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Monitoring the degradation of a thermally aged EPDM terpolymer by ^{1}H NMR relaxation measurements of solvent swelled samples

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Abstract

^{1}H nuclear magnetic resonance (NMR) relaxation times were investigated as a method for monitoring the degradation of polymeric materials. The properties of an ethylene–propylene–diene (EPDM) terpolymer, oven aged at 140°C, were first characterized by traditional mechanical and solution measurements including ultimate tensile elongation, tensile strength, tensile modulus, gel fraction, solvent uptake and density. The elongation and density results provided a characteristic lifetime for this material at 140°C. The other measurements demonstrated that the EPDM terpolymer undergoes predominately chain scission during the early stages of the degradation process and predominately cross-linking during the latter stages. ^{1}H NMR spin–spin relaxation times, T_2, of the solid polymer were insensitive to the degree of aging until the polymer was very heavily cross-linked after long exposure times. The ^{1}H NMR T_2s of the polymer swelled in deutero-chloroform were as sensitive to aging as any of the classical measurements cited above. The NMR measurements have the advantage of being rapid, requiring minimal amounts of sample and being applicable for unconventional sample forms such as films, foams and powders. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: EPDM terpolymer; Thermal oxidation; Degradation monitoring

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1. Introduction

Considerable effort has been extended to advance our scientific understanding of thermo-oxidative aging and stabilization against aging in polymers [1–9]. Increasingly sophisticated degradation monitoring methods are needed for developing a better understanding of the physical and chemical changes induced by the aging process. Desirable features of any analytical approach include such things as accessibility of the instrumentation, ease of sample preparation and measurement, and rapid analysis time. In addition, it is often advantageous to be able to make measurements on very small samples and/or on samples for which classical approaches may not be possible (e.g. mechanical property measurements on films, foams or powders).

It is well known that nuclear relaxation resonance (NMR) relaxation times are sensitive to the molecular dynamics of a polymer. Relaxation times have been traditionally used to investigate phase transitions attributed to both main chain and sub group motions. The frequencies probed range from hundred's of MHz (^{1}H and ^{13}C spin–lattice relaxation times, T_1) to kHz (^{1}H transverse or spin–spin relaxation times, T_2, and ^{13}C cross-polarization relaxation times, T_{1cp}) [10]. Changes in mechanical properties usually correlate most closely with the relaxation times controlled by low frequency dynamics that are reflective of main chain motions. Parker [11] and Marcinko [12] derived a relationship between the modulus of a polymer and its ^{13}C T_{cp} and demonstrated the relationship for a variety of polymeric materials. We have recently shown that this relationship can be used to monitor the thermal degradation of a hydroxy-terminated polybutadiene [13]. Although these measurements are quite sensitive to changes in the mechanical properties of the polymer, the experiments are lengthy and require approximately 200 mg of sample.

The goal of the work described in this paper was to develop a method that is not only sensitive to aging but is also rapid and uses minimal amounts of sample. The ^{1}H nucleus is employed because of the increased response of this nucleus compared to the ^{13}C nucleus with its low natural abundance. Simon et al. [14] have shown that the ^{1}H transverse relaxation time is a sensitive probe of cross-linking in polymer networks at temperatures well above their glass transition temperature. They derive an expression for the magnetization decay that includes a fast response from inter-cross-link chains and a slow response from the dangling chain ends. Menge et al. [15] adapted these

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equations to describe the transverse relaxation of solid and swollen poly(dimethylsiloxane) rubbers. Litvinov et al. [16] used transverse relaxation times to measure the cross-link densities of EPDM elastomers that had been prepared using various vulcanization conditions.

The transverse relaxation times of both solid and swollen samples of thermally aged EPDM elastomer were measured. The relaxation times of the solid samples showed little dependence on aging until the polymer was near the end of its useful life. When swollen, the dynamics of the polymer are a function of both the intra-molecular constraints provided by the cross-links and the relative polymer/solvent ratio. An increase in cross-link densities reduces the number of dangling chain ends and restricts the motion of the inter-cross-link chain segments. Both factors contribute to a reduction in segmental mobility. The ^{1}H NMR T_2 relaxation times of an EPDM terpolymer swollen in deuterated chloroform, exhibited greatly enhanced sensitivity to thermal aging. The relaxation times of the swollen sample show excellent correlation with traditional mechanical and solution property measurements.

