



VERIFYING THE GLASS TRANSITION TEMPERATURE OF POLYMERS (PS, PMMA AND PET) BY RAMAN SPECTROSCOPY

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ABSTRACT

In this work we show the possibility to verify the glass transition temperature of the polymers polystyrene, poly(methyl methacrylate) and poly(ethylene terephthalate) by using Raman spectroscopy. It is well known that the glass transition is a very important relaxation process for polymeric materials and this process has been related with the motion in the backbone chain of the polymers. We heated up the samples step by step and collected the Raman spectrum as a function of the temperature, which made it possible to verify the glass transition temperature with relative facility. Raman spectroscopy is a technique able to detect small changes in the backbone chain and, therefore, it reveals itself as one additional technique to perform the glass transition investigations in polymeric materials

KEYWORDS: The glass transition temperature, Raman spectroscopy, polystyrene, poly(methyl methacrylate), poly(ethylene terephthalate).

INTRODUCTION

There has been a lot of interest in the study of the physical properties of polymers, and of their glass transition (GT) in particular, since the control of the glass transition temperature (T_g) in polymers is crucial for materials engineering [1].

The GT is a fundamental process related to slow conformational exchange in molecular processes arrangements [2] and, therefore, a complex phenomenon due to the random variation of thermodynamic parameters [1]. The value of T_g depends on various factors, such as the composition of the polymer, flexibility of molecular chains, molecular weight [3], crystallinity content [4, 5], concentration of diluent and the number of lattice sites [6]. The GT is associated with electrical and thermal properties, but the nature of GT is still not perfectly understood [2].

The most accepted theoretical model claims that when increasing temperature up to T_g the molecular chains relax, and thermodynamic variables, (such as specific heat), change continuously. Above T_g , the polymer volume continuously begins to expand allowing conformers to finally relax independently [1].

There are many well-known characteristic methods to measure T_g , such as Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Analysis (DMA). There are also several studies in which where the relaxation processes have been detected by ultraviolet-visible (UV-VIS) spectroscopy; in this case the researchers made a polymeric blend using a non-luminescent polymer with a luminescent polymer, which was used as a probe to detect internal changes in polymeric chain [7, 8]. In the present work we show the possibility to

verify the glass transition temperature of the polymers polystyrene, poly(methyl methacrylate) and poly(ethylene terephthalate) by using Raman spectroscopy. The collected Raman spectra were integrated (defined as the entire area under the spectral profile) in order to plot the integrated intensity versus temperature. This experimental procedure allows a simple and fast verification of T_g of these polymeric materials with smaller effort.

Material and methods

All polymeric substances were acquired from Sigma-Aldrich: poly(1-phenylethene) (PS) $[-CH_2CH(C_6H_5)-]_n$, with molecular weight (M_w), $M_w=350,000$ g.mol⁻¹, and density (d), $d=1.04$ g.mL⁻¹, poly(methyl methacrylate) (PMMA) $[CH_2C(CH_3)(CO_2CH_3)]_n$, $M_w=350,000$ g.mol⁻¹ and $d=1.17$ g.mL⁻¹ and poly(ethylene terephthalate) (PET) $[-C_{10}H_{12}O_6-]_n$ and $d=1.37$ g.mL⁻¹.

All the Raman spectra of these polymers were acquired with the help of a Thermo Scientific™ DXR™ Raman microscope, equipped with an Olympus BX41 confocal microscope. The spectrometer system was operated with the Thermo Omnic acquisition software. A CW laser with an excitation wavelength of 532 nm (2.33 eV) was used. Using a 10x objective (NA=0.25) yields a laser spot diameter of 2.5 μm. The laser power on the sample was 9.0 mW, resulting in an irradiance of 458 μW μm⁻². Fifteen accumulations with an exposure time of 10.0 sec each were collected for all spectra in the spectra range from 100 to 3500 cm⁻¹ with spectra resolution of 5.0 cm⁻¹. We applied an automatic baseline correction to all spectra. The temperature of the polymeric

samples was controlled by a T95 System and a cooling Option LNP95, both from Linkam Scientific Instruments Ltd. A heating rate of $20\text{ }^{\circ}\text{C min}^{-1}$ was used. The temperature step size was $2.0\text{ }^{\circ}\text{C}$ for all polymers except for PS, where the step was set to $5.0\text{ }^{\circ}\text{C}$, with a precision of $\pm 0.1\text{ }^{\circ}\text{C}$ in all cases. The samples were measured without any physical or chemical pretreatment.

