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Article *in* Polymer · December 2013

DOI: 10.1016/j.polymer.2013.10.046

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Polymer 54 (2013) 7041–7047

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Something about amber: Fictive temperature and glass transition temperature of extremely old glasses from copal to Triassic amber

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ARTICLE INFO

Article history:
Received 14 September 2013
Received in revised form
22 October 2013
Accepted 24 October 2013
Available online 1 November 2013

Keywords:
Glass transition
Amber
Age

ABSTRACT

In previous work we successfully used a stable Dominican amber to investigate the sub-glass transition dynamics of an organic glass with extremely low fictive temperature. The results provided an incentive to seek other stable ambers with lower values of fictive temperature. In the present work, a series of fossil resins from different locations, and ages ranging from approximately 100 years–230 million years, has been investigated using differential scanning calorimetry. The measurement results show the thermal signatures for each fossil sample: copals are unstable, and have lower glass transition temperatures than the amber samples. For the amber samples, there is not a systematic age dependence for the amber's glass transition temperature. Furthermore, even for the same sort of amber, the thermal properties can be different for different samples. The stability of the fossil resins was studied and glass transition temperatures were determined. For the stable samples, fictive temperature was also determined.

1. Introduction

Fossil resins, such as amber, are very complex organic polymer/copolymer materials formed from plant resins that have aged for multiple millions of years [1,2]. The amber is formed via a fossilization process by crosslinking of the original organic resin by free radical polymerization [3]. In addition, the composition of the amber changes with time during the aging or fossilization process. Volatile fractions decrease during the long time aging and the fossil resin becomes hard over time [1]. Anderson et al. have reported a classification of fossil resins and most of the ambers have been, generally, placed into the Class I category [4]. The Anderson classification is summarized in Fig. 1 [1,3,4].

Due to its natural beauty and physical properties, amber has been used in different fields: jewelry [1,2,5,6], pharmaceuticals [6–10], oil varnish [11], archeology [12–14,2], geology [15] and glass physics [16–18]. Copal, a younger resin which has not completed the fossilization process, is normally softer than true amber [2,19]. Usually, copal is not considered to be true amber although it can be confused in the jewelry market. Therefore, it is useful to have a method to distinguish copal and amber. In addition, amber itself is a material of interest. It offers an opportunity to explore the behavior of a range of glasses that has not been previously examined. Amber might be a good material on the investigation of Boson peak due to its long time aging history [17,18]. Also, in a previous work we showed that a specific stable sample of Dominican amber provided a novel means to study the dynamics of glass-forming materials [16]. The over 40 °C gap between the glass transition temperature (T_g) and the fictive temperature (T_f) of the material provided the opportunity to investigate the temperature dependence of the upper bound to the relaxation times at temperatures far below T_g, with the result that strong evidence of deviations from classic theory were obtained. The low fictive temperature is thought to be due to the long time (millions of years) aging of amber [16,20–22], and the success of that study lead us to seek other amber samples having lower fictive temperatures among the older ambers. Our findings, however, show that the relationship between amber age and fictive temperature and glass transition temperature is not straight-forward and the result is the first systematic comparison of the glass response of ambers and other fossil resins in the age range of approximately 100 years–230 million (Ma) years.

Different methods have been applied to assess the age of fossil resins. Kimura et al. [3] applied ^{13}C NMR to several sorts of fossil resins, and estimated the age of the ambers by checking the crosslink formation. Ragazzi et al. [23] used thermogravimetry (TG) and differential thermogravimetry (DTG) to test different fossil resins, and found that the relationship between the age of fossil and DTG peak is linear. As the age of the resin increases, the value for

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0032-3861/$ – see front matter
http://dx.doi.org/10.1016/j.polymer.2013.10.046

