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*M.Ya. Kuzmenko, V.Kh. Shapka, O.M. Kuzmenko, A.O. Zhylicheva, T.G. Filinska***MODIFICATION OF TRIACETATE CELLULOSE POLYMER COMPOSITIONS BY OLIGODIURETHANEDIOLS****Ukrainian State University of Chemical Technology, Dnipro, Ukraine**

We carried out the research on the modification of triacetate cellulose composite materials by oligodiurethanedliols synthesized on the basis of a mixture of isomers of toluene diisocyanate and aliphatic diols (individual or oligomeric) which differ in the length of the aliphatic chain between the hydroxyl groups and the nature of the hydroxy group itself. It was shown that used oligodiurethanedliols are effective modifiers of the soluble triacetate cellulose compositions. At the stage of film casting, such additives allow governing the viscosity of the solution in a wide range and, at the same time, improving the physical and mechanical characteristics of the cast films (ensuring an increase in the tensile strength of the films by almost 2.5 times). This effect was achieved due to the presence of polar urethane groups in the structure of the modifier, which are formed at the stage of its synthesis, which have higher values of total cohesion energy (36.6 kJ/mol), in comparison with the ester groups (12.2 kJ/mol) of phthalate or adipinate plasticizers.

**Keywords:** cellulose triacetate, modification, oligodiurethanedliol, solution, films.**DOI:** 10.32434/0321-4095-2022-143-4-40-48**Introduction**

Triacetate cellulose (TAC) is widely used in the manufacture of packaging for bulk foods, polaroid films, in the production of man-made fibers and fabrics based on them, electrical insulating materials and in a number of other fields [1–5].

However, it has significant shortcomings those complicate both the technology of its production and the properties of the TAC itself. The batches of original cellulose obtained from softwoods differ significantly in molecular weight, which depends on the breed of raw materials used, and even for one species, the place of growth, as well as different climatic conditions and different soils. This, at the stage of acetylation of such cellulose, leads to batches of TAC with different molecular weight and different degrees of acetylation, which has a strong effect on the viscosity of the standard solution both in the film casting and in the production of threads: their quality requires for each batch of TAC readjustment of the casting equipment.

Such negative factors significantly affect the wide distribution of physical and mechanical

properties of the obtained films, threads, etc. In addition, TAC is a representative of the highly polar crystalline polymer, which is characterized by the formation of large supramolecular formations and, as a consequence, has high internal stresses that lead to reduced elasticity of products based on it and a wide range of strength characteristics. However, the reason for this behavior of products with TAC, in addition to the above factors, is mainly due to the difference in the degree of acetylation of hydroxyl groups in the elementary chain of the original cellulose and the tendency of such a polymer to crystallize. The cyclic structure of the TAC elementary unit, the presence of highly polarized ester, simple ether, glycosidic bonds, and partially non-esterified hydroxyl groups per unit leads to the implementation in the polymer matrix of a dense network of strong physical interactions between molecules. This rigid-chain nature of supramolecular formations in TAC, larger in size and their low mobility cause high fragility of products based on them, low elasticity, and wide distribution of mechanical characteristics.

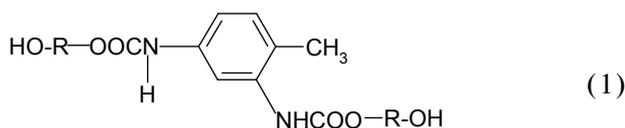
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This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).*M.Ya. Kuzmenko, V.Kh. Shapka, O.M. Kuzmenko, A.O. Zhylicheva, T.G. Filinska*

These shortcomings can be eliminated only by modifying the TAC in various ways: chemical ones, which consist in attaching lateral, large-sized radicals to the macromolecule, or physical ones, leading to the fragmentation of large supramolecular formations into smaller ones and reducing internal stresses in the polymer matrix.

The use of silicon alkoxy derivatives as effective modifiers of TAC-soluble compositions has previously been described in the literature [6–9].