RESULTS AND DISCUSSION

The glass transition relaxation is associated with molecular motion in the main chain of a polymer [9]. When the molecule receives enough thermal energy, motions are initiated making some molecules slide past one another [10]. In our case, the necessary energy comes from heating up the substance by using the Linkam T95 system. The glass transition relaxation

is considered to be a kinetic phenomenon [11], therefore the presence of side groups or cross-linking between chains can disturb the chain mobility and increase T_g . On the other hand, if the side groups of the chains have more flexibility, the T_g will decrease [12].

However, any variation in the polymeric structure might change molecular vibrations and, therefore, modify intensities encountered in Raman scattering. This is shown for the Raman spectra of PS, PMMA and PET in **figure 1**, in which the Raman signal intensity changes as a function of temperature, demonstrated for three different temperatures of each polymer. **Figure 1** shows selected ranges of the Raman shift for each spectrum to accentuate the parts where the intensity variation is more evident.

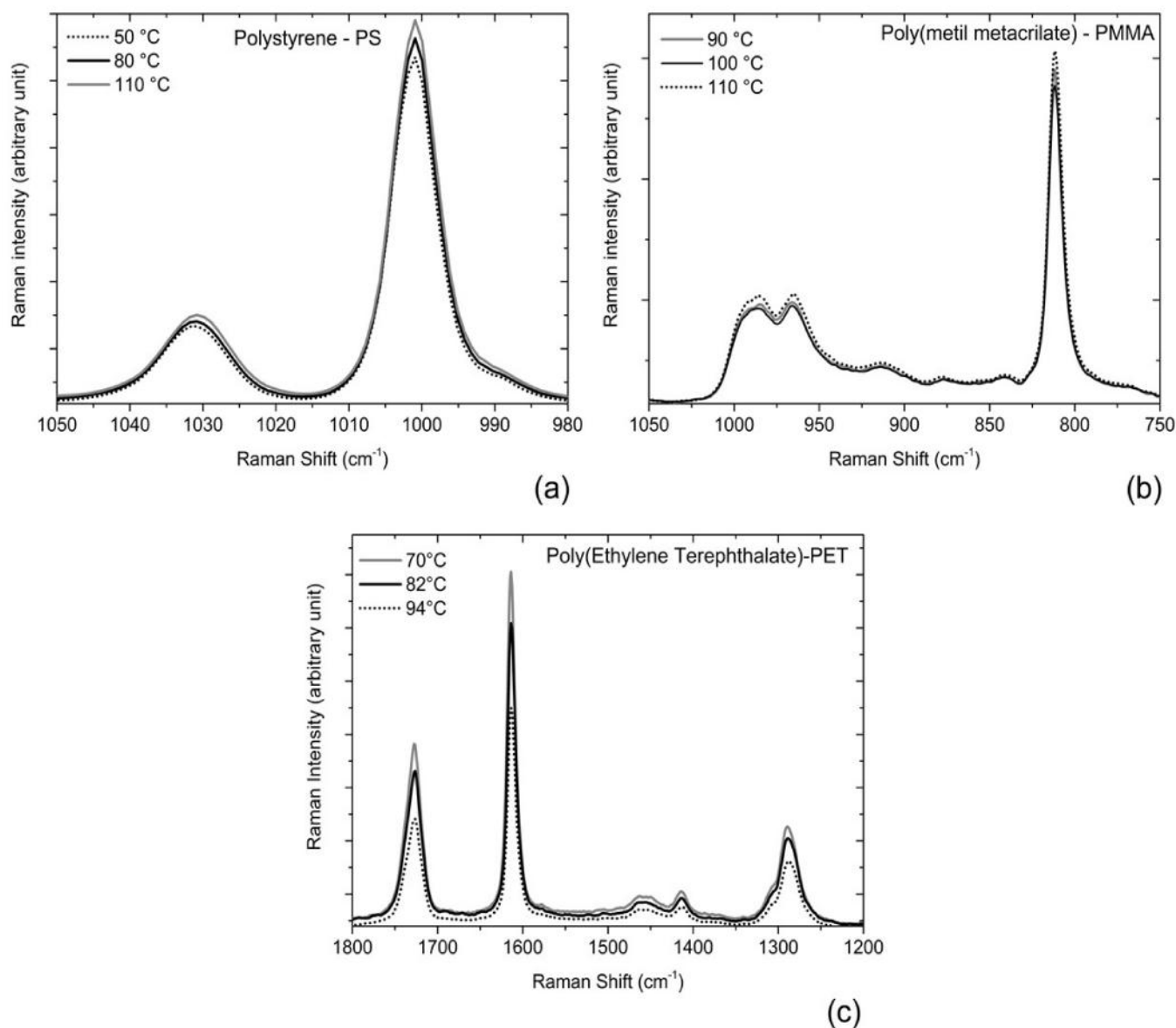


Figure 1. Part of the Raman spectra of the samples: **a)** PS, **b)** PMMA and **c)** PET, at three different temperatures around the glass transition temperature. It is possible to see that the spectrum intensity changes with increasing temperature

