Nuclear Magnetic Resonance Imaging Characterization of Resistance Properties of Polymers to Solvent Diffusion

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Abstract: Nuclear magnetic resonance (NMR) imaging (MRI) was applied to study the penetration of aggressive fluids, used as blowing agents for thermal insulators (polyurethane). The penetration profiles of cyclopentane and fluorotrichloromethane (Freon 11©) were obtained through a series of NMR images taken dynamically during saturation of polymer rods. The applied technique allowed efficient observation of radial diffusion of the solvents. The method provides quantitative measurements of the solvent penetration rate by determining the translational diffusion coefficients D_{TRL}. These parameters were applied in evaluating materials with different compositions, and they were useful in understanding the resistance properties to solvent aggression. Significant chemical and physical parameters influencing diffusion were identified.

INTRODUCTION

High-impact polystyrene (HIPS) is a two-phase material that is widely used in industrial manufacturing because of its interesting mechanical properties, determined by the presence of a dispersed rubbery phase distributed inside a hard polystyrene matrix.[1] However, such complex materials need careful design to fulfill selected requirements, particularly when special resistance to aggressive agents, e.g., fluids utilized in refrigerator liners, is necessary. Standard methods based on solvent penetration and weight uptaking measurements give only limited information with large experimental errors. Nuclear magnetic resonance (NMR) imaging (MRI) is a relatively recent technique increasingly applied in polymeric materials investigation.[2] Its interesting feature is mainly related to the possibility of investigating physical and chemical equilibria without damaging or interfering significantly with the materials. The real advantage of MRI is the possibility of making spatially localized diffusion measurements, allowing examination of concentration and location of a liquid permeating a solid material.[3–5] We have applied this technique in studying aggressive penetration of fluids used as blowing agents for polyurethanes (thermal insulators) inside several HIPS.

EXPERIMENTAL SECTION

Experimental Conditions and Materials

The MRI experiments were performed on a 2 T (85 MHz ^{1}H NMR resonance frequency) SISCO instrument (Varian, Palo Alto, Calif., USA) equipped with a 31 cm bore horizontal magnet and actively shielded gradients (7 gauss/cm). The diffusion measurements were performed at 20°C, on polymer rods (circa 4 mm o.d.) immersed in Freon 11$^©$ or cyclopentane and placed inside a solenoidal coil. In this way, the samples were imaged simultaneously. The images were acquired using a spin-echo sequence (echo time TE = 6 ms, recovery time TR = 1 s, total acquisition time = 4 min). Images, characterized by a resolution of $150 \times 150 \, \mu m$, were then analyzed using a dedicated software package running on a Sun Ultra Sparc 1 workstation, allowing extraction of shape and morphology parameters.

HIPS were produced and shaped by EniChem. Characteristic properties of polymers, such as swelling index and rubbery phase content, were determined according to the procedures reported in a previous article.[6] Swelling index is a parameter, obtained by solvent uptake measurement, related to the degree of cross-linking of the rubbery phase that is constituted of grafted rubber and polystyrene occlusions. The higher the

Table I. Characteristics of HIPS samples

Sample	Rubbery phase (% w/w)	Swelling index	Acrylonitrile content in matrix (% w/w)
SR 5	23.3	23.0	0
SR 7	38.5	15.1	0
DW 4	31.1	24.0	0
KR 2	36.0	13.5	0
SR 8	39.4	16.0	8
SW FG[a]	37.0	13.1	0
SW AD	39.9	18.1	0
RR 70	37.6	12.5	0
RR 15	40.1	12.1	0
SR 80	37.9	14.7	8

[a]Contains rubber with a high value of *cis* isomer.

swelling index, the lower the degree of cross-linking. The properties of the polymers are reported in Table I. It can be noted that, while almost all HIPS have a polystyrene matrix, the products SR8 and SR80 have a copolymer poly(styrene-*co*-acrylonitrile) matrix.

