Viscoelastic Characteristics of Pentane-Swollen Polystyrene Beads

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ABSTRACT: Expansion of pentane-swollen polystyrene beads was followed at and above the glass transition by using a very simple optical technique. Measurements allowed a suitable determination of the glass transition temperature and of the viscoelastic characteristics of the pentane-plasticized polystyrene chains inside the beads, at different pentane contents. This was achieved by combining the well-known Williams, Landel, and Ferry approach and some calculations derived from a recent micromechanical modeling of the expanded polystyrene microstructure. The results, analyzed in terms of free volume characteristics, revealed the peculiar plasticizing character of pentane, as compared to the usual polymer diluents. A value of 42°C was found as the lowest temperature for which the dimensional variation of the beads could result from glass transition motions. The relevance of these conclusions was discussed, not just in terms of the changes in dimensions of the individual beads at zero expansion time but also in terms of the dimensional evolution observed in the expanded polystyrene structures. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2463–2472, 1999

Key words: expanded polystyrene; swollen beads; pentane; plasticization; expansion; viscoelasticity

INTRODUCTION

For many years, solid polymeric foams have been the subject of extensive studies, dealing with both fundamental and technological aspects of synthesis, properties and applications (see, for example, ref. 1). One among the pending issues concerns the changes in dimensions that the foams can undergo after manufacturing.

The later point is especially crucial when dealing with expanded polystyrene (EPS), made from beads of pentane-swollen polystyrene.^{2–5} In that case, after temperature has been raised above both the pentane boiling point and pentane-swol-

len polystyrene glass transition temperature, the beads expand and acquire a cellular microstructure, as shown in Figure 1. Following this preexpansion, EPS slabs are produced by further expansion of a great number of preexpanded beads in a mold at temperatures between 100 and 115°C. After demolding, a temperature gradient exists across the cross-section of the slab until it uniformly reaches room temperature. At the end of the processing cycle, EPS is reported to still contain 2-3 wt % of blowing agent. The concentration of pentane in the EPS decreases with time as the blowing agent diffuses and is replaced by air. From this moment, EPS slabs dimensions are reported to increase slightly for a short period before decreasing (shrinkage). This phenomenon goes on even after the temperature has reached constant room temperature. Until six weeks after

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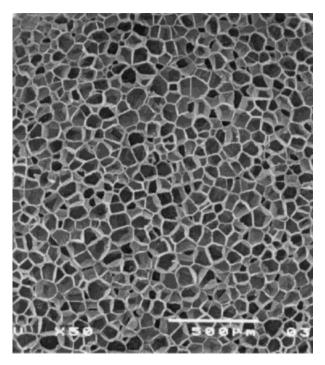


Figure 1 Cellular microstructure of a section of an isolated expanded polystyrene bead (scanning electron micrograph): the cell membranes appear in white or grey.

complete cooling, it can be high enough to prevent EPS panels from being stuck onto plaster panels for building applications, 6,7 such that foamed polystyrene needs to be cured for reaching stabilization.

In order to reduce this costly and long-lasting cure time, it is necessary to know more on the influence of processing parameters on the dimensional evolution of EPS. To this end, it can be anticipated that two factors play a prominent role in the process: (1) the intracellular pressure, governed by the exchange between residual pentane and air across the cell walls; and (2) the mechanical resistance of the walls, associated with the modulus and glass transition temperature of the pentane-plasticized polystyrene.

In this paper, we present a novel way of determining the thermomechanical behavior of EPS beads as a function of temperature and pentane content, based on the optical inspection of the expansion of individual beads. As will be shown, analysis of the experimental data requires the combined use of the viscoelastic equation of Williams, Landel, and Ferry, the so-called WLF equation, and of a recent micromechanical modeling of EPS cellular microstructure. 10

EXPERIMENTAL

Materials Characterization

As-Received Beads

The pentane-swollen polystyrene beads were provided by Shell Co. (Research and Technology Center, Louvain-La-Neuve, Belgium). The diameter of these beads ranges from 0.9 to 1.3 mm. Beads of similar diameter were selected by inspection of the individual samples under a microscope equipped with a micrometric reticle. This time-consuming procedure also allowed the elimination of some broken beads.