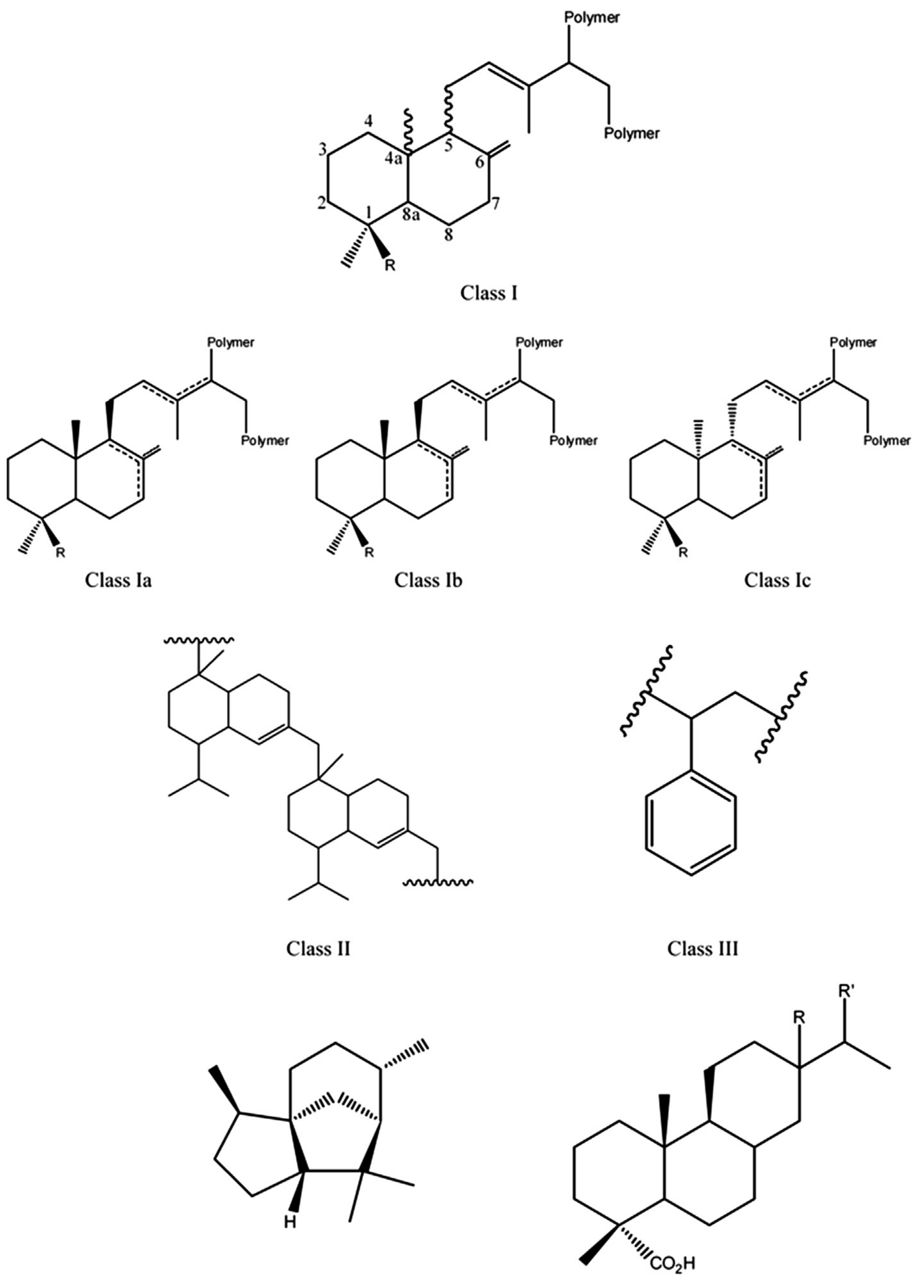

Fig. 1. Schematic description of Classification for fossil resins according to Anderson and Crelling [1].

the DTG peak increases. Furthermore, amber is a good matrix for keeping old and ancient insects and plants [2,14,24–26]. One method to determine the age of amber is by studying the DNA of the insect trapped inside the amber [6,27,28]. Fig. 2 shows an insect in one of the resins studied in this work, Madagascar copal. It is clear that the insect inside the copal has been well protected and preserved. In addition to the above technologies, mass spectrometry [19,29,30], infrared spectrometry [19,30–32], X-ray analyses [33,34] and differential scanning calorimetry (DSC) [28] have also been applied to test different fossil resins.

