

## Rosin Based Composites for Additive Manufacturing

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**Abstract.** Rosins are the non-volatile exudates of pine resins with hydrophobic characteristics that are widely used as a precursor for many industrial applications. In this paper we discuss the nature, process and its applications as a matrix for a composite material for additive manufacturing. The composite material has been tailored to chemical and mechanical properties with respect to their applications.

### Introduction

Additive Manufacturing (AM) is increasingly used in the manufacture of new products. The technique allows for the tailoring of each part individually, without a cost or time penalty. The introduction of AM has revolutionized the prototyping and manufacturing industry, which previously relied on more expensive and time consuming methods such as moulding, forming and machining [1]. This technology is capable of creating objects from 3d digital data, adding the material layer by layer in contrast with traditional methods.

Although significant progress has been made in AM, it has not yet been explored from a sustainable perspective. Nature provides a wide range of renewable raw materials with varying properties and different chemical compositions. These materials are particularly interesting as alternatives to fossil resources for energy generation and as starting materials for the manufacturing industry. In this article, rosin is presented as a matrix for composite materials for sustainable 3d printing.

Rosin is the non-volatile solid material that is left after distillation of the pine tree resin that is obtained by tapping the trees. The extraction process consumes little energy and it only produces clean water as waste [2].

Sustainable manufacturing is defined as the creation of manufactured products that use processes that minimize negative environmental impacts, conserve energy and natural resources and are also safe for employees, communities, and consumers as well as being economically sound [3].

Rosin is obtained from living pine trees and other plants typically belonging to the conifer family. The resin is then processed in a batch manner by heating fresh liquid resin to vaporize the volatile liquid terpene components separating the resin in to three basic components, clean water (15%), turpentine (15%) and rosin (70%) [2,4]. The process is very eco-friendly and it makes full use of gravity based flow. A schematic of the process is shown in Figure 1.

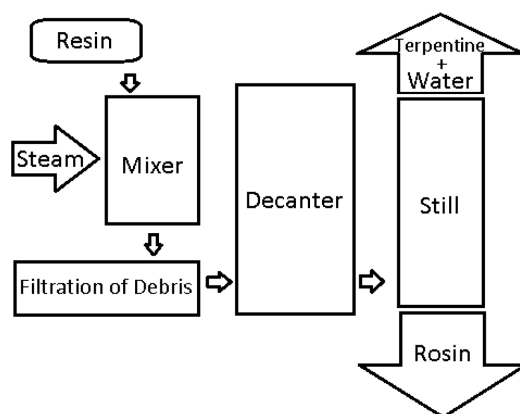


Fig. 1: Schematic of the process used to separate pine resin in to Rosin, water and turpentine.

The rosin produced by this method is a semi-transparent mass and readily fusible with glossy appearance, varying in colour from pale yellow to black. It is insoluble in water but soluble in alcohol, carbon disulphide, chloroform, ether, many fixed and volatile oils, glacial acetic acid and in light petroleum [5]. At room temperature it is a brittle glassy material but it softens at about 100° C.

Rosin consists of different resinous tricyclic diterpene monocarboxylic acids with a molecular formula  $C_{20}H_{30}O_2$  and thus belongs to the diterpenes (four isoprene units) [6]. The rosin acid molecules possess two chemically reactive centers: the double bonds and the carboxyl group. The double bonds in abietic acid are conjugated while in pimaric acid they are non-conjugated [7].

Pine rosin is a widely available source of abietic acid, the principle acid, the chemical structure is shown in Figure 2 along with levopimaric acid and pimaric acid. Shown in Figure 3 is an example of the amber translucent raw rosin glassy nuggets.

