RESEARCHES CONCERNING THE STRENGTH CHARACTERISTICS OF THE COMPOSITE MATERIALS WHICH USE WASTES FROM LEATHER INDUSTRY

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The present paper presents original results regarding the experimentation of a new composite material, made of elastomeric matrix (rubber) with proteic reinforcement . The composite material is realised in five structural variants, depending on the concentration of fibrous reinforcement obtained from wastes from leather. There are presented in particular, results regarding the mechanical characteristics of each variant of composite material, directly related to the concentration in material of fibres from proteic wastes. It highlights the correlation between the mechanical characteristics of composite material, both in the initial version (primary), and in artificially aged material version through experiments to accelerated requests.

Keywords: composite, elastomer, proteic reinforcement, mechanical strength

1. Introduction

The present paper, through the presented results, enrolls at the confluence of several technical - scientific priorities: obtaining new composite materials, waste recycling, creating products with high biodegradability, etc. The composite material, whose technical performances of resistance presented in this article, is made up of an elastomeric matrix with proteic reinforcement. The elastomeric matrix is obtained by valorisation of some NBR rubber waste type, resulting from the recycling of rubber footwear, soles shoes, rubber goods (skid plates, sealing gaskets, floor mats, etc.) The reinforcement is constitued of proteic wastes from processing of natural leather (tanning, tailoring, etc.) or from integrated sorting of some used footwear articles and leatherwear. Through this technical solution is bring an important contribution to reducing the impact of leather, footwear and

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leatherwear industry on the environment, [1]. Elastomeric/polymeric and leather wastes recovery represents a necessity of the clean, environmental technologies, because only 25% of raw leather is found as the final product, [2]. Also, there is in the literature a patent concerning a material based on a similar technology, called *compound*, [2]. The wastes recovery as the utility and as an ecological action is a maximum actuality theme in science and technology, [4–8]. Obtaining the material referred to this paper is based on the rolling technical process, similar to that used by other authors, [2]. The leather wastes used coming under heading 04 01 09 EWC 2002, [9]. The composite material thus obtained was called CAUFIPEL (CFP) and can be used for the manufacture of soles of shoes, insulating carpet and protective plates, gaskets etc.

2. Structural characterization of the composite material analyzed

A relevant structural characterization, necessary and sufficient for the aimed goal in this work is shown in Table 1.

Table 1

Composite material based on finite leather waste

Name of material	[UM]	CFP1	CFP2	FP3	CFP4	CFP5
Butadiene-coacrilonitric rubber (NBR)	g	300	300	300	300	300
Stearin	g	6	6	6	6	6
Zinc oxide	g	15	15	15	15	15
Calcium carbonate	g	75	75	75	75	75
Silicon dioxide	g	120	120	120	120	120
Leather waste	g	-	30	90	150	240
Carbon black	g	30	30	30	30	30
Sumparo oil	g	30	30	30	30	30
Antioxidant IPPD	g	9	9	9	9	9
Sulfur	g	6	6	6	6	6
Accelerator Th	g	4,5	4,5	4,5	4,5	4,5
Accelerator D	g	0,45	0,45	0,45	0,45	0,45
PEG 4000	g	1,8	1,8	1,8	1,8	1,8
Total	g	597,75	627,75	687,75	747,75	837,75

To describe the mechanical characteristics of the CFP composite material, are used the following standardized items: density, hardness, modulus of elasticity, tensile strength, elongation at break, residual elongation, tear resistance, wear resistance, all these on the newly produced material and also on the accelerated aging material (70º for 168 hours).

3. The research methodology

3.1 Materials and equipment required

In this article are made references to those mechanical properties of the CFP composite material that characterize the most useful properties in operation and not the rheological behavior of the material. From the point of view of classical characteristic tensile strength of the CFP composite material, has resulted a material having a quasi-known mechanical behaviour (Fig.1).

