MATERIALE PLASTICE
https://revmaterialeplastice.ro
https://doi.org/10.37358/Mat.Plast.1964

Researches Regarding the Mechanical Properties of a New Hybrid Vegetal Resin

COSMIN MIHAI MIRITOIU[1], MARIUS MARINEL STĂNESCU[2]*, DUMITRU BOLCU[1]
[1]Applied Mechanics and Civil Constructions Department, Faculty of Mechanics, University of Craiova, 107 Calea Bucuresti Str.., 200512, Craiova, Romania
[2]Applied Mathematics Department, University of Craiova, 13 .I. Cuza Str., 200396, Craiova, Romania

Abstract. *The paper presents the mechanical behaviour and properties of a new hybrid vegetal based resin. For this, through static loading tests, the main mechanical characteristics were determined: static Young modulus, breaking strength, breaking elongation and transversal Poisson ratio. Samples of the proposed materials were subjected also to free vibration tests, by clamping them at one end and leaving them free at the other. The observation and results from these were used for deduction of the first vibration mode eigenfrequency, the dynamic Young modulus, the loss and damping factors. Some representative SEM images with an electronic microscope were collected and the samples surface roughness was determined. By using the Thermogravimetric analysis (TGA), the mass loss up to 800° C was investigated. Compared to the other resins that have dammar in composition, the proposed dammar based resin from this research has a 15.32 times higher static Young modulus than the oil palm trunk and 8.885 times higher than the oil palm trunk (OPT) with 20% dammar resin.*

Keywords: *dammar, mechanical properties, static loading, dynamic behaviour, SEM images, TGA analysis.*

1.Introduction

The biomaterials have derived from renewable sources in many fields, from which we can express examples like polymers and nano-composites that opened great interest from both academic and industry point of view, owning their potential to replace fossil-based counterparts [1].

An epoxy resin modified by biobased reactive is presented in [2]. The structural, thermal, thermomechanical and mechanical properties and also the curing kinetics of the bio-based epoxy networks were investigated. The results obtained in [2] demonstrated the autocatalytic process of curing the analyzed samples. There were determined the next mechanical properties in [2]:

tensile strength 10-16 MPa
Young Modulus 900-1100 MPa
Flexural strength 54-64 MPa
Flexural modulus 3-4 GPa.

In Japan, a natural lacquer for bio-based hybrid resins is researched in [3]. It is called urushi and has a beautiful glossy appearance and high durability [3]. From this lacquer bio-based hybrid materials with epoxy, organic silane compounds were investigated in [4]. There were obtained improvements in drying and molding properties of the hybrid resin based on the chemical reactions among all components (natural lacquer, epoxy and organic silane).

Growing environmental awarness and new rules or regulations, scientists have researched and developed varios improved ecologically bio-composites [5].

That is why, in [6], its was developed a novel bio-resin made from banana sap for low end applications such as the interior components of motor vehicles. It was concluded that by adding 50% banana sap gave the best mechanical properties when compared to the control resin which is 100% petroleum-based unsaturated polyester resin.

**email: mamas1967@gmail.com*

From the vegetal resins, sandarac, copal and dammar are mentioned in [7]. The shellac is a part of animal resins and amber from fossils ones.

The dammar resin has also been included in many investigations. For example, in [8], the quality of reactive combination of oil palm trunk with the dammar resin has been investigated. Several quantities of dammar resin were used, from 0% up to 40%. The stress strain curves were obtained and also SEM and TGA investigations were made. The effect of poly(methyl methacrylate) (PMMA) on physical properties of dammar for coating paint application has been investigated in [9]. It was found that natural dammar resins are applicable for coating on cold rolled mild steel Q-panel when mixed with PMMA. The highest energy with impact indenter was found for dammar resin with PMMA in 1:1 ratio.

