A thermal analytical study of some modern and fossil resins from New Zealand

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Abstract

Differential and thermogravimetric analyses of New Zealand modern, Pleistocene (<30 000 years) and Tertiary (>40 000 000 years) *Agathis* resins show a progressive change in their combustion profiles with increasing age. Differences between modern resins and Pleistocene Kauri gums are minimal. Both exhibit thermal events in the low-temperature range, commencing near 100°C and extending to 300°C, that reflect the relative abundance of more reactive, undersaturated, carboxyl-rich, unpolymerized components in the younger samples. Diagenetic changes accompanying thermal maturation reveal a reduction in intensity of thermal responses below 200°C and a progression in the temperature of the major thermal combustion event, from 350–450°C in the younger resins, to 450–580°C in the 40 000 000-year-old copals. These variations in thermal behavior accord with a reduction in undersaturated bonds and functionalized groups, and an increase in the proportion of aromatized groups that characterize resin aging. Used judiciously, thermal behavior may indicate maturation histories and resin associations. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Fossil resin is composed principally of macromolecular structures that retain the chemical fingerprints of the original resin [1]. New Zealand is well served by such resins that occur in rocks ranging in age from Recent to Mesozoic [2] and between 1850 and 1915 exported 297×10^6 kg of the so-called Kauri gum [3]. With only ~1200 km² of the country suitable for resin extraction, and with not all this area worked, at least 250 000 kg km^{-2} of resin from *Agathis australis* accumulated in the northern part of New Zealand in the later stages of the Quaternary (but, cf. Ref. [4]). In addition, substantial amounts of the liptinite maceral, resinite, occur in New Zealand's low-rank, lower Tertiary coals, along with large discreet masses of copal, up to tens of kilograms in weight, and regarded as biogenetic with the resinite. Poinar [[5], p. 135] introduced the terms 'occluded resinites' and 'non-occluded resinites' to distinguish these two categories although such a distinction is somewhat arbitrary. Infra-red and gas chromatographic analysis of the coal-derived resins indicate that they too are derived from *A. australis*, although one Eocene resin showed differences that suggested another species may be involved [4]. However, such differences can also arise from maturation during diagenesis [6,7].

Table 1
Analyzed resins

	Sample and location	Age/(years) [a]	S.G. [b] (g cm^{-3})	Ether [c]	Alcohol [c]	Description	Collection
1	Modern resin, Northland	<100	1.055	soluble	soluble	medium brown yellow	SC [d] 1
2	Modern resin, Northland	<100	1.057	soluble	soluble	very light yellow	SC [d] 7
3	Modern resin, Northland	<100	1.055	soluble	soluble	very light yellow	P151 AU15256 [e]
4	Modern resin, Northland	<100	1.064	soluble	soluble	golden yellow	P34 [e]
5	Modern resin, Northland	<100	1.039	soluble	soluble	brown yellow, heavy crust	P153 AU15259 [e]
6	Modern resin, Northland	<100	1.042	soluble	soluble	golden yellow	P154 AU15254 [e]
7	Pleistocene Kauri gum	5–30 000	1.055	soluble	soluble	light yellow	P155 AU15259 [e]
8	Pleistocene Kauri gum	5–30 000	1.052	soluble	slightly soluble	golden yellow	P156 AU15256 [e]
9	Eocene copal, Waikato Coal measures	~45 000 000	porous	insoluble	insoluble	translucent grey brown	P158 AU 15029
10	Eocene copal, Waikato Coal measures	~45 000 000	1.051	insoluble	insoluble	translucent dull yellow brown	P159 AU15258 [e]
11	Eocene copal, Hikurangi Coal measures	~45 000 000	1.080	insoluble	insoluble	dark red brown	SC [d] 15
12	Eocene copal, Waikato Coal measures	~45 000 000	1.047–1.052	insoluble	insoluble	dull opaque brown, include coal	SC [d] 20
13	Baltic amber	>45 000 000	1.083	insoluble	insoluble	medium light yellow	SC [d] 9
14	Finnish amber	>45 000 000	1.072	insoluble	insoluble	medium golden yellow	SC [d] 10

[a] Age estimates are based on present understanding of the stratigraphic ages of the appropriate deposits and differ considerably from earlier estimates [4,5,11].
[b] Specific gravity determined by dilution of concentrated brine until sample suspended followed by determination of solution density with pycnometer.
[c] Solubility verified by holding a drop of solvent against a freshly broken surface for 30 s and observing outcome.
[d] Spencer Currie Collection.
[e] P&AU – University of Auckland, Paleontology Collection numbers.

