

## CREATING ENVIRONMENTALLY FRIENDLY POLYMER COATINGS FOR TEXTILE PACKAGING MATERIALS

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**Key words:**

*Styrene-acrylic dispersion  
Polyurethane dispersion  
Cross-linking agent  
Polymer coatings  
Textile packaging  
Materials*

**ABSTRACT**

The influence of formaldehydeless cross-linking agents — triglycidyl esters — on physico-mechanical and chemical properties of polymer films based on aqueous dispersions of styrene-acrylic and polyurethane polymers was studied. It has been found that polymer compositions Lacrytex 640/Laproxide 703 and Aquapol 14/Laproxide TMP possess the best complex of properties. The characteristics of textile materials with formed coatings based on selected polymer compositions have been determined. It is shown that these polymer compositions allow obtaining elastic, waterproof and wear-resistant coatings required for textile packaging materials.

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## СТВОРЕННЯ ЕКОЛОГІЧНО ЧИСТИХ ПОЛІМЕРНИХ ПОКРИТТІВ ДЛЯ ТЕКСТИЛЬНИХ ПАКУВАЛЬНИХ МАТЕРІАЛІВ

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*У статті досліджено вплив безформальдегідних зшиваючих агентів — тригліцидилових етерів — на фізико-механічні і хімічні властивості полімерних плівок на основі водних дисперсій стирол-акрилового та поліуретанового полімерів. Встановлено, що найкращий комплекс властивостей мають полімерні композиції Lacrytex 640/Laproxide 703 і Aquapol 14/Laproxide TMP. Визначено характеристики текстильних матеріалів зі сформованими покриттями на основі обраних композицій полімерів. Показано, що дані полімерні композиції дають змогу отримати еластичні, водостійкі та зносостійкі покриття, необхідні для текстильних пакувальних матеріалів.*

**Ключові слова:** *стирол-акрилова дисперсія, поліуретанова дисперсія, зшиваючий агент, полімерні покриття, текстильні пакувальні матеріали.*

**Introduction.** Currently, there is a rapid growth in the consumption of packaging from combined film materials. Such packaging not only fulfills its functional purpose for preserving the quality of the packaged goods, but also contributes to its quick sale.

Combined film materials are divided into the following three groups: multilayer films composed only of polymers; multilayer films using aluminum foil or metallized; films on textiles, paper or cardboard [1].

In Ukraine, the market for combined film materials is virtually non-existent, and materials produced with a monopolymer coating (mainly PVC) do not meet modern requirements for product quality. Solving the problems of providing the Ukrainian market with packaging products of its own production is also exacerbated by an insufficient assortment of compositions for the formation of polymer coatings on the surface of packaging materials. In addition, one of the main drawbacks, significantly limiting the scope of packaging materials, is the presence of formaldehyde-containing preparations in film-forming formulations.

Therefore, studies aimed at developing new economically beneficial and environmentally friendly polymer coatings for textile packaging materials are relevant.

**Literature review.** During operation, the textile package undergoes mechanical and atmospheric influences, which makes it necessary to form a protective film on the fabric surface with applying of various high-molecular compounds. Polymer protective films must meet such requirements as non-toxicity, elasticity, mechanical strength, transparency, high adhesion to the fiber, reduced stickiness and, consequently, low dirt retention.

Due to the combination of valuable properties and compliance with modern environmental requirements, aqueous dispersions of polymers have an important practical value in the production technology of packaging textile materials [2]. Due to the presence of hydrophilic groups in the molecular chain of the polymer, films based on aqueous dispersions are characterized by lower strength and resistance to water as compared to polymer films based on organic solvents. In this regard, cross-linking agents are introduced into the composition of the polymer compositions.

Traditional cross-linking agents are dangerous because of their toxicity, since they release volatile substances, such as formaldehyde, during the curing and use of products. An alternative is the use of multifunctional epoxy resins such as glycidyl esters, which are commercially available and well known for its properties, including high mechanical strength, heat resistance, etc. [3—5].

