

Composite Materials with the Hybrid Matrix Based on Rosin and the Reinforcement from Agricultural Waste - Chemical Structure and Mechanical Properties

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Abstract. *The manufacture of composite materials with hybrid matrix and reinforcements from agricultural waste, which have properties/structure corresponding to the field where they will be used, is a challenge both in terms of environmental protection and low production costs. Based on this premise, in this article, composite materials reinforced with crushed sunflower seed shells or chopped wheat straw were fabricated, and a hybrid resin matrix based on rosin was used. The chemical structure was studied, along with the influence of the reinforcement addition on the morphology of the materials and their behaviour under various mechanical solicitations: tension and compression.*

Keywords: *composite materials, rosin based matrix, sunflower seed shells, wheat straw, chemical structure, mechanical properties*

1. Introduction

Wheat straw has diverse applications, ranging from animal feed to composite materials used in construction or the automotive industry [1]. Bio-composite boards reinforced with straw have been produced by [2], and studies on improving their mechanical properties are presented in [3]. A disadvantage of using wheat straw is that it has inferior mechanical properties compared to traditional textile fibers. Additionally, the relatively weak surface properties of wheat straw and the presence of nodes can reduce the quality of the interfacial bond with various polymer binders [4]. These drawbacks can be overcome by separating the nodes and subjecting the internode portions to a series of treatments with hot water and steam, followed by drying [5]. Improving the surface compatibility between resin and fibers can be achieved through surface treatments of wheat straw using radiation or plasma [6], steam [7], or enzymes [8]. Beneficial results regarding the modification of the straw surface have been obtained through alkaline treatments [9], which enhance the matrix penetration into the cellular lumen [10]. In [11] the wheat straw was subjected to water-based and mild alkaline pre-treatments and subsequently densified. As a result, the average tensile strength and modulus of elasticity of straw strands improved. Simultaneously, chemical changes to the surface enabled better adhesive bonding. The resulting unidirectional straw composites exhibited a flexural strength and an elastic modulus, well within the range of established wood and bamboo-based materials. In [12] the effect on the flexural modulus and ultimate strength of three mass fractions of four agricultural residue fibers (AF) was evaluated, including two types of wheat strains, in bio composites with poly-hydroxybutyrate-co-hydroxyvalerate (PHBV). AF were combined with PHBV using two compatibilization treatments. It was found that modulus and strength increased with increasing fiber fraction, and the effect of using hollow stem wheat was comparable to that of hemp residue.

Sunflower seed shells are another example of agricultural waste that can be used as a reinforcement for composite materials. In this direction, some mechanical and thermal properties of composites reinforced with various mass proportions of sunflower husk powder and the matrix of polypropylene (PP) [13, 14], low-density polyethylene (PE) with very low density [15], polyamide (PA) [16] and poly

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urethanes [17], were studied. It was found that the tensile strength and elastic modulus improve when increasing proportion of seed shells and decreasing particle size used as filler. Studies on materials using sunflower seed shells as fillers have shown that increasing their volumetric proportion has led to a significant increase in the rigidity of the composites, which has affected their impact behaviour. This is explained by the fact that sunflower seed shells are mostly characterized by irregular shape and create stress concentration points [18]. The increase in the proportion of seed shells is also limited by the fact that it allows for the propagation of cracks along the interface between the polymer matrix and the reinforcement particles.

In recent years, there has been a growing interest in the complete or partial replacement of synthetic resins with natural resins such as sandarac, copal, dammar, rosin, or mastic. These resins are insoluble in water but soluble in alcohol, turpentine, oil, or gasoline. By dilution, liquid solutions can be obtained, which can be used as coating varnishes but require a combination with synthetic resins for hardening [19, 20]. Hybrid resins have been developed that exhibit mechanical properties suitable for use as matrices in composite materials [21]. Many types of bio-epoxy resins have been produced using renewable sources such as vegetable oils [22], lignin [23], rosin [24], cardanol [25], or chitosan [26]. Moreover, in [27, 28], composite materials based on hybrid resins have also been investigated.

