Dynamic Mechanical Behavior of Atactic and High-Impact Polystyrene

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ABSTRACT: Results of the dynamic mechanical behavior of atactic polystyrene (PS) and high-impact polystyrene (HIPS) for temperatures between 300 and 425 K at a frequency of the order of 50 kHz are presented. The storage Young's modulus, (E'), of the HIPS is lower than the PS value, being the relationship between them a function of the rubber phase volume fraction, independent of the measurement frequency. The glass transition temperature (T_g) of HIPS is shifted to lower temperature in respect to the PS. The γ relaxation appears at 308 K in PS at 50 kHz, while it seems to move toward lower temperatures in the HIPS. Both shifts are attributed to the presence of mineral oils in the HIPS. The values of E', T_g, and the temperature of the γ relaxation at 50 kHz are discussed within the scope of the theory of viscoelasticity. Finally, the effect of thermal treatments, using different annealing times, on the behavior of both materials is shown. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 865–873, 2000

Key words: dynamic mechanical behavior; polystyrene; high-impact polystyrene; glass transition; secondary relaxation

INTRODUCTION

Polystyrene is modified with polybutadiene in order to improve the impact resistance. The resulting polymer, termed high-impact polystyrene (HIPS), may be regarded as a two-phase blend of materials of widely different viscoelastic properties.

Recent works in HIPS are dedicated to the study of the modification of the impact strength, tensile strength, and relative elongation by using different types of elastomers, different elastomer particle size, etc.[1–5] However, the dynamic mechanical relaxation processes are intimately associated with the stiffness and impact toughness, among other physical properties.[6] There are a few measurements of dynamic mechanical properties and these were performed at frequencies in the order of 1 Hz[7–9] and no information was reported in the literature at frequencies near 50 kHz.

On the other hand, the dynamic mechanical properties of atactic polystyrene (PS) at frequencies below 10^3 Hz were studied by several authors.[10–18] However, there are few works dedicated to investigate the mechanical behavior of PS in the region of 10^4 Hz and none of them present data at temperatures near the glass transition temperature.[19–22] For example, Baccaredda et al.[20] measured the internal friction, *IF*, of PS in the temperature range from 60 to 300 K at 10 kHz. Yano and Wada[21] also studied PS for temperatures between 4 and 220 K, but at 34 kHz. It should also be mentioned that Yamamoto and Wada[22] reported the *IF* and the storage Young's modulus data of PS at frequencies of

Table I   Glass Transition Temperatures Obtained by DSC at 10 K/min and Tensile Young's Modulus at 300 K in PS and HIPS

Material	ρ (g/cm^3)	M_n (g/mol)	Polydispersity	E (GPa)	$T_{g(\text{DSC})}$ (K)
PS	1.04	1.221×10^5	2.15	3.174	376.7
HIPS	1.06	1.045×10^5	2.34	1.898	368.5

around 50 kHz and for temperatures between 273 and 345 K. Finally, it is interesting to note that there is scarce information about the presence of structural relaxation in both polystyrenes, and the little there is was obtained in PS by dilatometric[23,24] or thermal[25] tests.

In this work, results are presented concerning internal friction and the storage Young's modulus, E', of PS and HIPS (polystyrene with 8% of polybutadiene) at 50 kHz from room temperature to about 420 K. The results obtained for the dynamic modulus, glass transition temperatures, and secondary and intrinsic relaxation in both materials are compared, within the scope of the viscoelastic theory, with the available experimental data obtained from other tests (tensile and differential scanning calorimetry). Finally, the effect of the rubber phase volume fraction ϕ in the dynamic properties of HIPS was analyzed, taking into account the PS data measured at 50 kHz of the PS.

EXPERIMENTAL

Samples were cut from 2-mm-thick sheets of commercial PS and HIPS supplied by Monsanto Argentina S.A.I.C. (Buenos Aires). The supplier states an 8% polybutadiene (PB) content in the HIPS composition. The density, ρ, and the static Young's modulus, E, of these materials, as indicated by the supplier, are shown in Table I.

The molecular weight distribution of the specimens was determined by gel permeation chromatography (GPC) using a Shimadzu L-6A liquid chromatograph system. The glass transition temperature, T_g, was measured using a differential scanning calorimetry (DSC) Mettler TA3000 system at 10 K/min. The values obtained for the number-average molecular weight M_n, polydispersity, and $T_{g(\text{DSC})}$ for both polystyrenes are shown in Table I.