Glycidyl esters are multifunctional epoxy resins, when interacting with acrylic polymer, the reaction occurs with carboxyl and hydroxyl groups to form ester bonds, and in interaction with polyurethane polymers, the crosslinking reaction is based on the interaction of epoxy groups with hydroxyl and secondary amino groups [3].

The formation of the three-dimensional polymer structure of the matrix inhibits the hydrolysis of ester bonds in the case of epoxides, resulting in safe and resistant to external factors polymer systems.

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 glycidyl esters as formaldehydeless cross-linking agents.

**The goal of the study.** The goal of present work was to study the effect of glycidyl esters on the physico-mechanical and chemical properties of polymer films formed from aqueous dispersions, as well as the assessing the possibility of using the resulting polymer compositions to create coatings on textile packaging materials.

**Results of the study.** The following aqueous dispersions were used as the object of the study:

- Lacrytex 640 — aqueous dispersion of the acrylic copolymer modified by the addition of an adhesion promoter (dry residue — 55—57%, pH = 2—3, particle size  $\approx 0.2 \mu\text{m}$ , viscosity at 25° C — not less than 5000 mPa·s);

- Aquapol 14 – aqueous dispersion of aliphatic polyurethane (dry residue — 35%, pH = 7.36, particle size  $\approx 0.1 \mu\text{m}$ , viscosity at 25° C — 20.1 mPa·s).

Triglycidyl esters were used as cross-linking agents (NPC Macromer Ltd., Vladimir), the characteristics of which are given in Table. 1.

*Table 1. Characteristics of cross-linking agents*

Name	Chemical composition	Mass fraction of epoxy groups, %	Viscosity at 25° C, mPa·s
Laproxide 703	Triglycidyl ester of polyoxypropylenetriol	13.5—16.5	90—160
Laproxide 603	Triglycidyl ester of polyoxypropylenetriol	16.5—19.5	80—150
Laproxide TMP	Triglycidyl ester of trimethylolpropane	27.0—31.0	150—250

The effectiveness of the cross-linking action of the test esters was evaluated by the number of acetone-insoluble fractions of the formed polymer films. An analysis of the results shows that the individual polymer films formed from Lacrytex 640 are soluble in acetone and are not able to provide the necessary parameters for the quality of the polymer coating. It was found that the film formed only from the polyurethane dispersion Aquapol 14 has a limited resistance to the action of solvents.

In this connection, the effect of the concentration of the cross-linking agents on the cross-linking of styrene-acrylic and polyurethane polymers was studied.

The results of the experiment showed that in order to stabilize the Lacrytex 640 film, the optimum amount of Laproxide TMP cross-linking agent is in the range of 6—10%, which provides a sufficiently high curing degree of 54—84%. When to styrene-acrylic polymer Laproxides grades 603 and 703 are added at a concentration of 2%, the degree of curing is 78—79%, and when the concentration of cross-linking agents is increased to 10% — reaches a maximum value of 97—99%.

It has been found that for the modification of the polyurethane dispersion Aquapol 14, the optimal concentration of cross-linking agents Laproxide TMP, 703 and 603 is 4—6%, with a curing degree of 75—80%.

At the next stage of work, the influence of cross-linking agents on the physical and mechanical properties of polymer films was determined.

The conventional strength of polymer film samples and the elongation at break were determined in accordance with GOST 14236-81. The hardness of the polymer

coating was determined using a König pendulum. The method is based on the principle that the amplitude of oscillations of the pendulum touching the surface of the coating decreases the faster, the softer this surface. In the course of the study, the duration of the pendulum oscillations was determined with a decrease in the amplitude from 6° to 3°. Determination of the stickiness of polymer films was carried out by the method of FINAT (Test Method Number 9). The essence of the technique consists in lowering the 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 results of the study of the physical-mechanical properties of individual styrene-acrylic and polyurethane polymers and their compositions with cross-linking agents are given in Table 2.

