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MECHANICAL, THERMOOXIDATIVE AND BIODEGRADABLE PROPERTIES OF COMPOSITES FROM EPOXYURETHANES AND CHEMICALLY MODIFIED HEMP WOODY CORE

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Natural fibre reinforced polymer composites nowadays are considered to be attractive cheap, safe and eco-friendly materials. The main problem of such composites related to the hydrophilicity of plant fibres may be successfully solved by chemical modification of their surface. However, some characteristics of the materials may be suppressed after this procedure. Therefore, the aim of the research is to find out the impact of chemical modification of filler on thermooxidative stability, tensile and flexural strength, as well as on biodegradability of polymer composites. The novelty of this work is in the examining new materials on the basis of Si-containing epoxyurethanes and chemically treated hemp woody core (HWC). Woody core that is the side product of hemp industry requiring its apropriate utilization was exposed to mercerization with sodium hydroxide solution and to further functionalization with epoxidized soybean oil (ESO) or 3-aminopropyltriethoxysilane (APS). Raw and surface treated HWC was used as reinforcement for two types of organic-inorganic epoxyurethane matrices made from sodium silicate, polyurethane prepolymer based on polyisocyanate and castor oil, and either diglycidyl ether of bisphenol-A (DGEBA) or ESO as epoxy component.

Functionalization of HWC led to better mechanical properties of composites. Compared to the corresponding materials including untreated filler, maximum increase in flexural strength (26 %) was observed for the samples with ESO-containing epoxyurethane and silanized HWC, while maximum increase in tensile strength (53 %) was revealed for the ones with DGEBA-containing epoxyurethane and oil treated HWC. Thermooxidative stability was also higher for composites reinforced with functionalized HWC. The specimens with APS-treated HWC performed the best at thermal decomposition. The values of their $T_{50\%}$ were up to 68 °C more than those for composites with unmodified filler. At the same time, the samples based on APS- or ESO-treated HWC were the most resistant to biodegradation, which may be concluded from their smallest weight loss during soil burial test.

Keywords: *hemp woody core, chemical modification of filler, mercerization, silane treatment, epoxidized soybean oil treatment, epoxyurethanes, natural fiber reinforced polymer composites, interfacial adhesion, soil burial test, biodegradation*

INTRODUCTION

Current concern on ecological issues raised in regaining of scientific attention towards plant fibers reinforced polymer composites [1–3]. Except for being renewable, energy efficient and neutral or even positive with respect to carbon dioxide emissions, such natural fibers are inexpensive, available, have high specific strength and no potential health hazards as their synthetic counterparts do [4–7]. Among the most essential advantages of lignocellulosic fillers, some researchers [8, 9] also mention biodegradability, though the others [10] refer it as their downside. In this respect it should be noted that triggered biodegradability is demanded here. This term means that materials are stable during designated service life and prone to microbial attacks only

under the conditions of soil burial or composting [11]. Meanwhile, such characteristics as poor interfacial and mechanical strength along with low thermal and fire resistance are generally accepted as drawbacks of natural fiber based polymer composites [2, 10–12].

These limitations of materials may restrict the possibility of their practical application [2, 12], so in order to overcome them, the methods of fiber chemical modification are widely used [1, 6–8]. Mercerization involving exposure of fillers to alkaline solution and functionalization of their surface with organic compounds bearing functional groups are the examples of approaches purposed to improve mechanical properties of natural fibre reinforced composites by strengthening the interphase and to ensure an optimum stress

transfer [13]. Typically, the composites with modified plant fillers exhibit much better mechanical characteristics [4, 5, 14], but sometimes they may remain unchanged as in epoxy composites with silane treated cellulose fibers [15] or even deteriorated as reported by [16] for tensile strength of alkali and silane treated flax mats. Notwithstanding that application of triglycerides on the surface of fibers is not so widespread as the one of silanes, opposite effects of it also may be found. Particularly, exposure of pre-mercerised hemp to soybean and corn oils resulted in enhanced mechanical properties of polypropylene composites on its basis [6], whereas polyurethane foams reinforced with sunflower or tung oil impregnated hemp shives performed worse than those with non-treated filler [17].