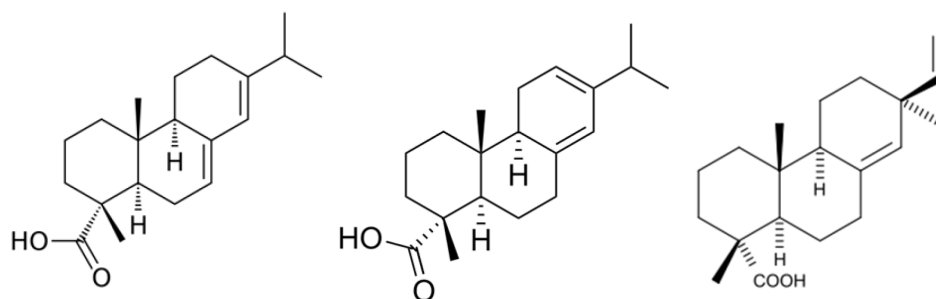


Fig. 2: (a) Abietic Acid, (b) Levopimaric acid, c) Pimaric acid.



Fig. 3: Piece of rosin glass (~2cm) as taken from the output of the separation process shown in Figure 1.

Rosin mainly consists of different rosin acids and are not polymers like hydrocarbon thermoplastic resins but a combination of molecules characterized by three fused six-carbon rings, double bonds that vary in number, location and a single carboxylic acid group as in Figure 2. The ratio of these isomers in rosin depends on the collection method and the species of the tree from which the rosin is

produced. The molecular weight of the rosin is fairly different compared with hydrocarbon resins. Rosin is classified into three main types; gum rosin, wood rosin and tall rosin.

## Materials

Gum rosins were obtained via local producers, Costa e Irmãos (Leiria, Portugal). Nanoclay, Montmorillonite modified with 25-30% of trimethyl stearyl ammonium was purchased from Aldrich and Chloroform from Alfa Aesar and used as received. Polycaprolactone, (PCL) polymer (CAPA 6500) from Perstorp Caprolactones (Cheshire, United Kingdom) with a molecular weight ( $M_w$ ) of 50 kDa was used. Experiments were conducted using standard laboratory glassware.

## Experimental Methods

### Wide Angle X-Ray Scattering

Wide angle x-ray scattering (WAXS) experiments were performed on the Bruker AXS Nanostar at the University of Reading Chemical Analysis Facility, UK. The equipment has a compact 3 pin hole collimation and a beam size  $\sim 0.6$  mm. 2D WAXS patterns were collected onto an image plate placed approximately 10 cm from the sample position. Data was collected from  $|Q| = 0.3 \text{ \AA}^{-1} - 4.6 \text{ \AA}^{-1}$  where  $|Q| = 4\pi\sin\theta/\lambda$ ,  $\lambda$  is the wavelength and  $2\theta$  is the scattering angle. A wavelength of  $1.5418 \text{ \AA}$  was employed. Varying compositions of solvent cast PCL/rosin mixtures were examined. A data collection time of 30 minutes was used for each sample. A corundum standard was subjected to WAXS and its corresponding scattering pattern, which has known  $Q$  values of the diffraction rings, was used for calibration of the sample to detector distance.

### Scanner

The extruded cube was digitized using a Steinbichler Comet 5 3D scanner. The nominal resolution obtained with this equipment is about 30 micron, but the opalescence of the material might reduce the effective resolution due to sub-surface scattering of the light pattern projected by the scanner.

### Compression tests

The compression tests were performed with an Instron Model 4505 H2464 testing system with a crosshead speed of 1mm/min at room temperature.

### Optical Microscopy

The optical microscope image was taken with a Daffodil MCX100 from Micros.

### Additive Manufacturing

Rosin is presented as a composite matrix for use in additive manufacturing. We are using Fused Deposition Modelling (FDM) technology to print 3d objects. FDM is an additive manufacturing technology that uses a preformed filament which is heated to above its melting or softening point in a temperature-controlled head and extruded as a jet of liquid material that is deposited layer by layer onto a build platform, the extruded hot material hardens and adheres to the preceding layer creating a three dimensional object.

The production of a preformed filament and the operation of the extrusion system are two stages that require optimization in the development of new materials. The first step is bypassed by using a pellet based extruder so there is no need for a preformed filament and the extrusion works by heating the material to above its melting or softening point and compressed air forces it down a screw through a nozzle on to a platform.

