DOI: 10.1002/masy.201300137

A Near-Infrared Spectroscopy Study on Thermal Transitions of PMMA and PMMA/SiO_2 Nanocomposites

Freddy A. Sanchez, Marta Redondo, Dania Olmos, Maja Kuzmanovic,
*Javier González-Benito**

Summary: In this work infrared spectroscopy in the near infrared (NIR) range is used to study the dynamics of polymethylmethacrylate (PMMA) as a pure polymer and when it is modified with silica nanoparticles. Different ways of analyzing FT-NIR spectra were explored taking the temperature as the variable of the systems: i) bands shifts in terms of the first moment of the wavenumber; ii) bands shifts in terms of an absorbance ratio method and iii) absorbance variations in terms of the integrated absorbance. The spectroscopic analysis allowed to study thermal transitions in PMMA and PMMA based nanocomposites. In particular the method based on the use of an absorbance ratio is the most sensible to analyze the thermal transitions. All bands considered could be used to detect thermal transitions reflecting how the vibrations of the groups CH_2; CH_3 and C=O are affected by changes in the free volume of the PMMA. It seems that the PMMA dynamics is more driven by the lateral groups than the backbone of the polymer. The presence of silica nanoparticles, at least when 1% by weight is used, restrains the PMMA motion increasing the relaxation temperatures that can be associated with the glass transitions.

Keywords: FT-NIR; nanocomposites; PMMA; polymer spectroscopy; thermal transitions

Introduction

In polymers science one of the main basic points to understand polymers properties and behavior is to know the dynamics of macromolecular chains. This dynamics is directly related with intra and intermolecular interactions and its deep knowledge can help to understand polymer processing, physical ageing, and mechanical properties among other things. There are several techniques that are conventionally used with the purpose of obtaining that information, differential scanning calorimetry, dynamic mechanical analysis and dielectric relaxation measurements. However, in general the information given is related with cooperative motions associated with the whole material under investigation or the so called thermal relaxation. A really interesting thing would be to understand what is exactly occurring during one of those relaxations, that is to say, to have the possibility of probing those relaxations at a molecular scale. In polymer spectroscopy, it is common to study the shapes and widths of absorption and emission bands because they are related to the distribution of local environments experienced by radiation absorbing or emitting moieties, the band due to a particular absorption or emission reflects the superimposition of different frequencies that are a result of interactions in slightly different local environments.[1–3] Some attempts have been done from the use of fluorescent probes and labels which allows to obtain information about the

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Dpt. Materials Science and Engineering and IQMAAB, Universidad Carlos III de Madrid, Av. Universidad 30, 28911 Leganés, Spain
E-mail: javid@ing.uc3m.es

dynamics of polymers exactly from the sites in where the fluorophores are localized.[4–7] In principle, the fluorescent response or the emission bands of those labels are used to locally extract information since, on average, they reflect physico-chemical properties of their surroundings. However, it would be even more instructive if the information is taken exactly from the polymer chains and, if possible, from different positions.

In the scientific literature, there are several articles concerning the special variations that certain infrared bands of polymers experience as a function of temperature either in the mid or the near ranges.[1,2] In general, it is proposed that this sensibility is a function of both conformational effects and vibrational relaxation effects. Painter et al.[2] argue that intensity and band changes observed for IR bands of PMMA studied in the mid range as a function of temperature are probably related not only to conformational energy differences but also to vibrational relaxation effects. In this case, as in fluorescence, there must be distribution of local environments and conformations in these materials and, as a result, there is not a single transition energy but a band which should change in terms of shape and/or intensity simply changing the local physico-chemical properties.

There are various effects that can lead to changes in infrared band intensities with increasing temperature. These include changes in the Boltzmann factors and density of the sample (hence refractive index), but these factors usually result in only small perturbations that can be neglected. In the spectra of polymers, changes in conformation can also lead to significant intensity changes. In the research of several polymers, mid-infrared (MIR) is a very useful technique. The main advantage is that there are several bands coming from the activation of molecular vibration simple of visualizing. However, the transmission measurement of mid-IR is limited to a thin sample due to high-absorption coefficient. This limitation requires remarkable sample preparation techniques and skills. In this sense near-infrared spectroscopy (NIR) may be a simple alternative because transition moment of overtones and combination bands are quite lower allowing the sample of analysis to be thicker. There are several articles in which FT-NIR is used to study thermal transitions in polymers.[8–11]

On the other hand, variations in hydrogen bonding and other interactions manifest themselves as changes in the force constants of the X-H bonds. Generally, bands will shift in frequency and broaden due to the formation of those interactions. Because combination bands result from the summation of two or more fundamental vibration, and overtones occur as the result of the multiples of fundamental vibrations, frequency shifts related to interactions have a greater relative effect on combination and overtone bands than on their corresponding fundamentals. This feature of the near infrared region alerts one to the importance of the relative hydrogen bonding and other interaction effects brought about by solvents and temperature variations. In general, the influence of hydrogen bonding and attracting interactions results in band shifts to lower frequencies; a decrease in attracting interactions due to dilution for instance and higher temperatures results in band shifts to higher frequencies that usually are from 10–100 cm^{-1}. On the other hand, as a disadvantage, near infrared sometimes gives difficulties in band assignation since they come from combination of normal modes and therefore some relaxations are not easy of being interpreted at a molecular scale.