Rosin, also known as colophony, is a natural resin that can be used to obtain hybrid resins for the production of composite materials. The main advantage lies in its low cost (rosin is over 10 times cheaper than epoxy resin). An up-to-date overview of rosin, presenting its intrinsic characteristics, its processing, and the development of material production for ecological science, was provided by [29]. The majority of articles in the specialized literature focus on the processing of rosin as a reinforcing agent for different types of matrices used in bio-composite materials. In this field, researchers are primarily focused on improving the mechanical properties of bio-composites through various methods. The blending of natural rubber-based magneto-rheological (MR) elastomers (MREs) based on natural rubber with rosin glycerin ester to enhance wettability and dispersibility of arboonyliron (CI) particles was studied in [30]. It has been found that the MR effect of these hybrid matrix MREs was higher and could reach up to 112% when the mass fraction of CI particles was only 60%. The use of a hemp oil-based polycarboxylic acid in combination with rosin-derived anhydride HO-polyacid/MPA as a curing agent for epoxy resins was proposed by [31]. It was found that the use of the co-curing agent allowed for efficient adjustment of the balance between rigidity and flexibility in the cured resins.

In [32], composites reinforced with carbon fibers and ramie fibers were developed by using a conceptual Resin Transfer Molding (RTM) approach based on a preform which supposes to sprinkle with solid rosin into the preform, followed by the injection of a low-viscosity nonreactive liquid resin into the matrix to infiltrate and wet the pre-loaded preform. The quality and mechanical properties of the resulting composites are comparable to those of autoclave-prepreg or compression moulded preparations.

Rosin can also be used in the structure of nanocomposites. An environmentally friendly mechano-chemical synthesis method of a rubber-compatible organomontmorillonite (OMMT) composed of raw bentonite mineral and rosin is employed by [33]. It has been demonstrated that during the grinding process, rosin gradually intercalates into montmorillonite - (MMT). Test results revealed that tensile strength, rupture resistance, and elongation significantly improved for (OMMT) compared to (MMT).

A derivative of rosin was utilized by [34] and [35] to enhance the properties of two types of vitrimers, more specifically it was used as the main monomer for the preparation of epoxy vitrimers (the first study) and polyurethane vitrimers (the second study). Both types of vitrimers exhibited good mechanical properties, including self-healing and reprocessing capabilities.

The antibacterial properties of rosin are highlighted in [36]. Rosin was blended with PE, PP, PLA, PA, and corn starch-based biopolymer (CS), proving to be compatible with all exposed polymers. Through tests, the best mechanical performance in terms of initial stiffness (Young's modulus), ultimate strength, and maximum deformation was recorded by PE and PP fibers. Regarding the antibacterial

response, PE containing 10% by weight of rosin exhibited significant antibacterial effects against *E. coli* DH5 and *Staphylococcus aureus* ATCC.

The use of rosin for modifying castor oil-based polyurethane PU foam is proposed by [37]. The results show that increasing the molar ratio of rosin enhances the density and compression strength of the PU foam. Models for TGA indicate that a PU foam with a 5% molar ratio of rosin is the most thermally stable.

Three types of hybrid resin with volumetric ratios of 45%, 55%, and 65% rosin are studied in [38]. The chemical composition and tensile behaviour were analysed and it was found that the values of rupture strength and elasticity modulus decrease with the increase in the volumetric proportion of rosin.

In this study, the chemical structure of composite materials with a hybrid rosin-based resin matrix and two types of reinforcements-chopped sunflower seed shells or chopped wheat straws-was investigated using energy dispersive X-ray analysis EDAX. The mechanical behaviour of these composites was established based on tensile and compression. After tensile testing, the fracture surface was examined using scanning electron microscopy to assess the influence of reinforcement addition on material morphology. To enhance certain properties, sandwich-type composites were manufactured with a core identical to the previously tested composite materials, but with added layers of flax and cotton fabric. It was found that the properties of these sandwich composites are comparable to those of MDF - Medium Density Fibreboard [39].

2. Materials and methods

2.1. Preparation of samples

The following types of resins were used for creating the composite materials:

- Epoxy resin - Resoltech 1050, and its corresponding hardener Resoltech 1058S;
- Hybrid resins - these included natural rosin resin in a volumetric ratio of 50% and 60%, with the remaining percentage being epoxy resin and its corresponding hardener.

It was found that exceeding the volumetric ratio of 60% rosin in the matrix produces slow polymerization of over 7 days, which is a disadvantage.

Composite materials were studied, including:

- Epoxy resin reinforced with chopped wheat straws, abbreviated as EPT;
- Hybrid resin with 50% rosin, reinforced with chopped wheat straws, abbreviated as CoPT5;
- Hybrid resin with 60% rosin, reinforced with chopped wheat straws, abbreviated as CoPT6;
- Epoxy resin reinforced with chopped sunflower seed shells, abbreviated as EST;
- Hybrid resin with 50% rosin, reinforced with chopped sunflower seed shells, abbreviated as CoST5;
- Hybrid resin with 60% rosin, reinforced with chopped sunflower seed shells, abbreviated as CoST6.