With the aim of characterizing the polystyrene that had been used for the bead preparation, the polymer was extracted from the as-received material. For this purpose, expandable beads were first dissolved in tetrahydrofurane to an amount of 5 wt % of beads. After 24 h under stirring, the solution was evaporated at 100°C under vacuum for 72 h in order to remove completely the volatile components (pentane and diluent). The dry solid residue was further dissolved in tetrahydrofurane at 0.1 wt % for gel permeation chromatography (GPC) analysis. It was found to consist of polystyrene (weight-average molecular weight around $185,000 \,\mathrm{g\cdot mol^{-1}}$, polydispersity close to 2), and of a small amount (1%) of low-molecular weight additives $(400-500 \text{ g} \cdot \text{mol}^{-1})$. These unidentified additives could not be separated from polystyrene by precipitation: indeed, the latter done by putting a 0.1 wt % beads toluene solution in a large excess of methanol led to a solid exhibiting the same GPC chromatogram as the material obtained by evaporation. The glass transition of this unplasticized polystyrene T_{g_0} was determined by differential scanning calorimetry (DSC) at a heating rate of 10°C/min. T_{g_0} , taken at the onset of the change in heat capacity, was found to be 97 ± 1 °C.

Determination of the Amount of Pentane in the Beads

It is worth mentioning that the blowing agent, which we call pentane to be consistent with the industrial usage, is not actually pure n-pentane but a n-pentane-rich mixture of different isomers. As a first approximation, we will consider in this study that the properties of the blowing agent are identical to those of pure n-pentane.

Firstly, the amount of pentane was determined in the as-received beads, so-called beads A, by using the GPC technique. For this purpose, the

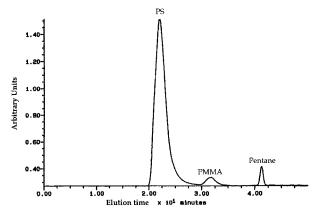


Figure 2 GPC chromatogram of dissolved expandable beads with PMMA as the reference material.

expandable beads were dissolved in tetrahydrofurane (THF) at about 5 wt %. Direct evaluation of the pentane/polystyrene ratio would be imprecise due to the huge difference between the areas of the relevant peaks, as shown in Figure 2. This difficulty was overcome by analyzing ternary systems of bead-PMMA-THF (PMMA: polymethylmethacrylate) instead of the bead-THF mixtures (Fig. 2). For this purpose, a weighted amount of a reference material, a PMMA of 1830 g · mol⁻¹, was added to a weighted amount of beads in the solution, in order to yield comparable GPC peak areas for PMMA and pentane. The amount of pentane in the beads was derived using a calibration curve, relating the ratio Mass (Pentane)/ Mass (PMMA) to the ratio Peak Area (Pentane)/ Peak Area (PMMA), and determined from GPC measurements on additional *n*-pentane–PMMA– THF solutions of known composition (Fig. 3).

Following this procedure, the weight fraction of pentane in the as-received beads (beads A) was found to be around 8 wt %. Two additional series of beads, exhibiting a lower pentane ratio, were prepared from the as-received beads. In the first procedure, the original beads were placed in a vacuum oven (1 mm Hg) for 65 h at room temperature before testing (beads B). The weight fraction of pentane in these beads was found to be reduced to 6 wt %. A more drastic pentane removal was achieved by following another procedure. The original beads were placed in the vacuum oven for 120 h at room temperature and then for 40 h at 40°C, and finally they were left for equilibration for 90 h at 67°C and atmospheric pressure (beads C). The weight fraction of pentane in these beads was shown to drop to 1 wt %.