PMMA/Silica nanocomposites have received much attention because of their potential applications in multiple areas. Apart from obtaining unique properties, the addition of inorganic particles to polymers usually changes their thermal properties[12]. In general, there are mainly two ways of visualizing the problem of changes in thermal properties under the effect of the presence of certain substrates: i) specific interactions polymer-substrate and ii) polymer chain ordering at the interfaces. Particularly in the case of PMMA there are studies pointing out the existence of conformational changes in the polymer backbone on an aluminum surface due to the existence of ionic bonds generated by the hydrolysis of ester groups over the aluminum surface.[13] However, other attribute their similar results to conformational changes due to the restrictions imposed by the surface to the chain motion.[14] Due to this more efforts should be done in order to clarify this issue.

Through this study, it will be demonstrated that NIR have the capability of being used to study the thermal transitions in PMMA. Different ways of analysis will be checked in order to choose the best one in terms of sensibility. The information given will be used to finally understand the physical process under consideration. Finally, silica nanoparticles will be introduced within the PMMA in order to study their influence in the dynamics of the polymer through the same experimental procedure an analysis.

Experimental Part

Materials and Sample Preparation

PMMA ($M_w = 75000$ mol/g) was purchased from Polysiences Inc. Fumed silica nanoparticles (99.8% pure silica, 200 m^2/g surface area, 2.2 g/cm^3 density and 14 nm diameter) and HPLC grade tetrahydrofurane, THF, were supplied by Sigma-Aldrich.

Films of PMMA and nano-silica filled PMMA composites were prepared as follows:

- In a glass vial the PMMA is firstly dissolved in THF.
- A particular amount of silica nanoparticles is added to the PMMA/THF solution.
- The mixture is subjected to a sonication process at room temperature for 1h obtaining a homogeneous suspension.
- The suspension is agitated at room temperature for at least 24 h.
- The mixture is poured over a PP mold to obtain a preformed material by casting.
- The preformed material is finally subjected to hot pressing process to obtain films (90 kN at 180 °C for 30 min).

Figure 1 shows three films with different silica content in which an extraordinary transparency is evidenced.

Techniques

Differential scanning calorimetry, DSC, was carried out in non-isothermal conditions in a Mettler Toledo 822e under

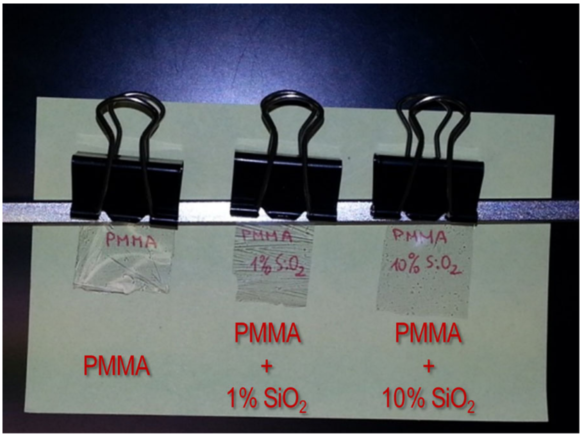

Figure 1.
Films of PMMA filled with different contents of silica nanoparticles: 0%, 1% and 10% by weight.

nitrogen atmosphere. Samples of about 2–4 mg were measured. Samples were first heated from 30 °C to 160 °C at 10 °C/min maintaining the sample at 160 °C for 5 min just to erase the thermal history. After that, the relaxation process associated with the glass transition was studied by cooling and heating scans at 10 °C/min from 160 °C to 40 °C and 40 °C to 160 °C respectively.

Fourier transformed infrared spectra in the near range, FT-NIR, were recorded with an FT-IR Spectrum GX (Perkin-Elmer) using a homemade program to collect spectra as a function of time (resolution of 4 cm^{-1} and five scans). The evolution of the PMMA spectrum was monitored at different temperatures from 40 °C to 150 °C using an oven (SPECAC) controlled with a homemade program which allows to subject the system to specific ramps of temperatures (in this case 1 °C/min). The samples were placed between two microscope–glass slides inside the oven.

