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## MECHANICAL PROPERTIES, CHEMICAL AND THERMO-OXIDATIVE RESISTANCE OF BIOPOLYMER MATRICES BASED ON THE EPOXY RESIN AND FUNCTIONALIZED SOYBEAN OIL

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*Biopolymer matrices has been synthesized on the basis of ED-20 epoxy resin and soybean oil (SbO) bearing cyclocarbonate and epoxy groups. Mono(cyanoethyl)diethylenetriamine (UP) and tris(2-hydroxyethyl)amine (TEA) were used as hardeners. Chemical structure, mechanical properties, thermo-oxidative resistance of the samples and their changes after contact with distilled water, alkaline or acidic environment were studied. By means of ATR-FTIR the possible formation of H-NIPU (hybrid non-isocyanate polyurethane) fragments between cyclocarbonate groups of SbO and amino groups of the hardener was demonstrated. Influence of the curing mode and the type of hardener on water absorption, chemical and thermal oxidation resistance of the developed biopolymer matrices was thoroughly investigated. UP-based biopolymer matrices showed water and alkali resistance similar to the ones of neat epoxy polymers, while TEA-based biopolymer matrices showed better resistance to the acidic medium. The thermo-oxidative stability of the chosen samples was revealed by the TGA method in an air atmosphere. It was demonstrated that epoxy polymer cured with TEA hardener were more stable than the one cured with UP hardener. The similar dependence is observed for biopolymer matrices based on TEA hardener. At the same time, the curing mode has almost no effect on ultimate tensile strength value of the samples with ED-20/UP composition. However, the addition of functionalized SbO to the epoxy matrix cured with both TEA and UP hardeners increases the ultimate tensile strength values regardless of the type of oil functionalization. As expected, all biopolymer matrices exhibited higher ultimate tensile strength compared with unmodified epoxy polymers, which provides the possibility of their further application to obtain multi-layered bioplastics.*

**Keywords:** *biopolymer matrices, epoxy resin, epoxidized and cyclocarbonated soybean oil, chemical and thermo-oxidative resistance, mechanical properties*

### INTRODUCTION

Certainly, polymeric materials occupy a leading place in science and technology, but the large volume of their production increases the burden on the environment and causes certain environmental problems. Therefore, the creation of new environmentally “friendly” polymer materials is important both in fundamental and, especially, in practical terms [1–5]. The use of biogenic materials represents an eco-friendly way to use these natural additives in composites. Such composite materials formed by a matrix and/or a filler derived from natural biomass and can effectively reduce the volume of plastic waste [6, 7].

Vegetable oils are one of the most important renewable and natural platform chemicals due to their universal availability, inherent biodegradability and recycling, low price, low ecotoxicity and low toxicity toward humans [8, 9]. These natural properties are now being taken

advantage of in research and development, with vegetable oil derived polymers/composites being used in numerous applications including paints and coatings, adhesives, and biomedicine [10]. Soybean oil (SbO) represents one of the cheapest, most abundant and easily functionalized natural chemical that makes it suitable for many technical applications [11–13]. Modified soybean oil containing active functional groups can be used to reduce the brittleness of epoxy materials obtained with amine hardeners. The number of such functional groups capable of interacting with the amino groups of the hardener is quite limited. Such groups include epoxy, and cyclocarbonate groups [14]. Epoxidized soybean oil offers very good miscibility with epoxy resins and can be co-crosslinked with the resins into homogenous matrix using typical hardeners [15, 16]. As a result, thermal stability and glass transition temperature of the materials were slightly decreased that could be caused by the low reduced cross-linking density of the epoxy network, however mechanical properties

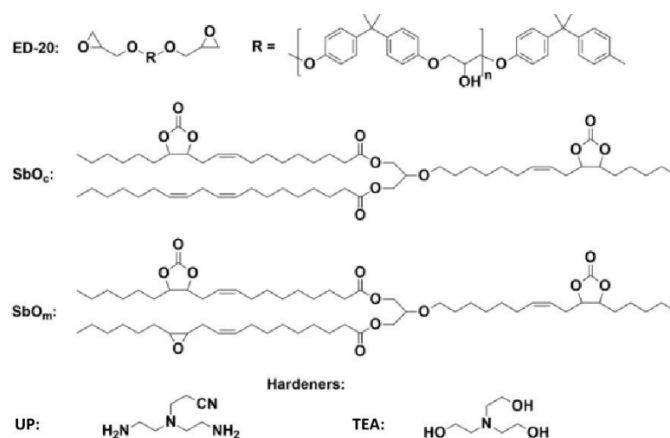
increased up to 10 wt. % epoxidized SbO content [16–19]. Five-membered carbonates react also with aliphatic primary and secondary amines under mild conditions to form  $\beta$ -hydroxyurethane bonds [14, 20–23]. Additionally, changing the chemical structure of the hardener and the curing conditions may also result in changes in such properties as chemical resistance, thermo-oxidative stability, toughness, flexibility, hardness, *etc.*

Therefore, the aim of this work was to receive modified epoxy resin with reactive epoxidized and cyclocarbonated SbO and investigate the influence of the type of hardener, functionality of modifier and curing conditions on the resistance to aggressive environments and mechanical properties of ED-20/SbO biocomposites.