NMR Imaging of Diffusion in Polymers: Theory and Methods

Diffusion behavior of solvents into polymers can be classified, according to Alfrey et al.,[7] into three categories:

1) Case I or Fickian diffusion in which the rate of diffusion of solvents is much less than that of polymer segmental relaxation rates (typical of rubbery polymers).
2) Case II or relaxation-controlled diffusion in which the rate of diffusion is much greater than that of the polymer segmental relaxation (typical of glassy polymers).
3) Non-Fickian or anomalous diffusion.

Systems subjected to diffusion of gas or liquids inside follow Fick's law (Equation (1)), which can be converted into a time-dependent form, also known as Fick's second law (Equation (2)):

$$J = -D\frac{\partial c}{\partial x} \tag{1}$$

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \tag{2}$$

In the above equations, J represents the flux, i.e., the mass passing through a unit area per unit time, D is the diffusion coefficient, x is the distance diffused, and c is solvent concentration. In general, the diffusion coefficient for polymer-solvent systems following Fickian behavior is concentration dependent, having the form:

$$D = D_0 e^{kc} \tag{3}$$

D_0 is the diffusion coefficient corresponding to surface concentration c_0. If D is a function of concentration only, a transformation can be applied[8] to Equation (2) to give

$$\left(\frac{\partial x}{\partial t}\right)_c = f(D, c) t^{1/2} \tag{4}$$

Therefore, for a given value of c/c_0, the distance diffused will be proportional to the square root of time. The time dependence of the distance diffused can be expressed as

$$\Delta x \propto \Delta t^n$$

or

$$\log(\Delta x) \propto n \, \log(\Delta t)$$

where n lies between 0.5 for pure Fickian diffusion and 1.0 for pure Case II diffusion.

Methodology

The experiments were performed simultaneously on three polymer rod samples immersed in the solvent as shown in Figure 1. A plane sheet, orthogonal to the main axis of the samples, was imaged to observe only radial diffusion. Lengths of samples were carefully chosen in order to be at least 10 times larger than the diameter to avoid flow artifacts. The NMR images, shown in Figure 2, were acquired at different times while solvent diffusion was occurring. Image analysis was performed by measuring the distance covered by the solvent front. This parameter was obtained by computing the difference between the initial diameter of the sample ($d_{initial}$) on the slice imaged (thickness $500 \, \mu m$) and the space not occupied by the solvent at acquisition time (d_{free}) as expressed in the following relation:

$$r_{diffusion} = \frac{d_{initial} - d_{free}}{2} \tag{5}$$
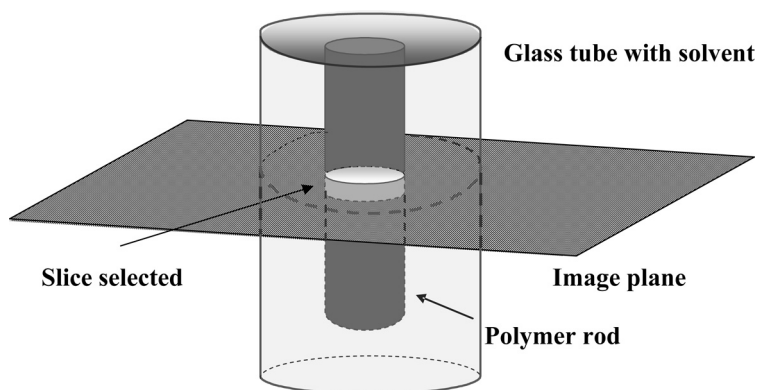
Figure 1. Experimental scheme showing the polymer rod immersed in the solvent and the image of the slice acquired by MRI.

