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THE INFLUENCE OF INORGANIC PARTICLES ON CHARACTERISTICS OF POLYMER MATRIX COMPOSITES

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Abstract: *The study presents simplified approximations that allow the evaluation of the unidirectional longitudinal and transverse modulus of a composite material, starting from the elastic properties of the constituents (inorganic particles, matrices) as well as its relative properties. In calculations, the response of the composite material is assimilated with an associated system of particles and matrices*

Key words: *polymer matrix composites, inorganic particles, modulus of composite material.*

1. INTRODUCTION

The influence of reinforcing agents – inorganic particles – on mechanical properties is undoubtedly the most important motivation for the development of research on polymer-type composites – inorganic particles. Numerous research have been done on systems containing micrometer-sized particles [1-3]. Broadly speaking, four important factors are considered in determining the mechanical characteristics of a composite system with inorganic particles, namely:

- the composition of the system, the choice of the matrix, the reinforcing agent and the fraction of the inorganic phase,
- the type of interaction at the polymer interface - the inorganic particle,
- geometric factors of inorganic charges,
- the state of dispersion of the particles.

It is worth emphasizing that these four parameters apparently of variable importance condition the properties we intend to investigate, and that their manifestations are interdependent. In this study, we try to approach relationships that are established between the morphological parameters and the mechanical properties of the composites considered.

A very important factor in determining the mechanical characteristics of the composite material is the relative proportion of the matrix and the curing agent. This proportion can be expressed either in volumetric fraction (or fraction in percentage of volume) or in mass fraction (or fraction in percentage of mass). The mass fraction is very difficult to measure when the material is obtained. The volumetric fraction intervenes directly in theoretical models, describing the behavior of materials. It is therefore necessary to know the relations of passage from one fraction to another. These relationships are established for a two-phase material and then extended for composites with more than two phases.

1. 1 Theoretical considerations

As mentioned, the use of inorganic fillers in thermoplastics leads to an increase in the values of modules that appear to be at high temperatures [4]. The effect of introducing inorganic particles into thermoplastic matrices becomes a strong effect as the temperature at which the process takes place approaches or even exceeds the main relaxation temperature of the matrix, which is illustrated in figure 1.

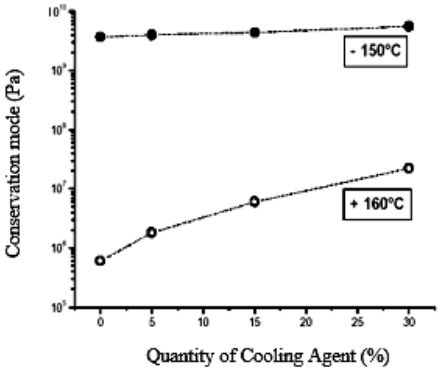


Figure 1. Evolution of the preservation of a polyhydroxyethyl methacrylate-silica composite of -150°C (in the vitreous domain) and +160°C (in the rubber domain)

To realize this increase, it is necessary for theoretical treatments to exploit the available information on different compounds whose parameters are easily accessible, the modules of the constituents, the volumetric fraction of the reinforcing agents, possibly their geometry. Unknown data are therefore subject to these assumptions.

It should be noted that the numerous approximations of these reinforcement problems, developed especially in the case of elasticity, can be understood by viscoelasticity by replacing the elastic constituents by their homologous complexes, as defined in Hashin's correspondence principle.

From the data in the literature [6], we can see that there are two very particular categories of approximations:
- hydrodynamic approximations, or theories of rigid inclusions in matrices that it does not have. They are generally based on the development of semi-empirical equations in rheology and transposed under various conditions. After these approximations (of Einstein and Mooney), Ahmed reserved a particular place for Kerner's approximation.

