SINTEZA I KARAKTERIZACIJA PREMAZA EPOKSIDNE SMOLE SA POBOLJŠANOM OTPORNOŠĆU NA PLAMEN UPOTREBOM MODIFIKOVANE TANINSKE KISELINE

SYNTHESIS AND CHARACTERIZATION OF EPOXY RESIN COATING WITH IMPROVED FIRE RESISTANCE BY THE ADDITION OF MODIFIED TANNIC ACID

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U radu je predstavljen novi postupak za dobijanje eko-epoksidnih materijala sa smanjenom zapaljivošću ili su potpuno negorovi, a koji se sintetišu iz bio-obnovljivih sirovina, čiji se proizvodni proces sastoji od dve faze. Poseban aspekt od višestrukog značaja za životnu sredinu je upotreba bio-obnovljivih resursa i smanjenje udela toksične epoksidne komponente u proizvodnji epoksidnih materijala. Prva faza razmatra sintezu derivata komponenata epoksidne smole: epoksi funkcionalizovana taninska kiselina (TA) - ETA i sinteza fosfatnih derivata TA - glicidil ester TA modifikovan fosforom kiselinom (PGET). Drugi faza razmatra sintezu bio-epoksi smole korišćenjem ETA, i PGET koji se koriste kao zamena komponente epoksidne smole (A) – bisfenol A epoksida u odnosu 25-100% kao reaktivni razblaživač za dobijanje proizvoda koji se mogu koristiti u građevinarstvu i drugim industrijskim oblastima, a imaju smanjenu zapaljivost ili potpuno su nezapaljivi. U drugom delu prikazani su rezultati termalnih i mehaničkih ispitivanja za neke od dobijenih derivata. Dodavanje 25% TA derivata poboljšalo je žilavost i zateznu čvrstoću epoksidnog materijala. Termogravimetrija je pokazala da uzorci koji sadrže taninski epoksid pokazuju više ostatka. Delimična ili potpuna zamena epoksidna komponenta sa produktom tanina koristi ekološki prihvatljiv materijal sa značajno povećanom otpornošću na vatru (V-2 do V-0).

Ključne reči: epoksid; tanijska kiselina; retardacija plamena; mehanička svojstva; termalna svojstva

The paper presents a new process for obtaining eco-epoxide materials with reduced combustibility or completely non-combustible, which are synthesized from bio-renewable raw materials, whose production process consists of two stages. A particular aspect of multiple environmental significance is the use of bio-renewable resources and the reduction of the share of the toxic epoxy component in the production of epoxy materials. The first stage considers the synthesis epoxy resin components: epoxy functionalized tannic acid (TA) – ETA, and synthesis of phosphate derivatives of TA - glycidyl ester of TA modified by phosphoric acid (PGET). The second stage considers the synthesis of bio-epoxy resins using ETA and PGET that are used as a replacement of the epoxy resin component (A) – bisphenol A based epoxy in a ratio 25-100% as a reactive diluent to obtain products that can be used in the construction and other industrial fields and have reduced combustibility or completely non-combustible. The second part presents the results of thermal and mechanical tests for some of the obtained derivatives. The addition of 25% of TA derivate improved the toughness as well as the tensile strength of epoxy material. Thermogravimetry showed that samples containing tannin epoxide showed more residue left. Partial or full replacement of the epoxy component with a tannin component produces eco-friendly material with while significantly increased fire resistance (V-2 to V-0).

Key words: epoxy; tannic acid; flame retardant; mechanical properties; thermal properties

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1 Introduction

The term 'epoxy resin' is used for both crosslinked and non-crosslinked resins. Only non-crosslinked resin contains epoxy - oxirane groups, after which they got their name. In the crosslinked, all reactive epoxy groups reacted. Although there are no longer any epoxy groups in crosslinked resins, they are still called epoxy resins.

Bis (4-hydroxyphenylene) -2,2-propane, also known as bisphenol A (BPA), is used as the base for most epoxides, and it is the monomer derived from fossil fuels. Aromatic compounds are widely used as materials of organic origin due to their stability, strength, toughness and especially the ability to establish intermolecular interactions by overlapping π -bonds, which allows BPA epoxides to have good thermal and mechanical properties, as well as anticorrosive and barrier properties [1,2]. Most epoxies, including BPA epoxy, are subject to hydrolysis to some extent, which can cause the release of BPA and its exposure and contact with humans and the environment [3,4].

