



# Preliminary thermal characterization of natural resins from different botanical sources and geological environments

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## Abstract

The preliminary studies on thermal behavior of differently aged natural resins from Russia (Khatanga), Dominican Republic (El Valle), Colombia and Poland (Jantar) were performed. Thermal stability and behavior under elevated temperature were investigated by thermogravimetry (TG) and differential scanning calorimetry (DSC), while the differences in the structure and composition by FT-IR spectroscopy. Analyzed resins show different thermal effects during heating suggesting that possible post-reactions and structural changes occurred. TG results indicated that Dominican, Russian and Colombian resins present relatively high thermal stability under air conditions in the range of 228–300 °C, whereas the mass loss of 5mass% at about 217 °C was observed for Baltic amber. During DSC experiments, the analyzed resins expose thermal events which make impossible determination of glass transition temperature in a raw sample. The results indicate that both TG and DSC cannot be considered as methods for age dating of natural resins and more advanced techniques should be applied. Careful analysis of FT-IR data in the carbonyl region may provide additional information about the composition and history of the natural resin.

**Keywords** Glass transition · DSC · Fossil resins · Copal · Fossilization

## Introduction

The term ‘amber’ is the most known and frequently used to indicate resinite or fossil resins formed when natural resin was exuded from the tree wounds and exposed to light and

oxygen. However, these fossil resins usually differ significantly in terms of geological age, provenience, botanical designation and chemistry [1]. Natural resins constitute a mixture of organic high molecular mass compounds with polymeric-like materials. Depending on the botanical source, geographical area and temperature–pressure conditions of their diagenesis, different resins occurring worldwide can be distinguished. There are five classes in the classification system of natural resins structure that group various natural polymers, non-polymeric material containing sesquiterpenoids and diterpenoids carboxylic acids [2, 3].

Various species of trees produce natural resins; however, only those resistant to decay may further undergo fossilization. During this process, the resins, preserved in various deposits, change its structure and composition over time by formation of higher molecular mass compounds and conversion of volatile and reactive components into stable species. The main process in fossils formation is polymerization, but also the curing process occurs which is equivalent to the synthetic curing process but much slower. This curing/maturation of natural resins depends not only on the duration of burial but also primary chemical

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composition and alteration processes in geological environment [4]. Moreover, natural resins even after millions of years still preserve a significant amount of unpolymerized material [5–7].

There are only few studies on thermal analysis of natural resins [7–11], where authors tried to correlate thermal properties (glass transition, combustion profiles) of resins with their age. However, there is no agreement whether the thermal analysis is appropriate tool for assessment of natural resins age. Some authors stated that TG and DSC can give information that helps in dating, while another postulate that the glass transition cannot be used for this. Therefore, a good understanding of fossilization process, thermal behavior of natural resins and their structural changes seems to be important in natural resins characterization. Besides, while Baltic amber is widely described and characterized [12], Dominican and Colombian resins still need more interest. On the other hand, to the best of our knowledge, there are no reports concerning Khatanga resin; only Kaliningrad materials were investigated [13, 14].

In this paper, we perform preliminary studies on the thermal properties of differently aged natural resins from Russia (Khatanga), Dominican Republic (El Valle), Colombia and Poland (Jantar). This work is a part of studies on properties of fossil resins, in which a larger set of specimens differentiated by geographical locality and age is investigated by various analytical methods. Initially, this group of four resins was tested according to thermal stability (TG) and behavior under elevated temperatures (DSC, FT-IR) to show that they have different structure and composition. Furthermore, we cross-evaluate our results with those from the literature to show that this complex subject still needs scientific attention.

## Materials and methods

The characteristics of the analyzed resin samples are given in Table 1. It provides information on the geographical origin of samples, their age, geological setting of deposit and short description of resins. The samples were denoted with a collection number belonging to the authors.

Before analysis, the samples of natural resins were cut and grinded in the laboratory mill equipped with a liquid nitrogen cooling system (Retsch CryoMill). First, the material was cooled down in about 15 min and then, three grinding steps were applied, each one for 5 min with frequency of 15 Hz. The total time of grinding was about 20 min.

The obtained powdered sample was then weighed and put in the corundum  $\text{Al}_2\text{O}_3$  (TG) or aluminum Al (DSC) crucible to test its thermal behavior. The materials were

tested from 25 to 700 °C in TG (TGA2 Mettler Toledo) and from – 60 °C to 200 °C in DSC (DSC1 Mettler Toledo) at 10 °C  $\text{min}^{-1}$  heating/cooling rate. DSC instrument was calibrated using indium and zinc standards. Nitrogen atmosphere (50 mL  $\text{min}^{-1}$ ) has been applied in DSC, to avoid oxygen effect on thermal properties of the material. TG experiments were performed under dynamic flow of air (30 mL  $\text{min}^{-1}$ ) to investigate degradation of the material under oxidative conditions.