To continue the work in the direction on the physical modification of TAC (search for effective modifiers of TAC-soluble compositions) and study the properties of film materials with their use, it will be interesting to use as modifiers a number of oligodiuretanediols of the general formula:



where R is an individual or oligomeric residue (based on propylene oxide, aliphatic diol) with a molecular weight in the range of 90 to 1,000 units.

The properties of the used compounds of the series are given below (Experimental). All of them are synthesized by the known urethane formation reaction, by the interaction of two moles of diol with a mole of a mixture of isomers of toluene diisocyanates. The influence of the molecular weight of the diol component (or the concentration of urethane groups in the target compounds) on the rheological characteristics of TAC solutions and the physicomechanical properties of film materials based on them was studied.

It is expected that concentrating oligodiuretanediols on the boundaries of supramolecular formations will allow the following:

- partially reduce the internal stresses between them and, to some extent, adjust the viscosity of TAC solutions in the desired direction;

- increase the strength characteristics of the films due to the formation in the polymer matrix, along with traditional hydrogen physical bonds, hydrogen interactions with urethane groups of the modifier, which as is known, have the total cohesion energy of 36.6 kJ/mol, which is three times higher than the total cohesion energy of the ester group (12.2 kJ/mol) of traditionally used oligoether plasticizers. At the same time, the presence in the structure of low-polar fatty aliphatic radicals (residues, diols) with –OH group at the end and

with a smaller value of total cohesion energy (24.3 kJ/mol) should act as a disintegrator of supramolecular formations (the component of the additive that disintegrates at high concentrations large supramolecular formations to smaller ones) and further crushing already small supramolecular formations to individual molecules, which is a positive phenomenon.

Regarding the possibility of a chemical reaction between residual non-acylated –OH groups of the TAC elementary unit and free –OH groups of oligodiurethanediols, which is possible at the temperatures above 200°C, this issue has not been considered because the TAC matrix is unstable and begins to destruct at the temperatures above 100°C.

Simultaneous interaction of the above factors will determine the total positive or negative effect from the use of this series of oligodiurethanediols as modifiers of TAC materials.

### Experimental

As the basic soluble of TAC composition, we used the following industrial composition (wt.%): TAC 15.0; dibutyl phthalate 0.75; triphenylphosphate (fire-resistant additive) 1.65; three-component solvent: methylene chloride 75.6; methyl alcohol 5.0; and butyl alcohol 2.0.

As a modifier, we used compounds of general formula (1), the method of synthesis of which is given below, and the structural formulas and properties are shown in Table.

For the convenience of homogenization of components in the process of synthesis and acceleration of production of prototypes of TAC composition, all modifiers were used in the form of 50% by weight of the solution in cyclohexanone, i.e. the concentration at which their synthesis was carried out. After 5 minutes of homogenization of the TAC composition with a modifier, transparent and almost colorless films were formed from the obtained homogeneous transparent solution by pouring onto glass, followed by drying.

To prepare the initial TAC composition, a sample of an equal mass mixture of five different batches of TAC with averaged characteristics was used: the content of acetate groups of 62.1 wt.%; the degree of substitution of hydroxyl groups by acetate of 2.83; the viscosity of the standard soluble TAC composition at 20°C of 2.94 Pa·s.

Rheological characteristics of the basic and experimental samples of TAC solutions (initial and modified) were determined on a rotary viscometer «Reotest-2» in the temperature range of 18–38°C and shear rates of 0.16–142.88 s<sup>-1</sup>. From the data obtained, according to the manual to the device,

the dynamic viscosity was calculated by the formula:

$$\eta = (z - \alpha) / (Dr - (v/50)), \quad (2)$$

where  $\eta$  is the dynamic viscosity (Pa·s);  $z$  is the constant of the measuring cylinder;  $\alpha$  is the instrument readings;  $Dr$  is the shear rate ( $s^{-1}$ ); and  $v$  is the real frequency of the current in the mains (Hz).