All the composite materials produced had a mass ratio of 60% matrix and 40% reinforcement. The use of a mass proportion of reinforcement greater than 40% showed that a part of the reinforcing agent did not mix sufficiently with the matrix, which led to interface bonding problems, and a mass proportion greater than 60% matrix showed that in the structure of the composite appeared a resin surplus. Since the plates produced were subjected to a uniform pressure of 10 N/cm² during the technological process, small amounts of resin were removed, causing the mass ratio of resin in the obtained plates to be 59-60%. The mixing of components and casting of composite plates were performed at an ambient temperature of 21 - 23°C, and the samples were cut after 5 days from casting.

From each previously mentioned composite material, a 7 mm thick plate was cast. From each plate, 15 samples with a length of 250 mm and a width of 25 mm were cut for tensile testing, following the ASTM D3039 standard. These samples were abbreviated in the same way as the composite materials they were made from.

Using the same composite materials as for the tensile testing, square-section bars with a side dimension of 20 mm were cast for compression testing. From these bars, 15 cubes with a side length of 20 mm each were cut, following the ASTM D3410 standard. The sets of cubes obtained were abbreviated by adding the letter "C" before the abbreviation used for the composite material they were made from.

In Figure 1, examples of samples made from studied composite materials which to be subjected to various mechanical stresses are presented.



Figure 1. Examples of samples made from the composite materials studied, with shredded wheat straw (a) and sunflower seed hulls (b) as reinforcing material, subjected to various mechanical stresses

2.2. Testing equipment

The chemical structure of the studied composites was determined using EDAX analysis. A PHENOM PURE PRO X scanning electron microscope was employed, equipped with an integrated EDS system and a conventional cathode designed for the microscopic study of the structure and surface of various materials. It allows for the determination of chemical composition and phases within the structure. The magnification capability ranges from 80 to 130.000 times. Among the materials for which this microscope is used are polymer matrix composites and metal matrix composites.

Tensile tests were conducted using the material testing machine mounted on a bench, with a single-column Lloyd Instruments LRX type for mechanical tests, featuring the following specifications: maximum force of 5 kN; stroke range of 1 - 750 mm; applied speed of 0.1-500 mm/min; 50 mm extensometer; cyclic loading frequency up to 40Hz, inclusive; data acquisition and analysis software NEXYGEN-Plus.

The compression tests were performed with a Walter+Bai universal machine for static and dynamic tests with a capacity of 300 kN.

A scanning electron microscope with a much higher magnification capacity than the EDAX analysis microscope was used for SEM analysis. The microscope used was the Hitachi model S3400N/Type II, magnification range: between x5 - x300.000; acceleration voltage: 0.3 kV - 30 kV; electron gun voltage: in steps with self-field and fixed-field with continuously adjustable voltage; image shift: minimum, 50 microns at WD = 10 mm.

3. Results and discussions

3.1. EDAX

The chemical structure of samples taken from the CoPT5, CoPT6, CoST5, and CoST6 composites is presented in Figure 2 a-d. Chemical characterization was performed using Energy Dispersive X-Ray Analysis - EDAX.

