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Thermogravimetric analysis

A tool to evaluate the ability of mixtures in consolidating waterlogged archaeological woods

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Abstract Waterlogged archaeological woods (*Pinus pinaster*, *Ulmus* cf. *minor* and *Fagus sylvatica* L.) were consolidated by using Colophony, Rosin 100, and a mixture of Poly(ethylene) glycol (PEG) 3000 and Poly(propylene) glycol (PPG) 425. The efficiency of the consolidants was estimated by determining the content entrapped into the cavity of degraded wood. For this purpose, thermogravimetry was demonstrated to be a reliable tool. In the case that the polymeric mixture was used for impregnation, it was also possible to discriminate the amount of PEG 3000 from that of PPG 425 captured by the wood capillaries. Regardless of the wood nature, all the consolidants were present in treated samples in large amount (at least 70% w/w). Thermogravimetric results were in agreement with those calculated by using the wood degradation degree and composition of the consolidant mixture. One of the advantages of using this technique consists into requiring very small amounts (a few mg) of sample against the grams necessary for the conventional experiments.

Keywords TG · Waterlogged archaeological wood · Consolidants · Colophony · Rosin 100 · PEG · PPG

Introduction

Wood is a rather complex material made up of cellulose, hemicelluloses, lignin and extractives. Within the cultural heritage issue, it plays a relevant role because many artworks are of wood, and their conservation is a challenging task. In fact, one has to remind that it is a complex problem to conserve ancient shipwrecks [1–3], which come from submerged environments and undergone complex degradation processes. Therefore, it is fundamental the availability of methodologies for conservation and preservation of waterlogged archaeological wood [4, 5] degraded by chemical and/or biotic processes [2, 4, 6–8]. The loss of water from the waterlogged wood shrinks and inevitably deforms the material. It may occur [5, 9] that only a few percent of the wet weight of an object is composed of wood, while the remaining part is formed by water and minerals from the soil. To avoid contraction and deformation, the cavity previously filled with water has to be refilled with consolidants, which not only provide robustness and stability, but also guarantee that all the characteristics of the object remain unchanged. In other words, the consolidant should reinforce any structure to ensure that the wooden object could not collapse and the handwork could be not destroyed.

Within this issue, a main objective is to find out the best consolidant mixtures compatible with the specific wooden *Taxon*, and to verify their capability in penetrating the cell wall of the wood. The best benefits may be reached when the application of mixtures with optimal composition of consolidant leads to the maximum penetration and pore filling and besides it remains in solid condition in a wide range of temperature and relative humidity.

Aqueous mixtures of poly(ethylene) glycols of different molecular weights are generally used to preserve archeological wood because they represent a fine combination of depth of impregnation and strength [10, 11]. Accordingly, a selective impregnation may occur depending on the poly(ethylene) glycol size and the diameters of the pores of

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degraded waterlogged wood. Consolidation by impregnation with solution of thermoplastic resins in organic solvents was also done [12]. The goodness of penetrating effect of the consolidant mixtures can be evaluated by determining quantitatively the amount of consolidant encapsulated within the wooden tissue in order to ascertain the filling degree of the pores in the wood material.

In this article, we will report results on consolidation of archeological woods monitored by thermogravimetry, which has been revealed to be proper technique to study woods [13, 14]. The consolidants are Colophony (a natural resin) and Rosin 100 (a colophony chemically modified, in particular, ester of pentaerythritol) as well as a mixture of Poly(ethylene) glycol, 3000 u.m.a (PEG 3000) and Poly(propylene) glycol, 425 u.m.a (PPG 425). The latter mixture was used to verify the eventual selectivity of the polymers toward the wood microstructures. The woods are of different species being *Ulmus* cf. *minor*, *Pinus pinaster*, and *Fagus sylvatica* L. Interestingly, it was demonstrated that thermogravimetric analysis is powerful: (1) to evidence quantitatively the impregnants entrapped into the wood, and (2) to discriminate the affinity of PEG 3000 and PPG 425 toward the different micropores of the cell wall wood.