In order to determine T_g , the resulting intensity as area below the spectra profile was integrated over a selected spectra range. Graphs of the integrated intensity Raman spectra (IIRS) versus temperature in temperature range 50-120°C for PS, 90-120°C for PMMA and 70-94°C for PET, are shown in **figure 2**. In these graphs the integrated intensity was normalized considering the highest integrated intensity as unit. Thus, **figure 2** shows how the IIRS changes when the temperature increases.

In this work, we used information from other papers about T_g of these samples [13, 14, 15, 18, 19, 20] and from these data we carefully sought in the shape of the integrated intensity temperature profiles some changes which could, in turn, be associated to the T_g of our samples.

Figure 2(a) shows the behavior of the IIRS as a function of temperature, where is possible to see that between 70 and 90 °C there is a linear dependence of the IIRS with the temperature, but in the range of 90 to 100 °C this linear

dependence disappears. However, starting with 100 °C a linear dependence comes up again. The center of this discontinuity was identified as the T_g of the PS, $T_g=95$ °C. This data is corroborated by other methods, e.g. Real Part of the Complex Electric Capacitance [13, 14] and Scanning Viscoelasticity Microscopy [15]. All these authors have found the same value for T_g .

In **figure 2(b)** it is possible to see for PMMA that at 104 °C the IIRS has a minimum, and this was identified as the T_g of this sample, i.e. $T_g=104$ °C. In comparison, by DSC the T_g of PMMA was determined at 100 °C [7,20].

A graph of IIRS versus temperature of the polymer PET is shown in **figure 2(c)**. There it is possible to see a significant discontinuity between 80 and 84°C, thus, as in PS, the middle point of this discontinuity was identified as PET's T_g . In literature, the values of 77 °C [18] and 81 °C [19] were allocated to T_g by DSC.

