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Restorative biocompatible polymer composites on the base of epoxy-resin filled by surface-modified disperse utilizated solid waste of industrial paper products

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Abstract:*The paper industry is one of the sources of environment pollution. Therefore, the problem of efficient utilization of such wastes is an urgent one. One of the possible effective methods of paper industry waste recycling can be the application in epoxy composites. The review of literature proves a high scientific and industrial actuality of this thematic. Optical microscopy shows that 20 wt% of micro- and meso-particles of lignocellulose from waste-paper utilization leads to changes in morphology of composite due to interactions between phases. As a result, the key mechanic (modulus at bending, resistance to wear) and resistant (swelling, fire- resistance) parameters changed. At the same time, 20wt% filling do not importantly change compression and bending strength parameters. Filled composites (as fresh as aged) are noticeable more resistant in acetone-containing solvents. Effect of filling on resistance in H_2O_2 depends on its concentration and age of templates: aged 20%-filled composites are more resistant than unfilled - in 35% H_2O_2, but fresh 10%-filled composite destruct quickly (unlike unfilled)-in high-concentrated (60%) H_2O_2.*

Keywords: *Paper industry waste; Epoxy-resin; Mechanical properties; Resistance to swelling.*

1. Introduction

The paper industry is one of the sources of environment pollution because of the consumption of a large amount of water and formation of a huge quantities of wastewaters, which differ in composition, depending on the range of products produced. The paper and cardboard manufacturing is a quite complex and multi-stage process. The equipment for paper formation produces wastewater with a high content of soluble and insoluble substances. In order to reduce the anthropogenic load, the implementation of using recycling water can be created. But this method is too difficult to perform, because of the formation and accumulation of dissolved mineral salts and mucus in system. During treatment of such wastewaters, a large amount of solid wastes which contains, not only natural fibers but also mineral components, is formed. The main part of this wastes remains unused and requires the development of effective disposal methods.

Methods for solid wastes of paper industry utilization have been described in many publications (as a component of concrete mixtures, in the manufacture of bricks, as a base of gypsum plaster, as a component of wood-fiber boards, as a filler of insulation blocks), but none of the investigated methods has acquired industrial use. For nowadays, only landfill or incineration is used on an industrial scale for the utilization of solid wastes of paper industry, which has a negative impact on the environment. Therefore, the problem of efficient utilization of such wastes is an urgent one. One of the possible effective methods of its utilization can be the application in epoxy composites.

Epoxy-resin is a good matrix for filling-utilization of various materials [1-5]. Salasinska et al. [6] investigated Epoxy-Composites (EC) with ground walnut shell used as organic waste fillers. Incorporation of the filler resulted in a decrease of composite material tensile strength and impact resistance. Results obtained from dynamic mechanical thermal analysis tests showed a growth in the composites' stiffness at elevated temperatures as a function of the increasing natural filler content. Thermogravimetric analysis (TGA) was found that the incorporation of ground walnut shell led to an improved thermal stability of composite materials. The analysis of the change in composite material properties, caused by natural filler incorporation, was complemented by material microstructure observations. According [6], various plant fillers used for natural composite production, such as: bamboo, coconut, kenaf, ramie, nettles, abaca, pineapple, sugar cane, rice, and grass, can

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be found in the literature and industrial applications [7,8]. Authors observed an increased interfacial adhesion between polymer and reinforcement. Although this conclusion does not see from corresponding SEM-images, but is good seen a difference of structures at various fillings. From the same study, it is seen that strength (at bending & impact) drops, but modulus & micro-hardness increases (especially at 30% of filler). It is in accordance with our results for epoxy-waste cellulose composites [9-11]. In our earlier works [9-10], an informative schema of interaction "epoxy – cellulose" is presented in Fig.1.

The research of Sarikaya et al. [12] aimed the production of epoxy resin composites reinforced by birch, palm, and eucalyptus fibers with resin transfer molding technique and molded fiber production technique combination. The tensile stress of birch, palm, and eucalyptus reinforced epoxy composites were determined as 30; 42 and 45 MPa, respectively (seriously less than Neat-Epoxy ≈78 MPa, but more than for neat fibers ≈ 3-8 MPa).

Bending stress of birch, palm and eucalyptus reinforced epoxy composites were found as 59, 69, and 80 MPa, respectively. The birch epoxy composite had 0.105 J impact energy while palm and eucalyptus epoxy composites were determined as 0.130 and 0.124 J, respectively (increases with filling). It is clearly observed that fiber type was very effective on mechanical properties of composites. The results of studies showed that molded fiber production method had a very promising future for the development of natural fiber reinforced composites.