Thermal stability was also revealed to depend differently on fiber chemical modification. For instance, application of two silane coupling agents had no impact on the thermal decomposition of hemp fibers [18]. At the same time, under the influence of silane treatment thermal stability of *C. indica* fiber improved significantly [19]. Altogether, given examples testify that some universal conclusion showing the relation between fiber treatments and the properties of resulting reinforced composites cannot be drawn. The behavior of material is at least determined by the combination of matrix, filler and a type of surface modification. So, in each unique case it is important to investigate the characteristics of polymer composites reinforced with chemically modified fibers.

Within a huge variety of cellulosic fillers hemp woody core (HWC) also known as hurds or shives was selected for the research presented. It is a chopped inner part of the hemp plant stem (60–80 % of its mass) that is a by-product of hemp industry having almost no proper utilization [17, 20]. HWC is not frequently used as reinforcement in polymer composites but owing to its good stability, viscoelastic and mechanical characteristics may be considered as very promising in this field [17]. In given study HWC was subjected to mercerization, oil treatment with epoxidized soybean oil (ESO) or aminosilane treatment with 3-aminopropyltriethoxysilane (APS).

To make completely renewable and biodegradable biocomposites the tendency to apply natural polymers is becoming popular. However, in this case it is challenging to meet the necessary requirements for materials and to maintain a balance between economics and ecology. Therefore,

composites derived from plant fibers and synthetic thermoplastics or thermosets are regarded as suitable alternatives [1, 3]. Among polymer matrices polyurethanes providing *in situ* formation of covalent bonds between isocyanate groups of matrices and hydroxyl groups of lignocellulosic fillers [21, 22] were chosen. Namely, two types of Si-containing epoxyurethanes including sodium silicate, polyurethane prepolymer based on polyisocyanate and castor oil, and either synthetic or plant-derived epoxy constituent were synthesized.

The novelty of the work lies in filling such matrices with chemically modified HWC and in evaluating the dependence of the properties of obtained composites upon a type of HWC treatment used.

The objective of this study is to investigate thermooxidative resistance, tensile and flexural strength, as well as biodegradability of fabricated composites under soil burial conditions.

EXPERIMENTAL

Materials. HWC used as filler was obtained from non-narcotic types of hemp and supplied by Institute of Bast Crops of the National Academy of Agrarian Sciences of Ukraine. Sodium hydroxide (NaOH) applied for mercerization was purchased from Chempol, Czech Republic. The treatment agents APS and ESO were obtained from Sigma-Aldrich, USA. The chemical structures of APS and main component of ESO (epoxidized linolein, ~ 51 %) are depicted in Fig. 1.

The chemicals listed below were used for matrix synthesis. Polyisocyanate (PIC) commercialized under the name of "Lupranat M 20S" IsoPMDI 92140 that is a mixture of isomers of diphenylmethane diisocyanate and oligomeric compounds (the content of NCO groups = 30.0 %, density = 1.2446 g/cm^3) was purchased from BASF Polyurethanes GmbH, Germany. Diglycidyl ether of bisphenol-A (DGEBA) commercialized under the name of DER-331 (M = 390 g/mol, the content of epoxy groups = 19.8 %, the content of OH groups = 1.9 %) was obtained from Dow Chemicals, Germany. Castor oil (CO, *Oleum Ricini*, density = 0.955 g/cm^3, hydroxyl number = 150), was purchased from Phitopharm, Ukraine. ESO (epoxy equivalent = 250 g/mol, epoxy group content = 6.1 %) was obtained from Sigma-Aldrich, USA. Aqueous solution of sodium silicate (SS) (silicate module = 2.9–3.0, the content of free water = 56.0 %) was supplied by Dniproskloservis, Ukraine.
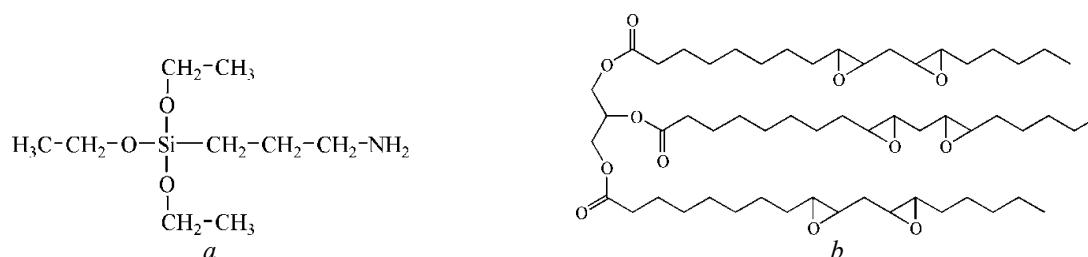
Fig. 1. Chemical structure of treatment agents: APS (*a*) and major component of ESO (*b*)