The obtained results were processed on a computer by using the «Origin 6» software. The obtained dependences of the logarithm of viscosity on the logarithm of the shear rate or the concentration of additives at different temperatures were analyzed.

When discussing the results of the experiment, we limited ourselves only to studies carried out at the temperature of 38°C (the temperature at which the films are cast in production) and the constant shear rate of 2.09  $s^{-1}$ .

The physical and mechanical properties of the samples of the films obtained (both basic and modified) were evaluated by the relative hardness of the film coating, which was determined on a pendulum dill TM 2124 at 20°C by the state standard GOST 5233-67. This indicator is quite sensitive to various internal structural changes in the polymer matrix. Tensile strength of free films was determined by the state standard GOST 18299-72 using a tensile machine FP-10 at the clamping speed of 20 mm/min. The relationship between the physical and mechanical properties of the films, the nature and amount of the modifier used in them were analyzed.

Films for determining the tensile strength index (100  $\mu m$  thick) were made by pouring a sample of the TAC-composition solution on glass plates 4 times with exposure of each layer at 20°C in a horizontal position for at least 2 hours to remove the bulk of the solvent and the following additional drying in an oven at 50°C for 4 hours.

To determine the relative hardness of the films, a solution of TAC composition was applied to a glass plate (photo glass) in two layers and after drying each layer, first at 20°C for 2 hours, and then at 50°C for 4 hours, received a coating of 40–50  $\mu m$  thick. To determine each point of the obtained graphical dependences, at least five parallel measurements were performed and the arithmetic mean value was calculated, having previously discarded the indicators that significantly differed from the array. Deviations did not exceed  $\pm 3\%$ . The modifier was added to the TAC solution in the amount of: 0.010; 0.025; 0.050; 0.075; 0.100; 1.000; 2.000; 3.000 and 5.000 wt.% by the TAC mass,

recalculated 100% substance.

Example: Synthesis of oligodiuretanediol by the interaction of triethylene glycol with a mixture of toluene diisocyanate (compound 3, Table).

150.06 g (1 mol) of triethylene glycol and 150.06 g of cyclohexanone were charged to a four-necked reactor with a stirrer, a reflux, a nitrogen supply tube, and a dropping funnel. In a nitrogen atmosphere, a mixture of 87.05 g (0.5 mol) of toluene diisocyanate isomers in 87.05 g and cyclohexanone was added dropwise to the reaction mixture with simultaneous stirring and heated to 68°C. The reaction rate and the temperature of the reaction mixture at a given level were regulated by the rate of dropping of a mixture of isomers of toluene diisocyanates. After dropping completed, the reaction mixture was kept at this temperature for another 4–5 hours, hourly taking a sample for the presence of free isocyanate groups in it.

After depletion of all isocyanate groups in the reaction mass, the reaction was stopped and the finished product was poured into a flask and analyzed. In the reactor, 469.30 g (98.97 wt.% calculated on 50% by weight of the solution from the theoretical one) of a viscous, transparent and homogeneous liquid were isolated, which, according to the results of the analysis, responded to compound 3 (Table). Molecular weight was determined in benzene using a precision ebulliometer EP-68.

Other oligomeric products were synthesized by a similar method.

### **Results and discussion**

Figure 1 shows the dependences of the change in the logarithm of the viscosity of the basic solution of the TAC composition on the logarithm of the shear rate in the temperature range from 22°C (curve 1) to 38°C (curve 5). It is seen that the logarithm of the viscosity of the basic sample of the TAC solution decreases with increasing the temperature (from 2.94 Pa·s to 0.5 Pa·s at 22°C and 38°C, respectively). This behavior of the solution is due to the destruction of the weakest hydrogen bonds both between the TAC molecules in the solution and their bonds with the solvent in this temperature range. It is characteristic practically both for solutions and for solvents.