A resin based on a silicone-dammar (SD) combination is presented in [10]. It was applied on an aluminum Q-panel and cured at room temperature. There were used from 0% up to 45% values for dammar weight. By using the Berkovich nano-indentation with Vickers Hardness formula, the SD with 10% dammar was found to be the hardest coating.

This paper deals with a new vegetal hybrid based resin that we have developed, with the main part being dammar resin (60%) combined with an epoxy resin (40%). The aim is to obtain a new bioresin with comparable mechanical properties in relation with the other existent resins in the engineering literature literature. The combination used in this study in new compared to the already known resins.

2.Methods of experimental investigation

2.1 Static test

Six samples from the hybrid resin with the mass between 22-23 g were made and tensile loaded on a universal testing machine (Walter Bai, Switzerland) with the maximum force of 300 kN, according to the SR EN ISO 6892-1:2010 standard. A general view with a representative sample is presented in Figure 1.

Figure 1. A general view with the used sample

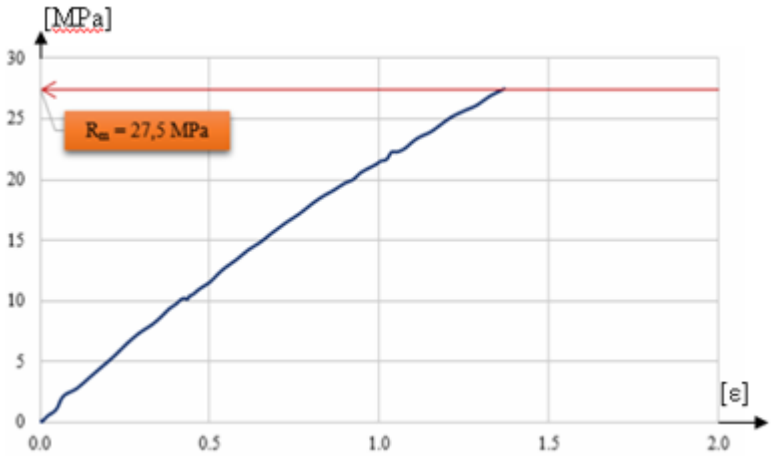

Figure 2. The characteristic curve for a dammar resin sample

2.2 Dynamic test

Two samples were made, geometrically characterized in this way:

- set 1: width = 25 mm, thickness= 4 mm;
- set 2: width = 10 mm, thickness= 4 mm.

A general view with the samples sets is presented in Figure 3. The bar was clamped at one end and the other end was left free. For the two samples we used the next free lengths: 330, 310, 290, 270 and 250 mm. A schematization of the experimental montage is presented in Figure 4. Several samples free lengths were used to study the damping factor per unit mass and length variation on the bar length. A similar experimental montage was used in [11], where accurate results were obtained for composite sandwich bars reinforced with steel fabric. An initial deformation was applied to the sample through a force, and the sample was left to freely vibrate. The vibration response was recorded with a Bruel&Kjaer accelerometer with the 0.04 pc/ms^{-2} sensitivity. The accelerometer was connected to a NEXUS 2692-A-0I4 signal conditioner (Bruel&Kjaer, Denmark). The signal conditioner was connected to a data acquisition system SPIDER 8 (HBM, Germany). The data acquisition system was connected to a notebook by an USB port. In order to eliminate any possible errors inserted by the measuring system, a high-pass Butterworth filtration of the signal at 3Hz cut-off frequency was made.

