Application of Magnetic Resonance Techniques in Investigation of Hydrocarbons Interaction with Composite Polymers

G. Maddinelli,[1] L. Montanari,[1] A. Ferrando,[2] C. Maestrini[2]

[1]*EniTecnologie S.p.A., via F. Maritano 26, 20097, S. Donato, Milano, Italy*
[2]*Polimeri Europa, via Taliercio 14, 46100 Mantova, Italy*

ABSTRACT: Composite polymers such as high impact polystirene (HIPS) or acrylonitrile–butadiene–styrene (ABS) are widely used in manufacturing industry. In special applications, such as refrigerator liners, a good resistance to fluids aggression is required. In this study we have applied NMR and ESR techniques to investigate the effect of diffusion of fluids (light hydrocarbons) used as blowing agents for polyurethanes (thermal insulators) inside selected HIPS materials. The application of NMR relaxation analysis on materials exposed to deuterated hydrocarbons (C_6D_{12}) allowed selective observation of rubber phase modification. Both longitudinal (T_1) and transversal (T_2) relaxation provided information on polymer chain dynamics effects, determined by solvent interactions. In fact, a consistent increase in relaxation times of polybutadiene rubber phase after solvent exposition was observed. Similar results were obtained by using hexachlorobutadiene as solvent. Another confirmation was also obtained by spin-probe ESR technique. This technique could give useful insight into the molecular mobility of the two phases of HIPS. This experimental investigation provided a clear demonstration of consistent solvent penetration inside the rubbery phase of such composite polymers. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 2810–2817, 2006

Key words: NMR imaging; high impact polystyrene (HIPS); spin-probe ESR; relaxometry

INTRODUCTION

Composite polymers, i.e., high impact polystyrene (HIPS) and acrylonitrile–styrene–butadiene (ABS), are widely applied in manufacturing industry because of their distinctive mechanical properties.[1] Among the wide range of industrial applications, manufacturing components for refrigerator liners is one of the most demanding. A careful design of production procedures is required to improve material performance, especially when resistance to aggressive agents is necessary. In fact, materials applied in refrigerators manufacturing are subjected to severe conditions determined by the low temperature and exposition to aggressive fluids, which could behave as solvents for the styrenic polymers. In a previous study,[2] we focused on phenomena related to the diffusion of cyclopentane and fluorinated fluids inside HIPS samples. The diffusion regime was characterized and a correlation between the extent of the rubber phase and the diffusion rate of hydrocarbon or fluorinated solvents was found. However, some uncertainties still remain on the mechanism involved in fluids penetration and on the structural modifications induced on the different phases constituting the composite materials. Especially the interaction of the hydrocarbon fluids with the rubber phase present in high impact polystyrenes has never been clearly observed by experimental techniques. A better knowledge in this field should be very helpful to understand the mechanism of fluids propagation inside this class of composite materials.

Rubber materials have been deeply investigated by NMR techniques. Most of the studies have been dedicated to the characterization of the degree of crosslinking, mainly by analyzing the spin-echo (Hahn echo) experimental relaxation decay curves.[3–6] In fact, the Gaussian decay of the initial part of the spin-echo curves is related to the anisotropic motion of the solid-like proton fraction of the rubber segments. However, in spite of a correct evaluation of short relaxation times, this type of methods are less efficient in fitting the longest relaxation components.[6] A different approach based on the observation of CPMG relaxation decays and the application of a continuous distribution model of transverse relaxation times was recently proposed.[7] This method is particularly suitable for the characterization of not highly crosslinked rubbery materials or in the evaluation of swelling processes (high segmental mobility), on which the shortest (solid-like) relaxation

components are negligible. The transverse ^{1}H-NMR relaxation (T_2) is caused by inter- and intramolecular dipolar interaction of protons. Its observation is very useful as a sensitive probe of local molecular dynamics, which is closely related to chain dynamics and chain structure of the polymer network above T_g. Diffusion of solvent and consequent swelling of the materials have an appreciable impact on polymer network, which is revealed by a consistent increase in transverse ^{1}H-NMR relaxation. This effect is strongly related to the increase in chain dynamics and probably reduction of physical loops (entanglements) constraints. Also longitudinal ^{1}H-NMR relaxation time (T_1) is sensitive to chain mobility and could provide good indications on solvent interactions with the polymer network.[6,7] Very recently, methods based on dipolar correlation effects (DCE) measurements and contrast filters for NMR imaging of residual ^{1}H dipolar coupling have been introduced as new techniques for elastomers characterization.[8,9] The following experimental description reports the measurements of relaxation data on samples exposed to solvents and describes the information obtained on structural mobility of the polymer chains.

