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SYNTHESIS AND MECHANICAL PROPERTIES OF NOVEL EPOXY-POLYURETHANE MATERIALS BASED ON MODIFIED SOYBEAN OIL

SYNTEZA I WŁAŚCIWOŚCI MECHANICZNE NOWYCH EPOKSYDOWO-POLIURETANOWYCH MATERIAŁÓW NA BAZIE MODYFIKOWANEGO OLEJU SOJOWEGO

Abstract

The paper presents the results of studies on the synthesis and mechanical properties of the fusion product of epoxidized soybean oil with bisphenol A, which are a part of the current research on environmentally friendly raw materials for the preparation and modification of modern polymeric materials. It has been shown that the use of 4,4'-methylene diphenyl diisocyanate in the cross-linking process of the fusion product in the presence of Dabco 33-LV and BYK-A530 or BYK-A525 gives hard materials with interesting mechanical properties.

Keywords: bisphenol A, diisocyanates, epoxidized soybean oil, epoxy fusion process

Streszczenie

W pracy przedstawiono wyniki badań nad syntezą i właściwościami mechanicznymi produktu stapiania epoksydowanego oleju sojowego z bisfenolem A, które wpisują się w nurt poszukiwań proekologicznych surowców do otrzymywania i modyfikacji nowoczesnych materiałów polimerowych. Wykazano, że użycie 4,4'-diizocyjanianu difenylometanu w procesie sieciowania produktu stapiania w obecności Dabco 33-LV oraz BYK-A530 lub BYK-A525 prowadzi do otrzymania twardych materiałów o ciekawych właściwościach mechanicznych.

Słowa kluczowe: bisfenol A, diizocyjaniany, epoksydowany olej sojowy, reakcje stapiania,

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1. Introduction

The big challenge for modern chemistry and chemical technology is, first of all, the need to seek new sources of raw materials, which would become the alternative to petroleum-derived feedstocks. Another very important challenge is the necessity to protect our natural environment; hence, the drive to meet the requirements of the so-called 'green chemistry'. The use of modified vegetable oils gathers these principles. Vegetable oils are substances of natural origin and from renewable sources. They are non-toxic, cheap and biodegradable. What is also important is that oils are materials differing in composition (depending on their origin, vegetable oils contain in their triglyceride molecules residues of various fatty acids in different amounts), but also in the chemical structure (fatty acid residues generally contain unsaturated bonds, however, in oils obtained from some plants, hydroxyl or epoxy groups are present naturally). Therefore, after suitable modification, for many years, vegetable oils have been used as plasticisers for thermoplastics (epoxide derivatives) [1], as well as natural components of polyol mixtures (hydroxyl derivatives) for the production of polyurethane materials [2–4]. Currently, around the world, studies on the application of vegetable oils as a source of many valuable derivatives, which could be used either for modification of other polymers [5] or as raw materials for their synthesis [6], are undertaken. Hence, on an industrial scale, vegetable oils are used, for example, for bio-polyamides production [7], for which, by modifying selected vegetable oils, both essential fatty acids and amines [8] could be obtained. From scientific and patent literature, there are known proposals for the use of derivatives of plant triglycerides as raw materials for the synthesis of the other polymers, such as: poly(hydroxyalcanoates) [9], polyesteramides [10], polyetheramides [11] and alkyds [12]. At the same time, efforts are also put on studies on the use of modified vegetable oils in epoxy resin technology, such as: reactive diluents [13], modifiers for increasing toughness and flexibility [14] or even raw materials in the synthesis of high-molecular-weight resins by polyaddition carried out in bulk by the fusion process [15–16].

In our group, numerous experiments have been performed on the application of a novel pro-ecological method of the synthesis of epoxy materials. This new and interesting reaction is based on a conventional method of the synthesis of high-molecular-weight (1,500–10,000 g/mol) epoxy resins in the epoxy fusion process involving low- and average-molecular-weight epoxies and bisphenols [17] (Fig. 1).

Our method, which meets the requirements of 'green chemistry', not only eliminates the necessity for the application of solvents that are harmful for environment, strong acids and alkali [18], which is particularly important for ecological awareness, but also is proposing partially replacing petrochemical raw materials by introducing modified vegetable oils in the form of epoxidized or hydroxylised derivatives. The elaborated process is simple and gives the opportunity of obtaining a product of the design properties and molecular weight, which is much higher than *via* the conventional solvent method. The introduction of vegetable oils in the process of synthesis of epoxy resins results in obtaining a pro-ecological product with better applicable characteristics (e.g. lower viscosity [13], [19–20] and higher resilience) than *via* the conventional method using petrochemical raw materials.

