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Optical Properties of Rosin/PMMA Nanocomposites

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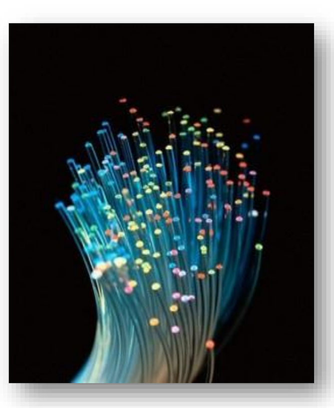
Optical plastics can acquire new physical characteristics, without losing transparency, by dissolving functional molecules in them. These physical characteristics could be for example an increased refractive index, fluorescence, phosphorescence, and absorption in ultraviolet, visible or infrared spectral region, etc. However, to avoid crystallization and precipitation of the organic solute, with formation of crystals capable to scatter the light, a high chemical affinity between the organic molecule and the polymer side-groups is required. Recently, some natural substances are being investigated as polymer additive for their unique optical properties. In particular, a wide number of fluorescent derivatives of **rosin (colophony)**, have been synthesized in order to modify the emission wavelength of this natural molecule. Structurally, the colophony has an hydrocarbon skeleton, containing a diene group, and it is functionalized by a carboxylic acid group (COOH). Similarly, acrylic polymers, like poly(methyl methacrylate) (PMMA), contain a hydrocarbon backbone chain and a side-group, which contains an ester function. Consequently, a strong physical interaction between polymer and rosin is possible and such property allows to obtain a solid solution, which is optically transparent. Optical transparency is a relevant characteristic for a fluorescent material since it allows to collect the emission of all dissolved molecules.

Here, rosin solid solutions in PMMA have been prepared by solvent casting technology and the obtained material has been characterized by fluorescence measurements. In addition, the thermal stability of these rosin-PMMA solid solutions has been investigated by thermo-gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The chemical composition has been identified by infrared spectroscopy (FT-IR).

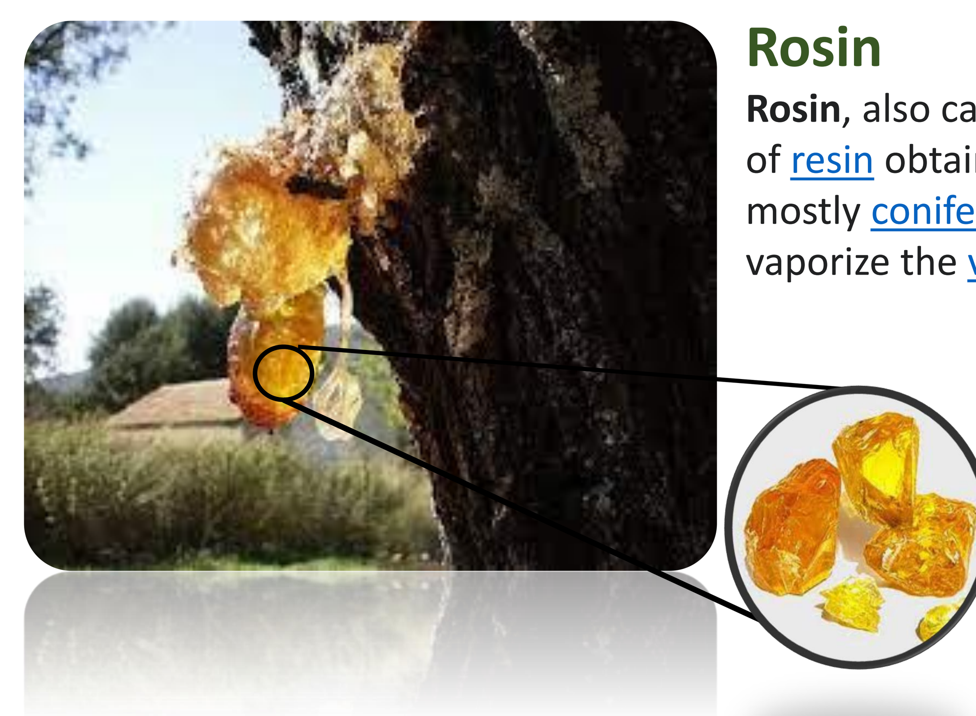


Optical plastics

Optical plastics are amorphous linear polymers with neutral optical characteristics (i.e., they are colourless, perfectly transparent and with a refractive index close to that of glass). Typical optical plastics are

