

DETECTION OF THE GLASS TRANSITION OF POLYMERS USED IN ART AND ART-CONSERVATION USING RAMAN SPECTROSCOPY

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Abstract

In this work Raman spectroscopy was employed for the detection of the glass transition temperatures (T_g) of some thermoplastic polymers and natural terpenoid resins. In particular, our attention was focused on evaluating the T_g of polystyrene and colophony. The measurements returned T_g values in accordance with those reported in the literature obtained using the DSC technique, thus confirming the reliability of the approach proposed herein. Further studies will be focused on the evaluation of T_g temperature changes depending on materials treatments and ageing.

1. Introduction

Glass transition is a second order transition occurring at a characteristic temperature (T_g), corresponding to the transformation of a solid (glassy) material to a softer state (rubbery) and vice versa. In amorphous materials this is the primary transition. T_g is a very important parameter to be considered in order to objectively evaluate the performance of a material because it primarily affects the chemical and physical properties such as heat capacity, linear coefficient of thermal expansion and elasticity [1]. Polymers have several different phases (glassy, LC, crystalline and isotropic). Glass transition in polymers has found great interest in the last years given that, under T_g conditions, they behave as a hard disordered solid with a microscopic glassy structure, while above they change considerably structure becoming rubber-like and comparatively softer, thus changing their physical properties over time [2]. The knowledge of T_g of polymers used in art and its conservation is important in order to achieve proper performance, especially when the material is intended for outdoor exposition. In this respect, polymers used in conservation generally have a T_g far enough away from the ambient temperature [3].

Besides, thermoplastic polymeric materials are widespread in modern art museum collections and they have been used extensively in the production of design objects [4]. Moreover, natural materials, such as dammar, mastic, sandarac, colophony, and shellac resins, commonly used in art, as well as in current conservation treatments, have been investigated.

In this work, Raman spectroscopy is proposed as an alternative technique to the most commonly used differential scanning calorimetry (DSC) and dilatometry techniques, for measuring T_g of thermoplastic polymers and natural resins used in art and conservation. Raman spectroscopy represents a non-invasive approach with a spatial resolution higher than DSC.

2. Materials and methods

A compact Raman device was assembled for the present purpose, using a spectrometer equipped with a deep-cooled (-60°C) InGaAs array detector and a monochromator covering the spectral range between 165-1825 cm⁻¹. The exciting source was a ultra-narrow linewidth diode pumped CW Nd:YAG (1064 nm) laser. Although at 1064 nm the absorption of the materials under study is low, an automated control of the laser power and energy release was used in order to prevent any undesired overheating effect within the irradiated volume. This included a thermoelectric sensor providing the feedback signal for suitably modulating the output power of the laser source, according to a method reported elsewhere [5].

The detection of T_g has been achieved by monitoring the frequency shifts in the Raman bands with increasing temperature in a range between 25-170 °C. T_g of commercial thermoplastic polymers such as Polyvinylacetate (PVAc), Polymethyl-methacrylate (PMMA), Polystyrene (PS) was measured. Besides, the T_g of natural materials, such as dammar, mastic, sandarac, colophony and shellac resins provided by Zecchi (Florence, Italy) and commonly used in art, was also detected. In order to have a homogeneous surface morphology for the analysis, the samples were prepared by heating pure synthetic and natural polymers products up to their melting point and then let them cool at environmental temperature. The determination of the frequency shift was achieved through the weighted average of specific Raman bands of the spectra, $\bar{\nu}$, on the basis of the equation:

$$\bar{\nu} = \frac{\sum_{i=1}^n (I_i \cdot \bar{\nu}_i)}{\sum_{i=1}^n I_i} \quad (1)$$

where I_i is the Raman intensity in an interval of wavenumbers ($\bar{\nu}_i$) within the peak's range. This approach provides a sort of "centre of mass" of the selected Raman band, which provided

more repeatable and then reliable determinations of the band centre with respect to the usual peak fitting approach.