Structural changes after thermal treatment were investigated by ATR FT-IR measurements. The spectra were recorded on the pristine resins samples and samples after DSC measurements with Bruker TENSOR27 device with a RT-DLaTGS detector and diamond crystal (32 scans, 4  $\text{cm}^{-1}$  resolution). Deconvolution of the spectra and fitting procedure was performed with the Grafit version 0.4.5 open source software, while the spectra were baseline-corrected and processed with OPUS software (version 6.0). In order to compare, the spectra were also normalized with respect to the most intense band in the spectrum. For each vibrational signal, its position, intensity (amplitude) and its full width at half maximum (FWHM) were recorded.

## Results and discussion

Natural resins, which are in fact natural polymers originated from different types of trees, were analyzed by thermal analysis methods (TG, DSC), and selected samples were structurally characterized (FT-IR). These kinds of biomaterials are known from their sensitivity to physico-chemical environmental factors, e.g., Baltic amber is extremely prone to progressive degradation and eventually to complete disintegration by atmospheric oxidation, accelerated by heat and light [22–24].

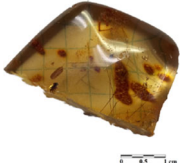



### Thermal stability—Thermogravimetry TG

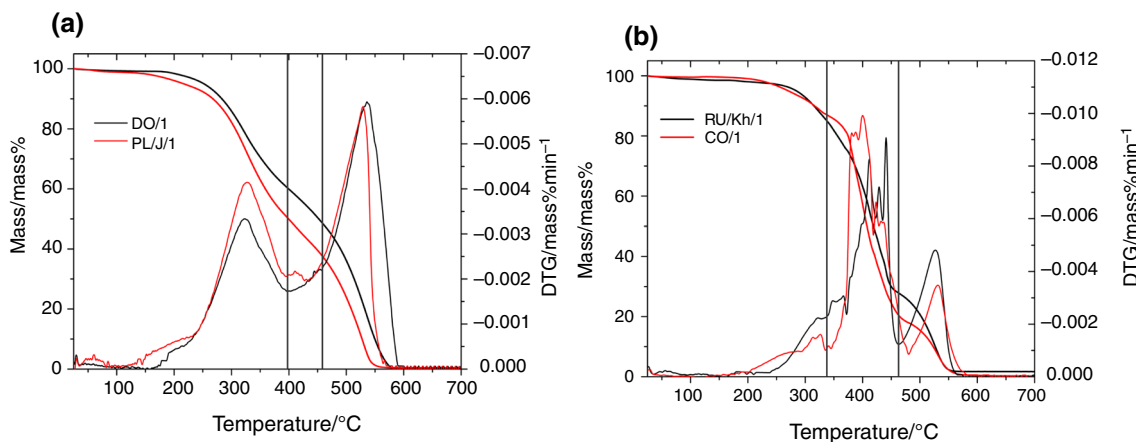
TG results have shown that resins continuously lose mass on heating through vaporization (low molecular mass products), possible post-curing reactions and decomposition. The slope of TG curves of tested materials allows to divide them into two groups, according to their thermal behavior: (I) Dominican DO/1 and Polish PL/J/1 and (II) Russian RU/Kh/1 and Colombian CO/1 resins.

In general, the first group (I—Fig. 1a) has shown two-step degradation with the main mass loss events in the range of 200–440 °C and 440–600 °C. The DTG profiles suggest that the degradation pathway is less complicated than in the case of other resins under investigation.

The Colombian (CO/1) and Russian (RU/Kh/1) resins were assigned to second group (II—Fig. 1b), and they are