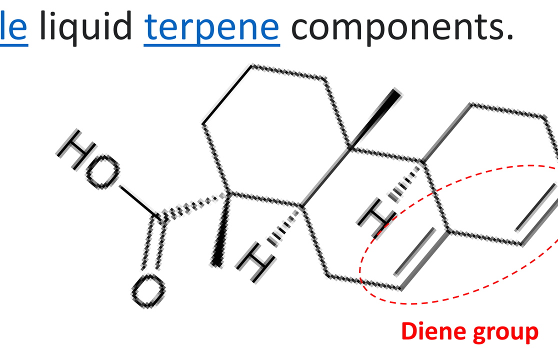
- **poly(methyl methacrylate) (PMMA),**
- **polycarbonate (PC),**
- **polystyrene (PS).**

These materials are widely exploited for several traditional and advanced technological applications (e.g., lenses, optical windows, waveguides, etc.).



Rosin

Rosin, also called **colophony** or **Greek pitch**, is a solid form of resin obtained from pines and some other plants, mostly conifers, produced by heating fresh liquid resin to vaporize the volatile liquid terpene components.



Chemical structure of the abietic acid, main component of rosin.

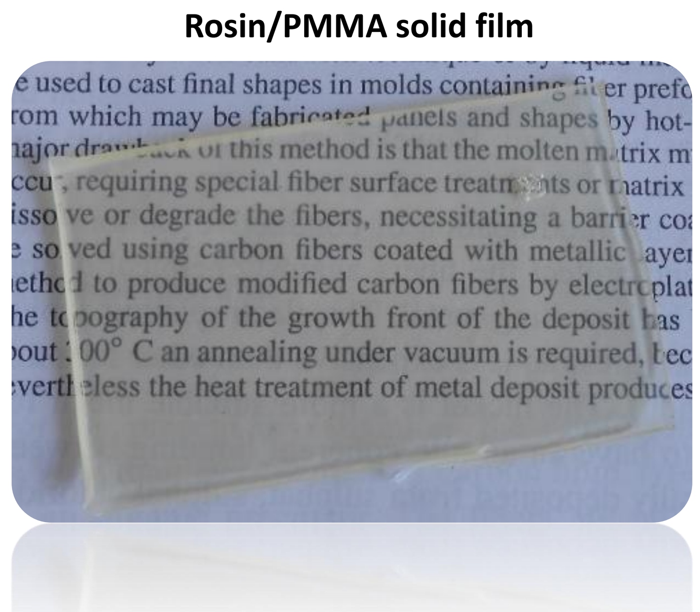
Rosin is a mixture of different resin acids, especially abietic acid. It looks a polymer but a blend of eight closely related rosin acids characterized by three fused six-carbon rings, with double bonds that vary in number and location, and a single carboxylic acid group. The advantages of the use the rosin like additive are: not toxicity ,sustainability, and availability at low cost.

Experimental Results

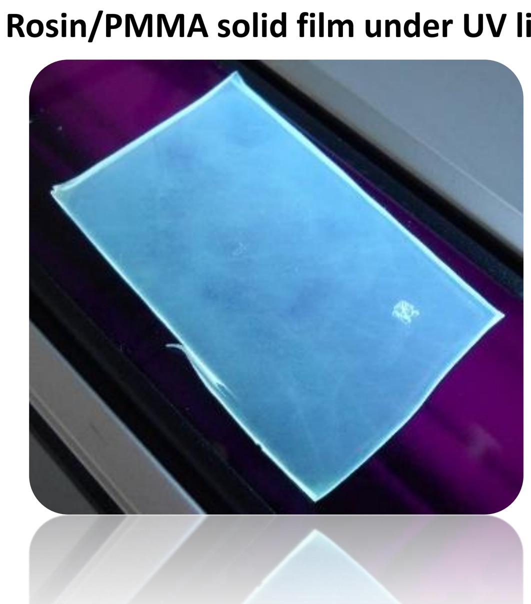
The commercial rosin was acquired to prepare a solid solution in PMMA by solution casting. The Transparent and fluorescent PMMA film was obtained by the presence of Rosin (about 1% by weight) dissolved inside