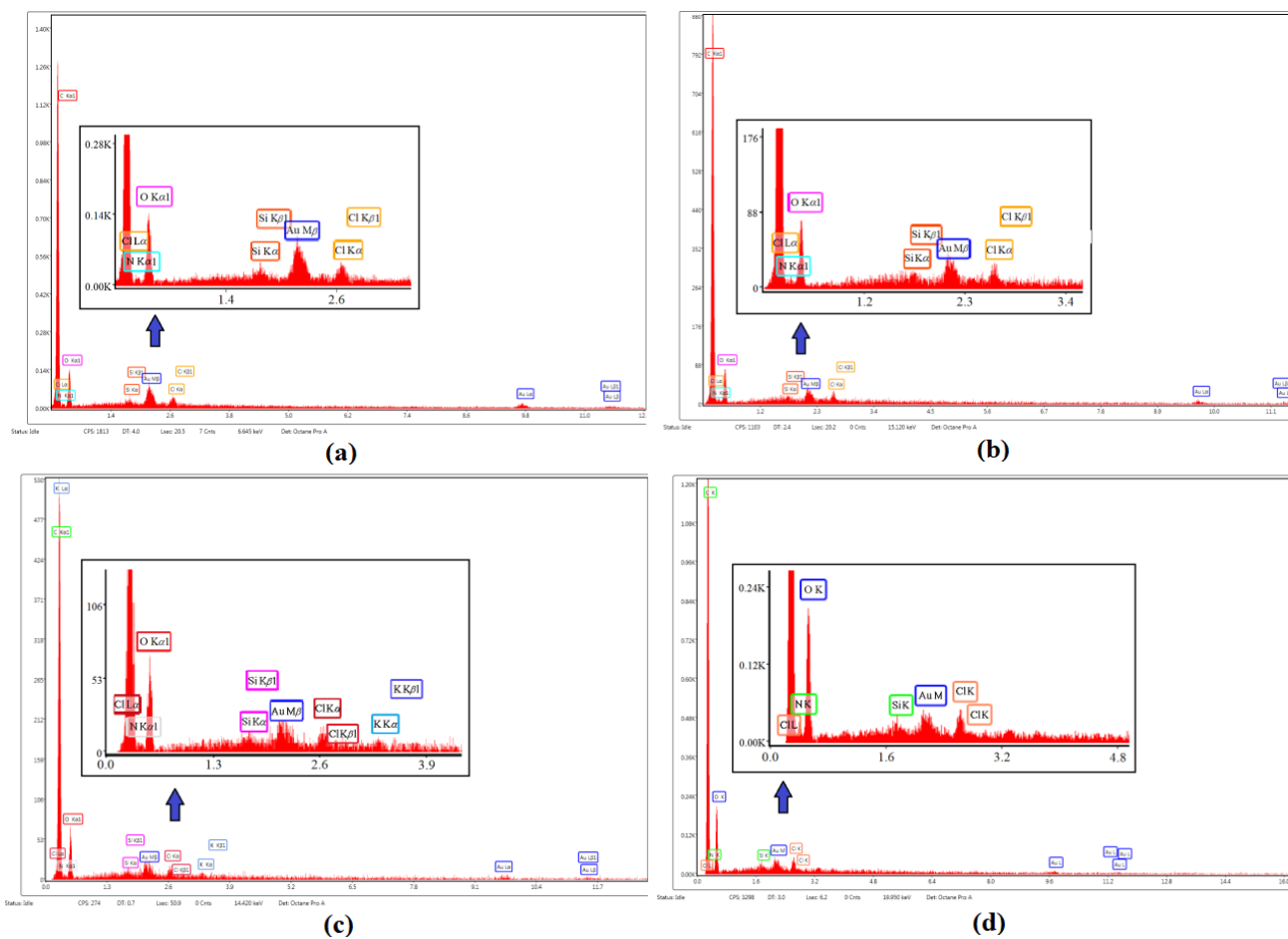


Figure 2. EDAX diagrams showing the distribution of atomic spectra of chemical elements from the sample: (a) CoPT5; (b) CoPT6; (c) CoST5; (d) CoST6

Based on the EDAX analysis, Tables 1 and 2 present the individual values of the chemical composition for the analysed areas of the CoPT5, CoPT6, CoST5, and CoST6 composites.

Table 1. Chemical composition of a sample taken from the CoPT5 and CoPT6 composites

	CoPT5					CoPT6				
	C K	N K	O K	Si K	Cl K	C K	N K	O K	Si K	Cl K
Weight %	73.23	7.36	18.77	0.27	0.38	75.77	8.1	15.66	0.2	0.27
Atomic %	78.01	6.72	15.01	0.12	0.14	80.06	7.34	12.42	0.09	0.1
Error %	4.69	27.64	14.99	26.81	19.72	4.5	30.73	17.42	39.83	24.99
Net Int.	669.04	10.95	65.91	18.36	29.37	476.49	7.78	35.03	9.97	15.84
K Ratio	0.5112	0.0052	0.0169	0.0017	0.0033	0.5592	0.0057	0.0136	0.0013	0.0024
Z	1.009	0.9886	0.9708	0.8923	0.8347	1.0078	0.9874	0.9696	0.8911	0.8336
A	0.6918	0.0716	0.0926	0.7343	1.0434	0.7322	0.0711	0.0898	0.7233	1.06
F	1	1	1	1.0063	1.0208	1	1	1	1.0064	1.0218

Table 2. Chemical composition of a sample taken from the CoST5 and CoST6 composites