3. Results

Raman measurements were carried out on the abovementioned thermoplastic polymers as well as natural resins. Two examples for each category are herein discussed. Figure 1a shows Raman spectra of polystyrene as acquired at different temperatures ranging from 24 to 168 °C.

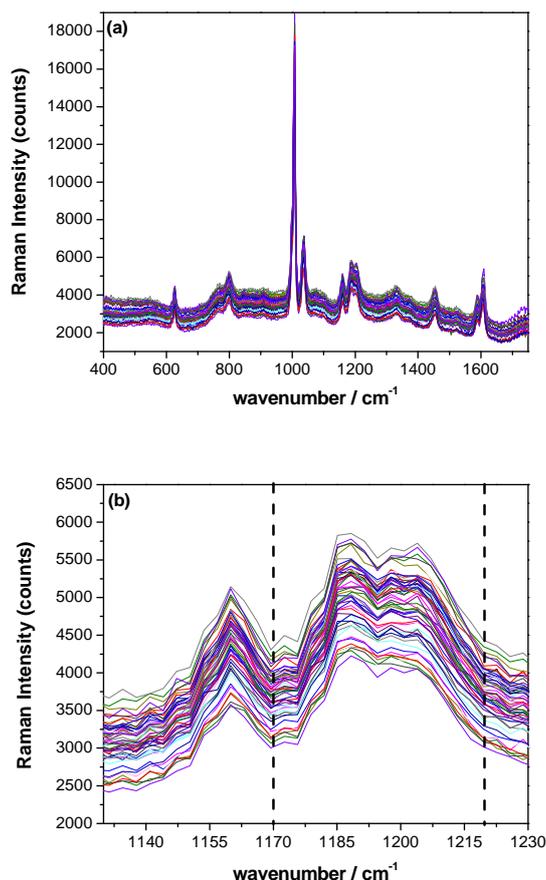


Fig. 1 Overview of the Raman spectra of polystyrene at different temperatures ranging between 24-168 °C: (a) whole fingerprint spectral region; (b) zoomed view of the spectral region used for deriving T_g (1170-1220 cm^{-1}).

Table 1: polystyrene vibrational modes assignment

Raman Frequency (cm^{-1})	Vibrational assignment
623	Aromatic ring deformation
765	C-H out of plane, $\rho(\text{C-H})$
1007	$\rho(\text{C-C})$
1033	$\nu(\text{H-C-H})$
1159	$\delta(\text{C-C})$
1188	$\nu(\text{C-C}), \delta(\text{H-C-H})$
1200	$\delta(\text{C-C-H}), \nu(\text{C-C})$
1329	$\rho(\text{H-C-H}), \delta(\text{C-C-H})$
1454	$\delta(\text{H-C-H})$

1590	$\nu(\text{C-C}), \delta(\text{C-C-H})$
1606	$\nu(\text{C-C}), \delta(\text{C-C-H})$

Vibrational modes assignments of polystyrene Raman bands shown in Fig- 1 are listed in Tab. 1 in accordance with the literature [6, 7]

In particular, the spectral region between 1170-1220 cm^{-1} was selected for monitoring frequency shifts with temperature according to Liem et al. [2]. Weighted averages (Eq. 1) were calculated for both the bands at 1188 and 1200 cm^{-1} in order to detect any minimal change in the molecular structure. Figure 1b shows a detail of the spectral region of interest: black dashed lines indicate the extremes of the interval for calculating weighted average.

Figure 2 shows weighted average values calculated from 1170 to 1220 cm^{-1} for each Raman spectrum of polystyrene as a function of temperature. A slope change is clearly observable around 110°C. This is the first time that glass transition is achieved by means of weighted average calculations on Raman spectroscopic data. For this reason, in accordance with what stated by Rieger [6] regarding the analysis of DSC curves, the onset glass transition temperature (T_{g0}) was defined as the intersection of the two lines obtained by fitting the two point-clouds with different slopes. The intersection of the two red lines shown in Fig. 2 therefore provided a $T_{g0} \approx 96^\circ\text{C}$, in good agreement with the corresponding value reported in the literature [2, 8]. The parameters of the mentioned linear fittings are reported in Tab. 2.