The developed method of the synthesis allows to obtain new and very interesting epoxy material, containing free epoxy and hydroxyl groups in their structure. It is possible to cross-link products of the epoxy fusion process with, e.g. diisocyanates, obtaining novel epoxy-

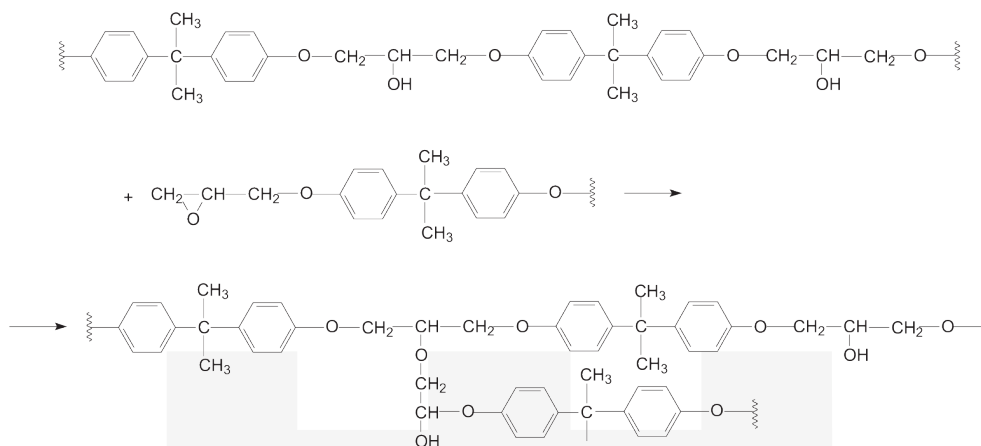


Fig. 1. The conventional method of the high-molecular-weight epoxy resins synthesis

polyurethane materials of which characteristics depend on the choice of the cross-linking method [21]. Therefore, the aim of this study was to obtain a product of fusion reaction of epoxidized soybean oil with bisphenol A, then cross-link it with 4,4'-methylene diphenyl diisocyanate under different conditions and to investigate the properties of the materials as well as to determine the relationship between the selected curing estate and mechanical strength of the cured compositions. In the presented part of the research, we concentrate on obtaining materials with good mechanical properties.

2. Materials and methods

2.1. Materials

In the performed epoxy fusion process, epoxidized soybean oil (ESBO, Ergoplast EG, Boryszew, EV = 0.363mol/100g), bisphenol A (BPA, GE Cartagenie, 99.93%) and LiCl (Merck, pure; in amount of 0.002 mol per 1 mol of bisphenol A) were used.

Cross-linking of synthesised epoxy fusion product was made with the use of:

- Desmodur VL (Bayer Material Science, Germany), used as a curing agent, an aromatic polyisocyanate based on 4,4'-methylene diphenyl diisocyanate [MDI] and containing 31.5 wt.% of free -NCO groups, viscosity of 90 mPa·s (at 25°C) and density of 1.24 g/cm³.
- Dabco 33-LV (Air Products and Chemicals, Inc., USA), a mixture of 33 wt.% of triethylene diamine and 67 wt.% of dipropylene glycol, used as catalyst.
- BYK A 530 and BYK 525 (BYK – Chemie GmbH, Germany), deaerators on the silicone basis, used for facilitation of vent and skimming of cured compositions.

2.2. Fusion process

Epoxidized product (ESBO), bisphenol A (BPA, GE Cartagenie, 99.93%) and LiCl (Merck, pure; in amount of 0.002 mol per 1 mol of bisphenol A) have been involved in the fusion reactions. The process was carried out in a nitrogen atmosphere. In the first step, epoxidized soybean oil was heated to 110°C and a calculated amount of the BPA was added. The reaction mixture was homogenised. Then, LiCl was added and the temperature was raised to 160°C. The progress of the epoxy fusion process was monitored in time by evaluating the epoxy group contents of the obtained samples.

