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T.F. Samoilenko, L.M. Yashchenko, N.V. Yarova, O.O. Brovko

PROPERTIES OF COMPOSITES BASED ON CHEMICALLY TREATED HEMP WOODY CORE AND EPOXYURETHANE CONTAINING EPOXIDIZED SOYBEAN OIL

Institute of Macromolecular Chemistry of National Academy of Sciences of Ukraine
48 Kharkivske shose, Kyiv, 02155, Ukraine, E-mail: s_t_f@ukr.net

In last two decades the intensive growth in the number of publications devoted to plant fibers as reinforcements for polymer matrices is observed. Considering ecological issues natural fibers are recognized as an appealing alternative to synthetic ones. Unlike hemp fiber, which is frequently used for given needs, its by-product named hemp woody core (HWC) has not yet gained much scientific attention in this sphere. Nevertheless, owing to the set of its unique properties HWC is also may be a promising filler. Application of HWC in composites would additionally contribute to its proper utilization. However, among the distinctions of lignocellulosic reinforcements is their hydrophilicity that requires to be reduced to ensure strong interface interaction with the matrix and good durability of the resulting composites. Herein, mercerization (alkali treatment) and/or subsequent modification of HWC with epoxidized soybean oil (ESO) or 3-aminopropyltriethoxysilane (APS) was used for this purpose. Si-containing epoxyurethane polymer matrix was synthesized from sodium silicate, polyisocyanate and ESO as epoxy component. Four series of molded samples with high plant filler content (60 wt. %) were elaborated. The results of contact angle and water uptake measurements showed that all applied types of treatment led to hydrophobization of the surface. Thus, the values of contact angles of composites with modified HWC exceeded 90 °, and their surface energy was lower than the one of neat samples. Regardless of quite high polarity of composites containing silanized HWC due the presence of amino and silanol groups, the formation of covalent bonds between filler and APS coupling agent turned out to be crucial for such characteristics as water resistance and mechanical performance. Particularly, equlibrium moisture content decreased by 31 % compared to that of the samples with pristine HWC, whereas tensile and flexural strength improved by 19 and 65 %, respectively. The highest microbial stability of the specimens with silane treated filler estimated within soil burial test is another evidence of enhanced interfacial adhesion in this case.

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

INTRODUCTION

Natural plant fibers like hemp, flax, jute, sisal and kenaf continue to gain considerable scientific interest as promising reinforcement for polymer matrices. It is attributed to their renewable nature, high specific strength, light weight, low cost, thermal and acoustic insulation, reduced energy consumption and biodegradability [1–3]. Although a set of these properties makes lignocellulosic fillers attractive alternative to synthetic glass and carbon fibers [1, 2], still they cannot substitute them in applications, where high mechanical performance and water resistance are required [3, 4]. Thus, the main restrictions of plant fibers are linked to their hydrophilicity and low interfacial adhesion to polymer matrices [5, 6]. Such approaches as physical, chemical and biological modification are practiced to moderate them [5, 7]. In the research given chemical treatment with alkali, also called mercerization, or/and further functionalization with either epoxidized soybean oil (ESO) or 3-aminopropyltriethoxysilane (APS) was used for hemp woody core (HWC) filler.

HWC (hurds or shives) is a chopped interior part of the hemp stem that comprises 60–80 % of the whole plant mass. The most amount of it, as of a side product of hemp industry, simply ends up in landfills [8]. However, HWC is believed to serve a good natural filler for composite fabrication [9]. There were already some studies in this field, particularly, HWC was used to reinforce MgO-cement for lightweight construction composites [10], cement, clay and starch for energy efficient building materials [11], polypropylene for composites with enhanced panel properties [12], polyvinyl alcohol for UV-shielding composites [13], polyurethane foams for materials with improved thermal stability and flame retardancy [9]. In majority of the studies mentioned HWC was exposed to different types of chemical modification. Mercerization of hemp hurds resulted in better water resistance although lower strength and thermal conductivity of composites [10]. Impregnation of hemp shives with sunflower or tung oil led to better thermal characteristics and water resistance but deteriorated mechanical performance [9]. The addition of a silane coupling agent contributed to suppressed water absorption and thickness swelling [12].