A 3d bioextrusion system, which was developed by the Centre for Rapid and Sustainable Product Development (CDRSP) of the Polytechnic Institute of Leiria (IPL, Portugal) is used to explore the

potential of rosin based resins for use in additive manufacturing. Figure 4 shows a schematic of the equipment used in this work [8].

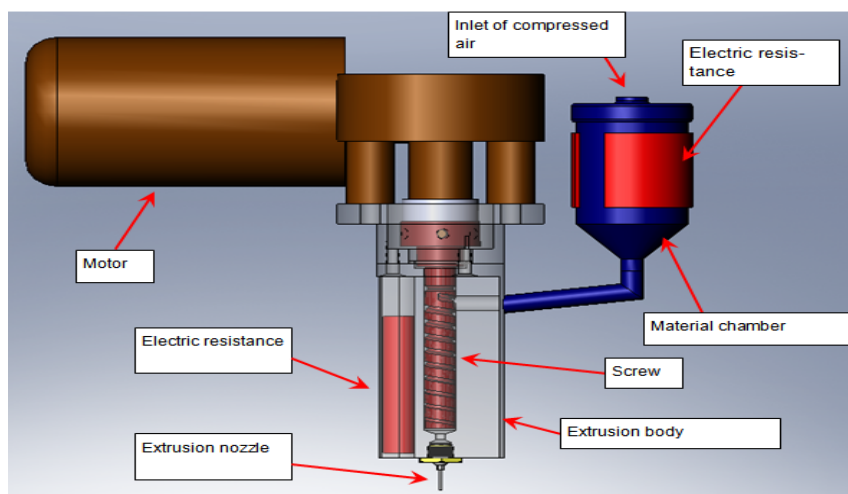


Fig. 4: The extruder based FDM system used in this work.

Rosin scaffolds were produced by deposition of fibers through a nozzle with a diameter of 400  $\mu\text{m}$ . Scaffolds with dimensions of 15 x 15 x 2 mm and pore configuration of 0°/90°, were processed at 115 °C, using deposition velocity of 300 mm/min and the screw rotation velocity of 40 rpm were found to be the optimum parameters to produce the scaffolds.

## Results and Discussion

Through additive manufacturing, we were able to produce scaffolds with the equipment described above. The scaffolds prepared with rosin lacked precision as the material flowed after deposition and they were extremely brittle. Several tests were made by adding of up to 30% (w/w) of nanoclay (Montmorillonite) in to the rosin at 115°C. Figure 5 shows the scaffolds produced using the extruder based FDM additive manufacturing technology. These objects are ~1.5cm in width with a strand thickness of ~400 $\mu\text{m}$ .

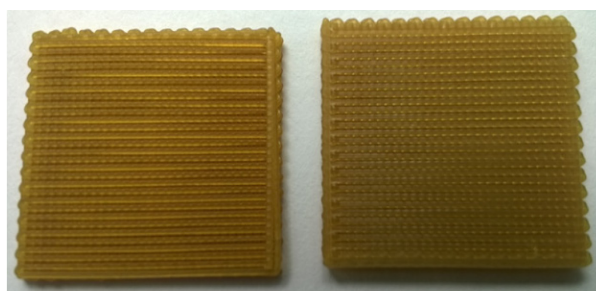


Fig. 5: Scaffold-like objects of ~1.5 cm of width produced using the extruder based FDM additive manufacturing technology.

Rosin composite scaffolds were successfully obtained in a process that is 100% green using our bio-extrusion system as mentioned above. We have explored a way that allows the processing of rosin with the addition of 30% of nanoclay, there is some improvement in the flow of the extruded filaments but the scaffold composites (Figure 5) are still very brittle. The brittleness is a drawback of the natural rosin and can be overcome by mixing it with a polymer with superior properties. Polycaprolactone a synthetic biodegradable polymer has been widely used due to its high flexibility and hydrophobic nature. To improve the properties we have explored the use of polycaprolactone with a  $M_w$  of 50 kDa, at different compositions. The components are mixed with mechanical mixing in chloroform, after which the dry solvent is allowed to evaporate and the solid mixture is fed to the extruder in order to produce cubic shapes on the order of ~1  $\text{cm}^3$  with a strand thickness of ~400 $\mu\text{m}$  as seen in Figure 6.