Analytical Approximations

In order to analyze possible changes appearing in any absorption band of the spectra different analytical methods were used:

a) Bands shifts in terms of the first moment of the absorption band, $<\nu>$

A simple way of obtaining the average shifts of the bands under analysis is to consider the absorption bands as a distribution of energies at which the absorption is taking place. Analytically this concept can be expressed by equation 1:

$$< \nu >= \frac{\Sigma A(\nu_i) \cdot \nu_i}{\Sigma A(\nu_i)} \qquad (1)$$

Where $<\nu>$ is the average number wavenumber or the first moment of the distribution of wavenumbers for a particular absorption band and $A(\nu_i)$ is the absorbance at particular i-value of the wavenumber.

To obtain the first moment values several steps were followed:

(i) Baseline correction: to built-up the straight line passing through the minima that delimit the band and subtract it from the band of the spectrum. (see Figure 2)
(ii) Application of equation 1 to the corrected band for every temperature.
(iii) Representation of the first moment value as a function of temperature.

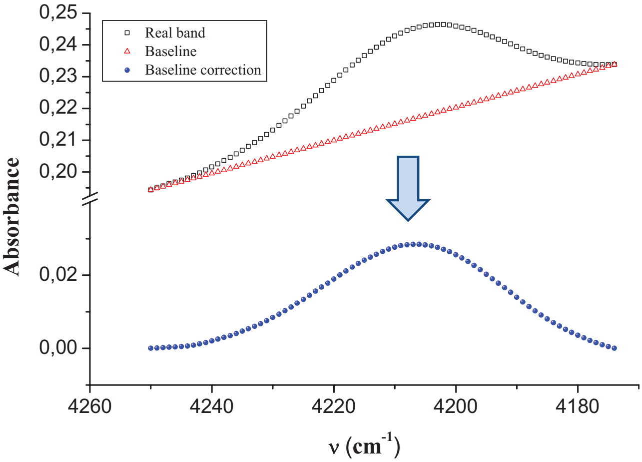

Figure 2.
Example of baseline correction for the FTNIR band centered at 4206 cm^{-1}.of PMMA in the composite with 1% by weight of silica nanoparticles.

b) Bands shifts in terms of an absorbance ratio method based on that proposed by Vatanparast et al.[15,16].

   (i) For a certain band in a whole experiment as a function of temperature the two spectra that show greater variation each other are taken (in this work that coincides with the spectra at the lowest temperature, 40 °C, and the spectrum at the highest temperature, 150 °C, respectively) (Figure 3a).
   (ii) The quotient between both bands is represented (Figure 3b).
   (iii) The values of wavenumber for which the above quotient was minimum and maximum are taken (in Figure 3b, 4190 cm^{-1} and 4233 cm^{-1} respectively).
   (iv) For all the spectra the ratio between the absorbances associated with the wavenumbers of the above highest spectra ratio, A_{HSR}, and the lowest spectra ratio, A_{LSR}, is obtained (Absorbance ratio = A_{HSR}/A_{LSR}) and represented as a function of temperature.

c) Absorbance variations in terms of the integrated absorbance.

   (i) Baseline correction (Figure 2).
   (ii) To obtain the integral associated with the corrected band (equation 2).

$$Int\,A = \Sigma A(\nu_i) \qquad (2)$$

   (iii) Representation of the integrated absorbance as a function of temperature.

Results and Discussion

In Figure 4 the PMMA FT-NIR spectra at different times of one experiment or temperatures are shown for the composite with 1% by weight of silica nanoparticles. A similar result for the neat PMMA was obtained.

The bands observed with their assignations are gathered in Table 1. As can be seen in Figure 4 none band shows large changes as a function of temperature. However, some of them experience small variations that could be analyzed by the use of the analytical methods above described and that can indirectly increase the accuracy. The bands under consideration are those shown as insets in Figure 4: i) bands found from 4800 cm^1 to 4625 cm^{-1} associated with combinations bands for the carbonyl group; ii) bands found from 4625 cm^1 to 4300 cm^{-1} associated with combinations bands for the methyl group and iii) bands

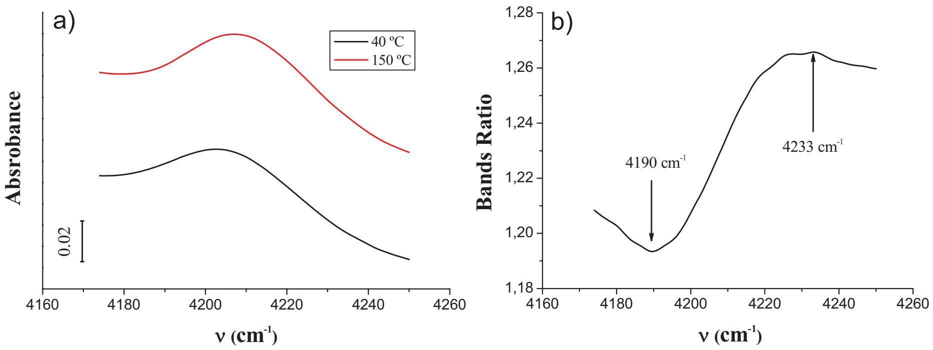

Figure 3.
Example for the calculation of the quotient between a certain band at the lowest temperature and that at the highest temperature for the FTNIR band centered at 4206 cm^{-1} of PMMA in the composite with 1% by weight of silica nanoparticles.