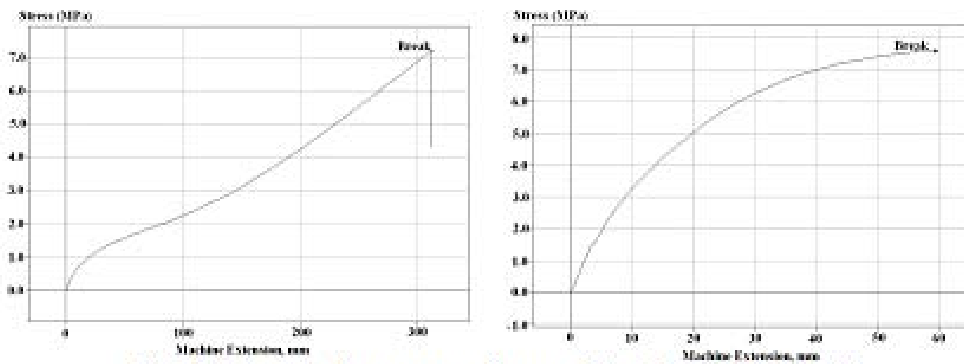

Fig. 1 Stress – strain diagrams to tensile tests of the CFP composite material

The laboratory equipment and the necessary materials for the determination of mechanical properties of the standardized specimens made of specific materials to the five variants of CFP composite are specified in current standards, [10-16]. Also, is used an extensive presentation of composite materials tests, [19].

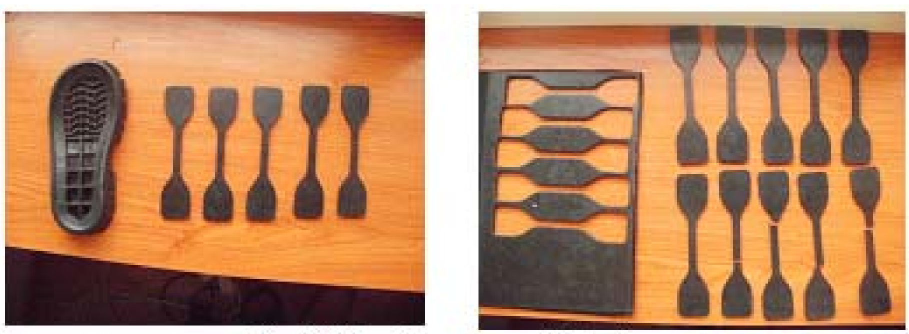

Fig. 2 CFP specimens prepared for testing

As mentioned above, the main purpose of this article is highlighting in a synthetic manner the mechanical properties of the CFP composite material, in the five experimental variants, as well as the variation of these properties depending on the leather fiber concentration in elastomeric matrix. Also, have been performed specific mechanical tests of tensile testing of the size standardized specimens (Fig. 2), for which the obtained values were calculated as the average of a series of at least three measurements.

The synthesis of the main experimental results obtained by standardized tests of the mechanical characteristics specific to the analyzed CFP composite material, is given in Table 2.

Table 2

The synthesis of the experimental results

No. crt.	**Mechanical characteristics** [UM]		**Obtained values**				
			CFP1	**CFP2**	**CFP3**	**CFP4**	**CFP5**
1	Hardness, °Sh A		62	66	81	84	92
2	Useful elasticity, %		24	28	16	16	10
3	The elongation module N/mm^2	100%	1,3	2,1	3,6	-	-
		300%	2,6	-	-	-	-
4	Tensile strength, N/mm^2		5	3,2	5,3	5,2	4.4
5	Elongation at break, %		500	273	300	100	80
6	Residual elongation, %		20	20	20	20	16
7	Tear resistance, N/mm		19	29	42	44,5	35,5
8	Density, g/cm^3		1,23	1,23	1,25	1,25	1,30
9	Wear resistance, mm^3		215	210	250	234	356
Accelerated aging 70° x 168 h							
10	Hardness, °Sh A		62	67	83	87	94
11	Useful elasticity, %		20	22	14	14	10
12	The elongation module, N/mm^2		1,2	2,2	7	-	-
13	Tensile strength, N/mm^2		3,9	3,8	7,1	5	4,4
14	Elongation at break, %		387	380	140	100	60
15	Residual elongation,%		18	24	20	22	14
16	Tear resistance, N/mm		20,5	27	46	45	43

3.2. Graphical representation of the experimental results

The variation of the mechanical characteristics specific to the CFP composite material depending on the leather fiber concentration of the proteic reinforcement is plotted on the bases of the values taken from Table 2 (see Fig. 3, Fig. 4, Fig.5 and Fig. 6). The leather fiber concentration in the composite mass is calculated as the ratio between the amount of proteic waste and the amount of elastomer (the matrix composite).