Bead Expansion Visualization Setup

Figure 4 shows the schematic diagram of the experimental setup. It consists of a thermally controlled Mettler hot-stage whose specimen compartment was modified to include a very small bath of silicone oil. One bead at a time was then plunged into this bath by means of a needle attached to a transparent glass slide. Above this slide was a microscope with a micrometric reticle that permits measurement of the diameter as the bead expands. Measurements were performed by eye in real time or by attaching to the binocular either a film or a video camera. In the former case, the diameter was measured after each 15 s in the first minute of expansion, then after each minute in the following 9 min, and finally after each 2 min until 20 min had gone by.

Figure 5 shows the expansion of one bead: it is worth noting that the bead remained spherical at any time, which means that the expansion proceeded, as desired, in a highly isotropic fashion.

RESULTS AND DATA ANALYSIS

The primary purpose of the experimental collection of the plots of bead diameter vs. expansion time at different temperatures (Fig. 6) was to determine the glass transition temperature $T_g(\tau)$, of the pentane-swollen polystyrene, as a function of initial pentane weight fraction τ . Due to the plasticizing effect of pentane, one may anticipate that $T_g(\tau)$ should be lower than T_{g_0} and should decrease with increasing initial pentane content in the beads. In addition, the rate of bead expan-

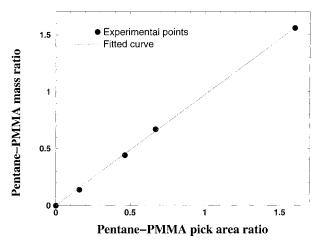


Figure 3 GPC calibration curve for pentane with PMMA as reference. The linear slope is found to be 0.98.

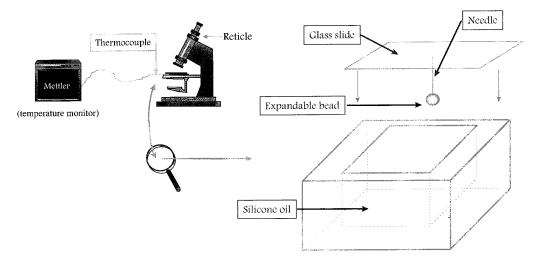


Figure 4 Schematic diagram of the experimental apparatus for the bead expansion experiments.

sion decreases with decreasing expansion temperature. For each series of pentane-swollen polystyrene beads, $T_{g}(\tau)$ is conventionally defined as the highest temperature for which no expansion was observed for 20 min under our setup. As shown in the second entry of Table I, the value of glass transition determined in this way decreases markedly with increasing pentane amount. By the way, it is worth pointing out that this procedure of the determination of T_g is much more accurate in expandable materials than the familiar DSC technique. The latter, indeed, suffers from severe limitations in this case, because the heat flow signal is disturbed at and above T_{σ} by the changes in contact area between the specimen and the detector, as the result of expansion.

Second, the experimental data (Fig. 6) can be used to extract the expansion rates from the slopes of the isothermal curves of bead diameter vs. time. Analysis of the curves of expansion rate vs. time yields the initial expansion rates $v_{0,T}$. Such quantities depend on the expansion temperature and also on the initial pentane content of the beads.

Analysis of $v_{0,T}$ values requires some theoretical assumptions with the aim of accounting for the bead mechanical behavior at the beginning of expansion. Let us first consider a foam with closed cells like an expanded bead as shown in Figure 1. This body is assumed to be at constant and uniform temperature with a traction-free boundary. The porosity is also supposed to be constant and uniform in the whole foam. As indicated in Figure 7, we consider the mechanical problem of predicting its changes in dimensions due to the presence of an intracellular pressure that is assumed to be identi-

cal in each cell. The mechanical behavior of the cell membranes (the matrix) is assumed to be linear, isotropic, and elastic. It can be shown¹⁰ that the elastic strain of such an isolated bead is given by