2.3. Cross-linking of the composition and samples for mechanical testing preparation

Cross-linking of epoxy fusion product was conducted with the use of selected isocyanate – Desmodur VL at a stoichiometric amount with the respect of hydroxyl groups in hardened the material. Each composition contained 1% of BYK A530 (BYK A525) deaerator. Additionally, the influence of different amounts of catalyst Dabco 33-LV on the cross-linking process and mechanical properties of cured compositions was observed. After intensive mixing, followed by venting in a vacuum dryer at 25°C, the prepared compositions were poured into forms made of PTFE and left for hardening at room temperature for 24 hours. Then, the samples were removed from forms and annealed at 80°C for another 24h.

2.4. Measurement methods

2.4.1. Spectroscopic measurements

The analysis of transmittance FT-IR spectroscopy was achieved using the FT-IR Perkin-Elmer precise system spectrophotometer (SPECTRUM 65 FT-IR, Perkin Elmer, UK). The measurements of liquid samples were performed in a form of liquid films between KBr cell windows. A drop of oil samples was placed between two KBr windows, and then it was spread evenly on their surface. Subsequently, oil samples absorbance spectra were obtained in the range of 4000–400 cm^{-1} at ambient temperature of 20–22°C, using the FT-IR spectrophotometer. Composition samples were analysed using a same spectrometer equipped with ZnSe crystal attenuated total reflectance unit. Spectra were recorded with a resolution of 4 cm^{-1} , from 4000 to 400 cm^{-1} , with an average of 32 scans. The obtained spectra are presented in the dependence of transmittance T [%] and wave number ν [cm^{-1}].

2.4.2. Epoxy and hydroxyl values determination

The epoxy and hydroxyl values were evaluated by the titration methods. The content of epoxy groups (epoxy value, EV) in the investigated products was evaluated according to the PN-87/C-89085/13 standard: samples were dissolved in HCl/1,4-dioxane solution and titrated by NaOH/methanol in the presence of cresol red as the indicator to the visual change of the tint to purple. In order to defined the hydroxyl value (HV), respectively, samples of soybean oil, its epoxidized and fusion products were dissolved in the solution of catalyst

[4-(dimethylamine) pyridine in DMF] and acetic anhydride in DMF, followed by intensive stirring for another 15 minutes and titration with KOH aqueous solution in a presence of thymolphthalein, until the tint changed from colourless to blue.

2.4.3. Mechanical properties

The mechanical properties of the prepared composition samples in the form of paddles, beams and rollers, were tested. Tensile strength, elongation at break, modulus elasticity, flexural strength, elasticity flexural modulus, deflection, compressive strength and compression set, were tested using the Zwick 1445 apparatus. However, specifically tensile strength, elongation at break, modulus elasticity, were determined according to the PN-EN ISO 527-1:2012 standard on samples in the form of paddles (type B) [section measurement with dimensions: 4×10 (at cross-section) and 50 mm (length)] and the use of the Zwick apparatus equipped with an extensometer. Measurements were conducted with a 5 mm/min testing speed. Flexural strength, elasticity flexural modulus, deflection were tested according to the PN-EN ISO 178:2011 standard, using samples in the form of cuboid beams with a cross-section of 4×10 mm, with 64 mm spacing between supports and a testing speed of 10 mm/min. Compressive strength and compression set were tested according to the PN-EN ISO 604:2006 standard, using samples prepared in the form of rollers with 10 mm diameter and 25 mm height, with a testing speed of 0.8 mm/min.

Hardness in the Shore's A scale was tested according to the PN-EN ISO 868:2005 standard with the use of the InSize apparatus.

Impact toughness by the Charpy's method (PN-EN ISO 179-2:2001) was tested on the ZORN PSW 4J Digital apparatus.