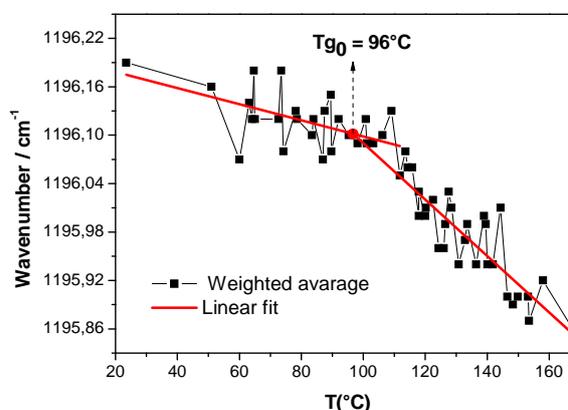


Fig. 2 Weighted averages of the peak position between 1170-1220 cm^{-1} of polystyrene as a function of temperature and associated linear fittings.

Table 2: linear fit parameters

	Value	Error
Intercept 1 (cm^{-1})	1196.20	0.02
Slope 1 ($\text{cm}^{-1}/^\circ\text{C}$)	-0.0010	$3 \cdot 10^{-4}$
Intercept 2 (cm^{-1})	1196.44	0.05
Slope 2 ($\text{cm}^{-1}/^\circ\text{C}$)	-0.0035	$4 \cdot 10^{-4}$

It is worth noting that the application of weighted average data allows detecting molecular changes resulting in very small frequency shifts (on the order of 1 cm^{-1}).

The frequency shift is due to the change of the relative amount of glassy and crystalline components of the material with the temperature [1]. Besides, at T_g , Raman modes are also affected by the discontinuity in the thermal expansion and other physical properties, which are directly correlated to intermolecular interactions.

Also natural resins underwent glass transitions and the value of T_g was determined in a similar way as for polystyrene.

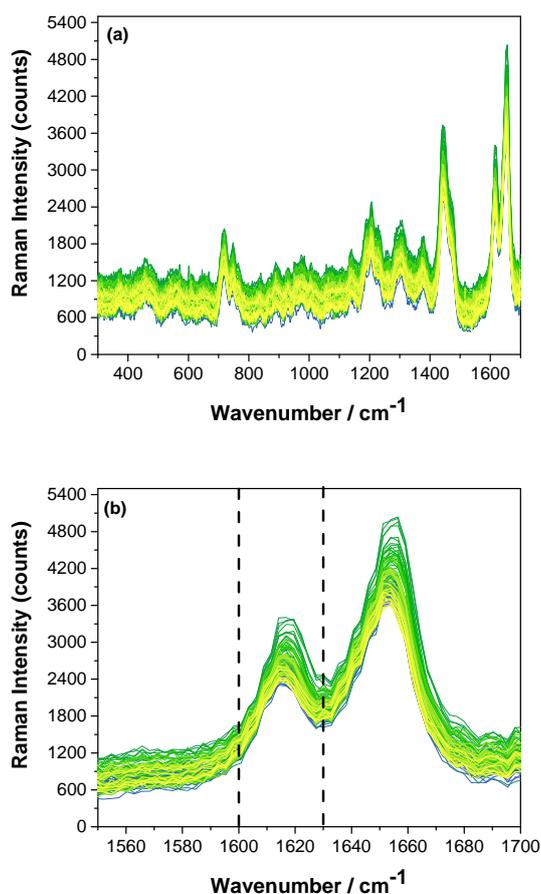


Fig. 3 Overview of the Raman spectra of colophony at different temperatures ranging from 24 to 127 °C: (a) whole fingerprint spectral region; (b) zoomed view of the spectral region used for deriving T_g ($1600\text{-}1630 \text{ cm}^{-1}$).