Thermogravimetric analysis has shown that resinite exerts a significant effect on the combustion of New Zealand high volatile subbituminous coals, such as those from the Waikato Coal Field [8]. The present study uses the same technology to compare the thermal behaviour of New Zealand fossil and modern *Agathis* resins as well as their classic Baltic counterparts. The opportunity was taken to evaluate modern thermal analysis as a way of characterising fossil plant resins. Previous attempts to use such techniques for characterising fossil resins were bedeviled by the inadequacies of earlier generation equipment than that employed here, resulting in unsatisfactory and inconclusive results [9]. The new data correlates with models proposed for the diagenetic changes occurring in resin structure on ageing.

2. Samples and methods

2.1. Samples

Samples analysed came from the Paleontology Research Collection of the Department of Geology, University of Auckland, and from the personal collection of Spencer Currie (Table 1). New Zealand *Agathis* resins are a mixture of monosesqui- and diterpenes. Despite ages in excess of many thousand years, New Zealand Pleistocene Kauri gums have been shown to retain appreciable volatiles [10,11]. In addition, two Baltic ambers were thermally analysed by way of comparison. Unlike *Agathis* resins, both of these contain considerable succinic acid [12].

XRF SemiQuant analyses of both, fossil and modern New Zealand resins showed no consistent differences with age for carbon (69–85%) and oxygen (6–11%). All contained appreciable trace amounts of Si (30–690 µg/g), Cl (35–135 µg/g), Al (30–625 µg/g), Ca (40–1160 µg/g), S (15–14 000 µg/g), Fe (10–200 µg/g) and K (15–100 µg/g). In addition, Mg (130–1700 µg/g), Mn (30–90 µg/g), Ti (15–40 µg/g) and P (35 µg/g) were occasionally present. The two Tertiary samples analysed contained 3000 and 14 000 µg/g S that, at least in part, represent contamination from the host coal. No behaviour was observed in the results of the thermal analytical runs, that might reflect these analytical levels.

2.2. Differential thermal analysis (DTA) and differential thermogravimetric analysis (DTG)

Combustion profiles (DTA and DTG) of each sample were obtained simultaneously by the method of Benfell, Beamish and Rodgers [13] using a Rheometric Scientific (formerly Stanton–Redcroft) simultaneous thermal analyser STA 1500. A type R (Pt–13%Rh/Pt) flat plate thermocouple system provided both, differential and sample temperature measurements. The samples (mass 5.0 ± 0.5 mg, particle size <75 µm) were contained in cylindrical alumina crucibles with 0.5 mm thick walls, placed directly on the thermocouple plates. The heating rate was $15°C$ min^{-1}, dry air purge 50 ml min^{-1}, and maximum temperature 900°C, giving a repeatability of $<\pm2°C$ [13]. The accompanying Polymer Laboratories PLus V software (v 5.40) derived DTG data from the recorded TG signal.

This procedure, unlike the closed-tube technique [9] produces a broad exothermic combustion curve, but yields results that are directly comparable with standard procedures adopted for coal analyses [8,13].

3. Results

The thermal analytical results show a progression in the character of the combustion profiles with increasing age of the New Zealand resins, as illustrated by examples given in Fig. 1. All weight loss events were exothermal.

Both, modern resins and Pleistocene Kauri gums are typified by a succession of small thermal events with maximum rates of weight loss at ca. 115–125°, 200–240°, 280–300°C (Fig. 1(a and b), profiles 1,7). There is a general increase in the maximum combustion rate over the 80–400°C interval, with a cumulative weight loss over this interval of some 52–56% of the original charge. Above 300°C, the younger resins show three major, distinct thermal events centred near 395–400°, 420–430°, and 530°C. The relative DTA intensity of these events varies but, in general, the rate of weight loss of all such young resins analysed to date, increases with increasing temperature. The final event terminates abruptly.