Materials and samples preparation

PEG 3000 and PPG 425 are from Fluka. Acetone was a J. T. Baker product. Colophony (from Phase) is a complex mixture essentially composed of isomers of abietic acid (90%) and the corresponding esters, aldehydes, and alcohols (10%) [15]. Rosin 100 (from Bresciani s.r.l.) is a pentaerythritol ester of Colophony. The waterlogged archeological woods from the ship Chrétienne C, (II century, BC), discovered over the coast of Provence and kindly provided by Prof. Patrice Pomey of C.N.R.S., Université de Provence (France).

Water from reverse osmosis (Elga model Option 3) with a specific resistivity higher than 1 MΩ cm was used.

Characteristics of woods

The woods were characterized according to the procedure of the Italian standard UNI 11205:2007 [16].

1. The identification of taxon wood was done by means of optical microscopy on thin sections along the three characteristic directions of wood; from this analysis and the comparison with the taxonomic tables [17] the woods samples were classified as *Ulmus* cf. *minor, P. pinaster* and *F. sylvatica* L.
2. The decay assessment was determined from the maximum water content (MWC %) which, in turn, was obtained from physical measurements.
3. The decay assessment was determined according to literature [18, 19] by means of chemical measurements of residual of holocellulose (H), lignin content (L) and H/L ratio. The latter is representative of the extent of chemical decay.

The taxon of samples, the MWC, porosity, and the H/L values are collected in Table 1.

Woods desalinization

Before every treatment, all the samples (2 × 2 × 4 cm) were immerged in deionized water to remove the salts. This procedure was carried out, at room temperature, several times until the water resistivity was higher than 0.1 MΩ cm.

Woods treatment with acetone

Each sample was kept in acetone which was regularly replaced. The diffusion of water from the wood pores to the bulk acetone, at room temperature, was monitored by measuring the refractive index of the mixtures. The treatment was stopped when the refractive index value was coincident with that of pure acetone.

Impregnation of woods with resins

Each sample was kept in a given volume of mixture acetone + resin (63% w/w of Colophony in acetone and 60% w/w of Rosin 100 in acetone) which was regularly changed. The impregnation process was performed at 30 °C over some months; the mixtures compositions were monitored by determining the viscosity at a selected temperature.

Table 1 Parameters representative of wood degradation

Wood	H/L[a]	H/L[b]	MWC/%
Ulmus cf. *minor*	0.18	2.1	491
Pinus pinaster	0.26	2.2	562
Fagus sylvatica L.	0.16	3.0	612

[a] Value for degraded wood

[b] Value for non-degraded wood (determined by using the same procedure for degraded wood [18, 19])

Impregnation of woods with the polymeric mixture

To remove easily water, each sample was first immersed in pure PPG 425 at 30 °C which was regularly replaced until the refractive index of the bulk mixture was equal to that of pure PPG 425. Then, the sample was immerged at 45 °C in a PEG 3000 + PPG 425 liquid mixture (50.0% w/w) which is an optimal composition for treating degraded woods. The composition of the mixture in contact with the sample was determined by density.

Thermogravimetry

Experiments were carried out by using a Q5000 IR apparatus (TA Instruments) under nitrogen flow of 25 cm^3 min^{-1} for the sample and 10 cm^3 min^{-1} for the balance. The explored temperature interval ranged between 25 and 600 °C at a heating rate of 10 °C min^{-1}. Recording the temperature dependence of mass loss (TG), the first-order differentiation curves of mass loss to temperature (DTG) were determined. The decomposition temperature (T_d) was taken at the maximum of the DTG peaks. The mass loss was calculated from the area of the peaks exhibited by the DTG curves. The sample (ca. 15 mg) was taken from the core of the treated wood in order to verify the consolidant capability to penetrate. Due to the inhomogeneity of the wood, each measurement was repeated thrice at least, so that the averaged values are discussed. The standard deviation for T_d and residual mass are ±2 °C and ±3%, respectively.