2. Experimental

2.1. Material

The EPDM analyzed was an o-ring material, designated E529-60 by the manufacturer, Parker Seal and contained the normal commercial antioxidants and fillers. The o-rings had a cross-sectional diameter of 0.178 cm and an inner diameter of 3.78 cm.

2.2. Oven aging

Thermal aging of the EPDM terpolymer was carried out in temperature-controlled (±1°C stability), commercial, air-circulating aging ovens equipped with thermocouples connected to continuous strip chart recorders under ambient atmospheric conditions (~630 mm Hg in Albuquerque).

2.3. Tensile strength and elongation

Tensile tests (5.1 cm initial jaw separation, 12.7 cm/min strain rate) were performed on o-rings that had been cut once so that they could be pulled as cylindrical specimens of approximately 12.0 cm original length. The tests were conducted on an Instron 1000 tensile testing machine equipped with pneumatic grips; an extensometer clamped on the sample allowed ultimate tensile elongation values to be obtained.

2.4. Modulus measurements

Modulus profiles with a resolution of ~50 μm were obtained on aged samples using a computer-controlled, automated version of our modulus profiling apparatus, which has been described in detail previously [17]. This instrument measures tensile compliance. The inverse of the tensile compliance, D^{-1}, which is closely related to the more commonly measured modulus for viscoelastic materials and is precisely equivalent for elastic materials is reported for convenience. For each aging condition, five measurements of were taken at random locations on the o-ring cross-sections and the average value reported. Typical scatter was $\sim \pm 10\%$ for D^{-1} values below 20 MPa and $\sim \pm 20\%$ above 30 MPa.

2.5. Solvent uptake and gel fraction

Solvent uptake measurements were carried out by first exposing a known weight of sample (w_0) to refluxing *p*-xylene for a minimum of 24 h. The sample was quickly recovered from the hot solvent and the weight of the swollen rubber (w_s) determined. The final weight w_f was determined after drying the swollen sample under vacuum. The solvent uptake factor is defined as the ratio of w_s to w_f. The percent gel is given by the ratio of w_f to w_0.

2.6. Density measurements

Density measurements were made using the Archimedes approach, where the sample (typically 50 mg) is weighed in air and then in isopropanol on a balance with a reproducibility of better than 10 μg [18,19].

2.7. NMR experiments

The ^{1}H relaxation times of the solid polymers and $CDCl_3$ swelled polymers were measured on a Bruker DRX spectrometer at 399.9 MHz using a 5 mm broadband solution probe. The T_2 relaxation times were measured using a spin–echo pulse sequence [20] consisting of $\{90° — \tau — 180° — \tau — \text{acquire}\}$ with a 90° pulse-width of 7.5 μs. The τ values ranged from 0.02 to 0.6 ms for the solid samples and from 0.1 to 20 ms for the swollen samples. The relaxation delay was 4 s and eight scans were accumulated for each τ value. The ratio of polymer to $CDCl_3$ for the solvent swelling experiments was 1:9 on a w/v basis. The samples were allowed to equilibrate overnight. These conditions yielded results that were independent of exact solvent concentration since a clear excess of solvent could be visually observed for each of the samples.

3. Results and discussion

A common property used to follow the degradation of elastomeric materials is the ultimate tensile elongation. Fig. 1a shows elongation results for the EPDM material versus aging time at 140°C. The mechanical lifetime of this sample is on the order of 80–90 days. Since monitoring properties beyond a material's mechanical lifetime is of little practical use, this study is limited to the first 90 days of exposure. When thermally aged at 140°C, the EPDM