EXPERIMENTAL

Materials and methods

The composite polymers studied were commercial High Impact Polystyrene (HIPS) products, supplied by Polimeri Europa Laboratories (Mantova, Italy). The HIPS samples are characterized by a typical cell-like rubber phase dispersion in the plastic matrix (PS), as shown in the micrograph reported in Figure 1. Therefore the dispersed phase or, as often called the rubbery phase, is constituted of rather spherical com-
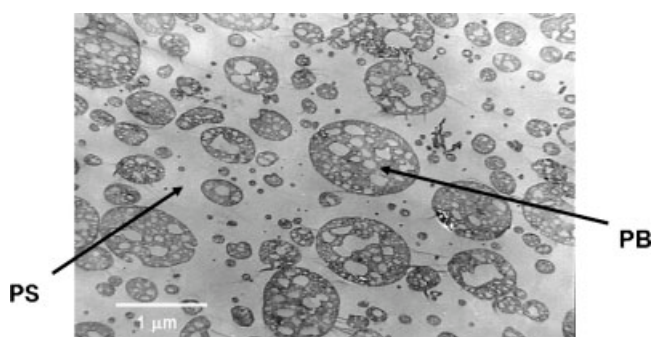
Figure 1 Transmission electron micrograph (TEM) of a thin section of a typical HIPS composite polymer, stained with osmium tetroxide. The image shows in a gray scale the characteristic cell-like morphology due to the rubber phase with distinct occlusions of PS (white) within PB (dark). The rubber phase cells are dispersed within the plastic matrix of PS.

TABLE I
Composition and Properties of HIPS Samples Examined

	Polybutadiene (%, w/w)	Rubber phase (%, w/w)	Mw ($\times 10^{-4}$) (g/mole)	Mw/Mn	Swelling index (a.u.)
HIPS1	8.5	31.4	15.7	2.26	14.0
HIPS2	8.0	24.4	14.3	1.68	24.5

posite particles of polybutadiene with occlusion of polystyrene. The determination of dispersed phase parameters, such as its fraction content on the total material weight (rubbery phase content) and morphological features, is extremely important to assess the physical and chemical properties of the final materials.[10] Characteristic properties of investigated polymers, such as swelling index and rubbery phase fraction content (reported on Table I) were determined according to the procedures previously reported.[11] The absorption of solvents was performed on HIPS rods (4 mm O.D.). These samples were immersed in standard cyclohexane (C_6H_{12}) for NMR imaging observation and in deuterated cyclohexane (C_6D_{12}) (Aldrich 99.6% w/w) for NMR relaxation measurements. A sample of commercial *cis-trans* 1,4 polybutadiene (PB) was used as a reference for solvent diffusion in a pure rubber phase. The samples were allowed to absorb solvents for 12 h.

Magnetic resonance techniques

The NMR imaging (MRI) and relaxation measurements were performed on a 2 T (85 MHz ^{1}H-NMR resonance frequency) SISCO instrument (Varian, Palo Alto, CA) equipped with a 31-cm bore horizontal magnet and shielded gradients (7 Gauss/cm).

^{1}H-NMR relaxation measurements were also performed at high field (300.13 MHz) on a Bruker Avance spectrometer. In this case, several samples obtained at different thermal curing times (at 200°C), were left in contact at ambient temperature, for 16 h, with the same weight amount of hexachloro-1,3-butadiene (Aldrich, 97% w/w). The hexachloro-1,3-butadiene (HCB) has a strong capacity to diffuse in the sample: in the test conditions the whole sample was permeated by the solvent. Relaxation measurements (pulse sequences: inversion recovery – IR for T_1, and Carr-Purcell-Meiboom-Gill – CPMG, for T_2) were performed at 25°C on both instruments. Processing of CPMG decay data to obtain the distribution of transversal relaxation times was performed with the UPEN software[12] based on application of an Inverse Laplace Transform algorithm. ESR spectra were acquired at 25°C using a Bruker ESP 300 E spectrometer equipped with a variable temperature control unit (100–520 K). The microwave frequency was controlled by a very accurate HP

frequency meter (1 Hz precision) able to evaluate fourth decimal digit of the g factor.

RESULTS AND DISCUSSION

NMR study of solvent absorption

Laboratory testing of resistance to solvents aggression on HIPS materials are generally performed using cyclopentane, which has now widely substituted fluorinated fluids as blowing agents in refrigeration industry. In this case, we have focused on cyclohexane because of commercial availability of the corresponding deuterated compound. In preliminary studies,[2] we characterized the penetration rate of such solvent inside HIPS materials. The diffusion of cyclohexane in the polymer was found to be comparable, if slightly slower than that of cyclopentane. The ingress of the standard cyclohexane (C_6H_{12}) was followed by MRI to check the absorption rate and the type of distribution in the HIPS1 (Table I) sample examined (Fig. 2). In the images shown, the bright circle is related to the solvent ingress inside the polymer rod section, while the polymer itself appears dark due to the lack of signal (short T_2). A careful selection of acquisition parameters allowed magnification of the solvent inside the polymer sample compared to bulk solvent itself outside (relaxation based contrast). Twelve hours were considered enough to get diffusion in about 70% of the sample area exposed. The relaxation measurements were performed with same procedure but using the deuter-