In the present work, 12 types of fossilizable and fossil resin with ages ranging from approximately one hundred years to over 200 million years were characterized using DSC. These 12 types of amber came from 9 locations. The stability of the amber and the relationship between the glass transition temperature, fictive temperature and age of the resins were investigated. Also, different pieces for the same sort of amber were tested and the results compared.

2. Experimental

After receipt, all the amber samples were stored under desiccant to keep the samples dry. Fig. 3 and Table 1 provide a picture of the resin samples, as-received, and general information for all the samples, respectively. A differential scanning calorimeter (DSC Q20 from TA Instruments) was used to measure the glass transition temperature and fictive temperature of different copal and amber samples. Three test loops were used with 10 °C/min heating/cooling rates. For each amber sample, the measurement temperature range was determined using the following rules. First, the highest temperature in the measurement is lower than the degradation

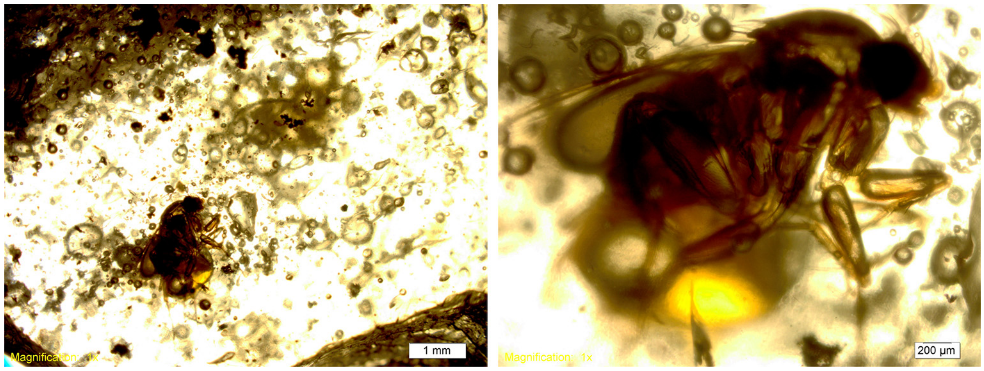

Fig. 2. Optical microscopy images of an insect in a Madagascar copal. Left image: 1.25× magnification. Right image: 5× magnification.

temperature of the specific amber [19,23]. Secondly, the measurement temperature range covers the whole glass transition process and, consequently, the equilibrium glass/liquid line of heat capacity could be determined. Finally, for the stable amber samples, the glass line and liquid line for the first and second heating traces overlap. Both the fictive temperature (only for stable samples) and glass transition temperature (limiting fictive temperature) were calculated using Moynihan's method. [46]

$$\int_{T \gg T_g}^{T_f} \left(C_{pl} - C_{pg}\right) dT = \int_{T \gg T_g}^{T \ll T_g} \left(C_p - C_{pg}\right) dT \quad (1)$$

where C_p is the measured heat capacity, C_{pl} is the liquid heat capacity, and C_{pg} is the glassy heat capacity. [46]

3. Results and discussion

As mentioned above, copal is younger than amber, has different maturities, and is not completely fossilized. Due to the younger age, copal is less stable than amber [2]. In Fig. 4 we present the DSC thermograms for the three different copal samples investigated. The trace for the first heating shows a large enthalpy overshoot which is due to the long aging time, and the second and third heating curves overlap and show the glass transition process. As seen from the figure, all three copals are unstable over the measurement temperature range, as evidenced by the fact that the liquid lines of heat capacity for the three testing loops do not overlap. During the heating process, there are chemical/physical reactions going on and the properties of the sample change [1,2]. There is no mass change for the Madagascar copal and Congo copal, and 0.7% weight loss for the Colombia copal. Therefore, the three tested copals do not have good thermal stability, and fictive temperatures of the aged materials cannot be determined from the DSC measurements. The glass transition temperatures for the samples after the initial heating are shown in Table 2.