The latter author determines in fact the mechanical response of a hydrostatic pressure of an assembly consisting of a spherical rigid particle inserted into a matrix, with a perfect interfacial adhesion. In the case of reinforcing agents with a modulus greater than that of the matrix, the shear modulus Gc of the composite can be determined starting from the following equation:

$$\frac{G_c}{G_m} = 1 + \frac{V_f}{1 - V_f} \cdot \frac{15(1-\nu_m)}{8 - 10\nu_m}$$

with V_f the volumetric fraction of the reinforcing agent, ν_m and G_m the Poisson coefficient and the shear modulus of the matrix.
- micromechanical approximations or the theory of rigid inclusions in a rigid matrix, or homogeneity theories that are particularly addressed here and the finite element method.

The principle of this type of approximation consists in determining the macroscopic behavior of a charged system starting from the answer given by a sample or the Representative Elementary Volume (V.E.R.), which is in fact the smallest structure that we can define from inside the composite and which preserves all the characteristics of the phases present (it is schematically represented for a composite with inorganic particles (figure 2) [7-9].

In approaching this approximation, the localization stage is the stage of determining the localized mechanical fields that take place inside the Representative Volume starting from the microscopic data, being the most difficult stage.

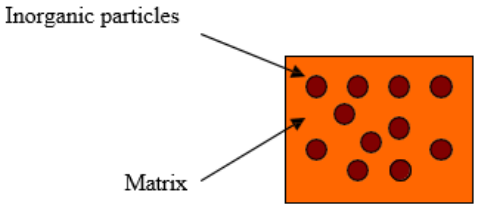


Figure 2. Schematic representation of the morphology of a polymer reinforced with inorganic particles – Representative Elementary Volume (V.E.R.)

A possible solution to the localization problems consists in using the energetic criteria (the approximations being called variational) that lead to the determination of the limits, defining a domain for the researched modules. According to Reuss and Voigt, limits are the simplest arrangements for a material consisting of two phases (the limits are also called the law of mixtures), of external stresses (Reuss) or of deformation (Voigt). Also, the boundaries are defined as uniform in the two phases.

These limits were also confirmed by Hashim and Shtrickman, considering the Poisson tension of the two constituents. In particular, the difference between the upper and lower bound of this approximation depends on the ratio of the particle's modulus to that of the matrix. The limits defined by Hashim and Shtrickman delimit a model corresponding to the series-parallel models proposed by Reuss and Voigt.
These limits, however, define a field of validity for exact theoretical approximations. The latter allows the evaluation of the elastic constants of the composite system starting from the behavior of an equivalent homogeneous environment, subjected to a field of external stresses and deformations. Among other models, the generalized self-coherent approximation is of clear interest. The representative inclusion (V.E.R.) of the loaded polymers is introduced into a reference medium, which we consider to be equal to the medium to be investigated. The choice of the reference medium allows the estimation of the elastic properties of the composite system by solving the self-coherence equation. In the case of the simplest model, figure 3, which defines the representative cell of the material: V.E.R., consisting of three phases: the reference medium, also called the equivalent homogeneous medium. The self-coherent equation defined on a similar system is of secondary order.

The correspondence between the self-coherent models and the experimental results obtained by mechanical spectrometry was illustrated in the case of polymers with low percentage of reinforcement, with very well distributed spherical micron agents over the entire temperature range used by the material.

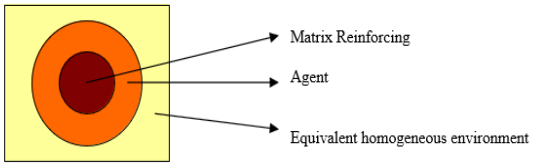


Figure 3. Schematic representation of a composite system according to a generalized self-coherent three-phase model

But the founding hypothesis of this type of approximation (elliptical and well-dispersed charges, perfect interfacial adhesion, fraction of limited reinforcing agent) remains the field morphological logic of the materials that can describe the behavior. Also, these models have been adopted and can be modified taking into account the effects of size, aggregation, form factor of the reinforced agent observed on the composition of the loaded polymers [10, 11].