Combination of lignocellulosic fibers with urethane or epoxyurethane polymer matrices is especially efficient since it ensures *in situ* formation of covalent bonds via isocyanate groups of matrices and hydroxyl groups of fillers [14, 15]. In our previous works chemically treated HWC was used for reinforcing of epoxyurethane matrices obtained from prepolymers containing castor oil as a polyol constituent [16, 17]. Herein, Si-containing epoxyurethane on the basis of polyisocyanate, sodium silicate, and ESO as an epoxy component have been synthesized.

The aim of this research is to investigate the effect of HWC chemical treatment on surface properties, water absorption, mechanical performance and biodegradability of the composites.

EXPERIMENTAL

Materials. HWC applied as filler was derived from non-narcotic types of hemp and given by Institute of Bast Crops of the National Academy of Agrarian Sciences of Ukraine. Sodium hydroxide (NaOH) used for mercerization was obtained from Chempol, Czech Republic. Functionalization agents APS and ESO were supplied from Sigma-Aldrich, USA.

For polymer matrix synthesis the following reagents were used. Polyisocyanate 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. ESO (epoxy equivalent = 250 g/mol, epoxy group content = 6.1 %) was obtained from Sigma-Aldrich, USA. Aqueous solution of sodium silicate (silicate module = 2.9–3.0, the content of free water = 56.0 %) was supplied by Dniproskloservis, Ukraine.

Treatment of filler. Initially HWC was washed with water, dried at 80 °C for 4 hours to constant weight and then chopped. The particles of the desired size, particularly of (0.05–5.0) mm, were selected by fractionation through a sieve (model 029). For mercerization HWC was immersed in 5 wt. % solution of sodium hydroxide at room temperature for 24 hours. Then the particles were rinsed with acidified water to neutralize alkali residues, washed with distilled water and dried at 80 °C for 8 hours. Mercerization was applied separately or as pre-treatment for further modification of HWC. Oil treatment was conducted by immersing pre-mercerized HWC into 3 wt. % ESO solution in acetone, followed by mixing at room temperature for 3 hours and drying at 80 °C to constant weight. Silane treatment was performed by immersing pre-mercerized HWC into 5 wt. % aminosilane solution at room temperature for 24 hours. After that 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 ensure a complete silane hydrolysis.

Polymer matrix synthesis. Epoxyurethane matrices were obtained from three components, namely, isocyanate (polyisocyanate), epoxy (ESO) and inorganic (sodium silicate) ones combined in a weight ratio of 80/20/20. ESO was introduced into the polyisocyanate and stirred at 900 rpm for 3 min at 20±1 °C. Then sodium silicate, which was used to provide UV-, fire- and thermal stability of matrices, was added under 3 min stirring at 900–1000 rpm and 20±1 °C.

Composites preparation. To obtain composites 60 wt. % of unmodified, mercerized or functionalized HWC was soaked into liquid epoxyurethane mixture under stirring. Then the samples were fabricated in the molds at 140 °C and 10 MPa by a hot press machine.

Contact angle measurements. The contact angles (θ) of water and linseed oil as liquids of different polarities were measured. Using a digital ocular camera of a horizontal microscope MG, microphotographs of the droplets reached equilibrium were taken. The photographs were adapted by the image processing software package ImageJ [18]. The contact angles were computed by DropSnake algorithm implemented in the Drop Shape Analysis plug-in. The contact angle values reported were obtained from the mean of at least five measurements at different locations on the same substrate. They were used to evaluate surface energy by means of Owens and Wendt equation [19]:

$$\gamma_L(1 + cos\theta) = 2(\gamma_S^d \cdot \gamma_L^d)^{\frac{1}{2}} + 2(\gamma_S^p \cdot \gamma_L^p)^{\frac{1}{2}}, \quad (1)$$

where γ_L – surface tension of liquids;
γ_L^{p} and γ_L^d – polar and dispersive components of surface energy for liquids, respectively;
γ_S^{p} and γ_S^d – polar and dispersive components of surface energy for solids, respectively.