## EXPERIMENT AND RESULTS DISCUSSION

**Materials.** Commercial epoxy resin ED-20 (2,2'-di(4-glycidyl phenylene)-propane based resin; DGEBA (mass fraction of epoxy groups is 20.0–22.5 %) and TEA hardener (tris(2-hydroxyethyl) amine, “Dafna”, Ukraine) and UP hardener (mono(cyanoethyl)diethylenetriamine, UP-0633M, “RIAP”, Ukraine), were used as received without additional purification.

Two types of functionalized soybean oils were prepared and supplied by the group of researchers headed by V.K. Grishchenko [24]. SbOm was a mixture of soybean oil functionalized with epoxy (12.5 %) and cyclocarbonate (24.6 %) groups, while the SbOc contained soybean oil functionalized only with cyclocarbonate (27.03 %) groups.



**Fig. 1.** Molecular structures of the raw materials used

**Sample preparation.** Compositions of pristine as well as modified ED-20 samples were synthesized with UP hardener (20 wt. %) or with TEA hardener (10 wt. %). Mass fraction of functionalized SbO for all biocomposite samples was 10 wt. %. The homogenized reaction mixture was poured into molds and cured under three different temperature regimes. The curing mode **I** was performed at 25° for 4 hours; curing mode **II** at 80° for 2 hours, 7 hours at 100°; and curing mode **III** was for 1 hour at 80°, 1 hour at 100°, 3 hours at 120°, and 2 hours at 160°. Sample abbreviation reflects its composition and curing mode.

**Characterization.** To analyse chemical structure, Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra (4000–400  $\text{cm}^{-1}$ ) of all synthesized materials were

recorded on a TENSOR 37, Bruker spectrometer at 20°.

The chemical resistance of the synthesized samples to the action of aggressive media was determined in accordance with water absorption tests by ASTM D-570 - 98(2018) “Standard Test Method for Water Absorption of Plastics” and ISO 175:2010 “Plastics – Methods of test for the determination of the effects of immersion in liquid chemicals”. The dried preweighed specimens were immersed into a definite volume of distilled water, 10 % acid solution ( $\text{H}_2\text{SO}_4$ ) and 10 % alkaline solution ( $\text{NaOH}$ ) at 25° for different intervals of time (due to 50 days). Weight changes were recorded by periodic removal of the specimens from the solution and weighing.

The degree of absorption ( $W$ , %; also called Percent chemical resistance) of the samples was

determined gravimetrically and calculated by Eq. (1):

$$W = (m_1 - m_0) / m_0 \times 100\%, \quad (1)$$

where  $m_0$  and  $m_1$  are the sample initial mass and mass after certain interval in an aggressive environment, respectively.

The percentage at equilibrium water absorption ( $W_{\max}$ ), was calculated as the average value of several consecutive measurements that showed no appreciable additional absorption.

For calculating diffusion coefficient of water (or aqueous solutions) into the polymer sample Eq. (2) was used:

$$D = 0.0494 \times (t_{1/2} / l), \quad (2)$$

where  $D$  is the diffusion coefficient of water ( $\text{cm}^2/\text{s}$ ) and,  $l$  is the initial thickness of the dry polymer sample ( $\mu\text{m}$ ),  $t_{1/2}$  is the time corresponding to the  $W_{\max}/2$ .

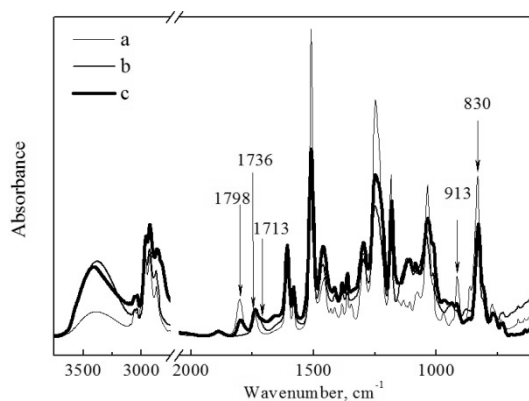
The morphology of the samples was studied by scanning electron microscopy (SEM) using a MIRA 3 microscope (Tescan GmbH, Czech Republic) with an electron beam energy of 2.0 kV in the secondary electron mode. The resolution of the device was 4–5 nm.

The thermo-oxidative stability of samples was studied by thermogravimetric analysis (TGA) on a TA Instruments Q-50 apparatus (USA) in air atmosphere. A heating rate of  $20 \text{ }^\circ\text{C min}^{-1}$  with a temperature range from 25 to  $700 \text{ }^\circ\text{C}$  was applied.

Tensile tests were performed using a “P-5” tensile testing machine with uniaxial tension applied at the rate of clamp movement of 50 mm/min. The standard type-I specimen specified in ASTM D638–99 (2000) had  $\sim 0.04 \text{ cm}$  thickness with 25 mm overall length, and 5.0 mm overall width. The ultimate tensile strength ( $\sigma$ , MPa) and – ultimate deformation (percentage elongation at break  $\epsilon$ , %) were measured.

