

Characterization of Indian pine Oleoresin and Evidence for the existence of Silicon compounds

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(Received 14 April 2019, Accepted 28 April 2019, Published 30 April 2019)

Abstract

Herein we report the thermal behavior of the Indian pine oleoresin by thermogravimetric, differential thermal analysis (TG-DTA) and powder XRD studies. The natural oleoresin is amorphous as seen from powder XRD studies. However, when heated to a high temperature, it forms crystalline SiO₂ with characteristic reflections of alpha-quartz (SiO₂) as seen in powder XRD patterns. TG-DTA analysis shows that the amount of SiO₂ obtained upon heating is about 75% of the initial resin mass, a huge proportion compared to a maximum of 20% reported in the literature from other plant sources. The FTIR spectra of the oleoresin and its organic extract show a band around 1013-1081 cm⁻¹, indicating the presence of compounds containing Si-O or Si-O-R groups in oleoresin. Our results suggest that the oleoresin contains a substantial amount of dispersed biosilica and/or several organosilicon compounds, not reported till date.

Keywords: Pine oleoresin, resin, silica, X-ray diffraction, thermogravimetry, FT-IR.

1. Introduction

Pine is a coniferous tree in the genus *Pinus*. These trees have a highly developed resin duct system and synthesize abundant amounts of oleoresin containing volatile and non-volatile terpenes. The oleoresin is commercially tapped from living trees for various industrial applications. The steam distillation of pine oleoresin gives turpentine oil (gum turpentine), which is a common solvent and thinner for paints along with several other applications. The solid remaining after steam distillation is the rosin (colophony), which is used in printer inks, varnishes, soldering fluxes, and sealing wax. Chemically, turpentine oil is a complex mixture of several hydrocarbons, mainly the monoterpenes, α - and β -pinene, whereas rosin consists of various resin acids, especially abietic and levopimaric acid [1]. Chirpine (*Pinus roxburghii*), also known as three-needled pine, is an Indian

conifer that grows mainly in the Himalayan region at an elevation of 500-2200 meters [2]. In India, chirpine oleoresin is also used to produce fragrant smoke which is considered as a disinfectant. The burning of oleoresin produces volatile and nonvolatile solid residues. The chemical and physical changes associated with the burning process are not well-understood phenomena despite its extensive use. Herein the chemical and physical changes in oleoresin were investigated, and the presence of a significant amount of silicon is inferred from our experiments. The detailed observations made from TG-DTA, XRD and IR studies of oleoresin subjected to different heating conditions are being reported.

2. Method

The samples of pine oleoresin used in the studies here were obtained from a local market, where it is sold as “Dhoop”. The commercial samples were used directly in all the experiments. The hard and waxy translucent chunks of as-obtained oleoresin were fragmented into pieces. The decomposition behaviors were investigated by a simultaneous TG-DTA setup (Setaram, France) and by powder XRD (Rigaku Smart Lab powder XRD unit). The TG-DTA traces were recorded while heating the sample in a platinum crucible at a heating rate of 10°C/min to 600°C in flowing air. The FTIR spectra of the samples were recorded in transmission mode, from 500 to 4800 cm⁻¹, using the sample either as Nujol mull or direct gel. Crushed chunks of oleoresin were heated on a hotplate, and melting was visually observed before the formation of white crystalline residues. To separate the inorganic and organic components of the oleoresin, the specimen was sequentially washed with a series of organic solvents, toluene, chloroform, and dichloromethane. The dissolved organic components of the oleoresin in three solvents were pooled together and allowed to evaporate slowly at room temperature in a fume hood. A yellow gel-like organic extract of the oleoresin obtained after evaporating organic solvents was characterized by FTIR and compared with the pine oleoresin samples.

3. Results and Discussion

The selected translucent chunks of the pine oleoresin, its organic extract and inorganic components (residues) were amorphous as observed from the broad hump in their XRD patterns (Figure-1). This is, in general, attributed to the polymeric nature of the oleoresin. The FTIR spectra of the oleoresin and its organic extract are shown in Figure-2. Overall the IR traces for both the samples are identical except the modes are broadened in the oleoresin when compared with its organic extract. The observed IR modes of the oleoresin samples are tabulated in Table-1. The IR traces are closely similar to those reported earlier for other pine oleoresins [3, 4]. The modes observed at 1377, 1453, 1700, 2870 and 2923 cm⁻¹ are the characteristics modes of the oleoresin which are present in both the samples. The band around 1700 cm⁻¹ is the characteristic of a carbonyl group. The broad absorption band observed at around 3400 cm⁻¹ is characteristic of stretching mode

of OH group. Interestingly, some of the modes observed in the range 1013-1081 cm^{-1} are the characteristics of Si-O or Si-O-R groups (see Table-1) [5] indicating the presence of either biosilica or organosilicon compounds in the oleoresin.