3. Results and discussion

The basic epoxy product, which was then used as a reactant in the fusion process, was synthesised using commercially manufactured soybean oil, wherein its modification was performed in the typical process of epoxidation of natural oil. In general, this reaction is carried out in a system of hydrogen peroxide and an aliphatic carboxylic acid, in the presence of an acid catalyst (Fig. 2, reaction 1: A – soybean oil, B – epoxidized soybean oil, C – epoxy fusion dimer, D – epoxy fusion product), although, the actual oxidising agent is created *in situ* by reaction of the acid with hydrogen peroxide and the formation of an organic peracid, which then reacts with unsaturated bonds of oil macromolecules [22]. In the performed epoxy fusion process (Fig. 2, reaction 2), reagents were applied in a 1:1 molar ratio with the calculation of the amount of BPA based on the change of quantity of functional groups in substrates and products of the reaction as well with an assumption that the obtained product should contain epoxy groups on the level of 0.100 mol/100g [15–16]. Epoxy fusion process was conducted for a period of 18 h at a temperature of 160°C (the time of conducted process was established experimentally, by monitoring the epoxy value of the reacting mixture) in the presence of LiCl (0.002 mol per 1 mol of bisphenol) [23], which favours reactions of phenol groups of bisphenol A with epoxy groups over possible reaction of secondary hydroxyl groups (obtained by oxirane ring opening) with epoxy groups, as well as inhibits branching reaction and, at the same time, prevents gelling of the reacting mixture. In general, the first stage of

the bio-synthesis of novel epoxy resin involves the formation of a dimer (C) (Fig. 2, reaction 2), due to the reaction of one epoxy group of epoxidized vegetable oil with one hydroxyl group of bisphenol A. In the next stage, reactions involving subsequent molecules of either epoxidized vegetable oil (B) (with the utilisation of free hydroxyl group of bisphenol A) or BPA (reaction with the use of remaining epoxy groups) are possible, leading to the formation of linear (D1) or branched structure (D2) of epoxy fusion product (D).

After 18 h of conducting the process, it was possible to obtain decrease of epoxy group content to the level of 0.204 mol/100 g, while the hydroxyl value was 130 mgKOH/g. The structure of epoxy product was characterised by FT-IR (Fig. 4), GPC and functional group determination (epoxy and hydroxyl group contents).

On the FT-IR image of the epoxidized soybean oil, signals with little intensity, characteristic for epoxy group, are visible at $\nu = 1240 \text{ cm}^{-1}$ and $\nu = 832 \text{ cm}^{-1}$, respectively. They are still