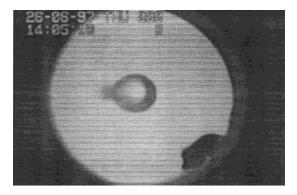
$$\varepsilon_{\tau,T} = \frac{c_{\tau}}{1 - c_{\tau}} \cdot \frac{1 - \nu_{\tau,T}}{2 \cdot (1 - 2 \cdot \nu_{\tau,T})} \cdot \frac{1}{k_{\tau,T}} \cdot P_{\tau,T} \quad (1)$$

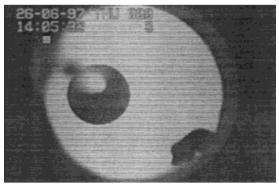
where $\varepsilon_{\tau,T}$ is the elastic strain undergone by an isolated bead at temperature T, c_{τ} is the porosity of the foam (volume fraction of cells), $k_{\tau,T}$ and $\nu_{\tau,T}$ are the bulk modulus and the Poisson ratio of the matrix, respectively, and $P_{\tau,T}$ is the intracellular pressure in excess of the atmospheric pressure. All of these quantities depend on the temperature T and on the pentane content τ of the bead. If the cell membranes are supposed to present a linear and isotropic viscoelastic behavior, and if the Poisson ratio and the pentane content are assumed to be constant, then by means of the correspondence principle, 11 eq. (1) can be converted to

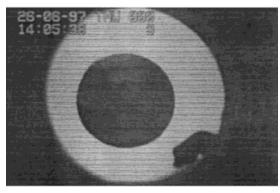
$$\varepsilon_{\tau,T}(t) = \frac{c_{\tau}}{1 - c_{\tau}} \cdot \frac{1 - \nu}{2 \cdot (1 - 2 \cdot \nu)} \cdot J_{\tau,T}(t) \otimes \frac{d}{dt} P_{\tau,T}(t)$$

$$= \frac{c_{\tau}}{1 - c_{\tau}} \cdot \frac{1 - \nu}{2 \cdot (1 - 2 \cdot \nu)} \cdot \left\{ \int_{-\infty}^{t} J_{\tau,T}(t - u) \cdot \frac{d}{du} P_{\tau,T}(u) \cdot du + \sum_{i} J_{\tau,T}(t - t_{i}) \cdot ||P_{\tau,T}||_{i} \right\}$$
(2)

in which t is time, \otimes is the Riemann-convolution product, and $J_{\tau,T}(t)$ is the creep matrix bulk com-







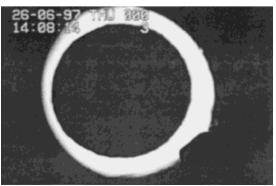


Figure 5 Observation of the expansion of an isolated bead with an optical microscope. The initial bead is at the top and the expanded bead at the bottom. The end of the thermocouple can be distinguished in the right corner of the cell.

pliance [convolution-inverse of the pentane-swollen polystyrene bulk relaxation modulus $k_{\tau,T}(t)$], and $\|P_{\tau,T}\|_i$ is any pressure discontinuity occurring at time t_i .

Equations (1) and (2) were derived to predict the strain of an expanded bead between two relatively close states. This can be extended for an initial state corresponding to the beginning of the expansion. In this way, τ is the initial pentane wt % content of the bead and the intracellular pressure can be considered equal to the vapor pressure of pentane at temperature T, $P_{\rm vs}(T)$. It is assumed that the temperature of each expandable bead instantaneously reaches the temperature T of the silicone oil bath, such that the intracellular pressure is proportional to the Unit-Step function H(t):

$$P_{\tau,T}(t) = P_{vs}(T) \cdot H(t). \tag{3}$$

By deriving eq. (2) with respect to time, and by substitution of eq. (3) for $P_{\tau,T}$, we obtain the expression of the bead initial expansion strain rate $v_{0,T}$ at t=0:

$$\begin{split} \boldsymbol{v}_{0,T} &= \left[\frac{d}{dt} \, \boldsymbol{\varepsilon}_T\right]_{t=0} \\ &= \, \frac{\boldsymbol{c}_{\tau}}{1 \, - \, \boldsymbol{c}_{\tau}} \cdot \frac{1 \, - \, \boldsymbol{\nu}}{2 \cdot (1 \, - \, 2 \cdot \boldsymbol{\nu})} \cdot \left[\frac{d}{dt} \boldsymbol{J}_{\tau,T}\right]_{t=0} \cdot \boldsymbol{P}_{\text{vs}}(\mathbf{T}) \end{split} \tag{4}$$

It is worth noting that eq. (4) is not applicable to large times of beads expansion because in this case the intracellular pressure is no longer constant and the matrix behavior becomes elastovisco-plastic. As shown by eq. (4), consideration of the initial expansion strain rates at different temperatures for identical series of beads with a given τ wt % pentane content gives a means of deducing the type of (thermo)mechanical behavior of the cell membranes as a function of initial pentane content. For instance, if the time–temperature equivalence principle is assumed above the glass transition of pentane-swollen polystyrene, the translation factor can be easily calculated:

$$\begin{split} \frac{\boldsymbol{v}_{0,T}}{\boldsymbol{P}_{\text{vs}}(T)} &= \frac{\left[(d/dt) \boldsymbol{J}_{\tau,T} \right]_{t=0}}{\left[(d/dt) \boldsymbol{J}_{\tau,T_g(\tau)} \right]_{t=0}} \cdot \frac{\boldsymbol{v}_{0,T_g(\tau)}}{\boldsymbol{P}_{\text{vs}}[T_g(\tau)]} \\ &= \boldsymbol{a}_{T_g(\tau)}(T) \cdot \frac{\boldsymbol{v}_{0,T_g(\tau)}}{\boldsymbol{P}_{\text{vs}}[T_g(\tau)]}, \quad (5) \end{split}$$

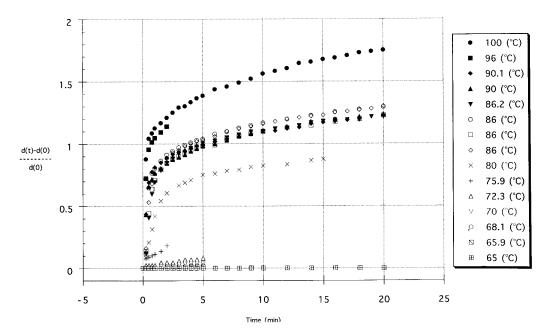


Figure 6 Bead diameter vs expansion time. Example of 8 wt % pentane-swollen beads at various temperatures above $T_{\rm g}$.

where $a_{T_g(\tau)}$ is the shift factor of the WLF equation between the temperature T and T_g , taken as the reference temperature.

Comparing eq. (5) with the experimental results needs the relative vapor pressure to be known. This is done by using literature data for the absolute vapor pressure of pentane¹² and by subtracting the atmospheric pressure (about 0.1 MPa). In such calculations, the hydrostatic pressure of silicone oil (about 44 Pa) is negligible. The temperature dependence of the intracellular pressure of pentane is given by the phenomenological Dupré's law¹²:

$$\log[P_{vs}(T)] \approx -6.5 + \frac{30}{T} + 3 \cdot \log(T),$$
 (6)

where T holds for the temperature in Celsius and log is the decimal logarithm.