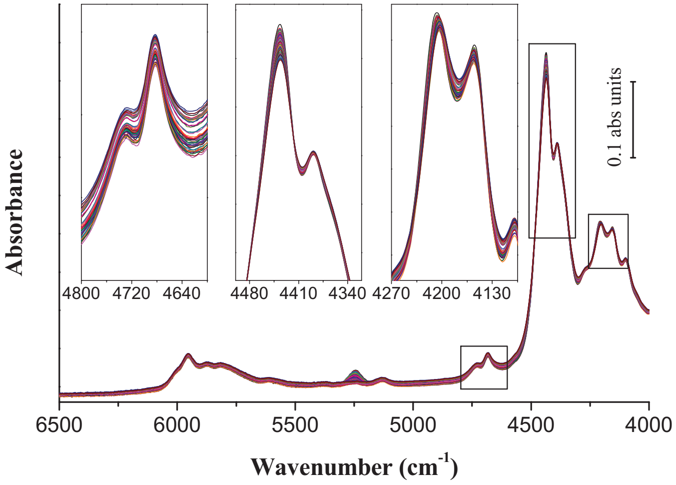

Figure 4.
PMMA FT-NIR spectra at different times or temperatures is shown for the composite with 1% by weight of silica nanoparticles.

found from 4300 cm^1 to 4115 cm^{-1} associated with combinations bands for the C—C bond.

Let us analyze the three bands considered in terms of the three methods described.

Band 1 (4174–4250 cm^{-1})

In Figure 5 the values of the first moment as a function of temperature are represented for the two samples under consideration: neat PMMA (left) and PMMA filled with 1% wt of silica nanoparticles (right).

In both cases it is observed a decrease of $<\nu>$ as the temperature increases meaning that, on average, there is band shift to lower energies with temperature. This effect can be simply associated to thermal activation. In fact, the global shift in both cases is of about 4 cm^{-1} which is within the order of magnitude for a thermal activation of 110 °C. However, at a certain value of

Table 1.
Bands observed in the FT.NIR spectra with their assignations.

Vibration	Frequency (cm^{-1})	Observacions	Band (cm^{-1})
(2ν) CH (overtone)	5960	C-H of CH_3 of C=OCH_3 [17]	5953
	5946	C-H methyl, carbonyl associated as one C removed (C=OCH_2CH_3) [18]	5953
	5951	−CH_3 asymmetric str. of the C_3CH_3 [18]	5953
	5880	C—H methyl, esther associated as (R-O-CH_3) [17]	5876
	5862	—CH_3 asymmetric str. of the C_3CH_3 [18]	5876
	5806	CH_3 asymmetric str.qCH_3 symmetric str. [18]	5815
(3ν) C=O (overtone)	5128	—C=O esthers and acids (C=OOR) [17]	5128
(4ν) C=O-O (overtone)	4762	C=O—O polymeric (C=O and C-O stretching). [17]	4730
C-H/C=O (combination)	4729	C=O str.-CH_3 asymmetric str. [18]	4730
	4673	C-H str. and C=O stretching combination and C-H deformation combination [17]	4683
−CH_3 (combination)	4484	—CH_3 antisymmetric str. plus bending vibration of the C-H bonds of the −CH_3 group.	4435
	4405	—CH_3 symmetric str. plus bending vibration of the C-H bonds of the —CH_3 group.	4391
C-H/C-C (combination)	4202	C—H stretching and C—C stretching combination [17]	4203

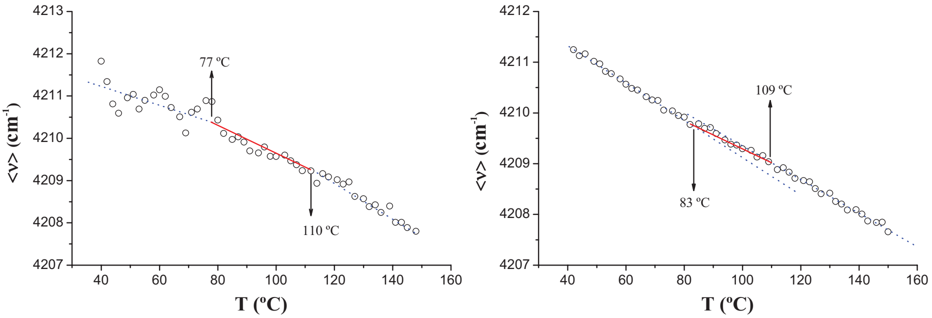

Figure 5.
First moment of the FTNIR band centered at 4206 cm^{-1}: neat PMMA (left) and PMMA/silica composite with 1% by weight of silica nanoparticles (right).

temperature a change in the slope of the plots is observed (Figure 5). In the case of neat PMMA from 77 °C to 110 °C while in the case of the nanocomposite from 83 °C to 109 °C. It is well known that the glass transition temperature of PMMA is around 110 °C so the slope change for the representation of the first moment with temperature seems to point out the glass transition of the PMMA.