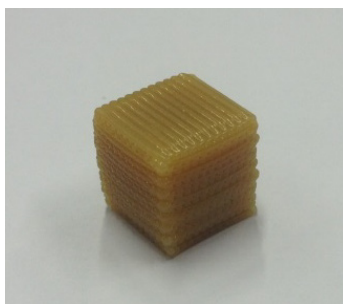


Fig. 6: A  $\sim 1\text{cm}^3$  cube-like object produced using the extruder based FDM additive manufacturing technology.

Figure 7 shows a scanned cube and the dimensions estimated from the digitized model along each of the main axes were: 10.09 mm (width), 9.63 mm (depth, top), 10.32 mm (depth, bottom) and 9.90 mm (height).

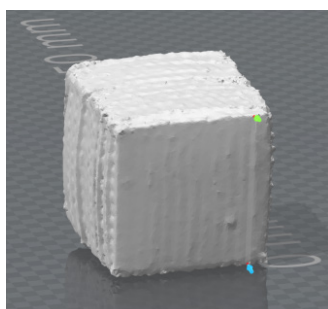


Fig. 7: An image from a 3d scan of a  $\sim 1\text{cm}^3$  cube prepared using the FDM system shown in Figure 4 using a thermoplastic resin based on (rosin, nanoclay) and polycaprolactone (50w/w%).

The Compression Stress-Strain was measured for all the cubic objects and is presented in Figure 8 from where the compressive modulus was taken and this is shown in figure 9.

The brittleness of the rosin/nanoclay material is overcome with the addition of PCL, at 30w/w% PCL the compressive modulus increases drastically when compared to 20w/w% PCL. The printed sample has good mechanical properties and this composite (30w/w% PCL) can be used to produce printed objects for various applications.

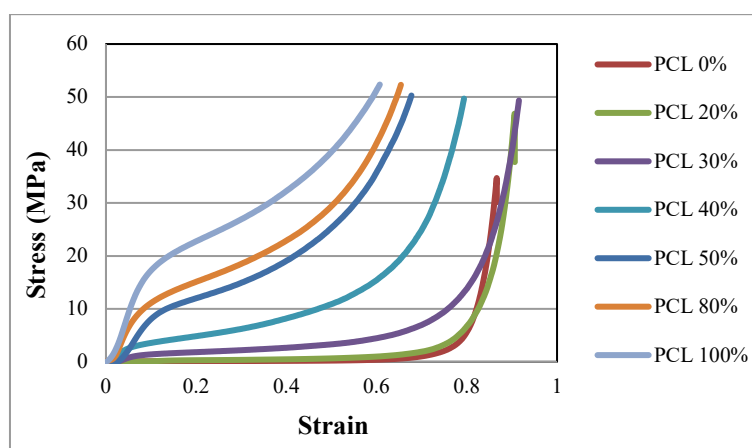


Fig. 8: Compression stress-strain curve for different percentages of PCL.

It shows that an increase in PCL increases the compressive modulus. The rapid increase in modulus with concentration above 20% we attribute to the formation of a percolated network of PCL spherulites.