Modification of HWC. Before modification HWC was washed with water to remove impurities, dried at 80 °C for 4 hours to constant weight and then chopped. The particles of the desired size (between 0.05 and 5.0 mm) were selected by fractionation through a sieve (model 029). For mercerization HWC was immersed in 5 wt. % NaOH solution (assumed to be optimal in [7, 23]) at 20±2 °C for 24 hours. After that the particles were rinsed with acidified water to neutralize any remnants of alkali and washed with distilled water. Mercerized HWC were dried at 80 °C for 8 hours. This alkali treatment was used solely or as pre-treatment for further functionalization of HWC. Oil treatment was performed by immersing pre-mercerized HWC into 3 wt. % acetone solution of ESO (assumed to be optimal from preliminary experiments), followed by mixing at 20±2 °C for 3 hours and drying at 80 °C to constant weight. Silane treatment was done by immersing pre-mercerized HWC into 5 wt. % APS solution (shown to be optimal in [24, 25]) at 20±2 °C for 24 h. Afterwards, HWC particles were washed with distilled water and dried at 80 °C to constant weight. APS solution was prepared in 50/50 w/w

ethanol/water mixture by stirring it during 1 hour to provide a complete silane hydrolysis.

Polymer matrix synthesis. Two types of organic-inorganic Si-containing epoxyurethane (EU) matrices were obtained. SS serves as an inorganic component of given polymers providing their UV-, fire- and thermal stability. Urethane component was synthesized through the stage of polyurethane prepolymer based on PIC and CO as a polyol in a mass ratio of 80/20. The reaction was conducted under stirring at 60±2 °C until theore-tically calculated amount of isocyanate groups was reached. The matrices differ in the nature of epoxy component used. For the first epoxyurethane (EU-D) it is synthetic epoxy resin DGEBA, while for the second one (EU-E) it is plant-derived ESO. Epoxy component (either DGEBA or ESO) was introduced into the polyurethane prepolymer and stirred at 900 rpm for 3 min at 20±2 °C. Then SS was added into the mixture under 3 min stirring at 900–1000 rpm at 20±2 °C. The total weight ratio between components and the codes of synthesized polymer matrices are given in the Table 1.

Table 1. Composition of EU matrices

Code	Weight parts		
	Inorganic component	Urethane component	Epoxy component
EU-D	20 (SS)	80 (PIC/CO=80/20)	20 (DGEBA)
EU-E	20 (SS)	80 (PIC/CO=80/20)	20 (ESO)

Composites fabrication. To obtain unfilled polymers the reactive mixtures were poured into Teflon molds and cured at 140 °C. To form composites unmodified, mercerized or functionalized HWC (60 wt. %) was soaked into liquid epoxyurethane mixture under stirring. As it was studied before [26], such a high filler content

ensure the best mechanical properties of composites. The samples were then fabricated in the molds at 140 °C and under a 10 MPa pressure by a hot press machine. The composites codes depending on the matrix and type of chemical modification the filler was exposed to are given in Table 2.

Mechanical testing. Mechanical characteristics of composites were determined for molded samples with a size of 150×20×5 mm according to State standard 11262-80 for tensile strength and according to ASTM D790-17 for flexural strength. The tests were carried out for five different samples, and the average values are represented below.

Thermogravimetric analysis (TGA). Thermooxidative degradation of composites was investigated using a thermogravimetric analyzer TGA Q 50 (TA Instruments). The specimens were heated from 20 to 600 °C under air atmosphere at a rate of 20 °C/min. For major stages of thermooxidative destruction activation energy was computed by means of Broido equation [27]:

$$E_{act} = R \times tan\,\varphi,$$

where R is a gas constant equals to 8.314 J/mol·K, φ is a slope of a straight line of $ln(ln1/y)$ dependence versus $1/T \cdot 10^{-3}$, ($y=w_t/w_0$, w_t is weight at any time within considered decomposition stage, w_0 is initial weight, and T is temperature, K).

