickiness) of individual styrene-acrylic polymers and their compositions with crosslinking agents;
– to study physical and mechanical properties (bending rigidity, water and air permeability, abrasion resistance) of a textile material with a formed polymer coating.

4. Materials and methods for studying chemical, physical-chemical and physical and mechanical properties of film-forming polymers and coatings based on them

4. 1. Materials studied in the experiment

The aqueous dispersions of styrene-acrylic polymers were studied as film-forming substances included to the polymer composition, Table 1.

Mono-, di- and triglycidyl esters were used as crosslinking agents. A modified dimethylolethoxyethylenyl ether – Appretta ECO, was used to compare the effectiveness of a cross-linking action of the preparations, Table 2.

Table 1

| Characteristic of film-forming substances | Chemical composition | Solid residue, % | pH | Size of particles, µm | Viscosity at 25 °C, mPa·s |
|----------------------------------------|----------------------|----------------|----|---------------------|--------------------------|
| Lacrytex 306 | aqueous dispersion of thermocrosslinking copolymer of butyl acrylate and styrene | 50 | 4.0–7.0 | ≈0.2 | 100–1,000 |
| Lacrytex 430 | aqueous dispersion of copolymer of ester of acrylic acid and styrene | 50 | 7.5–8.5 | ≈0.1 | 5,000–15,000 |
| Lacrytex 640 | aqueous dispersion of acrylic copolymer modified by addition of adhesion promoter | 55–57 | 2.0–3.0 | ≈0.2 | Not less than 5,000 |

Polymer coating was formed on a calico cotton fabric Art. 125, produced by Ternopil JSC “Teksterno” (Ukraine), Table 3.

Table 3

| Characteristics of textile material | Fabric, article | Width, cm | Surface density, g/m² | Number of threads per 10 cm | Breaking load, kgf | Shrinkage, % |
|-----------------------------------|----------------|-----------|----------------------|---------------------------|-----------------|-------------|
| Calico, art. 125                   | 220           | 125       | 252±5/218±7          | 75/45                     | –3.5/±2.0       |

4. 2. Methods for studying the properties of film-forming polymers

The determination of the amount of the acetone-insoluble fraction was carried out by extraction of polymer films with acetone in the Soxhlet apparatus for 24 hours. The degree of films hardening was calculated after extraction and drying of the films to constant weight, %:

\[
C = \frac{W_i}{W_0} \times 100, \tag{1}
\]

where \(W_i\) is an initial mass of the film, g; \(W_0\) is the mass of the film after extraction, g.

For the sol-gel analysis of polymer films, film samples were placed in the Soxhlet apparatus and extracted with acetone for 18 hours. Then films were dried in a thermostat at 60 °C for 2 hours and held at room temperature for 30 minutes.

The samples were further extracted with benzol in another Soxhlet apparatus for 16 hours. The films were weighed after extraction with acetone and benzol. The amount of benzol extract (in %) corresponded to the content of the sol fraction \(S\):

\[
S = \frac{m_e - m_b}{m_e} \times 100, \tag{2}
\]
where $m_j$ is the mass of the sample after extraction with acetone, g; $m_0$ is the mass of the sample after extraction with benzol, g.

The degree of crosslinking of the polymer $j$:

$$j = \frac{1}{S + \sqrt{S}} \tag{3}$$

The fraction of active chains $V_j$:

$$V_j = (1-S) - (1-2jS)(1+2jS). \tag{4}$$

Structural parameters of the grid were calculated according to the theory of equilibrium swelling of Flory-Reny
ner, which relates the number of active chains of the $1/M^r$ grid to the relative polymer fraction in the swollen system:

$$\frac{1}{M^r} = \frac{V_j + x V_j^2 + \ln(1-V_j)}{\rho_j V_j (V_j^{1/2} - 0.5V_j)} \tag{5}$$

where $V_j$ is the volume fraction of the polymer in the swollen sample; $\gamma$ is the constant of polymer-solvent interaction (Huggins constant); $\rho_j$ is the polymer density, g/cm$^3$; $V_j$ is the partial molar volume of the solvent.

The density of the crosslinking $\nu$ was determined by formula:

$$\nu = \frac{1}{2M^r}.$$  

Determination of stickiness of polymeric films was carried out using the FINAT method (Test Method Number 9). The essence of the technique consisted in lowering a loop from the polymer to a rigid plate of a known area and measuring the force necessary to detach the loop from the substrate. The measurement was performed on LT-1000 Loop Tack Tester (“Ichemco”, Italy).

Conditional strength of the samples and breaking length of the films were determined on the tensile machine RT-250M according to GOST 2580-87.