Results and discussion

Thermal stability of pristine wood

Shape of TG curve of untreated waterlogged wood is independent of the taxon (Fig. 1). A comparable mass loss observed at ca. 100° C for all the sampled tested is ascribable to water elimination. At higher temperature the thermal degradation takes place.

The mass loss due to water (WL), the residual matter, representing the non-degraded wood present between 150 and 600 °C (RM$_W$), and the degradation temperature (T_d) are given in Table 2. Under no-oxidant conditions, the wood degradation is not complete as only ca. 55% w/w of the total mass is decomposed up to 600 °C. The RM$_W$ values are nearly equal for *P. pinaster* and *F. sylvatica* L. which are slightly larger than RM$_W$ of *Ulmus* cf. *minor*. It is interesting to note that T_d values are comparable for *Ulmus* cf. *minor* and *F.* sylvatica L. and higher than that for *P. pinaster*. The T_d values may be correlated to those of *H/L*. In fact, from data in Table 1, one observes that *Ulmus* cf. *minor* and *F. sylvatica* L. exhibit comparable *H/L* values which are smaller than that of *P. pinaster*. Similarly, recent thermal analysis studies [20] on different wood species revealed that the thermal stability is correlated to the amount of cellulose and lignin. Nevertheless, the different microstructure may take into account for these findings. According to literature [17], *Ulmus* cf. *minor* and *F. sylvatica* L. exhibit a polydispersion in the pore radii while *P. pinaster* presents large and monodisperse pores (Fig. 2).

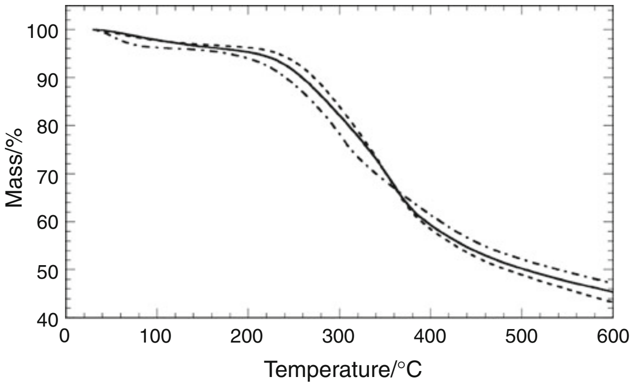

Fig. 1 Thermal degradation as functions of temperature for the *Pinus pinaster* (*dashed dotted line*), *Ulmus* cf. *minor* (*dashed line*) and *Fagus sylvatica* L. (*solid line*)

The experiments were also performed on the same samples of waterlogged wood treated with pure acetone. This was done because for the consolidation process acetonic mixtures of resins (Colophony or Rosin 100) were used and, therefore, it was thought important to verify whether acetone affects the thermal degradation of the wood. The obtained results are reported in Table 2. The treatment of the wood samples with acetone essentially does not affect the T_d values, which are close to those of pristine woods, while it does the RM$_W$ values which slightly decrease. Such a result might reflect the thermal stabilization of extractives as a consequence of their solubilization in acetone. A recent study showed that the wood thermal stability improved by removing the extractives [20].

Thermal stability of woods consolidated with resins

Initially, the study (from 25 to 600 °C) dealt with the thermal degradation of Colophony and Rosin 100 after the solubilization and the evaporation of acetone. As shown in Fig. 3, both the resins exhibit degradation and a negligible moisture content. The T_d values of 250 and 474 °C for Colophony and Rosin 100 were obtained, respectively. The chemical modification present in Rosin 100 confers to the resin itself a strong enhancement of the thermal stability. The mass loss due to the thermal degradation is almost