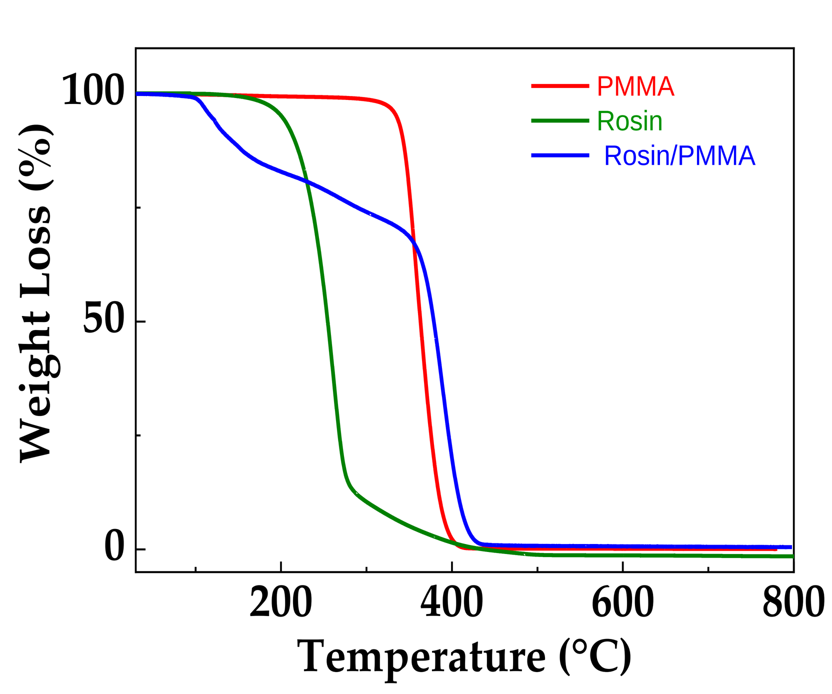
Rosin under UV light

Rosin/PMMA solid film



Rosin/PMMA solid film under UV light

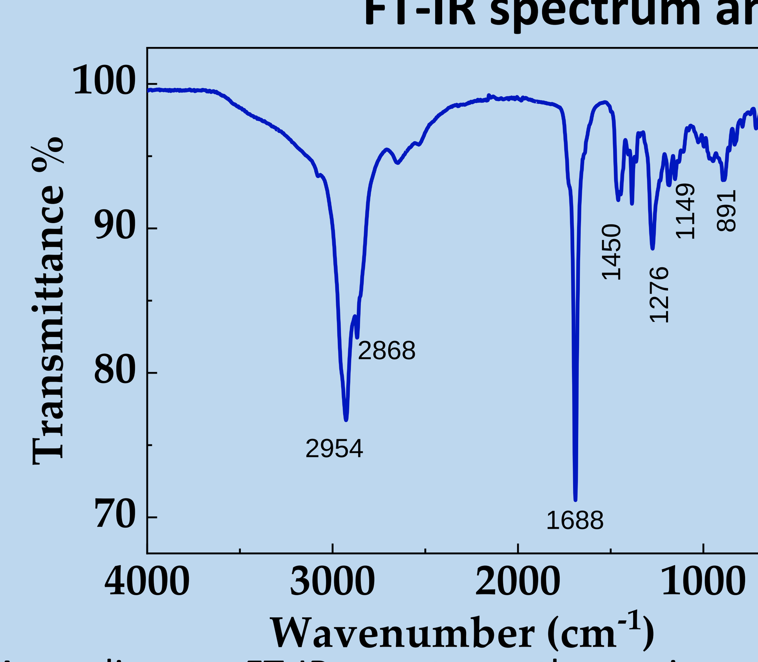


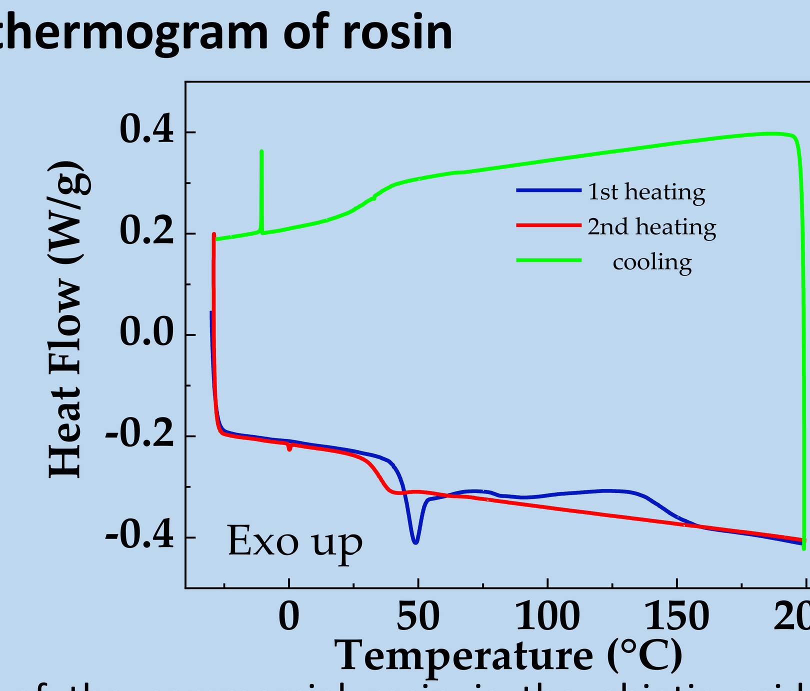


TGA thermograms

The TGA curve of Rosin shows as the thermal decomposition occurs at temperatures ranging from 190 to 310 °C. These results also show