Hardness of the polymers was determined using a Koenig pendulum. The method was based on a principle that an amplitude of oscillations of the pendulum, which touches a surface of a coating, decreases the faster, the softer is a surface. The duration of oscillations of the pendulum was determined with a decrease in the amplitude from 6° to 3° in the course of the study.

4.3. Methods for formation of a polymer coating on textile material and investigation of its properties

The formation of polymer coating on a textile material was carried out by the method of directly applying the polymer composition to the textile material, followed by forming the polymer film during the drying process.

The determination of the rigidity of the textile material with a formed polymer coating during bending was performed using a cantilever contactless method on the PT-2 device in accordance with GOST 10550-93.

Air permeability was determined on VPTM.2 device according to GOST 12088-77.

Water resistance was determined on a penetrometer under normal climatic conditions in accordance with GOST 3816-81.

5. Results of study of structural parameters of individual styrene-acrylic polymers and their compositions with crosslinking agents

Structural parameters of styrene-acrylic polymers were evaluated by the number of acetone-insoluble fractions of formed polymer films when samples were extracted in a solvent.

The analysis of the results shows that films based on styrene-acrylic polymers Lacrytex 309 and 430 are characterized by a significant amount of acetone-insoluble fraction—97 and 68 %, respectively.

The additional introduction of Laproxide and Appretta ECO into the composition reduces the amount of the acetone-insoluble fraction.

Individual polymer films formed from Lacrytex 640 are soluble in acetone and are not able to provide quality characteristics to the polymer coating, and therefore require the introduction of crosslinking agents.

Fig. 5 shows a chart of the influence of various types of crosslinking agents on the resistance of polymer films to the action of an organic solvent.

The data in Fig. 5 show that the optimum amount of crosslinking agents of 301B, AF, 702 and TMP Laproxide for the stabilization of the Lacrytex 640 film is in the range of 6–10 %. This provides a sufficiently high hardening degree of 54–84 %. When Laproxide of 603 and 703 grades are added with a concentration of 2 %, the degree of hardening of the Lacrytex 640 film is 78–79 %. When the concentration of crosslinking agents is increased to 10 %, the degree of hardening reaches a maximum value of 97–99 %.

Characteristics of the spatial grid of individual styrene-acrylic polymers and their compositions with crosslinking agents are presented in Table 4.

An analysis of the data presented in Table 4 shows that films based on styrene-acrylic polymers Lacrytex 309 and 430 are distinguished by a high degree of intermolecular cross-linking. Taking into account that the individual Lacrytex 640 film is unstable to solvents, the introduction of crosslinking agents increases the degree of structuring of the polymer. The 4 % concentration of Laproxide 703 as the crosslinking agent gives the lowest average molecular weight of the chain segment, 50 g/mol, which results in a significant increase in the crosslinking density of the Lacrytex 640/Laproxide 703 – 10×10$^{-3}$ mol/cm$^3$ composite.
6. Results of study of hydrolytic stability of individual styrene-acrylic polymers and their compositions with crosslinking agents

Long term effective use of polymer coating is the most important task for polymer modification. Decomposition processes begin to proceed quickly and the products of destruction accumulate under the influence of sunlight, temperature, water, oxygen of air in polymer products. One of the most common types of chemical destruction of polymers for textile packaging is hydrolysis, it affects the resistance of products to moisture. The tendency to hydrolysis is determined by the nature of functional groups and bonds that make up the polymer. The chemical composition of the polymer changes in the hydrolysis of the side functional groups. And when the hydrolysis of bonds in the main molecular chain occurs, the molecular weight of the polymer decreases.

A process of interaction of low-molecular liquids with polymers, without dissolution of the chain, is observed with a low thermodynamic affinity between a polymer and a solvent. Absence of dissolution is also characteristic of polymers; their macromolecules are connected by strong crosslinks to a spatial grid. The rare transverse bonds between macromolecules in the first stage of polymer swelling do not impede the diffusion of solvent molecules into it. Solvent molecules penetrate the space between polymer chains and move apart their flexible regions. Therefore, the first swelling period occurs at the maximum rate. However, solution of the solvent by the links of macromolecules, which are located between the nodes of the grid, reduces their mobility and leads to an increase in the distances between them, stretching and straightening of macromolecules, reducing the entropy of the system, the appearance of strong mechanical stresses and rupture of some overstressed areas. The swelling rate decreases. If short transverse bridges in macromolecules are close to each other (dense rigid grids), then such a polymer does not swell.

Since the films obtained from styrene-acrylic and polyurethane dispersions undergo hydrolytic degradation, the stability of individual films and polymer compositions with crosslinking agents to the action of moisture at different temperatures was studied in the work (Fig. 6).

According to the data obtained, which characterize the process of dissolution of polymer films, it can be seen that almost all the samples undergo various degrees of hydrolytic destruction.