In general, the beginning of homogeneity calculations consists in determining the fields of stresses and deformations inside V.E.R. imposing certain conditions of them at its border. Starting from this information it is possible to calculate the average voltages in the direction *of i* inside the volume element, according to the equation:

$$\overline{\sigma_i} = \frac{1}{V}\int_V \sigma_i dV$$

in the same way, the average deformation is given by the equation

$$\overline{\varepsilon_i} = \frac{1}{V}\int_V \varepsilon_i dV \text{ , cu i = 1.....6}$$

Starting from the average of stresses and deformations on the V.E.R. assembly, it is theoretically possible to determine the elastic properties of the homogenized material. The exact solutions are given by the field of stresses and deformations at each point of the V.E.R., these can only be obtained in the case of simple and idealized geometric models.
In practice, we can also obtain samples of the moduli of the material by approximations based on simplified assumptions of the mechanical behavior of the V.E.R. The simplest model being that of a unidirectional material [12].

1.2 Young's Modulus

Young's longitudinal modulus is determined by a tensile test in the X direction.

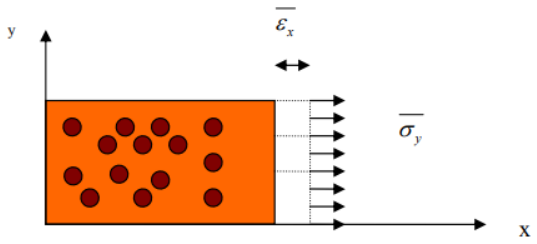


Figure 4. Simple diagram of a longitudinal traction

Starting with the expressions (2) and (3) we can write:

$$\overline{\sigma_x} = \frac{1}{V_p}\int_{V_p} \sigma_x dV + \frac{1}{V_m}\int_{V_m} \sigma_x dV$$

where $\overline{\sigma_x}$ is the average tensile voltage of the V.E.R.

From this data we can deduce the relationships for the average voltage in the particles and the matrix, respectively:

$$\overline{\sigma_{px}} = \frac{1}{V_p}\int_{V_p} \sigma_x dV \quad \text{si} \quad \overline{\sigma_{mx}} = \frac{1}{V_m}\int_{V_m} \sigma_x dV$$

where $\overline{\sigma_{px}}$ and $\overline{\sigma_{\mu\xi}}$ are the average voltages in particles and matrices.
Thus:

$$\overline{\sigma_x} = v_p\overline{\sigma_{px}} + v_m\overline{\sigma_{mx}}$$

A simplified hypothesis consists in considering that the deformation is uniform and identical both in the particles and in the matrix so: $\overline{\varepsilon_x} - \overline{\varepsilon_m} - \overline{\varepsilon_p}$

If we hypothetically consider linear elastic behavior (Hooke's law) for particles and matrices, we also obtain:

$$\overline{\sigma_x} = \left(v_p E_p + v_m E_m\right)\overline{\varepsilon_x}$$

Thus, the expression of Young's modulus is given by the relation:

$$E_x = v_p E_p + v_m E_m$$

1.3 Transversal Module

Requesting V.E.R. previously defined in the transverse direction y, $\overline{\varepsilon_y}$ is defined as the average strain and is given by the reality

$$\overline{\varepsilon_y} = v_p\overline{\varepsilon_{py}} + v_m\overline{\varepsilon_{my}}$$

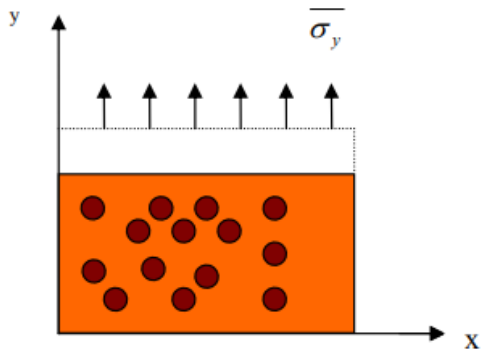


Figure 5. Simple diagram of a transverse traction

The transversely applied force can be transmitted entirely in particles and matrices, so the applied load is uniform and identical in particles and matrices.

$$\overline{\sigma_y} = E_m \overline{\varepsilon_{my}} = E_p \overline{\varepsilon_{py}}$$

we obtain:

$$\overline{\varepsilon_x} = \left(\frac{\nu_p}{E_p} + \frac{\nu_m}{E_m} \right) \overline{\sigma_y}$$