As an example, Fig. 3a displays Raman spectra of colophony acquired at different temperatures (24-127 °C). In particular, the spectral region between $1600\text{-}1630 \text{ cm}^{-1}$ was selected for monitoring frequency shifts with temperature (Fig. 3b).

Vibrational modes assignments of Raman bands of colophony shown in Fig. 3 are listed in table 3 in accordance with the literature [9].

Table 3: colophony vibrational modes assignment

Raman Frequency (cm^{-1})	Vibrational assignment
710-750	$\nu(\text{C-C})$
885	$\nu(\text{C-C})$
974	$\rho(\text{CH}_3)$
1138	$\nu(\text{C-C}), \nu(\text{COC})$
1207	$\delta(\text{H-C=C-H})$
1293	$\tau(\text{H-C-H})$
1379	$\delta(\text{H-C-H}), \delta(\text{CH}_3)$
1449	$\delta(\text{H-C-H}), \delta(\text{CH}_3)$
1620	$\nu(\text{C=C})$
1657	$\nu(\text{C=C})$

Figure 4 reports the weighted averages of the peak position between $1600\text{-}1630 \text{ cm}^{-1}$ of colophony as a function of temperature. In order to evaluate the data-set reproducibility, five Raman spectra for each temperature value were acquired. As in polystyrene, the intersection between the two linear fittings the scatter plot led to $T_{g0} \cong 53 \text{ }^\circ\text{C}$, in agreement with the range of temperatures reported in the literature for terpenoid resins [2]. In fact, it is known that glass transition of these materials undergoes significant changes and it strongly depends on the composition and degree of purity, which can vary depending on provenance, harvesting conditions, processing, and subsequent storage of the raw material. Besides, when applied as protective coatings, ageing, pollution, and many other causes affect their physical and chemical properties. Linear fit parameters are reported in Tab. 4.

Table 4: linear fit parameters

	Value	Error
Intercept 1 (cm^{-1})	1614.20	0.03
Slope 1 ($\text{cm}^{-1}/^\circ\text{C}$)	-0.0010	$7 \cdot 10^{-4}$
Intercept 2 (cm^{-1})	1614.51	0.04
Slope 2 ($\text{cm}^{-1}/^\circ\text{C}$)	-0.0068	$4 \cdot 10^{-4}$

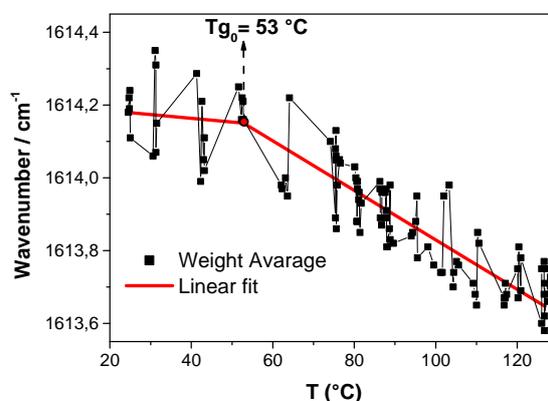


Fig. 4 Weighted average of the peak position of colophony between $1600\text{-}1630 \text{ cm}^{-1}$ as a function of temperature and associated linear fittings.

4. Conclusions

Glass transition temperatures of polystyrene and colophony were successfully detected through Raman spectroscopy measurements. The T_g values determined were in accordance to those detected using DSC. The possibility of measuring T_g using a non-invasive portable technique allowing for spatial resolution appears of particular interest in order to assess the state of conservation of polymeric artifacts. Furthermore, the present approach might be also of interest for optimizing and assessing laser conservation treatments, which involve photothermal processes. In particular, the Raman technique could provide direct information on the energy coupling to the material layers to be safeguarded and then on the overall selectivity of the laser irradiation treatment.

Further studies will be focused on the evaluation of T_g changes associated with ageing and conservation treatments of various artifacts of cultural interest.

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