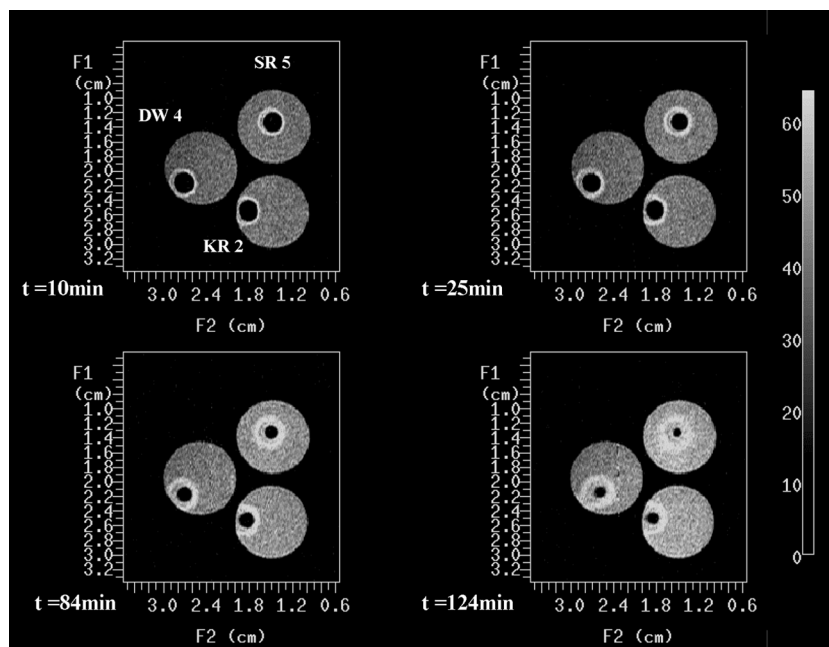**Figure 2.** In situ diffusion of cyclopentane through HIPS rods (4 mm diameter) as a function of time. ^{1}H NMR imaging parameters: 256×256 pixels (spatial resolution: $150 \times 150\,\mu$m), 128 phase encode steps, TR = 1 s, TE = 6 ms, 2 scans, slice thickness = 0.5 mm, total experimental time, 4 min.

where $r_{diffusion}$ is simply the spatial component with radial symmetry of the solvent front diffusion inside the sample. In this way, every artifact related to sample swelling is neglected.[9]