As discussed previously, our initial motivation for the present study was to seek an amber that is stable and has a low fictive temperature relative to the glass transition temperature. Therefore, we tested 6 sorts of fossilized resins (ambers) with different ages

Fig. 3. Different fossil resin samples and the different pieces for the same sort of amber.

Table 1
Information for different copal and amber samples.

Name	Location	Age	Color	Source	Class[a]	Ref.[b]
Madagascar copal	Madagascar	10,000–100 y	Yellow	Galactic Stone and Ironworks	Ic	[23,35,36]
Congo copal	Congo	40,000–5000 y	Dark red	Galactic Stone and Ironworks	1c	[1,37]
Colombia copal	Colombia	2.5 Ma–200 y	Yellow	Galactic Stone and Ironworks	Ic	[23,38]
Dominican amber 1	Dominican Republic	20 Ma	Yellow	The Dead Bug in Amber Club	Ic	[39,40]
Dominican amber 2	Dominican Republic	20 Ma	Dark yellow	The Dead Bug in Amber Club	Ic	[39,40]
Baltic amber	Around the Baltic sea	40–35 Ma	Yellow	Galactic Stone and Ironworks	Ia	[23,39]
New Jersey amber	NJ, USA	94–90 Ma	Dark yellow	The Dead Bug in Amber Club	Ib, III	[23,39,41]
Burmese amber	Burma/Myanmar	100–90 Ma	Brownish	Galactic Stone and Ironworks	Ib, II	[1,39,42]
Spanish amber 1	El Soplao, Spain	110 Ma	Yellow	M. A. Ramos	Ib	[43]
Spanish amber 2	El Soplao, Spain	110 Ma	Brownish	M. A. Ramos	Ib	[43]
Triassic amber 1	Southern Alps, Italy	230 Ma	Dark red	E. Ragazzi	I, II	[13,44,45]
Triassic amber 2	Southern Alps, Italy	230 Ma	Dark yellow	E. Ragazzi	I, II	[13,44,45]

[a] According to Anderson's [1,4]classification.
[b] References are to both age and classification.

and from different locations, and investigated the relationship between T_g, T_f and the age of the amber. In addition, different sample pieces for the same sort of amber were tested and compared. Fig. 5 shows the DSC thermograms for all the amber samples in order of age. The fictive temperatures (for stable samples) and glass transition temperatures are shown in Table 2. Interestingly, most of the ambers are unstable (the undershoot of heat capacity indicates chemical reaction during the measurement) even though the samples have aged for millions of years. And the stability has no obvious relationship to the age of the amber. For example, one of the youngest ambers, Dominican amber 1 (which is the sample tested in Ref. [16]) is stable, but the Burmese amber, which is 80 Ma older than the Dominican amber, is unstable. In addition, different pieces of sample for the same sort of amber were also compared. Examination of Fig. 5 (compare Dominican amber 1 with Dominican amber 2; Spanish amber 1 with Spanish amber 2; Triassic amber 1 with Triassic amber 2) shows that, even for the same kind of amber, two different pieces may have different thermal signatures. Because even if the ambers were deposited at the same period and same location, different geothermal gradients can provide different environments, e.g. temperature, pressure etc. In addition, the plant resins also have variability typical of living systems, i.e., they are expected to be non-uniform and heterogeneous [1]. These differences affect the chemical process of amber fossilization and, consequently, lead to different properties [1]. Therefore, in studying amber behavior, it is important to examine

