Polymeric Composite Materials Reinforced with Protein Fibers - Variation of the Mechanical Properties Depending on the Concentration of the Reinforced Material

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The paper presents the results obtained by the authors in the research of the mechanical behaviour variation of the polymeric reinforced with protein fibers composite (CFP) depending on the reinforcing material concentration in the elastomeric matrix. The determination of the mechanical behavior variation depending on the reinforcing material concentration is important not only to establish a convenient concentration to obtain some mechanical properties required in any field of application, but for obtaining an optimal method of choice of some values in its concentration, so that the composite material to satisfy a certain property (value) or even a number of mechanical properties.

Keywords: CFP, variation, mechanical properties, reinforcing concentration

The mechanical properties of the composite materials have a great importance for use in their high performance and maximum safety conditions in various fields of application.

The polymeric reinforced with protein fibers composite material based on elastomer butadiene-co-acrylonitrile and the protein wastes resulted from the leather industry as reinforcing material, is designed for a wide range of products used in aggressive working environments (solvents, petroleum oils, acids, bases etc.): gaskets, shoe soles, carpet protection, etc. To satisfy a large range of applications it is necessary to have available a tool with which we can vary, in the manufacturing process, the mechanical properties of plastic or composite material. For the CFP composite material, a parameter whose choice leads to obtaining some desired properties is the leather wastes concentration in the elastomeric matrix. Obvious that the polymer materials used in composites benefit from such a possibility for the prediction of properties, some can have even more eligible parameters so that to be realized as accurately certain values of concerned mechanical properties. In this article is illustrated the used technique for obtaining some properties to the desired values by the user. Obviously, the study can be intensively generalized (up to total mathematization) and extensive (in a wide range of materials). Moreover, can be built functions or estimators of economic efficiency starting from the same accurate determination of the mechanical properties variation depending on the variation of the concentration of a material constituent. The results can be also applied to the chemical properties or other kind of the material. Our approaches are not entirely unique, the study of the mechanical properties in general has been widely investigated for plastic materials, [1-5]. The variations problem of these properties with the concentration of some constituents was also approached, but not carried to complex applications of these variations, [6-8].

Experimental parts

Material and methods

Making the CFP based on elastomeric wastes followed several steps:

- grinding elastomeric waste;
- making the mixtures;
- chemical and physico- mechanical characterization of the resulted materials.

Each of these phases is characterized by working conditions, equipment and various materials.

Grinding the elastomeric waste was carried out with the knives and site mill for waste used in compounds of plastics.

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Name of material	[UM]	CFP1	CFP2	CFP3	CFP4	CFP5
Butadiene-co-acrylonitrile 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
Oil Sumparo	g	30	30	30	30	30
Antioxidant IPPD	g	9	9	9	9	9
Sulfur	g	6	6	6	6	6
Th Accelerator	g	4,5	4,5	4,5	4,5	4,5
D Accelerator	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

Table 1
POLYMER COMPOSITE FORMULATIONS WITH VARYING PROPORTIONS OF LEATHER WASTE

Making the mixtures was performed on a laboratory roller with electric heating. There were made several types of compounds depending on the varied content of leather waste, according to table 1.

The order of the materials introduction, and processing time in the roller of the polymeric compounds are listed in the table below:

Nr.c rt.	The order of entry	The times for the materials introduction (min.)
1	The elastomer	0
2	Antioxidant + Stabiliser	2
3	Finite leather waste	5
4	Plastifiant + batches	17
5	Protective agent	26
6	Discharge and refining	35

The test specimens were made by compression in specific molds and vulcanization.
Chemical and physico- mechanical characterization of resulted composite materials was performed according to the standards.

The mechanical tests of the composite materials are regulated by standards, [9-15]. In the fig. 1, 2, 3, 4, 5, 6, 7 and 8 are plotted the experimental results obtained for the tested mechanical properties of the CFP material, for a new material and for an accelerated aging material.

The accurate experimental values are represented by the broken lines peaks, the segments between them being only interpolation line segments.