RESULTS AND DISCUSSION

Translational diffusion measurements of cyclopentane were performed on different HIPS samples by acquiring images at different times as shown in Figure 2. The careful choice of the NMR sequence acquisition parameters gave an efficient contrast of solvents diffusing inside the polymer. In fact, from the images one can easily observe the shape of the solvent penetrated inside the polymer rods (bright areas); the dry polymer appears rather dark due to the lack of signal related to the fast relaxation of solid-state protons (transverse relaxation time $T_2 < 2\,ms$). As previously described in the methodology section, the distance diffused was determined by image analysis. Data plots, as shown in Figures 3 and 4, revealed a consistent linear correlation of diffusion distance with $t^{1/2}$, as also confirmed by the values of linear correlation coefficients (R^2) reported in Table II. These results confirmed the existence of an apparent
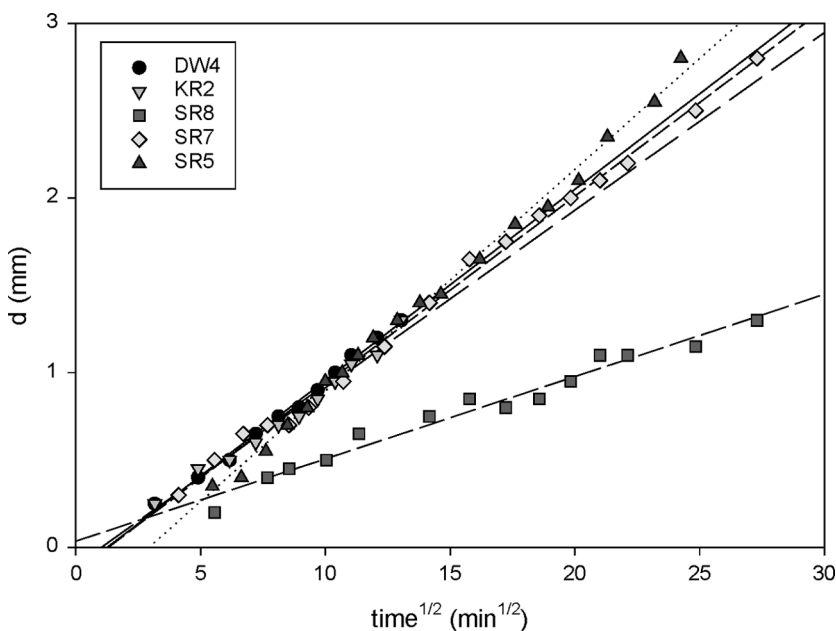
Figure 3. Diffusion distance of cyclopentane inside HIPS rods vs. square root of time.
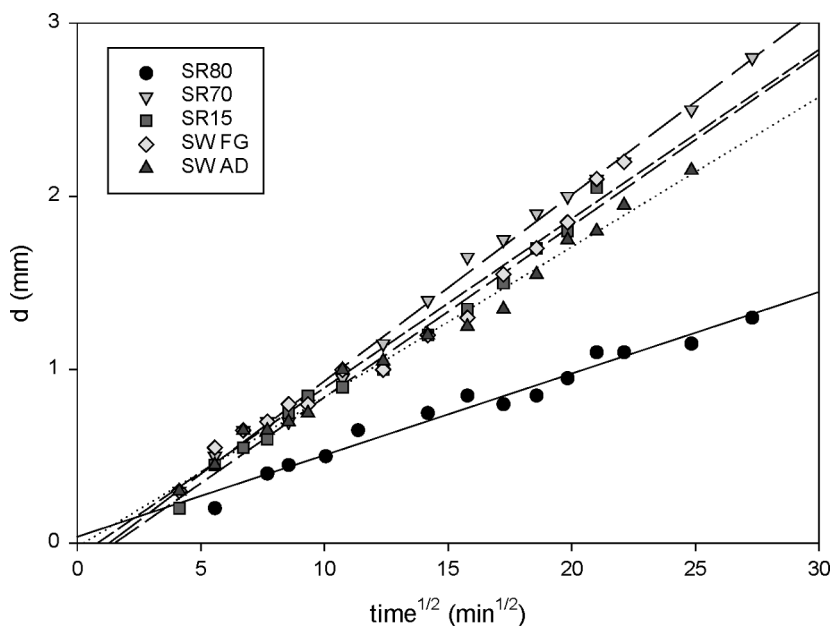
Figure 4. Diffusion distance of cyclopentane inside HIPS rods vs. square root of time.

Fickian diffusion regime for this type of two-phase polymeric system. This behavior could be related to the lowering of Tg in the polystyrene phase as a result of solvent penetration. This affects considerably the relaxation rate of polystyrene chains, giving rise to an average Fickian diffusion regime.

Table II. Translational diffusion coefficients (D_{TRL}) and linear correlation coefficients (R^2) for solvents diffusing in HIPS rods

Sample	D_{TRL} in cyclopentane (m^{2}s^{-1})	R^2	D_{TRL} in Freon 11$^©$(m^{2}s^{-1})	R^2
SR 5	2.78×10^{-10}	0.995	1.81×10^{-10}	0.989
SR 7	1.30×10^{-10}	0.996	1.68×10^{-10}	0.992
DW 4	2.04×10^{-10}	0.994	1.24×10^{-10}	0.991
KR 2	1.37×10^{-10}	0.982	1.20×10^{-10}	0.973
SR 8	4.86×10^{-11}	0.971	6.26×10^{-11}	0.981
SW FG	1.59×10^{-10}	0.978	—	—
SW AD	1.25×10^{-10}	0.989	—	—
RR 70	1.90×10^{-10}	0.996	—	—
RR 15	1.63×10^{-10}	0.988	—	—
SR 80	6.55×10^{-11}	0.970	—	—