BPA epoxide in hydrolyzed form is classified as carcinogenic, mutagenic and reprotoxic (respiratory poisoning) - CMR substance, and is also registered as a cause of endocrine problems (destroyer / hormone disruptor - impact on the sterility of human and animal species) [3-5]. With all this in mind, and the fact that fossil fuels are a non-renewable resource and will eventually deplete, it should be replaced with a naturally found monomer from renewable resources.

Tannins are a secondary biodegradable/biorenewable source of natural aromatic derivatives and the third most common component that can be extracted from wood biomass (cellulose is the most abundant, closely followed by lignin). Tannins are found in the soft tissue of wood, bark, leaves, needles, roots and fruits of many plants, it leaves a dried feeling in the mouth, and it has a bitter, basic taste [6]. It helps with cardiovascular problems, regulates blood pressure and circulation if used properly, it is mostly found in urns and teas such as black, green and white tea. In the plant, they play a protective role from external influences and regulate the growth of the plant, and also give the tissue strength.

Tannins are polyphenolic derivatives, a natural polymer of low molar mass, an undefined structure of molecules that can be divided into three main categories: Hydrolyzable tannins, condensed tannins and complex or compact tannins, complex or compact tannins are a combination of the first two [7]. Tannin can easily be converted into tannic acid (TA).

Fire hazard is a combination of factors, including ignitability, ease of extinction, flammability of the volatile products generated, amount of heat released on burning, rate of heat release, flame spread, smoke obscuration, and smoke toxicity, as well as the fire scenario. Fire fatalities are usually reported as resulting from the lethal atmosphere generated by fires. Carbon monoxide concentrations measured in real fires can reach up to 7500 ppm, which would probably result in a loss of consciousness in 4 minutes. Other components of acute toxicity found in real fires play a secondary role.

The combustion reaction involves two factors: one or more combustibles (reducing agents) and a combusting (oxidizing agent). The combusting is generally the oxygen in the air. The whole process usually starts with an increase in the temperature of the polymeric material due to a heat source, to such an extent that it induces polymer bond scissions. The volatile fraction of the resulting polymer fragments diffuses into the air and creates a combustible gaseous mixture (also called fuel) [8]. This gaseous mixture ignites when the auto-ignition temperature (defined as the temperature at which the activation energy of the combustion reaction is attained) is reached, liberating heat. Alternatively, the fuel can also ignite at a lower temperature (called the flash point) upon reaction with an external source of intense energy (spark, flame, etc.). The decomposition mechanism is highly dependent on the weakest bonds, and also on the presence or absence of oxygen in the solid and gas phases. Generally, thermal decomposition is the result of a combination of the effects of heat and oxygen. We can therefore distinguish between non-oxidizing thermal degradation and oxidizing thermal degradation [8].

Flame retardancy and inhibition of inflammation are very often spoken of as one and the same phenomena and are easily mixed up. Even though quite similar in end results there is some difference to how they prevent flame hazards. Flame inhibition refers to increasing the activation energy of inflammation reaction and therefore making the material burn on much higher temperature than

originally. Flame inhibition does not make inflammation reaction any different in its products and heat generated, it just delays the beginning temperature of the reaction, and once reaction starts it will continue spontaneously until it has finished or forcefully stopped. Therefore inhibition is not enough and it is always combined with another mechanism that will slow the reaction, stop it, adsorb the heat generated and/or isolate the burning material from the source of heat by making a protective barrier, which is collectively classified as flame retardancy. So flame retardancy includes all effects that will prevent a material from ignition.

Flame retardant systems are intended to inhibit or to stop the polymer combustion process previously described. In function of their nature, flame retardant systems can either act physically (by cooling, formation of a protective layer or fuel dilution) or chemically (reaction in the condensed or gas phase). They can interfere with the various processes involved in polymer combustion (heating, pyrolysis, ignition, propagation of thermal degradation). The main modes of action of flame retardant systems are reported and discussed below [9, 10].

Initially, halogenated epoxy materials were used, which had very good flame retardant and mechanical properties, but released very toxic halogen gases harmful to humans and the environment, which is why their use is prohibited [9, 10].