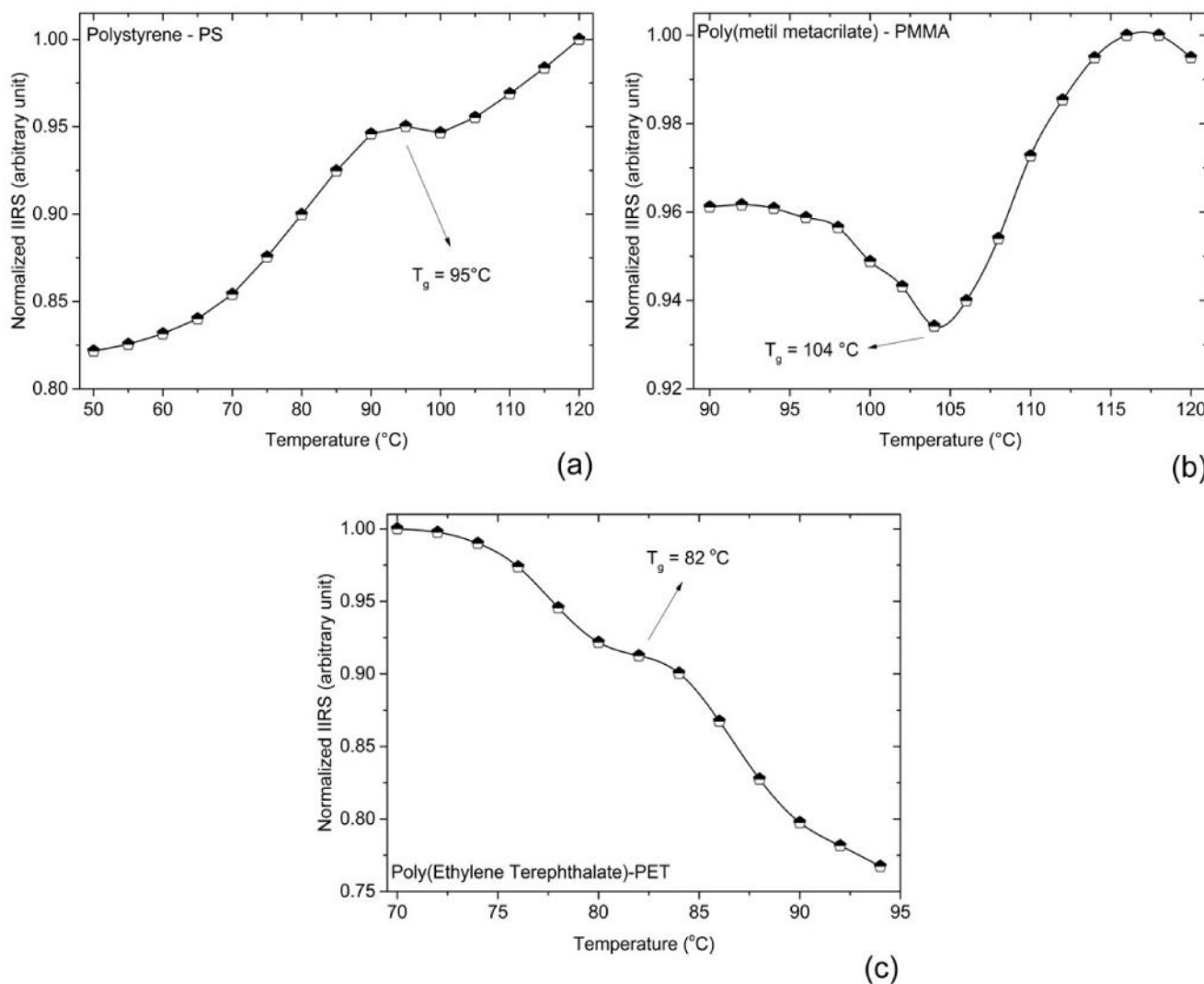


Figure 2. Integrated intensity Raman spectra (IIRS) as a function of temperature of the samples, for **a)** PS, **b)** PMMA and **c)** PET (integration range 100 – 3500 cm^{-1}). The IIRS curves show marked changes around the glass transition temperature (T_g), which enable the identification of the T_g value.

In **figure 3** the FWHM of the peaks around 1001 cm^{-1} for PS, 811 cm^{-1} for PMMA and 1727 cm^{-1} for PET, are shown. These peaks were fitted by Gaussian profiles, enabling us to analyze the FWHM behavior of every peak of the spectrum as function of temperature. It is evident that the FWHM remains constant at different temperatures for all polymers,

i.e. the Raman bands did not noticeable enlargement; thus we can conclude that the change of IIRS is a function of Raman intensity only. Intensity is affected around T_g because of discontinuity in thermal expansion and other physical properties directly influencing intermolecular interactions [2].