![Hydrolytic stability of styrene-acrylic polymers](image)

Fig. 6. Hydrolytic stability of styrene-acrylic polymers

Lacrytex 309 films retain 100 % stability at all hydrolysis temperatures under study. The decrease in the mass of the sample of Lacrytex 430 during hydrolytic degradation at 100 °C occurs by 5 %, with films remaining stable at 20 and 40 °C.

Investigation of hydrolytic stability of Lacrytex 640 films showed a decrease in the sample mass by 8–15 %, which depends on the hydrolytic degradation temperature used. Introduction of Laproxide of 603 and 703 grades leads to complete stability of composite films at 20 and 40 °C. When the temperature is raised to 100 °C, the mass of the sample is reduced by 2 %.

7. Results of study of physical-mechanical properties of individual styrene-acrylic polymers and their compositions with crosslinking agents

Textile package undergoes mechanical and atmospheric influences during operation. This necessitates the application of various high-molecular compounds, which form a protective film on a surface of a fiber, to the fabric. The following requirements are imposed on polymer protective films: non-toxicity, elasticity, mechanical strength, transparency, high adhesion to a fiber, reduced stickiness and, consequently, low dirt retention.

Results of the study of physical and mechanical properties of individual styrene-acrylic polymers and their compositions with cross-linking agents are given in Table 5.

Individual styrene-acrylic films Lacrytex 430 and 309, as shown in Table 5, have a high tensile strength of 8 and 14 MPa. Stickiness in both types of polymer films is absent, but hardness and breakage length are significantly different. For the Lacrytex 430 film, the Koenig hardness has a value of 9 s at ε=470 %, and for Lacrytex 309, the breakage length is 120 % with a hardness of 32 s.

### Table 4

| Composition | Volume fraction of a polymer (V) | Huggins constant (ξ) | Average molecular weight of the chain segment (Mc, g/mol) | Crosslinking degree (%, %) | Density of a polymer (ρ, g/cm³) | Density of crosslinking (x10³, mol/cm³) |
|-------------|---------------------------------|----------------------|----------------------------------------------------------|---------------------------|-------------------------------|---------------------------------------|
| Lacrytex 430 | 0.98                            | 0.88                 | 52                                                       | 7.30                      | 1.0325                        | 9.6                                   |
| Lacrytex 309 | 0.88                            | 0.83                 | 67                                                       | 34.48                     | 1.015                         | 7.4                                   |
| Lacrytex 640/Laproxide 702 | 0.39            | 0.57                 | 2,403                                                    | 4.43                      | 1.0175                        | 0.21                                  |
| Lacrytex 640/Laproxide TMP 703 | 0.56             | 0.66                 | 792                                                      | 4.65                      | 1.0175                        | 0.63                                  |
| Lacrytex 640/Laproxide 603 | 0.67             | 0.72                 | 437                                                      | 4.80                      | 1.0175                        | 1.14                                  |
The obtained results indicate a different influence of crosslinking agents on the change in the properties of the Lacrytex 640 film. The individual styrene-acrylic polymer has a stickiness of 20 kPa, strength and breakage length of which corresponds to 6 MPa and 800 %, respectively. Introduction Laproxide of TMP grade reduces breakage length up to 670 % and does not affect other physical and mechanical properties of the original polymer. The use of Laproxide 702 and 603 crosslinking agents results in a slight increase in the stickiness of composites, an increase in tensile strength at breaks greater than 1000 %, and a reduction in strength up to 3–5 MPa. The use of Laproxide 703 eliminates the stickiness of the resulting Lacrytex 640-based composite, and the sample hardness is 5 seconds. There is a decrease in breakage length up to 640 %, while the strength at break remains unchanged.

8. Results of the study of physical and mechanical properties of a textile material with a formed polymer coating

To characterize materials with a polymer coating, we considered:
- mechanical properties of the material, namely, bending rigidity;
- physical properties of the material, namely water and air permeability;
- abrasion resistance of the material (Table 6).

9. Discussion of results of studying properties of the film-forming polymers and coatings that were made based on them

As a result of the conducted investigations it was revealed that the use of Lacrytex 309 polymer for obtaining a polymer coating on a textile material makes it possible to obtain a product with a hard stamp, which is unacceptable for the developed composite composition. The formation of a strong three-dimensional spatial structure of films provides a styrene-acrylic polymer Lacrytex 430, which allows the use of this polymer without crosslinking agents. The additional introduction of Laproxide and Appretta ECO into the composition lowers the degree of structuring of polymer films. This phenomenon is a consequence of the action of crosslinking agents as solvents. As a result, the degree of crosslinking of the polymer decreases and the quality of the composition deteriorates.