Halogenated reduced flammability materials have been replaced by materials containing additives based on phosphorus compounds that form polymerized phosphoric acid at elevated temperature and / or condensed structures that serve as an improved flame retardant and inhibition of inflammation barrier [9, 10].

Chemical modification of tannic acid yielded an epoxide with improved flame retardant properties, which were achieved by modifying tannic acid molecules with phosphorus oxychloride. Epoxidation was performed by adding glycidol to phosphorus oxychloride modified tannic acid molecules, or by modification of TA with epichlorohydrin (EPH).

The aim of this study is to investigate the thermal and mechanical properties of products obtained from TA by process of epoxidation, reduce BPA epoxy content or completely replace BPA epoxy in cured samples of obtained epoxide. Methods used for characterization are FTIR Analysis, UL94 V test, thermogravimetry analysis (TG) and tensile strength test.

2 Experimental session

2.1 Materials

Chemicals used in synthesis of modified TA: epichlorohydrin (EPH), sodium hydroxide (NaOH), Chloroform, N-methyl-2-pyrrolidone (NMP), phosphorus oxychloride (POCl_3), glycidol (G), N,N-Dimethylformamide (DMF), deionized water (MiliQ), magnesium sulphate (MgSO_4), calcium chloride (CaCl_2) were used as received and supplied from Sigma Aldrich, USA. Reference adhesive was selected to be BPA based epoxy (LG700 epoxy component and HG 700R curing agent) was supplied from GI-NI ltd. Belgrade, Serbia (epoxy value 0.62, epoxy equivalent weight is 160 g / mol, $T_g = 79.4^\circ\text{C}$).

2.2 Synthesis of glycidyl phosphate ester of TA (PGET)

In 250ml three-neck round-bottomed flask equipped with magnetic stirrer 6g of TA was added and dissolved in 40 to 50ml of 1:1 ratio mixture of chloroform and NMP at room temperature for 30 minutes. After 30 minutes had passed, temperature of the oil bath should be set to the value of 70°C , 250ml three-neck round-bottomed flask should be equipped with vacuum condenser, and if all of the tannic acid hasn't been dissolved 1 to 2ml of DMF should be added to the reaction mixture. Two vacuum dropping funnels should also be equipped to the reactor, one should contain 9.75g of POCl_3 diluted to 20ml with chloroform, and the other one should contain 9.42g of G diluted to 40ml with chloroform. As soon as reaction temperature reaches 70°C reaction should be initiated by addition of POCl_3 solution under constant stirring and low vacuum. POCl_3 should be added dropwise for duration of 1 minute, then reaction should be left to occur for 10 minutes after which G should be added also dropwise for duration of 2 minutes, reaction should be yet again be left to occur for 10 minutes. POCl_3 and G should be added the same way in ratio of 1 : 2 until all of the reactants are added, after which

temperature should be risen to the value of 80 or 85°C and vacuum should be gradually be increased, until all the chloroform had been removed. Reaction should be left to occur for at least 12 more hours after which maximum vacuum should be applied in order to remove NMP. When the reaction is finally over PGET should be left in air dryer for a few days or in vacuum desiccator with MgSO₄ and CaCl₂ drying mixture overnight. In order to purify the product following procedure is followed. To the solution was slowly added to 200 mL cold MiliQ water. Extraction of the product with toluene (3 times 70 mL) was followed by drying of organic extract with MgSO₄ overnight. After filtration toluene solution was transferred to flask equipped with short distillation column, Liebig condenser and recipient fitted well to sustain high vacuum (app. 1000 Pa). Concomitant increase of temperature (2 °C/min) was followed by pressure decrease in order to remove all volatile residual compounds in mixture. TA and segment of a modified TA (ETA and PGET) made for the purpose of this research will be presented on figure 1.