Table 2 Thermogravimetric analysis results for pristine woods

Wood	WL/%[a]	WL/%[b]	RM_W/%[a]	RM_W/%[b]	T_d/°C[a]	T_d/°C[b]
Ulmus cf. *minor*	3.6	4.7	41.8	31.8	364	364
Pinus pinaster	3.5	4.8	46.7	44.9	295	300
Fagus sylvatica L.	3.3	5.6	45.9	38.7	363	355

[a] Waterlogged wood samples dried at 103 °C

[b] After treatment of waterlogged wood samples with acetone and dried at 103 °C

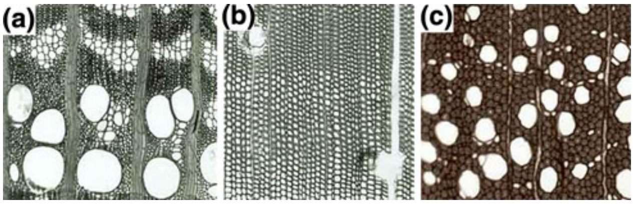

Fig. 2 Microstructure of *Ulmus* cf. *minor* (**a**), *Pinus pinaster* (**b**), *Fagus sylvatica* L. (**c**), Ref. [17]

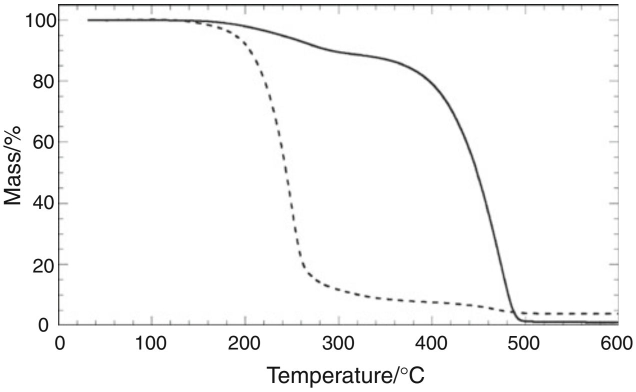

Fig. 3 Thermal degradation as functions of temperature for Colophony (*dashed line*) and Rosin 100 (*solid line*)

quantitative as shown by the consolidant residual matter at 600 °C (RM_C) values of 1.1 and 3.7% w/w determined for Rosin 100 and Colophony, respectively.

The consolidated woods present a moisture content (ca. 2% w/w) which is comparable to that of untreated woods. Moreover, the residual matter at 600 °C for the wood + consolidant system (RM_{W+C}) is comprised between the RM_W and RM_C values (Table 3).

All the samples treated with Colophony showed a complex degradation process as the TG and, more clearly, the DTG curves in Fig. 4 show. Being that the T_d values of pristine wood and resin are rather close the decomposition could be generated by the overlapping of the degradation of each component. Nevertheless, many authors reported in literature [20–22] that mixtures featured by weak interactions between the components generate thermograms characterized by degradation steps similar to those of each precursor with small shift of T_d values. This was also observed for blend components differing in T_d by ca. 60 °C [22]. Therefore, one may deduce that interactions between wood and Colophony are present in some extent. In the case of wood + Rosin 100 systems, the TG curve is dominated by a degradation process around 455 °C (Fig. 5) which is lower by ca. 20 °C than pure Rosin 100 and much larger than those for untreated woods (Table 2). The T_d shifts observed for both resins might be ascribed to the hydrogen bonding between lignin (that is the predominant wood component) and the consolidant.

Based on these findings, one may rule out the possibility of determining the amount of resin entrapped within the wood by simply separating the degradation processes of the two components. Nevertheless, insights may be drawn by expressing the residual matter at 600 °C for the wood + resin system as a linear combination of those of the precursors. On this basis, one can estimate the consolidant mass percent into the wood + resin system (CW%) as

$$\mathrm{CW\%} = 100 - \frac{\mathrm{RM_{W+C}} - \mathrm{RM_C}}{\mathrm{RM_W} - \mathrm{RM_C}} \times 100 \qquad (1)$$

where RM_{W+C}, RM_C, and RM_W assume the same meaning as above.The CW% data are reported in Table 4.