	CoST5						CoST6				
	C K	N K	O K	Si K	Cl K	K K	C K	N K	O K	Si K	Cl K
Weight %	70.47	7.45	21.63	0.13	0.21	0.1	71.71	6.65	21.15	0.13	0.36
Atomic %	75.57	6.85	17.41	0.06	0.08	0.03	76.73	6.1	16.99	0.06	0.13
Error %	5.21	34.21	15.93	66.18	51.93	63.46	5.04	37.39	16.39	67.69	20.54
Net Int.	105.73	1.88	12.84	1.52	2.85	1.32	1357.24	20.45	156.41	16.58	47.3
K Ratio	0.4958	0.0055	0.0201	0.0009	0.0019	0.001	0.4949	0.0047	0.0197	0.0009	0.0032
Z	1.0098	0.9894	0.9717	0.8931	0.8355	0.8336	1.0096	0.9892	0.9714	0.8929	0.8352
A	0.6968	0.0747	0.0956	0.7118	1.0394	1.1009	0.6837	0.0713	0.0961	0.7634	1.0326
F	1	1	1	1.0062	1.0215	1.0418	1	1	1	1.0063	1.0207

It is observed that with the increase in the percentage of rosin, there is an increase in the percentage of carbon and a decrease in the percentage of oxygen. The percentages of nitrogen and silicon in the composition of all analysed samples could come from the fertilization of wheat and sunflower crops, respectively, while chlorine is from the coolant used for cutting the samples.

3.2. Tensile testing

Hereinafter, a representative specimen from a set will refer to the specimen whose determined mechanical properties are closest to the calculated average values for the 15 tested samples. Tensile testing was conducted at a loading rate of 5 mm/min. Based on the tensile testing, the stress-strain curve, tensile strength R_m [MPa], elasticity modulus E [N/mm²], and percentage elongation after rupture A [%] were obtained.

The tensile strength-strain curves for representative samples from sets of composite materials reinforced with chopped wheat straws (a) and chopped sunflower seed shells (b) are presented in the Figure 3.

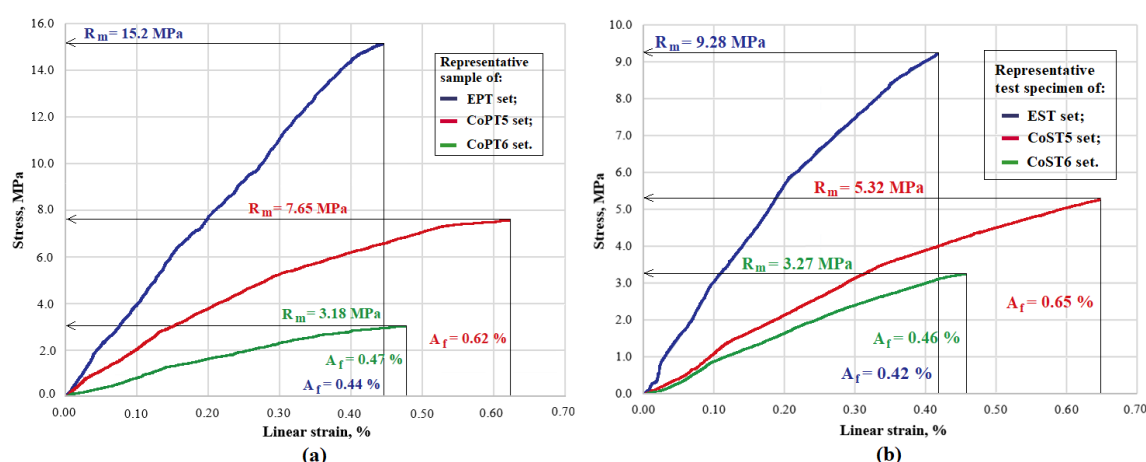


Figure 3. Tensile strength-strain diagram for representative samples from the: (a) EPT, CoPT5, and CoPT6 sets; (b) EST, CoST5, and CoST6 sets

The average value and standard deviation for the elasticity modulus E [N/mm²], tensile strength R_m [MPa], and percentage elongation at break A [%] for the sets of samples from the six types of composite materials are given in Table 3.