ated compound (C_6D_{12}). After 12 h, the external solvent was thoroughly removed, to minimize the effect of dissolved material on NMR signal. In fact, some polystyrene was found in the bulk liquid which acts as solvent for it and possible influence on NMR spectra was considered. Therefore, the polymer samples were carefully cleaned removing all solvent in excess. The static ^{1}H-NMR spectra relative to the HIPS1 sample (Table I), before and after solvent treatment, are shown in Figures 3(a) and 3(b), respectively. In spite of the large line broadening, determined by the non spinning acquisition and the low field instrument (85 MHz) a moderate peak resolution is still observed. In fact, the peaks of polybutadiene at approximately 2 and 5 ppm are distinguishable in the spectra. In the acquisition conditions adopted, which are typical of liquid state spectroscopy, only the soft rubber phase signal is reasonably recorded, due to the quite different signal decay of the "solid" PS phase characterized by a T_2^*, which is at least two orders of magnitude shorter than that of polybutadiene. The application of a CPMG type sequence allows determination of longer transversal relaxation times which is particularly suitable for the characterization of swelling effects on the rubber structure. Therefore, relaxation times were measured by selecting the two different peaks at 2 and 5 ppm and results compared to the measurements on the pure PB sample. NMR relaxation measurements on the solvent exposed samples show a significant increase in both T_1 and T_2 (Table II). This variation of relaxation times was also clearly observed on pure PB treated with
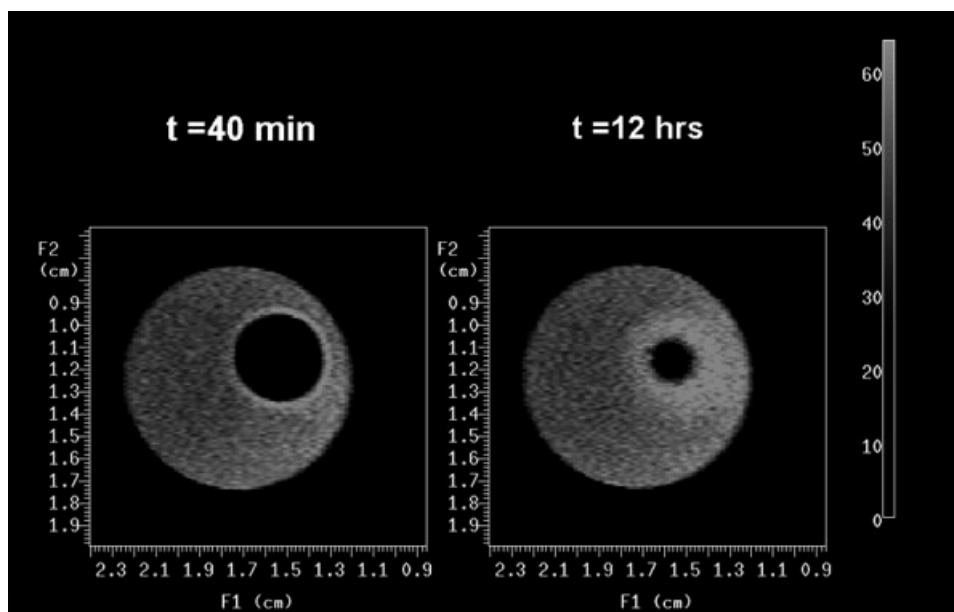
Figure 2 ^{1}H-NMR images of *in situ* diffusion of cyclohexane through HIPS rods (4 mm in diameter) at two different times ($t = 42$ min and $t = 12$ h). The images show at different steps the invasion of solvent (white) inside a transverse section of the polymer rod (black) immersed in a tube filled with standard cyclohexane (C_6H_{12}). ^{1}H-NMR imaging parameters (standard spin–echo sequence): 256 × 256 pixels, 128 phase encode steps, recovery time TR = 1 s, echo time TE = 6 ms, 2 scans, slice thickness = 0.5 mm, total experimental time = 4 min.