NMR measurement on the PS and HIPS was done. The ^{1}H spectra of the samples was recorded on a Bruker AC-200 spectrometer at 200 MHz

using approximately a 20 mg/mL solution in Cl_3CD at 300 K.

Because physical aging has been found to affect the dynamical mechanical properties of polymers, thermal treatments were performed on the samples before testing. All heat treatments were carried out with the specimens located inside a metallic can partially submerged in a oil bath at 393 K. Annealing times of 30, 60, and 120 min were used. After being annealed, all specimens were slowly cooled inside the bath by shutting off the power in the oil heater.

The dynamic mechanical measurements were performed using a three-component composite oscillator, which has been described in previous works.[26,27] It involves a specimen vibrating longitudinally through a technique based on the Marx[28] oscillator. Essentially, it consists of four basic components (a drive piezoelectric crystal, a gauge piezoelectric crystal, a dummy rod, and the specimen), each of which is cut to resonate in longitudinal vibrations at 50 kHz. The dummy rod is inserted between the specimen and the driver crystal so that the temperature of the specimen may be changed while the crystals are maintained at room temperature. The technique allows one to determine the damping and storage Young's modulus as a function of temperature from the measurement of drive and gauge voltage and the resonant frequency of the system.[26–29] This measuring device is completely instrumented both in its control and data acquisition systems, and it is commanded by a PC-AT.

The dynamic mechanical measurements were performed between 293 and 400 K and employed a heating rate of 10 K/h. It is interesting to note that the dynamic mechanical measurements of Yamamoto et al.[22] and Yano et al.[21] were performed using a two-component composite oscillator, which is similar to that employed here.

RESULTS

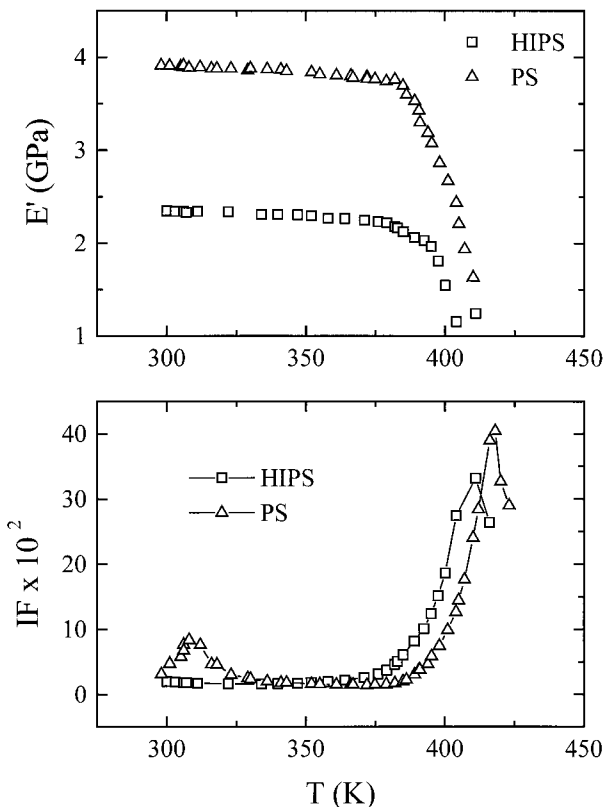Dynamic mechanical results for PS and HIPS are plotted as the storage Young's modulus (E') and

Figure 1 Storage Young's modulus and internal friction of PS and HIPS as a function of temperature.

internal friction (*IF*) versus temperature in Figure 1. Below 375 K, the E' values in HIPS are substantially lower than those in PS but the slight decrease with increasing temperature, which is caused by thermal expansion,[30,31] is approximately the same. The strong drop in storage modulus observed above 375 K is related to the α relaxation, as it can be easily noticed from the *IF* peaks.