A slightly different picture of the change in the logarithm of the viscosity of the basic solution of the TAC composition is observed with the introduction of additive 2 (Table) (Fig. 2). After introduction into the basic solution of 0.010; 0.025; 0.050 wt.% of additive 2 by weight of TAC, there is a rapid increase in the value of  $\ln \eta$  from 0.5 Pa·s to 2.38 Pa·s. It can be explained by the growth of physical bonds of

Physicochemical constants of oligodiuretanediols

Structural formula	Yield, wt.% (50% by weight of the solution)	$n_D^{20}$ (50% by weight of the solution)	Molar mass (100% product)		Equivalent by (-OH) determined (100% product)	% NCO, (50% by weight of the solution)
			calculated	determined (ebullioscopy)		
	99.80	1.4813	354.17	365.00	177.08	0
	99.76	1.5015	386.17	397.00	193.08	0
	98.97	1.4909	474.19	485.00	237.095	0
	98.81	1.4904	562.25	570.00	281.12	0
	99.69	1.4798	694.09	706.00	347.05	0
	98.92	1.4647	1114.09	1125.00	557.05	0
	99.91	1.4648	2174.09	2203.00	1087.05	0

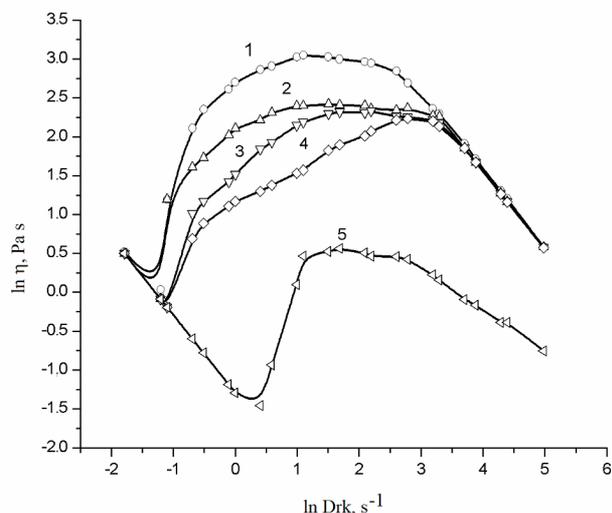


Fig. 1. Dependences of the change in the logarithm of the viscosity of the basic solution of the TAC composition on the logarithm of the change in the shear rate at the temperatures: 1 – 22°C; 2 – 24°C; 3 – 30°C; 4 – 34°C; and 5 – 38°C

urethane groups of the additive with already partially fragmented supramolecular formations of TAC in solution. When adding the additive at the level of 0.075% by weight, this process ends. With a further addition of oligodiurethanediol 2 ( $\geq 0.075\%$  by weight), the  $\ln\eta$  value gradually decreases to almost 1.85 Pa·s (an inflection in the curve of the dependence of  $\ln\eta$  on the concentration of the additive is observed at  $\ln\eta = 1.85$  Pa·s). This phenomenon is associated with the beginning of penetration of oligodiurethanediol 2 molecules from the solution into the supramolecular formations (i.e. their plasticization is observed), separation of individual molecules from these formations, and their transfer into the solution. As the amount of additive added increases, these processes increase. However, along with this, there are processes of formation of a new type of associations of TAC macromolecules with oligodiurethanediol due to the formation of stronger physical hydrogen bonds between urethane groups and TAC molecules. The molecular weight of the associates increases and this is manifested in an increase in the  $\ln\eta$  value of the test sample of the soluble TAC composition.

Figure 3 shows the dependences of  $\ln\eta$  of the experimental samples of the soluble TAC composition at 38°C on the number of added oligodiurethanediols of the series 1–7 to this solution (Table) at the constant shear rate of  $2.09 \text{ s}^{-1}$ . In all curves with a small number of additives introduced into the basic solution (0.010; 0.025; 0.050; and 0.075), there is a sharp increase in the  $\ln\eta$  value to 2.37 Pa·s. Then, in