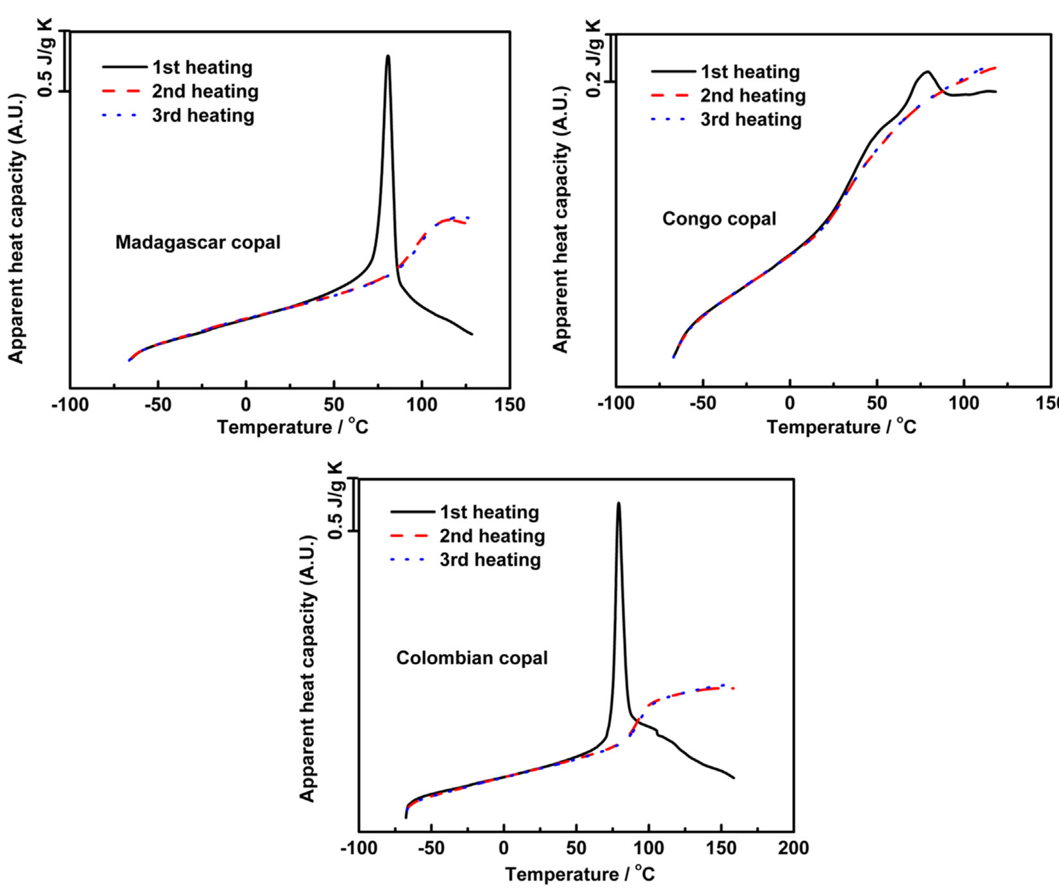

Fig. 4. DSC thermograms for three different copal samples, as indicated.

Table 2
DSC measurement results summary.

	Stability	T_g (°C)	T_f (°C)	T_g–T_f (°C)	Number
Madagascar copal	Unstable	92	–	–	1
Congo copal	Unstable	41.2	–	–	2
Colombia copal	Unstable	90.7	–	–	3
Dominican amber 1	**Stable**	136.2	92.6	43.6	4
Dominican amber 2	Unstable	162.2	–	–	5
Baltic amber	Unstable	117.8	–	–	6
New Jersey amber	Unstable	149.1	–	–	7
Burmese amber	Unstable	180.4	–	–	8
Spanish amber 1	**Stable**	142.5	101.1	41.4	9
Spanish amber 2	Unstable	125.2	–	–	10
Triassic amber 1	**Stable**	121.8	103.9	17.9	11
Triassic amber 2	Unstable	134.5	–	–	12

multiple pieces for a given material. Different pieces can exhibit different thermal and other properties. There may also be a subtle effect of the classification scheme into which the amber falls, but the present study was not able to provide insight into this issue.