For Lacrytex 640, which has a low structuring index, the introduction of the glycidyl ester of Laproxide 703 trade mark results in an increase in the degree of crosslinking of the films to 7.9 %. A consequence of this is an increase in the stability of films to the action of organic solvents, a reduction in hydrolytic degradation at high temperatures, and an increase in the physical-mechanical indexes. A probable mechanism of interaction of glycidyl esters with styrene-acrylic polymers is shown in Fig. 7.

When multifunctional epoxy resins (glycidyl esters) are used, both carboxylic and hydroxyl functional groups of acrylic polymers are used as crosslinking agents, which leads to the formation of ester bonds (Fig. 7). The formation of the three-dimensional polymer structure of the matrix inhibits the hydrolysis of ester bonds more effectively in the case of application of epoxides than application of melamine-formaldehyde resins (Appretta ECO preparation). As a result, polymer systems are safer and more resistant to external factors. After analysis of the experimental data on physical and mechanical characteristics of polymer films, it can be concluded that films of the individual polymer Lacrytex 430 and with the Lacrytex 640/Laproxide 703 crosslinking agent are characterized by elasticity, high breaking load and degree of structuring. These polymeric compositions can be used as polymer matrices.

### Table 5

| Composition          | Conditional tensile strength G, MPa | Relative breakage length εb, % | Koenig hardness K, s | Stickiness, kPa |
|----------------------|------------------------------------|--------------------------------|----------------------|----------------|
| Lacrytex 430         | 8                                  | 470                            | 9                    | –              |
| Lacrytex 309         | 14                                 | 120                            | 32                   | –              |
| Lacrytex 640         | 6                                  | 800                            | –                    | 20             |
| Lacrytex 640/Laproxide 702 | 3–5                               | >1,000                         | –                    | 22             |
| Lacrytex 640/Laproxide TMP | 6                                 | 670                            | –                    | 20             |
| Lacrytex 640/Laproxide 703 | 6                                 | 640                            | 5                    | –              |
| Lacrytex 640/Laproxide 603 | 3–5                               | >1,000                         | –                    | 24             |

### Table 6

| Composition          | Rigidity, E, μN/cm² | Air permeability R, dm³/(m²·s) | Water resistance Pa | Abra-  | | |
|----------------------|---------------------|-------------------------------|--------------------|--------| |
| Base weft            | 280                 | 165.7                         | 363.8              | 65     | 1,400 |
| Without finish       | 280                 | 165.7                         | 363.8              | 65     | 1,400 |
| Lacrytex 430         | 356.7               | 216.1                         | 7,651.8            | 780    | 63,000 |
| Lacrytex 640/Laproxide 703 | 356.7               | 216.1                         | 7,651.8            | 780    | 63,000 |

According to the data given in Table 6, a textile material with a polymer coating in the form of an individual styrene-acrylic film Lacrytex 409 has excessive rigidity, low air permeability, high water resistance and abrasion resistance. Textile materials with individual styrene-acrylic film Lacrytex 430 and with Lacrytex 640/Laproxide 703 crosslinking agent are characterized by sufficient elasticity and air permeability. High indexes of water resistance and abrasion resistance should be noted.

![Fig. 7. Reaction between epoxide and carboxyl (hydroxyl) groups of styrene-acrylic polymers](image)
to immobilize additives with different applications on a surface of a textile material.

Further studies may be aimed at giving antimicrobial properties to polymeric compositions of textile packaging designed using silver citrates.

10. Conclusions

1. It was determined that films based on styrene-acrylic polymers Lacrytex 430 and 309 have a high degree of intermolecular crosslinking, which results in a significant amount of acetone-insoluble fraction of 97 % and 68 %, respectively. Individual polymer films formed from Lacrytex 640 are not able to provide quality characteristics to a polymer coating, and therefore require the addition of crosslinking agents.

2. It was established that the films Lacrytex 309 and Lacrytex 430 retain 95–100 % stability at all hydrolysis temperatures under study. The hydrolytic stability of individual Lacrytex 640 films at the level of 85–92 %, the introduction of Laproxide grades 603 and 703 leads to the complete stability of composite films (97–100 %).

3. It was found that individual styrene-acrylic films Lacrytex 430 and 309 have high tensile strength and hardness, they do not have stickiness and significantly differ in breakage length (470 % and 120 %, respectively). The most satisfactory results in the study of physical-mechanical properties of Lacrytex 640 films were obtained when it was used together with Lapatex 703.

4. It was determined that textile material with polymer coating in the form of individual styrene-acrylic film Lacrytex 409 possesses excessive rigidity, low air permeability, high indicators of water resistance and abrasion resistance. Textile materials with individual styrene-acrylic film Lacrytex 430 and composition with Lapatex 640/Laproxide 703 crosslinking agent are characterized by sufficient elasticity and air permeability, high water resistance and abrasion resistance.

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