It is a well-known fact that HIPS gives two glassy loss peaks, one for PS and other for PB since the PS is not miscible with PB.[18] The results of Figure 1 show that the relaxation peak associated to the T_g of the PB is not observed for the temperature range of measurement and that all the relaxation that appears in the *IF* curve of HIPS corresponds to the relaxation of the polystyrene phase present in this material. However, the values of the glass transition temperature, T_g, obtained from the *IF* curves as the location of the α peak, for the HIPS and PS samples were T_g = 409 K and T_g = 417 K, respectively. This shift of the relaxation peak in the HIPS was also re-

ported by Kraus et al.[9] and by Turley[7] in styrene–butadiene rubber (SBR)-modified PS.

A second relaxation process is observed about 308 K in PS, but it disappears or is displaced to lower temperatures in HIPS. In an early work, Yamamoto and Wada[22] reported the same peak at about 306 K at 50 kHz and at 310 K at 100 kHz in commercial PS. The authors noted that this peak is not an experimental error. Finally, it should be also mentioned that the values of the *IF* background in both polystyrenes were of the order of those reported by other authors.[7,16,22]

Figure 2(a,b) shows the ^{1}H spectra of PS and HIPS, respectively. In both spectra, it can be observed that two anomalous peaks appear around 0.85 and 1.25 ppm, which can be associated with the presence of mineral oil. Figure 2(c) shows the ^{1}H spectrum of the mineral oil used by Monsanto Argentina S.A.I.C. during the manufacture of both polystyrenes. It clearly shows that only two peaks are detected: one around 0.85 ppm and other around 1.25 ppm.

Figure 3 shows the effect of the thermal treatments on the *IF* curves of the samples studied here. A small peak appears in the *IF* curves of the samples without thermal treatment around 380 K; its amplitude decreases for an annealing time of t_a = 30 min and the peak disappears for $t_a > 60$ min. This structural relaxation is more discernible in the HIPS samples than in the PS samples. Although the intensity of the structural relaxation is small, the magnitude of the difference in the *IF* values between curves with different thermal history is greater than is the experimental error, which is of the order of 1%.

DISCUSSION

Storage Young's Modulus

As shown in Table I, the static Young's modulus in HIPS is lower than in PS. This result is in agreement with the known fact that the tensile modulus of the composite PS/PB decreases with an increasing rubber phase volume fraction ϕ (fraction of rubber + occluded polystyrene). Taking into account the experimental relationship between both magnitudes given by Braun et al.[3] or Maestrini et al.,[2] the HIPS modulus from Table I corresponds to $\phi \approx 0.2$.

