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https://doi.org/10.37358/Mat.Plast.1964

Chemical and Mechanical Properties for Rosin-based Hybrid Resins

ALEXANDRU BOLCU[1], NICOLETA CIOATERA[2], DUMITRU BOLCU[1*], MARIUS MARINEL STANESCU[1], ION CIUCA[3], ALIN DINITA[4], IULIAN CONSTANTIN[5]

[1] University of Craiova, Faculty of Mechanics, 107 Calea Bucuresti, 200512, Craiova, Romania
[2] University of Craiova, Faculty of Sciences, Department of Chemistry, 107 Calea Bucuresti, 200478, Craiova, Romania
[3] Politehnica University of Bucharest, Faculty of Engineering and Materials Science, 313 Splaiul Independenței, 060042, Bucharest, Romania
[4] University of Petrolium-Gas, Faculty of Mechanical and Electrical Engineering, 39 București Blvd., 100680, Ploiești, Romania
[5] Universitatea Dunarea de Jos, Facultatea de Medicina si Farmacie, 35 Al. I. Cuza Str., 800010, Galati, Romania

Abstract*. The increasing concern for the protection of the environment, through the use of renewable natural resources, has led in the last decades to the realization of a number of natural polymers or hybrids to be able to replace petroleum-based polymeric materials. Rosin is a low-cost wood resin extracted from conifers. In this paper, based on FTIR and Raman analyses, the spectra of natural Rosin resin and some hybrid resins with volume proportions of 45, 55 and 65% Rosin were studied. Some mechanical properties such as modulus of elasticity, elongation at break, tensile strength were determined from stress-strain diagrams obtained from tensile stress. Increasing the volume proportion of Rosin leads to a decrease in stiffness and strength properties and obtaining a visco-elastic behavior.*

Keywords*: Rosin, hybrid resin, FTIR and Raman analyses, chemical and mechanical properties*

1. Introduction

The composite materials mainly use as matrices synthetic resins of the epoxy, polyester, etc. type. Numerous studies have investigated the mechanical behavior of composites based on epoxy resin [1-3]. The influence of the shelf life of an epoxy matrix on the mechanical properties of glass fiber reinforced composites was studied in [4].

Because fiber-reinforced polymer composites are light and have high strength values, their fields of use are increasingly varied. In recent years, biobased production of these composites has gained importance due to their low cost and environmentally friendly properties. In particular, the production of bio-based polymers and the use of these polymers in the production of composite materials have become some of the important topics that scientists are interested in [5-7].

It is important to produce bio-based materials because the need for environmentally sustainable materials is constantly increasing day by day. Many types of bio-epoxy resins have been produced from renewable sources, such as vegetable oils [8,9], lignin [10,11], rosin [12,13], cardanol [14,15] and chitosan [16,17]. Hybrid resins based on dammar have been used to obtain composite materials reinforced with natural fibers [18] and whose mechanical properties can be modified in a controlled manner [19].

Rosin, as a natural polymer extracted from pine trees, is renewable, abundant and inexpensive. The major component in rosin is abietic acid, a partially unsaturated compound with three fused six-membered rings and a carboxyl group, which gives it good hydrophobic properties [20]. Raw pine resin obtained by "wounding" trees contains approximately 70% rosin, 15% turpentine and 15% waste and water [21].

Among the primary applications associated with rosin are: soap making, printing inks, surface coatings, adhesives and rubber additives. In recent years, it has been widely used in papermaking and polymer synthesis as a natural filler or a source of monomers [22]. Due to its hydrophobic character and

**email: dbolcu@yahoo.com*

affinity for wood, rosin has the potential to improve the properties of wood. Several studies have been done using rosin and its derivatives to fix copper in wood, to preserve it, as well as to increase the water resistance of wood joints [23,24]. Due to its unique properties (hydrophobicity, biocompatibility, and chemical reactivity), rosin is used in a wide range of products, such as emulsifier [25], waterproofing agent, and insulating material [26]. However, its potential applications as advanced materials are somewhat limited due to certain properties such as low softening point (700^{o}C), poor mechanical properties (fragility at room temperature), and high acidity [27].