According to this approach total surface energy (γ_S) consists of dispersive and polar components [19, 20]:

$$\gamma_S = \gamma_S^d + \gamma_S^{\mathrm{p}}. \quad (2)$$

Water absorption studies. To estimate water resistance of the composites investigation of water absorption behaviour and diffusion parameters were performed following the ASTM D570. For this 50×50×5 mm sized samples were immersed in distilled water at constant room temperature. They were taken out periodically and, after wiping out the water from the surface by filter paper, weighed immediately on a precise five-digit balance Kern ABT 120-DM. Then the specimens were submerged into water again. The measurements were carried out once an hour during the first day of experiment and then once a day till the constant gain in mass was reached. Altogether, the testing was performed for 310 hours (13 days). The percentage of water absorbed at any time was calculated using given equation:

$$\Delta W = \frac{W_t - W_0}{W_0} \times 100, \quad (3)$$

where W_t is the weight of the sample at time t and W_0 is its initial weight (at $t = 0$).

At the saturation level W_t. is equal to equilibrium moisture content (W_m), from which sorption coefficient (S) can be calculated by the following equation:

$$S = \frac{W_m}{W_0}. \quad (4)$$

Another quantitative parameter is diffusion coefficient (D, mm^2/s), which is computed from the initial slope of W_t / W_m dependence on $t^{1/2}/h$ (where t is soaking time, hours; h is the thickness of the sample, mm) by means of the formula given:

$$D = \frac{\pi}{16}\left[\frac{\Delta\,(\mathrm{Wt/\,Wm})}{\Delta\,(\mathrm{t}^{1/2}/\mathrm{h})}\right]^2. \quad (5)$$

By production of the values of sorption and diffusion coefficients permeation coefficient (P, mm^2/s) can be found [21, 22]:

$$P = D \times S. \quad (6)$$

Mechanical testing. Tensile and flexural strength of obtained composites were measured for molded samples with a size of 150×20×5 mm each. The average values of five determinations are presented.

Soil burial testing. Previously dried and weighted samples of composites were buried in soil (pH = 6). After 14 months they were removed, washed with distilled water, and dried to a constant mass.

RESULTS AND DISCUSSION

Surface properties. Contact angles of epoxyurethane composites were measured to estimate the changes in their wettability due to chemical treatment of HWC. The values of contact angles (θ) of water and linseed oil together with that of surface energy (γ_S) and its components, namely dispersive (γ_S^d) and polar (γ_S^{p}) ones, calculated on their basis, are given in the Table 1.

Table 1. Surface parameters of composites

Type of HWC modification	θ, degree		Surface energy, mJ/m^2		
	water	linseed oil	γ_s^d	γ_s^p	γ_s
Untreated	83	10.3	32.67	3.93	36.60
Mercerized	103	12.1	32.47	0.03	32.70
Oil treated	104	14.0	32.22	0.02	32.44
Silanized	94	8.9	32.79	2.92	35.71

From the Table 1 it can be seen that the specimen filled with untreated HWC exhibits the lowest value of contact angle of water indicating its highest hydrophilicity. This is quite expected taking into account the large amount of hydroxyl groups on the surface of lignocellulosic fillers. In the meantime, all the types of HWC chemical modification lead to less water wettability of composites with the values of contact angles even above 90 °, which is considered to be a criterion of hydrophobic surface. In the case of alkali treatment it is accounted for the dissolution of hemicelulloses known to be the most hydrophilic components of plant fibers [23]. Their removal during mercerization of HWC has been evidenced by means of FTIR investigations [16]. For composites with functionalized filler the masking of surface hydroxyl groups may also occur [24] along with their additional consumption for formation of bonds with modifiers. Among the specimens with chemically treated HWC, the ones containing aminosilanized filler are characterized with the lowest contact angle of water. Despite the introduction of additional polar $–NH_2$ and –Si–OH groups onto the surface of HWC, its hydrophilicity decreases after APS treatment. Similar behavior of aminosilane treated samples was observed by other scientists and explained by the consumption of polar functionalities via formation of hydrogen bonds between amino and hydroxyl groups [25] as well as via rapid self-condensation of –Si–OH groups and their condensation with C–OH groups of filler induced by the catalytic effect of the amine group [24, 25]. The proceeding of both condensation reactions for given samples were confirmed before [16].