*Table 2. Physical-mechanical properties of polymer films*

Composition	Conditional tensile strength $\sigma$ , MPa	Elongation at break $\epsilon$ , %	König hardness Kö, c	Stickiness, kPa
styrene-acrylic polymer				
Lacrytex 640	6	800	—	20
Lacrytex 640/ Laproxide 603	3-5	>1000	—	24
Lacrytex 640/ Laproxide TMP	6	670	—	20
Lacrytex 640/ Laproxide 703	6	640	5	—
polyurethane polymer				
Aquapol 14	11	340	55	—
Aquapol 14/ Laproxide 603	12	240	74	—
Aquapol 14/ Laproxide TMP	12	200	80	—
Aquapol 14/ Laproxide 703	12	180	91	—

The obtained results testify to the different influence of cross-linking agents on the change in the properties of the Lacrytex 640 film. The individual styrene-acrylic polymer has a tackiness of 20 kPa, strength and elongation at break of which corresponds to 6 kPa and 800% respectively. Introduction Laproxide TMP reduces elongation at break up to 670%, without affecting other physical-mechanical parameters of the initial polymer. The use of the cross-linking agent Laproxide 603 results in a slight increase in the stickiness of the composites, an increase in tensile strength at breaks greater than 1000%, and a reduction in strength to 4 kPa. The use of Laproxide 703 eliminates the stickiness of the resulting Lacrytex 640-based composite, and the sample hardness is 5 s. There is a decrease in elongation at break up to 640%, while the tensile strength is unchanged.

The properties of composite films obtained from Aquapol 14 also depend on the type of cross-linking agent used. Laproxide 703, Laproxide 603, Laproxide TMP help to reduce the elongation at break of films based on Aquapol 14 by a factor of 2. While the use of Laproxide 703 leads to an increase in the hardness of the

polymer compositions to 91 s, and when a similar concentration of Laproxide TMP and Laproxide 603 are introduced, the hardness is increased to 80 s.

Long term effective use of polymer coating is the most important task for polymer modification. Under the influence of sunlight, high temperature, water, oxygen of air in polymer coatings, decay processes begin to proceed quickly, and the products of destruction accumulate. To one of the most common types of chemical destruction of polymers is hydrolysis, which affects the index of resistance of coatings to wet treatments. The tendency to hydrolysis is determined by the nature of the functional groups and bonds in the polymer. In the hydrolysis of the side functional groups, the chemical composition of the polymer changes; when the bonds that form part of the main molecular chain hydrolyze, the molecular weight of the polymer decreases.

Since packaging textile materials with polymer coatings are exposed to moisture during operation, the stability of individual films and polymer compositions with cross-linking agents to hydrolytic degradation at different temperatures was studied at the next stage of the work (Table 3).

*Table 3. Effect of aqueous treatments on the hydrolytic stability of polymers*

Composition	Hydrolytic stability, %		
	20° C	40° C	100° C
styrene-acrylic polymer			
Lacrytex 640	92	89	85
Lacrytex 640/ Laproxide 603	100	100	98
Lacrytex 640/ Laproxide TMP	98	97	96
Lacrytex 640/ Laproxide 703	100	100	98
polyurethane polymer			
Aquapol 14	98	98	93
Aquapol 14/ Laproxide 603	100	100	99
Aquapol 14/ Laproxide TMP	100	100	99
Aquapol 14/ Laproxide 703	100	100	99

According to the data obtained (Table 3), which characterizes the process of dissolution of polymer films, it can be seen that practically all the samples undergo various degrees of hydrolytic destruction.

Investigation of the hydrolytic stability of Lacrytex 640 films showed a decrease in the sample mass by 8—15%, depending on the hydrolytic degradation temperature used. However, the introduction of Laproxide 603 and Laproxide 703 results in complete stability of the composite films at 20° C and 40° C, and at 100° C the sample weight is reduced by 2%.