Figure 3. The dammar samples from sets 1 and 2

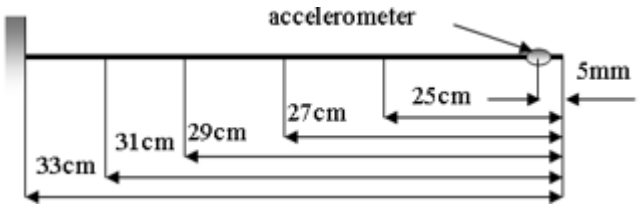

Figure 4. The experimental montage scheme

According to [11], from the experimental recording of free vibrations damping factor per unit mass can be determined in this way:

- the values where the displacement is zero are determined;
- the cancellation movement period is determined (more precisely the *T* parameter is the double time gap between two consecutive cancellations);
- the frequency ν, pulsation ω and the damping factor per unit mass μ are determined with (1), (2) and (3):

$$\nu = \frac{1}{T} \tag{1}$$

$$\omega = \frac{2 \cdot \pi}{T} \tag{2}$$

$$\mu = k^{-1} \cdot T^{-1} \cdot \ln\left(\frac{\psi_i}{\psi_{i+k}}\right) \tag{3}$$

In (3) it was marked with *k* the number of cycles and with ψ_i and ψ_{i+k} the maximums separated by *k* cycles.

According to [12], the stiffness *EI* for composite bars can be determined with (4), the dynamic elasticity modulus E_{dyn} with (5), the loss factor η with (6) and the damping factor per unit length *C* with (7):

$$EI = 39.478418 \cdot \rho \cdot g \cdot w \cdot \left(\frac{\nu \cdot l^2}{\xi^2} \right)^2 \quad (4)$$

$$E_{dyn} \approx 38.32 \cdot \rho \cdot \left(\frac{l^2 \cdot \nu}{g} \right)^2 \quad (5)$$

$$\eta \approx 0.3183099 \cdot \mu \cdot \nu^{-1} \quad (6)$$

$$C = 2 \cdot \mu \cdot \rho \cdot g \cdot w \quad (7)$$

In the relations (4), (5), (6) and (7), the next parameters were marked in this way : ρ the material density, *g* and *w* the samples thickness and width, ξ is a parameter from the samples supporting conditions which is 1.875 for a bar clamped at one end and free at the other [13], *l* is the bar free length.

In Figure 5, the experimental recording of the free vibration for a representative sample with 25 mm width and 290 mm free length is presented. In fig. 6, the damping factor per unit mass calculus for 5 cycles is presented. The cycles are delimited by the two vertical dotted lines.