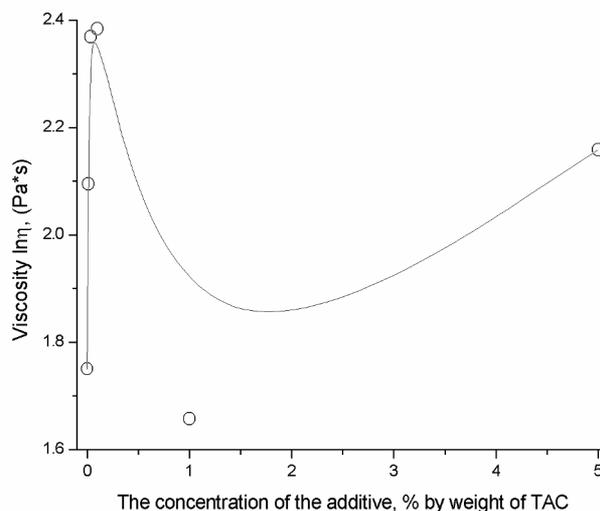


Fig. 2. The dependence of the logarithm of the viscosity of the TAC composition solution at 38°C on the concentration of oligourethanediol 2 (Table) at the constant shear rate of  $2.09 \text{ s}^{-1}$

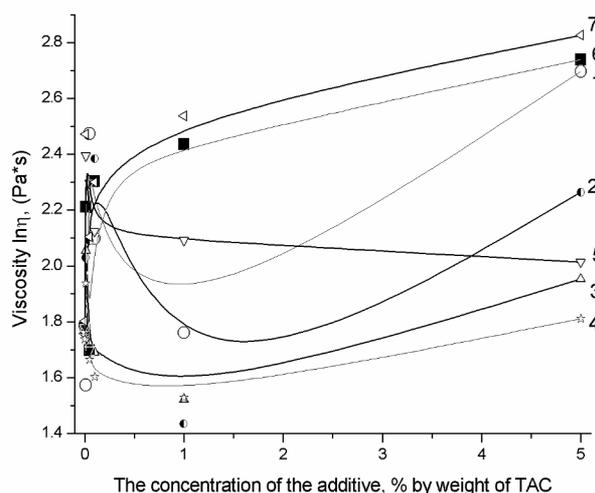


Fig. 3. The dependence of the logarithm of the viscosity of the TCA composition solution at 38°C on the concentration of oligourethanediols 1–7 (Table) at the constant shear rate of  $2.09 \text{ s}^{-1}$ . The curve number corresponds to the number of oligourethanediol in Table

the concentration range of 0.075–1.000 wt.%, there is a decrease in the  $\ln\eta$  value to 1.85 Pa·s. After the introduction of 1.0–1.5 wt.% of the additives, there is a gradual increase in the viscosity of the experimental solutions of the TAC composition again.

A complete analogy in the behavior of the viscous characteristics of the experimental samples of the TAC compositions depending on the number of the test additives indicates the identity of the processes occurring in them.

However, some differences have been also

observed. The largest increase in the  $\ln\eta$  value at 5% by weight of the additive in the basic solution (at 2.8 Pa·s) is observed when using compound 7 as an additive (Table). In the structure of its diol part, the length of the oxypropylene residue increases to 1,000 units and the number of polarized oxypropylene chain links increases as well.

Moreover, in some compounds 1–4 (Table), with an increase in the length of the hydroxyl-containing component (synchronously with a decrease in the structure of the proportion of polar urethane groups that form cohesive interactions in the solution of TAC composition), there is a decrease (5% by weight of the additive) of the maximum achieved  $\ln\eta$  value from 2.65 Pa·s (compound 1) to 2.28 Pa·s (compound 2), to 1.94 Pa·s (compound 3) and 1.82 Pa·s (compounds 4). This fact is explained by a decrease in the concentration of more polar urethane groups in the structure of this series of additives from 33.35 wt.% (compound 1) to 20.92 wt.% (compound 4, Table).

In the series of compounds 5–7 (Table), the opposite pattern is observed. The maximum achieved  $\ln\eta$  value is fixed with the introduction of additive 5 into the soluble TAC-composition (Table) at the level of 2.05 Pa·s, and then, it increases up to 2.73 Pa·s (compound 6) and it reaches 2.8 Pa·s (compound 7).