**Table 1** Natural resins characterization

Name	Location	Age	Appearance	Geological setting	Description
CO/1	Colombia	Pliocene/Recent 2.5 Ma–200 y		Quaternary sands [15]	Light yellow; transparent; numerous inclusions
DO/1	Dominican Republic, El Valle	Lower Miocene-middle Miocene 15–20 Ma		The Yanigua Formation (YF): conglomerates, dark clays, laminated sandy clays, lignite and carbonaceous clays and sandstones [16–18]	Dark yellow–orange yellow; transparent–translucent; small, dark inclusions
PL/J/1	Baltic amber, Jantar	Upper Eocene (Priabonian) 40.4 Ma [19]		Gray–green sandy-mud and mud sand with glauconite and muscovite, phosphorites, seashell fragments and fossil resins; below are non-calcareous or slightly calcareous sandy mudstones with micas and glauconite [20]	Brown; translucent–opaque
RU/Kh/1	Russia, Khatanga	Lower Cretaceous (Aptian–Albian) 125–100.5 Ma/upper Cretaceous (Santonian) 85.8 Ma [21]		Lagoon and coastal sediments of alluvial origin; sands, sandstones, lignites, siliceous rocks, siderites and carbonized wood fragments [20]	Yellow–brown; transparent; numerous inclusions



**Fig. 1** Thermal behavior of the natural resins under air atmosphere: **a** group I and **b** group II

characterized by three-step decomposition with the main mass losses in the range of 220–340 °C, 340–480 °C and 480–600 °C.

In the first decomposition step, most probably low molecular mass components are evolved, such as water and organic species produced during post-curing reactions. The intensive mass loss observed between 200 and 400 °C for the (I) group of resins is related to the decomposition of less stable structures of the resin. Above 450–580 °C, the

main decomposition takes place and this process was registered as more intensive in the (I) group of resins, as compared to the height of DTG signals between low- and high-temperature region. For the (II) group, several extrema were observed on DTG profile in the range of 340–480 °C. This is likely due to melting and subsequent foaming upon heating, that is common for organic systems. It may also suggest that complex reactions of decomposition take place; however, we have found that these signals

are not reproducible and this supports our first observation with foaming process. Thermogravimetric step in this range is the most intensive of all, with 49–69 mass% mass loss.

Analyzing the char residue after TG measurements, one can conclude that Russian material seems to be more resistant and produces more solid residue than other resins under investigation. All materials decompose completely or with slight char residue. A comparison of the samples is given in Table 2, where the characteristic temperatures and mass losses for three thermal decomposition regions are presented.

The presented results are close to those obtained by Ragazzi et al. [8], who investigated different kinds of natural resins, including Dominican amber, Colombian copal and Baltic amber. The most complicated thermal degradation profile was registered for Baltic amber, but all of those materials expose the main mass loss at about 400 °C. In contrary to those results, for the materials of (I) group, the ‘main’ DTG peak (i.e., the first major thermal event) was observed about 320 °C, while RU/Kh/1 and CO/1 resins from second group showed the main DTG signal above 400 °C. The discrepancy between our results and those reported in the literature may be caused by variability of physico-chemical properties of resin specimens from the same localization or different experimental setups (different sample masses, measurement parameters and procedure for the preparation). This requires more material to be tested; however, the availability of specimens from the same deposit is very limited. Moreover, the resins may undergo structural reorganization when are exposed to air. Nevertheless, the presented here results contain a basic knowledge and will be useful for further more detailed studies.

Despite their geological age, both samples of (II) group followed similar main degradation route, but CO/1 showed additionally low temperature degradation peaks, which can be more meaningful than the ‘main’ DTG peak itself. These thermal events may come from the chemical composition of Colombian copal and also its relatively ‘young’ structure. Moreover, similar observations we have made for the

(I) group of resins exposed thermal signals between about 125 °C and 240 °C, which may be related to the presence of reactive species in the resin [9]. This stays in accordance with the earliest reports on natural resins. For example, Poinar [25] suggests that the qualities of copal, as younger resins which contain unpolymerized fraction, may preserve this reactivity for even 3 or 4 millions of years.

As it was previously reported [3], the resin fossilization runs through polymerization of nonvolatile ingredients, cross-linking and isomerization, after low molecular mass compounds have been evaporated. This means that thermal behavior may reflect maturation histories and resin transformations [26].

Here, as a general conclusion from the comparative analysis of the data, one can say that there is no clear dependence on thermal stability vs age of the resin; hence, more complex and statistical studies should be performed. The analytical data cited above show that there is no evident dependence between thermal stability of resins and their geological age. For example, the oldest Khatanga resin (RU/Kh/1) has the ‘main’ DTG peak about 439 °C and further samples, respectively, to their age: PL/J/1 (about 40 Ma) – 327 °C, DO/1 (15–0 Ma) – 323 °C and the youngest one CO/1 (2.5 Ma – 200 y) – 400 °C.

Certainly, these results indicate that larger number of specimens should be investigated to confirm whether there is correlation between thermal stability and geological age of the resin or not. Also, statistical analysis should be performed that will require numerous specimens from the same location in order to assess variability in the structure of resins of the same botanical and geographical origin and age. Besides, more complex studies are needed that also involve a chemical control of the resin composition and detailed physical analysis of the materials structure.