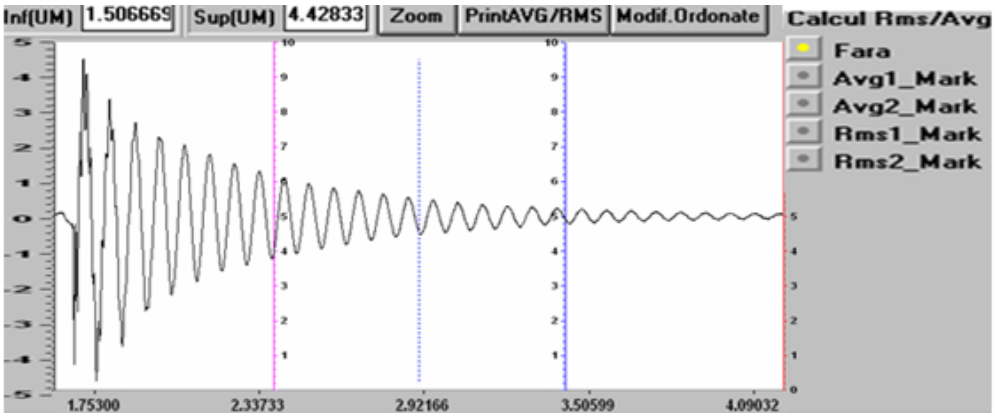

Figure 5. Experimental recordings for a 29 cm free length – set 1 sample

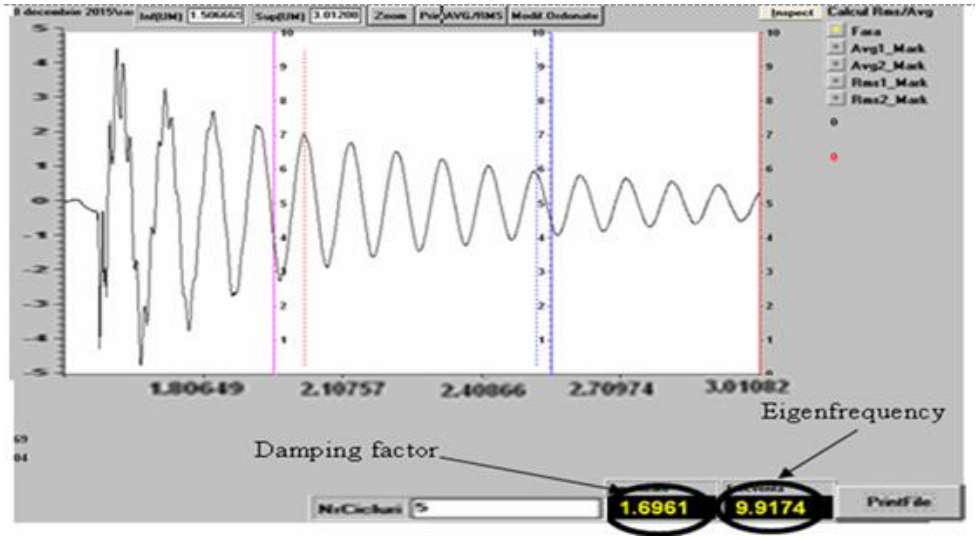

Figure 6. The damping factor per unit mass determination for a 29 cm free length – set 1 sample

Important remark: because the form of the bars deformed medium fiber is similar to their first vibration eigenmode, the measured frequency was considered as the one of the first eigenmode.

2.3 Thermogravimetric (TGA) analysis

The resin was analyzed for determining the weight change (loss) because of the heating up phenomenon. The TGA can be used to characterize any material that has weight change upon heating and to detect change due to decomposition [8]. A TGA Q 50 (TA Instruments, USA) was used for this purpose, connected to a desktop, that can heat up a sample up to 1000^0C. From the resin samples, a sample with the mass of 0.631000 mg was collected and loaded into the apparatus pan. The sample for TGA analysis was collected with the cutting blade of a scissor used to turn it into a powder. This is presented in Figure 7. The next experimental data were also used:

- the pan is made from platinum;
- the heating was made up to 800°C with a ramp of 10^0C/min;
- gas used: nitrogen;
- air cool time after the experiment: 10 min.

Figure 7. Powder from the resin sample for TGA analysis

The resin weight variation with the temperature is presented in Figure 8.

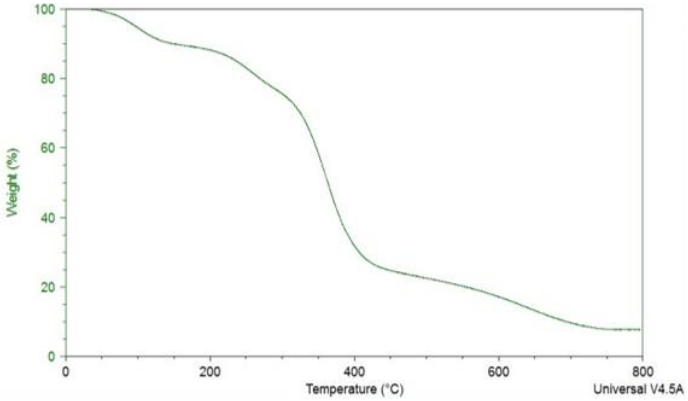

Figure 8. Weight variation versus temperature

A time derivative of the graphic and then a peak integration were made and the software gave the mass loss determination at certain temperature values. This fact is presented in Figure 9.