This is explained by the fact that when changing the nature of the diol component in the structure of the used oligodiurethanediol or when replacing the individual diol residue (1,4-butanediol, diethylene glycol, triethylene glycol, and tetraethylene glycol) on polyoxypropylene glycol, there are two effects of such additives on the viscosity of the soluble TAC composition.

Initially, in the series of additives 1–4, with a decrease in the structure of the proportion of polar urethane groups, their influence on the growth of cohesive interactions in the modified solution of TAC composition decreases. This leads to a decrease in the viscosity logarithm. This pattern is maintained when using additives 5–7.

Another process occurs simultaneously with the process described above when compounds 5–7 are used as additives. The ether bond in the oxypropylene chain of the additive, due to the donor effect of the methyl group, leads to a greater polarization of the ether group of the link as compared with the polarity of the ether bond in compounds 2–4, which begins to manifest itself in increasing the cohesive interactions in the solution with an increase in oxypropylene links in such a chain.

At the same time, as the increase in the length

of the oxyethylene chain in the compounds 2–4 leads to a decrease in the concentration of urethane groups and their effect on the growth of cohesive interactions in the soluble composition (synchronously manifested in a decrease in the value of  $\ln\eta$  solution), in the compositions of TAC solutions with additives 5–7, the growth in the residues of the diol component of oxypropylene polarized ether groups compensates for the loss of impact on viscosity by a decreasing number of urethane groups and even, as can be seen from Fig. 3, can completely replace them.

The total effect of these processes is registered as positive at the stage of regulating the viscosity of the solution.

In addition, the effect on the viscosity and hydrodynamic effects of the increasing molecular weight of the additive itself should not be ruled out.

At the same time, it was of interest to investigate the influence of the nature of the additives used and their number on the change in values: the relative hardness of the coating (Fig. 4), the tensile strength of free films (Fig. 5), and the relative elongation at rupture (Fig. 6).

Considering the results of the experiment shown in Fig. 4, to change the value of the relative hardness of the coating from the amount of additives 1–7 (Table) added to the soluble basic TAC composition, we can conclude that the largest values of relative hardness coating test samples of films, in comparison with the base, are achieved when introducing the

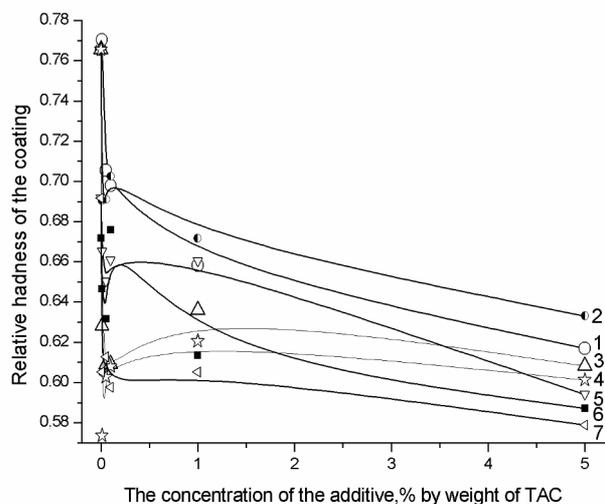


Fig. 4. Dependence of the value of the relative hardness of the coating for the base and experimental TAC compositions on the concentration of oligourethanediol in their composition.