In Figure 6 the values of the absorption ratio as a function of temperature are represented for the two samples under consideration: neat PMMA (left) and PMMA filled with 1% wt of silica nanoparticles (right).

In both cases is observed a continuous decrease of the absorbance ratio with temperature indicating a continuous band shift to lower energies as indicated the variation of the first moment with temperature. However, the plot of this parameter shows a sharp change in its slope which clearer points out the PMMA glass transition of the samples under study. This result indicates that this analytical method is more sensible to detect thermal relaxations in PMMA. On the other hand, it is observed that the slope change in the absorbance ratio as a function of temperature occurs at higher temperatures for the sample with 1% by weight of silica nanoparticles (Figure 6) which suggests that someway the nanoparticles inhibit the PMMA macromolecular chain motion.

In Figure 7 the integrated absorbance as a function of temperature is represented for the two samples under consideration: neat PMMA (left) and PMMA filled with 1% wt of silica nanoparticles (right).

A continuous decrease of the integrated absorbance with temperature is observed

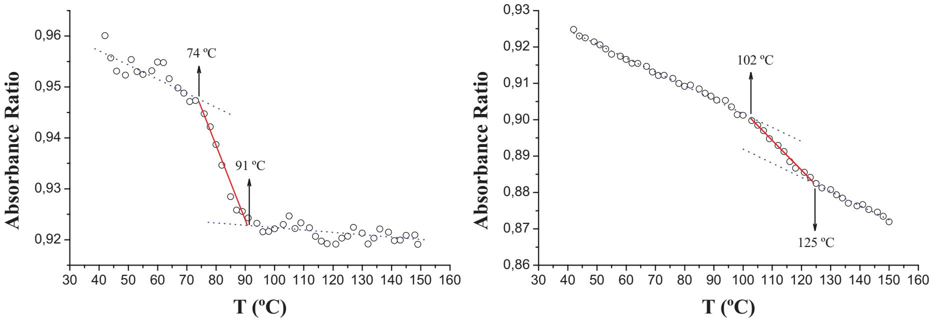

Figure 6.
Absorbance ratio of the FTNIR band centered at 4206 cm^{-1}: neat PMMA (left); PMMA/silica composite with 1% by weight of silica nanoparticles (right).

in both samples that may be attributed to simple density decrease as temperature increases. However, at certain temperature, close to that of the glass transition, there is an increase of the slope which is in accordance with the sharp increase of the specific volume usually observed in a glass transition. Although this slope change is not as sensible as that observed for the absorbance ratio method, again it occurs at higher temperatures for the nanocomposite indicating PMMA chain motion restrain under the presence of silica nanoparticles, at least when 1% wt is present.

Band 2 (4300–4550 cm^{-1})

The same representations were considered for band 2 (Figure 8, Figure 9 and Figure 10).

It is observed similar results than in the case of band 1, therefore, the same discussion can be done attaining the same conclusions. However, in the case of using the absorption ratio parameter it is easier to visualize the slope changes ascribable to the glass transition probably because the changes experienced by these vibrations are more sensible to the macromolecular chains dynamics. However, the profiles of the plots can be clearly described as follows: first moment decrease, firstly with a certain negative slope, then stabilization or lower slope and finally, again, higher slope. From the points at which the slope of the plots changes more than 10% it can be draw the interval of temperatures (lines) in which it is considered the thermal transition to occur.

Band 3 (4710–4619 cm^{-1})

The same representations were considered for band 3 (Figure 11, Figure 12 and Figure 13).

For the two samples under study, as a summary for better comparisons, Table 2

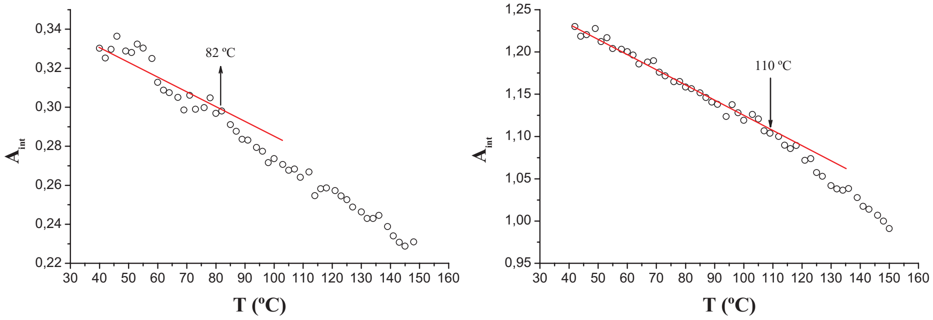

Figure 7.
Integrated absorbance of the FTNIR band centered at 4206 cm^{-1}: neat PMMA (left); PMMA/silica composite with 1% by weight of silica nanoparticles (right).

