VIII Congresso Nazionale di Archeometria
Scienze e Beni Culturali: stato dell'arte e prospettive
Bologna 5 - 7 Febbraio 2014

THERMAL DEGRADATION CHEMISTRY OF ARCHAEOLOGICAL PINE PITCH: ALONE AND MIXED WITH BEESWAX

M.P.Colombini[1], C. Duce[1], S Orsini[1*], E. Ribechini[1], A. Spepi[1], M.R. Tinè[1]

[1] Department of Chemistry and Industrial Chemistry, Scibec group, University of Pisa, sibilla.orsini@gmail.com

Since early times, the resinous substances secreted by trees have been widely used in their natural form or as tar and pitch to waterproof the planking of ships and the vessels, and to transport and store fluids such as wine and plant oils [1-3]. Tar or pitch were obtained subjecting resinous materials to hard-heating treatments and to distillation-type processes. Tar and pitch have been of great importance for their properties, such as insolubility in water, adhesion and glasslike characteristics. During the pyrolysis process to obtain the pitch the terpenoids, the main compounds of resins, experience chemical modifications, such as aromatization, demethylation and decarboxylation, with the formation of new compounds with a lower molecular weight and a high degree of aromatization. The mixtures found in several archaeological objects demonstrate the to modify the physical chemical properties of pitch and tar, a wide variety of organic materials, such as waxes or animal fats, could be added [4,5]. Traditionally, mixtures of pine pitch and beeswax were used to obtain lower melting point materials during their application.

The aim of this work is to evaluate the physicochemical effects that pine pitch undertakes added with beeswax as additive. For this scope, pine pitch replicas from *Pinus sylvestris* prepared following traditional procedures were added with different proportion of beeswax and studied by a multi-analytical approach comprising the use of gas chromatography/mass spectrometry (GC/MS) and thermal analysis techniques (DSC, TGA and TGA-FTIR). GC/MS was use to assess the molecular composition of pitch replica and to identify a series of species acting as markers of technological manipulation and eventually of degradation. In addition, GC/MS analysis was applied to pine pitch heated for a second time up 300°C with a dynamic process (TGA) both with nitrogen (pyrolysis of a pyrolysed sample) and air atmosphere (combustion of a pyrolysed sample) (Tab. 1). Studying the mixtures of pine pitch with different amount of additive by thermal analysis (Fig.1) allowed us to extend the knowledge of the techniques used in the past and to define the reason why in some archaeological objects pine pitch was applied used in mixture with beeswax.

Tab. 1. Percentage amount of diterpenoid acids in the pine pitch residues at 300°C under nitrogen and air condition; DHA: dehydroabietic.

Compound	% at 300°C (N2)	% at 300°C (air)	Oxidat. degree	% at 300°C (N2)	% at 300°C (air)
Abietic Ac.	4.10	0	**0**	4.10	0
methyl-DHA	6.92	3.28	**I**	41.04	39.74
diDHA Ac.	5.01	10.02			
DHA Ac.	29.11	26.43			
15-hydroxy-diDHA Ac.	1.98	3.69	**II**	29.76	32.41
15-hydroxy-DHA Ac.	9.74	3.73			
7-oxo-DHA Ac.	18.04	23.45			
methyl-7-oxo-DHA	0	1.54			
7,15-dimethoxy-DHA Ac.	12.49	8.78	**III**	14.94	19.68
7,15-dimethoxy-6-methyl-DHA Ac.	0	2.20			
methyl-7,15-dimethoxy-diDHA	0	6.89			
7-oxo-15-hydroxy-DHA Ac.	2.46	1.80			

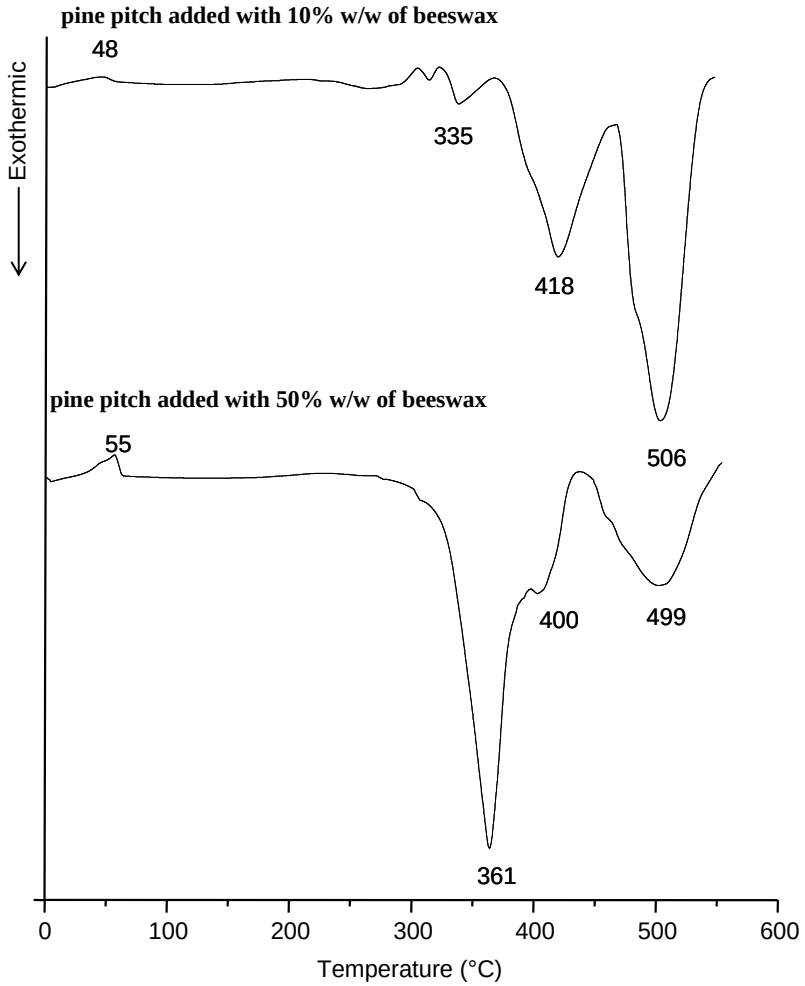

Fig. 1. DSC analysis of pine pitch added with different percentage of beeswax.

References

[1] Colombini M. P.,Giachi G., Modugno F., Pallecchi P., Ribechini E., 2003.The characterization of paints and waterproofing materials from the shipwrecks found at the archaeological site of the Etruscan and Roman Harbour of Pisa (Italy), Archaeometry, 45:659-674.

[2] Romanus K., Baeten J., Poblome J., Accardo S., Degryse P., Jacobs P., De Vos D., Waelkens M. 2009. Wine and olive oil permeation in pitched and non-pitched ceramics: relation with results from archaeological amphorae from Sagalassos, Turkey, J. Archaeological Science, 36:900-909.

[3] Connan j., Nissenbaum A. 2003. Conifer tar on the keel and hull planking of the Ma'agan Mikhael ship (Israel, 5th century BC): identification and comparison with natural products and artifacts employed in boat construction, J. Archaeological Science,30:709-719.

[4] Ribechini E., Orsini S., Silvano F., Colombini M.P., 2009. Analytica Chimica Acta, 638(1):79-87.

[5] Regert M., Langlois J., Colinart S., 2005. Characterisation of wax works of art by gas chromatographic procedures. Journal of Chromatography A, 1091(1-2):124-136.