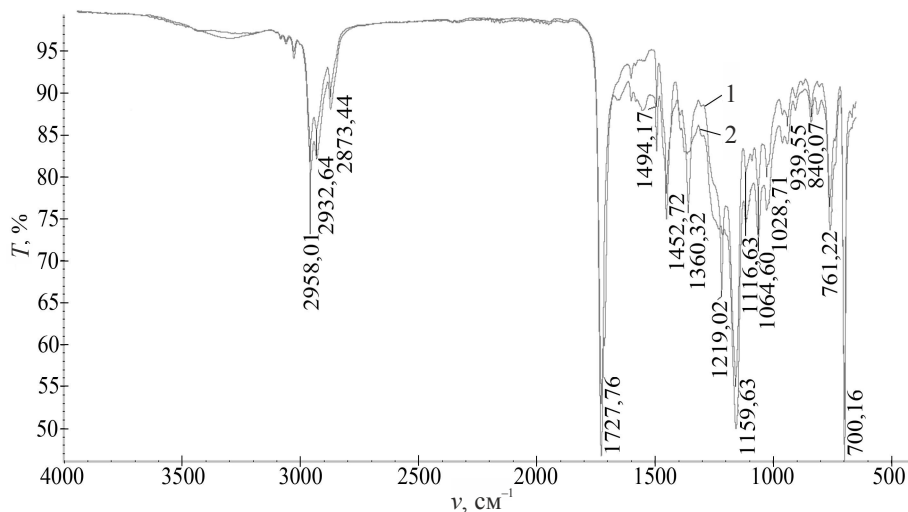
Individual film Aquapol 14 (Table 3) has a high resistance to water treatment, which is 98% at 20° C and 40° C and 93% at 100° C. The introduction of all cross-linking agents into the polymer composition makes it possible to increase the hydrolytic stability of the films to 100% at 20° C and 40° C, and also to increase resistance to water degradation at 100° C by 6%.

Based on the results of the studies, the optimal compositions based on the polymer compositions of Lacrytex 640/Laproxide 703 and Aquapol 14/Laproxide TMP were selected to form coatings on textile packaging materials.

In order to study the nature of the effect of cross-linking agents on the chemical structure of selected polymers, the IR-spectra of individual films and their compositions with cross-linking agents were studied.

The IR-spectra of the polymers were obtained using a Nicolet-iS10 FTIR spectrometer (Thermo Fisher Scientific, USA) using a DTGS detector, a KBr beam splitter and a Smart Performer attachment equipped with a ZnSe crystal. The measurement was carried out at a resolution of  $4\text{ cm}^{-1}$ ; zone of the spectrum  $4000\text{—}650\text{ cm}^{-1}$ . The spectra were processed using OMNIC-7.0.

The IR-spectra of the individual Lacrytex 640 film and the Lacrytex 640/Laproxide 703 composition are shown in Fig. 1.



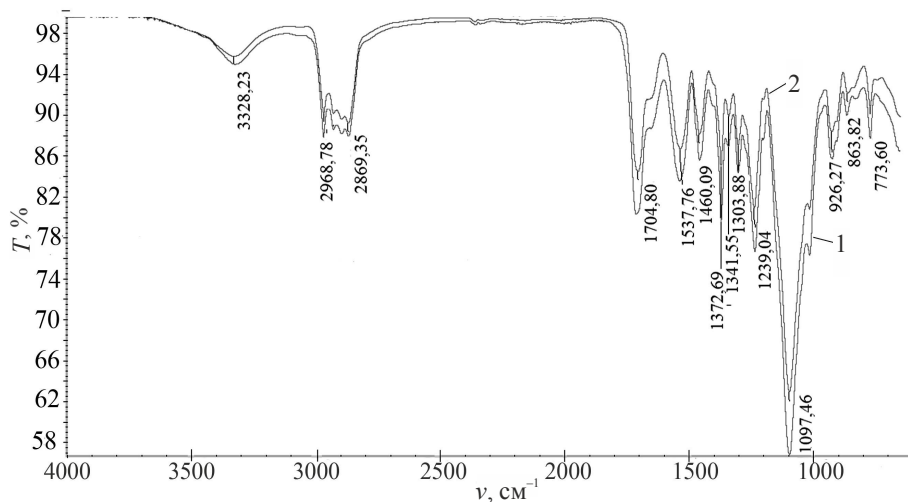
**Fig. 1. IR-spectra of styrene-acrylic polymer films:**  
1 — Lacrytex 640; 2 — Lacrytex 640/Laproxide 703 composition