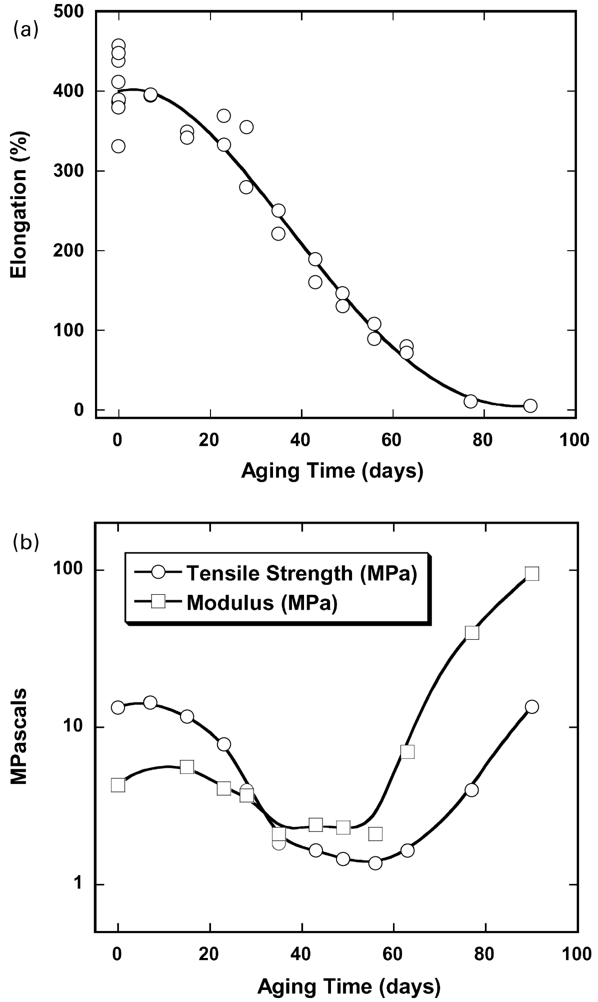

Fig. 1. The (a) ultimate tensile elongation and (b) tensile strength and modulus of an EPDM terpolymer vs. aging time at 140°C.

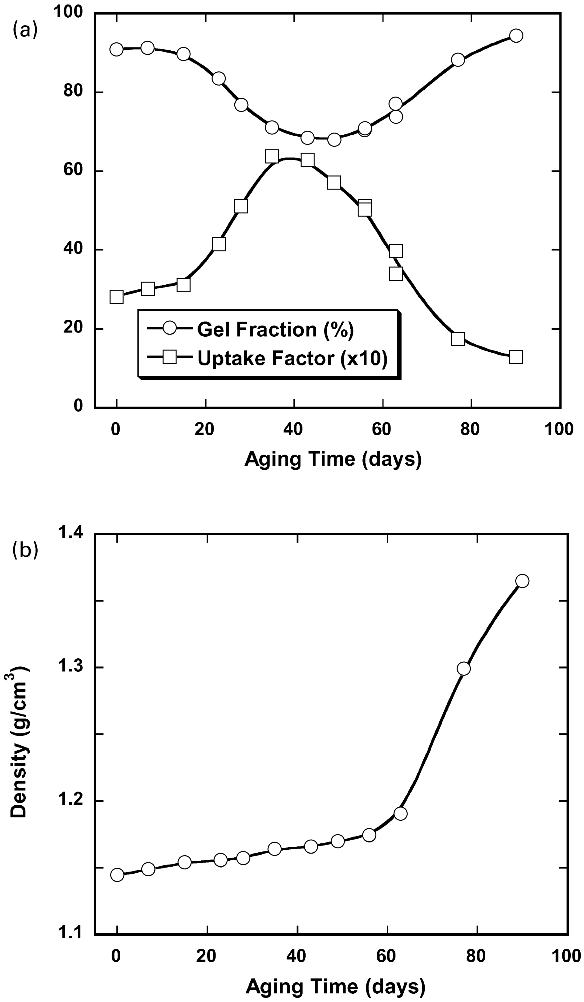

Fig. 2. The (a) gel fraction and uptake factor and (b) density of an EPDM terpolymer vs. aging time at 140°C.

terpolymer undergoes both chain scission and cross-linking. The competing role of these two mechanisms can easily be seen from the mechanical properties presented in Fig. 1b. This figure shows the tensile strength and modulus of the EPDM terpolymer vs. aging time at 140°C. Both quantities display a decreasing trend from 0 to 50 days associated with chain scission processes. From 50 to 90 days, the tensile strength and modulus show an upward trend associated with cross-linking processes. The competition between chain scission and cross-linking is comparable to that reported in the literature for a polybutadiene aged in air at 130°C [21]. The overall changes in the properties of EPDM for each stage of the aging process are substantial.