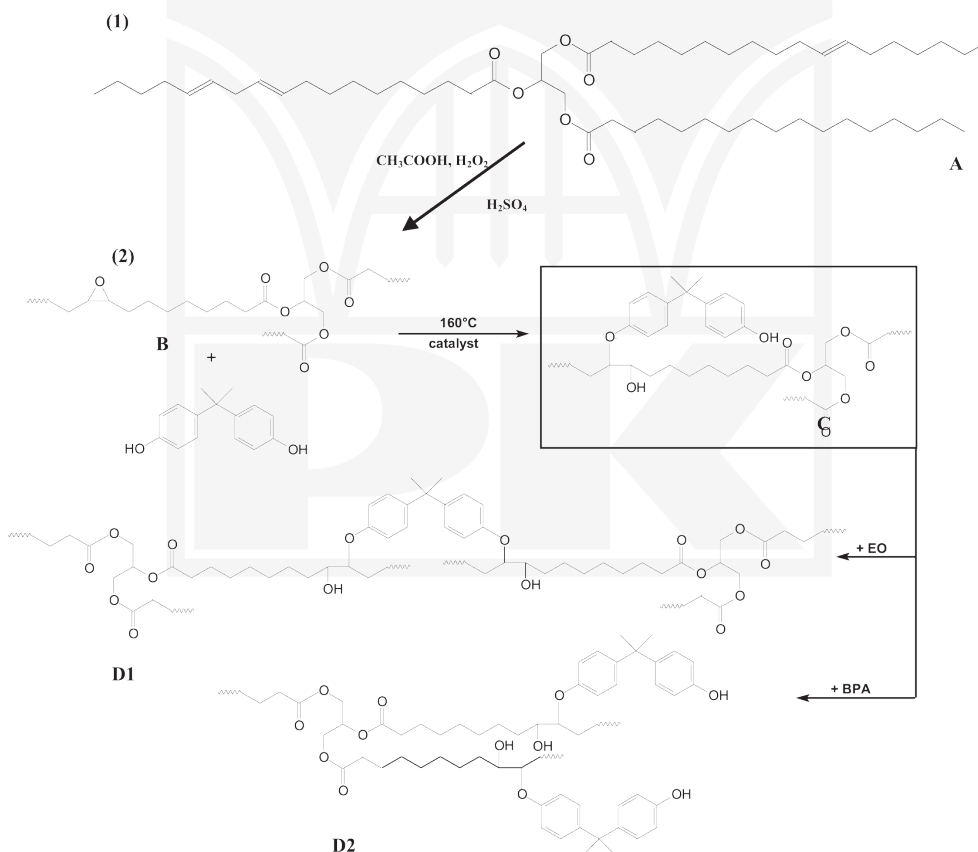


Fig. 2. Scheme of the innovative, pro-ecological method of the bio-based epoxy-polyurethane materials' synthesis – PART I: 1 – epoxidation, 2 – epoxy fusion process; A – soybean oil (SO), B – epoxidized soybean oil (ESBO), C – epoxy fusion dimer, D1 – linear epoxy fusion product formation, D2 – branched epoxy fusion product formation

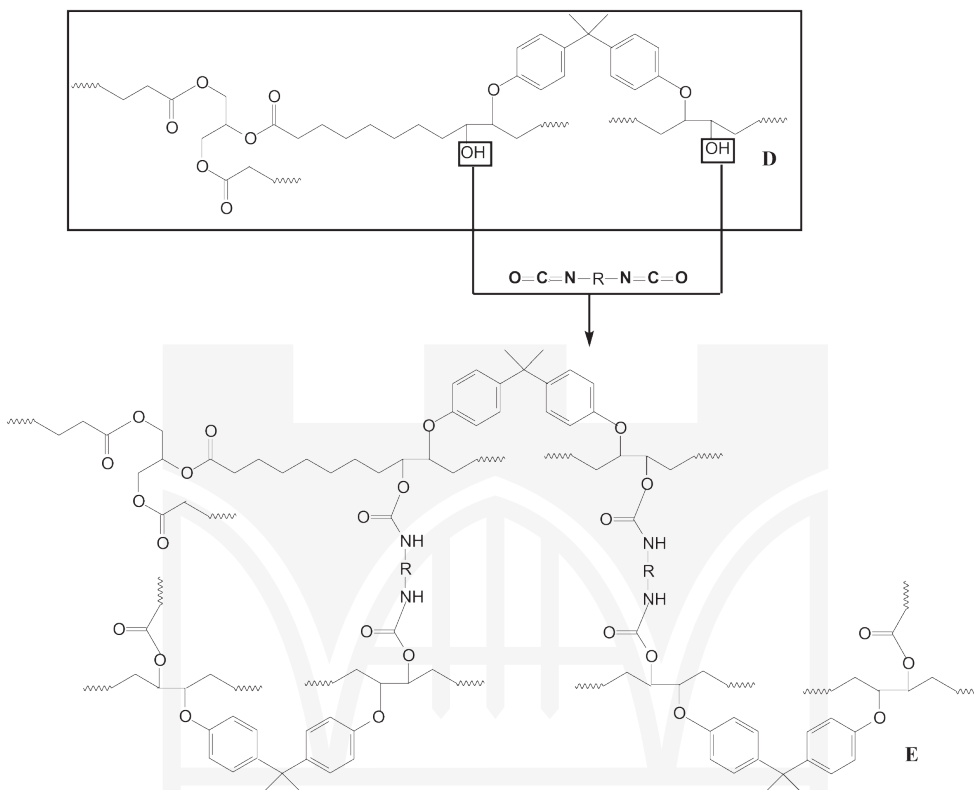


Fig. 3. Scheme of the innovative, pro-ecological method of the bio-based epoxy-polyurethane materials' synthesis – PART II: cross-linking process, D – epoxy fusion product, E – bio-based epoxy-polyurethane material

present on the spectrum of ESBO_BPA, however, their intensities decreased and they are just visible at $\nu = 1238\text{ cm}^{-1}$. The absorption signal at $\nu = 832\text{ cm}^{-1}$, due to its very little intensity, is not visible and might be covered by the signal from the covalent bond of *t*-butyl group ($\nu = 842\text{ cm}^{-1}$) from bisphenol A, which has relatively high intensity. Additionally, there is a wide signal at $\nu = 3412\text{ cm}^{-1}$, which can be assign to hydroxyl groups. Comparison of spectrogram images of ESBO and ESBO_BPA confirms that the reaction between epoxidized soybean oil and bisphenol A took place, and the obtained product consists of both the epoxy and hydroxyl group. The above observations were additionally proven by titration designation of the functional group's contents. Both epoxy and hydroxyl groups might be successfully utilised for the cross-linking process, wherein the selection of cross-linking agent and the condition of the cross-linking reaction are crucial for the mechanical properties of the obtained epoxy materials. In the technology of epoxies, different curing agents might be used, including: aliphatic amines and polyamines, aromatic amines and acidic anhydrides. The research presented here not only shows the application of an innovative method of the synthesis of novel bio-based epoxy fusion products,