In order to understand the thermal decomposition behavior of the oleoresin, they were first heated on a hotplate or in an open flame such that they do not catch fire. The weight loss observed was around 48 %. The powder XRD pattern of the residues left after heating (52%), shown in Figure-3, indicates the formation of SiO_2 . However, when oleoresin sample was heated in a furnace to 800°C at a heating rate of 5°C/min the weight loss was 98 %. The powder XRD pattern of the residues left after heating (<2%) shows the formation of CaO or $\text{Ca}(\text{OH})_2$ (Figure-3). The variation could be due to different extent of volatilization or decomposition of the sample during burning as discussed below.

To get a better insight into the thermal behavior and stabilities of oleoresin, TG-DTA traces (shown in Figure-4) were analyzed. A weak, but sharp, endothermic peak is observed around 235°C, and the weight loss initiates around this temperature. This endothermic peak can be attributed to the melting of the oleoresin. The weight losses of the oleoresin occur in multiple steps—the initial loss could be due to volatilization of the organic components while subsequent losses can be due to decomposition and burning of the oleoresin. A broad endothermic peak observed in a wider range of temperature, viz. 325-425°C could be due to the decomposition of carboxylic acids and other hydroxyl compounds. The losses observed at a still higher temperature appear as a sharp exothermic peak, which can be attributed to the burning of organic molecules upon decarboxylation or dehydroxylation. The net weight loss of the oleoresin, when heated to 600°C, was found to be only 25 % in TG. The residues left after TG-DTA runs was SiO_2 (quartz), as inferred from their powder XRD pattern.

Several reports in literature suggest the presence of dispersed nano SiO_2 in different parts of the plant [6]. The finely dispersed SiO_2 , if present in the oleoresin, may sublime along with the volatile organic molecules during heating experiments in open crucibles, resulting in a more significant loss. It might be the case that while heating in the furnace, the sample catches fire leading to a significant loss (98 %). However, while heating oleoresin in open flame, care was taken not to allow the samples to catch fire and hence weight loss was significantly less (48 %). The TG-DTA experiments, therefore, gives better insight. The TG-DTA results indicate that the SiO_2 obtained upon heating the oleoresin to 600°C is about 75 % of the initial oleoresin mass, a surprisingly huge proportion compared to a maximum of 10-20 % reported in literature from other plant sources [6-9].

Thus, the formation of silica on heating suggests the presence of either biosilica/nano-silica (SiO_2) or organosilicon compounds in the natural pine oleoresin. The organosilicon compounds having Si-O-R groups may decompose into silica at an intermediate temperature, and grow to larger crystallites of SiO_2 . The nano-silica or biosilica can also grow to larger crystallites of SiO_2 under suitable thermodynamic conditions.

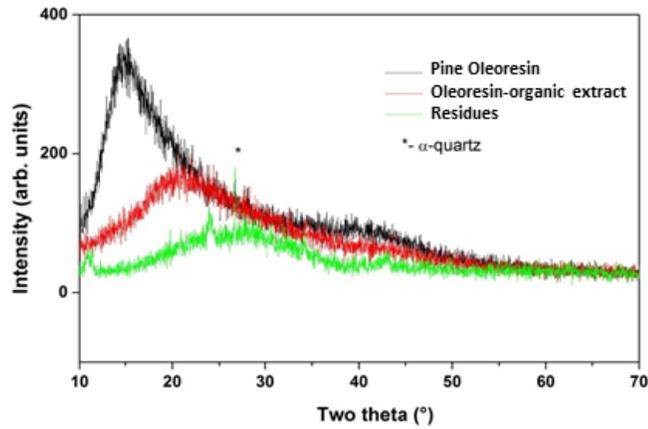


Figure-1. Powder XRD pattern of pine oleoresin, its organic extract, and the inorganic residues left after organic extract. Two broad peaks observed in the residue left after organic extract may be due some crystalline impurity phase which could not be identified in this study.