The transverse modulus E_y is defined by:

$$\frac{1}{E_v} = \frac{\nu_p}{E_p} + \frac{\nu_m}{E_m}$$

1.4 Longitudinal Shear Module

Considering the same V.E.R., we can write that the average shear stresses in the matrix and particles are identical and equal with τ.

$$\overline{\gamma_p} = \frac{\bar{\tau}}{G_p} \quad \text{si} \quad \overline{\gamma_m} = \frac{\bar{\tau}}{G_m}$$

with G_p and G_m the shear modules from particles and matrices. Analogously we can write:

$$\frac{1}{G_{xy}} = \frac{\nu_p}{G_p} + \frac{\nu_m}{G_m}$$

If the approximation of the parallel model gives the correct results for Ex, the series model generally gives the values below the values E_y. This translates into the fact that a transversely stressed unidirectional composite is not a pure serial model [7].

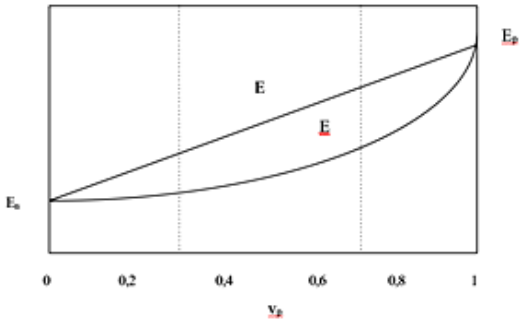


Figure 6. E_x and E_y values according to the amount of reinforcing agent

In general, we can consider that, for a given v_f value, the values E_x and E_y defined above give a range of the possible values of the modulus of the composites even if we change the shape (particles, fibers) or the dispersion (tissue, material) of the reinforcing agent [7].

There are significant differences between longitudinal and transverse elastic modulus, for the same proportion of reinforcement material, in the case of fiber reinforcement. This behavior can be seen in Figure 6.
In case of spherical particle reinforcement, the elastic behavior is the same in either direction and the curves Figure 6 overlap.

2. THE EXPERIMENTAL PART

The experimental program contains two steps: obtaining composite material from epoxy resin (polymer matrix) and chalk powder (as filler) followed by the observation of the structural changes produced after tensile testing of the composite material. The tests were performed on specimens having inorganic particles (calcium carbonate powder) in their constitution at nanoscopic scale.

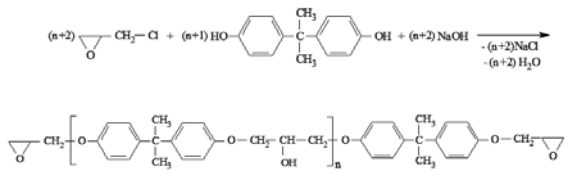
2.1 Obtaining the macromolecular composite material

Incorporating inorganic powders into the polymer matrix aims to improve certain mechanical properties or modify the surface properties of the matrix. The filler, a material with a low price, contributes to the significant decrease in the cost price of the composite.

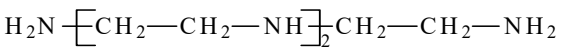
The polymer matrix

Epoxy resins occupy an important place in the production of composite materials due to their very good physical-mechanical properties.

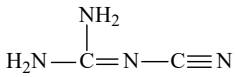
Epoxy resins for general use are obtained by the polyaddition of bisphenol A with epichlorohydrin, according to the following general reaction:



The oxiranic groups give the resin the reactivity required for crosslinking. Curing of epoxy resins can be done at room temperature with primary or secondary amines (eg TETA - triethylenetetramine), or at high temperatures (t~180^{0}C) with amines (dicyandiamide) or with anhydrides.



Chemical formula a triethylenetetraamine



Chemical formula a dicyandiamides

The reinforcing agent

The properties of the composite depend mainly on the chemical nature and granulation of the powder. Micronized chalk is obtained by finely grinding limestone. To avoid the formation of agglomerations, the powder must be dry.