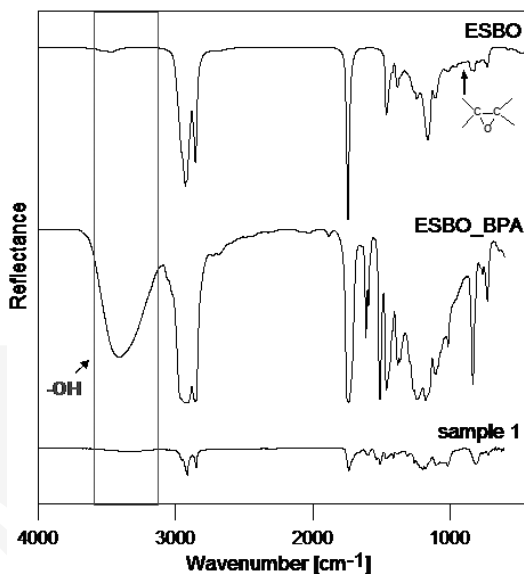


Fig. 4. FT-IR spectra of the soybean oil: epoxidized soybean oil (a) and epoxy fusion product of epoxidized soybean oil and bisphenol A (b), cross-linked epoxy-polyurethane material (c)

but also introduces diisocyanate as a curing agent for this type of materials, leading to obtaining novel materials with interesting mechanical properties. 4,4'-methylene diphenyl diisocyanate is commonly used in the technology of PU for materials, both in the form of rigid foams and elastomers. The selection of particular (aliphatic or aromatic) structure of isocyanate for the cross-linking process significantly influences the mechanical properties of the final product. As it was observed, for aliphatic isocyanates, the products are characterised by low mechanical strength and high elongation at break, while these obtained with the use of aromatic hardeners have better mechanical properties. In the part of the research presented here, we concentrate on obtaining materials with good mechanical properties. Application of 4,4'-methylene diphenyl diisocyanate for the cross-linking process is based on the reaction of hydroxyl groups of epoxy fusion product (D) and -NCO groups of diisocyanate (Fig. 3), leading to formation of hybrid epoxy-polyurethane material (E). In other words, the performed reaction utilises hydroxyl groups in the networking process, which is clearly visible on the comparison FT-IR spectrogram (Fig. 4: b-c), where the signal from hydroxyl groups present at $\nu = 3412 \text{ cm}^{-1}$ for ESBO_BPA is not visible for cured product.

Based on the performed cross-linking tests, five compositions were prepared and their mechanical properties were tested. Individual samples consisted of epoxy fusion product ESBO_BPA, MDI, the catalyst (Dabco 33-LV, in about 0.00, 0.15 or 0.30 wt.%) and 1 wt.% of the deaerator (BYK A530 or BYK A525) (Table 1). Dabco 33-LV (commonly used in the polyurethane technology) has a strong influence on promoting the urethane reaction (polyol with isocyanate) in a variety of both flexible and rigid foams as well as elastomer applications.

Table 1

List of the cured compositions submitted to mechanical properties testing

Sample	Epoxy fusion product	Isocyanate	Catalyst	Deaerator
1	ESBO_BPA EV = 0.204 mol/100g HV = 130 mgKOH/g	MDI -NCO =31.5 wt.%	No catalyst added	BYK A530
2			Dabco 33-LV (0.3%)	
3			Dabco 33-LV (0.15%)	
4			No catalyst added	BYK A525
5			Dabco 33-LV (0.15%)	

The amount of cross-linking agent was calculated with the respect to the hydroxyl group content in the epoxy fusion product. The process was performed in open forms at room temperature for 24 h, followed by final post-curing at a temperature of 80°C for another 24 h. During both the preparation and the casting, there were no significant differences observed between the compositions. After 24 h, the cured samples were easy to remove from their forms. All of them maintained rigidity and non-transparency.

The prepared samples were subjected to mechanical tests, determining their tensile strength, elongation at break, modulus elasticity, flexural strength, elasticity flexural modulus, deflection, compressive strength, compression, hardness on the Shore'a A scale and toughness by the Charpy's method (Fig. 5–7, Table 2).