The numbers of the curves correspond to the number of oligourethanediol in Table

additives in the amount of up to 0.075 wt.% by the TAC mass into the soluble TAC composition. The value of the relative hardness of the coating increases from 0.58 for the films based on the basic sample, to 0.77 based on the test samples with the addition of oligodiuretanediols 1 and 2 (Table) with the highest concentration of polar urethane groups. The least effect on increasing the value of the relative hardness of the coating at the level of 0.64 is achieved by adding oligodiurethanediol 7 to the composition

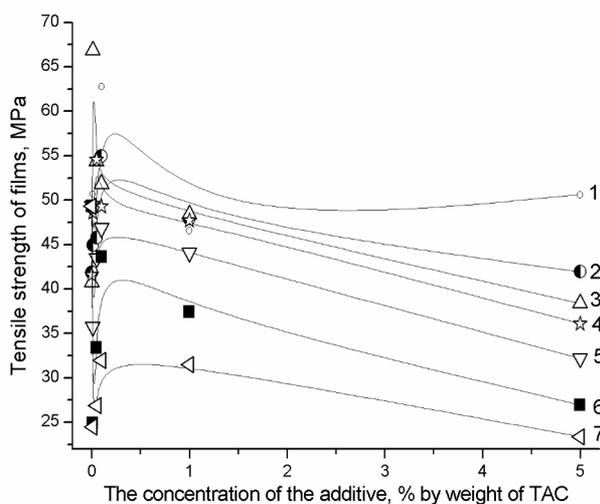


Fig. 5. Dependence of the value of the tensile strength of the films for the basic and experimental TAC compositions on the concentration of oligourethanediol in their composition. The numbers of the curves correspond to the number of oligourethanediol in Table

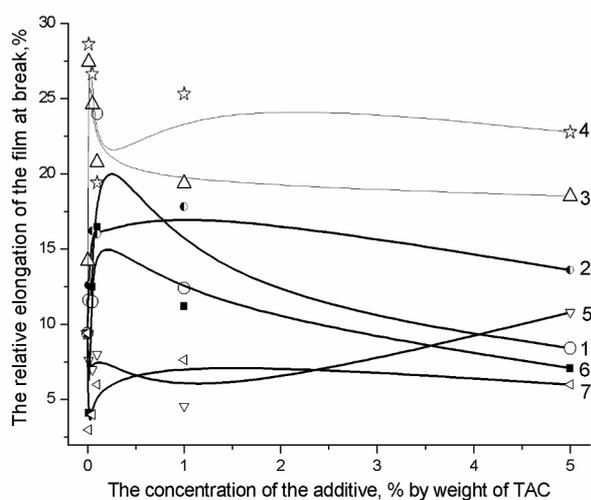


Fig. 6. Dependence of the value of the relative elongation of the films for the basic and experimental TAC compositions on the concentration of oligourethanediol in their composition.

The numbers of the curves correspond to the number of oligourethanediol in Table

(Table).

However, there is a general pattern to a gradual decrease in the value of the relative hardness of the coating with increasing the proportion of additives 1–7 in the soluble part of the TAC composition.

The obtained result indicates that the total effect from the addition of the studied series of oligodiurethanediols to the TAC composition promotes the growth of intermolecular interactions in the polymer matrix, which is manifested in increasing the relative hardness of the films compared to the basic case. However, the excess of additives in more than 0.1 wt.% leads to a gradual decrease in this indicator. Oligourethanediols considered in the work act as plasticizers of the rigid-chain TAC polymer. This conclusion is confirmed by the results of the experiments shown in Fig. 5 and 6 by changing the values of the tensile strength of the films and the relative elongation at break from the number of additives added to the soluble TAC composition.

The tensile strength of the films increases from 25 MPa for the basic sample to 62 MPa when compound 1 is used as an additive (Table) with the highest concentration of polar urethane groups in the molecule structure. The lowest increase in the tensile strength of films up to 32 MPa is observed when using compound 7 as an additive (with the lowest concentration of polar urethane groups in the structure).

The value of the relative elongation of films at rupture also changes almost synchronously. The greater the tensile strength of the films, due to the growth of cohesive interactions in the polymer matrix when adding additives 1–7 (Table) in the soluble recipe, the lower the relative elongation of the films at rupture.

However, the addition to the experimental soluble TAC composition of the studied series of oligodiurethanediols contributes to the destruction of large supramolecular TAC formations, which is confirmed by increasing the relative elongation of the films at rupture from 6–7% to 30%, that is, it is accompanied by an increase in the elasticity of products made from such a modified matrix.