The next step of our data analysis was to consider the temperature dependence of the initial strain rates $v_{0,T}$ at a given pentane content. The temperature dependence of the translation factor can be inferred by fitting the quantity $\log[v_0]$ $P_{\rm vs}(T)] - \log\{v_{0,T_g(\tau)}/P_{\rm vs}[T_g(\tau)]\}, \mbox{which equals } \log[a_{T_g(\tau)}(T)] \mbox{ according to eq. (5). Since } T_g(\tau) \mbox{ has}$ been defined as the highest temperature for which no expansion was observed for 20 min, it can be determined according to the precision of our optical measurements (half a micrometer graduation, i.e., 10 µm) and to the mean expandable beads diameter (about 1 mm). It turns out that $v_{0,T_c(\tau)}$ is equal to about 4.8 10^{-4} min⁻¹ whatever the class of beads (A, B, or C) under consideration. Figures 8(a-c) show the temperature dependence of the normalized bead initial expansion rate for beads A, B, and C, respectively. If the capability of a bead to expand is assumed to be

Table I WLF Parameters of Pentane-Swollen Polystyrene (The WLF Coefficients for Pure Polystyrene are Extracted from Ref. 13)

τ (%)	T_g (°C)	C_1^g	C_2^g (°C)	$f(T_g)/B$ (%)	$\alpha / B \ (10^{-4} {}^{\circ}\mathrm{C}^{-1})$	T_{∞} (°C)
0	97 ± 1	13.4 ± 0.2	55 ± 2	3.24 ± 0.05	5.9 ± 0.3	42 ± 3
1 ± 0.5	88 ± 1	8.3 ± 0.2	50 ± 2	5.24 ± 0.13	10.5 ± 0.7	38 ± 3
6 ± 0.5	72 ± 1	6.1 ± 0.2	32 ± 2	7.13 ± 0.23	22.3 ± 2.1	40 ± 3
8 ± 0.5	65 ± 1	5.6 ± 0.2	18 ± 2	7.76 ± 0.28	43.1 ± 6.3	47 ± 3

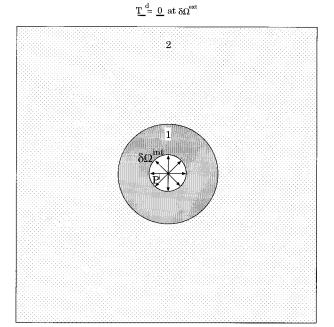


Figure 7 Micromechanical analysis of an intracellular-pressurized foam with closed cells. Medium 1 is a cell with its membrane, medium 2 is made up of an infinity of medium 1. The considered problem consists of deriving the overall strain of the foam with linear, isotropic, and elastic cells membranes, subjected to a traction-free outer boundary.

controlled, in the initial stages, by the ability of the polymer chains to develop glass transition motions, the temperature dependence of the initial expansion rate, or more precisely, of the quantity $\log[a_T(T)]$ can be analyzed by using the well-known WLF equation⁹:

$$\begin{split} \log[a_{T_g}(T)] &= \log\left[\frac{v_{0,T}}{P_{\text{vs}}(T)}\right] - \log\left[\frac{v_{0,T_g}}{P_{\text{vs}}(T_g)}\right] \\ &= C_1^g \cdot \frac{T - T_g}{C_2^g + (T - T_g)} \,. \quad (7) \end{split}$$

As shown in Figure 8(a–c), the fits of the experimental data by eq. (7) are satisfactory in all cases. The values of the viscoelastic coefficients of the WLF equation, C_1^g and C_2^g taken at the reference temperature T_g , are given in Table I, together with the critical glass transition temperature of the pentane-swollen polystyrene at infinitely long observation time $T_{\infty}(\tau)$, defined as

$$T_{\infty}(\tau) = T_{\sigma}(\tau) - C_{2}^{g}(\tau). \tag{8}$$

Below this temperature, the glass transition-like molecular motions cannot be observed even if the experimental time window were be infinite. $T_{\infty}(\tau)$ does not seem to vary with the pentane content of the beads within the error bar on the determinations (about $\pm 5^{\circ}\mathrm{C}$).