Thermal events prior to 200°C in combustion profiles of the older fossil resins, both the New Zealand
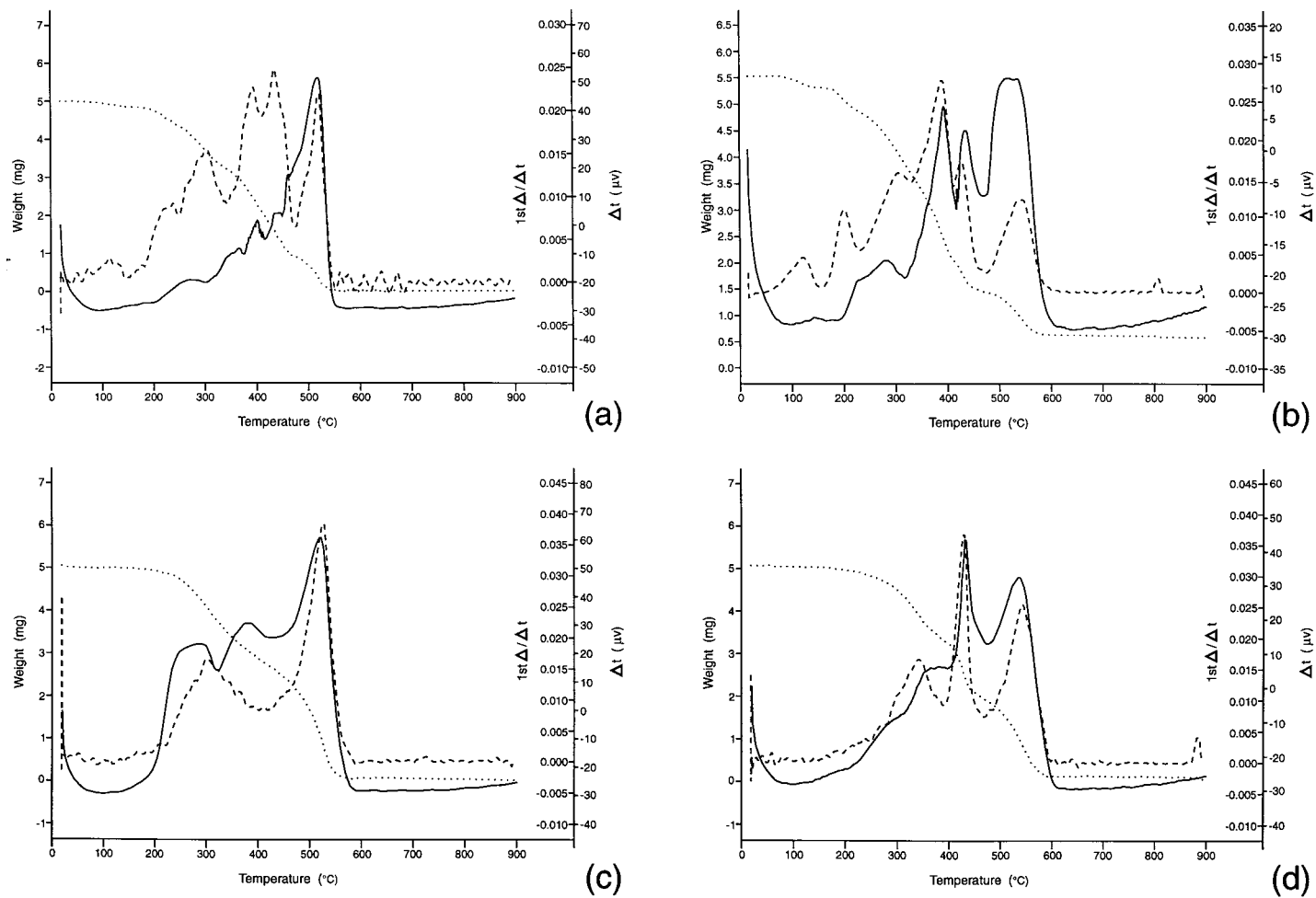
Fig. 1. Examples of TG combustion profiles of modern and fossil resins: (———) DTA; (· · ·) TG; (- - -) DTG. (a) modern Kauri resin, 1, Northland, New Zealand; (b) Pleistocene Kauri gum, 7, New Zealand, AU15259; (c) Eocene copal, 9, Waikato Coal Measures, New Zealand, AU15029; and (d) Baltic amber, 13, SC9. (Sample numbers as for Table 1.)