Obvious that can be obtained much better quality interpolation, but a satisfactory accuracy is guaranteed only by a large number of experimental data.

From elementary graphical representations of the experimental data can be drawn several important conclusions for the development that follows.

It can be noticed that some mechanical characteristics (the fewest as number), have a monotonic variation in relation to the concentration of leather wastes in the material (the Shore hardness, density and elongation at break in the version of aged material, according to the standard [13]).

Another part of the mechanical characteristics varies with the concentration of leather wastes in the elastomer matrix, having a well-defined global direction (increasing or decreasing) with negligible local minimum or maximum (elasticity, elongation at break in the version of the new material (new manufactured material, unused), the residual elongation and the Shore hardness).

Finally, a third category of characteristic curves is formed by those curves having not negligible extreme points (tensile strength, tear strength, maybe even the elongation at break in the version of aged material, according to the standard [13]).

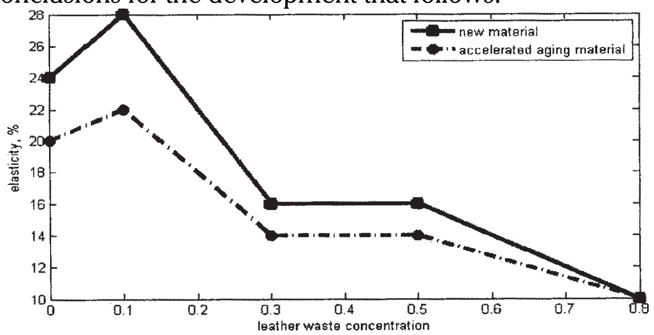

Fig. 1. CFP elasticity variation depending on the concentration in leather +wastes

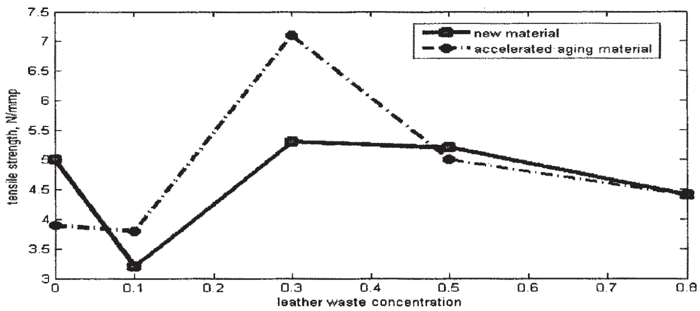

Fig. 2. CFP tensile strength variation depending on the concentration in leather wastes.

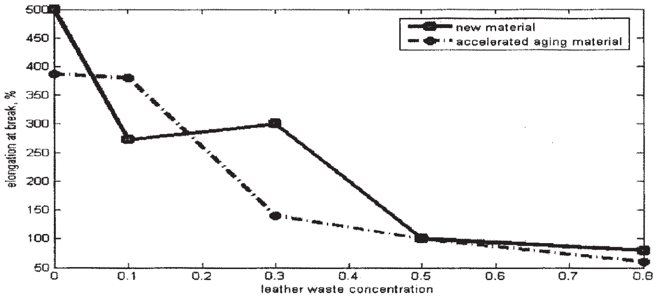

Fig. 3. CFP elongation at break variation depending on the concentration in leather wastes

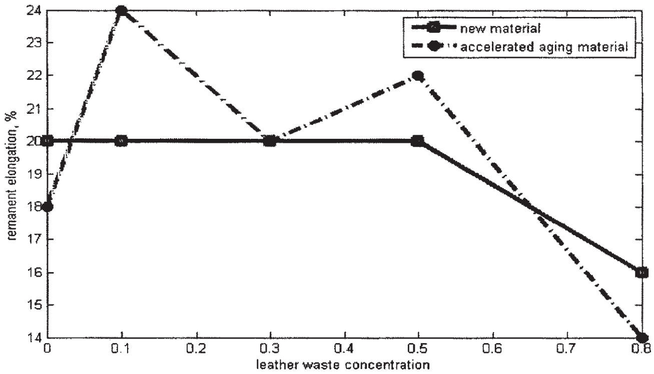

Fig. 4. CFP residual elongation depending on the concentration in leather wastes.