Analyzing the values of surface energy and its constituents it may be noticed that dispersion component remain almost unchanged. According to data available in literature [24], such phenomenon is predictable. Alternatively, total surface energy increases with the augment in its polar component. Furthermore, the lower values of surface energy correlate well with the higher ones of contact angles of water. This trend demonstrated in Fig. 1 was also noticed in [24] for silane treated cellulose. At the same time, analogous correlation with the contact angles of linseed oil, which serve as auxiliary parameters, is not so pronounced due to small difference between their values. Therefore, their contribution in computing surface energy is less than the one of contact angles of water.

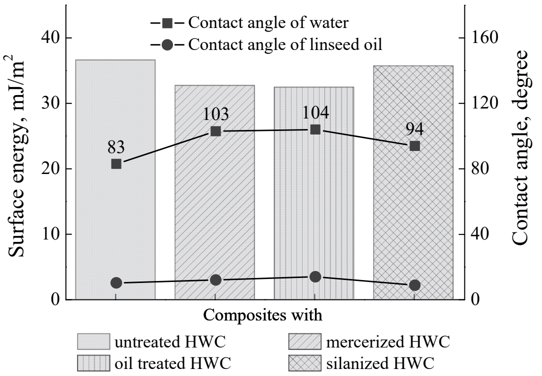

Fig. 1. Contact angles and surface energy of composites

Water uptake. The water uptake profiles of the composites with different reinforcements are plotted in Fig. 2. The slope of the curves indicates that the samples containing functionalized HWC absorb water slower than the ones containing raw or mercerized HWC. After some period of time the velocity of gain in weight of the specimen with alkali treated filler also starts to decrease resulting in medium equilibrium moisture content after levelling off. The values of qualitative water absorption parameters obtained by formulae 4–6 together with the ones of thickness swelling (*TS*) are collected in the Table 2.

Naturally, the values of equilibrium moisture content (W_m), diffusion (D) and permeation (P) coefficients are the largest for composites with untreated filler (Table 2), as it is the most hydrophilic among them (Table 1). From the data in the Table 2 it may be also noticed that even providing similar values of water contact angle and surface energy to the ones of composites with ESO treated reinforcement (Fig. 1), mercerization of HWC almost does not ensure changes in the diffusion coefficient. Like in other works [26] mere alkali treatment cannot be as efficient in improving water resistance as its combination with further functionalization that in our case evokes *in situ* formation of extra bonds with polyurethane matrix via amino groups of APS or epoxy groups of ESO as well as simultaneous minimization of microvoids in the resulting composites.

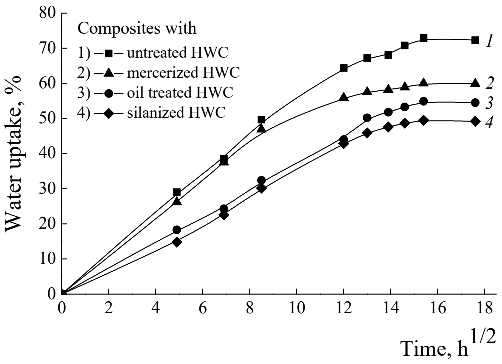

Fig. 2. Water absorption curves of composites

Table 2. Water absorption parameters of composites

Type of HWC modification	W_m, %	TS, %	S	D, mm^2/s	P, mm^2/s
Untreated	72.3	5.40	1.34	$1.57\cdot10^{-5}$	$2.10\cdot10^{-5}$
Mercerized	59.9	6.98	1.11	$1.51\cdot10^{-5}$	$1.67\cdot10^{-5}$
Oil treated	54.5	6.06	1.36	$7.03\cdot10^{-6}$	$9.56\cdot10^{-6}$
Silanized	49.2	6.63	1.45	$6.25\cdot10^{-6}$	$9.06\cdot10^{-6}$