Figure 1. Tannic acid molecule and a segment of modified TA epoxy molecule

2.3 Synthesis of glycidyl ether of TA (ETA)

Epoxy functionalized tannic acid – ETA, or glycidyl ether of TA was obtained by reaction of TA with EPH at 80°C and at 1:1.5 wt. ratio of of TA to 20% NaOH solution in ethanol (or alternatively saturated water solution) [11]. EPH (15 g) was mixed with 10 mL of water at room temperature under magnetic stirring for 30 min. In meanwhile, the solution was placed in a 100 mL three-neck round-bottomed flask equipped with a reflux condenser, pressure equalizing dropping funnel and nitrogen inlet tube, and followed by addition of TA (3 g) and heating to 80 °C under magnetic stirring for 1h. Afterward, 22.5 ml 20% NaOH ethanol solution (or 4.5 g NaOH in 4.5 mL of water NaOH solution) was added dropwise using a dropping funnel while continuing to stir. The reaction was heated at 80 °C for 4 h to achieve completion of reaction. After that, the solution was left to cool down, and after was purified in the same way as PGET. ETA modified segment of TA, along with PGET is also shown on figure 1.

2.4 Curing of Eco-epoxy

The crosslinking of the components of the epoxy system was performed with or without the use of solvents in order to improve homogenization (ethanol or methanol). Mixtures of epoxide based on tannic acid (PGET) and commercial epoxy - LG 700 (component A) were made in different molar

ratios so that component A was replaced with 25%, 50% and 75 % and 100% of the synthesized epoxy component of PGET to give the materials TA-epoks 25%, TA-epoks50%, TA-epoks 75% and TA-epoks 100%, respectively. TA-epoks and component A in the mixture should have total weight of 2g and curing agent - HG 700R (component B) should weight 1g. The prepared reaction mixture is homogenized by a combined mixing and ultrasound treatment. In case of using solvents, it is necessary to heat the reaction mixture to 50 °C until the solvent evaporates, it was treated in an ultrasonic bath and under reduced pressure. The epoxy mixture is then poured into molds and crosslinked at 50 and 80 °C for 12 hours, 120 and 150 °C for 6 hours, and at 180 °C for 4 hours. Epoxy functionalized tannic acid (TA) – ETA was cured in analog way.

3 Characterization methods

3.1 FTIR Analysis

Analysis was done using a Nicolet™ iS™10 6700 spectrometer (Thermo Scientific) in the attenuated total reflectance (ATR) mode with a single bounce 45 °F Golden Gate ATR accessory with a diamond crystal, and DTGS detector. FTIR spectra were obtained at 4 cm⁻¹ resolution with ATR correction. The FTIR spectrometer was equipped with OMNIC software and recorded the spectra in the wavelength range from 2.5 μm to 20 μm (i.e., 4000 –500 cm⁻¹).

3.2 UL94 V test

This test is the subject of an international standard (IEC 60695-11-10) for small flames (50 W). It is a simple test of vertical combustion that classifies materials as V-0, V-1 or V-2. The corresponding experimental device is shown in Figure 2. And test parameters are shown on table 1.

Table 1. UL94 V test parameters

Fire Classification	Experiment
V - 0	t_1 and t_2 less than 10s for each specimen $t_1 + t_2$ less than 50s for the five specimens $t_1 + t_2$ less than 30s for each specimen No afterflame or afterglow up to the holding clamp No burning drops
V - 1	t_1 and t_2 less than 30s for each specimen $t_1 + t_2$ less than 250s for the five specimens $t_1 + t_2$ less than 60s for each specimen No afterflame or afterglow up to the holding clamp No burning drops
V - 2	t_1 and t_2 less than 10s for each specimen $t_1 + t_2$ less than 50s for the five specimens $t_1 + t_2$ less than 30s for each specimen No afterflame or afterglow up to the holding clamp Burning drops allowed

Figure 2. Experimental set-up for the UL94 V flammability test

3.3 Tensile strength test

Determination of tensile strength during axial (static) stretching of standard-sized specimens was done according to the ASTM D882 method on the AG-X plus Universal testing machine, Shimadzu. Test resin tubes, standard dimensions (80 x 10 x4 mm), All tests were performed at 25 °C with a shear rate of 0.5 mm/min.

3.4 Thermogravimetry

For thermogravimetry analysis (TG) SDT Q600 simulated TGA-DTA instrument (TA Instruments) coupled with mass spectrometer Hiden HPR-20/QIC was used. Samples were heated to 800 °C for thermal analysis.

