

^1H T_2 -NMR Monitoring of Crosslinked Polyolefin Aging

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ABSTRACT: This work examines the correlation between the ^1H -NMR T_2 relaxation constant and the mechanical properties of aged crosslinked polyolefin cable insulation. T_2 experiments on unswollen samples could not differentiate between unaged and highly aged materials; all exhibited ^1H T_2 constants of approximately 0.5 ms. To accentuate the effects of aging, samples were swollen in various solvents. Unaged samples had T_2 values of approximately 15 ms in good solvents. With thermal aging, T_2 values decreased as

the ultimate tensile elongation decreased. However, the correlation between T_2 and elongation differed for samples irradiated with high-energy radiation and for materials aged above versus below the crystalline melting temperature. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2578–2582, 2003

Key words: NMR; polyethylene (PE); polyolefins; degradation; irradiation

INTRODUCTION

Accelerated aging of polymers¹ allows prediction of service lifetimes (often many decades) from data obtained in a reasonable time period. Mechanical techniques, such as tensile testing, provide the most applicable results but usually are destructive and require large samples. This is often unacceptable for condition monitoring where nondestructive testing of materials under active service conditions must be performed. Several methods have been used to study polymer degradation in crosslinked polymers including density,^{2,3} gel content,³ and solvent uptake. These techniques, however, currently suffer from several disadvantages including long experimental measurement times and the need for a relatively large sample size (10's to 100's of milligrams).

NMR spectroscopy has several potential advantages for quantifying polymer degradation including improved reliability, reduced use of hazardous solvents, and shortened experiment time. Some of these advantages were illustrated by recent work^{4–14} on transversal ^1H -NMR relaxation (T_2) for characterizing structural and motional parameters in polymer networks at temperatures well above the glass transition temperature, T_g . Specifically, both theoretical and experimental results showed that crosslinks result in anisotropic segmental motions and, thus, a nonzero average of dipolar cou-

pling despite fast dynamics.¹¹ The high motional rates assumed in the data analysis can be achieved experimentally by swelling the gel with a good solvent.¹³ The degree of swelling is dependent on both the chemical structure of the network and the polarity of the solvent.^{14,15} Other articles have described successful determination of the crosslink density by analyzing the residual ^1H dipolar interactions in dry and swelled natural rubber,^{6–8,10,12} butadiene rubber,^{5,8,9} styrene–butadiene rubber,¹¹ and crosslinked poly(dimethyl siloxane).^{4,8,13}

The goal of this research was to ascertain parameters that are necessary to design effective ^1H - T_2 NMR experiments for monitoring crosslinked polyolefin cable insulation degradation. The procedure was then applied to study materials subjected to accelerated thermal aging or irradiation. Finally, the NMR results were correlated to ultimate elongation and solvent-uptake values.

EXPERIMENTAL

Materials

The material studied in this research was crosslinked polyolefin cable insulation commonly used in power cables. The thermal–mechanical properties of this material have been reported previously.³ The flame retardants were antimony oxide in combination with chlorinated and brominated organics (dodecachloro–dodecahydro–dimethano–dibenzo–cyclooctene, and decabromo–diphenyl ether). A small amount of TiO_2 was also present. The XPLO content of the insulation was estimated to be approximately 65%. FTIR identified the polymer matrix as an ethylene–vinylacetate copolymer. Samples were aged in convection ovens at temperatures of 100, 110, 125, and 152°C. Other sam-

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ples were subjected to ^{60}Co radiation with a dose rate of 200 Gy/h at ambient temperatures.

DSC

The melting characteristics were investigated using a Perkin-Elmer Model DSC-7 after calibration with an indium standard. A sample weighing of 15.9 mg was sealed in an aluminum pan and analyzed with a scanning rate of $10^\circ\text{C}/\text{min}$.

Mechanical testing

Tensile tests were performed with an Instron table model testing machine (Model 1000) equipped with pneumatic grips and an extensometer. The initial crosshead separation was 5.1 cm and the strain rate was $12.7\text{ cm}/\text{min}$.