Recently, rosin has received increasing attention as a bio-source of renewable raw material in thermosetting polymer science. From rosin acid, an anhydride-type epoxy curing agent was synthesized as maleopimaric acid (RAM) [28]. Using RAM to harden a two-component resin consisting of an E51-type epoxy and a solid phenolic epoxy, a prepreg epoxy resin with a bio content of approximately 30% was developed [29]. Research has shown that the obtained resin can be used for pre-impregnation in the production of "green composites" for autoclave casting. Compared to composites pre-impregnated with 100% petroleum-derived products, green rosin-based composite generally exhibits higher application performance [30]. Given the increased use of polymer-based composites in the aerospace industry, rosin green composites have attracted great interest as quasi-structural aircraft interiors [31,32].

In this paper, some chemical and mechanical properties of some hybrid resins obtained by combining, in different proportions, rosin with a synthetic epoxy resin are studied.

2. Materials and methods

Natural rosin resin diluted with turpentine hardens over time if applied in thin layers, and if kept in closed containers remains in a liquid state. Therefore, the composite materials that have this natural resin as a matrix have a very long curing time. To overcome this drawback, a natural resin polymerization process using Resoltech 1050 epoxy resin and related hardener Resoltech 1058S was generated. This resin will hereafter be called rosin-based hybrid resin.

From this hybrid resin were made three sets of 15 samples, depending on the volume proportion of rosin, as follows:

- the first combination, which had a volume proportion of 45% rosin and 55% epoxy resin, with a density of 1.12 g/cm^3; the samples were abbreviated CE45-xx;
- the second combination, which had a volume proportion of 55% rosin and 45% epoxy resin, with a density of 1.10 g/cm^3; the specimens were abbreviated CE55-xx;
- the third combination, which had a volume proportion of 65% rosin and 35% epoxy resin, with a density of 1.09 g/cm^3; the specimens were abbreviated CE65-xx.

It has been found that for resins with volume proportions of rosin greater than 70% the curing time increases greatly, obtaining materials that deform under the action of very small forces.

It should be noted that the casting and storage of the specimens was carried out at an ambient temperature of 21-23^{o}C. In order to ensure complete polymerization, the specimens were removed from the molds 14 days after casting.

Equipment used

The 15 specimens from each set of hybrid resin CE45, CE55 and CE65 were subjected to the tensile test. The samples were made in accordance with the provisions of SR EN ISO 6892-1:2010. For this request, the LLOYD Instruments Lrx PLU mechanical testing machine was used, with a maximum force of 2.5 kN, a maximum race of the crossbar of 1400 mm, strain gauge on 50 mm. The test speed was 5 mm per minute.

The ATR-FTIR spectra of all resins were recorded using a Bruker Alpha spectrometer. Raman spectra were recorded at room temperature using an inVia confocal Raman microscope (Renishaw) with a 785 nm laser source and a Peltier cooled CCD detector. The single beam power of the laser was 150 mW and the 50x objective of the microscope was used.

3. Results and discussions

Next, representative sample of a set means the sample with average values of the studied mechanical properties.

On the basis of subjecting the samples to the tensile test we obtained following results. The main mechanical characteristics obtained for the 45% rosin and 55% epoxy resin specimens are:

- breaking strength between 17.79-19.21 MPa;
- elongation at break between 3.21-3.60%;
- modulus of elasticity between 805-880 MPa.

Figure 1 shows the characteristic curve for a representative specimen from the combination of 45% rosin and 55% epoxy resin.

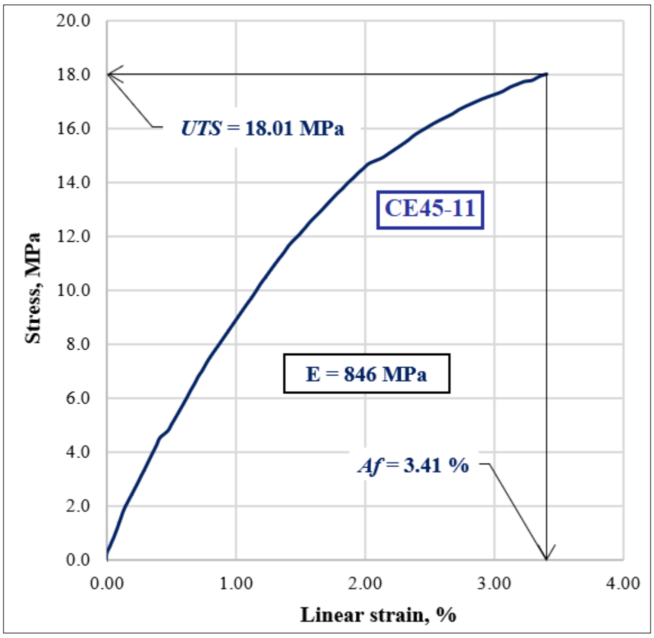

Figure 1. Characteristic curve for a representative sample from the combination of 45% rosin and 55% epoxy resin