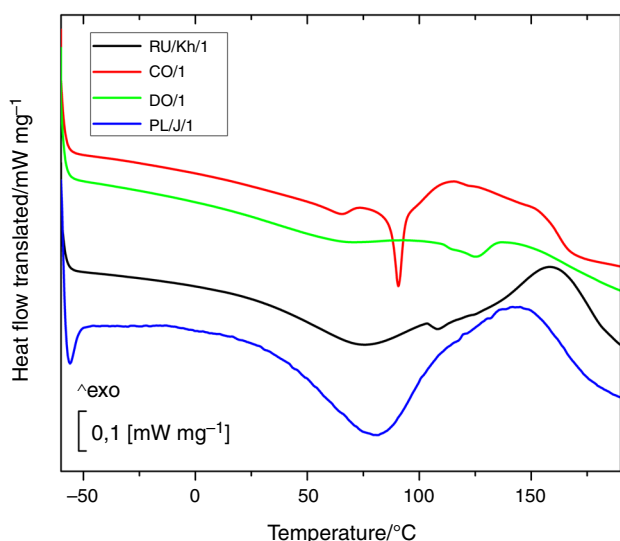
### Thermal properties—differential scanning calorimetry DSC

Phase transitions under programmed temperature changes were investigated by DSC analysis, and in Fig. 2, DSC curves for analyzed resins are presented. The profile of the

**Table 2** Parameters of thermogravimetric analysis of natural resins under oxidative atmosphere

Sample	$T_{5\%}/^{\circ}\text{C}$	$T_{\text{DTG}}/^{\circ}\text{C}$			$\Delta m/\text{mass}\%$			Residue/mass%
		I	II	III	I	II	III	
CO/1	270	323	400	530	13.4	68.9	17.6	0.2
DO/1	270	324	429	538	36.3	11.3	51.8	0.7
PL/J/1	217	327	408	526	49.4	7.5	42.8	0.4
RU/Kh/1	284	323/363	412/439	526	23.9	48.7	25.8	1.7

$T_{5\%}$ —temperature at 5 mass% of mass loss,  $T_{\text{DTG}}$ —main DTG extrema in different temperature regions (I, II and III) for thermal decomposition of analyzed resins,  $\Delta m$ —the mass loss at particular temperature region of I, II and III



**Fig. 2** Normalized DSC curves recorded with the natural resins under investigation

first heating scan has shown variation of heat capacity of the materials due to chemical changes (softening, melting, post-curing reactions, vaporization).

The glass transition  $T_g$  of natural resins in the first heating scan is usually overlapped with other effects, such as enthalpy relaxation and post-curing reactions. The course of DSC profile with increasing temperature has shown both endothermic and exothermic effects, which correspond to the softening and partial melting of the resin, evolution of volatiles, possible relaxation and post-curing reactions. In Table 3, the evaluated results are presented.

The analyzed resins during heating liberate heat due to post-curing reactions, which can be clearly observed on DSC curves as an exothermic effect (Fig. 2). The material also may lose some volatiles, and this evaporation is endothermic and compete with the exothermic reaction of curing. Other ‘endo’ events observed are mainly related to the softening and partial melting.

The distinctive DSC profile was observed for Colombian copal (CO/1), which shows the presence of a sharp endothermic signal at 91 °C corresponding probably to the melting of the material. The appearance of the sample after DSC measurement confirms this observation.

On cooling profiles (Fig. S1), a glass transition can be distinguished, that is overlapped on first heating curves by the melting, vaporization and curing effects. This indicates that conventional DSC analysis is not an appropriate tool for pristine resin properties determination, because the glass transition temperature can only be determined from the cooling or second heating run, so after thermal treatment of the resin. Thermal history of the natural resin is removed in the first heating run, and only subsequent thermal behavior might be observed, while the most important are thermal effects related to the complex resin composition and its age.