At this stage of our investigations, a pending question concerns the possibility of reducing the curves of Figure 8(a–c) to a unique master curve that should account for the initial pentane content of the beads. Simple replacement in eq. (5) of c/(1-c) by $\rho_{_{\rm PS}}/\rho_{_{\rm C5}} \cdot \tau/(1-\tau)$, where $\rho_{_{\rm PS}}=1050~{\rm g} \cdot {\rm dm}^{-3}$ and $\rho_{_{C5}}=626.2~{\rm g} \cdot {\rm dm}^{-3}$ are the densities of pure polystyrene and of pentane, 12 respectively, would be misleading because it supposes that the whole pentane population is only in the cells; this assumption is in contradiction with the plasticizing effect that we have evidenced for pentane in the form of a polystyrene T_g depression.

The viscoelastic coefficients C_1^g and C_2^g can be discussed in the framework of the free volume models by assuming the validity of two simple concepts⁹:

1. At $T \ge T_g$, the viscosity depends on the fractional free volume according to the Doolittle equation:

$$\ln \eta(T) = \ln A + \frac{B}{f(T)}, \qquad (9)$$

where f(T) is the fractional free volume available at temperature T, A and B are constants, the latter being usually taken to be unity.

2. The fractional free volume above T_g , f(T), increases with temperature according to

$$f(T) = f(T_g) + \alpha_f \cdot (T - T_g), \tag{10}$$

where $f(T_g)$ is the fractional free volume available at T_g , and α_f the free volume thermal expansion coefficient above T_g . These quantities are related to the WLF coefficients by

$$f\left[T_g(\tau)\right] = \frac{B}{2.3 \cdot C_1^g(\tau)} \text{ and } \alpha_f(\tau) = \frac{f\left[T_g(\tau)\right]}{C_2^g(\tau)}. \quad (11)$$

The values of $f[T_g(\tau)]$ and $\alpha_f(\tau)$ are also given in Table I.

It turns out that both fractional free volume available at T_g and thermal expansion coefficient of the free volume above T_g are found to drasti-

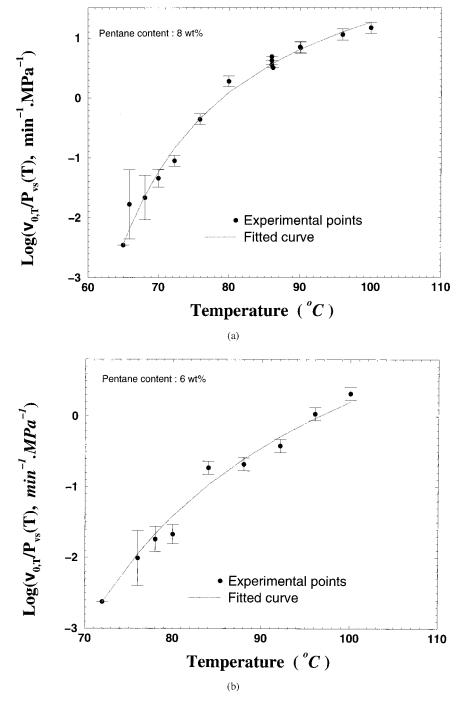


Figure 8 Experimental data treatment by WLF analysis: (a) 8 wt % pentane swollen PS, (b) 6 wt % pentane-swollen PS, and (c) 1 wt % pentane-swollen PS.

cally increase with increasing pentane weight content.

DISCUSSION

The above results need to be discussed in two separate ways, depending on whether emphasis is

laid on the phenomenon of polystyrene plasticization or on the issue of the dimensional variations of EPS after manufacturing.

As far as plasticization of polystyrene in the beads is concerned, let us focus on the variations of $T_g(\tau)$, $f[T_g(\tau)]$, and $\alpha_f(\tau)$ as a function of the pentane weight fraction τ (Table I). Even though