### Conclusions

The influence of the structure and molecular weight of additives of the homologous investigated series of oligodiurethanediols on the change of viscosity characteristics of the basic composition of the soluble TAC composition has been studied. It has been shown that in all cases, with the addition of such additives in very small amounts from 0.01 to 0.075 wt.% by the TAC mass, there is a sharp increase in the viscosity of the test samples from 0.5–2.4 Pa·s

due to the increase of cohesive interaction forces between urethane groups of the additive and polarized bonds of TAC and simultaneous further destruction of the TAC supramolecular formations. This phenomenon is positive when working with low molecular weight TAC samples.

Such additives, with an increase in their concentration in the soluble TAC composition (almost up to 5 wt.% by the TAC mass), to a greater extent, penetrate the most supramolecular formations and act as plasticizers.

It has been found that simultaneously with the increase in the viscosity of the basic solution of the TCA composition, the addition to its composition, as an additive, of the investigated series of oligodiurethanediols contributes to an increase in the physical-mechanical parameters of films based on it: the relative hardness of the coating changes from 0.6 to 0.77; the tensile strength of the films changes from 25.0 MPa to 62 MPa; and the relative elongation changes from 6–7% to 30%.

The obtained positive research results are especially relevant for the disposal of waste products of the TAC production, for the processing of appropriate containers, products, etc.

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## МОДИФІКАЦІЯ ТРИАЦЕТАТЦЕЛЮЛОЗНИХ ПОЛІМЕРНИХ КОМПОЗИЦІЙ ОЛІГОДИУРЕТАНДІОЛАМИ

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Виконані дослідження з модифікації триацетатцелюлозних композиційних матеріалів олігодиуретандіолами, синтезованими на основі суміші ізомерів толуїлендіізоціанату та аліфатичних діолів (індивідуальних або олігомерних), які відрізняються довжиною аліфатичного ланцюга між гідроксильними групами і природою самої гідроксильної групи. Показано, що використані олігодиуретандіоли є ефективними модифікаторами розчинних триацетат-целюлозних композицій. На стадії відливу плівок такі добавки дозволяють регулювати в'язкість розчину в широкому діапазоні і, одночасно, сприяють покращенню фізико-механічних характеристик відлитої плівки, (забезпечуючи зростання показника міцності плівки на розрив майже в 2,5 рази). Такий ефект досягається за рахунок наявності в структурі модифікатора, сформованих ще на стадії його синтезу, полярних уретанових груп, які мають більш високі значення повної енергії когезії (36,6 кДж/моль) у порівнянні з естерними групами (12,2 кДж/моль) фталатних або адипінатних пластифікаторів.

**Ключові слова:** триацетат целюлоза; модифікація; олігодиуретандіол; розчин; плівки.

**MODIFICATION OF TRIACETATE CELLULOSE  
POLYMER COMPOSITIONS BY  
OLIGODIURETHANEDIOLS**

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We carried out the research on the modification of triacetate cellulose composite materials by oligodiurethanedioles synthesized on the basis of a mixture of isomers of toluene diisocyanate and aliphatic diols (individual or oligomeric) which differ in the length of the aliphatic chain between the hydroxyl groups and the nature of the hydroxy group itself. It was shown that used oligodiurethanedioles are effective modifiers of the soluble triacetate cellulose compositions. At the stage of film casting, such additives allow governing the viscosity of the solution in a wide range and, at the same time, improving the physical and mechanical characteristics of the cast films (ensuring an increase in the tensile strength of the films by almost 2.5 times). This effect was achieved due to the presence of polar urethane groups in the structure of the modifier, which are formed at the stage of its synthesis, which have higher values of total cohesion energy (36.6 kJ/mol), in comparison with the ester groups (12.2 kJ/mol) of phthalate or adipinate plasticizers.

**Keywords:** cellulose triacetate; modification; oligodiurethanediol; solution; films.

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