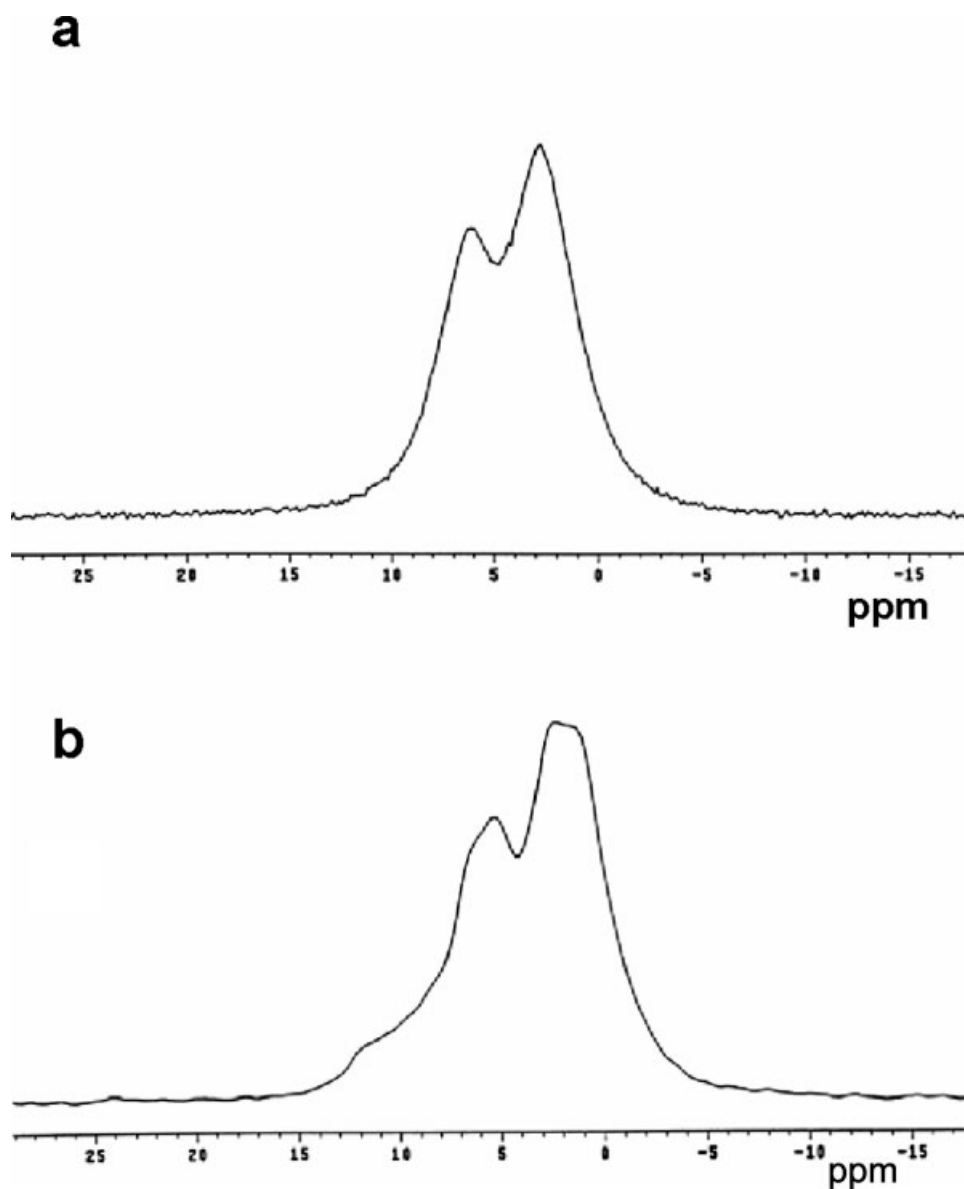**Figure 3** ^{1}H-NMR (85 MHz) spectra of the dry (a) and the C_6D_{12} exposed (b) HIPS sample.

cyclopentane (T_1 is doubled and T_2 is rather 40 times) as reported in Table II. This effect is mainly due to increased mobility of network chains, determined by swelling, which makes relaxation phenomena less efficient. The same effect was observed on T_1 measured on the composite polymer sample HIPS1 exposed to deuterated cyclohexane (C_6D_{12}) and is comparable to what was observed on pure PB. It is noticeable that T_1 and T_2 values of PB and HIPS are rather similar, because the NMR signal acquired on HIPS is almost completely due to the liquid-like rubber phase (more favorable signal decay). Therefore, variations in the relaxation times are certainly determined by network structural changes of the rubber, induced by solvent diffusion, confirming the penetration of the solvent in the rubber itself. Moreover, T_2 relaxation decay curves of the rubber phase in the HIPS1 sample signals $M(t)$ can be expressed using a sum of exponentials, according to eq. (1):

$$M(t) = \sum_{i=1}^{N} W_i(-t/T_{2i}) \qquad (1)$$

where N is the number of components, T_{2i} refers to the transversal relaxation times, and W_i refers to the constants related to the proton fractions. The results of this kind of fitting are graphically described in Figure 4 where the distribution of the T_2 components is plotted, clearly showing two large areas, centered around 5 and 100 ms respectively.