Interesting enough, notwithstanding the higher hydrophilicity and surface energy of the samples containing silanized HWC as compared to those containing oil modified HWC (Table 1), they exhibit the lowest values of both permeation coefficient and equilibrium moisture content with the last being by 31 % and 10 % less than the ones of composites with pristine and ESO treated filler, respectively. Indeed, the presence of polar groups in the structure of APS may contribute to the high sorption of water (*S*). However, most attention should be paid to the permeation coefficient that is the smallest here. Depending on both the rate of water movement through the sample (diffusion) and the relative weight of absorbed water at the saturation point (sorption) [21, 22] it seems to be the most informative among the absorption parameters. Retarded diffusion of water molecules inside the composite with silane treated HWC determines its less overall permeation. Such behavior may be originated from the character of interaction of a modifier with lignocellulosic filler. Its treatment with ESO gives rise to hydrogen bonding between hydroxyl groups of HWC and ester or epoxy groups of triglyceride, whereas during treatment with APS not only formation of hydrogen bonds via silanol or amino groups is possible but also of Si–O–C covalent bonds with the surface of plant filler as it was shown in [16]. In other words, in comparison with the application of modified oil the one of aminosilane leads to denser structure caused by stronger matrix/filler interfacial connection.

Mechanical characteristics. Fig. 3 demonstrates the results of flexural and tensile strength testing for the composites on the basis of chemically treated and untreated HWC. As it has been turned out, modification of filler is especially effective for improving flexural strength of composites. Changes in tensile strength of the samples are not so remarkable. Still, in both instances the specimens with APS treated HWC show the best mechanical performance with 19 and 65 % increase in tensile and flexural strength, respectively, if compared to that of composites with raw hemp filler. Thus, like in the case of impact on water resistance, the presence of additional covalent bonds provided by silanization is found to be crucial for mechanical properties.

Biodegradability. The biodegradability of composites is commonly estimated by their weight loss within soil burial test [27]. Weight loss by the samples of composites after testing is given in Fig. 4.

It is generally known that unlike neat synthetic polymers composites reinforced with natural fibers acquire ability to degrade in biological environment. It is accounted for increased hydrophilicity and moisture absorption that along with the occurrence of cavities due to filler loading promote the adhesion of microorganisms [28, 29]. The reason of quite significant entire decrement in weight observed in given research (Fig. 4) may be associated with the high content of plant filler, which has been reported to enhance the degradability of composites under soil exposure [29, 30]. Like in other investigations [30, 31], the specimens with untreated filler degrade better than those with alkali treated one that is accounted for higher sensitivity to water and weaker matrix/filler interaction. In accordance with similar studies [29, 31], functionalization of pre-mercerized HWC particles results in more retarded biodegradation of composites. Once again, in spite of polar functional groups in the structure of aminosilane coupling agent, composites fabricated by means of its application are the least susceptible to the action of microbiota, since strong interfacial adhesion is believed to play the pivotal role in the resistance of composites to biodegradation [28].