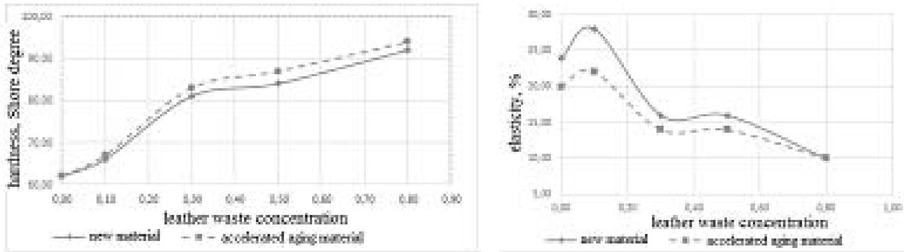

Fig. 3 The variation of hardness and elasticity of CFP with the leather fiber concentration

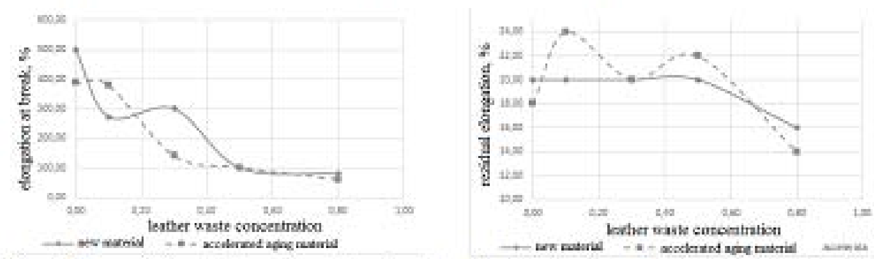

Fig. 4 The variation of elongation at break and residual elongation of CFP with the leather fiber concentration

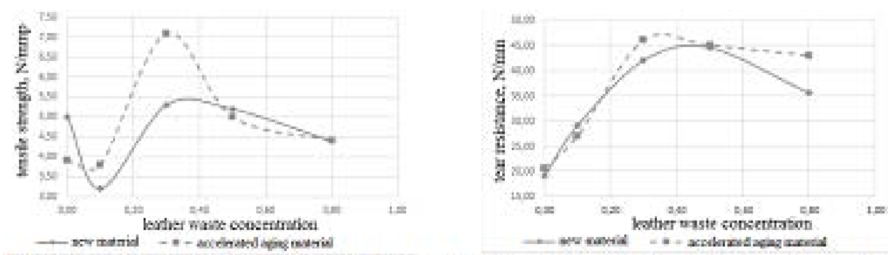

Fig. 5 The variation of tensile strength and tear resistance of CFP composite material with the leather fiber concentration

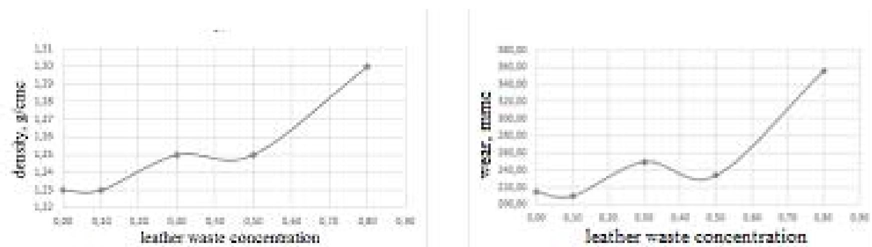

Fig. 6 The variation of density and wear resistance of CFP with the leather fiber concentration

3.3. Analysis of the correlation matrix of the obtained mechanical characteristics

One of the interesting statistical parameters for the collective behavior study of a composite material properties generally, and in particular for the analyzed CFP composite material, is the correlation between the vectors of these properties when the concentration of a component in the composite varies, in this case, the proteic fiber. We first analyze the correlation between parameters of the new composite material manufactured and then is calculated the correlation between mechanical characteristics of the same material after exposure to the accelerated aging process, in order to highlight the conservation or not, of the initial correlation properties. Also, is analyzed the correlation degree of the variation curve of a initial composite material mechanical characteristics with the one corresponding to the artificially aged material.

In table 3 is presented the correlation matrix of all the mechanical characteristics of the initial material (without aging), these varying with the concentration of proteic fibers.

Table 3

The correlation matrix of initial composite material characteristics

	Hardness	Useful elasticity	Tensile strength	Elongation at break	Residual elongation	Tear resistance	Density	Wear resistance
Hardness	1.00	-0.95	0.31	-0.86	0.66	0.78	0.88	0.81
Useful elasticity	-0.95	1.00	-0.51	0.67	0.69	-0.64	-0.89	-0.84
Tensile strength	0.31	-0.51	1.00	0.08	0.14	0.35	0.10	0.05
Elongation at break	-0.86	0.67	0.08	1.00	0.56	-0.75	-0.71	-0.62
Residual elongation	-0.66	0.69	0.14	0.56	1.00	-0.08	-0.94	-0.96
Tear resistance	0.78	-0.64	0.35	-0.75	-0.08	1.00	0.40	0.29
Density	0.88	-0.89	0.10	-0.71	-0.94	0.40	1.00	0.99
Wear resistance	0.81	-0.84	0.05	-0.62	-0.96	0.29	0.99	1.00

For the artificially aged material, the same correlation matrix excepting density and wear resistance that are not determined after the aging, is shown in Table 4.