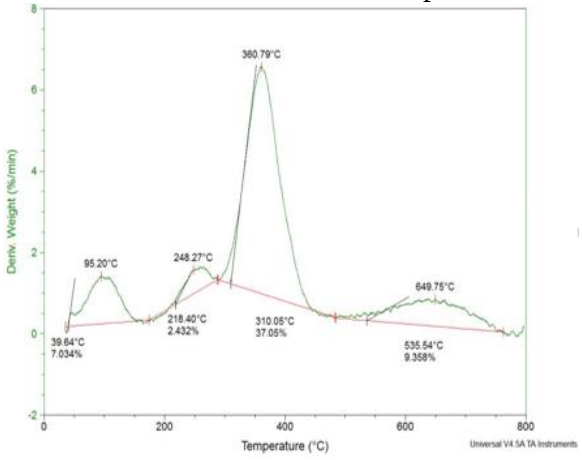

Figure 9. TGA analysis of the sample

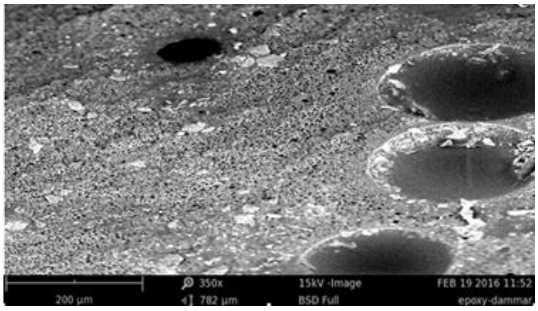

Figure 10. Sample SEM investigation

2.4 Scanning electron microscopy (SEM) analysis

In the last part of the experimental investigations regarding the resin a SEM investigation was made for one of the breaking section. The PHENOM PROX electronic microscope (PHENOM WORLD BV, Netherlands) was used. The SEM image is presented in fig. 10. The 3D reconstruction of the first picture from fig. 10 is presented in fig. 11. The reconstruction was automatically made by the PHENOM PROX software. There was also automatically determined through the software the surface roughness.

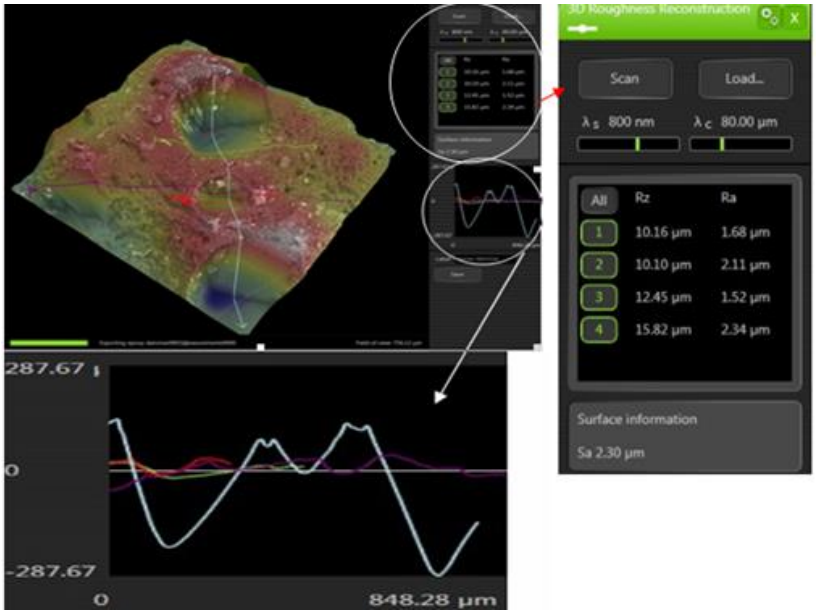

Figure 11. 3D reconstruction and roughness analysis of the sample

3.Results and discussions

3.1Static mechanical characteristics

For a representative sample, the next mechanical characteristics from the tensile test were obtained:

- the breaking strength R_m= 27.5 MPa;
- the static elasticity modulus E= 1740 MPa;
- the transversal Poisson ratio μ_p= 0.6;
- the breaking elongation A= 1.4 %.