## RESULTS AND DISCUSSION

**ATR-FTIR spectra.** The chemical structures of all initial components and synthesizes samples were analyzed by ATR-FTIR. It is detected that the characteristics bands of both epoxy resin and functionalized SbO appeared in all spectra of the initial reaction mixture. For example, spectra of ED-20/TEA/SbOc sample before curing is given in Fig. 2 *a*.



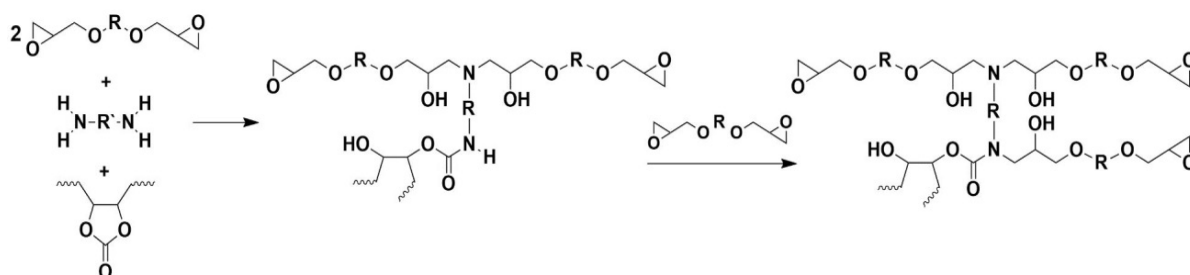
**Fig. 2.** ATR-FTIR spectra of ED-20/TEA/SbOc sample before (*a*) and after (*b*) curing; ED-20/UP/ SbOc sample after curing (*c*)

For epoxy resin, the main peaks at 913 and  $830 \text{ cm}^{-1}$  are attributed to epoxy -O- vibration; the peaks at 1241 and  $1160 \text{ cm}^{-1}$  are assigned to aryl and alkyl ether linkages, correspondingly; while the bands at 1635, 1410 and  $810 \text{ cm}^{-1}$  are ascribed to  $\text{C}=\text{C}_{\text{Ar}}$  vibration. Samples after curing revealed significant decrease of absorption bands at 913 and  $830 \text{ cm}^{-1}$  (ex., ED-20/TEA/SbOc sample after curing by curing mode III is shown in Fig. 2 *b*). However, the signals of epoxy -O- group didn't

disappear completely even when complete conversion was reached, which was caused by the peak overlapping with the in-plane flexural vibration of  $-\text{CH}_3$  groups [14]. The main characteristic band of cyclocarbonated SbO is also observed in the ATR-FTIR spectra in the initial mixture before curing (Fig. 2 *a*), namely stretching vibrations of carbonyl groups in the starting cyclocarbonates ( $1798 \text{ cm}^{-1}$ ), which disappears after curing mode. These results substantiated the

formation of netted structure of epoxy polymer and opening of cyclocarbonate groups of SbOc. The absorption band at  $1736\text{ cm}^{-1}$  refers to the stretching vibrations of C=O of the ester group of the residue of the fatty acid molecule in the oil molecules. After samples curing this band shifts slightly to the low frequency region and might be overlapped with the absorption band at  $1713\text{ cm}^{-1}$  that corresponds to the C=O group of

hydroxyurethanes in the case of UP hardener (ex., ED-20/UP/SbOc-III sample in Fig. 2 c) [25] and confirms possible interaction between cyclocarbonate groups of SbO and amino-groups of UP hardener with formation of H-NIPU (Hybrid Non-Isocyanate PolyUrethane) fragments between them. This interaction contributes to the grafting between epoxy matrix and soybean oil (Fig. 3) [20, 23].



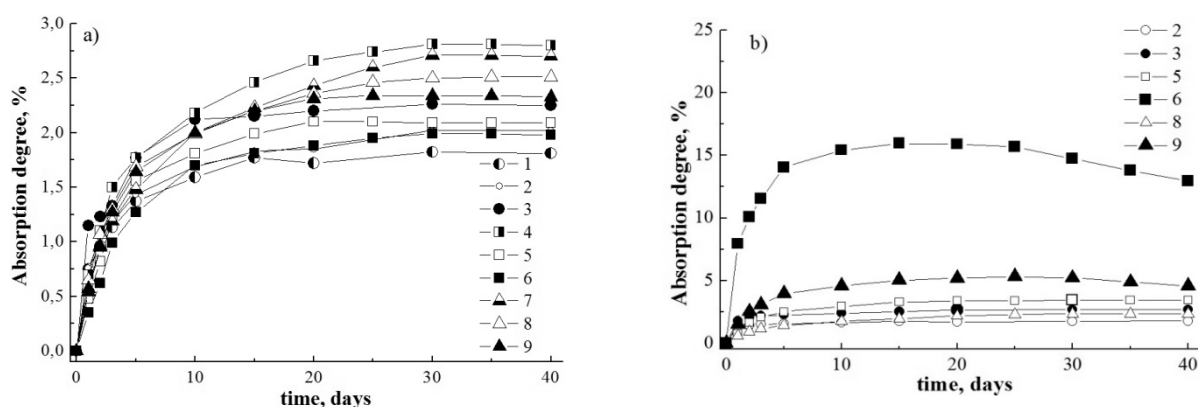
**Fig. 3.** Schematic representation of interaction between epoxy resin, cyclocarbonate group of functionalized SbO and UP hardener as diamine with formation of hydroxyurethane fragment

Small characteristic -OH bands around  $3400\text{ cm}^{-1}$  increased in the final spectrum of all of the samples. This indicated that some internal alkoxide ions produced during the curing reaction could be converted into -OH groups by the action of traces of moisture.