Musaeva [13] investigated a composition of "epoxy + 10-25wt% nut shells". It is proved that filling enhances a heat-viscosity, density and hardness (micro-hardness?) of polymer-composites. Unlike existence of all these researches and other [14-24] information, now we have a lack of experimental data about epoxy-cellulose and epoxy-paper compositions for a practical use. The aim of this new paper is to do a new step into investigation in this field.

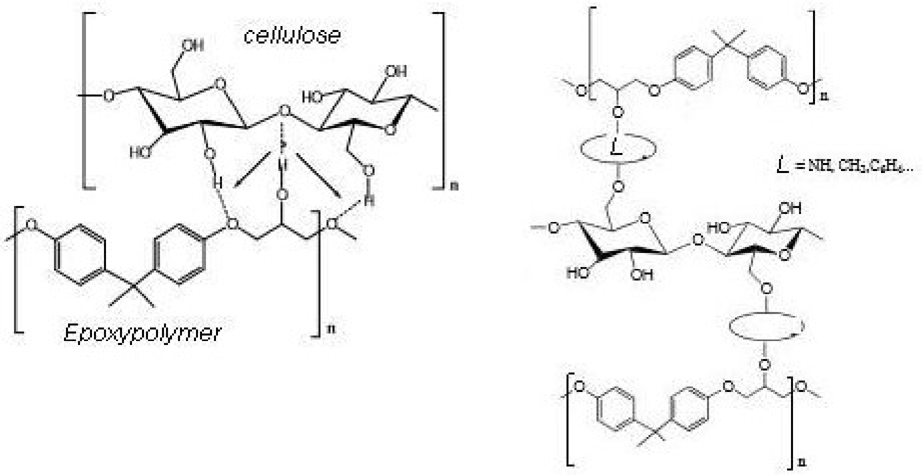


***Fig.1**. Schematic physical (H-bonds) and chemical (if cellulose is modified) interaction between epoxy and cellulose.*

2. Materials and methods

In this work solid waste of paper (WP) industry in the form of fibrous material was used as the raw material. According to sertificate-concluison (22/4904, 2.09.2008, Ukrainian Marzeev institute of hygiene & ecology, see [25]) it is classified as "low-dangerous waste". WP fibrous material consists from greeze-brown fiber lignocellulose particles, without smell. They consist from 8 % of organic and 92 % mineral substances.

According [25], the value of the redox potential (pH) is 6.5, humidity - 85.4%. The mineral constituent includes ions of Pb(II), Zn(II), Cu(II), Cd(II), Cr(II), Ni(II), Mn(II). The commercially available epoxy resin CHS-EPOXY-520 and polyethylene polyamine (a curing agent) were used to prepare composites. The content of FM in composites was 20 %. It was added immediately after stirring main components, and then the composition was homogenized and formed into samples. The polymerization was occurred at a room temperature during 72 h.

Compositions of epoxy-WP were prepared by mixing weights of waste-paper derivatives 10 wt % to 20 wt% with Epoxy520 epoxy resin (Czech production), followed by the addition of PEPA hardener (resin: hardener ratio 5:1) and constant mechanical stirring under normal conditions (Fig.2).

After 3 days of initial curing, samples of the obtained composites were subjected to heat treatment at a temperature of 65 °C for 5-7 hours for mechanical and thermal tests or at 30 °C for at least 5-7 days for tests on swelling and resistance in aggressive liquids. Mechanical tests of the obtained samples were carried out in accordance with standard methods (Fig.3):

A) Compression (ISO 604: 2002), - on cylindrical samples D = 6.5 mm, height = 11 ± 0.5 mm - on a L.Shopper press-machine.

B) Brinell microhardness was determined on a hard-meter PIM (USSR), with 3 mm steel hemisphere.
C) For bending tests (ISO 178, GOST 56810-2015), plates with a size of 6 × 1 × 0.2 cm were made. Their break during bending was carried out on the basis of L = 3 cm of a testing bending machine going to yours.
D) Tests on the resistance in liquids were carried out according to ISO 62:2008 – by measuring the weight gain of tablets 1 × 1 × 0.1 cm after removal from the liquid, wiping and short-term (5-10 min) drying at norm. conditions Solutions of acetone, 35% and 60% H_2O_2 and 20% nitric acid concentration (produced in Ukraine and Russia) were used without further purification.

Fig.2. *Photo of typical epoxy – wastepaper composition before hardening.*

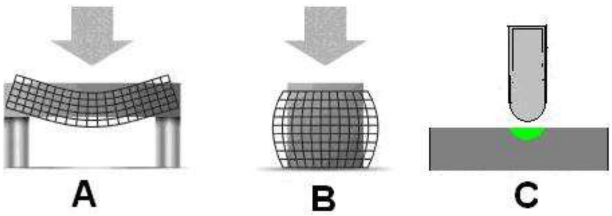


Fig.3. *Tests on: A – tensile; B – compression; C – microhardness.*

3. Results and discussion

Optical microscopy observation obtained on “BRESSER LCD Micro” microscope shows that mesoscale cellulose is distributed in epoxy in large interlacing agglomerates up to 200-300 microns in size (Fig.4). Investigation of the mechanical properties of obtained composite testifies about good compatibility between epoxy and WP (due to the fact that both materials contain a significant content of hydroxyl groups) and about high strength and flexibility of the composites. The results of the laboratory experiments are shown in Table 1. As can be seen the addition of WP in the composition of composites leads to the increase in some parameters.