Table 3 Thermogravimetric characterisation of consolidated wood samples

Wood	Colophony		Rosin 100		PEG + PPG	
	RM_{W+C}/%	T_d/°C	RM_{W+C}/%	T_d/°C	RM_{W+C}/%	T_d/°C
Ulmus cf. *minor*	11.0	273	11.4	455	6.3	260; 404
Pinus pinaster	14.2	277	8.0	455	5.9	264; 403
Fagus sylvatica L.	9.2	263	9.7	454	6.3	275; 385

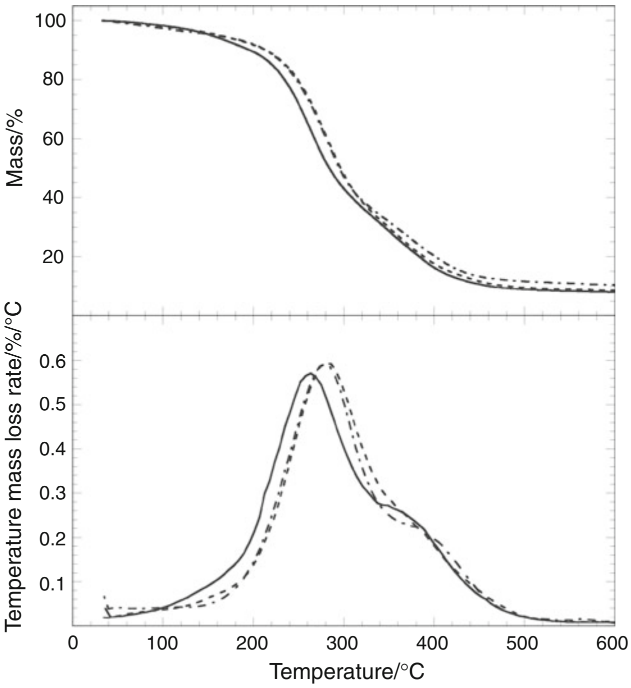

Fig. 4 Curves of mass loss to temperature (top) and the first order differentiation curves of mass loss to temperature (bottom) for the *Pinus pinaster* (*dashed dotted line*), *Ulmus* cf. *minor* (*dashed line*) and *Fagus sylvatica* L. (*solid line*) consolidated with Colophony

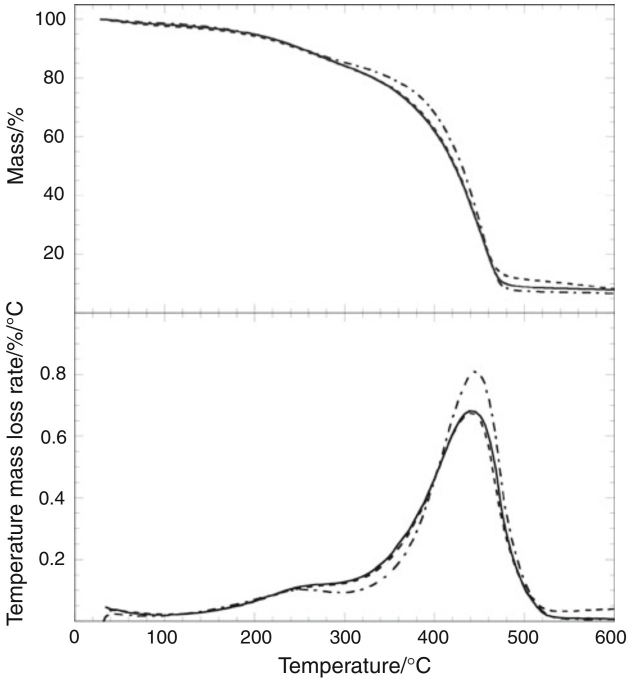

Fig. 5 Curves of mass loss to temperature (*top*) and the first order differentiation curves of mass loss to temperature (*bottom*) for the *Pinus pinaster* (*dashed dotted line*), *Ulmus* cf. *minor* (*dashed line*) and *Fagus sylvatica* L. (*solid line*) consolidated with Rosin 100