It has been previously reported, from a smaller dataset, that the older the amber, the higher the glass transition temperature [28]. However, the data from the present work show different results. Fig. 6 shows the glass transition temperature of the fossilizable and fossil resins as a function of age. The inset shows the data on the log scale of time. First, by comparing the T_g value for the copal and amber samples, we found that the copals have lower glass transition temperatures than the ambers. This result is consistent with the Jablonski et al. report [28]. However, when the glass transition temperatures for all the amber samples are compared, the figure

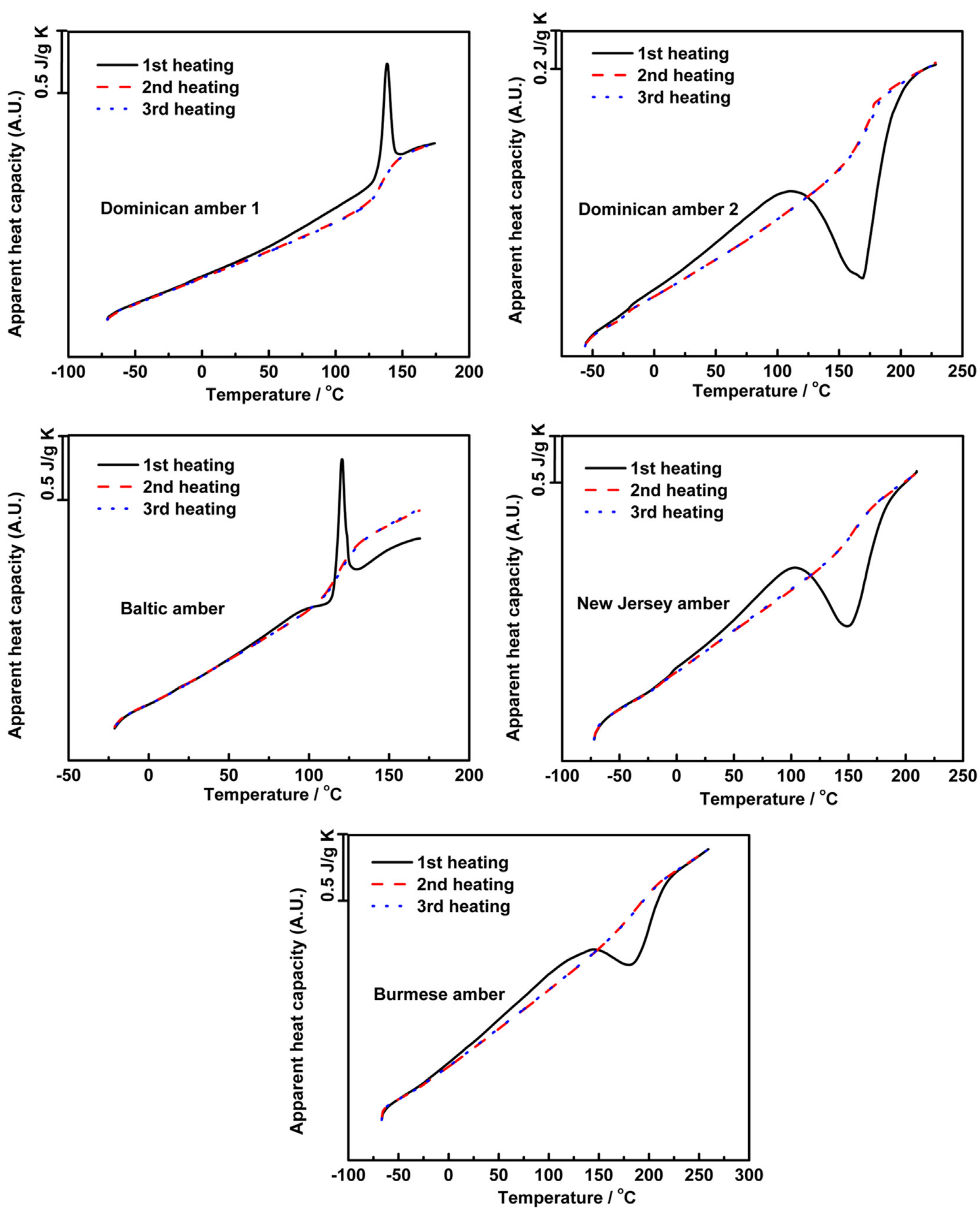

Fig. 5. DSC thermograms for different amber samples, as indicated.