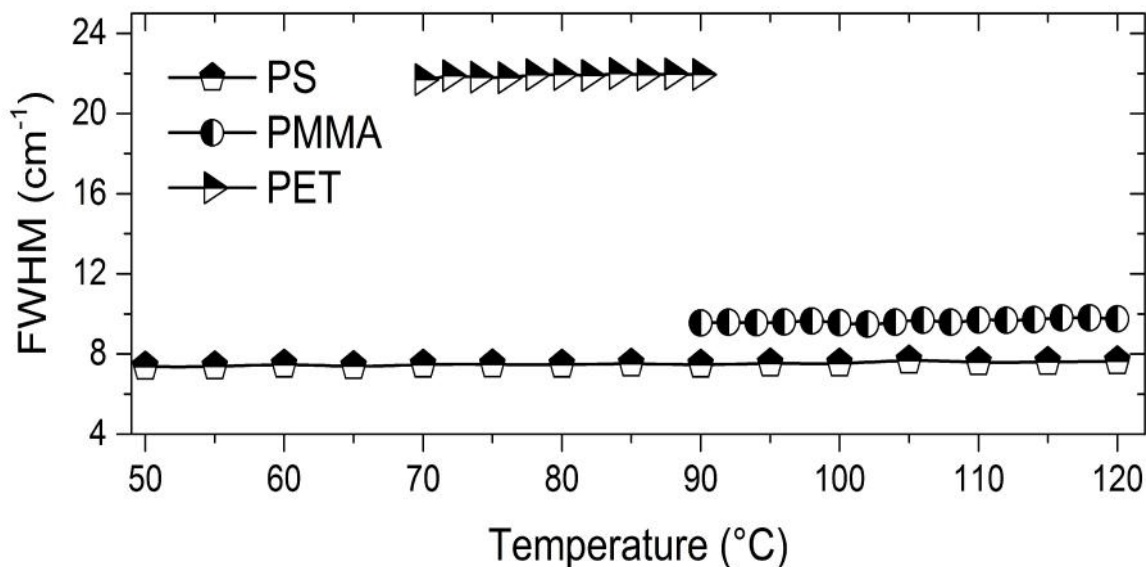


Figure 3. Full width at half-maximum (FWHM) of selected Raman peaks as a function of temperature at around 1727 cm^{-1} for PET, 1001 cm^{-1} for PS and 811 cm^{-1} for PMMA. The FWHM of these peaks is almost invariant.

The largest deviation found between FWHM data was at around 4% for PS, 1% for PMMA and 3% for PET. Therefore, it is also possible to verify the T_g through the maximum height of the Raman peak (HR) as a function of temperature, since in this case the IIRS depends mostly on the

height of these peaks. In **figure 4** the maximum height of the selected Raman peaks from every polymer is shown (the same peaks as in **figure 3**). The T_g was identified via the peak height that exhibits a discontinuity or a change in the rate of intensity decrease.