The physical explanation of this kind of model is very likely related to portions of PB experiencing a different surrounding and therefore dynamics. The two T_2 areas could be associated to PB swollen by the

TABLE II
T_1 and T_2 Relaxation Times Obtained by Single and Double Exponential (2-exp) Fitting on PB and HIPS Samples Dry and with Solvent Absorption

		Polybutadiene (PB)	PB + cyclopentane	HIPS	HIPS + C_6D_{12}	T_{2a}	(%)	T_{2b}	(%)
						HIPS + C_6D_{12} (2-exp fitting)[a]			
T_1 (ms)	2 ppm	158	1884[b]	175	390				
	5 ppm	151	446	176	455				
T_2 (ms)	2 ppm	6.8	–	7.1	–	6	76	105	24
	5 ppm	7.2	288	6.9	–	6	74	118	26

[a] Double exponential fitting (2-exp fitting) best approximates experimental decay.
[b] The high value of T_1 is determined by the contribution of overlapping cyclopentane.

solvent and the other not yet influenced by diffusion. The fractions of the two components are reported as percentage (%) in the last column of Table II. The percentage associated to the long T_2 component (T_{2b}) indicates therefore the amount of PB protons modified by the solvent. This amount (about ¼ of the total rubber protons) is reasonable considering the rather incomplete penetration of the solvent inside the sample as shown in the NMR imaging tests of Figure 2.

Study of crosslinked samples

Another set of T_1 measurements was performed at high field at the proton frequency of 300.13 MHz, using HCB as solvent. This solvent was chosen because it is known to diffuse thoroughly inside the polymer. This guarantees a complete contact between the whole polymer and the solvent. Several samples were obtained by curing the original polymer HIPS 1 at different times. The thermal treatment was applied at 200°C, under vacuum, for 2, 4, 8, 16, and 24 h. After annealing, the