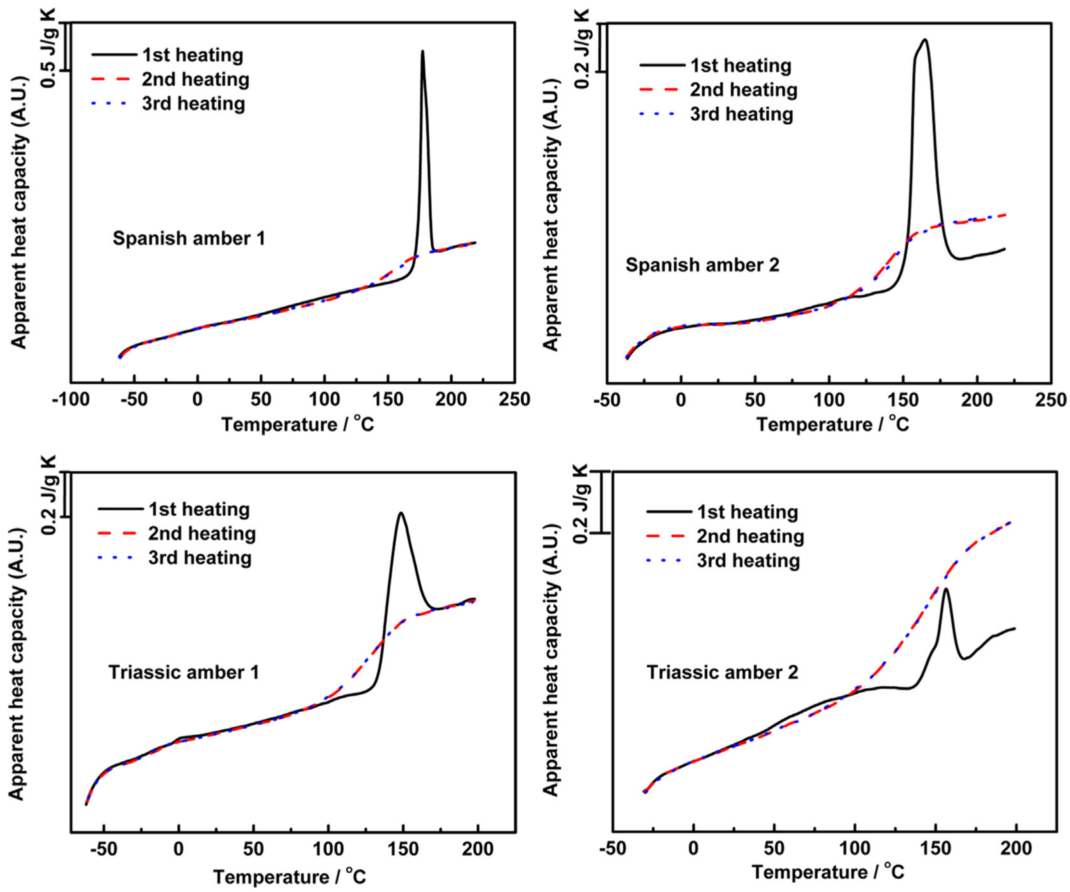

Fig. 5. (*continued*).

shows that there is no systematic age dependence for the glass transition temperature of the ambers (after heating above the T_g to remove prior thermal history). Therefore, the glass transition temperature cannot be used to determine the age of amber. This result shows that the aging of amber is a complex combination of the chemistry of fossilization and the physical aspects of the environment, such as temperature, pressure, and humidity.