Epoxy plastics are quite resistant to many aggressive mediums. But there are a number of solvents and mediums, such as acetone and its solutions with ethyl acetate, nitric acid, chlorocarbons, peroxides, that are very aggressive for polyepoxides. Our laboratory has an essential experimental knowledge about investigation of resistance of epoxy-polymers in aggressive media [1-5, 9-11].

Fig.4. *Optical photo of filler in EPOXY-520.*

The effects of acetone and hydrogen peroxide onto epoxy composites swelling degree are shown in Fig.5 and Table 2. As seen from Fig.5, the filling of epoxy composites with WP leads to an increase in its resistance to acetone. If unfilled cannot stand in acetone for more than 2 days, then filled sample can withstand more than 10 days. At the same time, the lower degree of swelling is observed for filled sample.

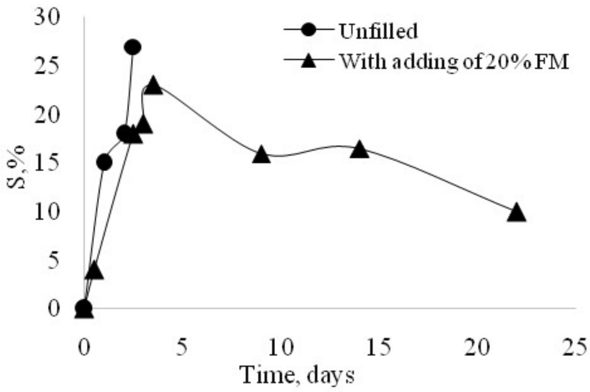


Fig.5. *Swelling degree effect of epoxy composites (1 month old, without thermo-treatment) after endurance in acetone.*

Table 1
Strength parameters of epoxy composites.

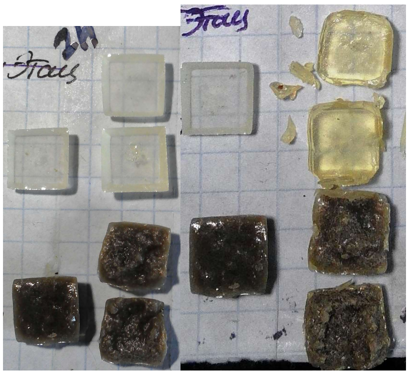
Strength parameters	Unfilled	With adding of 20% WP
Bending strength, kg/mm^2	5.0	5.1
Bending Modulus I×1000, kg/cm^2	16.2	20
Compression strength, MPa	100	66
Compression Modulus E×1000,	13	13*
Microhardness, N^x (x – immersion, mcm)	300^{20}; 400^{30}; 550^{50}	200^{20}; 330^{30}; 400^{50}
Abrasion resistance, 1000\mg	10	11
Fire resistance, sec	1	2

Table 2
Swelling degree effect of epoxy composites (aged 6-month-old, without thermo-treatment) after endurance in acetone+ethylacetate (1:1).

Days	H (Unfilled)	W20 (With adding of 20% WP-fibre)
0	0.0	0.0
0.08	8.0	6.3
0.25	11.4	6.3
1	25.0	7.8
2	destructed	13.0
3		17.7
6		25.0
8		25.0
		Not destruct in next days

Roughly the same picture with swelling in a mixture "acetone-ethyl acetate" (known as a solvent for nail polish). It can be seen that the filled composite is much more stable in this solvent. Unfilled for a few hours of exposure swells by more than 10%, and after 1 day - by 25%, after which it quickly degrades. Filled does not degrade at all, although it can swell up to 25% over time

When fresh (made the day before testing) compositions are used, the percentages of swelling increase (Table 3), but swelling dynamics in acetone+ethylacetate does not generally change. Destruction of unfilled samples is visible in first hours (Fig.6), and filled are more resistant. For example, filled ones can swell up to 50-70% without destructing (Table 3).



2 hours 4 hours

Fig.6. *Filled (initial W in left and endured W1, W2 in right) and unfilled (initial H in left, and H1, H2 in right) templates in Acetone-Ethylacetate mix (1:1)*

Table 3
Effects of acetone-ethylacetate mix (1:1) onto swelling of fresh epoxy-composite templates (H - unfilled, W - with 10 wt % of WP-fiber).