the presence of a small amount of volatile molecules in rosin sample such as terpene from the turpentine residues.
In addition, Rosin dissolved in PMMA leaves the solid solution at a temperature of 100°C whic represents maximum temperature for the use of this materials.

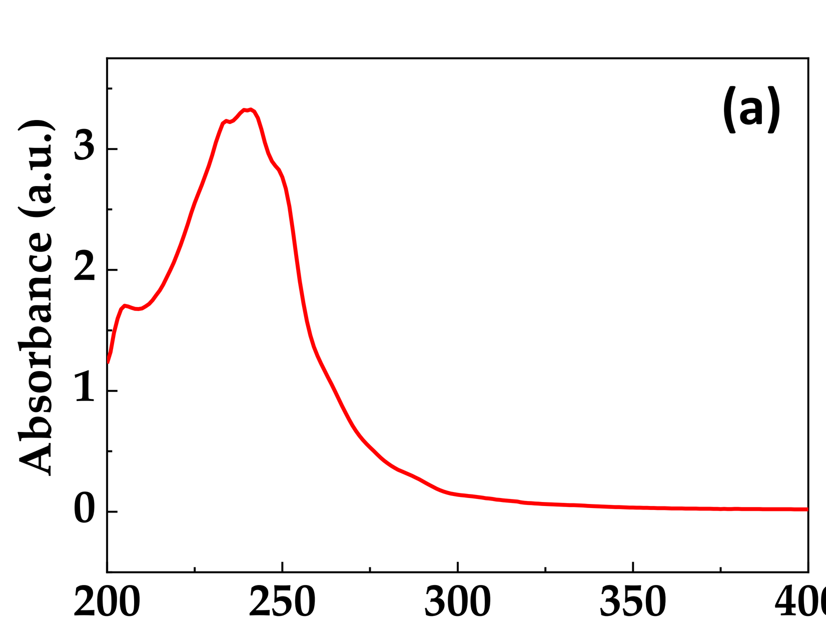
FT-IR spectrum and DSC thermogram of rosin