sample was kept in contact at ambient temperature, for 16 h, with an equal amount in weight of HCB. These conditions fulfilled a complete absorption of solvent in the polymer. The thermal treatment, as well known, induces a crosslinking of the rubber chains, without affecting the styrene matrix. The proton spectra, acquired directly [Fig. 5(a)] on the original sample, before solvent contact, show a broad peak at about 4 ppm, due to the soft rubber phase and represent the olefinic and the aliphatic protons together (the two resonances were collapsed because peaks are too broad to be resolved). After solvent contact [Fig. 5(b)], the spectra show two peaks, one at about 7–8 ppm and the other at about 2 ppm. The HCB solvent gives mobility to all the system and the resonances could be assigned at 7–8 ppm for the aromatic styrenic units and at 2 ppm for the polybutadiene and the styrenic backbone protons. Figure 5 (c) and 5(d) show the spectra of the sample with 24 h of thermal curing, before (C) and after (D) contact with the solvent. Almost the same resonances are present. On the all samples thermally cured, T_1 for each peak were measured and the results are reported
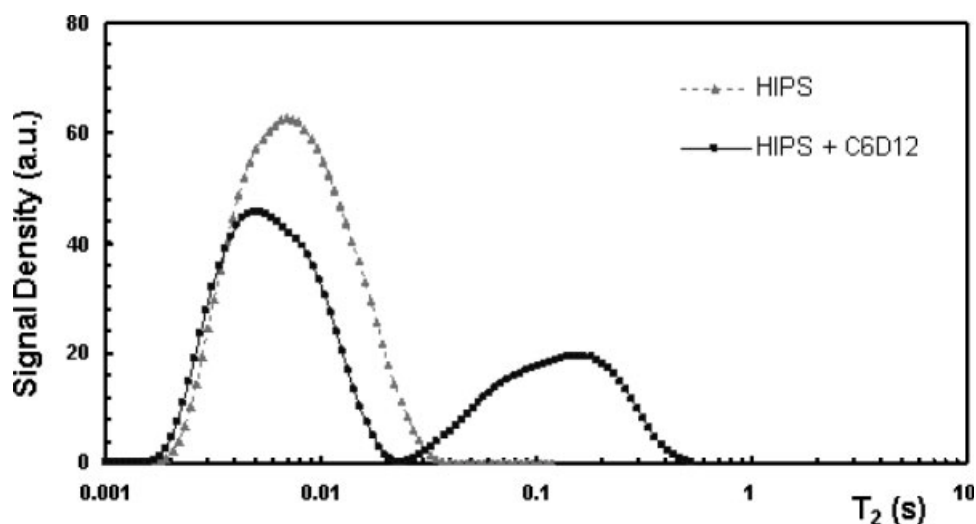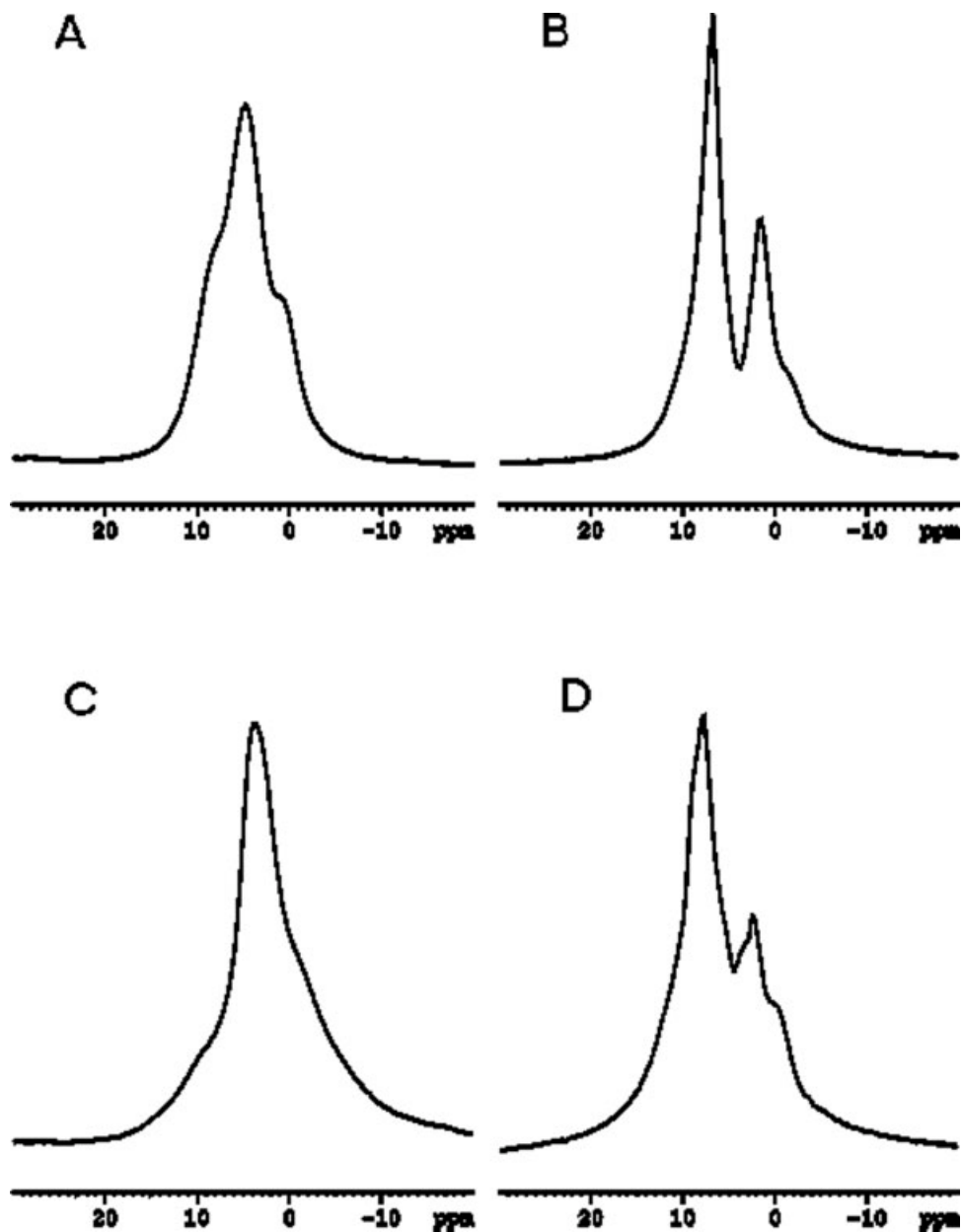

Figure 4 Distribution of the experimental transverse relaxation time (T_2) decay data on an HIPS sample before and after being exposed to deuterated solvent (C_6D_{12}). The continuous distribution model (processed with UPEN algorithm) showed the best fitting of the CPMG relaxation decay curve obtained after solvent exposition.

Figure 5 ^{1}H-NMR spectra of dry and exposed HIPS 1 samples (300.13 MHz): original sample before (A) and after solvent absorption (B), thermal cured 24 h sample before (C) and after solvent absorption (D).

in Table III. On the basis of these results, some observations can be drawn. In the dry samples, only the signal from the soft rubber phase is observable, in the instrumental conditions adopted, and the T_1 values became longer with the increase of thermally induced crosslink degree. After solvent absorption, also signal from polystyrenic matrix was observed. The T_1 values of the aromatic component (8 ppm) were almost constant, as expected, that means no significant variations were induced by annealing on polystyrene. On the opposite, the T_1 values of aliphatic component (2 ppm) were a composition of T_1 from polystyrenic backbone, which were constant, and from rubber, which vary with the crosslink degree (Fig. 6). Fitting the data by a linear

regression, as a guide for the eye, we can observe a higher intercept and a lower slope for solvent exposed samples than for dry samples. This behavior could be explained keeping in mind that the T_1 values of aliphatic components (2 ppm) in exposed samples, are averaged by the rubber protons, whose T_1 values are increasing with curing time and from styrenic backbone protons (greater and constant), resulting therefore in an higher intercept. The lower slope is an evidence of solvent interaction which enhances the mobility of rubber crosslinks and at the same time reduces the T_1 values if compared to the dry samples. In fact, T_1 measured on the dry samples showed a great variation (high slope) because of the reduced segmental mobility