The solution properties, represented by the gel fraction and the solvent uptake factor in Fig. 2a, confirm that chain scission followed by chain cross-linking dominate the aging process for short and long aging times, respectively. The density, shown in Fig. 2b, increases slowly for the first 60 days and then increases dramatically from 60 to 90 days. Oxidation of polymers normally leads to density increases due to the introduction of higher density oxidation groups with time [22]. In addition, cross-linking processes normally lead to sample shrinkage and therefore represent a second mechanism contributing to density increases [23]. For similar reasons, one would expect that scission processes would lead to volume expansion and therefore density decreases. These expectations, coupled with the results in Figs. 1b and 2a, are clearly consistent with the density results of Fig. 2b. For the first 50 days of aging, density increases caused by incorporation of oxidation species appear to slightly dominate density decreases caused by chain scission. After approximately 50 days, cross-link processes dominate the scission processes, and the combination of two density-increasing effects leads to a rapid increase in density with aging time.

The early time behavior of the mechanical and solution properties, represented by 0–14 days of aging, does not provide clear evidence for the direction or extent of aging. The tensile strength, Fig. 1b, and solution properties, Fig. 2a, however, provide a clear indication that chain scission has occurred when the samples have been aged for 23 and 28 days. A useful measure of polymer aging, based on NMR

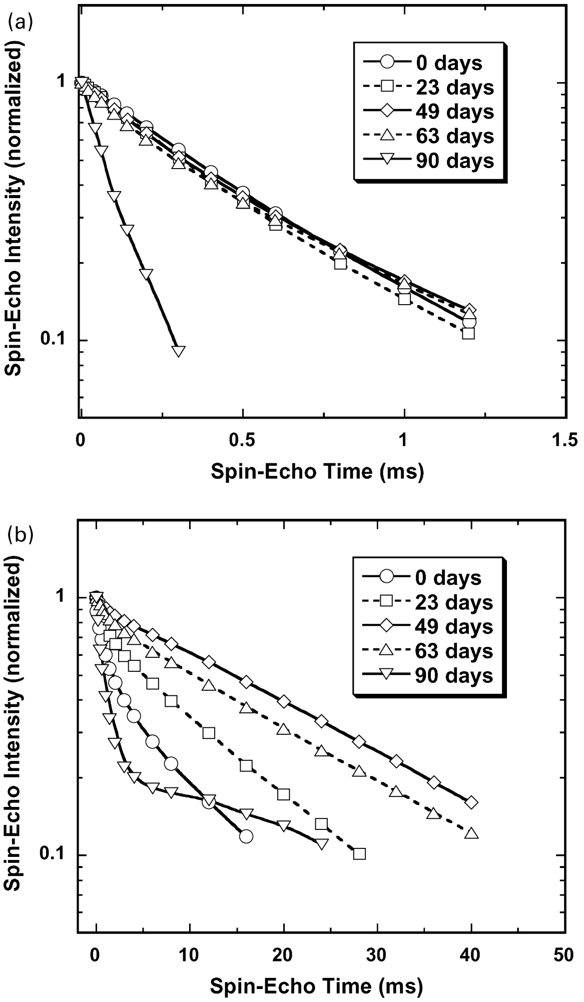

Fig. 3. The ^{1}H NMR spin–echo decay curves of an EPDM terpolymer aged at 140°C for 0, 23, 49, 63 and 90 days: (a) solid and (b) swelled in deuterochloroform.

relaxation, would need to exhibit sensitivity to these levels of aging. In addition, we would expect that the relaxation measurements would reach an extreme before reversing itself for aging times longer than 50 days.

Fig. 3a shows the ^{1}H NMR spin–echo decay curves for an unaged EPDM sample and for EPDM samples aged 23, 49, 63 and 90 days. Little difference in the shape or rate of decay of these samples is observed except for the sample aged 90 days, at the end of the useful life of the material. Chain scission processes during the early stages of degradation are expected to increase chain mobility and increase the relaxation time. No evidence of this behavior is seen. The expected changes in mobility caused by chain scission and cross-linking events are only evident for the spin–echo decay curve of the sample aged for 90 days. A quantitative analysis of the spin–echo decay curves for all of samples will be presented later in this paper.

Fig. 3b shows the spin–echo decay curves for the same five samples that have been swollen in $CDCl_3$. Substantial differences in both the shape and rate of decay of the spin–echo curves are observed as a function of aging time. Up to and including 49 days, the decay rate of the spin–echo decreases, corresponding to increased mobility. The increased mobility is attributed to fewer constraints since many of the chains have been severed. In addition, the local viscosity experienced by the polymer chain decreases since it swells to a greater extent and behaves as a more dilute solution. The decay rates of the samples aged for 63 and 90 days increase, corresponding to decreased mobility as the chains are becoming more heavily cross-linked. All of the curves are nonexponential and cannot be fit by a simple exponential decay function.