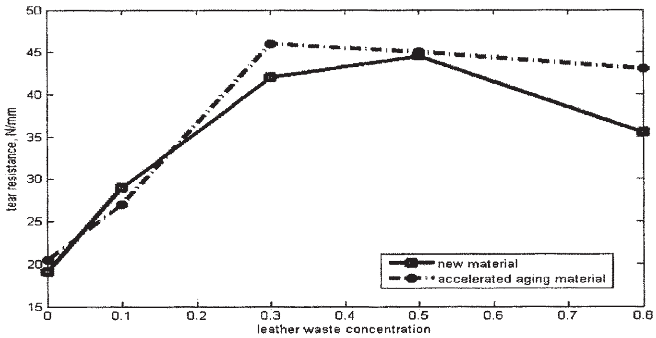

Fig. 5. CFP tear resistance depending on the concentration in leather wastes

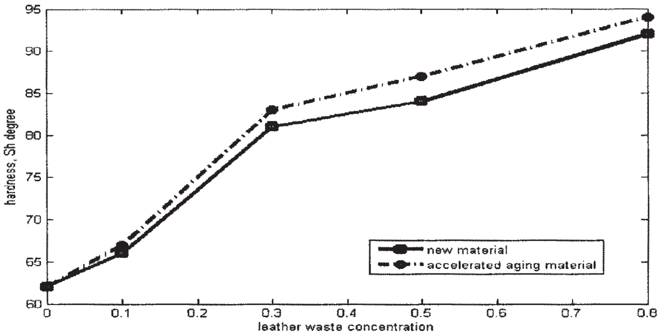

Fig. 6. CFP Shore hardness depending on the concentration in leather wastes

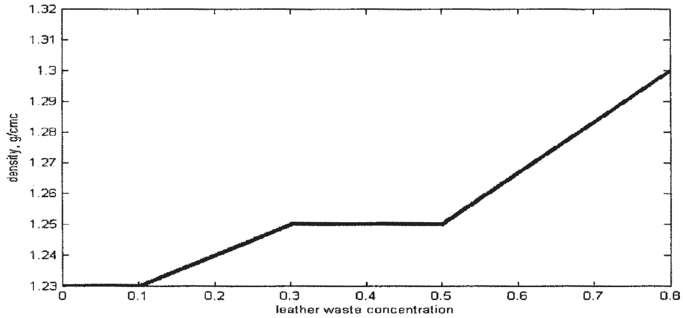

Fig. 7. CFP density variation depending on the concentration in leather wastes

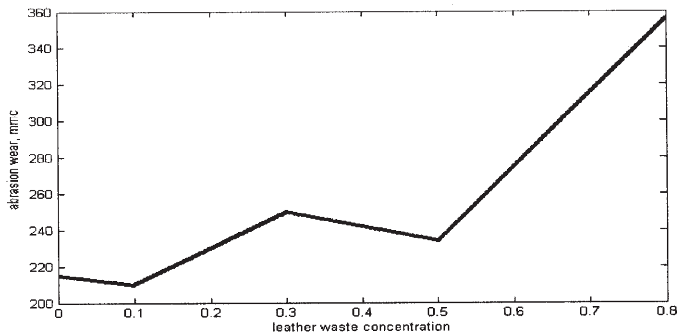

Fig. 8. CFP abrasion wear variation depending on the concentration in leather wastes

Phenomena like mechanical characteristics that present not negligible extreme points (when, for example is interpolated such a curve), are not new, [7, 16]. Obvious that these variations should be explained, very likely through the structure of the material, but this is a different problem than the one addressed in this article. In this article we will show how we can take advantage of the mechanical characteristics obtained to choose a convenient concentration to obtain a material as close to the client's needs.

Results and discussions

In order to facilitate the understanding of the presented ideas in the article, will be given a few examples illustrating the use of the experimental data in order to elaborate some varieties of the CFP material to match the various customers' requirements.