   Analogous results were found by studying the absorption of fluoro-
trichloromethane (Freon 11[©]). In this case, ^{19}F NMR imaging technique
was applied, and sufficient contrast to analyze the absorption of solvent
was found. Compared to previous experiments, as shown in Figure 5, the
signal intensity decreases when solvent protons are inside the material
due to unfavorable relaxation of solvent fluorine nuclei absorbed by
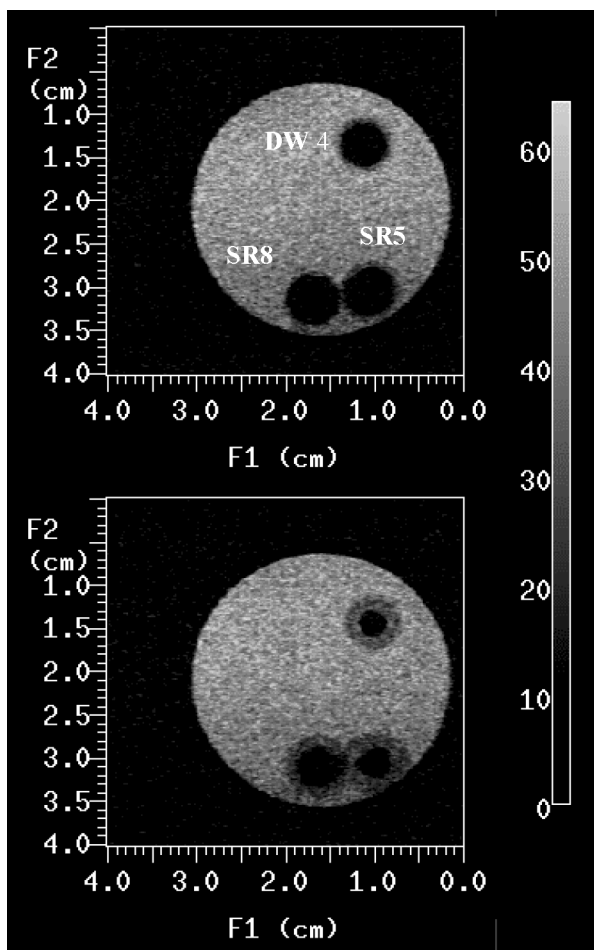the polymer. Also, in this case, diffusion was in agreement with apparent

Figure 5. In situ diffusion of Freon 11[©] through HIPS rods as a function of
time. ^{19}F NMR imaging parameters: 256×256 pixels spatial resolution
($150 \times 150 \,\mu m$), 128 phase encode steps, TR $= 1$ s, TE $= 4$ ms, 4 scans, slice thick-
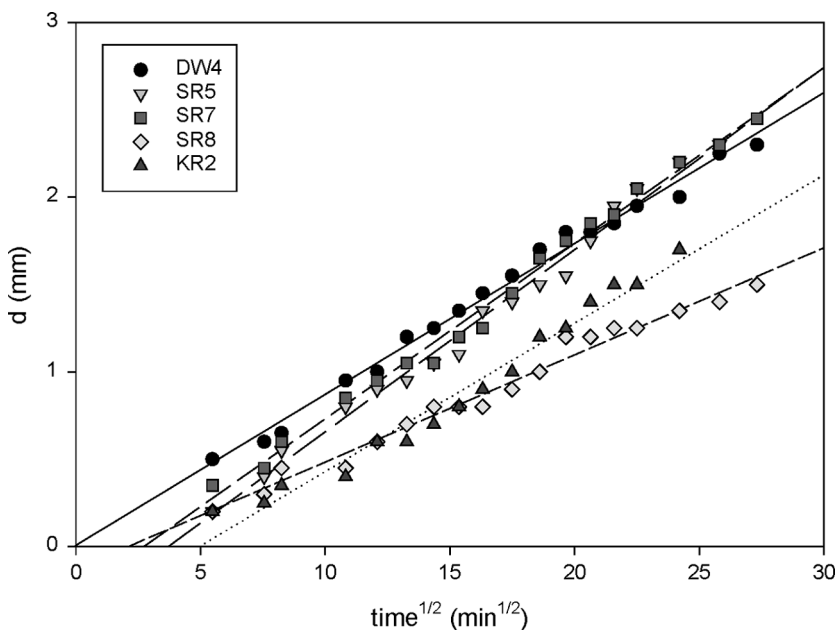ness $= 0.2$ cm, total experimental time, 8 min.