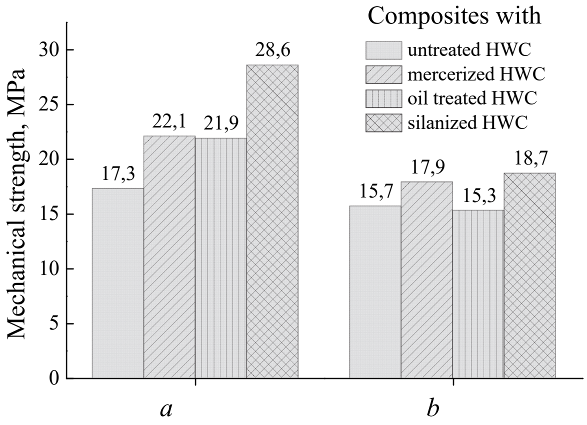

Fig. 3. Mechanical strength of composites: *a* – flexural and *b* – tensile

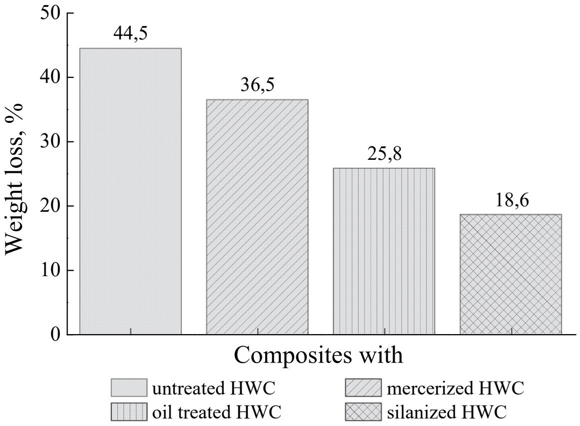

Fig. 4. Weight loss after soil burial exposure

CONCLUSIONS

Composites on the basis of epoxyurethane matrix with ESO as an epoxy component were elaborated. Four types of HWC particles served as natural reinforcement: raw, mercerized and functionalized after previous mercerization either with ESO or APS. Surface, mechanical and biodegradable properties of obtained composites as well as their water absorption were investigated. Contact angle determination and calculation of surface energy together with its components evidenced hydrophobization of the surface as an outcome of application of all types of chemical modification. The effect of silanization was not so pronounced owing to the presence of polar amino and silanol groups in its structure. However, the results of other measurements indicated that the strength of interfacial matrix/filler adhesion rather than hydrophobicity was responsible for acquiring important characteristics. Thus, treatment of HWC with epoxidized triglyceride leading to formation of only hydrogen bonds between filler and modifier was found to be less efficient than modification with aminosilane providing the occurrence of corresponding covalent bonds also. Particularly, composites containing silanized filler exhibited the best water resistance manifested in the lowest values of equilibrium moisture content, diffusion and permeation coefficients. Moreover, they demonstrated the utmost mechanical performance, including 19 % higher tensile strength and 65 % higher flexural strength as compared to the samples with unmodified reinforcement. The appearance of dense interface in the case of APS treated filler prevented attacks of microorganisms during biodegradability test that resulted in 18 % of weight loss after 14 month of exposure under soil burial conditions against 44 % of the one by the composite containing untreated hemp woody core.

Властивості композитів на основі хімічно обробленої конопляної костриці й епоксиуретанів з епоксидованою соєвою олією

Т.Ф. Самойленко, Л.М. Ященко, Н.В. Ярова, О.О. Бровко

Інститут хімії високомолекулярних сполук Національної Академії Наук України
Харківське шосе, 48, Київ, 02155, Україна, s_t_f@ukr.net

За останні два десятиріччя спостерігаємо інтенсивне зростання кількості публікацій, присвячених рослинним волокнам як підсилювачам полімерних матриць. З урахуванням екологічних проблем природні волокна розглядають як привабливі альтернативи синтетичним. На відміну від конопляного волокна, яке часто використовують для цих потреб, його побічний продукт під назвою конопляна костриця (КК) ще не привернув достатньо уваги науковців у цій галузі. Проте завдяки низці унікальних властивостей КК також може бути перспективним наповнювачем. Застосування КК в композитах додатково сприяло би її раціональній утилізації. Однак, до особливостей лігноцелюлозних наповнювачів належить і їхня гідрофільність, яку необхідно знизити, щоб забезпечити міцну міжфазову взаємодію з матрицею та задовільну довговічність виготовлених композитів. У роботі з цією метою використали мерсеризацію (лужну обробку) та/або подальшу модифікацію епоксидованою соєвою олією (ЕСО) або 3-аміно-пропілтриетоксисиланом (АПС). Si-вмісну епоксиуретанову полімерну матрицю синтезували з натрій силікату, поліізоціанату та ЕСО як епоксидної складової. Було виготовлено чотири серії формованих зразків з високим вмістом рослинного наповнювача (60 мас. %). Результати вимірювання кутів змочування та водопоглинання показали, що усі використані типи обробки зумовили гідрофобізацію поверхні. Так, значення кутів змочування композитів з модифікованою КК перевищили 90 °, а їхня поверхнева енергія була нижчою, ніж для вихідних зразків. Незважаючи на досить високу полярність композитів з силанізованою КК внаслідок наявності аміно- та силанольних груп, утворення ковалентних зв'язків між наповнювачем та аміносилановим сполучним аґентом АПС виявилося ключовим для таких характеристик як водостійкість і механічна міцність. Зокрема, рівноважний вміст вологи зменшився на 31 % порівняно з таким для зразків з немодифікованою КК, а міцність на розрив і на вигин поліпшилися на 19 і 65 %, відповідно. Найвища мікробна стабільність зразків з наповнювачем, обробленим силаном, визначена під час тесту при закопуванні в ґрунт, є ще одним доказом поліпшеної міжфазової адгезії в цьому випадку.