Elastic and low hardness

Suppose that we need to use a CFP composite in the manufacture of some footwear soles to be elastic (elastic sole primarily) and soft (hardness as small as possible). The question is whether there is a value of the residues leather concentration in the composite with rubber matrix, which realize the best composite from this point of view, namely to satisfy in the the greatest extent the requirements of a potential customer. The problem is actually an optimization problem. We have an optimization parameter: leather wastes concentration in the composite, we have two objective functions (elasticity, which must be maximized and hardness, which must be minimized) and we have a restriction on which we cannot passes for reasons of experimental substantiation: limiting the concentration of leather residues in the composite. These values are not allowed to exceed the experimental limits, namely they must be between 0 and 29%.

Complexity of the problem is given by the fact that we have two objective functions, not one, because the footwear must be not only elastic but also to have adhesion to the movement surface. And because a function must be maximized and the other one minimized, can form a single objective function as the ratio between the two, a compromise between the two requirements.

For example, if we note the elasticity with *e* and the composite material hardness with *d*, then the objective function will be of the form:

$$f(c) = \frac{e(c)}{d(c)} \qquad (1)$$

where *c* is the concentration of the leather residues in the composite material. Obviously, intuitive should to maximize

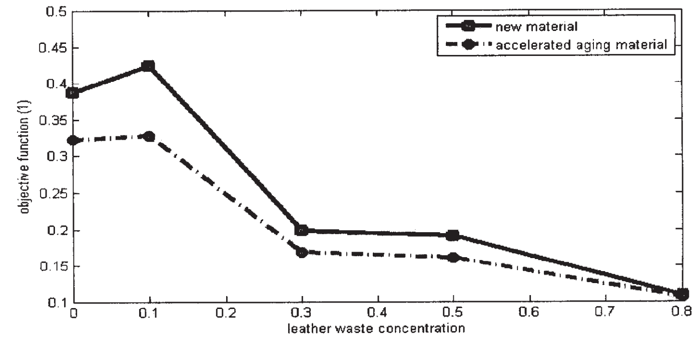

Fig. 9. CFP elasticity / hardness Shore ratio variation depending on the concentration in leather wastes

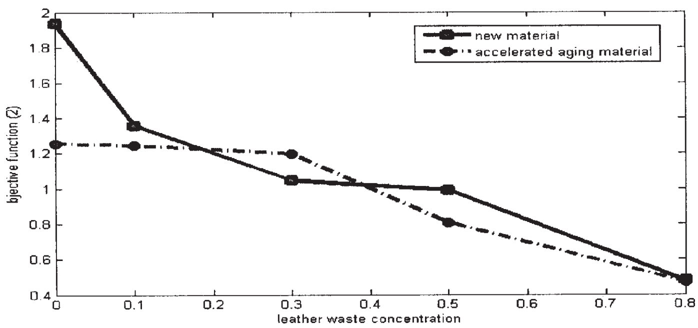

Fig. 10. Variation of the objective function (2) in relation to the concentration in leather waste

the function f defined by (1). The functions of this kind being only numeric functions, actually strings of real numbers, can be extended by various interpolation between the points empirically determined.

A simple graphical representation shows if there is an extreme point of interest, in this case a maximum (fig. 9). It can be noticed that the best percentage to produce a composite with high elasticity and minimum hardness qualities is about 10%.

As a result of such an optimal study we can provide to a potential producer of soft and elastic rubber material, such a composite, with the optimal percentage of leather wastes that achieves both proposed goals.

As an addition it is mentioned that the entire study can be repeated on the mathematical interpolated functions through exact formulas with which the optimal points to be found, possible, analytically. However in this case too, the accuracy depends on the set of the experimental data used.

In addition, must be shown that according to figure 1 and figure 8, the hardness has somewhat lower values in the area of percentages below 15%, and the elasticity has itself a maximum in the vicinity of 10%.

Therefore it was anticipated that such an optimal point for the objective function (1) exists and is located somewhere in the vicinity of the 10% concentration.

Elastic, low hardness and tensile resistant material

Except for the high elasticity and low hardness may be requested in a composite material used for various purposes (footwear sole), for example, must also be tensile resistant.