Figure 6. Diffusion distance of Freon 11© inside HIPS rods vs. square root of time.

Fickian regime as demonstrated by the appreciable linear correlation found in Figure 6.

From obtained data, the apparent translational diffusion coefficient[5] D_{TRL} can be determined (Table II) from the square root of the slope of the resulting plots. A 5% relative experimental error is associated with the data (determined by repetitive measurements on random samples). Differentiation of diffusion resistance of HIPS materials is possible, and a good range of D_{TRL} values is obtained both for cyclopentane and Freon 11©. The best-performing materials are those containing acrylonitrile in the polymer matrix (SR8 and SR80 for cyclopentane, SR8 for Freon 11©), due to the low affinity between matrix and diffusing solvent.

To better understand the different diffusion resistance of HIPS, we carried out further investigations on three selected HIPS samples (SR5, SR7, SR8), following the ingress of cyclopentane inside the polymer rods for several hours until complete saturation. The samples analyzed were representative of the entire group of products and were chosen according to their appreciable difference in D_{TRL} values.

By applying an inversion recovery-IR spin-echo NMR imaging sequence,[10] it was possible to measure a longitudinal relaxation time (T_1) map of solvent saturating the selected slice of the polymer rods.

Longitudinal relaxation times (T_1) are parameters related to nuclear magnetic relaxation of solvent protons that give important information on surrounding nuclei, revealing the change in mobility of segmental polymer chains and therefore the interaction between cyclopentane and the material[2]. Different values of T_1 indicate the interaction of the solvent with polymer chains, which could be eventually subjected to structural modification. The results obtained are shown in Figure 7, which refers to a transverse section acquired on three different tubes containing the materials surrounded by the cyclopentane solvent. The T_1 map, based on different grey levels, clearly revealed the strong resistance of sample SR8 to solvent diffusion, confirming appreciable structural resistance: In fact a swelled shell (high T_1) surrounds a rather intact core poorly affected by the solvent (low T_1). The other two samples lost their shape after 20 h, being almost completely dissolved by the solvent, resulting in an average uniform T_1 value.