We wanted to extract a single number from each of the curves that would quantitatively characterize the extent of aging and would not be dependent on the fitting model. To accomplish this, the times for the signals to reach 1/*e* of their initial values were calculated as described in Section 2.

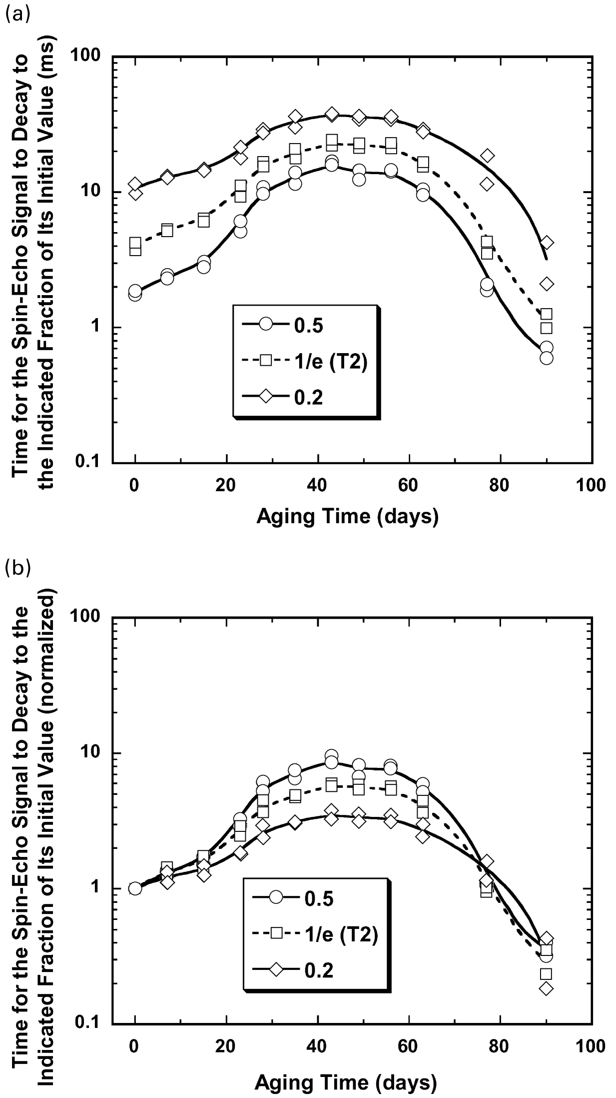

Fig. 4. The (a) absolute and (b) normalized times for the ^{1}H NMR spin–echo signal to decay to various fractional losses as a function of aging time at 140°C.

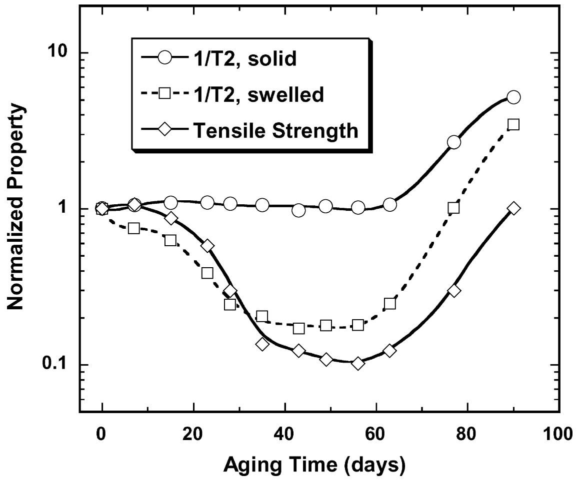

Fig. 5. Comparison of the inverse of the normalized ^{1}H NMR T_2 (solid and swollen) with the normalized tensile strength as a function of aging time at 140°C.