It is denoted by σ_r, the tensile strength of the material. In order to obtain a function which, to give an optimal point for this version of material, is proposed the objective function:

$$f(c) = \frac{e(c)\sigma_r(c)}{d(c)} \quad (2)$$

The graphical representation of the function tensile strength (fig. 2) and the one of the elasticity function, show that these functions have clear maximum in the experimental range.

However, the objective function (2) has no extreme points, as seen in figure 10.

Elastic, low hardness, tensile and tear resistant material

For this material is required, in addition to the material from the previous section, tear resistance. After the technique described above, is looking for a possible maximum point of the objective function:

$$f(c) = \frac{e(c)\sigma_r(c)\sigma_s(c)}{d(c)} \quad (3)$$

where σ_s is the tear resistance.

The graphical representation of the objective function variation (3) in relation to the leather wastes concentration in the composite material is given in figure 11.

Elastic, low hardness and light material

A composite material of the type discussed in this paper can be called elastic, soft (hardness as small) and light (the smaller the density), when its concentration in leather residue minimizes the objective function:

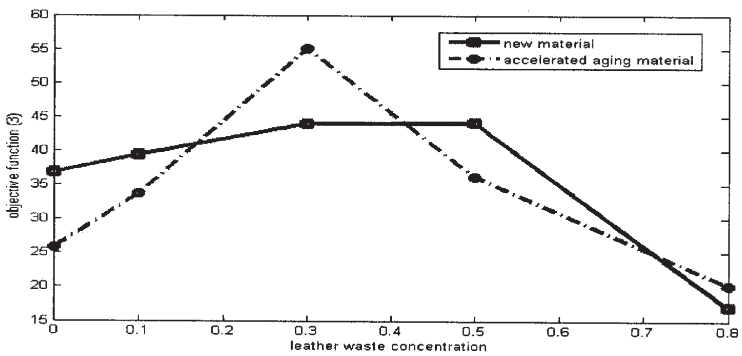

Fig. 11. Objective function variation (3) in relation to the leather wastes concentrations

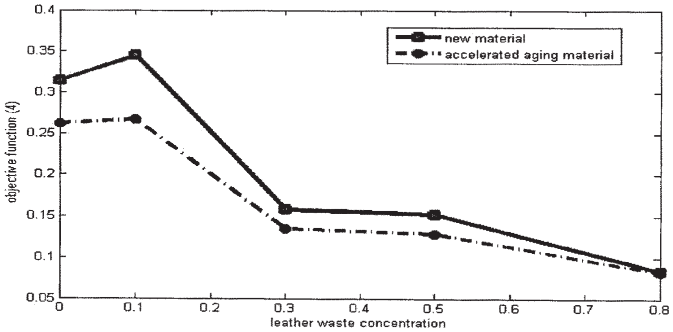

Fig. 12. Objective function variation (4) in relation to the leather wastes concentration

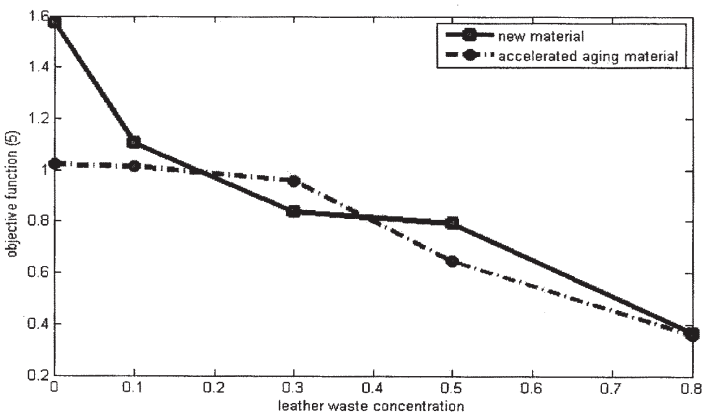

Fig. 13. Objective function variation (5) in relation to the leather wastes concentration