and European, are generally absent or poorly defined (Fig. 1(c), profile 9). The weight loss over this initial interval for these samples is <3%. Occasionally, a small exothermic event is observed near 190°C, but the profiles of all New Zealand Tertiary copals are characterised by the abrupt onset of a major, broad thermal event at 200 ± 10°C, that climaxes over 295–325°C. This event accounts for the majority of a 45% weight loss, to 400°C, of the initial mass of the oldest samples. Only one other thermal event characterizes major weight losses among older New Zealand copals, but in many resin profiles it proves to be the most intense and sharpest event, occurring above 450–550°C, with a maximum rate near 525°C. It is notable in having a fairly abrupt cutoff following maximum combustion.

A distinct exotherm near 375°C is present in the New Zealand Tertiary copal profiles and corresponds to the minimum weight loss rate over the entire 250–550°C interval. The behaviour reported for resinite from Waikato's Rotowaro field [8], is identical to that of all copals analysed here, but no comment was made on the 375°C DTA event although it is clearly present in the figure d trace Fig. 1(a).

Both the ambers show similar combustion profiles that differ from that of Fig. 1(d) (profile 13). The general sequence of thermal events is similar to that of the New Zealand Tertiary copals but the relative intensities of these events are quite different. There is a continual, incremental, increasing weight loss commencing near 100° and culminating at 340°C. The rate of this weight loss varies throughout this temperature range. As with the New Zealand resins, a moderate exotherm occurs near 380–390°C that is close to a minimum weight loss, but the most pronounced event in both, the DTA and DTG profiles is centred at 430°C and occupies a relatively narrow range of 90°C with a weight loss of some 25% of the original charge. A final event, corresponding to a weight loss of 30% and centred near 530–540°C, shows a less abrupt cutoff than with New Zealand resins.

4. Discussion

The variation in thermal reactivities, recognised here, is in more or less broad agreement with chemical differences that have been identified between modern, Pleistocene and Tertiary *Agathis* resins.

Freshly bled resin of *A. australis* rapidly loses water and some monoterpene hydrocarbon to yield a soft transparent surface film that gradually hardens on further exposure to air and light [10,11]. The main constituents at this point consist of agathic acid, *trans-* and *cis-* communic acids, sandaracopimaric acid, abietic acid, *d*-α-pinene and subsidiary monoterpenes, with a water-soluble fraction that includes some phenols [10]. Upon hardening, the conjugated dienes polymerize, incorporating other components of the resin, and accompanied by cross-linking through peroxidation and polyester formation. Even after many thousands of years, 30–50% of unpolymerized material still persists, particularly in larger masses [10]. In the present combustion profiles, differences between modern resin and Pleistocene Kauri gums are minimal. Both show a series of thermal events in the low-temperature range, commencing near 100°C and extending to 300°C. Such responses are presumably related to an enduring relative abundance of more reactive components in resins of <30 000 years age.

Subsequent changes in the resin take place very slowly. With increasing resin age, there is a progressive loss of undersaturated bonds, a decrease in functionalised groups, and an increase in the proportion of aromatised groups [1]. The net effect is a continued, progressive reduction in unpolymerized (acetone-soluble) constituents, particularly communic-acid-type compounds, and an increase in less reactive (and less soluble) polycommunic acid containing some communol units [14]. The exceedingly low rate of polymerisation is demonstrated in some 5% hexane-soluble (unpolymerized) material still remaining in the 20 000 000-year-old resin from Roxburgh, from which both, agathic and sandaracopimaric acids and their esters were isolated [11]. No resins of similar age were available for analysis in the present study but it would be expected that such a resin would continue to show low but perceptible thermal response(s) over the 100–300°C range.

In contrast, 40 000 000-year-old fossil resins from New Zealand's Waikato Coal Field contained neither sandaracopimarinol nor sandaracopimaric esters [4]. The combustion profiles of the similar copals analysed here are consistent with such a stage in thermal maturation. The more reactive constituents have been largely eliminated and decarboxylation has given way to aromatisation reactions [15], producing a suite of

materials that require increasingly elevated temperatures for combustion. The exothermic nature of the 375°C event, coupled with minimal weight loss, points to it arising from a structural change associated, presumably, with the remaining, less reactive portion of the polymer, perhaps a depolymerisation.