Table 4 Percent consolidant content in wood samples

Wood	Colophony		Rosin 100		PEG + PPG	
	CW%[a]	CW%[b]	CW%[a]	CW%[b]	CW%[a]	CW%[b]
Ulmus cf. *minor*	76	75	70	73	84	83
Pinus pinaster	77	77	82	76	89	85
Fagus sylvatica L.	84	81	77	80	87	88

[a] Calculated from TG data

[b] Calculated from MWC

A different route was pursued to calculate the CW% values. From the MWC values (Table 1), the amount of water penetrated into the wood pores was calculated. Assuming that the impregnating mixture occupies the same volume as water and based on the concentration of the consolidant mixture, the CW% value was computed and collected in Table 4. The CW% values obtained from the two routes show an average deviation of 3%. Considering that the archeological wood is not a homogenous sample, one may state that the agreement between the two CW% series is very good. This result is rather interesting because it demonstrates that the TG method is powerful for determining the amount of consolidant in the wood pores using a very easy and fast protocol. Furthermore, it requires very small amounts (a few mg) of sample against the usual sample size (some grams) necessary for the gravimetric determination.

As a general feature, regardless of the nature of both the resin and the wood, the amount of consolidant encapsulated into the wood is very large being at least 70% w/w. Within the errors, the Colophony impregnation follows the same trend as MWC (Table 1). As far as Rosin 100 is concerned, the CW% follows the order *P. pinaster* > *F. sylvatica* L. > *Ulmus* cf. *minor*. The larger size of Rosin 100 compared to Colophony may be invoked to explain the selectivity of the consolidation. The high CW% values indicate that the wood material is highly porous even considering that the used procedure does not allow to fill all of the pores being that the consolidant mixtures are based on acetone which is removed during the consolidation process.

Thermal stability of woods consolidated with polymeric mixture

The DTG curve for the PEG 3000 + PPG 425 mixture (Fig. 6) exhibits two degradation peaks at 264.7 and 413.2 °C which are nearly close to those of pure precursors (they are 282.3 and 416.6 °C for pure PPG 425 and PEG 3000, respectively). It is interesting to note that copolymers based on poly(ethylene glycol) and poly(propylene glycol) blocks exhibit [21, 23] a single degradation peak upon

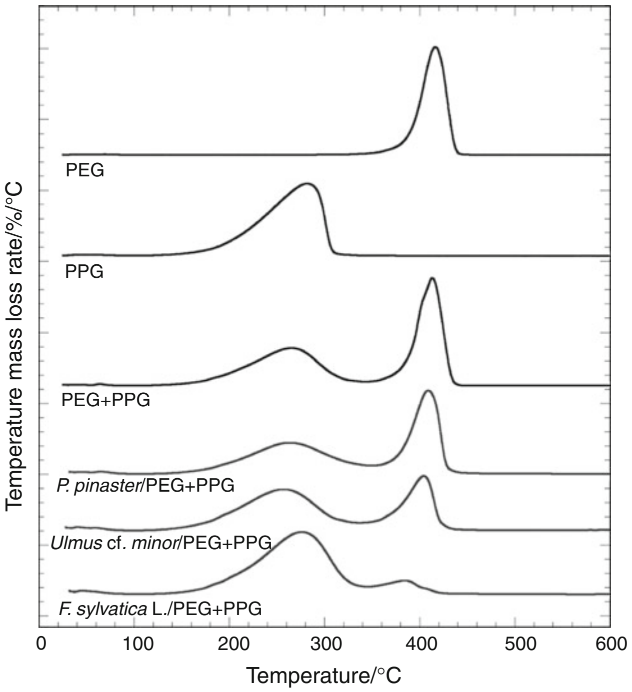

Fig. 6 Thermal degradation rates as functions of temperature for the woods consolidated with the PEG 3000 + PPG 425 mixture