***Ключові слова**: коноплянa кострицяб хімічна модифікація наповнювача, мерсеризація, обробіток силаном, обробка епоксидованою соєвою олією, епоксиуретани, підсилені природними волокнами полімерні композити, гідрофобність, тестування при закопуванні в ґрунт, біорозкладання*

REFERENCES

1. Malkapuram R., Kumar V., Negi Y.S. Recent development in natural fiber reinforced polypropylene composites. *J. Reinf. Plast. Compos.* 2009. **28**(10): 1169.
2. Brosius D. Natural fiber composites slowly take root. *Compos. Technol.* 2006. **12**(1): 32.
3. Begum K., Islam M.A. Natural fiber as a substitute to synthetic fiber in polymer composites: a review. *Res. J. Eng. Sci.* 2013. **2**(4): 46.
4. Dittenber D.B., GangaRao H.V.S. Critical review of recent publications on use of natural composites in infrastructure. *Composites, Part A.* 2012. **43**(8): 1419.
5. Lu N., Oza S., Tajabadi M.G. Surface modification of natural fibers for reinforcement in polymeric composites. In: *Surface Modification of Biopolymers*. (New York: Wiley, 2015).
6. Chen T., Wu Y., Qiu J., Fei M., Qiu R., Liu W. Interfacial compatibilization via in-situ polymerization of epoxidized soybean oil for bamboo fibers reinforced poly(lactic acid) biocomposites. *Composites, Part A.* 2020. **138**: 106066.
7. Le Moigne N., Otazaghine B., Corn S., Angellier-Coussy H., Bergeret A. Modification of the interface/interphase in natural fibre reinforced composites: Treatments and processes. In: *Surfaces and Interfaces in Natural Fibre Reinforced Composites: Fundamentals, Modifications and Characterization*. (Cham: Springer Cham, 2018).
8. Stevulova N., Estokova A., Cigasova J., Schwarzova I., Kacik F., Geffert A. Thermal degradation of natural and treated hemp hurds under air and nitrogen atmosphere. *J. Therm. Anal. Calorim*. 2017. **128**: 1649.
9. Członka S., Strakowska A., Kairyte A. The impact of hemp shives impregnated with selected plant oils on mechanical, thermal, and insulating properties of polyurethane composite foams. *Materials*. 2020. **13**(21): 4709.
10. Stevulova N., Cigasova J., Schwarzova I., Sicakova A., Junak J. Sustainable bio-aggregate-based composites containing hemp hurds and alternative binder. *Buildings*. 2018. **8**(2): 25.
11. Balčiūnas G., Vėjelis S., Vaitkus S., Kairytė A. Physical properties and structure of composite made by using hemp hurds and different binding materials. *Procedia Eng.* 2013. **57**: 159.
12. Li X., Xiao R., Morrell J.J., Zhou X., Du G. Improving the performance of hemp hurd/polypropylene composites using pectinase pre-treatments. *Ind. Crops. Prod.* 2017. **97**: 465.
13. Zhang Y., Remadevi R., Hinestroza J.P., Wang X., Naebe M. Transparent ultraviolet (UV)-shielding films made from waste hemp hurd and polyvinyl alcohol (PVA). *Polymers.* 2020. **12**(1190): 2.
14. Cuinat-Guerraz N., Dumont M.-J., Hubert P. Environmental resistance of flax/bio-based epoxy and flax/polyurethane composites manufactured by resin transfer moulding. *Composites, Part A*. 2016. **88**: 140.
15. Samoilenko T., Yashchenko L., Yarova N., Brovko O.O. Epoxyurethane polymer matrices for hemp woody core reinforced biocomposites synthesized with the use of plant-originated oils. *Iran. Polym. J.* 2023. **32**: 403.
16. Samoilenko T., Yashchenko L., Yarova N., Brovko O. Impact of hemp woody core surface chemical modification on wettability of epoxyurethane composites. *Compos. Interfaces*. 2023. **30**(12): 1429.
17. Samoilenko T.F., Yashchenko L.M., Yarova N.V., Leta O.O., Brovko O.O. Mechanical, thermooxidative and biodegradable properties of composites from epoxyurethanes and chemically modified hemp woody core. *Him. Fiz. Tehnol. Poverhni*. 2024. **15**(1): 67.
18. Stalder A.F., Kulik G., Sage D., Barbieri L. Hoffmann P. A snake-based approach to accurate determination of both contact points and contact angles. *Colloid. Surface A*. 2006. **286**(1–3): 92.
19. Owens D.K., Wendt R.C. Estimation of the surface free energy of polymers. *J. Appl. Polym. Sci.* 1969. **13**(8): 1741.
20. Heng J.Y.Y., Pearse D.F., Thielmann F., Lampke T., Bismarck A. Methods to determine surface energies of natural fibres: a review. *Compos. Interfaces.* 2007. **14**(7–9): 581.
21. Panthapulakkal S., Sain M. Studies on the water absorption properties of short hemp-glass fiber hybrid polypropylene composites. *J. Compos. Mater.* 2007. **41**(15): 1871.
22. Manaila E., Craciun G., Ighigeanu D. Water absorption kinetics in natural rubber composites reinforced with natural fibers processed by electron beam irradiation. *Polymers*. 2020. **12**(11): 2437.
23. Stevulova N., Cigasova J., Purcz P., Schwarzova I., Kacik F., Geffert A. Water absorption behavior of hemp hurds composites. *Materials*. 2015. **8**(5): 2243.