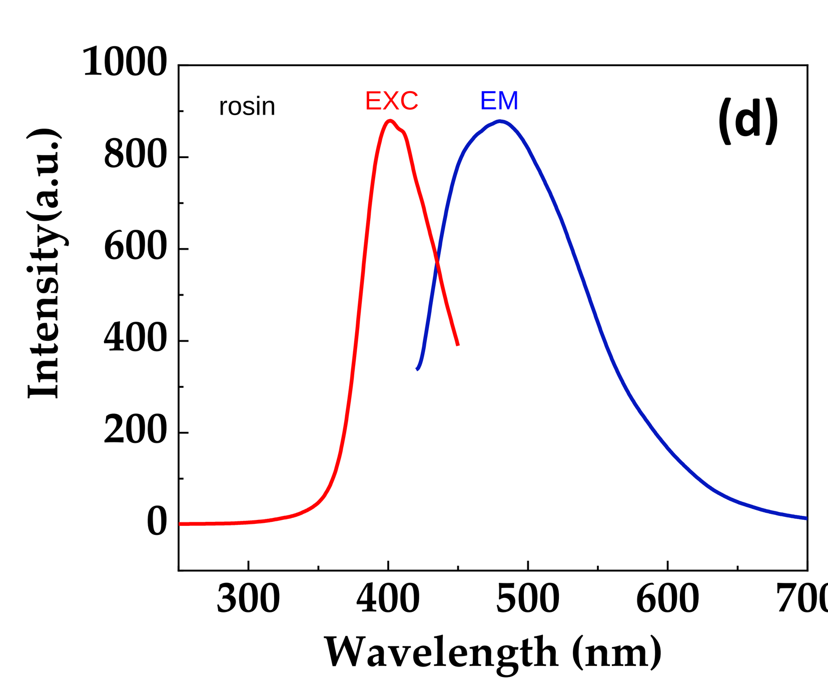


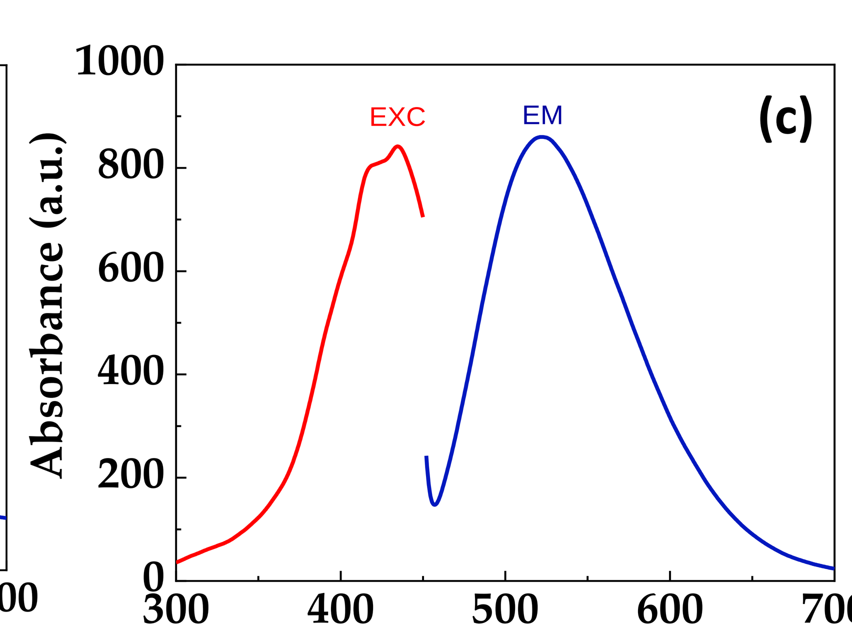
According to FT-IR spectrum the main component of the commercial rosin is the abietic acid. The stretching absorption of the -OH, visible at 3427cm^{-1}, is a broad band of low intensity. The tight and very intensive absorption band of the carbonyl group is clearly visible at 1688cm^{-1}. The absorption band located at ca. 1450cm^{-1} is generated by the bending vibration of hydroxyl group and the absorption band at 1276cm^{-1} is generated by the stretching of the C-O bond. The infrared spectrum contains also an absorption band located at 1654cm^{-1} belonging to the diene stretching resonance and an absorption band located at 891cm^{-1} generated by the bending of the C=C bond. Further absorption is generated by the olefinic =C-H group that is located at 1450cm^{-1} and corresponds to the bending vibration (rocking). Other aliphatic hydrocarbon groups (CH_3, CH_2 and CH) present in the molecule generate strong symmetric/antisymmetric stretching absorption at 2954cm^{-1}, 2868cm^{-1}. In addition, the DSC thermo-ghram shows an exothermal signal at a temperature above Tg (48°C), which is indicative of a chemical transformation.

Optical characterisation by UV-Vis absorption and emission spectroscopies



Absorption spectrum of rosin





Excitation and emission spectra of rosin and rosin/PMMA film

Rosin has a quite intensive optical absorption band in the UV spectral region. In particular, two peaks located at 205nm and a stronger absorption at 240nm can be observed, while there are not visible absorption bands **(a)**.
As visible in the fluorescence spectrum of the pure compound **(b)** the emission band is placed at 480nm.
A red-shift of this emission band occurs when rosin is dissolved in PMMA **(c)**.
Finally, rosin solutions in PMMA are both optically-transparent and strongly fluorescent.

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