Table 2. Codes and composition of the composites

Epoxyurethane matrix	HWC surface modification	Code for HWC	Composite code
EU-D (DGEBA as an epoxy component)	Untreated HWC	UH	UH/EU-D
	Mercerization of HWC	MH	MH/EU-D
	Treatment of premercerized HWC with ESO	OH	OH/EU-D
	Silanization of premercerized HWC	SH	SH/EU-D
EU-E (ESO as an epoxy component)	Untreated HWC	UH	UH/EU-E
	Mercerzation of HWC	MH	MH/EU-E
	Treatment of premercerized HWC with ESO	OH	OH/EU-E
	Silanization of premercerized HWC	SH	SH/EU-E

Soil burial test. Previously dried and weighted composites along with unfilled epoxyurethane matrices were buried in soil (pH = 6). After 1 year, the samples were removed, washed with distilled water, and dried to a constant mass. Mass was measured using a precise five-digit balance Kern ABT 120-DM.

RESULTS AND DISCUSSION

Mechanical properties. The results of flexural and tensile strength measurements for the composites based on HWC with different types of chemical modification are displayed in Fig. 2.
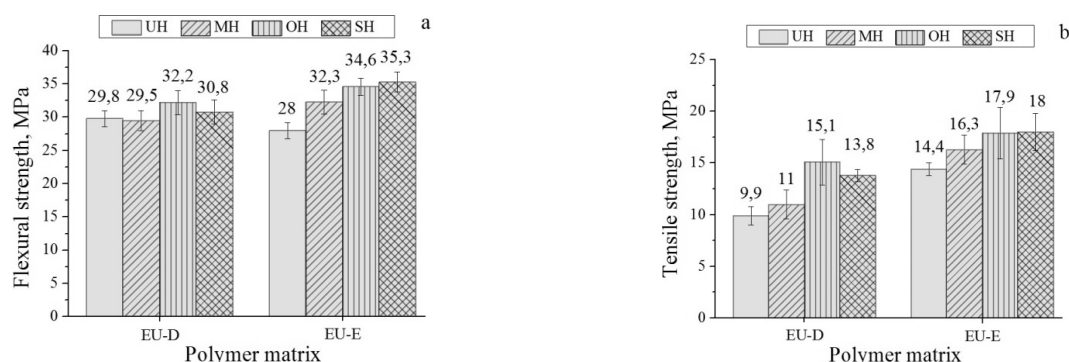

Fig 2. Mechanical properties of composites: *a* – flexural and *b* – tensile strength

From Fig. 2 it can be seen that all polymers reinforced with functionalized HWC exhibit higher values of flexural and tensile strength than the ones reinforced with unfunctionalized HWC. Alkali treatment of HWC is found to be not so effective for strengthening composites as

treatment with coupling agents. The slight increase in mechanical characteristics after mercerization was also declared by other researchers. For instance, tensile strength was 8 % higher for polyethylene composites filled with hemp fibers [28] and 9 % higher for poly(lactic acid) composites filled with short sisal fiber [8] respective to the ones with untreated reinforcements. Similar results are commonly explained by better wettability of filler that is a result of increased contact area after mercerization [28].

Sometimes alkali treatment leads to considerable augment in mechanical characteristics, like in [14], where epoxy composites filled with bamboo cellulose fibers exposed to NaOH reached 34 and 31 % improvement in tensile strength and elongation at break, respectively. The same authors [14] report about 71 % enhancement in tensile strength and 53 % increase in elongation at break after application of silane coupling agent. In the research presented, as compared to the composites with untreated HWC, the biggest relative increase in flexural strength is observed for the sample SH/EU-E (26 %), while the one in tensile strength is revealed for OH/EU-D (53 %).