Finally, we have tried to correlate D_{TRL} data with the morphological and structural parameters of materials in order to understand their
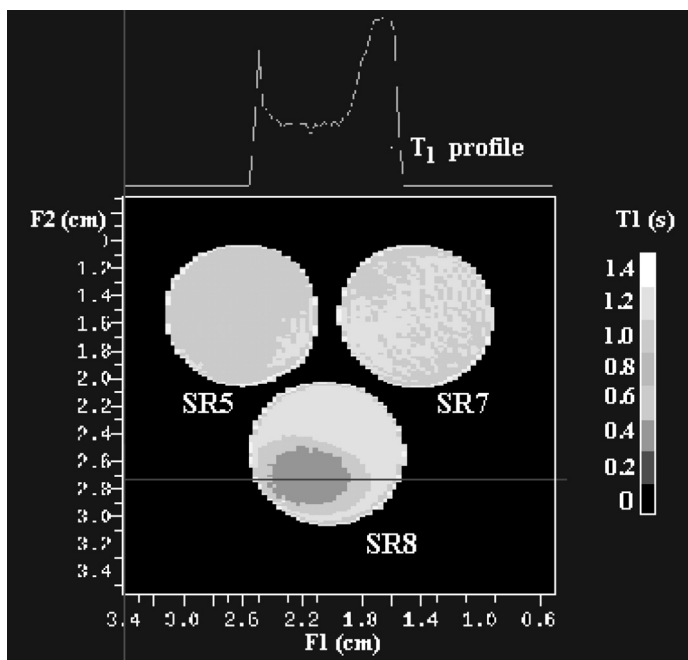
Figure 7. Calculated T_1 map of cyclopentane inside three different HIPS samples (SR5, SR7, SR8) subjected to solvent penetration (pixel-by-pixel fitting of 10 images obtained by an IR-spin-echo sequence). On the top is the profile of the SR8 sample across its diameter.
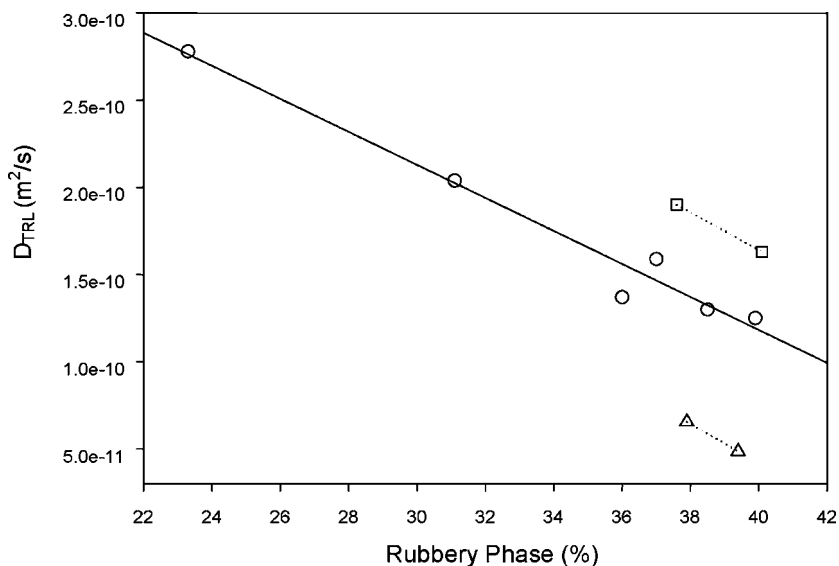
Figure 8. Correlation between experimental translational diffusion coefficients D_{TRL} and rubbery-phase content. Symbols: $\square$, RR15 and RR70; $\circ$, SR5, SR7, DW4, KR2, SW FG, and SW AD; $\triangle$, SR8 and SR80. Dotted lines are only guides, while the continuous straight line is a linear regression for the circles.

influence on the diffusion process. Results for cyclopentane are reported in Figure 8. An inverse linear correlation between D_{TRL} and rubbery phase content is evident, suggesting a consistent effect of the rubbery phase on decreasing diffusion rate. The cross-linking of the rubbery phase seems to have no effect on D_{TRL} for values of the swelling index in the range 13.5–24.0. A particular highly cross-linked rubbery phase (swelling index 12.1–12.5) instead allows faster diffusion of cyclopentane, probably because cyclopentane is less adsorbed inside the phase and is free to diffuse in the polystyrene matrix in which it has a higher diffusion coefficient. It is also confirmed that the presence inside the matrix of a polar comonomer (acrylonitrile) greatly reduces the diffusion of cyclopentane due to lower affinity. Similar correlations have not been tested for Freon 11© due to the limited number of samples analyzed.

CONCLUSIONS

NMR imaging could be applicable to complex materials, such as two-phase polymer systems (HIPS). Diffusion of solvents into such materials was studied using translational diffusion coefficients (D_{TRL}) and was

established to follow a pure Fickian diffusion model. A longitudinal relaxation time (T_1) map of solvent penetrating into the polymer was also successfully obtained on some samples, confirming the ability to discriminate between polymers having different solvent permeability.

An attempt was made to correlate the translational diffusion coefficients with physicochemical characteristics of the materials. Good results were obtained for cyclopentane. The presence of acrylonitrile in the polymer matrix greatly reduces the solvent diffusivity into the polymer, due to the remarkable polarity difference between acrylonitrile and cyclopentane. The rubbery-phase content has an important role in the diffusion resistance of the materials. The higher the rubbery phase content, the lower the diffusivity of cyclopentane. Furthermore, samples with a particular highly cross-linked rubbery phase show high diffusivity of cyclopentane.

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