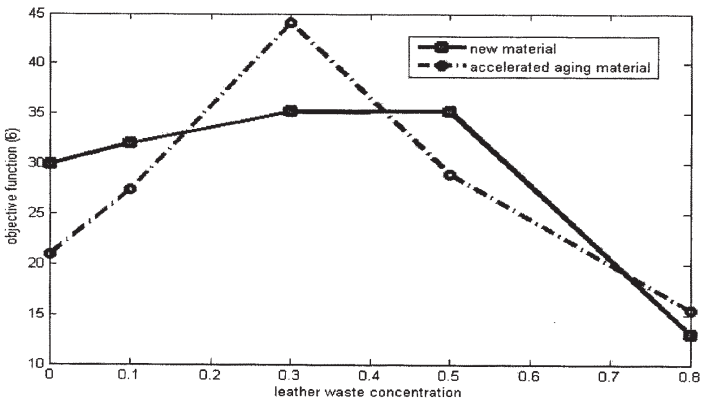

Fig. 14. Objective function variation (6) in relation to the leather wastes concentration

$$f(c) = \frac{e(c)}{d(c)\rho(c)} \qquad (4)$$

where $\rho(c)$ is the density of the composite material.

As can be seen from figure 12, this composite material exists, corresponding to concentration that realize the maximum of the curve which represents the graphical representation of the objective function (4). This concentration represents the recipe for the most elastic, soft and light achievable material with this composite (about 10% for both original material and for the aged one).

Elastic, tear resistant, soft and light material

Another type composite material that forms the subject of these works can be defined to be of good quality, when satisfies the conditions required of elasticity, tear resistance, and also to be soft and light.

The definition of this type of composite material studied (rubber with leather residues insertion) is obtained by the function that is defined to maximize these properties:

$$f(c) = \frac{e(c)\sigma_r(c)}{d(c)\rho(c)} \qquad (5)$$

If the function (5) admits a global maximum point then the concentration of the leather residue corresponds to the manufacturing recipe of the composite material with the required properties.

This brief theory is valid for all types of requirements expressed in this study.

The curve that plots the objective function (5) is shown in figur e 13.

The curve shows that the only point of global maximum is in the left extremity of the experimental interval of the leather residues concentrations, namely at the null value of this concentration.

In conclusion, the material that satisfies the condition of this example is pure rubber (both for the original material and for the aged one).

Elastic, tear resistant, low hardness and light material

Finally a last possible material gave as an example, is a composite material elastic, tensile resistant, tear resistant, light and soft, with the proper function of the form:

$$f(c) = \frac{e(c)\sigma_r(c)\sigma(c)}{d(c)\rho(c)} \qquad (6)$$

The graphical representation of the objective function (6) is the curve from figure 14. The curve shows that there is a global maximum point that indicate for the material with the proposed properties a concentration of the leather residues between 30 and 55% for the initial material and 30% for the aged material.

Conclusions

The obtained results confirm the possibility to obtain variants of the CFP material with optional properties, depending on the choice of leather wastes concentration in material.

The qualities required to the CFP material composite variants are expressed at the level of this article in unquantified terms, specific to the ordinary consumers: elastic, *low or high hardness*, light. The next step will need to quantify these properties.

For example, will be able to make difference between a sole that allows slip on a surface under certain conditions and another that is fixed and does not allow slippage.

Achieving this high accuracy keep of two extremely important factors: performing a large number of experiments to cover denser the range of interest of concentrations in leather wastes and, the calculation of some interpolation functions how higher accuracy (precision).

Achieving these two conditions can lead to the construction of a mathematical model of the manufacturing process of the material, to be put in the form of algorithms and writing in a computer program to assist the production.

Are thus placed the bases to achieve a production assisted by the variants of CFP with mechanical properties of an increased precision.

In a wider mathematical context you can add functions to achieve optimal solutions at the global level (energetic).

Aknowlegement: The work of Natalia Popa was supported by Project POSDRU/107/1.5/S/76903. The work of Viorel Stefan Minciuna was supported by Project SOP HRD - PERFORM /159/1.5/S/138963

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Manuscript received: 29.04.2014