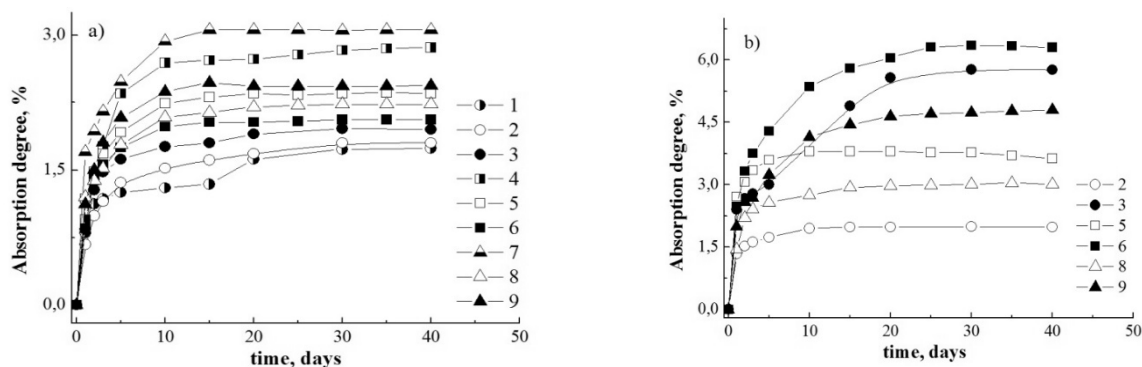
#### Chemical and Thermo-Oxidative Resistance.

The influence of environmental conditions on the biopolymer matrices has been investigated under various conditions in many studies. The

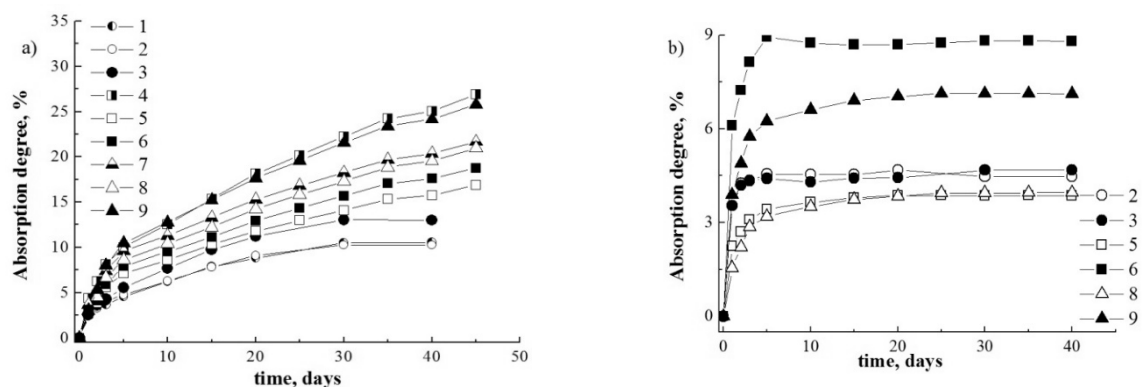
commercial practicability of the fabricated biopolymers lies in their physical and chemical resistance behaviour. As a result, a study on chemical resistance behaviour against water, 10 wt. % H<sub>2</sub>SO<sub>4</sub> and 10 wt. % NaOH, and swelling behaviour of polymer composites modified by functionalized SbO has been carried out (Figs. 4–6) and the percentage at equilibrium water absorption ( $W_{max}$ ) was determined (Table 1).



**Fig. 4.** Water absorption curves (in distilled water) of epoxy polymers based on the ED-20 and their composites made with *a* – UP as a curing agent: 1, 2, 3 – ED-20/UP; 4, 5, 6 – ED-20/UP/SbOc; 7, 8, 9 – ED-20/UP/SbOm; *b* – TEA as a curing agent: 2, 3 – ED-20/TEA; 5, 6 – ED-20/TEA/SbOc; 8, 9 – ED-20/TEA/SbOm. 1, 4, 7 – curing mode I; 2, 5, 8 – curing mode II; 3, 6, 9 – curing mode III