In previous reports [10], Dominican and Baltic ambers showed glass transition at 133–163 °C and 117 °C, respectively. The authors did not observe the age- $T_g$  dependence; however, another report by Jablonski et al. [5] showed the relation between the  $T_g$  value and age of the material. We also observed such relation, and we have found that the older is the resin and the higher is the glass

**Table 3** Evaluated DSC results for analyzed resins and samples appearance after DSC analysis

Sample	$T_g/^\circ\text{C}$	$\Delta H_{pc}/\text{J g}^{-1}$ (Peak temperature/ $^\circ\text{C}$ )	$\Delta H_1/\text{J g}^{-1}$	$\Delta H_2/\text{J g}^{-1}$	$T_f/^\circ\text{C}$	Appearance
CO/1	98	3.65 (112)	0.91 (66)	4.71 (91)	97	
DO/1	124	4.17 (146)	4.96 (64)	1.02 (124)	123	
PL/J/1	145	31.5 (149)	68.7 (81)*	–	137	
RU/Kh/1	154	25.2 (160)	13.6 (73)	0.84 (109)	142	

$T_g$ —Glass transition from the cooling scan in DSC measurements,  $\Delta H_{pc}$ —enthalpy of post-curing reaction from DSC measurement,  $\Delta H_1$ —enthalpy of endothermic effects observed on DSC scan 1—most probably evaporation, 2—relaxation or fusion process,  $T_f$ —fictive temperature from the cooling scan

\*Mixed process



transition value. However, it should be noted that proper comparison of the results is difficult by the fact that different instrument and measurement parameters were applied. In our studies, Dominican amber (DO/1) presents lower  $T_g$  than those from the literature. For Baltic amber, different  $T_g$  values were reported ranging from 117 °C [10] to 143 °C [27], which are close to our results.

Feist and coworkers [11] described different resin and copal materials from Baltic Sea area, Dominican Republic, Colombia and Madagascar. The differential thermal analysis (DTA) exhibited weak overlapping phenomena, both endothermic and exothermic character, which authors assigned to evaporation processes and decomposition

reactions. On the other hand, Bogdasarov [28] observed in DTA profile of Baltic resins similar endo- and exothermic effects during heating to 200 °C and described them as the partial molecular reorganization inside of the material.

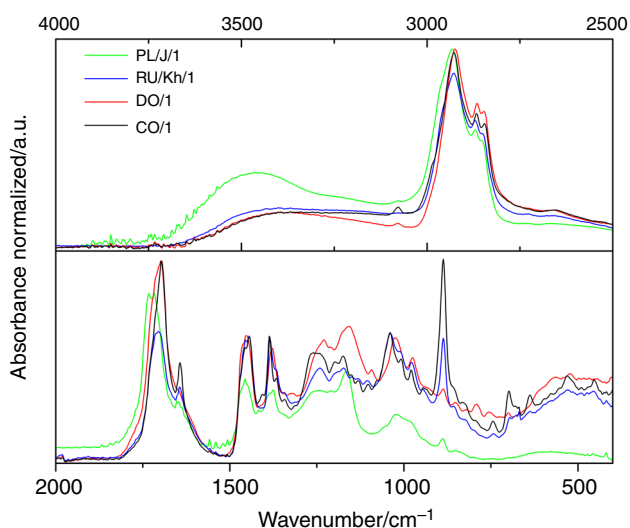
Our preliminary results and those from the literature suggest that for better elucidation of the natural resins characteristics, systematic studies by the use of DSC and DTA combined with chemical and more sophisticated methods should be performed.

### Structural changes—FT-IR

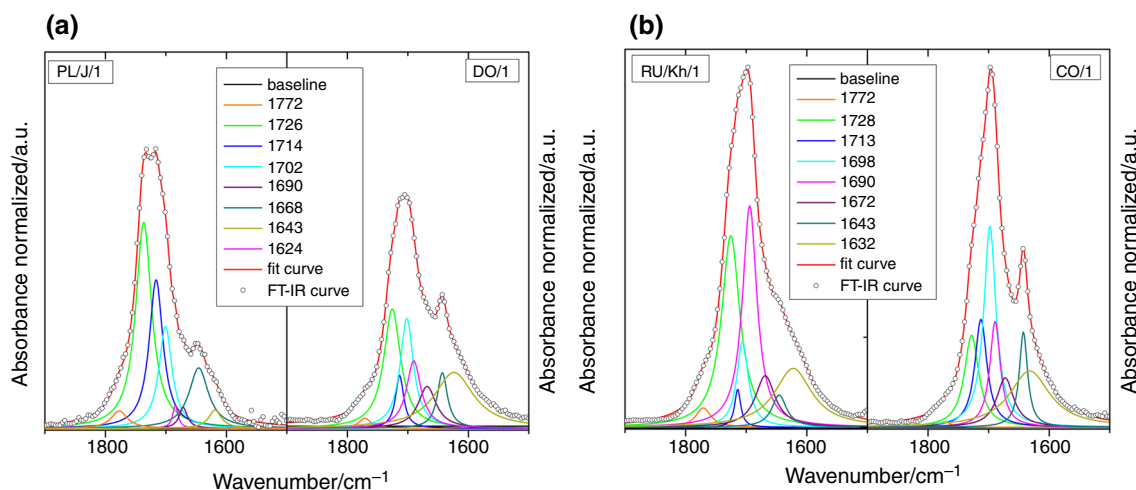
FT-IR is one of the most useful and popular methods for amber identification and characterization [6, 12, 29–31, 34–42]. The prominent features which can be found in the natural resins spectra are methyl/methylene stretching (2860/2920  $\text{cm}^{-1}$ ), carbonyl group stretching in the region of 1690–1740  $\text{cm}^{-1}$ , broad signal due to stretching in the hydroxyl group around 3420  $\text{cm}^{-1}$ , deformative O–H vibrations around 1640  $\text{cm}^{-1}$  and weak signal of C=C vibrations around 1610  $\text{cm}^{-1}$  [35].