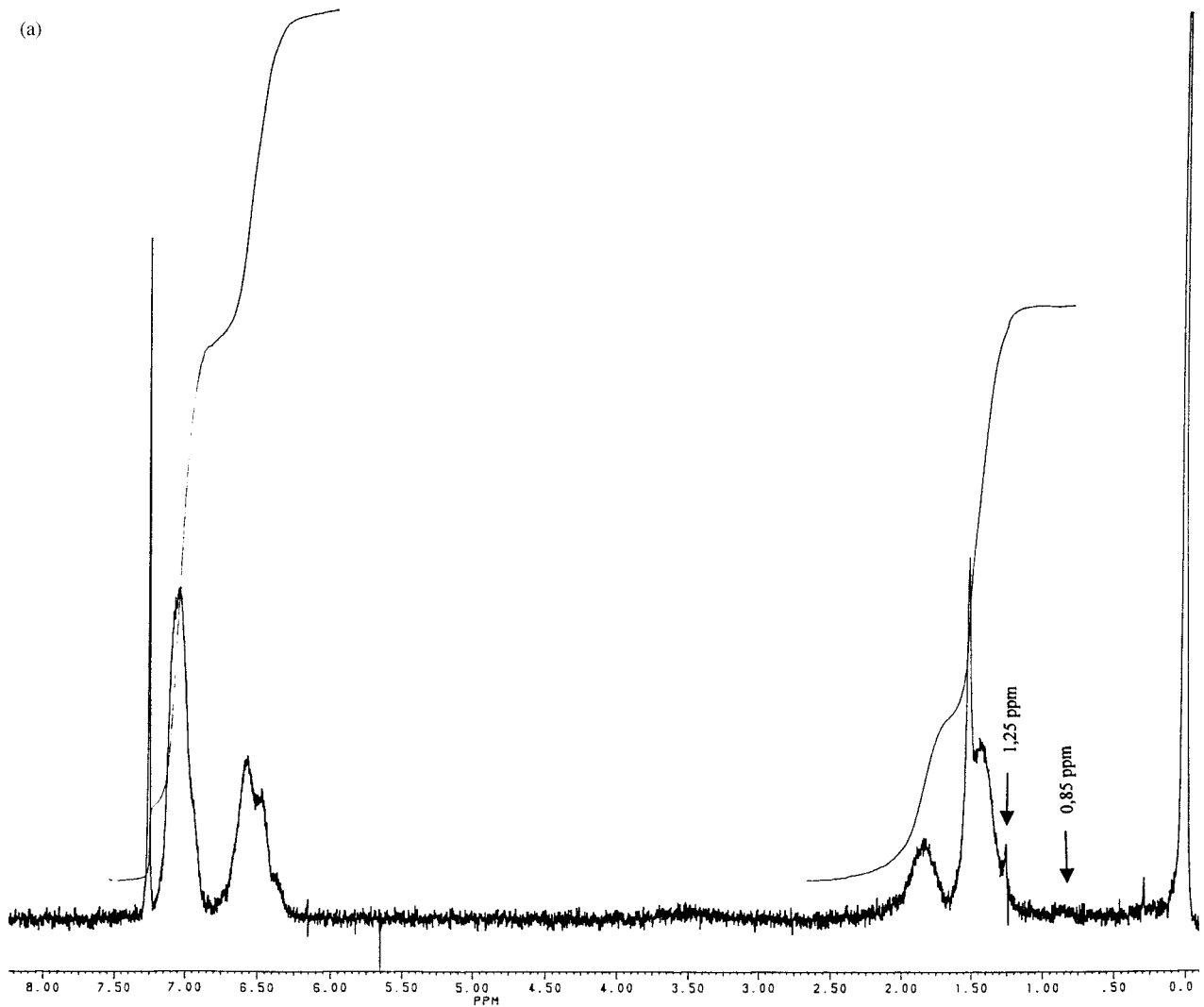Wagner and Robeson[8] showed, for the type of HIPS studied here, that the Young's modulus de-

(a)

Figure 2 ^{1}H spectra of both polystyrenes and the mineral oil at 300 K: (a) PS; (b) HIPS; (c) mineral oil.

creases with ϕ according to the following equation:

$$E_{\mathrm{HIPS}} = E_{\mathrm{PS}}\left[1 - 15\left(\frac{1 - \nu}{7 - 5\nu}\right)\phi \right] \qquad (1)$$

where E_{HIPS} and E_{PS} are the Young's modulus for the HIPS and PS, respectively, and ν is the Poisson ratio ($\nu = 0.35$ for PS). It is interesting to note that, by replacing the values of the tensile modulus for the HIPS and PS of Table I in eq. (1), a value of $\phi = 0.21$ is again found.

When eq. (1) is applied to the values of the storage Young's modulus at room temperature given in Figure 1, a value of $\phi = 0.22$ is obtained.

All these facts lead to the idea that eq. (1) holds independently of the test frequency.

On the other hand, the values at room temperature of the storage Young's modulus, given in Figure 1, are higher than those obtained by the tensile tests. This result is in accordance with the modulus dependence with the test frequency, f, proposed in the viscoelasticity theory.[32,33] Lagacos et al.[34] showed for hard plastics that, in regions away from transitions, this dependence has the following simple form:

$$E' = A \log(f) + B \qquad (2)$$

where A and B are constants. In the case of PS, $A = 0.061$ GPa and $B = 3.57$ GPa; then, eq. (2) leads
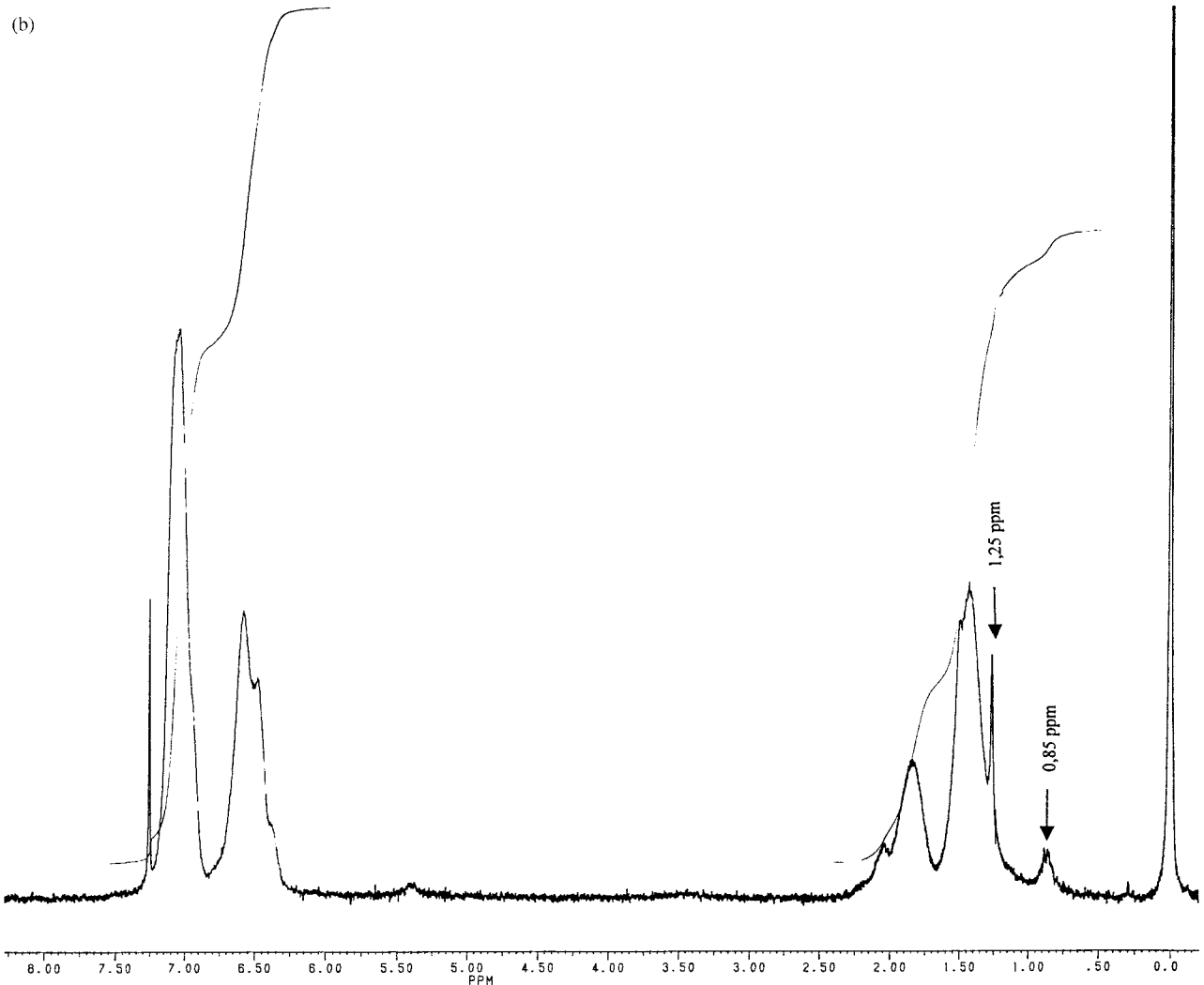
Figure 2   (*Continued from previous page*)

to $E' = 3.85$ GPa, which is in good agreement with the experimental value as can be seen from Figure 1.

The foregoing discussion allows one to say that the A and B constants in eq. (2) can be estimated by HIPS using the values for PS and applying to them a similar relationship to that in eq. (1) for the modulus.

Internal Friction

Glass Transition Temperature

The values of the glass transition temperature, obtained from the *IF* curves, are greater than those obtained, in the same materials, by DSC (Table I). However, it should be remembered that both tests were performed at different heating rates and frequencies. The correction of the T_g values by the heating rate can be made by using the relationship proposed by Schwartz[35]:

$$T_{gc} = T_{gc_0} + a \, \log\left(\frac{c}{c_0}\right) \qquad (3)$$

where T_{gc_0} and T_{gc} are the glass transition temperatures measured at the heating rates c_0 and c, respectively, and a is a constant of around 3.2 for most vinyl polymers.[35] Because the heating rate of the DSC measurements is greater than that of the *IF* measurements, the correction given by eq. (3) increases the difference between the T_g values obtained by both methods. This fact means that the difference between the T_g values at the same
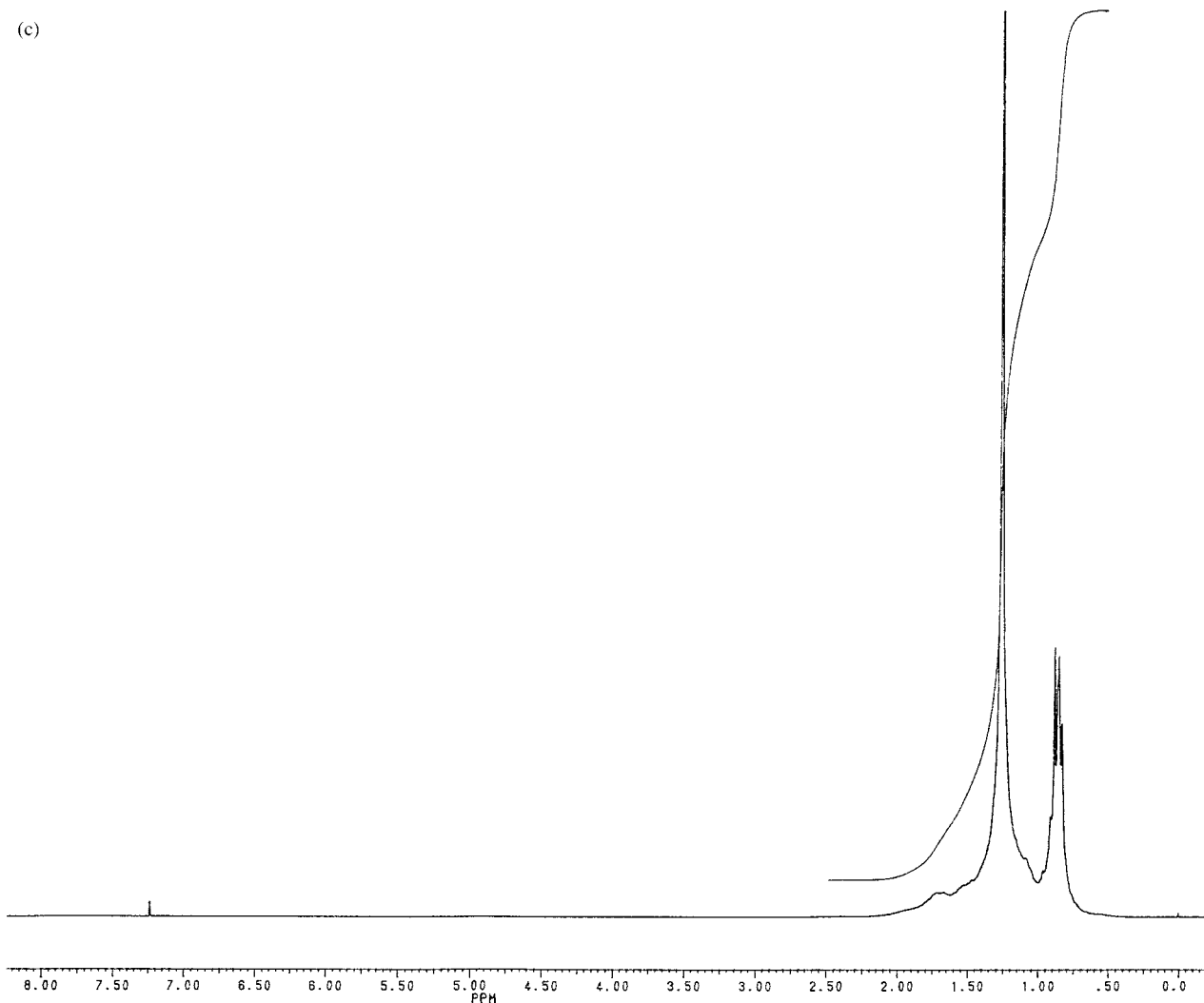
(c)

Figure 2   (*Continued from the previous page*)

heating rate must be corrected by the frequency effect.