24. Abdelmouleh M., Boufi S., Belgacem M.N., Duarte A.P., Ben Salah A., Gandini A. Modification of cellulosic fibres with functionalised silanes: development of surface properties. *Int. J. Adhes. Adhes*. 2004. **24**(1): 43.
25. Oushabi A., Hassani F.O., Abboud Y., Sair S., Tanane O., El Bouari A. Improvement of the interface bonding between date palm fibers and polymeric matrices using alkali-silane treatments. *Int. J. Ind. Chem*. 2018. **9**: 335.
26. Bisanda E.T.N., Ansell M.P. The effect of silane treatment on the mechanical and physical properties of sisal-epoxy composites. *Compos. Sci. Technol*. 1991. **41**(2): 165.
27. Karthika M., Shaji N., Johnson A., Santhosh N.M., Gopakumar D.A., Thomas S. Biodegradation of composite materials. In: *Bio monomers for green polymeric composite materials*. (NY: John Wiley & Sons, Ltd., 2019).
28. Batista K.C., Silva D.A.K., Coelho L.A.F., Pezzin S.H., Pezzin A.P.T. Soil biodegradation of PHBV/peach palm particles biocomposites. *J. Polym. Environ*. 2010. **18**: 346.
29. Pang A.L., Arsad A., Ahmadipour M., Ismail H., Bakar A.A. Effect of soil burial on silane treated and untreated kenaf fiber filled linear low-density polyethylene/polyvinyl alcohol composites. *BioResources*. 2020. **15**(4): 8648.
30. Rajesh G., Prasad A.V.R., Gupta A.V.S.S.K.S. Mechanical and degradation properties of successive alkali treated completely biodegradable sisal fiber reinforced poly lactic acid composites. *J. Reinf. Plast. Compos*. 2015. **34**(12): 951.
31. Jacob M., Thomas S., Varughese K.T. Biodegradability and aging studies of hybrid biofiber reinforced natural rubber biocomposites. *J. Biobased Mater. Bioenergy*. 2007. **1**(1): 118.

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