TABLE III
T_1 Relaxation Times Obtained on HIPS1 Samples Dry and with Solvent (HCB) Absorption

Curing time (h)	Dry samples 4 ppm (ms)	+ HCB absorption	
		7 ppm (ms)	2 ppm (ms)
0	365	596	1130
2	392	630	1360
4	450	728	1400
8	508	709	1400
16	836	816	1480
24	1130	918	1310

determined by the increased degree of crosslinking. The choice of examining different crosslinked samples allowed to separate the effect of the solvent on polystyrene (equal on all samples) and on polybutadiene (differing in crosslink degree). The global results provide evidence of solvent absorption both from matrix and dispersed phase.

Spin probe ESR study

The spin-probe ESR technique has been applied to verify the solvent diffusion into both HIPS phases. The TEMPO spin probes were dissolved at low concentration ($3.2 \times 10^{-4}M$) in cyclopentane. The samples rods were dipped into the solution and the solvent was allowed to diffuse into the polymer overnight. It is assumed that the TEMPO molecules follow reasonably the diffusion of cyclopentane. A necessary condition to apply the spin-probe technique to our aim is that the ESR lineshapes of TEMPO molecules inside the rubbery PB and the plastic PS phases are different. To verify it, pure polystyrene and polybutadiene samples were used and, after solvent evaporation at 90°C for
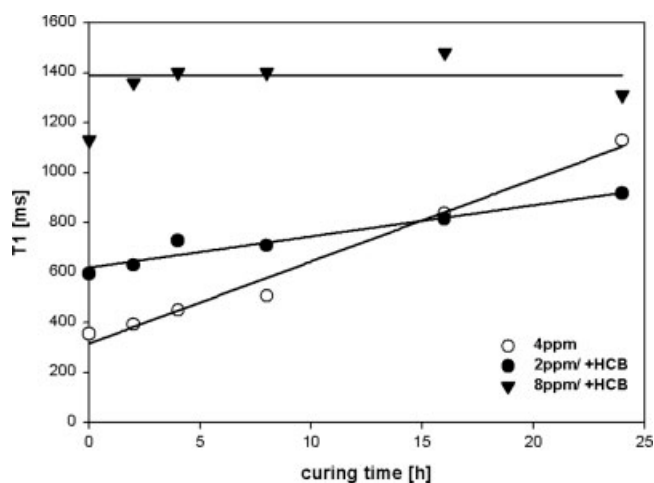
Figure 6 Proton T_1 of studied samples. The data relative to 4 ppm signal (empty circles), are collected on the dry samples. The data relative to 2 ppm and 8 ppm (filled circles and triangles), are collected on the wet samples, on the aliphatic and aromatic protons.

5 min, the ESR signals of entrapped TEMPO molecules were collected (Fig. 7). ESR signals of TEMPO in the two samples are quite different: the ESR signals are sharp and nearly isotropic in polybutadiene, which are typical of a fluid system, while the ESR signals are broader in the polystyrene due to a much more viscous matrix. The differences observed in the ESR lineshapes are caused by the dynamics of the spin-probe molecules which are determined by different "rotational correlation time" τ_R, defined as the time required for complete rotation of a radical about its axis. τ_R values vary from "fast motions" (10^{-11} to 10^{-9} s) to "slow motions" (10^{-8} to 10^{-7}s).[13]

With the assumption of isotropic Brownian motion, relatively precise values of τ_R in the range of 10^{-11} to 10^{-9}s can be estimated by using the following formula based on Kivelson's theory:[14]

$$\tau_R = 0.65 \times 10^{-5}\Delta B\left\{\left[\frac{I(0)}{I(-1)}\right]^{1/2} + \left[\frac{I(0)}{I(+1)}\right]^{1/2} - 2\right\} \quad (2)$$

where $I(-1)$, $I(0)$, and $I(+1)$ are intensities of low, central, and high field lines, respectively, and ΔB is the linewidth of the central line.

Applying eq. (2), the τ_R values of 9.5×10^{-12} s and 1.7×10^{-10} s for polybutadiene and polystyrene, respectively, were obtained. These values confirm a greater mobility of the polybutadiene matrix than of the polystyrene one.