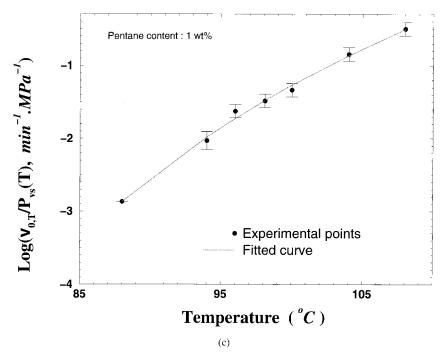


Figure 8 (Continued from previous page)

there is no proof that all the pentane molecules are in interaction with the polystyrene segments and actually act as a plasticizer, the weakly scattered plots shown in Figure 9 demonstrate that the observed evolutions make sense, at least from a qualitative viewpoint. The increase by a factor of 2.4 of the free volume available at T_g when T_g is depressed from 97 down to 65°C looks reasonable, and in agreement with the order of magnitude of $f(T_g)$. More striking is the observed huge

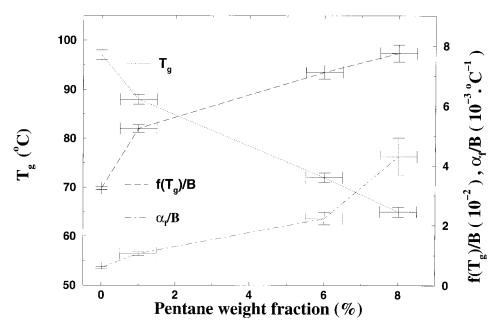


Figure 9 Glass transition, $T_g(\tau)$, fractional free volume available at T_g , $f(T_g(\tau))$, and free volume thermal expansion coefficient above T_g , $\alpha_f(\tau)$, as a function of pentane weight fraction.

increase in α_f even for τ as small as 6 wt %. To our knowledge, such an effect has never been reported in the literature. However, the usual diluents (as those used to modify the mechanical characteristics of polyvinylchloride) are bulky and low vapor pressure molecules. One may suggest that the peculiarity observed here would be the result of the numerous motional degrees of freedom available in the flexible molecule of pentane over the temperature range of interest. As a direct consequence of the large sensitivity of α_f on τ , C_2^g (τ) drastically decreases and $T_{\infty}(\tau)$ becomes closer and closer to $T_g\left(au \right)$ when au is increased. At the same time, $T_g(\tau)$ decreases markedly; hence, according to eq. (8), $T_{\infty}(\tau)$ is roughly independent of τ .

The next point of interest deals with the value found for T_{∞} , i.e., around 42°C. This result means that the relaxation associated with the glass transition motions of polystyrene chains in the beads is unlikely to occur below 42°C. This conclusion holds whatever the actual expansion degree of the beads is, since T_{∞} was shown not to depend on the residual pentane amount. On the other hand, it does not mean that at room temperature molecular relaxation is impossible: it might occur on a very large time scale, provided some short spatial scale motions, analogous to those evidenced in low temperature creep experiments, are liable to develop.

Transposition of the above conclusions, relative to individual EPS beads, to the case (of industrial interest) of manufactured structures could be achieved only with prudence. In particular, one should bear in mind that the thickness of the cell walls is very much smaller than the diameter of the beads. As a consequence, the viscoelastic behavior of the plasticized polystyrene chains might be affected by the passage from volume to surface properties, leading to possible changes in the values of T_g and T_∞ .

CONCLUSION

It is clear that the present study was not able to settle definitely the question of dimensional evolution in expanded polystyrene foams, a problem which has had much concentrated effort in the literature, especially from a technological viewpoint (see, for instance, refs. 1 and 4). As a matter of fact, the present contribution aimed at providing an insight in the relevant physicochemical phenomena. With this respect, three main objectives

tives have been reached: (1) a novel methodology has been developed for studying the blowing of individual EPS beads at and above their glass transition temperature; (2) an original method for the data analysis has been derived, based on the combination of a very recent micromechanical modeling with the well-known WLF equation; and (3) quantitative results have been obtained in this way regarding the plasticization of polystyrene by the residual blowing agent.

This approach may be of interest for future work on polymeric foams, including the detailed behavior of EPS industrial structures and, tentatively, that of extruded polystyrene foams.

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