In agreement with the viscoelasticity theory, the frequency effect can be taken into account with the Williams–Landel–Ferry (WLF) equation[32,33]:

$$T_{g\text{cal}(50\text{ kHz, }10\text{K/min})} = T_{g(\text{DSC})}$$
$$- \frac{C_2 \log(f_{(\text{DSC})}/50\text{ kHz})}{C_1 + \log(f_{(\text{DSC})}/50\text{ kHz})} \quad (4)$$

where the left member is the T_g value measured at 50 kHz and corrected by eq. (3) to the heating rate of DSC, $f_{(\text{DSC})}$ is a equivalent frequency for the DSC measurement, and $C_1 = 17.4$ and C_2

$= 51.6$ K are the values of the universal constants of the WLF equation.[34]

When eqs. (3) and (4) are applied to the results in PS and HIPS materials, the T_g values obtained from DSC and *IF* measurements become similar when $f_{(\text{DSC})} = 2.6 \times 10^{-4}$. Such an equivalent frequency was found by Hagen et al.[36] in elastomeric material, by extrapolating dynamic data with the WLF equation.

Return to the discussion about the shift of T_g values of HIPS in respect to that of PS. This fact can be attributed to the presence of a plasticizer, mineral oil, antioxidants, or other low molecular weight additives.[6,37] According to Chartoff,[6] the glass transition and the relaxation behavior associated with it in amorphous polymers are very

sensitive to the addition of a small amount of plasticizer. Since the plasticizer molecules are more mobile, they act to effectively increase the available free volume and the rate of segmental motion.[6] On comparing the ^{1}H spectra of both materials [Fig. 2(a,b)], it is clear that the content of mineral oil is very low in the case of PS while it is very important in the case of HIPS.

Secondary Relaxation

The loss peak observed at 308 K in PS was not affected by its thermal history, this result suggesting that it is a true relaxation. According to Heijboer,[38] the dependence of a secondary maximum temperature, T_m, with the measurement frequency follows an Arrhenius equation. With the literature data of T_m and the activation energy for secondary transitions in PS, it is easy to see that the relaxation at 308 K in Figure 1 could only be the γ relaxation.

Figure 4 shows a plot of the frequencies against

Figure 4 Relaxation map of PS. Nos. refer to references. ($\triangledown$) Datum from the present work; ($\square$) Yamamoto and Wada data.
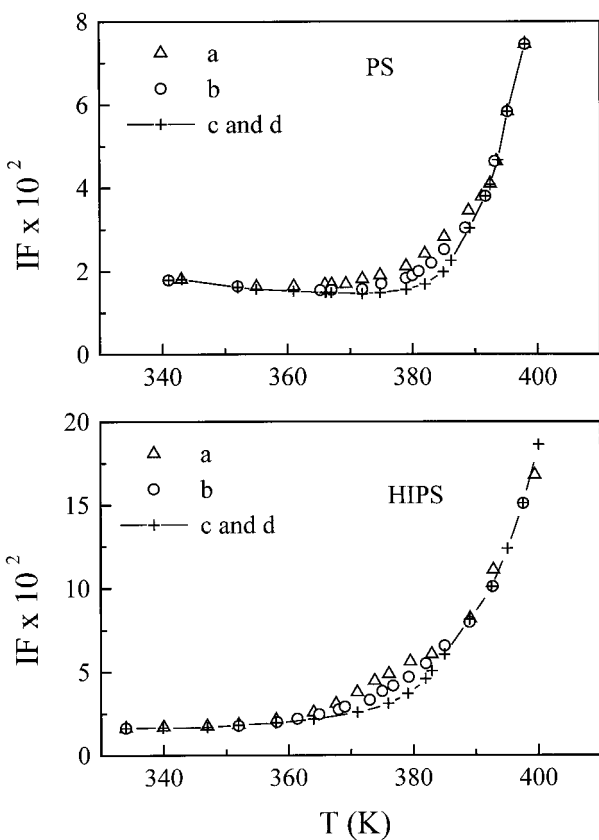