The thermal behaviour of the Rotowaro New Zealand fossil resin [8] most closely resembled those fossil Atlantic coastal plain resins [9] and differed, as do the modern or fossil *Agathis* resins described here, from European ambers. Both the amber samples analysed presumably contain a notable component of dicarboxylic acid(s), typically succinic [12]. Along with other differences in their chemical structure, decomposition and combustion of the acid would account for the distinct differences in the ambers' combustion profiles (Fig. 1).

5. Conclusion

Broughton [9] characterised fossilisation of resins in terms of a progressive reduction in the proportion of volatile components. Gemmologists effectively measure the same process in terms of a reduction of proportion of industrial alcohol- or ether-soluble components [2]. Both, volatility and solubility are expressions of the polymerisation process, the net effect of which is to increase the molecular weight of the resin constituents and reduce their reactivity. In the present instance, such changes are discerned by the progression in temperature of the major thermal combustion event; the contrast being clearly seen in overlay of the DTG combustion profiles of Fig. 2. The dominant weight-loss events of the younger resins occur over the 350–450°C interval. In the course of 40 000 000 years this has increased to 450–580°C.

Thermal behaviour alone cannot elucidate the botanical affinities of any resin, nor may it be invoked as some crude geothermometer. It may, however, be used to supplement other data used to describe maturation histories and associations. Although fossil resins generally retain chemical signposts pointing towards their past, the older a resin, the further it is removed from the structural chemistry of its original latex. Fossil
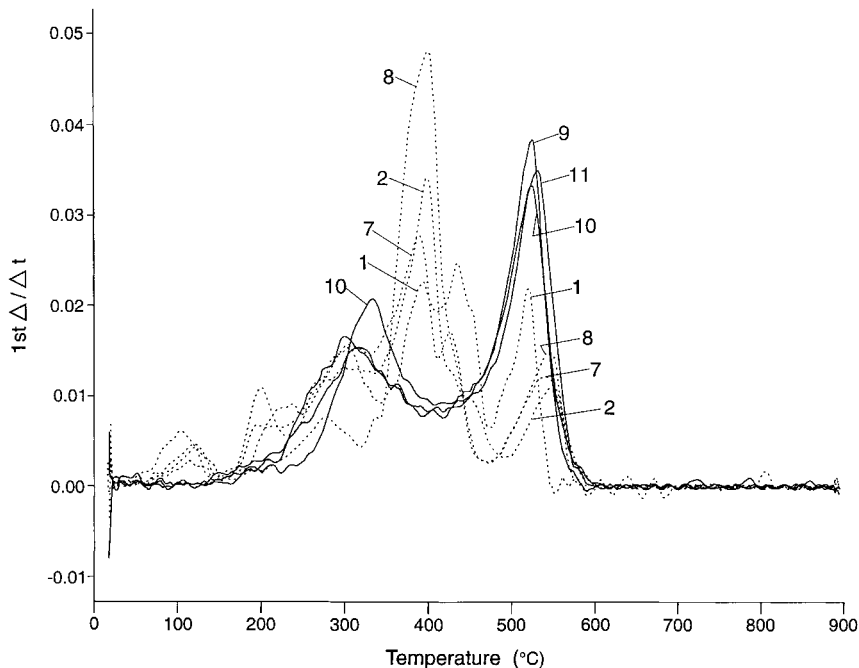

Fig. 2. Composite of DTG air-combustion profiles of modern and Pleistocene resins compared with Tertiary copals from low-rank New Zealand coals. Note the difference in temperatures of combustion activity between the younger (· · ·) and older (———) resins, particularly the temperature of maximum rate of weight loss. (Sample numbers as for Table 1.)

resins, even of different botanical affinities, preserved under similar conditions for sufficient time, may ultimately yield similar products and exhibit similar physical behaviour. If, as has been suggested by some researchers, European ambers have been derived from an *Agathis*-like source, they clearly have not been subjected to a similar diagenetic and, subsequent, geological history to that enjoyed by the ancient New Zealand *Agathis*-related resins.

Acknowledgements

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