heating; therefore, one may conclude that the linkage between the blocks strongly alters the thermal degradation feature, while the physical mixture of PEG and PPG does not affect the decomposition of the two polymers. Similar results were reported for the physical mixtures composed of poly(ε-caprolactone) (PCL) and poly(D,L-lactide) (PLA) and PLA/poly(glycolide) [22]. Moreover, the decomposition temperatures of blends and pure polymers (PCL and poly(vinyl acetate)) are quite close indicating the lack of interactions between the polymers [20]. Therefore, the small changes in the T_d values for our mixture are likely due to the weak interactions between the polymers in the mixture.

In the investigated temperature range, the degradation of the single polymers and their mixture is nearly quantitative (the residual mass at 600 °C is always less than 1% w/w). The degradation mass loss value of 49.1% w/w to the first step represents the PPG 425 content in the mixture; that is in a very good agreement with the stoichiometric value of 50.0% w/w.

Some examples of the DTG curves for the consolidated woods are illustrated in Fig. 6. Two degradation peaks are observed at temperatures close to those of the PEG 3000 + PPG 425 mixture. The lowering of the T_d values for PEG 3000 may reflect the interactions with lignin according to literature findings [24] based on NMR studies which evidenced that about 30% of PEG entrapped in archaeological woods is strictly interacting with lignin. Similarly to the case of the woods consolidated with resins, the TG curves are dominated by the signal of the consolidant which is likely the main component of the system (Table 3). The CW% values obtained from Eq. 1 and from MWC are in a good agreement, and demonstrate that a very large amount of polymer is entrapped into wood pores. Going further, it is worth noting that the two degradation processes are separated with a rather good resolution. Based on the evidences that the wood mass percent in the consolidated sample is low, the mass loss as a consequence of thermal decomposition is of 50% w/w and the T_d values for each component, one may deduce that the peak at lower temperature is practically generated by the PPG 425 degradation while the peak at higher temperature is essentially ascribable to the PEG 3000 degradation. Based on these arguments, one may quantify the PEG 3000/PPG 425 mass ratio ($R_{PEG/PPG}$) within the wood pores. It is interesting to note that the $R_{PEG/PPG}$ values of 0.8, 0.27, and 0.14 are obtained for *P. pinaster*, *Ulmus* cf. *minor*, and *F. sylvatica* L., respectively, indicating a preferential affinity toward one of the polymers. These findings can be understood to the light of the wood microstructure [17]; namely, as Fig. 2 shows, *P. pinaster* possesses pores that are almost monodisperse which can properly host the polymeric mixture while *Ulmus* cf. *minor* and *F. sylvatica* L. do have variable pores size which may preferentially accommodate the smaller polymeric chains of PPG 425 making selective the impregnation process. It was proved [9, 11] that polyethylene glycols with different molecular weights allow a differential impregnation of woods.

Conclusions

Different species (*P. pinaster*, *Ulmus* cf. *minor*, and *F. sylvatica* L.) of ancient woods were consolidated by using: (1) Colophony natural resin and its form chemically modified (Rosin 100); (2) a mixture of PEG 3000 and PPG 425. The versatility of the consolidant mixtures was evaluated through the determination of the amount of the consolidant entrapped within the wood pores. To this aim, the thermogravimetric analysis was proved to be a good tool. Accordingly, even for the degradation processes that cannot be resolved, the amount of consolidant in the wood was determined from the residual matters of the wood + consolidant system and the pristine components. In the case of polymeric mixture used as consolidant, it was also possible to discriminate the amount of PEG 3000 from that of PPG 425 entrapped into the wood pores highlighting the selective impregnation. These findings demonstrate that the thermogravimetric analysis is an easy and fast protocol for evaluating the capability of compounds in consolidating archaeological woods. Moreover, the very small amount of sample required for each experiment (a few mg) may allow determining the profile of impregnation of all the archaeological object, thus avoiding any deformation and damaging of the artwork.

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