Figure 3 Temperature dependence of the internal friction measured of both polystyrenes after different annealing times: (a) raw samples; (b) t_a = 30 min; (c) t_a = 60 min; (d) t_a = 120 min.
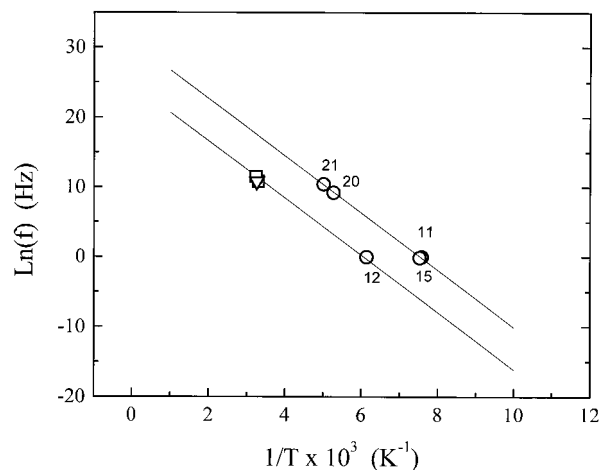
the temperatures of the γ relaxation peak using literature data for PS. With the exception of the point measured by Turley and Keskkula[12] and those measured at 50 and 100 kHz, the data can be fitted by a straight line whose slope leads to a value of the activation energy E_a = 8.14 kcal/mol. This value is within the range usually reported for the γ relaxation in PS. The points not used in this fitting lay on a straight line parallel to the one previously obtained. This is probably due to the method used to obtain these materials and in its plasticizer content or residual solvent. According to Boyer and Turley,[18] the type and number of end groups could cause modifications in the γ relaxation, and following Chartoff,[6] the plasticizer content reduces the temperature and strength of the γ relaxation.

In the case of HIPS, the peak associated with the γ relaxation was not observed but it should be remembered that a slight increment in the tail of the *IF* curve at low temperatures was measured (Fig. 1). Although there is no information in the literature, neither there are reasons that the γ relaxation is suppressed in the HIPS. Taking into account the high content of mineral oils present in the HIPS (Fig. 2), one may expect that the temperature of the γ relaxation in HIPS becomes lower than in PS.

The results of Figure 3 show that there is a structural secondary relaxation around 380 K in both studied materials, that is, a relaxation that disappears after adequate thermal treatment. In the case of PS, this result was observed before by dilatometric, mechanical, and thermal analy-

ses.[23–25,39] For example, Moraglio and Danusso[23] found a peculiarity in the expansion coefficient between 320 and 328 K, while Bianchi and Rossi[24] indicated, around 323 K, an anomaly in the internal pressure. According to Petrie,[39] the mechanical loss curve measured at low frequency shows a subsidiary transition in the neighborhood of 333 K and it disappears completely by annealing the sample for approximately 70 h at 365 K. Brunacci et al.[25] performed calorimetry experiments with different thermal treatments. Their results show a small change in the slope of the heat-capacity curves around 365 K, both for the raw sample and the one put at an aging temperature of 348 K for 1000 min. This slope change disappears with increase of the aging temperature.

At first sight, the subsidiary transition observed at 380 K and 50 kHz would be assigned to the same molecular origin of the results listed above if it is sensitive to the test frequency. Finally, it must be mentioned that there is no information in the literature about structural relaxations in HIPS. However, one should bear in mind that this relaxation type is normally associated with local relaxations in the backbone of the molecule and that this backbone is the same in both polystyrenes.

CONCLUSIONS

It has been shown that the storage Young's modulus of HIPS is lower than that of PS, being the relationship between them a function of the rubber phase volume fraction, independent of the test frequency. The modulus dependence with the test frequency in each material can be represented by the Lagacos equation. Besides, a method was given to obtain the constants of the Lagacos equation[34] by HIPS using the values for PS and applying to them a similar relationship to that given for the modulus at a fixed frequency.

The measurement of the internal friction at 50 kHz has allowed us to observe the behavior of the glass transition and of the γ relaxation in both materials. The glass transition temperature of HIPS is shifted to lower temperature in respect to its value for PS. The γ relaxation at 308 K and 50 kHz in PS seems to move toward lower temperatures in HIPS. Both shifts were ascribed to the presence of mineral oils in HIPS. In agreement with the viscoelasticity theory, the frequency effects were taken into account with the WLF equation[32,33] for the glass transition temperature and with an Arrhenius equation for the dependence of the γ relaxation temperature.[38]

Finally, study of the effect of thermal treatments at 393 K on the mechanical properties has shown that these do not affect the γ relaxation. Besides, these treatments also have shown that the shoulders observed in the IF experimental curves at 380 K should be associated with structural relaxations because they disappeared after enough annealing time.

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