The samples fracture was brittle, no yield stress could be determined. The samples had values between 1740-1812 MPa for the static Young modulus, 25-27.5 MPa for the breaking strength, 0.50-0.60 for the Poisson ratio and 1.2-1.4% for the breaking elongation. For each mechanical parameter, the standard deviation s, the sample variance S, coefficient of variation Cv were determined by using the relations (8), (9) and (10) [14].

$$s = \sqrt{\frac{1}{j-1} \cdot \sum_{i=1}^{j} (\xi_i - \xi_{med})^2} \tag{8}$$

$$S^2 = \frac{1}{j} \cdot \sum_{i=1}^{j} (\xi_i - \xi_{med})^2 \tag{9}$$

$$C_v = \frac{s}{\xi_{med}} \tag{10}$$

In (8), (9) and (10) the next parameters were marked: ξ_i the experimental value that corresponds to sample *i*, ξ_{med} the arithmetic mean of the experimental values and with *j* the number of the used samples (in our case j=6). For each mechanical characteristic, the next results were obtained:

- the breaking strength: s= 1.125, S^2= 1.056, C_v= 0.043;
- the static elasticity modulus: s= 28.654, S^2= 684.222, C_v= 0.016;

- the transversal Poisson ratio: s= 0.045, S^2= 0.0017, C_v= 0.082;
- the breaking elongation: s= 0.103, S^2= 0.094, C_v= 0.082.

3.2. Dynamic mechanical characteristics

All the results with the samples dimensions and the mechanical parameters obtained from the free vibrations recordings are written in table 1. The next deviations were obtained compared to the mean value in the dynamic elasticity modulus case: 2.809% for the set 1 and 1.148% for the set 2. For the dynamic Young modulus and stiffness, if we make the arithmetic mean of the values, there are obtained the next values:

- set 1: E_{dyn}= 2207.8 MPa; EI= 0.2952 Nm^2;
- set 2: E_{dyn}= 2050.2 MPa; EI= 0.11 Nm^2.

The error between the mean value of the dynamic Young modulus for the two sample sets is 7.138%. This error can be explained by the fact that the studied material is non-isotropic, and it is complicated to obtain a perfectly constant value.

Table 1. Geometrical characteristics, experimental results and mechanical characteristics determined from the dynamic test

ρ (kg/m^3)	l (mm)	ν (1/s)	μ [(Ns/m)/kg]	ρ·w·g (kg/m)	C [(Ns/m)/m]	η	E_{dyn} [MPa]	EI [Nm^2]	set
1307	330	7.7369	1.2095	0.131	0.317	0.05	2222	0.297	1
1307	310	8.8106	1.4671	0.131	0.384	0.053	2244	0.3	1
1307	290	9.9174	1.6961	0.131	0.444	0.054	2178	0.291	1
1307	270	11.631	2.1002	0.131	0.55	0.057	2250	0.301	1
1307	250	13.245	2.4972	0.131	0.654	0.06	2145	0.287	1
1467	330	7.0547	1.0919	0.059	0.129	0.049	2074	0.111	2
1467	310	7.9576	1.2189	0.059	0.144	0.049	2055	0.11	2
1467	290	8.8561	1.3703	0.059	0.154	0.046	2029	0.109	2
1467	270	10.462	1.5012	0.059	0.177	0.046	2044	0.11	2
1467	250	12.22	1.6683	0.059	0.197	0.043	2049	0.11	2

The standard deviation *s*, the sample variance *S*, coefficient of variation C_v were obtained for the dynamic mechanical characteristics by using the relations (8), (9) and (10).

We have obtained the next results:

- dynamic elasticity modulus: set 1 - s= 45.069, S^2= 1625, C_v= 0.02; set 2 - s= 16.423, S^2= 215.76, C_v= 0.00801;
- stiffness: set 1 - s= 0.006017, S^2= 0.00002896, C_v= 0.02; set 2 - s= 0.0007071, S^2= $4\cdot10^{-7}$, C_v= 0.006428;
- loss factor: set 1 - s= 0.003834, S^2= 0.00001176, C_v= 0.07; set 2 - s= 0.00251, S^2= $5{,}04\cdot10^{-6}$, C_v= 0.054.