**Fig. 5.** Water absorption curves (in alkaline medium) of epoxy polymers based on the ED-20 and their composites made with *a* – UP as a curing agent: 1, 2, 3 – ED-20/UP; 4, 5, 6 – ED-20/UP/SbOc; 7, 8, 9 – ED-20/UP/SbOm; *b* – TEA as a curing agent: 2, 3 – ED-20/TEA; 5, 6 – ED-20/TEA/SbOc; 8, 9 – ED-20/TEA/SbOm. 1, 4, 7 – curing mode I; 2, 5, 8 – curing mode II; 3, 6, 9 – curing mode III



**Fig. 6.** Water absorption curves (in acidic medium) of epoxy polymers based on the ED-20 and their composites made with *a* – UP as a curing agent: 1, 2, 3 – ED-20/UP; 4, 5, 6 – ED-20/UP/SbOc; 7, 8, 9 – ED-20/UP/SbOm; *b* – TEA as a curing agent: 1, 2 – ED-20/TEA; 3, 4 – ED-20/TEA/SbOc; 5, 6 – ED-20/TEA/SbOm. 1, 4, 7 – curing mode I; 2, 5, 8 – curing mode II; 3, 6, 9 – curing mode III

**Table 1.** Equilibrium water absorption ( $W_{max}$ ) and diffusion coefficient ( $D$ ) in different aggressive media of pristine and modified epoxy resins cured with different hardeners and by different modes

| Sample abbreviation | distilled water |  | alkaline medium |  | acidic medium |  |
|---------------------|-----------------|--|-----------------|--|---------------|--|
|                     | $W_{max}$ , %   | $D \cdot 10^{-10}$ , $\text{cm}^2 \cdot \text{s}^{-1}$ | $W_{max}$ , %   | $D \cdot 10^{-10}$ , $\text{cm}^2 \cdot \text{s}^{-1}$ | $W_{max}$ , % | $D \cdot 10^{-10}$ , $\text{cm}^2 \cdot \text{s}^{-1}$ |
| ED-20/UP-I          | 1.8             | 5.8  | 1.7             | 7.8  | 10.5          | 1.3  |
| ED-20/UP/SbOc-I     | 2.8             | 3.8  | 2.9             | 5.0  | 26.9          | 0.9  |
| ED-20/UP/SbOm-I     | 2.7             | 2.6  | 3.0             | 12.3   | 21.7          | 1.3  |
| ED-20/UP-II         | 1.0             | 4.4  | 1.8             | 4.8  | 10.3          | 1.4  |
| ED-20/UP/SbOc-II    | 2.1             | 3.8  | 2.4             | 9.6  | 16.9          | 1.0  |
| ED-20/UP/SbOm-II    | 2.5             | 3.1  | 2.2             | 9.2  | 21.0          | 0.8  |
| ED-20/UP-III        | 1.1             | 9.3  | 2.0             | 7.1  | 13.0          | 1.3  |
| ED-20/UP/SbOc-III   | 2.0             | 3.5  | 2.1             | 7.8  | 18.7          | 1.1  |
| ED-20/UP/SbOm-III   | 2.3             | 3.8  | 2.5             | 7.6  | 25.8          | 0.5  |
| ED-20/TEA-II        | 1.8             | 12.2   | 2.0             | 10.9   | 4.6           | 13.0   |
| ED-20/TEA/SbOc-II   | 3.4             | 4.6  | 3.8             | 13.9   | 3.9           | 12.0   |
| ED-20/TEA/SbOm-II   | 2.3             | 3.5  | 3.0             | 10.2   | 4.0           | 7.0  |
| ED-20/TEA-III       | 2.7             | 12.0   | 5.8             | 2.3  | 4.7           | 14.9   |
| ED-20/TEA/SbOc-III  | 15.9            | 9.7  | 6.4             | 5.5  | 8.8           | 12.9   |
| ED-20/TEA/SbOm-III  | 5.3             | 4.4  | 4.8             | 6.0  | 7.2           | 16.0   |

The general character of the absorption curves in different media indicates that all samples obtained with UP as well as with TEA reached sorption equilibrium without destruction regardless the type of curing mode (Figs. 4–6). The introduction of functionalized SbO (Figs. 4–6) significantly changes the chemical stability of biopolymer matrices. Thus, in an aqueous medium (Fig. 4 *a*), the swelling curves of samples 5 (ED-20/UP/SbOc(II)) and 6 (ED-20/UP/SbOc(III)) lie below the curves of the initial samples that do not contain SbO. It means that the structure of the sample in the aqueous medium is compacted and the sorption characteristics decrease. The formation of such network structures is important from a practical point of view, because it opens up the possibility of obtaining water-resistant bioplastics.

The use of TEA hardener cannot be performed at room temperature and requires higher temperatures to cure epoxy resin. For this reason, only curing modes II and III were applied for ED-20/TEA formulations. Among the samples obtained with the TEA hardener, sample 6 (ED-20/TEA/SbOc(III)) turned out to be the most unstable in an aqueous medium (Fig. 4 *b*), since its water uptake is equal to 15 %. In this case, a loose network structure is formed compared to the samples of the primary epoxy resin. The percentages of swelling in water for other modified samples are close to the ones of initial formulations in the range of (2–4) %. When the medium is alkaline (Fig. 5 *a*), the degree of swelling of the SbO-modified samples with the UP hardener are higher than the ones of initial samples, which indicates a decrease in their chemical resistance. When using the TEA hardener in an alkaline medium (Fig. 5 *b*), samples 9 (ED-20/TEA/SbOm(III)), 5 (ED-20/TEA/SbOc(II)) and 8 (ED-20/TEA/SbOm(II)) according to the location of the swelling curves, showed a higher chemical resistance compared to the initial sample 3. Such network structures are important from a practical point of view, because it opens up the possibility of obtaining alkali-resistant bioplastics.