4 Results and discussion

4.1 FTIR analysis

It can be noticed that at wave number of about 3260 cm^{-1} there was a significant decrease in -OH groups and an increase in band intensity at 2955 and 2820 cm^{-1} peaks represent C-H stretching of methylene groups due to the introduction of glycidol into the TA structure. Peaks at about 1190 and 750 cm^{-1} occur upon reaction with POCl_3 represent P=O stretch and P-aryl stretch, respectively. The peaks at about 875 and 825 cm^{-1} represent the vibrations of the epoxy group, while the peak observed at 875 to 1150 cm^{-1} represents the conjugate spectrum caused by the shift due to the mutual influence of the phosphine group bound to the epoxy ring and their mutual interactions. This is the most significant indicator of successfully synthesized PGET. ETA doesn't show conjugate spectrum as PGET does show increase of -OH groups at about 3300 cm^{-1} (which may represent oxirane ring opening) and stretching of C-O-C ethers at about 1050 cm^{-1} wavenumbers [12]. Another characteristic change on FTIR during epoxidation is at a wave number of about 915 cm^{-1} which belongs to the oxirane group and represents the C-O vibration deformation, and the group belonging to the C-O-C stretch of the oxirane group - epoxy ring appears at a wave number of about 830 cm^{-1} [12]. FTIR spectrum that compares TA with PGET and ETA epoxy is shown on figure 3.

Figure 3. FTIR spectrum of TA, PGET and ETA comparison.

4.2 Tensile strength test

The results of determining the tensile properties of the obtained samples are given in Figure 4. Analysis of the tensile test results shows an increase in the toughness of the material with an increase in the amount of PGET, a decrease in the modulus of elasticity, losses on the tensile strength and an increase in relative deformation up to 4 times.

Figure 4. Mechanical properties of TA-epoxy materials obtained by replacement of epoxy component A by modified TA (PGET)

4.3 UL94 V test

Results of UL94 V test are shown in table 2. Each sample burns superficially while the interior remains undamaged, there is no burning drip and there are no burning burns in the receiving place. Sample of 25% ETA didn't show significant flame retardant effects, but it burned for about 3 minutes longer period of time than 0% samples.

Table 2. UL94 V test results

Test results category, UL94 V	Tested specimen
V - 0	Epoxy+100% PGET
V - 1	Epoxy+50% and 75% PGET / 75% and 100% ETA
V - 2	Epoxy+25% PGET / 50% ETA

4.4 Thermogravimetry

Thermogravimetry showed that the initial temperature of thermal degradation is higher for the TA-epoks 25% sample than for the Komerc-epoks sample. The residue after heat treatment obtained for the TA-epoks 25% sample can be attributed to obtaining a more stable crosslinked sample structure at high temperatures, due to the presence of PGET. The results of thermogravimetric analysis show that improved thermal stability of epoxy material was achieved with the addition of TA component, which is presented on figure 5. Similar results were obtained for all other samples, so for better illustration only commercial bisphenol A epoxy and TA epoxy of PGET 25% sample were used. With same amounts of PGET and ETA results were quite similar, which indicates that solely TA contributes to residue/char levels.

Figure 5. Thermogravimetric diagram for commercial epoxy and for 25% PGET epoxy.

5 Conclusions

Tannic acid was modified in process of epoxidation with with epichlorohydrin / POCl₃ and glycidol in order to make ETA / PGET respectively. ETA and PGET were used as a replacement of the epoxy resin component (A) – bisphenol A based epoxy in a ratio 25-100% as a reactive diluent to obtain test samples for thermal and mechanical experiments. The tensile test results indicate an increase in toughness with increase in the amount of PGET at 25% and a decrease in toughness with higher PGET amounts, a decrease in the modulus of elasticity, and an increase in relative deformation. Results of UL94 V test show an increase of flame retardant properties of PGET and ETA. PGET had shown much better thermal properties than ETA. Thermogravimetric analysis indicates that there is a slight improvement in the thermal stability of the material with an increase in PGET in the product, products with higher amounts of PGET would start degrading at higher temperatures and have more solid residue. In contrast to the above properties, a significant improvement was obtained in terms of reducing flammability: (PGET) material TA-epoks 100% has no practical significance due to poor mechanical properties. Optimal mechanical and thermal properties show TA-epoks 25% and TA-epoks 50%.

6 References

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