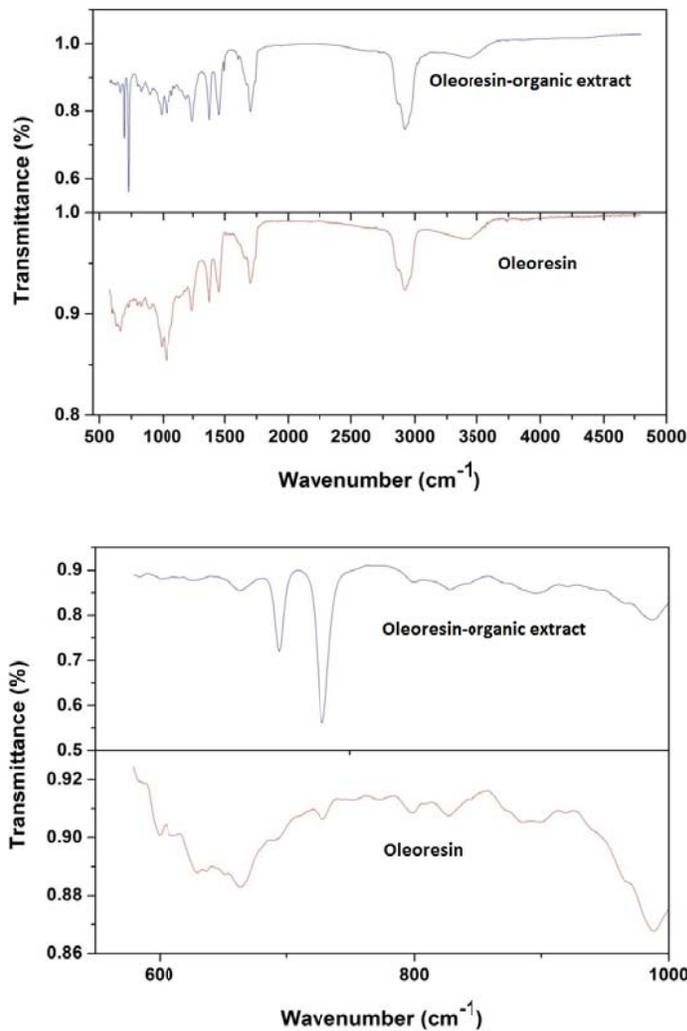


Figure-2. FTIR spectra of the pine oleoresin and its organic extract.

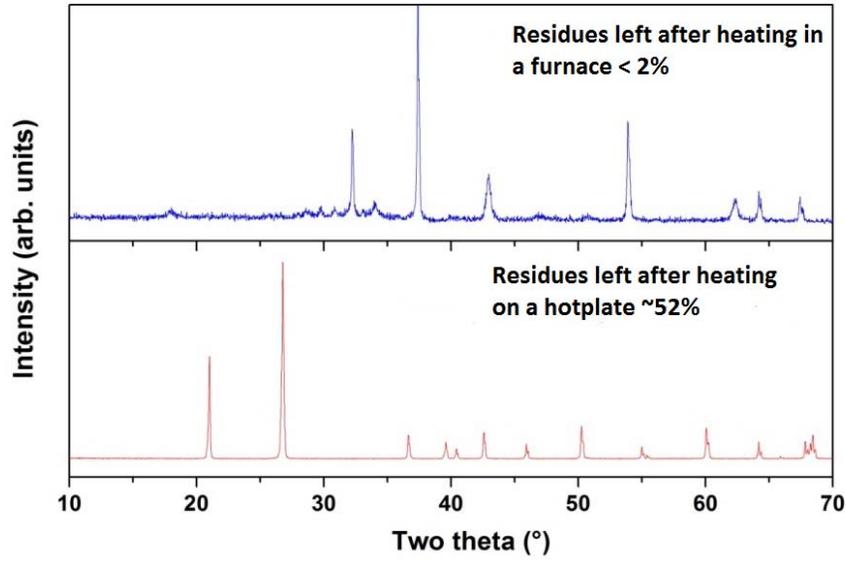


Figure-3. Powder XRD pattern of the pine oleoresin after heating to 800°C in the furnace (blue trace) and after heating on a hotplate (red trace).