The main mechanical characteristics obtained for the 55% rosin and 45% epoxy resin specimens are:

- breaking strength between 8.94-9.95 MPa;
- elongation at break between 8.56-10.08%;
- modulus of elasticity between 378-442 MPa.

Figure 2 shows the characteristic curve for a representative specimen from the combination of 55% rosin and 45% epoxy resin.

The main mechanical characteristics obtained for the 65% rosin and 35% epoxy resin specimens are:

- breaking strength between 2.20-2.65 MPa;
- elongation at break between 25.7-30.2%;
- modulus of elasticity between 11-14 MPa.

Figure 3 shows the characteristic curve for a representative specimen from the combination of 65% rosin and 35% epoxy resin.

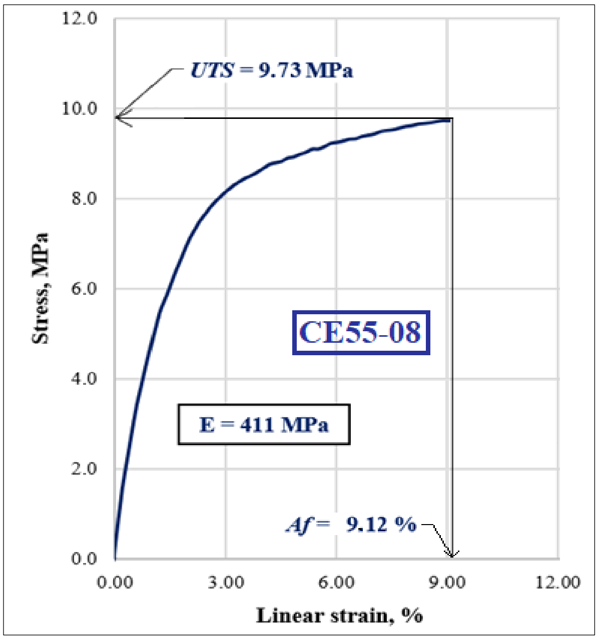

Figure 2. Characteristic curve for a representative
sample from the combination with 55% rosin and 45% epoxy resin

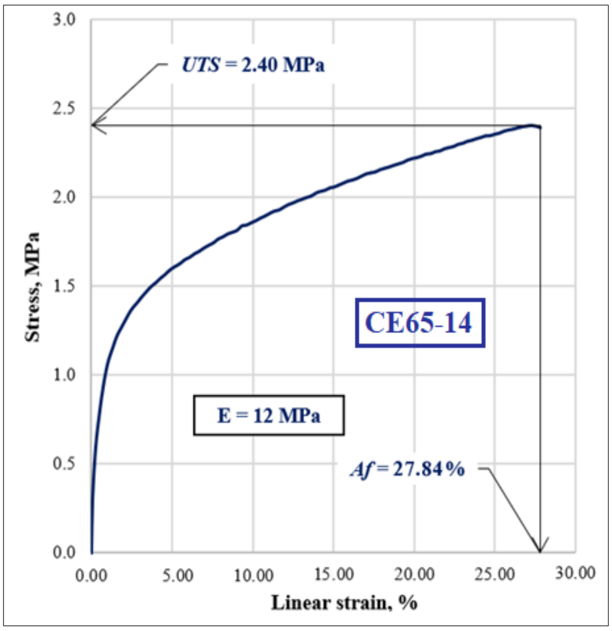

Figure 3. Characteristic curve for a representative
sample from the combination with 65% rosin and 35% epoxy resin

It is observed that in the case of the combination with 65% rosin and 35% epoxy resin, the modulus of elasticity and the resistance to breaking have much lower values than the other combinations. Also, the modulus of elasticity and tensile strength increase with increasing proportion of epoxy resin. This finding may be explained by the fact that epoxy resin has better elasticity and strength properties than rosin.