Table 3. Average value and standard deviation for elastic modulus, tensile strength, and elongation at break for the tensile tested samples

Specimen type	Modulus of elasticity E [N/mm ²]	Tensile strength R_m [MPa]	Elongation at break A [%]
EPT	4624 (\pm 281)	15.25 (\pm 0.95)	0.45 (\pm 0.04)
CoPT5	2850 (\pm 193)	7.64 (\pm 0.54)	0.62 (\pm 0.05)
CoPT6	1214 (\pm 81)	3.43 (\pm 0.29)	0.47 (\pm 0.04)
EST	2924 (\pm 120)	9.35 (\pm 0.55)	0.43 (\pm 0.04)
CoST5	1480 (\pm 108)	5.41 (\pm 0.40)	0.62 (\pm 0.05)
CoST6	1048 (\pm 68)	3.30 (\pm 0.32)	0.45 (\pm 0.03)

For the composite materials made with the three types of resin, a wide variation in values is observed both for tensile strength and elasticity modulus. For the composite materials made with the hybrid resin containing 50% rosin, the values of tensile strength and elastic modulus are practically half compared to those obtained for composites with epoxy resin. Comparatively, the mechanical properties of straw reinforced composites are superior to those for composites reinforced with chopped sunflower seed shells. This can be explained by differences in mechanical properties as well as differences in the particle

sizes of the reinforcing materials. The dimensions of the straw pieces embedded in the composite materials are significantly larger than those of sunflower seed shell particles. Because the length of the straw pieces is much larger than their thickness, they favourably absorb stresses in the direction of loading. In the case of the hybrid resin with 60% rosin, the differences in properties between composites with the two reinforcing materials are much smaller. The explanation lies in the fact that in this case, mechanical properties are mainly determined by the resin properties. An interesting trend is observed for elongation at break. It increases for composite materials made with the hybrid resin containing 50% rosin compared to those made with epoxy resin. This can be explained by the fact that the rosin-based hybrid resin has larger deformations than epoxy resin [38]. The decrease in elongation at break for composite materials with the hybrid resin containing 60% rosin is due to the significant drop in the resin's tensile strength, leading to rapid rupture.

3.3. SEM

The influence of the reinforcing agent addition on the morphology of the materials was assessed through scanning electron microscopy. The analysis was conducted on cross sectional surfaces, following the ASTM STP1203 standard.

In Figure 4a-d, the results of this analysis on a specimen from the set are presented: 4a - CoPT5; 4b - CoPT6; 4c - CoST5; 4d - CoST6.