Material	Properties
Epoxy resin DINOX 010-S	Density ρ_R = 1,25 g/cm^3
TETA or DDA	
Dibutilftalat	
Calcium Carbonate (Powder)	Density ρ_C = 2,71 g/cm^3
Demoulding agent (petroleum wax in CCl_4)	
250 ml flask equipped with a stirring system and thermostated	
Die	

1. The ratio between the reinforcing agent and the resin is chosen. (A = 20 %)

2. The volume of the VM mold is determined.

In our case, the volume of the mold (a parallelepiped with dimensions: L=12 cm, l=10cm, h=2cm) is: V= LxWxH= 12x10x2=240cm^3.

Considering the additivity of the volumes, the volume of the mold is described by the relation:

$$V_M = V_C + V_R$$

where: V_C is the volume of calcium carbonate powder; V_R is the volume of epoxy resin.

3. Calculate the required amounts of resin (m_R) and calcium carbonate powder (m_C), knowing the mold volume (V_M) and the densities:

$$m_R = 1{,}15 \cdot \frac{100 - A}{100} \cdot V_M \cdot \rho_R$$

$$m_R = 1{,}15 \cdot \frac{100 - 20}{100} \cdot 240 \cdot 1{,}25 = 276g$$

$$m_C = 1{,}15 \cdot \frac{A}{100} \cdot V_M \cdot \rho_C$$

$$m_C = 1{,}15 \cdot \frac{20}{100} \cdot 240 \cdot 2{,}71 = 149{,}6g$$

4. Dibutyl phthalate is added to improve the elasticity of the composite material. (10% compared to the resin).
5. TETA or DDA (hardening agent) 7% to the resin.

Work procedure

Calcium carbonate - micronized powder is placed in the oven at 100-120^{0}C for one hour to remove moisture.
To avoid adhesion of the mold resin, the active surfaces are smeared with a release agent.

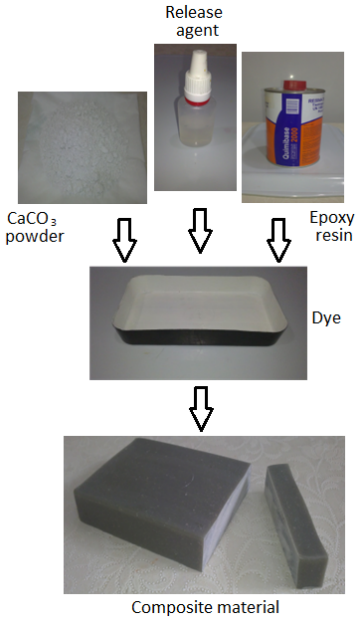


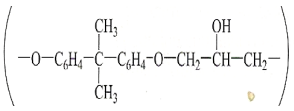
Figure 7. Obtaining the composite material

The casting resin is prepared by introducing the epoxy resin and the plasticizer into a flask equipped with a stirring and heating system. Heating to 60^0C ensures fluidization of the resin (decrease in viscosity) in order to incorporate the powder more easily and avoid the formation of air inclusions.

After approx. 15 min from the beginning of the heating, add the calcium carbonate powder in 6 portions, at intervals of 15 min. Advanced homogenization is essential to obtain a material with the designed properties.

The casting resin thus prepared is emptied into a glass and allowed to cool for approx. 20 min, after which the hardener is added. The mixture is homogenized for about 5 minutes, after which it is poured into the mold and left for 24 hours to complete the crosslinking reaction.

The general formula for epoxy resin is:



3. RESULTS AND DISCUSSIONS

In Figure 8 it can be seen the differences in microstructure of a pure polymer matrix (left) and the microstructure of a composite material reinforced with $CaCO_3$ (right). In the left side there are only long molecular chains (covalent bonding) and in the right side the structure is more compact (ionic bonding between molecular chains).