These achievements confirm the presence of intensive matrix/filler interaction in case of functionalized HWC that is the result of several factors. Firstly, treatment with organic compounds blocks surface hydroxyl groups and lessens hydrophilicity of HWC thus favoring its compatibility with polymer matrices and wetting by them. Secondly, applied modifiers provide formation of additional chemical links between filler and polymer. Within ESO treatment hydrogen bonding is possible via hydroxyl groups of HWC and ester or epoxy groups of the modifier. Other epoxy rings of ESO can further react with urethane groups of polymer matrix. During APS treatment hydrogen bonding emerges between its silanol or amino groups and lignocellulosic OH groups. Besides, APS grafting onto the surface of the filler gives rise to Si–O–C covalent bonds. Afterwards, free amino groups of aminosilane can react with epoxy and isocyanate groups of matrix in the process of composite formation. All this contributes to strong matrix/filler interfacial adhesion and, consequently, improved mechanical properties of composites.

It also may be noticed that the values of both tensile and flexural strength are in general higher for composites based on ESO-containing matrices. Similar results were reported in [29]

and [30], where mechanical properties were studied as a function of DGEBA/ESO ratio in unfilled and filled materials, respectively. In these works the addition of small quantities of ESO enhanced tensile strength, relative elongation [29, 30] and impact resistance [30] of the samples as well as lowered their glass transition temperature and crosslinking density of polymer networks [29]. Being more flexible component than DGEBA, ESO provides higher molecular mobility and elastification of the material thus making it more resistant to applied stress.

Thermogravimetric analysis. The integral curves of weight loss (DTA) and the derivative curves of weight loss (DTG) for composites and neat materials are presented in Figs. 3 and 4 for matrices based on DGEBA and ESO, respectively.

From the general view of decomposition profiles (Figs. 3 *a* and 4 *a*) it may be concluded that HWC displays the fastest weight loss, while unfilled epoxyurethanes – the slowest one, especially at the initial stage. It is an anticipated result, since thermooxidative stability of natural fiber reinforced composites based on epoxies and urethanes is known to be limited by lignocellulosic fillers [2] bearing C–O and O-H groups sensitive to oxidation [31]. DTG curves (Figs. 3 *b* and 4 *b*) and parameters found from TGA data (Table 3) can elucidate more information on thermal resistance of the specimens. Some researchers of fiber reinforced composites [32] consider first 5 wt. % losses as inappropriate for evaluation of thermal degradation due to significant content of moisture in the materials. Hence, the results from 20 [32] or 30 wt. % loss [19] are proposed to analyze the actual degradation. Herein, temperatures of 20 ($T_{20\%}$) and 50 wt. % ($T_{50\%}$) loss are selected as standards for comparison of thermooxidative properties of the samples.

From comparison of thermal stability of different epoxyurethanes it is apparent that the one based on DGEBA is more resistant. Thus, owing to higher cross-linking density and the presence of considerable amount of aromatic structures EU-D exhibits larger values of both $T_{20\%}$ and $T_{50\%}$, temperature at maximum decomposition rate (T_{max}) of the first stage, activation energy and char residue than EU-E. Equally, both matrices undergo two-step decomposition processes. The first stage occurring at temperature range between 250 and 350 °C includes the breakdown of urethane and urea bonds, cyclic structures, epoxy networks and ester groups of ESO [33, 34]. The second stage from 400 to

500–550 °C is related to further oxidative decomposition of the carbon skeleton of the matrices.