FT-IR spectroscopy allowed to observe several differences in the structure of analyzed materials (Fig. 3), and selected samples were tested according to structural changes after heating in DSC experiment. The resulted spectra are presented in Figs. 3–5, and their respective assignments are summarized in Tables 4 and 5. The infrared spectra show characteristic indicative bands for different regions, i.e., 2700–3100  $\text{cm}^{-1}$ , 3100–3700  $\text{cm}^{-1}$  and 730–1890  $\text{cm}^{-1}$ .

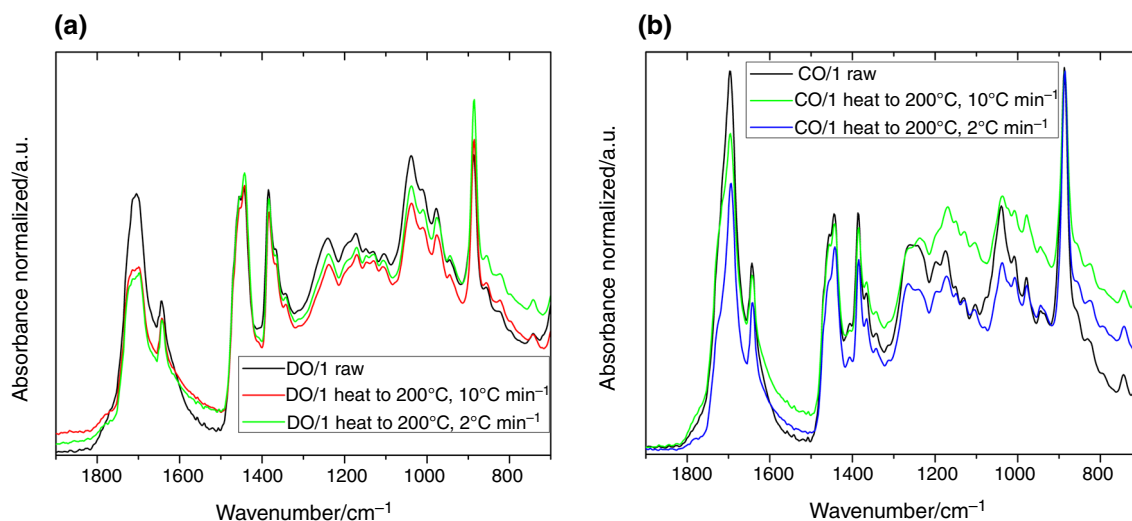
FT-IR results have shown that pristine Baltic amber (PL/1) is composed of ester part (mainly succinic ester) and acidic part (e.g., succinic acid), which may suggest that it was exposed on humid and acidic conditions. Moreover,



**Fig. 3** FT-IR spectra of the resins under investigation at room temperature in two spectral regions of 4000–2500  $\text{cm}^{-1}$  (up) and 2000–400  $\text{cm}^{-1}$  (bottom)



**Fig. 4** Normalized and deconvoluted FT-IR spectra of the analyzed resins in the spectral range of 1900–1500  $\text{cm}^{-1}$  at room temperature: **a** group I, **b** group II



**Fig. 5** Normalized FT-IR spectra of the DO/1 **a** and CO/1 **b** resins in the spectral range of 1900–700  $\text{cm}^{-1}$  (after different thermal treatments)

**Table 4** Main bands observed on the FT-IR spectra of the resins under investigation and their assignments based on the literature data