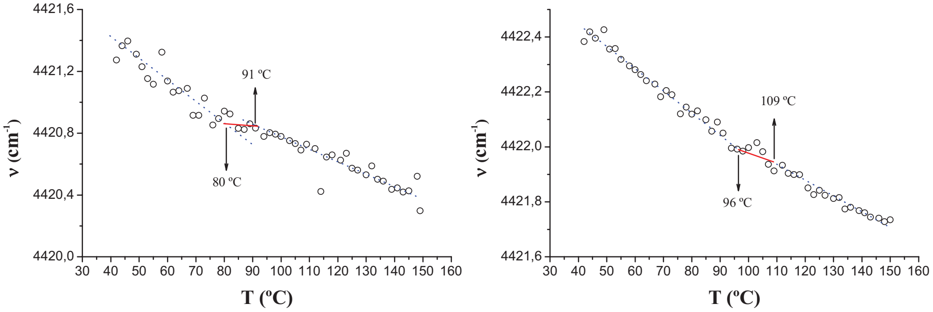

Figure 8.
First moment of the FTNIR band centered at about 4435 cm^{-1}: neat PMMA (left); PMMA/silica composite with 1% by weight of silica nanoparticles (right).

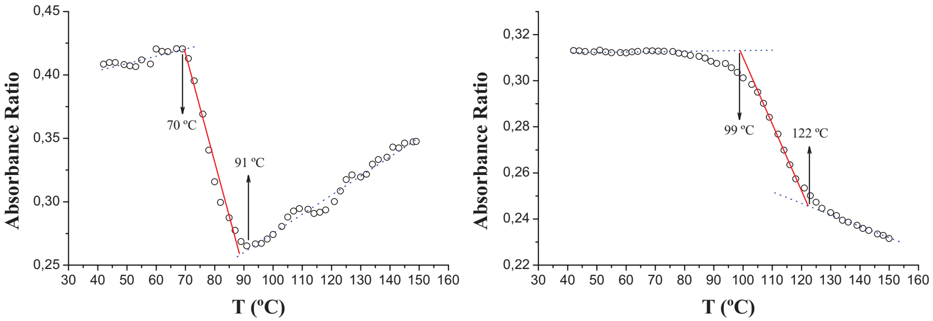

Figure 9.
Absorbance ratio of the FTNIR band centered at about 4435 cm^{-1}: neat PMMA (left); PMMA/silica composite with 1% by weight of silica nanoparticles (right).

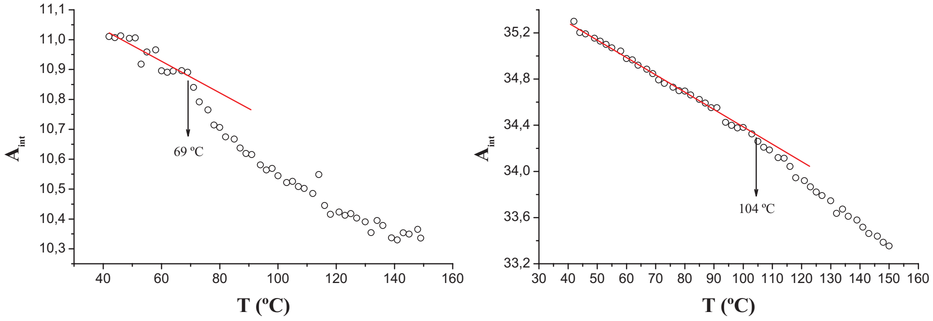

Figure 10.
Integrated absorbance of the FTNIR band centered at about 4435 cm^{-1}: neat PMMA (left); PMMA/silica composite with 1% by weight of silica nanoparticles (right).

gathers all the values of thermal transition obtained after studying every parameter extracted from the bands under analysis.

Similar arguments than in the case of band 2 can be given when analyzing the variation of the spectral parameter chosen associated with band 3. In fact, there is a coincidence in both cases; the bands correspond to combination bands in which the carbonyl stretching is involved while in the

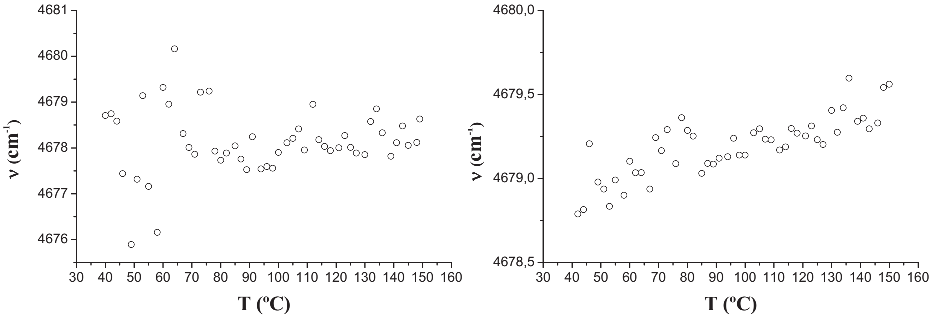

Figure 11.
First moment of the FTNIR band centered at 4680 cm^{-1}: neat PMMA (left); right PMMA/silica composite with 1% by weight of silica nanoparticles (right).