Data obtained for HWC show that its initial peak corresponding to 4 % weight loss appears at 55 °C. Likewise for other plant fillers showing weight loss below 100 °C [16, 19, 35], this peak can be ascribed to removal of inherent moisture. The second broad peak at 250–385 °C involves decomposition of hemicelluloses, pectin, cellulose and lignin [18, 35]. Small peak centered at 448 °C is attributed to further thermal degradation of lignin [6, 20].
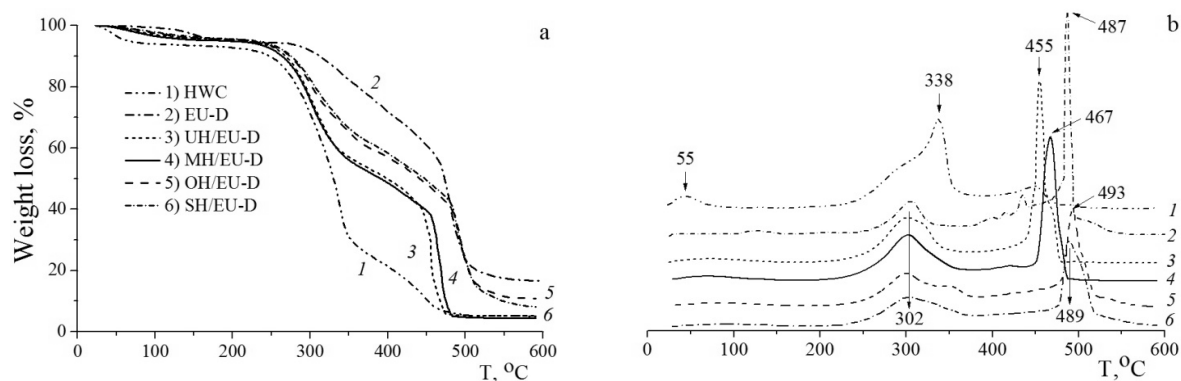
Fig. 3. DTA (*a*) and DTG (*b*) curves of the composites based on EU-D matrix as well as of neat substances
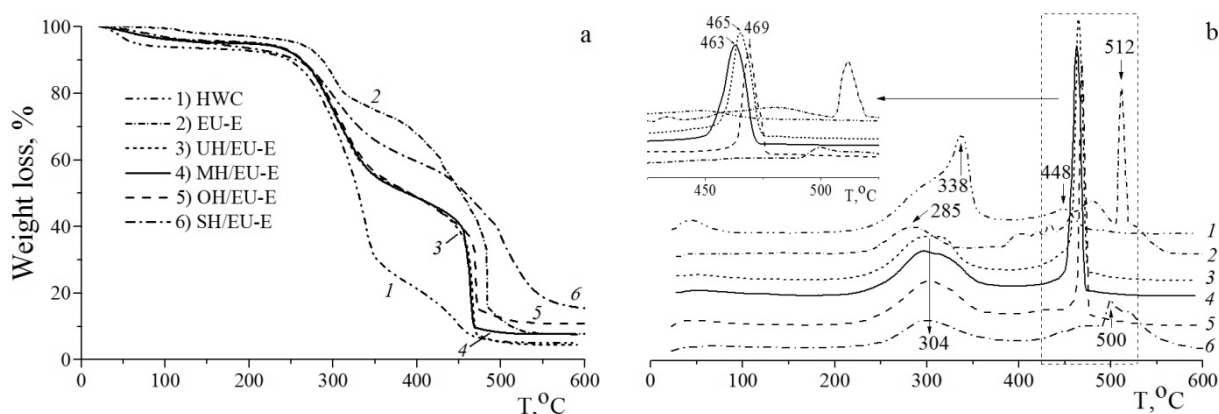
Fig. 4. DTA (*a*) and DTG (*b*) curves of the composites based on EU-E matrix as well as of neat substances

Table 3. TGA parameters of the samples

Samples	$T_{20\%}$, °C	$T_{50\%}$, °C	T_{max}, °C		Weight loss at T_{max}, %		E_{act}, kJ/mol		Char residue,%
			Stage I	Stage II	Stage I	Stage II	Stage I	Stage II	
HWC	283	330	55	338	4.0	58.6	104.34	148.22	5.1
EU-D	361	473	304	487	8.7	66.5	101.33	308.57	16.6
UH/EU-D	293	399	302	455	24.6	70.6	99.77	238.04	5.1
MH/EU-D	292	391	302	467	25.4	77.1	103.46	275.37	4.5
OH/EU-D	302	442	299	493	18.6	69.2	112.07	332.31	10.9
SH/EU-D	306	447	303	489	18.7	65.5	104.69	304.77	8.2
EU-E	314	453	285	512	9.9	89.8	118.63	215.74	7.9
UH/EU-E	290	391	308	465	29.2	75.7	80.04	222.62	4.5
MH/EU-E	290	389	296	463	22.8	75.6	84.06	310.90	7.7
OH/EU-E	293	391	304	469	25.7	67.5	89.95	317.51	10.9
SH/EU-E	298	459	298	500	19.9	63.0	96.31	178.32	15.5

Sometimes composites are also characterized by low-temperature loss of water that may cause porosity and deterioration of materials properties [2]. But on DTG curves of the fabricated composites such peaks are absent that is a consequence of HWC protection by polymers as well as of consumption of OH groups by the reaction with NCO groups of matrices. Decomposition processes of all the composites are characterized by two stages with the maxima at around 300 and 455–500 °C, respectively.