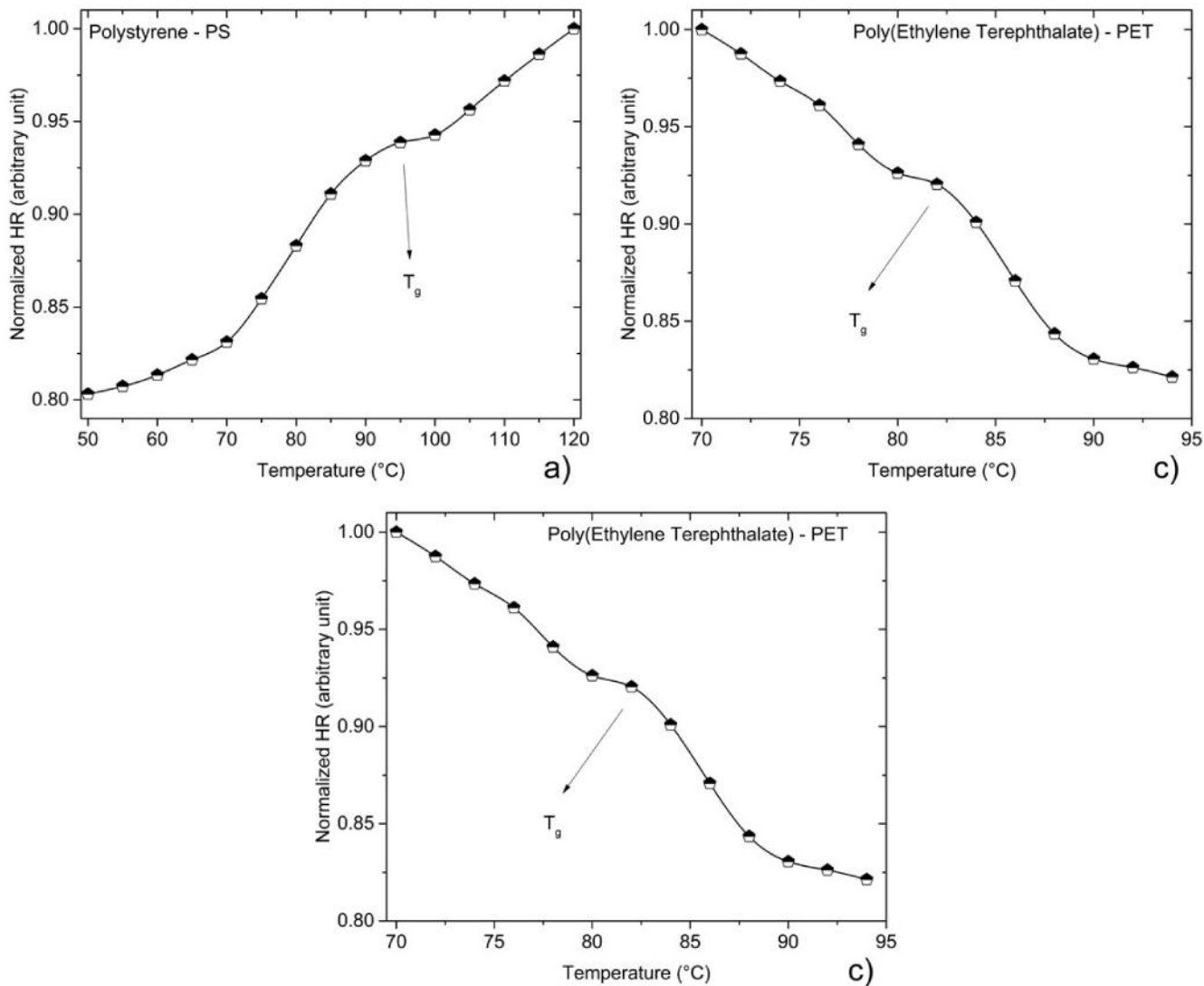


Figure 4. Normalized height of selected Raman peaks (HR) as a function of temperature: **a)** at around 1001 cm⁻¹ for PS, **b)** 811 cm⁻¹ for PMMA and **c)** 1727 cm⁻¹ for PET. This analysis method it also allows to find the glass transition temperature (T_g) of the chosen polymers.

The same values for T_g , as found in **figure 2**, could be located with this analysis method, as it is observable in **figure 4** for

all investigated polymeric substances. In **table 1** the consolidated data of this work is summarized.

Sample	Glass Transition Temperature T_g (°C)	Other Values Found T_g (°C)	Reference
PS	95.0 ± 2.0	95	[13, 14, 15]
PMMA	104.0 ± 2.0	100	[20, 7]
		77	[18]
PET	82.0 ± 2.0	81	[19]

Table 1. Consolidated data of the glass transition temperature (T_g) investigation by Raman spectroscopy

CONCLUSIONS

By using Raman spectroscopy, we determined the glass transition temperature T_g of the polystyrene, poly(methyl methacrylate) and poly(ethylene terephthalate) and compared our results with literature data (found by different techniques), obtaining consistent results. We used both the intensity of the collected Raman spectra integrated over the spectral range 100 – 3500 cm^{-1} , and the height of the peaks Raman at around 1001 cm^{-1} for PS, 811 cm^{-1} for PMMA and 1727 cm^{-1} for PET in order to identify T_g , since the rather constant full width at half-maximum (FWHM) shows that the change in intensity as function of temperature was only due to the variations of the Raman peak height. Each type of polymers showed a different behavior of the IIRS and HR as a function of temperature, this happened due, maybe, to distinct chemical structure of these polymers. Considering the analyzed data, it can be concluded that the intensity of Raman scattering is influenced by the glass transition, allowing to determine the temperature where these transitions happen and, thus, showing that with the Raman scattering measures it is possible to verify the T_g of these polymeric materials.

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