3.3. TGA results and discussions

Thermogravimetry analysis of resin showed five stages of decomposition (according to fig. 8 and 9):

- a weight loss of 7.034% from 39° up to 187°, with a peak value to 95.20°C; this mostly appears due to water parts evaporation that compound the resin;
- a weight loss of 2,432% up to 300°C with a peak value at 248.27°C; there remain residue values from epoxy and dammar resins;
- a weight loss of 37.05% up to around 500°C, with a peak value at 360.79°C; there remain residue values from epoxy and dammar resins;
- a weight loss of 9.358% up to around 750°C, with a peak value at 649.75°C;
- from 750 to 800°C, the graphic is characterized by a very small thermal decomposition.

3.4. SEM results and discussions

For the measuring lines, the next values for the surface roughness were obtained:
- first line: Rz=10.16μm; Ra= 1.68μm;
- second line Rz=10.10μm; Ra= 2.11μm;
- third line: Rz=12.45μm; Ra= 1.52μm;
- fourth line: Rz=15.82 μm; Ra= 2.34μm.

4. Conclusions

In this paper an original vegetal based resin was presented, where the dammar is the main part (60%) combined with a small quantity of synthetic resin (epoxy resin) in order to decrease the hardening time. For this new resin four major experimental investigations were made: static loading to tensile test, dynamic research regarding the dammar based samples free vibrations, TGA analysis and SEM analysis to study the surface shape or roughness. All the results are original, because the proposed resin is new.

From the static loading, the breaking strength, the static Young modulus, the elongation at break and the transversal Poisson ratio were determined. The representative values for the tested samples were presented.

From the dynamic loading, the damping factors per units mass and length, the dynamic Young modulus, the loss factor, the frequency of the first eigenmode and the samples stiffness were determined. The dynamic elasticity modulus is 2207 ± 45.069 MPa for set 1 and 2050.2 ± 16.423 MPa for set 2. If an arithmetic mean is made from the mean values of the experimental results, the 2129 MPa value was obtained. If the dynamic Young modulus is compared to the static one, its value is 1.224 times higher and the error between the values is 18.271%. This result was expected for an-isotropic and non-homogenous materials because in most researches this conclusion is obtained. Results of static and dynamic Young modulus between different materials, especially from the rocks study area, are presented in [15], with an increased valued for the dynamic one. The same conclusion regarding a higher value for the dynamic Young modulus can be extracted from [16]. Another explanation of the increased value of the dynamic Young modulus can appear if there is not enough time during the application of the force for the strain to occur, the overall strain appears smaller and the modulus from the dynamic method becomes higher than the one from the static one. Also the strain from the static method is of macro proportions and in the vibration technique the atoms are barely moved from their equilibrium sites. The first derivative of the applied force with respect to atomic displacement decreases as the atoms of the lattice are separated. So, the Young modulus for the static method is lower than the dynamic one, because the atoms displacement is larger. An increased value of the dynamic Young modulus compared to the static one was also found in [17]. Errors of 3% between that static and dynamic Young modulus were found for different types of steel [18]. Another explanation is that the samples came from different batches. Also the natural materials can have unsubstantial values when determining their mechanical properties [19, 20, 21]. Not for all materials the dynamic modulus is higher than the static one. For example, in [22] the static Young modulus is larger than the dynamic one by the factor 2.

Compared to the resins developed in [8], it can be concluded that the dammar based resin proposed in this research has a 15.32 times higher static Young modulus than the oil palm trunk and 8.885 times higher than the oil palm trunk (OPT) with 20% dammar resin. Instead, our proposed resin has a decreased thermal stability above 400°C than the OPT with 20% dammar, but an increased one compared only to OPT. Above 1000°C, decomposition of volatile compounds from the dammar based resin occurs.