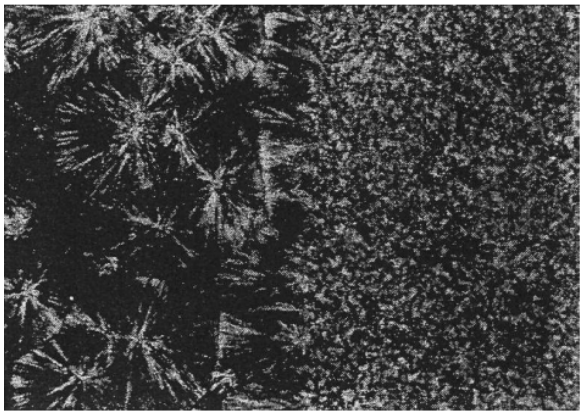


Figure 8. Polarized light optical microscopy of simple epoxy resin (left) and a Resin /$CaCO_3$ mixture (right) [13]

It has been performed tensile tests on manufactured materials in order to measure the tensile strengths and Young module. The experimental curves for a simple epoxy resin, a composite material with $CaCO_3$ reinforcing agent and a composite material with $CaCO_3$ reinforcing agent treated with stearic acid are shown in Figure 9.

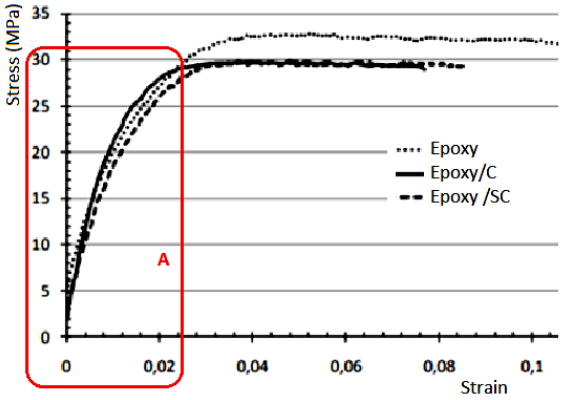


Figure 9. Tensile curves for simple epoxy resin and reinforced with $CaCO_3$ (Epoxy/C) and Ca stearate (Epoxy/SC)

The tests were performed according to the ISO 527-1 standard. The traction curves have a classical shape specific for polymeric materials with a relatively well-represented flowing region [14].

It can be observed that the tensile strength of pure resin is slightly higher (33 MPa) than in case of reinforced ones (30 MPa) (Figure 9). The matrix became discontinuous due to the presence of particles and the number of polymer chains which support the traction force decreases. As effect the tensile strength also decreases.

It is obvious that the calcium carbonate particles cannot provide a real reinforcement in comparison with case of composite materials reinforced with fiber.

However, as it can be shown in Fig.10, the elastic modulus of material reinforced with calcium carbonate is higher (the particles have a positive influence on the stiffness of material).

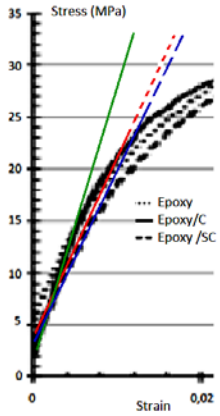


Figure 10. Stress-strain curves (detail A)

The superior stiffness of composite with calcium carbonate (3077 MPa) in comparison with stiffness of pure resin (2083 MPa) demonstrates that additional bonds are created between the resin and the particle.

4. CONCLUSIONS

The object of this work was to experiment the behavior of polymers reinforced with inorganic nanoparticles and provides elements that help to understand their behavior in general outside the established rules for materials loaded with micrometric particles.

Our objective was to study in particular the effective dispersion of calcium carbonate particles in an epoxy resin matrix and the interactions and effects of the dispersion on the performance properties of these materials.

The formed composite materials show increased stiffness, due to the appearance of new bonds between the polymer matrix and the reinforcing agent.
The calcium stearate formed by treating $CaCO_3$ with stearic acid favors this de-agglomeration and limits the re-agglomeration of inorganic particles, giving the macromolecular compound an increased rigidity

The presence of inorganic particles has an influence on the mechanical properties of the reinforced polymers.

The order of the morphological parameters approached will be as follows: the influence of the amount of reinforcing agent, the form factor of the particles used and the effect of the dispersion state of the reinforcing agents that will be confronted with different mechanical approximations.