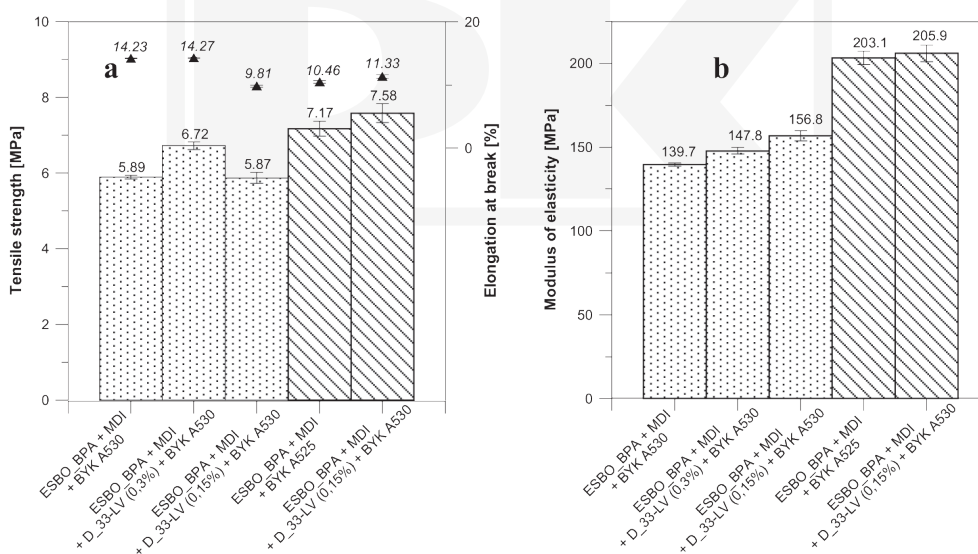


Fig. 5. Mechanical properties of epoxy fusion product, ESBO_BPA, cross-linked with the isocyanate: tensile strength and elongation at break (a), modulus of elasticity (b)

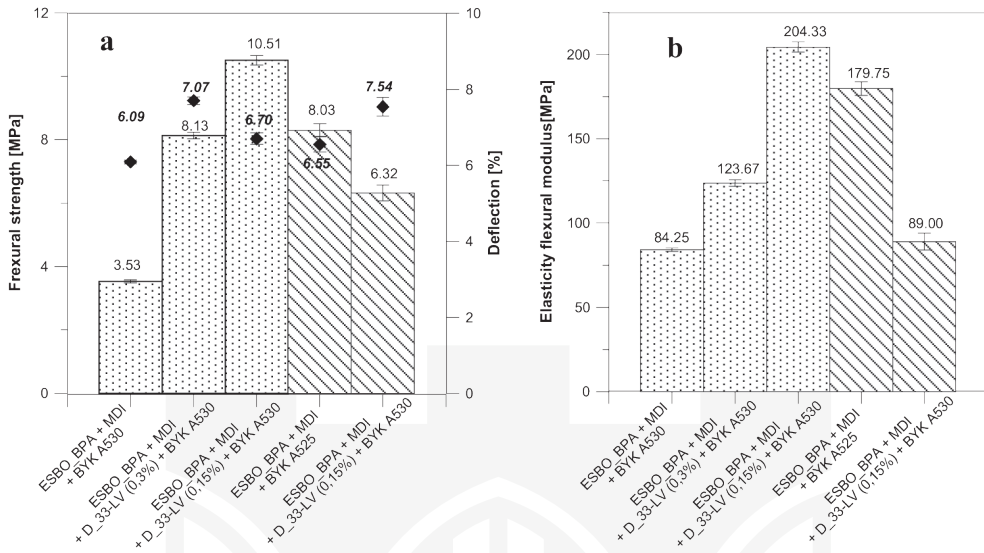


Fig. 6. Mechanical properties of epoxy fusion product, ESBO_BPA, cross-linked with the isocyanate: flexural strength and deflection (a), elasticity flexural modulus (b)