We also determined the relationship between the age of the ambers that were stable and the difference ΔT between the fictive temperature and the glass temperature ($\Delta T = T_g - T_f$). By comparing the three different stable ambers, we found that ΔT does not increase with the age of the amber as had been expected. In other words, the aging time or age of the amber does not determine the fictive temperature. Surprisingly, the Triassic amber is significantly different from either the Dominican or Spanish ambers, when stable. The latter two have similar T_g and ΔT, while the Triassic amber, in spite of its extreme age, has a lower glass transition temperature and a very small $\Delta T = 17.9$ °C. Similar to the case of the copal and unstable amber samples, it is clear that there are other factors besides the resin age that determine the properties of amber, e.g. temperature, pressure, humidity, and compositional differences among resins. This is an observation that has not been fully appreciated nor studied systematically in terms of the glassy response of the resins.

4. Summary and conclusions

The thermal properties of a series of fossilizable and fossil resins were investigated using DSC with the initial purpose of finding a stable amber for studies of very low fictive temperature glasses. The results show that the three copals investigated were unstable in the testing temperature range, and they have lower glass transition temperatures than the true amber samples. For the ambers, most of them are also unstable, and the fictive temperature cannot be

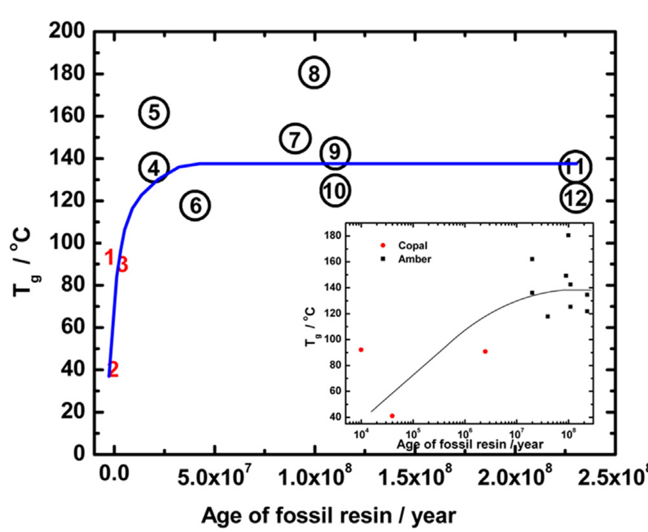

Fig. 6. The age dependence of the glass transition temperature for different fossilizable and fossil resins. Numbers correspond to sample designations in Table 2. The red numbers show the T_gs of the three copals investigated; the circled black numbers show the T_gs of the ambers; the blue line shows the changing trend of T_g as the resins age. The inset shows the T_g vs. logarithm of time. Circles (red) copal and squares (black) amber. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

determined when this is the case. We also find that, for the Dominican amber, Spanish amber and Triassic amber, although stable pieces could be obtained, these ambers can also be unstable. In other words, if one piece of amber is stable, it does not mean that all the other pieces of the nominally identical amber are stable, and vice versa. The results also show that there is not a clear relationship between the age of the amber and the glass transition temperature, and the glass transition temperature cannot be used to assess the age of fossil resins. Furthermore, the difference between the glass transition temperature and fictive temperature does not increase with the age of the amber. Although the Triassic amber is approximately 200 Ma older than the Dominican amber, the difference between T_g and T_f is less than half of the value for the latter. Full exploitation of amber as a stable glass requires care in the characterization and selection of appropriate samples, as done previously [16] with Dominican amber sample 1. Further investigations may well provide more insights into this remarkable material.

Acknowledgments

The authors thank the National Science Foundation under award DMR-1207070 and the John R. Bradford endowment at Texas Tech University, each for partial support of this work. We also thank M.A. Ramos for providing us with the Spanish amber samples.

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