Band no	RU/Kh/1	DO/1	CO/1	PL/J/1
1	3412	3420	3392	3460
2	3079 w	3078	3078	3077
3	2928	2924	2927	2932
4	2871	2865	2867	2870
5	2850 sh	2848	2845	2848 w
6	2726	2659	2654	2730
7	nd	nd	nd	1733
8	nd	nd	nd	1717
9	1698	1705	1696	–
10	1644	1644	1643	1652
11	1453	1444	1444	1456
12	–	–	1406	1418
13	1378	1385	1386/1366	1386/1375
14	1346sh/1326	1342 w	1343	1340 vw
15	1230	1241	1261/1243	1243
16	1158	1173	1174	1165
17	1093	1105	1102	1062
18	1025	1039	1039	1020
19	975	978	978	981 sh
20	887	887	887 s	889
21	853	860 w	832	852
22	792	–	792 w	800
23	757	743	744	742

\*sh shoulder, vw very weak, w weak, s strong, nd not determined

possible thermal aging occurred which is indicated by the presence of band at 1652  $\text{cm}^{-1}$ , corresponding to C=C bond vibrations. The carbonyl band characteristic for

pristine amber was found to be split into two bands at 1717  $\text{cm}^{-1}$  (C=O in ketones) and 1733  $\text{cm}^{-1}$  (C=O in esters) [29].

Carbonyl group vibrations are usually the most intense signals on the FT-IR spectra; however, in some cases are also difficult in the precise interpretation because the signals for different carbonyl compounds overlapped each other. The complex composition of the natural resins can be clearly visible on the FT-IR spectra, especially in the carbonyl stretching region. In order to qualify the signals in the carbonyl region, we followed a spectral deconvolution and fitting approach. The most adequate fitting was achieved with a sum of Lorentzians for vibrational signals, in which intensity differs depending on the resin. The signals observed at around 1702  $\text{cm}^{-1}$  and 1695  $\text{cm}^{-1}$ , which correspond to the carboxylic acid groups, can be in fact one signal about 1700  $\text{cm}^{-1}$ ; however, their presence did not affect the fitting quality. Within the experimental and calculation inaccuracy, the results did not show significant differences to those from the literature. The obtained resolved spectra are presented in Fig. 4. According to the previous reports [29, 42], we have found several signals overlapping in the region of 1500–1900  $\text{cm}^{-1}$ , which are presented in Table 6. The resolved spectra showed bands characteristic for esters, ketones, carboxylic acids and double bonds vibrations.

We have observed (Fig. 4) that while the key band positions in the spectra range of 1500–900  $\text{cm}^{-1}$  did not change significantly, their relative intensities did. This indicates that the composition of the resin differs in terms of carbonyl compounds content and double bonds presence in the structure of the material. In turn, one can conclude that is probably caused by the aging process of tested resins.

**Table 5** List of characteristic absorption bands in FT-IR spectra recorded using the ATR [29–34]

Band no	Wavenumber/cm <sup>-1</sup>	Reference	Annotation
1	3550–3230	3400, 3070–3477	Stretch. O–H, hydrogen bonds
2	> 3000	3048	Stretch. C–H or CH=CH
3	2970–2950	2924	Asym. stretch. CH <sub>3</sub>
4	2880–2860	2867	Sym. stretch. CH <sub>3</sub>
5	2865–2845	2847	Sym. stretch.=CH <sub>2</sub>
6	1740–1725/2800–2700	2730*	Aldehyde
7	1750–1725	1735	C=O stretching esters
8	1725–1705	1716–1712	C=O stretching ketone
9	1725–1700	1702 + 1695	C=O stretching carboxylic acid
10	1650–1633	1642	C=C stretching
11	1485–1445	1450	Bending CH <sub>2</sub>
	1470–1430	1443	Bending asym. CH <sub>3</sub>
12	1440–1395	1418*	In-plane O–H bend
13	1380–1370	1384/1375	Bending sym. CH <sub>3</sub>
	1385–1380/1370–1365		Iso-dimethyl CH <sub>3</sub>
	1395–1385/1365		Trimethyl CH <sub>3</sub>
14	1350–1260	1346*	In-plane O–H bend phenol
15	1260–1238	1236–1243	δ(CH <sub>2</sub> ), δ(CH <sub>3</sub> ) stretch. C–C–O esters
16	1200–1155	1157 s	ν(C–O–C) esters
17	~ 1100	1115–1095	O–H in alcohols stretch.
	1150–1050		ν(O–C–C) esters
18	1060–1020	1018	Stretch. C–O in alcohols
19	970–960	974	Out-of-plane C=C def.
20	915–890	889	Def. out-of-plane C=CH <sub>2</sub> , CH=CH
21	850–790	846–823	In phenolic resins (after heating), C–H out-of-plane def. vibration
22	840–790	792	Rocking CH <sub>3</sub>
23	750–720	742	Methylene rocking –(CH <sub>2</sub> ) <sub>3</sub> n > 3 out-of-plane C–H bending