In Figure 4, the FTIR spectra of the investigated samples are shown.

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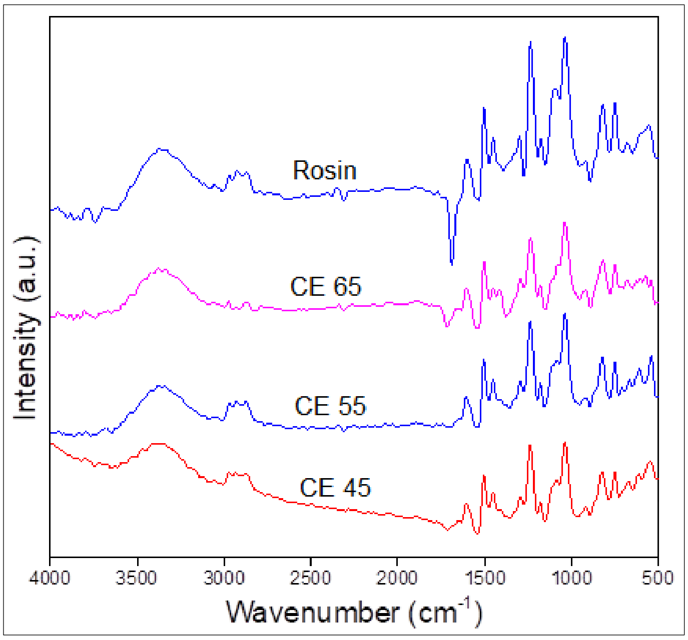

Figure 4. FTIR spectra of colophony (rosin) and hybrid resins

Four regions can be distinguished in the ATR-FT-IR spectra of all investigated samples:

- the hydroxyl region - ranging between 3700 cm^{-1} and 2700 cm^{-1};
- C-H stretching region - from 3000 cm^{-1} down to 2850 cm^{-1};
- Carbonyl region - from 1900 cm^{-1} to 1500 cm^{-1};
- the fingerprint region - from 1300 cm^{-1} and 600 cm^{-1}.

Slight changes in IR band intensity can be noticed after mixing with hardener and epoxy resin, indicating possible modifications at molecular level (Table 1). Thus, the absorption bands attributed to CH_3 asymmetric and symmetric stretching are centered at 2969 cm^{-1} and 2870 cm^{-1}, respectively, for pure rosin, being shifted toward slightly higher values in the mixtures with epoxy resin (Figure 4 and Table 1). The absorption bands located at about 1605 cm^{-1}, attributed to the C=C stretchinh vibration are present in all investigated samples. The intensity of the specific bands from the fingerprint region decreases when the rosin is mixed with epoxy resin (Figure 4).

Table 1. Frequencies corresponding to the most intensive infrared absorption peaks of the investigated samples (in wavenumer/cm^{-1})

Rosin	CE 65	CE 55	CE 45	Assignment
3375	3384	3376	3378	ν(O-H)
2969	2971	2978	2972	$\nu_{as}(CH_3)$
2925	2932	2929	2931	$\nu_{as}(CH_2)$
2870	2874	2875	2875	$\nu_{s}(CH_3)$
1772	-	1775	-	ν(C=O) in cyclic esters
-	1651	-	1656	ν(C=C)
1604	1605	1606	1605	ν(C=C) in aromatic rings
1452	1453	1453	1452	$\delta_{as}(CH_3)$
1299	1295	1295	1295	ν(C-O)
1236	1238	1238	1236	ν(C-O), ω,τ(C-H), ν(C-O-O)
1176	1180	1180	1180	ω,τ(C-H), ν(C-O-O)
1038	1039	1039	1039	ν(C-O), ν(C-C)
822	825	824	822	-
752	752	753	751	ν(C-C) in aromatic rings
683	674	668	682	-
555	548	540	541	δ(C-C-O)

ν- stretching; δ - bending; ω - wagging; τ - twisting; as – asymmetric; s – symmetric

In Figure 5, Raman spectra of the investigated samples are shown.