Introduction of functionalized SbO leads to sharp increase in sorption capacity of biopolymer matrices cured with UP hardener. The absorption process of such biopolymers does not reach equilibrium even for 50 days, regardless of the curing mode (Fig. 6 *a*). Samples 4 (ED-20/UP/SbOc(I)) and 9 (ED-20/UP/SbOm(III))

were noticed to be the most unstable ones, the degree of swelling of which increases to almost 25 %. Interesting to note, TEA hardener provides formation of more acid resistant materials than the UP hardener (Fig. 6 *b*). Thus, the swelling curves of samples 5 (ED-20/TEA/SbOc(II)) and 8 (ED-20/TEA/SbOm(II)) almost coincide and lie below the ones of initial samples.

As can be seen in Table 1, increase in curing temperature has insignificant effect on equilibrium absorption degree of ED-20/UP samples in distilled water as well as in alkaline media, namely  $W_{max}$  value was in the range of 1.0–2.0 % for such samples. For the samples ED-20/UP/SbOc and ED-20/UP/SbOm  $W_{max}$  values were in the range of 2.0–2.9 % and 2.1–3.0 %, respectively. These changes within one percent mean that introduction of functionalized SbO into epoxy matrix leads to slightly less dense network structure formation comparing with pristine epoxy samples. It should be noted that an increase in the curing temperature also has no significant effect on water absorption limit in both aqueous and alkaline medium for biopolymer matrices cured with UP hardener.

Chemical resistance of network ED-20/TEA samples to water and alkaline media decreases by 0.8–1.6 % and 0.2–3.8 %, respectively, comparing to the ED-20/UP samples. However, the chemical resistance of ED-20/TEA/SbO biopolymer matrices decreases more apparently in the case of curing mode III. It may indicate that curing mode II is more suitable for biopolymer matrices samples synthesized with TEA hardener than mode III.

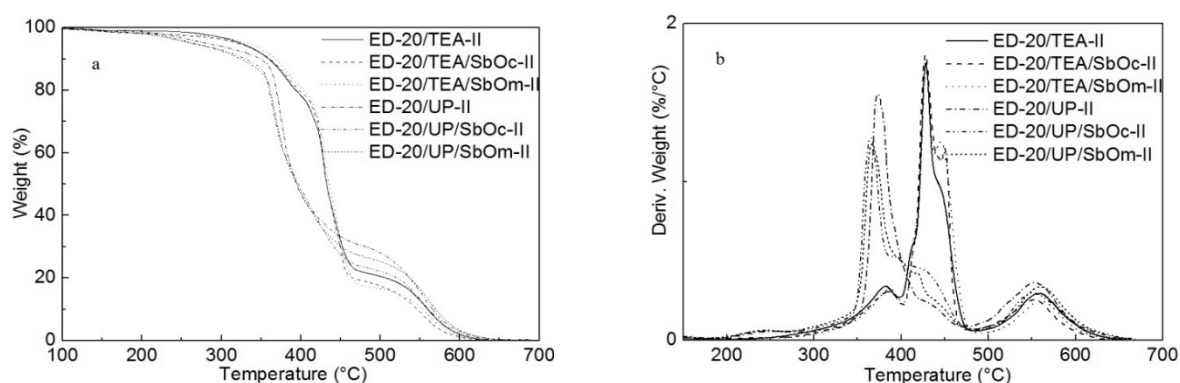
Additionally, the diffusion coefficient ( $D$ ) was calculated using Equation 2, and the values of this parameters are also given in Table 1 for all synthesized samples. The general character of the reduction of  $D$  values in distilled water and acidic environment, as a quantitative characteristic of the diffusion rate, indicates that the equilibrium water absorption for the biopolymer matrices occurs later comparing with the pristine ED-20 samples of corresponding cure mode. Namely, the presence of functionalized SbO during the formation of the epoxy network leads to a more tortuous diffusion path, and as a consequence, to slow down the movement of diffusion water molecules inside the composites (Table 1). However, the  $D$  value for alkaline medium resistance increases slightly compared to the corresponding samples in distilled water.

It should be noted that none of the biopolymer matrices after exposure to aggressive media did not

detect such defects in the surface of the films as cracking, delamination, discoloration, weight loss. Therefore, it can be concluded that destruction of the synthesized samples did not occur.

Thermo-oxidative stability of the chosen samples was evaluated by TGA analysis in air atmosphere. The biopolymer matrices exhibited two main stages of decomposition with a negligible

weight loss up to  $\sim 350$  °C (Fig. 7). The first main stage in the range  $\sim 350$ – $480$  °C is the combination of several peaks belonging to the structural fragments of different aliphatic chemical nature. The second stage in the region of  $\sim 485$ – $650$  °C is believed to correspond to aromatic fragments of ED-20.