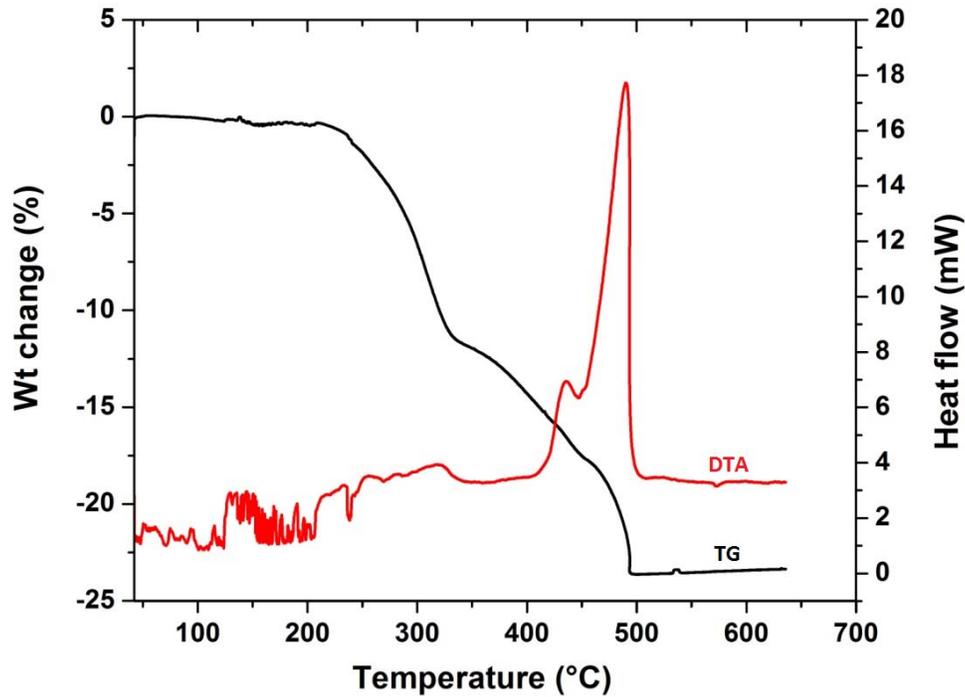


Figure-4. TG-DTA traces of pine oleoresin. Black trace-TG, Red trace-DTA.

Table-1. Peaks in FTIR spectra

Pine Oleoresin (IR peaks in cm^{-1})	Peak characteristics	Oleoresin-organic extract (IR peaks in cm^{-1})	Peak characteristics	Assigned groups
583		585	weak	
600		601	weak	
611				
630		629	weak	
636				
652				
664		663	broad weak	
691		694	sharp & strong	
710	shoulder			
729		728	sharp & strong	
750	Broad weak	754	sharp & weak	Si-CH ₃
771		772	weak	
798		799	weak	
809				
825		827	weak	
846		844		
871		872		
885				
898		896	broad & strong	
919		920	weak	
936	shoulder			
		943	weak & shoulder	
964		966	weak & shoulder	
987	sharp	988	broad & strong	
		1013	weak & shoulder	Si-O-Si/Si-OR
1025	sharp	1027		Si-O-Si/Si-OR
		1039		Si-O-Si/Si-OR
1049		1053		Si-O-Si/Si-OR
1076		1081		Si-O-Si/Si-OR
1107	weak shoulder	1106		Si-O-Si/Si-OR
1128		1126	weak	
1142		1143		

1165				Si-O-Si
		1177		
1187		1190		
1199		1195		
1240		1242	sharp & strong	Si-CH ₃
1340	weak shoulder			
1378	sharp	1377	sharp & strong	Si-OCH ₃
1439	shoulder			
1452	sharp	1453	sharp & strong	
		1496	weak	
1513	weak			
1542				
1604	shoulder	1605	sharp & weak	
1663	sharp	1671	sharp & strong	
1700	sharp	1702	sharp & strong	
1738	strong and overlapping	1739	sharp & strong	
		2623	strong & broad	
		2729	sharp & weak	
2870	sharp	2866	sharp & strong	
2923	sharp	2923	sharp & strong	
		2948	sharp & strong	
		3027	sharp & weak	
3395	broad and strong	3418	sharp & strong	
3742	sharp and weak	3739	weak	Isolated Si-OH

4. Conclusion

The specimen sample of the Indian pine oleoresin was characterized by TG-DTA, XRD and IR spectroscopy. Our results indicate that the oleoresin contains substantial amount of silicon component, which on heating produces crystalline silica. It is important to note that oleoresins contain a colossal amount silicon compound compared to other plant sources. The FTIR spectra of the oleoresin and its XRD patterns after thermal treatment provide evidences for the presence of Si-O-R group and crystalline SiO₂, respectively. It is unlikely that the growing parts of a plant would contain such a significant amount of silicon as it would require the recruitment of specialized cellular machinery (enzymes, transporters, etc) to take care of its utilization and metabolism. The

occurrence of silicon compounds in the oleoresin—a plant secretion devoid of cells—may have a role in plant defense. More experimental investigations are desired on such oleoresins to understand the nature and origin of silicon in them.

Acknowledgement

I thank Dr. S. N. Achary, Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai-400085, India for all the help in analysis and interpretation of the experimental results. This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

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