The correlation matrix between the variations in the composite material characteristics with the concentration of proteic fibers in the material, before and after accelerated aging process, is given in Table 5.

Table 4

The correlation matrix of accelerated aging composite material characteristics

	Hardness	Useful elasticity	Tensile strength	Elongation at break	Residual elongation	Tear resistance
Hardness	1.00	-0.95	0.44	-0.99	-0.43	0.92
Useful elasticity	-0.95	1.00	-0.46	0.97	0.64	-0.85
Tensile strength	0.44	-0.46	1.00	-0.53	0.03	0.71
Elongation at break	-0.99	0.97	-0.53	1.00	0.42	-0.95
Residual elongation	-0.43	0.64	0.03	0.42	1.00	-0.16
Tear resistance	0.92	-0.85	0.71	-0.95	-0.16	1.00

Table 5

The correlation matrix of composite material characteristics before and after accelerated aging

	Hardness	Useful elasticity	Tensile strength	Elongation at break	Residual elongation	Tear resistance
Hardness	1.00	-0.96	0.43	-0.98	-0.46	0.91
Useful elasticity	-0.94	1.00	-0.45	0.95	0.67	-0.83
Tensile strength	0.31	-0.48	0.61	-0.46	-0.30	0.43
Elongation at break	-0.87	0.70	-0.10	0.80	0.12	-0.76
Residual elongation	-0.63	0.68	0.18	0.54	0.81	-0.32
Tear resistance	0.81	-0.67	0.69	-0.84	0.14	0.95

3. Conclusions and suggestions

The mechanical properties of the obtained composite material vary appreciably with the content of proteic fibers (from leather).

The hardness of the CFP composite material (see Fig.3) increases monotonically with the leather fiber content, both for the initial material, and for the aging material. The hardness increases with the concentration of fiber reinforcement in the new composite material and in the one accelerated aging are perfectly correlated in a 1:1 ratio. By accelerated aging, the hardness increases slightly in relation to the new or the initial material.

The useful elasticity of the CFP composite material (see Fig. 3) generally decreases with the concentration of protein fibers, but not monotonically, presenting two local maximum around the values of 8.5% and 46% and a local minimum around the value of 33%. However, these values should be analyzed more deeply, the simple interpolation by splines not being able to guarantee the certainty and the interpretations for these extreme points. Certain is only global decrease in the considered range of leather fibers concentrations. Artificially aged material behaves similarly as variation in relation to the leather fibers concentration, with the new material, from the point of view of elasticity. Its variations for both cases (new and aged material) in relation to the percentage concentration of fibers in the leather are very similar, and the correlation between them has the maximum value, 1. By aging, modulus of elasticity decreases substantially to the composite material with small fibers concentrations and insignificant or not at all at concentrations above 10% of leather fibers.

The tensile strength, for both the new composite material and for the accelerated aging material, shows a variation in relation to the leather fibers concentration having a pronounced maximum percentage around the value of 26 - 27%. The variations of tensile strength of the new material and of the aged material are very similar (see Fig. 5), the correlation between these results having the value of 0.61 (see Table 5). In the case of the tensile strength variation of the material in relation to the concentration of fibers in the leather, the similarity of the new material behavior with the one of aged material it is not so pronounced as in the case of the hardness and of the modulus of elasticity, but existing correlation shows a remarkable similarity behavior. There are points of intersection of the two curves, marking the new composite material and the accelerated aged material dependence on the concentration of protein fibers. If their existence is real, then the exact identification of fibrous material concentrations can provide information on how to obtain variants of composite material which through aging they increase or decrease their tensile strength.

The elongation at break of the new, respectively aged material varies in a similar way descending (see Fig. 4), in relation to the fibrous material leather concentration even if there are some extreme which however are not significant. The correlation between variations of elongation at break of the new material and the one aged is large, larger than for similar tensile strength, having the value of 0.80 (see Table 5). As can be seen in Fig. 4, the variation curves of elongation at break for the new material and the aged one show the intersection points that require to be treated and commented as those in the case of variation curves corresponding the tensile strength. The allure of both curves is generally decreasing, so the elongation at break for both, the new material and the aged material in relation to the concentration of leather fibers in the mass of composite material, is decreasing or can be considered generally decreasing.