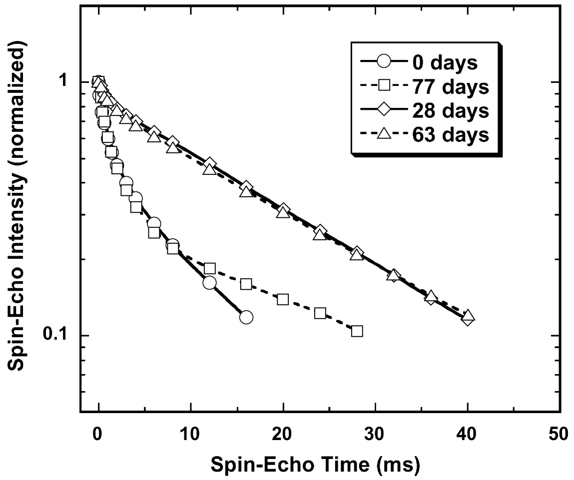

Fig. 6. Comparison of the entire spin–echo decay curves for two sets of samples (0, 77 and 28, 63 days) that exhibit equivalent ^{1}H NMR T_2 in the early and late stages of degradation.

Fig. 4a shows the results of these calculations as a function of aging time. These measurements were performed twice using a separate sample for each measurement in order to illustrate reproducibility. In addition, the times for the signals to decay to 0.5 and 0.2 of their initial values were calculated. These calculations are also shown in Fig. 4a. The normalized values for each of these measurements are shown in Fig. 4b. Although the sensitivity to aging decreases modestly as the signal fraction is reduced from 0.5 to $1/e$ to 0.2, the character of the behavior remains the same. We have standardized on the value of $1/e$ for the remaining discussion, defining T_2 as the time required for the spin–echo to reach $1/e$ of its initial value.

Fig. 5 shows a comparison of the normalized relaxation rate of both the solid and solvent swelled samples with the tensile strength as a function of aging time. The relaxation rate (inverse of the relaxation time) was employed so that the trends caused by chain scission and cross-linking would track that of the tensile strength. Little change was observed in the relaxation rate of the solid sample except for a small increase early in the aging process and a substantial increase when the polymer has approached the end of its lifetime. Excellent correspondence is observed, however, for both the direction and magnitude of the changes in the relaxation rate of the swollen sample as a function of aging time. It is also worth noting that the NMR relaxation rate appears to show more sensitivity to aging in the first 14 days than does the tensile strength or the other traditional measurements shown in Figs. 2 and 3.

A single value of the NMR spin–echo decay time or the tensile strength may correspond to two distinct aging times. For example, the $1/e$ times for the spin–echo of the unaged sample and of the sample aged for 77 days are similar. The time for the spin–echo decay to reach $1/e$ of its initial value is a simple quantity used to characterize a complex relaxation curve. Other characteristics of the NMR relaxation curve were examined in order to determine if they could be used to determine if a sample was in the early or latter stages of degradation. Pairs of samples (0 and 77, and 28 and 63 days) that had similar $1/e$ values were selected. These pairs are plotted in Fig. 6 These curves show little difference in their shape or decay rates except for the very long time behavior of the samples aged for 0 and 77 days. Since the long-time behavior is difficult to measure accurately and is subject to more uncertainty, this issue was not pursued.

The fast and slow components of the spin–echo decay curves are suggestive of a two-phase system. Solvent extraction experiments have shown that the EPDM terpolymer consists of soluble and gel components. It is appealing to assign the faster decaying component to the gel phase and the slower decaying component to the soluble phase. To assess the validity of such an assignment, the spin–echo decay curves were fit to the sum of two exponential components. The fraction of intensity attributed to the fast component is shown in Fig. 7 along with the gel fraction as a function of aging time. Both measurements show an initial decrease followed by an increase. This behavior is expected for a material that undergoes chain scission followed by cross-linking. The fraction of fast component is much less than the gel fraction for all aging times although it undergoes a larger change as a function of aging time than does the gel fraction. Because of this observation, we conclude that a simple 1:1 correspondence between the fast decaying component and the gel fraction does not exist. A detailed analysis by Simon et al. [14] describes the nonexponential behavior of a polybutadiene material in terms of a combination of contributions including a nonexponential component from the inter-cross-link chains, an exponential component with an intermediate relaxation time from the dangling ends and an exponential component with a very long relaxation time from the sol molecules.