The change in the form of bands of valent vibrations indicates structural and conformational changes resulting from the introduction of the Laproxide 703 cross-linking agent into the matrix of styrene-acrylic polymer Lacrytex 640. The absence of characteristic intense peaks for Lacrytex 640 at  $1219\text{ cm}^{-1}$  (C–O–H) and  $1360\text{ cm}^{-1}$  (C–CH<sub>3</sub>), as well as a shift in the vibrations of the carboxyl group –C=O from  $1715$  to  $1727\text{ cm}^{-1}$  indicates the formation of cross-links between the hydroxyl and carboxyl groups of the styrene-acrylic polymer and the epoxy groups of the cross-linking agent [6].

The IR-spectra of the individual Aquapol 14 film and the Aquapol 14/Laproxide TMP composition are shown in Fig. 2.

The introduction of the cross-linking agent Laproxide TMP into the polyurethane dispersion Aquapol 14 leads to an increase in the relative intensity of the =C=O group band at  $1700\text{ cm}^{-1}$ , the vibrations of the =NH band at  $3320\text{ cm}^{-1}$ , –CN and =NH groups at  $1540\text{ cm}^{-1}$ . The increase in the relative intensity of vibration  $\equiv\text{C–H}$  at  $2969\text{ cm}^{-1}$  is also noticeable. In addition, the IR-spectrum shows characteristic vibrations of  $\equiv\text{C–O–C}\equiv$  bands of polyglycol at  $1236$  and  $1097\text{ cm}^{-1}$ .

The shift in the peaks of the carboxyl group  $=C=O$  indicates the formation of hydrogen bonds with the epoxy groups of the cross-linking agent, which contributes to an increase in the degree of cross-linking of the polymer.



**Fig. 2. IR-spectra of polyurethane polymer films:**  
1 — Aquapol 14; 2 — Aquapol 14/Laproxide TMP composition

At the next stage of the work, the influence of the formed polymer coating on the properties of the textile material was studied. The formation of the polymer coating on the textile material was carried out by the method of directly applying these polymer compositions to the cotton fabric, followed by forming the polymer film during the drying process.

- To characterize textile materials with a polymer coating, were considered:
- mechanical properties of the material (rigidity for bending);
  - physical properties of the material (water resistance and air permeability);
  - wear resistance of a polymer coating during abrasion.

Determination of the rigidity for bending of a textile material with a formed polymer coating was performed using a cantilever contactless method in accordance with GOST 10550–93. The air permeability was determined according to GOST 12088–77. The water resistance was determined on a penetrometer under normal climatic conditions in accordance with GOST 3816–81.

The characteristics of a textile material with formed polymer coatings are presented in Table 4.

*Table 4. Characteristics of a textile material with a formed polymer coating*

Composition	Rigidity, $\mu\text{N}\cdot\text{cm}^2$		Air permeability, $\text{dm}^3/(\text{m}^2\cdot\text{s})$	Water resistance		Wear resistance, cycles
	warp	weft		Pa	mm wg	
Without coating	280	85,5	277,7	637,8	65	1400
Lacrytex 640/ Laproxide 703	356,7	161,5	23,6	7651,8	780	63000
Aquapol 14/ Laproxide TMP	373,4	170,5	20,2	>9810	>1000	64000

According to the data given in Table 4, a textile materials with composition of Lacrytex 640/Laproxide 703 and Aquapol 14/Laproxide TMP are characterized by sufficient elasticity and air permeability, high water resistance and wear resistance.

### Conclusions

The analysis of physical-mechanical and chemical characteristics of polymer films based on aqueous dispersions of styrene-acrylic and polyurethane polymers and their compositions with triglycidyl esters as formaldehydeless cross-linking agents is carried out. It has been found that the use of the polymer compositions of Lacrytex 640/Laproxide 703 and Aquapol 14/Laproxide TMP provides an elastic, durable and resistance coating. These polymeric compositions can be used as polymer matrices to immobilize additives with different applications on the surface of a textile packaging materials.

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