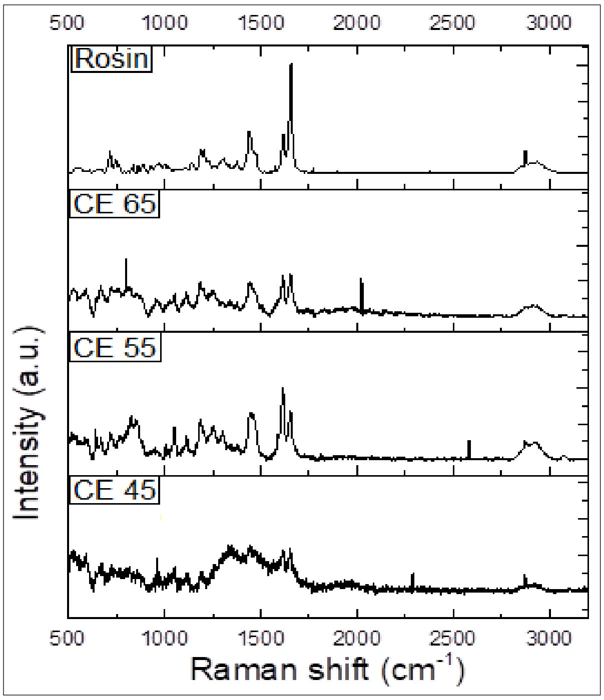

Figure 5. Raman spectra of colophony and hibrid resins

The band from about 1230 cm^{-1} are assigned to the stretching vibration of carboxylic bonds, while stretching of the ester bonds occurs at ~1170 cm^{-1}. The bands from about 1040 cm^{-1} can be attributed to ν(C-O) and ν(C-C) stretching vibrations.

Due to their terpenoid origin, they contain C=C structural units which led to Raman bands above 1600 cm^{-1} attributed to ν(C=C) stretching vibrations. Raman bands located in the range 1480 - 950cm^{-1} can be ascribed to δ(CH), δ(CH_2) and δ(CH_3) deformations and to ν(C-C) stretching vibrations. The most intensive bands of colophony are located at about 1660 cm^{-1} and 1450 cm^{-1}, the first being related to the C=CH_2 stretching vibrations, while the last is usually assigned to the deformations of CH_2 and CH_3 groups. The Raman spectrum of the mixture of hadener and epoxy resin exhibited the most intensive band at about 1625 cm^{-1}. The intensity of the Raman bands in all the investigated samples is proportional to the concentration of solid resins.

4. Conclusions

In order to be able to compare the mechanical characteristics of the epoxy resin (together its hardener) with those of hybrid resins based on mechanical rosin, it should be stated that the properties, given by the manufacturer, of the Resoltech 1050 epoxy resin with the hardener Resoltech 1058S are: breaking strength 82 MPa; modulus of elasticity 3500 MPa; elongation at break 2.4%. From the analysis of the characteristic curves, it can be found that the hybrid resins studied have lower values of the breaking strength and modulus of elasticity and higher values of the elongation at break, compared to those of the epoxy resin.

A comparison of the mechanical properties between the studied hybrid resins shows that the values of breaking strength and modulus of elasticity decrease, and the elongation at break increases, with increasing volume proportion of rosin. Thus, for the CE55 hybrid resin, the breaking strength and the modulus of elasticity have half the values of those obtained for the CE45 hybrid resin, although the difference in volume proportions of rosin is just 10%. Even more significant decreases were obtained for the CE65 hybrid resin.

The characteristic curves showing the specific stress-strain dependence differ greatly for the three types of hybrid resins. Although all show nonlinearities from the beginning of stress, the nonlinearity is more evident for the CE55 and CE65 resins. A flow phenomenon occurs in these, the elongation increasing greatly at a small increase in tension. A tripling of the elongation at break is obtained when increasing the proportion of rosin from 45 to 55% and an additional triple for the CE65 resin.

The use of hybrid resin based on rosin is recommended in various fields of activity, for example in the field of dental medicine when making molds for implants, surgical guides, drilling templates, etc. This is due to the advantages offered by the chemical structure, low cost and mechanical property values of this resin.

The studied hybrid resins can be used to make some composite materials because their mechanical behaviour depends especially on the properties of the reinforcing materials. Due to the low price of rosin, about 10 times lower than that of synthetic resins, economically profitable composite materials can be obtained.

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Manuscript received: 25.01.2023