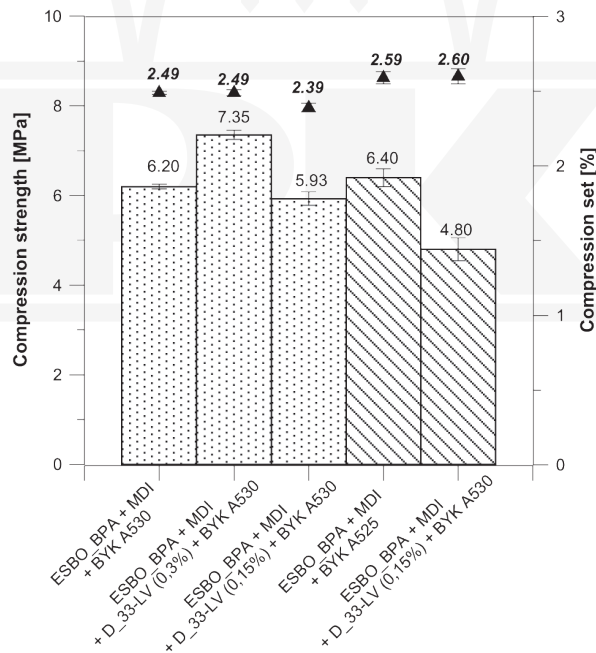


Fig. 7. Mechanical properties of epoxy fusion product, ESBO_BPA, cross-linked with the isocyanate: compressive strength and compression set

Mechanical properties of cross-linked epoxy-polyurethane material based on epoxy fusion product of epoxidized soybean oil and bisphenol A

Mechanical property	Composition				
	1	2	3	4	5
Impact toughness [kJ/m ²]	11.96 ± 1.50	9.04 ± 1.34	6.93 ± 0.81	6.75 ± 0.82	13.40 ± 1.46
Shore Hardness [Sh°A]	90 ± 1.5	91 ± 1.2	92 ± 0.9	92 ± 0.8	93 ± 1.5
Resilience [%]	14.2 ± 0.6	18.4 ± 0.5	18.2 ± 0.8	8.8 ± 0.6	13.2 ± 0.6

The analysis of the obtained mechanical test results might be divided into two groups upon the use of different deaerators. In the first group, obtained with BYK 530 application, a comparison between compositions 1–3 shows that the cured product containing 0.3 wt.% of catalyst Dabco 33-LV (composition 2) presents the highest tensile strength and elongation at break. At the same time, this material has the highest, from all prepared samples, resilience and compression strength. On the other hand, composition 3 presents the highest flexural strength and elasticity flexural modulus. Similarly, within the group of BYK A525 deaerator, application of the catalyst leads to an increase of the tensile strength, elongation at break, impact strength and resilience, simultaneous decrease of the flexural strength and elasticity flexural modulus. All of the obtained compositions have a comparable hardness on the Shore A scale. Additionally, it had been observed that the application of the deaerator BYK A525 leads to an increase of the tensile strength and elongation at break of the obtained material. It is worth to mention here that supplementary mechanical properties are closely related to the amount as well as the type (according to results of different experiments performed in our research group) of applied catalyst. Comparison of hybrid epoxy-polyurethane materials cured with 4,4'-methylene diphenyl diisocyanate with other polymeric materials indicates that mechanical resistance of obtained compositions is higher not only than commercial low molecular weight epoxy resin Ruetapox 162 cured with methyltetrahydrophthalic anhydride, but also elastic polyurethane materials based on hydroxyl soybean oil [24–25]. On the other hand, our materials have worse mechanical strength than epoxy resin cross-linked with isophoronediamine [21].

4. Conclusions

Our research presented in above paper is closely related to the latest environmental concerns, paying special attention to bio- and renewable resources as feedstock for the chemical industry. Application of vegetable oils gives the opportunity to obtain novel epoxy materials with various interesting properties, which may be designed by the proper selection of hardener, catalyst and deaerator of the curing process. The above-discussed investigations describe the synthesis and selected mechanical properties of compositions based on the product of the fusion reaction of the modified soybean oil and bisphenol A, subsequently cross-linked with MDI in the presence of various amounts of catalyst Dabco 33-LV and

two different deaerators on silicone basis (BYK A530 and BYK 525). It has been found that an application of the deaerator BYK A525 leads to an increase of the tensile strength and elongation at break of the obtained material without significant differences in the sample's appearance. Additionally, compositions prepared in the presence of catalyst Dabco 33-LV show a higher value of tensile strength, elongation at break, impact strength and resilience, when compared with samples without the use of catalyst.

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