Though many authors report that thermal stability is better for alkali treated fibers than for untreated ones [19, 20, 35], in the work presented the difference in most thermogravimetric parameters is unnoticeable. Only the values of activation energy are higher for mercerized-containing composites. At the same time, in literature data it is described that functionalization may both improve [19, 35] or does not affect thermal decomposition [18]. However, in this case composites reinforced with ESO and APS-treated HWC are obviously more thermally stable. Particularly, the values of $T_{20\%}$ and $T_{50\%}$ are mostly higher for the samples with functionalized filler. Unlike oil treatment, which effect is less pronounced for composites based on ESO-containing epoxyurethane, application of silane has a considerable impact on thermal properties irrespectively of the type of matrix. Thus, compared with specimens including raw HWC the values of $T_{20\%}$ were increased by 8–9 °C and the values of $T_{50\%}$ were increased by 48 and 68 °C in case of SH/EU-D and SH/EU-E, respectively. The presence of Si-O-C bonds with filler seems to contribute to thermal resistance significantly. The percentages of carbonaceous residue for the samples filled with ESO or APS-treated HWC are notably larger than the ones for composites with raw or mercerized filler. The same is true for activation energies of the first decomposition stage that can be explained by higher bond energies after chemical treatment [35].

Overall, composites with functionalized HWC display higher thermooxidation resistance as respect to their corresponding counterparts, which is in a good agreement with the results of mechanical properties investigation showing the best performance for the same composites.

Biodegradability. The biodegradability of composites is generally determined by their weight loss within soil burial test [9]. Percentage of weight reduced after testing is presented in the Table 4.

Table 4. Weight loss after soil burial exposure, %

Filler	Matrix	
	EU-D	EU-E
None	6.4	3.7
UH	26.5	20.4
MH	31.5	22.8
OH	13.1	13.5
SH	7.1	19.3

As expected, the weight loss of unfilled matrices is the smallest. It has been reported [36] that the urethane bond is predisposed to impact of microorganisms. The mechanism of polyurethane biodegradation implies the hydrolysis of ester group. It is noteworthy that ESO-containing neat epoxyurethane exhibits less weight loss than its counterpart including synthetic epoxy resin. Such a fact may be due to highly hydrophobic nature of ESO as triglyceride derivative.

Naturally, the presence of hydrophilic plant reinforcement contributes to biodegradation significantly (Table 4). The same is, particularly, observed in [37] and [38], where the addition of kenaf or peach palm particles, respectively, into polymer matrices made composites degrade faster than the neat polymers. It is believed to be associated with the formation of cavities from introduction of natural fillers [37] or, more likely, with the higher moisture absorption [38] favoring the adhesion of microorganisms [10, 37].

Interesting enough, the composites filled with mercerized HWC degrade more as compared to the ones filled with unmodified one. Usually, the researches declare opposite observations, as in [8] and [39], where the weight loss after soil burial of unmodified sisal fiber reinforced composites is higher than one of composites with mercerized fibers. The authors claim it to be attributed to better matrix/filler adhesion in the case of hydrophobized fiber surface after alkaline treatment. Indeed, the dissolution of hemicelluloses reduces both moisture adsorption and biodegradation [10], but other processes that occur during mercerization also should be considered. For instance, more pronounced biodegradation of composites reinforced with mercerized HWC here may be explained by partial removal of such non-cellulosic cementing impurities as lignin, wax and pectin [11] and

availability of hydrophilic hydroxyl groups on the surface.

At the same time, the results showing slower degradation of the samples filled with functionalized HWC are in good agreement with the other scientific reports. Thus, composites reinforced with silane treated kenaf [38], sisal and oil palm fibers [39] are shown to be more durable to biodegradation owing to enhanced interfacial adhesion. Within given research strengthen matrix/filler interphase endowes composites with higher resistance to the effect of microorganisms.