The ESR spectra of entrapped TEMPO obtained, operating in the same way on the two HIPS samples reported in Table I in which the polybutadiene is 14% mol/mol, are shown in Figure 8. They show two overlapping signals due to TEMPO molecules in the polybutadiene (more mobile, sharper ESR signals) and in the polystyrene phases. By deconvoluting the ESR spectra, the TEMPO radical's molar percentage inside the polybutadiene phase was found nearly 20% for both HIPS samples. From the assumption that during solvent evaporation no migration of TEMPO molecules
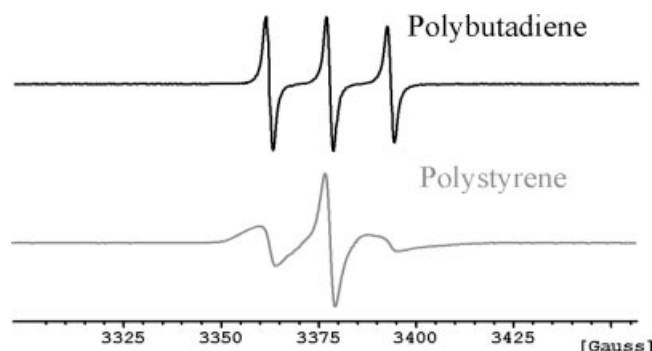
Figure 7 ESR spectra measured on standard polystyrene (PS) and polybutadiene (PB) samples with the spin probe molecule (TEMPO) entrapped.
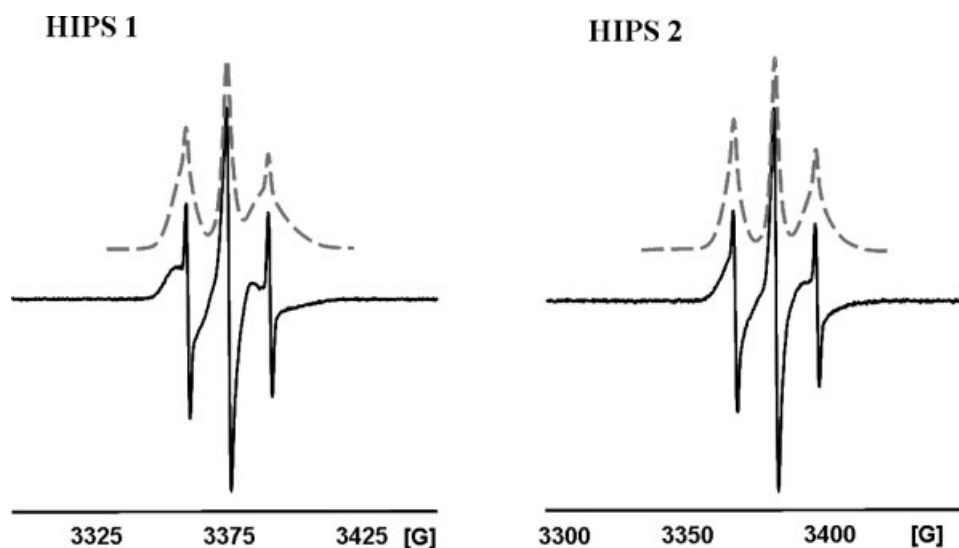
Figure 8 ESR spectra of two HIPS samples (HIPS1 and HIPS2) with the spin probe molecule (TEMPO) entrapped. The absorption spectrum is shown on the top as dashed line.

occurred, the molar percentage of TEMPO is a direct measure of the cyclopentane present in the rubbery phase. For this reason the percentage observed in the rubbery phase (nearly 20%) results higher than the molar rubber content (14%). This could indicate a slightly preferential diffusion of cyclopentane in the rubber than in the polystyrene matrix, confirming the NMR observation of a significant swelling of the rubber phase, as indicated by relaxation time measurements. The increased diffusion of cyclopentane in the rubber could be reasonably associated to its chemical affinity for the polybutadiene.

CONCLUSIONS

The application of different experimental techniques allowed the study of the interaction of hydrocarbon solvents with the rubber phase in composite polymers. The results obtained could confirm some of the hypothesis behind solvent diffusion in such materials. In fact, the hypothesis of the ingress of the hydrocarbon fluids inside the rubber phase, which is essential for designing new materials with high resistance, was not completely assessed previously by a clear experimental demonstration. The different magnetic resonance techniques provided a clear evidence of the interaction between the fluids and the PB phase. Moreover, a determination of the fraction of solvents in the different phases was also possible. These data indicate an appreciable diffusion of the hydrocarbons (cyclopentane and cyclohexane) inside the rubber phase. These fluids should act as solvents for the polystyrene phase (decreasing its T_g and softening the materials) and as swelling agents for the rubber

phase. In fact, this behavior would explain the dynamic changes found on the rubber phase as suggested by the consistent variation of the relaxation times (T_1 and T_2) of the PB protons. The swelling effect of the PB chains will cause an accumulation of hydrocarbons inside the cell-like rubber areas of the HIPS materials. The methods described here could be generally applied to characterize the behavior of fluids and their effect on composite materials.

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