\*Not in natural resins, s strong

**Table 6** FT-IR band positions with intensities after normalization of the carbonyl region of the spectra, and their relevant assignments [32, 33]

Band/cm <sup>-1</sup>	Material/Intensity				Assignment
	RU/Kh/1	DO/1	CO/1	PL/J/1	
1771–1777	0.054	0.028	0.016	0.048	1768/1828 anhydride
1725–1736	0.532	0.333	0.258	0.575	1735 ester
1713–1716	0.106	0.148	0.297	0.415	1716–1712 ketone
1698–1706	0.239	0.307	0.532	0.285	1702 and 1695 carboxylic acid groups
1684–1694	0.615	0.188	0.326	0.064	
1669–1672	0.143	0.117	0.134	0.058	1670 C=C
1643–1646	0.089	0.155	0.265	0.169	1642 C=C
1619–1632	0.164	0.156	0.156	0.051	1623 COO–

For the oldest resin, i.e., Khatanga (RU/Kh/1) and Baltic amber (PL/J/1), the intensity of a band at about 1737 cm<sup>-1</sup> corresponding to the C=O vibration in ester groups is

clearly higher than for other materials. The same was observed for the intensity of a band at 1714 cm<sup>-1</sup> of carboxylic groups in succinic acid which is the dominant



marker for Baltic amber [43]. Another interesting observation is that the intensity of band related to the double bond vibration at  $1642\text{ cm}^{-1}$  lowers as the resin is older, suggesting that it can be useful for the age assessment purposes. Some of the authors [44] determine the degree of resin maturity based on the ratio of  $1650/1440\text{ cm}^{-1}$  bands in Raman spectroscopy. Recent investigations [26, 34] did not confirm such relation. Correlation of spectral properties of resins with their age and maturity still requires more investigations.

For the materials after heating in DSC measurement (Fig. 5), we did not observe significant structural changes—the positions of the characteristic bands stayed the same, but the intensity of the band related to carbonyl group vibrations became lower as material was thermally treated. One can point out that the older resins, i.e., RU/Kh/1 and PL/J/1, did not show any changes under thermal conditions applied ( $200\text{ }^{\circ}\text{C}$ ), which can be explained by heat resistance of the resins or low FT-IR sensitivity for observation of such subtle effects.

## Conclusions

Actually, advanced analytical methods and techniques allow to shed a new light on the complexed natural products, such as natural resins. The present study was devoted to preliminary investigation of selected samples of resins by means of thermal analysis and structural (FT-IR) studies.

Thermogravimetric results showed that there is no direct correlation between the age of the resin and its thermal stability and decomposition pathway. However, we have observed similarities between Baltic amber (PL/J/1) and Dominican amber (DO/1) under heating in air atmosphere. This was expected as they stand close in the classification of the fossil resins—both resins belong to class I of resins containing labdatriene carboxylic acids in their structure. The course of TG profile indicates that Russian resin (RU/Kh/1) and Colombian copal (CO/1) decompose in a more complex way; however, only the Russian material presents slightly higher thermal stability than other resins under investigation.

For investigated resins, the relative dependence between the glass transition  $T_g$  and age was found—as the resin is older the glass transition value is higher. Considering that  $T_g$  values were evaluated on the cooling scan, this observation should be precisely confirmed by more advanced techniques. One of them is modulated-temperature DSC, which allows to separate complex heat flow signal and thus determines the extent of overlapping thermal transitions in the raw material.

FT-IR investigations have shown significant differences in the structure between tested materials. Deconvolution of the FT-IR spectra allowed to extract characteristic bands in the region of carbonyl group vibrations of  $1500\text{--}1900\text{ cm}^{-1}$ , which in turn brought potential information about the amount of particular carbonyl compounds in the resin. It was also observed that the intensity of the band related to the double bond vibrations gets lower as the resin is older, which can be a significant observation in terms of resin age assessment.

In general conclusion, our results showed that systematic thermal studies followed by structural FT-IR studies are recommended for the natural resins to help in classification of this material according to the maturation grade. At the same time, further research is needed on statistically larger number of samples from the same deposit, as well as specimens with different geographical locations, but similar age or botanical origin. We plan to follow this subject in our future papers, where more detailed studies will be presented.

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