Days	H1 (m_o=210 mg)	H2 (m_o= 237 mg)	W1 (m_o=254 mg)	W2 (m_o=270 mg)
0	0.0	0.0	0.0	0.0
0.014	6.7	8.9	5.5	6.7
0.15	14.3	22.4	15.0	14.4
1	31.0	30.8	32.7	34.8
2	31.0	Destruct	41.7	43.0
3	Destruct		48.4	51.9
4			47.2	51.9
7			47.2	66.7
9			47.2	66.7

One of effective destructive mediums for epoxypolymers is H_2O_2 in highest (35-60%) concentrations. Table 4 shows that filling of epoxy composite with 20% of FM also leads to an increase in resistance to concentrated hydrogen peroxide. This is effect is pronounced during first month of investigation. However, increasing the duration of the experiment indicates that the swelling values becomes are almost the same for both unfilled and filled composites.

However, fresh composites (3 days after hardening) behave differently in H_2O_2 than aged ones. They destruct on the 4th-7th day of exposure (unfilled ones do not destroy - Tables 5 and 6), and before that they swell much more actively than unfilled ones. Table 6 shows that compositions can reach a serious weight gain (in 1.6-3 times).

However, it cannot be said that the filling increases the resistance to all aggressive environments. So, filled composites are less stable in acid (HNO_3) solution. For example, in the first 9 days, unfilled composites absorb no more than 4% (Table 5). At the same time, composites with 10 wt% show swelling of 15-20% (Table 5).

Table 4
Effects of 35% hydrogen peroxide onto epoxy composite (aged templates) swelling degree.

Days	Swelling degree, %	
	H (Unfilled)	W20 (With adding of 20% FM)
0	0	0
1	2.1	0
2	6.2	1.0
3	6.2	2.4
4	6.2	2.9
19	12.4	9.0
55	19.6	20.0

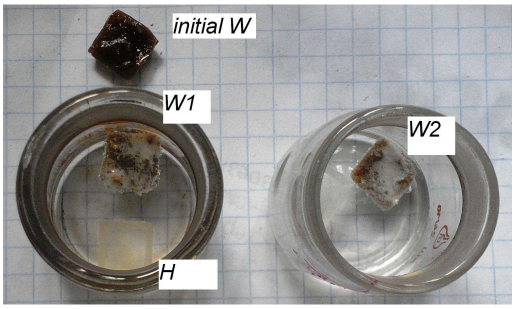


***Fig.7**. Filled (W1, W2) and unfilled (H) templates in 60% H_2O_2, the first seconds of endurance.*

20 minutes 30 minutes 3 days

***Fig.8.** Filled (initial W in left and endured W1, W2 in right) and unfilled (initial H in left, and H1, H2 in right) templates in H_2O_2 (60%).*

Table 5

Effects of 20% HNO3 onto fresh epoxy-composite templates swelling (H - unfilled, W - with 10 wt% of FM).

	Mass of templates, mg			
Days	H1	H2	W1	W2
0	202	242	270	214
0.08 (2 hours)	198	242	268	221
1	198	247	280	227
2	200	249	284	231
4	200	250	297	242
7	203	253	305	249
9	204	252	314	258

Table 6

Effects of super-concentrated H_2O_2 (60%) onto fresh epoxy-composite templates swelling (H - unfilled, W - with 10 wt% of FM).

	H1	H2	W1	W2
Days	(m_o=193 mg)	(m_o=221 mg)	(m_o=217 mg)	(m_o=184 mg)
0	0.0	0.0	0.0	0.0
0.014	1.0	0.9	5.5	9.8
0.06	11.4	10.4	15.2	19.6
0.15	26.9	21.7	31.8	38.0
1	103.6	73.8	177.9	145.7
2	125.9	85.5	257.1	189.7
3	130.1	122.2	296.3	263.6
4	144.6	129.9	destructed	266.8
7	168.4	191.0		destructed
9	186.5	240.7		

4. Conclusion

Composites of epoxy with utilized lignocellulose are good formable, esthetic and cheaper analogue of pure epoxy polymer materials. Filling (20 wt%) by utilized lignocellulose let enhances a row of important characteristics (modulus, fire\abrasion resistance, adhesion), other characteristics (strength at compression and bending) are unchanged. The resistance to swelling in H_2O_2 depends on his concentration (35-60%), and age of filled (10-20 wt%) templates. Aged filled templates are more resistant than unfilled, but fresh filled templates swell and destruct quickly (unfilled not destruct) in 60% H_2O_2. Filling due to noticeable growth of resistance in aggressive acetone solutions - in which they not destruct (unfilled destruct after 1-2 days of endurance). In general, it can be concluded that solid wastes after paper production can be regarded as perspective and promising material for application as a filler of epoxy composites, which is confirmed by the results of the present studies.

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