The proposed bioresin, combined with natural fibers, can be used to replace the synthetic resins combined with natural fibers, obtaining in the end a more eco-friendly material. For example, the proposed vegetal resin reinforced with flax fibers can be used to replace the classical composite made of epoxy reinforced with flax fibers for interior door paneling at the passenger cars. Combined with natural fibers, the proposed bioresin can be used to make reusable formworks for some construction elements, can be used as an alternative to wood and PVC at parquet blocks being an almost environment-friendly material.

Acknowlegments: This article was presented at Polymer Processing in Engineering Conference - PPE 2019, 7- 9 October 2019, Galati - Romania.

References

LI, C., LI, S., YAN, S., Rsc. Adv., 6, 2016, p. 62572.
ZOLGHANDR, M., ET. AL., Termochimica Acta, 673, 2019, p.147.
KUMANOTANI, J., Prog Org Coat, 51, 1995, p.238.
KANEHASHI, S., ET. AL., Prog Org Coat, 77, 2014, p.24.
IL'INA, A., VARMALOV, V., Appl. Biochem. Microbiol., 40, 2004, p. 300.
PAUL, V., KANNY, K., REDHI, G., G., J. Geosci., 43, 2013, p.496.
SCHWARZ, M., Encyclopedia of Materials, Parts and Finishes, CRC Press, London, 2002.
NURFAJRIANI, WIDIARTI, L., GEA, S., THAMRIN, WIRJOSENTONO, B, Int J Pharmtech Res , 8, nr. 1, 2015, p.74.
NASIR, K.M., HALIM, N.A., TAJUDDIN, H.A., AROF, A.K., ABIDIN, Z.H.Z., Pigm Resin Technol, 42, 1972, p.137.
ZAKARIA, R., AHMAD, A.H., Int. J. Adv. Sci. Eng. Inf. Techno, 42, 2012, p.33.
MIRIŢOIU, C.M., BOLCU, D., STĂNESCU, M.M., CIUCĂ, I., CORMOS, R., Mat Plast, 49, nr. 2, 2012, p.118.
BURADA, C.O., MIRIŢOIU, C.M., STĂNESCU, M.M., BOLCU, D., Rev Rom Mater, 45, nr. 3, 2015, p.244.
STĂNESCU, M.M., BOLCU, D., MANEA, I., CIUCĂ, I., BAYER, M., SEMENESCU, A., Materiale Plastice, 46, nr. 1, 2009, p.73.
STANIMIR, A., PASCU, I., Genessa Publishing House, Craiova, 2014.
MOCKOVCIAKOVA, A., PANDULA, B., Metalurgija, 42, nr. 1, 2003, p. 37.
POPOVICS, J.S., from www.concreteresearchcouncil.org /portals/7/files/pdfs/crc_43.pdf, 2008. (accessed on 7th of May 2019)
MARIANO, D.R., FELICISIMA, L., ET. AL., 19th International Congress on Acoustics Madrid, 2007, p.1.
HAMMOND, J.P., RATCLIFF, L.T., BRINKMAN, C.R., MOYER, M.W., NESTOR, C.W., Oak Ridge National Laboratory, Tennesee, 1979.
OKSMAN, K., Appl Compos Mater, 7, nr. 5, 2000, p.403.
CANTERO, G., ARBELAIZ, A., LLANO-PONTE, R., MONDRAGON, I., Compos Sci Technol, 63, nr. 9, 2003, p.1247.
MALKAPURAM R., KUMAR V., YUVRAJ SN., J Reinf Plast Comp, 28, nr. 10, 2008, p.1169.
22.BRAHMA, J., SIRCAR, A., J. Geosci., 5, 2014, p.184.

Manuscript received: 24.02.2020