**Fig. 7.** TGA (a) and DTG (b) curves of epoxy polymers based on the ED-20 and their biopolymer matrices

**Table 2.** TGA data of epoxy polymers based on the ED-20 and their biopolymer matrices

| Sample abbreviation | $T_{d10\%}, ^\circ\text{C}$ | $T_{dmax}, ^\circ\text{C}$ |
|---------------------|-----------------------------|----------------------------|
| ED20-TEA-II         | 360                         | 428                        |
| ED20-TEA-SbOc-II    | 351                         | 428                        |
| ED20-TEA-SbOm-II    | 368                         | 429                        |
| ED20-UP-II          | 349                         | 373                        |
| ED20-UP-SbOc-II     | 330                         | 365                        |
| ED20-UP-SbOm-II     | 324                         | 366                        |

We can see from the received data (Table 2) that epoxy polymer made with TEA hardener is more stable than that made with UP hardener, thus  $T_{dmax}$  of the latter is lower for 55 °C. The similar dependence is observed for biopolymer matrices received with TEA hardener, they are characterized with higher  $T_{dmax}$  value comparing with samples made with UP hardener for 63 °C. It should be noted that introduction of functionalized SbO into composition of biopolymer matrices made with TEA hardener did not reveal any changes in  $T_{dmax}$  value whereas biopolymer matrices with UP hardener had lower  $T_{dmax}$  value comparing with ED20/UP sample (on  $\sim 8$  °C).

**Morphology.** Morphological studies of ED-20/UP/SbOm biopolymer matrices were carried out using SEM. Micrographs of fractured specimens ED-20/UP/SbOm(I) and ED-20/UP/SbOm(II) are shown (Fig. 8). The fracture

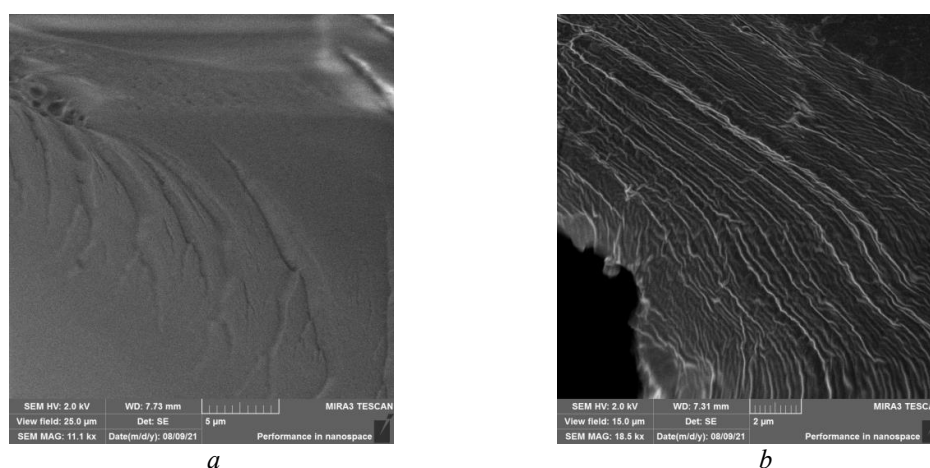
surface of the sample ED-20/UP/SbOm(I) (Fig. 8 a) is smooth, isolated inclusions of SbOm are observed, the system is mostly homogeneous, which may indicate grafting of functionalized soybean oil to the epoxy matrix [20]. There is no visible phase separation on the fracture surfaces, so the structure of such obtained polymer materials is homogeneous. However, the formation of layered structure on the fracture surface of the ED-20/UP/SbOm(II) film (Fig. 8 b) is characteristic of increasing material stiffness [18].

**Mechanical properties.** The mechanical properties i.e. ultimate tensile strength ( $\sigma$ , MPa) and ultimate deformation (elongation  $\epsilon$ , %) for the prepared samples were investigated and the results are presented in Table 3.

The curing of the ED-20/TEA sample by temperature mode III leads to an increase in

tensile strength by 1.4 times in comparison with the system of the same composition formed by curing mode **II**. At the same time, the curing mode has almost no effect on  $\sigma$  value for samples with ED-20/UP composition. However, the addition of functionalized SbO to the epoxy matrix cured with TEA hardener as well as UP hardener increases the  $\sigma$  values regardless of the type of oil functionalization. For example,  $\sigma$  rises to 1.3–1.6 times for ED-20/UP/SbOc comparing with correspondent ED-20/UP. It should be noted

that the curing mode almost does not affect the value of the ultimate deformation for biocomposites in the case of TEA hardener, and  $\epsilon$  value slightly decreases for these samples due to flexible nature of functionalized SbO. In contrast, an increase in the curing temperature of the biocomposites made with UP hardener promotes some increase in tensile strength. The value of the ultimate deformation varies randomly and unpredictably for ED-20/UP/SbO samples.