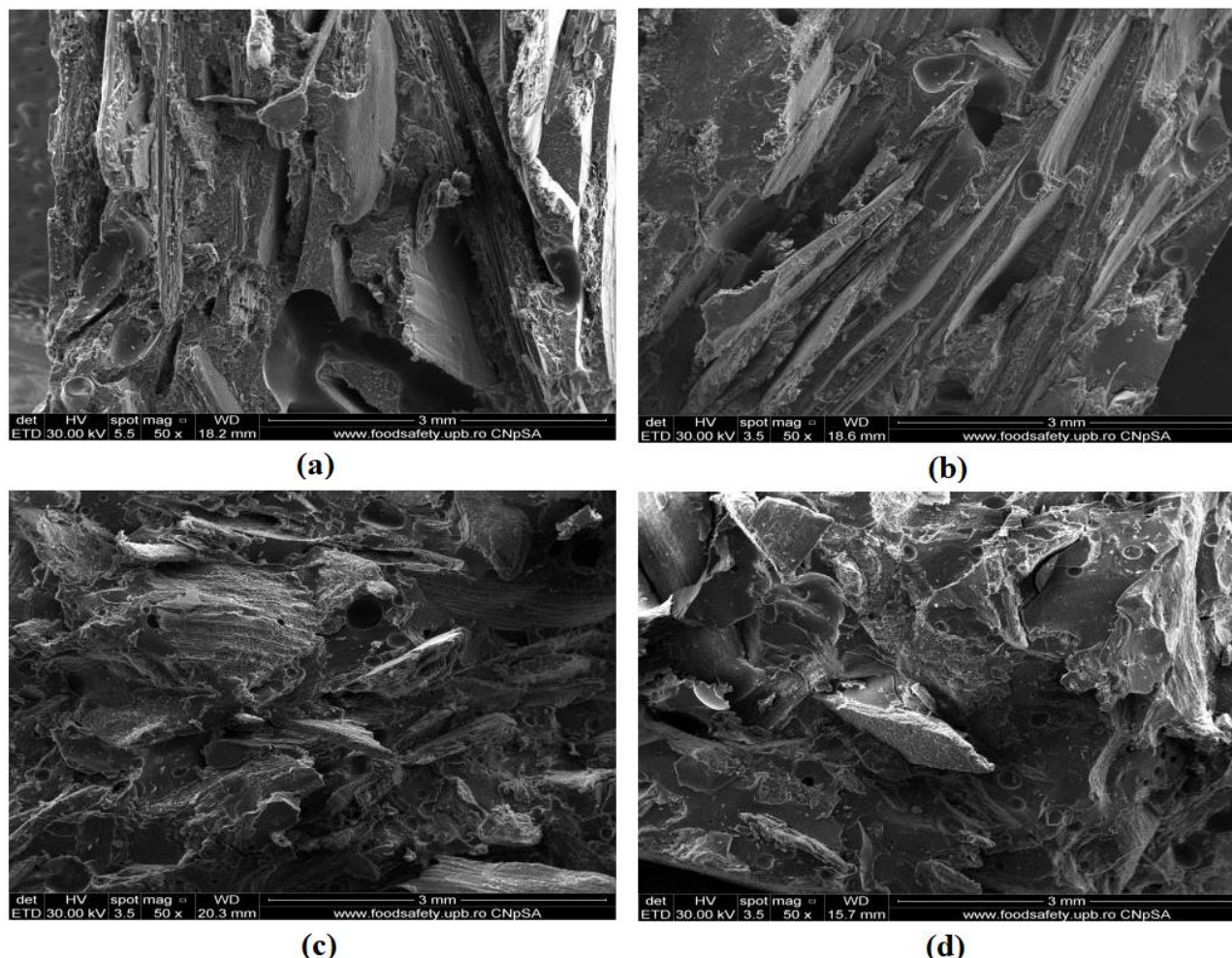


Figure 4. Fracture surface resulting from tensile testing, analyzed by using scanning electron microscopy, for a specimen from the set: (a) CoPT5; (b) CoPT6; (c) CoST5; (d) CoST6

From the analysis of Figure 4a-d, the massive presence of reinforcement elements (chopped wheat straws and crushed sunflower seed shells) in the hybrid matrix is observed. Samples reinforced with chopped straws, presented in Figure 4a and 4b, have a small number of irregularly shaped air voids in the matrix, ranging in size from 0.5 to 1.0 mm. Samples reinforced with crushed seed shells, shown in Figure 4c and 4d, have a larger number of uniformly distributed, smaller, round-shaped air voids in the matrix, ranging in size from 0.1 to 0.6 mm.

At the same mass fraction, the reinforcement made of chopped straws contains a larger amount of air compared to the reinforcement made of crushed seed shells. The justification is that chopped straws contain air inside them, have irregular shapes, and non-uniform sizes, whereas crushed seed shells do not contain air inside them, have regular shapes, and nearly uniform sizes. Because chopped straws compact better than crushed seed shells (which are more rigid), it follows that during the compaction of the resin reinforcement mixture, more air will be expelled from composites with straw reinforcement than from those with seed shell reinforcement. Some of the larger air bubbles in the composite with chopped straws will be expelled through compaction (although some will still remain trapped in the resin), while the smaller bubbles in the composite with seed shells will remain in greater numbers trapped in the hybrid resin, which, as it begins to polymerize, becomes increasingly viscous.

The absence of voids at the interface between the matrix and the reinforcement suggests a strong bond between the matrix and the reinforcement. An additional indication of this strong adhesion is the lack of detachment of the reinforcement after the tensile test, especially noticeable in the samples reinforced with seeds.

3.4. Compression test

Based on the compression test, the force-deformation diagram, maximum load force F_{max} [N], maximum deformation L_{max} [mm], and compressive permissible stress σ_{ac} [MPa] were determined.

Compression testing was conducted at a loading rate of 1 mm/min.

The force-deformation diagrams for representative samples from the sets of composite materials reinforced with chopped wheat straws (a) and crushed sunflower seed shells (b) are shown in Figure 5.