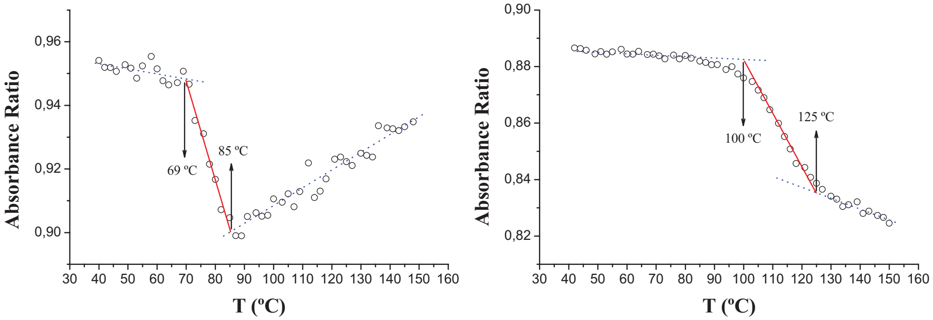

Figure 12.
Absorbance ratio of the FTNIR band centered at 4680 cm^{-1}: neat PMMA (left); PMMA/silica composite with 1% by weight of silica nanoparticles (right).

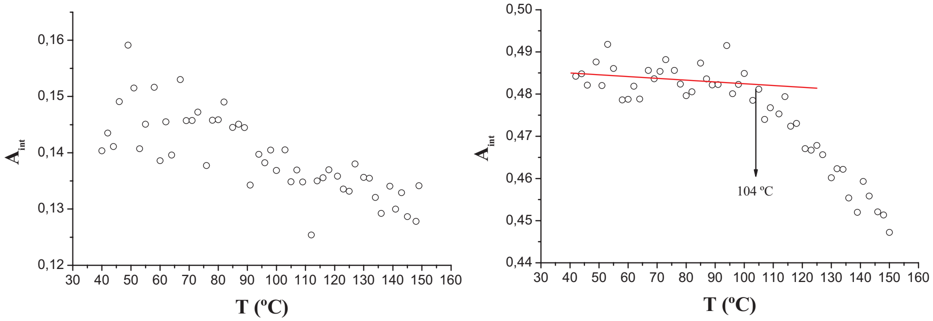

Figure 13.
Integrated absorbance of the FTNIR band centered at 4680 cm^{-1}: neat PMMA (left); PMMA/silica composite with 1% by weight of silica nanoparticles (right).

case of band 1 is not but C-C stretching. This result suggests that the PMMA dynamics is driven more by the lateral groups than the backbone.

It is interesting to highlight that glass transitions obtained are similar to those obtained by FTIR but in the middle range for similar systems formed by PMMA and PMMA filled with silica nanoparticles[1]. However, it is important to mention here that in that case the materials were subjected to high energy ball milling to immerse the particles into the polymer, being the milling process

Table 2.
Thermal transition of the two samples under consideration on heating.

	Band (cm^{-1})	4174–4250	4300–4550	4720–4619
$T_{<\nu>}$ (°C)	PMMA	77–90	74–90	82
	PMMA/1% SiO_2	83–109	102–125	110
$T_{Band\ Ratio}$ (°C)	PMMA	80–91	70–91	69
	PMMA/1% SiO_2	96–109	99–122	104
T_{Aint} (°C)	PMMA		69–85	
	PMMA/1% SiO_2		100–125	104
T_{DSC} (°C) Cooling	PMMA	97.7		
	PMMA/1% SiO_2	101.9		
T_{DSC} (°C) Heating	PMMA	103.3		
	PMMA/1% SiO_2	105.1		