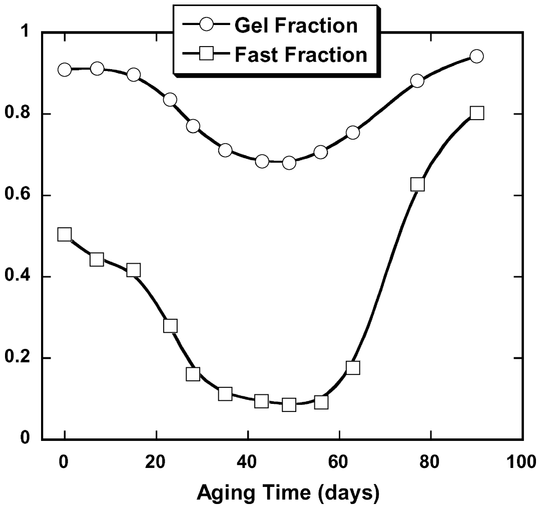

Fig. 7. Comparison of the rapidly decaying fraction of the spin–echo decay curve with the gel fraction of the EPDM terpolymer as a function of aging time.

An advantage of ^{1}H NMR relaxation measurements is the ability to measure very small samples. The previous results utilized 10 mg samples and eight scans for each delay time. The eight scans are used in order for the instrument to complete the phase cycling of the pulse sequence and minimize spectral artifacts. Much smaller samples, however, can be analyzed. Fig. 8 compares the spin–echo decays of 10 and 0.1 mg samples. The spin–echo decay of the 0.1 mg sample used a single scan per delay time in order to test the limits of detection. The two measurements provide nearly equivalent results for the first 1/*e* portion of the decay that is used for analysis. These measurements demonstrate that, if necessary, even much smaller samples could be analyzed. Recording 8 scans would provide a factor of $(8)^{1/2}$ or 2.8 times more signal-to-noise. In addition, a normal 'X' band probe with ^{1}H observed on the decoupling channel was used for these experiments. Sensitivity can be increased by a factor of 2 if a dedicated ^{1}H or inverse probe were used. These two modifications would enable samples of 20 μg to be measured with the same sensitivity as that shown for the 0.1 mg sample. Samples smaller than 0.1 mg may require handling and preparation by microscopic techniques. It is difficult to keep the polymer ratio at 1:9 w/v ratio for very small samples because of rapid solvent evaporation. For this reason, the 0.1 mg sample was measured with a large solvent excess. These experiments required the use of high purity $CDCl_3$ (99.96% D) to prevent interference from residual $CHCl_3$ signal.

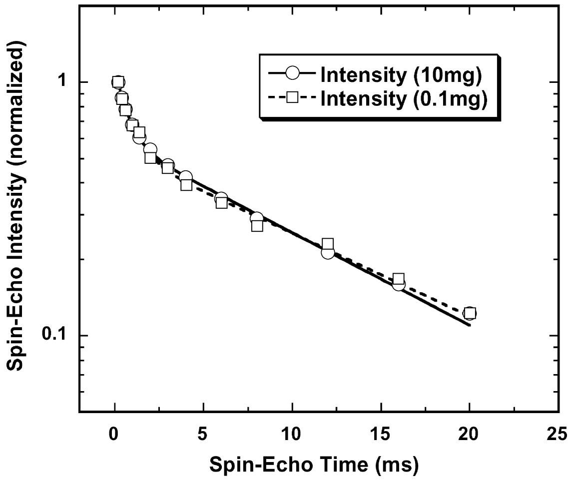

Fig. 8. The spin–echo decay curves for EPDM samples weighing 10 and 0.1 mg. Eight scans at each delay time were recorded for the 10 mg sample while a single scan at each delay time was recorded for the 0.1 mg sample.

Perhaps more important than the ability to measure samples smaller than 10 mg is the ability to perform these measurements on less sensitive and thus less expensive and more portable instrumentation. The factor of 500 (10 mg/20 μg) increase in sensitivity implies that much lower magnetic fields can be employed. Spectrometers based on permanent magnets operating in the 20–40 MHz range should be adequate for these measurements.

4. Conclusion

Swelling enhanced ^{1}H NMR T_2 relaxation measurements provide a rapid degradation monitoring tool for the thermal degradation of an EPDM terpolymer. Its sensitivity to thermal aging is comparable to that of conventional mechanical and solution property measurements. In additional to requiring minimal amounts of sample, the approach can easily be adapted to nonconventional sample forms such as films, foams and powders.

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