The residual elongation shows a variation up to a plateau approximately constant corresponding to a concentration of leather fibers of about 50%, then decreases monotonically, in case of the initial material (see Fig. 4). The variation of characteristic curve of the same residual elongation for the aged material shows two maxima and a minimum up to 50% concentration of leather fibers then decreases monotonically (see Fig. 4). The correlation of the two sequences of results has a value of 0.81, enough to say that the aged material does not fundamentally change the relative behavior to the residual elongation, in the range of experimental values of leather fibers concentration in the composite mass.

The tear resistance of the new composite material depends on the concentration of protein fibers, as shown in Fig. 5, with a slightly parabolic allure with a maximum around the value of 42%. The tear resistance dependence of the artificially aged composite material of residual concentration of leather fibers is plotted in Fig. 5, having a different allure of the one corresponding to the new composite material with a maximum located around the value of 37%. The correlation between the rows of empirical results with which were made graphics, has a value of 0.95, which means that the two rows of results are highly correlated. Interesting is that both curves show that there is a concentration of leather fibers in the composite mass that maximizes the tear resistance.

The density of the composite material was determined only for its initial state. The variation of the material density with the leather fibers concentration (see Fig. 6), is almost everywhere monotonically increasing, in other words, except for some small intervals in relation to the range of protein fibers concentrations in the composite mass, the material density increases with fibers concentration increasing.

Abrasive wear resistance of the CFP composite material, has a relatively similar variation with the density in relation to the leather fibers concentration (see Fig. 6). The high value of the correlation between wear and density (see Table 3) confirm the similarity of variation of these two characteristics with the waste fibrous mass concentration in the composite structure.

It was found that variation of many characteristic curves of the CFP composite material mechanical properties, as a function of leather fibrous mass concentration, presents the extreme points nonnegligible (the residual elongation of aged material, tensile strength). Other mechanical characteristics have extremes less pronounced, which can be, eventually, ignored in the interpolation calculation (hardness, density, wear resistance). The existence of these extreme, nonmonotonic variation of some characteristics, are interesting properties of the composite materials, properties that should be explained, possible by the internal structure of these materials. This kind of composite material behavior was also explained by others researchers, [17], [20]. Significant for concrete technical and industrial applications are the intervals in which the composite material mechanical properties take values in their general meaning of variation. These characteristics are important for the manufacturers in order to obtain some materials with predicted properties for use in certain areas.

Table 6

Extreme values and the global sense of the CFP characteristics

Mecanical characteristic	Extreme values of the initial material		Extreme values of the artifcially aged material		Monotonically character of the variation
	minimum	maximum	minimum	maximum	
Hardness, °Sh A	62.00	92.00	62.00	94.00	increasing
Useful elasticity, %	10.00	28.00	10.00	22.00	decreasing
Tensile strength, MPa	3.20	5.30	3.80	7.10	variable
Elongation at break, %	80.00	500.00	60.00	387.00	decreasing
Residual elongation, %	16.00	20.00	14.00	24.00	weakly decreasing
Tear resistance, N/mm	19.00	44.50	20.50	46.00	variable
Density, g/cm^3	1.23	1.30	-	-	increasing
Wear resistance, mm^3	210.00	356.00	-	-	increasing

Variation of leather fibers concentration in the composite material does not produces large variations of the initial material hardness range (see Table 6), in other words, the hardness is a property less sensitive to the artificial aging process standardized. The elasticity suffers (as a measure of the range of values), an appreciable contraction by artificial aging (Table 6), a reduction of about 33%. By aging, the material becomes more resistant, tensile strength expands its range of values with over 57%. However, the tear resistance increases as the absolute value, less, negligible, and the measure of the range of values is preserved. Elongation at break, suffer, through the aging process, not only a translation to lower values, but but a contraction of the range of values with over 22%. The residual elongation also suffers a translation to lower values, but in contrast to elongation at break, the range of values expands by artificial aging at 150%.

Therefore, the conducted analysis can contribute decisively to obtain a composite material with properties requested by the user. Because we know the mechanical performances of the composite material depending on the leather fibers concentration, the manufacturer can choose that concentration that gives to the customer satisfactory mechanical properties. Furthermore, the manufacturer, in some limits can choose that fibrous mass concentration that leads at a minimum energy consumption.

For example, using the wide range of values of the new CFP material composite mechanical properties, the facilitated range of the choosing possibility of the leather fibers concentration can provide a CFPx structural solution that satisfy the material requirements for sealing elements which are generally made from butadiene-coacrilonitric rubber, NBR type. Also, with the new CFP material composite can be tried obtaining other sealing elements whose properties are specified in the manufacturer's catalog, [18].

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