Inorganic charges in thermoplastics lead to an increase in the values of the modules that occur at high temperatures.

REFERENCES:

[1] Ahmed S., Jones F. R., A review of particulate reinforcement theories for polymer composites, Jour. Mat. Sci., 1990, vol. 25, n°12, p. 4933-4942

[2] Georgeta Comeleata, Cristiana Enescu, Mirela Zaharia Materiale compozite cu matrice polimerica, vol. I, Ed. Printech, Bucuresti, 2006, ISBN (10) 973-718-506-4 ; ISBN (13) 978-973-718-506-8.

[3] E.Gacoin, C.Fretigny, A. Chateauminois Measurement of the mechanical properties of thin films mechanically confined within contacts'Tribology Letters 21, N°3 (2006) 245-252

[4] George Frederic Vander Voort, G.M. Lucas, E.P. Manilova, Metallography and Microstructures ofStainless Steels and Maraging Steels, ASM Handbook, Volume 9: Metallography and Microstructures, G.F. Vander Voort, editor, p670, DOI: 10.1361/asmhba0003767,2004.

[5] Bonet M. Homogeneisation des milieux aléatoires;Bornes et estimations d'ordre deux. Méthodes d'homogeneisation en Mécanique des matériaux. Notes de cours. Ecole thématique du CNRS, La Londe les Maures, septembre 1998, p. 169 – 199.

[6] Maria Cristiana Enescu – La simulation de rézistence à la traction et compression dans un composite macromoléculaire Revista 'Buletinul Stiintific al Universitatii Politehica Bucuresti', seria B : Chimie si stiinta materialelor – ISSN 1454-2331

[7] J.M.Berthelot, Materiaux composites. Comportament mecaniques et analyse des structures, 3^e edition, TECHNIQUES &DOCUMENTATION,1999

[8] Elena Valentina Stoian, Experimental research and compaction behaviour modelling of materials composite with polymeric matrix, The Scientific Bulletin of Valahia University, Materials and Mechanics, vol. (9), nr.12, 2014, pag.7-11, ISSN 1844-1076

[9] Elena Valentina Stoian, Ionita Gheorghe, Cristiana Zizi Rizescu, Jana Pintea, Dan Nicolae Ungureanu, Polymeric Composite Armed with Powder, RECENT RESEARCHES in COMMUNICATIONS, AUTOMATION, SIGNAL PROCESSING, NANOTECHNOLOGY, ASTRONOMY and NUCLEAR PHYSICS, 3rd WSEAS International Conference on NANOTECHNOLOGY (NANOTECHNOLOGY '11), Cambridge, UK February 23-25, 2011, pp.271-276, ISBN:978-960-474-276-9

[10] S.YFu , X.Q. Feng, Bernd Lauke , Yiu-Wing Mai, Effects of particle size, particle/matrix interface adhesion and particle loading on mechanical properties of particulate–polymer composites, Composites Part B: Engineering,Volume 39, Issue 6, 2008, P. 933-961,

[11] J. Z. Liang, A. Li, Inorganic Particle Size and Content Effects on Tensile Strength of Polymer Composites, Journal of Reinforced Plastic AND COMPOSITE, 29(14):2744-2752, DOI: 10.1177/0731684409359216, 2010

[12] Ting Liu, Jihui Zhong, Effect of Dispersion of Nano-inorganic Particles on the Properties of Polymer Nanocomposites, IOP Conf. Series: Materials Science and Engineering 563 (2019) 022026 IOP Publishing doi:10.1088/1757-899X/563/2/022026,2019

[13] B. Pukánszky, K. Belina, A. Rockenbauer, F. H .J. Maurer. Effect of nucleation, filler anisotropy and orientation on the properties of PP composites. Composites, Vol. 25(3), pp. 205–214, 1994

[14] Anna Rudawska, Experimental Study of Mechanical Properties of Epoxy Compounds Modified with Calcium Carbonate and Carbon after Hygrothermal Exposure, Materials 2020, 13, 5439; doi:10.3390/ma13235439, p.1-30