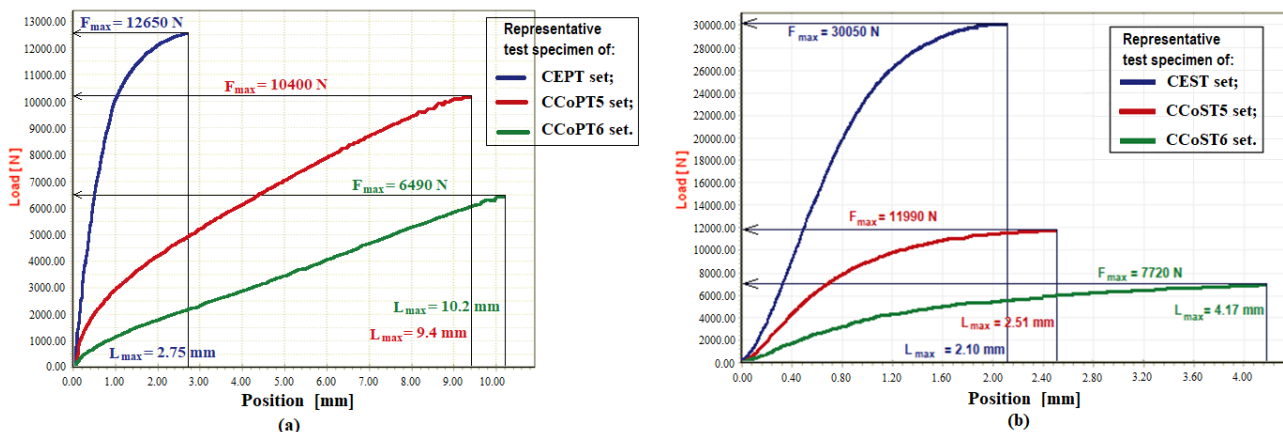


Figure 5. Force-position diagrams for representative samples from the composite sets: (a) CEPT, CCoPT5 and CCoPT6; (b) CEST, CCoST5 and CCoST6

Average values and standard deviation for maximum load F_{max} [N], maximum deformation L_{max} [mm], as well as compressive strength σ_{ac} [MPa] for samples from the six types of composite materials are provided in Table 4.

Table 4. Mean value and standard deviation for maximum load, maximum deformation, and compressive strength for the sets of samples subjected to compression

Specimen type	Maximum load F_{\max} [N]	Maximum extension at F_{\max} L_{\max} [mm]	Compressive strength σ_{ac} [MPa]
CEPT	12750 (\pm 570)	2.70 (\pm 0.2)	31.8 (\pm 1.5)
CCoPT5	10550 (\pm 480)	9.45 (\pm 0.8)	26.4 (\pm 1.2)
CCoPT6	6550 (\pm 350)	10.3 (\pm 0.8)	16.4 (\pm 0.9)
CEST	30240 (\pm 970)	2.15 (\pm 0.2)	75.6 (\pm 2.4)
CCoST5	12030 (\pm 510)	2.45 (\pm 0.3)	30.1 (\pm 1.3)
CcoST6	7690 (\pm 390)	4.30 (\pm 0.3)	19.2 (\pm 1.0)

Unlike tension, in compression, composite materials reinforced with chopped sunflower seed shells exhibit superior behaviour compared to those reinforced with wheat straw. This phenomenon is due to the fact that the particles of ground seed shells are more compact and have a shape closer to spherical, thus uniformly distributing the stresses encountered in compression. The differences between composites with these two types of reinforcement are smaller in materials utilizing hybrid resins with rosin as the matrix, indicating that in these cases, the stresses are primarily absorbed by the matrix. This is also justified by the fact that the deformations of cubes with matrices made of hybrid resins are much larger than those of cubes with epoxy resin matrices.

In all studied composite materials, the maximum stresses encountered in compression were significantly higher than the tensile strengths observed during tensile testing. Therefore, it is advisable for composite materials utilizing rosin based hybrid resins and reinforced with chopped sunflower seed shells or wheat straw to be employed in the manufacturing of components subjected primarily to compression loads.

4. Conclusions

Using wheat straw or sunflower seed shells as reinforcements, in combination with natural or hybrid resins, to create composite materials represents an environmentally friendly alternative that also offers economic advantages.

Composite materials with a hybrid resin matrix based on rosin exhibited lower mechanical strength and stiffness compared to those reinforced with epoxy resin. Increasing the proportion of rosin in the hybrid resin led to a significant decrease in tensile strength and modulus of elasticity. The fracture surfaces analysed indicated abrupt, non-elongated fractures, a characteristic feature of brittle materials.

The studied composite materials handle compressive stresses much better than tensile stresses. Therefore, composite materials with agricultural waste reinforcements such as wheat straw and sunflower seed shells are suitable for industrial products or semifinished goods primarily subjected to compression loads.

The mechanical properties investigated and the chemical structure determined for composite materials made from hybrid resin based on rosin and reinforced with chopped wheat straw or chopped sunflower seed shells, shows that these materials are comparable to MDF - Medium Density Fibreboard if they have the same thickness. The addition of natural fabrics over the initially obtained composites makes it possible to use of researched sandwich composites in the furniture industry or for decoration instead of veneered MDF. There are several advantages of using sandwich composites instead of veneered MDF. Among these can be: the lower cost of approximately 30-50% of the cost of the gray straw, respectively sunflower seed husks compared to sawdust; better behaviour in a high humidity environment.

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