**Fig. 8.** SEM micrographs of samples: *a* – ED-20/UP/SbOm(I), *b* – ED-20/UP/SbOm(II)

**Table 3.** Mechanical properties of epoxy polymers based on the ED-20 and their biopolymer matrices

| Sample abbreviation | $\sigma$ , MPa | $\epsilon$ , % |
|---------------------|----------------|----------------|
| ED20-TEA-II         | 29.5           | 12.3           |
| ED20-TEA-III        | 42.4           | 11.4           |
| ED20-TEA-SbOc-II    | 55.8           | 8.0            |
| ED20-TEA-SbOc- III  | 23.8           | 9.2            |
| ED20-TEA-SbOm-II    | 52.6           | 9.7            |
| ED20-TEA-SbOm- III  | 53.3           | 7.2            |
| ED20-UP-I           | 43.5           | 7.2            |
| ED20-UP-II          | 35.4           | 9.0            |
| ED20-UP-III         | 40.8           | 8.0            |
| ED20-UP-SbOc-I      | 57.4           | 7.3            |
| ED20-UP-SbOc-II     | 63.2           | 7.1            |
| ED20-UP-SbOc-III    | 66.9           | 8.9            |
| ED20-UP-SbOm-I      | 62.7           | 1.9            |
| ED20-UP-SbOm-II     | 10.8           | 3.2            |
| ED20-UP-SbOm-III    | 36.9           | 1.7            |

## CONCLUSIONS

In this work, cyclic carbonated soybean oil (SbOc) and a mixture of epoxidized and cyclic carbonated soybean oil (SbOm) were used to modify the epoxy resin. Modified systems were obtained by means of two types of hardeners UP

and TEA under three different hardening modes. The influence of hardener and hardening modes on the properties of ED-20/SbO biopolymer matrices, such as water absorption, chemical resistance, and mechanical resistance, was studied. It is shown that the introduction of



functionalized SbO, the change of hardeners and hardening modes significantly affects the chemical stability of biopolymer matrices. Thus, biopolymer matrices cured by UP show better stability in an aqueous medium, and those cured by TEA are stable in alkaline and acidic environments. The formation of such network structures is important from a practical point of view, because it opens up the possibility of obtaining multilayer bioplastics resistant to water, alkali and acid. Generally, incorporation of functionalized SbO into epoxy biocomposites has been shown to improve their mechanical

properties, such as ultimate tensile strength, compared to initial epoxy polymers. In the case of biocomposites with SbOc, the ultimate tensile strength reached a maximum value of 66.9 MPa and 55.8 MPa for those made with UP hardener at curing mode III and made with TEA hardener at curing mode II, respectively.

Thus, the obtained results have shown that the choice of hardener, curing modes and modifier SbOc or SbOm provide an opportunity to obtain biopolymer matrices with improved mechanical properties and resistance to water, alkali or acid, compared to the original epoxy polymers.

## Механічні властивості, хімічна та термоокисна стійкість біополімерних матриць на основі епоксидної смоли та функціоналізованої соєвої олії

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Синтезовано біополімерні матриці на основі епоксидної смоли ЕД-20 та соєвої олії (СО), що містить циклокарбонатні та епоксидні групи. Як твердники використовували моно(ціаноетил)діетилентриамін (УП) і трис(2-гідроксіетил)амін (ТЕА). Досліджено хімічну структуру, механічні властивості, термоокисну стійкість зразків та їхні зміни після контакту з дистильованою водою, лужним або кислим середовищем. За допомогою АТР-FTIR було продемонстровано можливе утворення фрагментів гібридного неізоціанатного поліуретану (Н-НІРУ) між циклокарбонатними групами СО та аміногрупами твердника. Ретельно досліджено вплив режиму тверднення та типу твердника на водопоглинання, хімічну та термоокисну стійкість розроблених біополімерних матриць. Біополімерні матриці на основі УП показали стійкість до води та лугів, подібну до стійкості чистих епоксидних полімерів, тоді як біополімерні матриці на основі ТЕА показали кращу стійкість до лужного та кислого середовища. Термоокисну стійкість відібраних зразків оцінювали методом ТГА в атмосфері повітря. Було продемонстровано, що епоксидний полімер, затверджений твердником ТЕА, був більш стабільним, ніж полімер, затверджений УП. Аналогічна залежність спостерігається для біополімерних матриць на основі твердника ТЕА. Режим тверднення практично не впливає на показники міцності на розрив зразків із складом ЕД-20/УП. Однак додавання функціоналізованої СО до епоксидної матриці, затвердженої за допомогою твердників ТЕА і УП, підвищує кінцеві значення міцності на розрив незалежно від типу функціональної групи. Як і очікувалося, усі біополімерні матриці показали вищі показники міцності на розрив, стійкість до води, лугу або кислоти, порівняно з немодифікованими епоксидними полімерами, що надає можливість їхнього подальшого застосування для отримання багатощарових біопластиків.

**Ключові слова:** біополімерні матриці, епоксидна смола, епоксидована та циклокарбонатна соєва олія, хімічна та термоокисна стійкість, механічні властивості

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