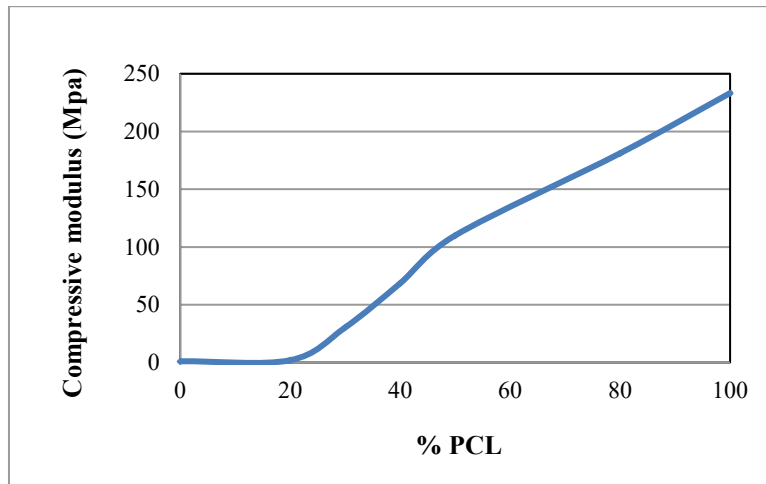


Fig 9: Compressive Modulus vs % PCL

In order to investigate the microstructure of the PCL component in rosin/PCL blends, WAXS patterns were measured (Figure 10). It is found that the microstructure of the rosin/PCL is characterized by an amorphous halo (rosin) and crystalline diffraction peaks that correspond to the PCL crystal. The scattering patterns show that with a decrease in PCL content there is a corresponding decrease in the intensity of the crystalline scattering peaks and an increase in the amorphous halo attributed to the rosin. The wide-angle x-ray scattering confirms that the rosin and PCL are phase separated and maintain their molecular organization.

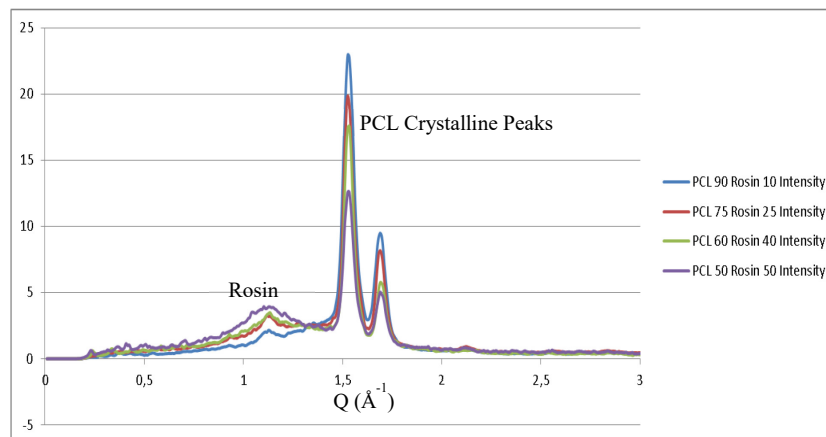


Fig. 10: Wide-angle x-ray scattering for rosin and PCL mixtures. Scattered Intensities are scaled to sample thickness.

The morphological investigation shows the PCL spherulites among the rosin/nanoclay (figure 11). The increase in the mechanical properties can be explained by percolation as the PCL has a reinforcing effect on the structure by forming a stiff continuous network. This can be seen for compositions as low as 30w/w% PCL.

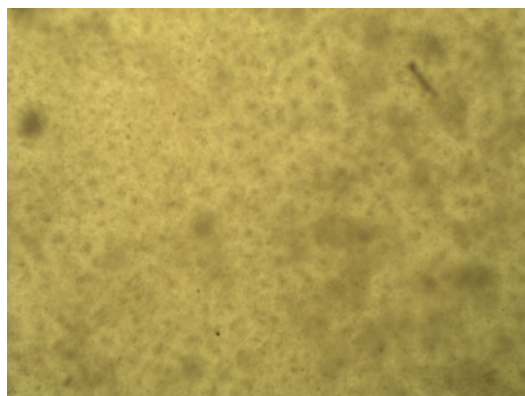


Fig. 11: Optical microscope image of (rosin/nanoclay) PCL (30w/w%). The image corresponds to a sample width of 1000  $\mu\text{m}$ .

## Conclusion

Rosin has been effectively used as a versatile natural material to successfully produce Rosin based components using 3d printing. We have shown that rosin can be mixed with other sustainable products without any further treatment thereby minimizing energy consumption and waste products for use in additive manufacturing.

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