CONCLUSIONS

Mechanical, thermooxidative and biodegradable properties of polymer composites reinforced with hemp woody core were investigated. Epoxyurethanes differing in the nature of epoxy component (either DGEBA or ESO) were used as matrices. Unmodified, mercerized and functionalized (with ESO or APS) HWC was applied as plant filler. Mechanical characteristics were found to be higher for composites based on functionalized HWC with the improvement in flexural strength up to 26 % for SH/EU-E and the one in tensile strength up to 53 % for OH/EU-D in regard to

composites based on raw filler. Alkali treatment was found to be no so effective for strengthening the samples. Comparison of the effect of polymer matrix revealed that in general mechanical performance was better for composites with epoxyurethanes containing flexible ESO fragments. However, such a chemical structure resulted in slightly poorer thermal characteristics of composites on the basis of plant-originated epoxy component. TGA data also showed that the samples with functionalized HWC were more resistant to thermooxidative decomposition than the ones with untreated or alkali treated filler. Modification with APS was particularly efficient for enhancing thermal properties of composites. Thus, 8–9 °C augment in the values of $T_{20\%}$ as well as 48 and 68 °C augment in the values of $T_{50\%}$ were noticed for SH/EU-D and SH/EU-E, respectively. The results of soil burial test have shown that the introduction of natural filler to both epoxyurethane polymer matrices accelerates their biodegradation. The samples with alkali treated HWC were the most prone to influence of microbiota, whereas the ones with oil or silane treated HWC were the most stable to it.

Механічні, термоокисні та біорозкладні властивості композитів з епоксиуретанів і хімічно модифікованої конопляної костриці

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Підсилені природними волокнами полімерні композити нині розглядають як привабливі дешеві, безпечні й екологічні матеріали. Головну проблему таких композитів, пов'язану з гідрофільністю рослинних волокон, можна успішно вирішити хімічним модифікуванням їхньої поверхні. Однак, після цього деякі характеристики матеріалів можуть погіршуватися. Зважаючи на це, метою дослідження є з'ясувати вплив хімічного модифікування наповнювача на термоокисну стабільність полімерних композитів, міцність на згин і на розрив, а також на здатність до біорозкладання. Новизною даної роботи є дослідження нових матеріалів на основі Si-вмісних епоксиуретанів і хімічно обробленої конопляної костриці (КК). Кострицю, яка є побічним продуктом конопляної промисловості з необхідністю раціональної утилізації, мерсеризували розчином натрій гідроксиду, а надалі функціоналізували епоксидованою соєвою олією (ЕСО) або 3-амінопропілтриетоксисиланом (АПС). Нативну та поверхнево оброблену КК використовували як підсилювач для двох типів органо-неорганічних епоксиуретанових матриць, виготовлених з натрій силікату, поліуретанового форполімера на основі поліізоціанату та рицинової олії, та дигліцидилового етеру бісфенолу-А (ДГЕБА) або ЕСО як епоксидної складової.

Функціоналізація КК зумовила поліпшення механічних властивостей композитів. Порівняно з відповідними матеріалами, які містять необроблений наповнювач, найбільше зростання міцності на згин

(26 %) спостерігали для зразків з ECO-вмісним епоксиуретаном і силанізованою КК, тоді як найбільше зростання міцності на розрив (53 %) виявили для зразків з ДГЕБА-вмісним епоксиуретаном і КК, обробленою олією. Термоокисна стабільність також була вищою для композитів, підсилених функціоналізованою КК. При термічному розкладанні найкраще зарекомендували себе зразки з КК, обробленою АПС. Їхні значення $T_{50\%}$ були до 68 °C вищими, ніж у композитів з немодифікованим наповнювачем. Водночас, зразки на основі КК, обробленої АПС або ECO, були найбільш стійкими до біорозкладання, про що можна зробити висновок з їхньої найменшої втрати маси під час тестування при закопуванні в ґрунт.

Ключові слова: коноплина костриця, хімічна модифікація наповнювача, мерсеризація, обробка силаном, обробка епоксидованою соєвою олією, епоксиуретани, підсилені природними волокнами полімерні композити, міжфазна адгезія, тестування при закопуванні в ґрунт, біорозкладання

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