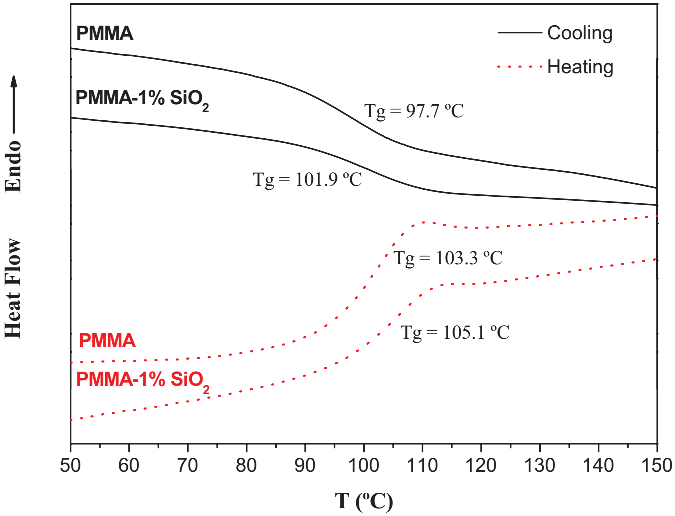

Figure 14.
DSC traces from the cooling and heating scans for PMMA and PMMA-SiO_2 nanocomposite (1% wt of silica nanoparticles).

the main factor affecting the polymer thermal relaxations.

Finally, DSC experiments were done to support the FTIR results and reasoning given above. In Figure 14 the DSC traces from the cooling and heating scans are shown for PMMA and PMMA-SiO_2 nanocomposite (1% wt of silica nanoparticles). Clear heat capacity change is observed for both temperature ramps (cooling and heating) that are assigned to the PMMA glass transition. The value of the glass transition temperature was extracted from the corresponding inflexion points on the curves (T_{DSC} in Table 2). As can be observed, there is a good correspondence between DSC and FTIR results, being the Tg's obtained from DSC higher for the sample with 1% of silica nanoparticles than for the neat PMMA.

Conclusion

Fourier transformed in the near infrared range spectroscopy, FT-NIR, has been demonstrated to be capable of being used to study thermal transitions in PMMA and PMMA based nanocomposites. It has been shown that a method based on the use of an absorbance ratio is the most sensible to analyze thermal transitions from the FTIR spectra in the near range. All bands considered can be used to detect thermal transitions reflecting how the vibrations of the groups CH_2; CH_3 and C=O are affected by changes in the free volume of the PMMA. It seems that the PMMA dynamics is driven more by the lateral groups than the backbone. The presence of silica nanoparticles, at least when 1% by weight is used, restrains the PMMA motion increasing the thermal transition that can be associated with the glass transition.

Acknowledgments: Authors gratefully acknowledge financial support of the Ministerio de Ciencia e Innovación (MAT2010-16815).

[1] J. González-Benito, G. González-Gaitano, *Macromolecules* **2008**, *41*, 4777.
[2] P. Painter, H. Huang, *Macromolecules* **2008**, *41*, 2494.
[3] R. L. Moron, D. Olmos, J. González-Benito, *J. Compos. Sci. Technol.* **2006**, *66*, 2758.
[4] R. Albalá, D. Olmos, A. J. Aznar, J. Baselga, J. González-Benito, *J. Colloid Inter. Sci.* **2004**, *277*, 71.

[5] S. G. Turrión, D. Olmos, N. Ekizoglou, J. González-Benito, *Polymer* **2005**, *46*, 4023.

[6] I. Barroso, J. González-Benito, *Polymer Composites* **2011**, *32*, 1874.

[7] D. Olmos, A. García-López, J. González-Benito, *Materials Letters* **2013**, *97*, 8.

[8] M. Mizushima, T. Kawamura, K. Takahashi, K. Nitta, *Polymer J.* **2012**, *44*, 162.

[9] S. Watanabe, I. Noda, Y. Ozaki, *Polymer* **2008**, *49*, 774.

[10] S. Watanabe, J. Dybal, K. Tashiro, Y. Ozaki, *Polymer* **2006**, *47*, 2010.

[11] Y. Ozaki, Y. Liu, I. Noda, *Macromolecules* **1997**, *30*, 2391.

[12] R. Pantaleón, J. González-Benito, *Polym. Compos.* **2010**, *31*, 1585.

[13] K. Konstadinis, B. Thakkar, A. Chakraborty, L. W. Potts, R. Tannenbaum, M. Tirrell, J. F. Evans, *Langmuir* **1992**, *8*, 1307.

[14] Y. Grohens, M. Brogly, C. Labbe, J. Schultz, *Polymer* **1997**, *38*, 5913.

[15] R. Vatanparast, S. Li, K. Hakala, H. Lemmetyinen, *Macromolecules* **2000**, *33*, 438.

[16] J. González-Benito, F. Mikes, J. Baselga, H. Lemmetyinen, *J. App. Polym. Sci.* **2002**, *86*, 2992.

[17] J. Workman, L. Weyer, "*Practical Guide to Interpretive Near-Infrared Spectroscopy*", CRC Press, Taylor and Francis Group, Boca Raton **2008**.

[18] Y. Ren, A. Matsushita, K. Matsukawa, H. Inoue, Y. Minami, I. Noda, Y. Ozaki, *Vibrational Spectroscopy* **2000**, *23*, 207.