^1H T_2 -NMR measurements

Approximately 10 mg of each sample was placed in 5-mm NMR tubes. The polymers were then swelled with $100\ \mu\text{L}$ of various solvents. The following deuterated solvents were used with solubility parameters, δ , ranging from 7.4 to 12.0 (cal/cm^3) $^{1/2}$: heptane- d_{16} , $\delta = 7.4$; methyl cyclohexane- d_{14} , $\delta = 7.8$; cyclohexane- d_{12} , $\delta = 8.2$; toluene- d_8 , $\delta = 8.9$; benzene- d_6 , $\delta = 9.2$; chlorobenzene- d_5 , $\delta = 9.5$; nitrobenzene- d_5 , $\delta = 10.0$; acetic acid- d_4 , $\delta = 10.1$; acetonitrile- d_3 , $\delta = 1.9$; and dimethyl sulfoxide- d_6 , $\delta = 12.0$. In addition, benzene mixtures containing 10, 20, 30, and 40 vol % acetonitrile were used to swell the insulation.

The ^1H spectra were obtained on a Bruker DRX400 operating at a frequency of 399.9 MHz. The 5-mm HX probe was heated to 70°C and samples were allowed to equilibrate for 5 min prior to the start of the experiments. Greater amounts of solvent or longer swelling times were shown to have no impact on the relaxation curves. The Hahn spin-echo pulse sequence, $90-\tau-180-\tau\text{-acq}$, was used to determine the relaxation rate. Four scans (plus two dummy scans) with a recycle delay of 2 s were acquired for each value of τ . The relaxation curve was calculated using 16 echo times ranging from 0.1 to 10 ms. The Bruker routine "abs2" corrected the baseline of each spectrum. The chemical shifts of the spectra were referenced to the small solvent peak. For each echo delay, the integral between -10 and 20 ppm was determined. The echo time dependence of the integrated signal area was nonexponential, as observed in a previous article.¹³ We, therefore, arbitrarily defined T_2 as the value $I_{2\tau} = I_0/e$, where $I_{2\tau}$ is the signal area after a Hahn echo time of τ . The initial signal area, I_0 , was determined by logarithmically extrapolating the shortest three echo lengths to time zero. The value of T_2 was calculated by linear extrap-

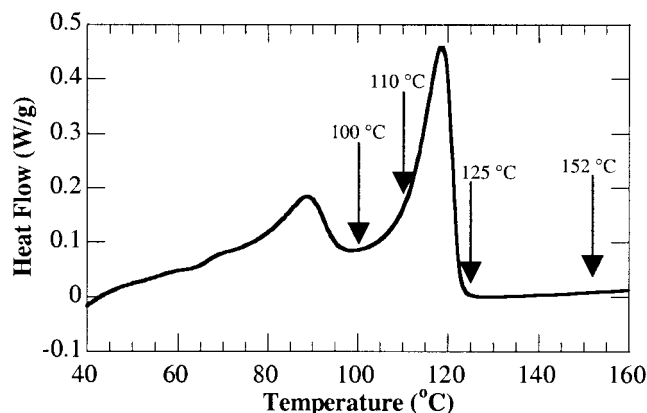


Figure 1 DSC scan of unaged cable insulation. The arrows show the temperatures used in the aging study.

olation between the values of 2τ that provided signals spanning I_0/e .

RESULTS AND DISCUSSION

The DSC scan of the unaged material (Fig. 1) shows a broad melting behavior with maxima at 88 and 119°C . The temperatures used in the thermal-aging study are marked on the trace with arrows. The two lowest aging temperatures (100 and 110°C) lie below the peak melting transition, while the insulation is completely amorphous in the 125 and 152°C experiments. The significance of the melting transition on the aging behavior is shown later in this article.

In the absence of a solvent, both aged and unaged samples exhibited similar T_2 relaxation constants. The measured values were 0.52 , 0.49 , and 0.51 ms for samples aged 0, 1540, and 2353 days, respectively. The invariant values are in stark contrast with the decrease in ultimate elongation from 310% for the unaged sample to 46% for the samples aged for 2353 days. The NMR relaxation measurements are therefore insensitive to aging for unswollen samples.

Swelling with a good solvent proved very useful to achieve fast chain dynamics and to accentuate the differences between unaged and aged samples. The degree of swelling in refluxing benzene was gravimetrically determined for unaged insulation and samples aged 1540 and 2353 days at 110°C to be $Q = 4.6$, 2.0 , and 1.5 , respectively. The swelling resulted in a narrowing of the peak in the ^1H spectrum of the cable insulation (Fig. 2). The signal from an unaged sample [Fig. 2(b)] has a full-width at half-maximum (fwhm) of 0.3 kHz due to increased motional averaging of dipolar interactions. Without swelling [Fig. (2)a], the fwhm is 2.5 kHz. More highly aged material swelled by benzene- d_6 [Fig. 2(c,d)] exhibited intermediate line widths of 1 kHz due to a lower degree of swelling and higher crosslink density.

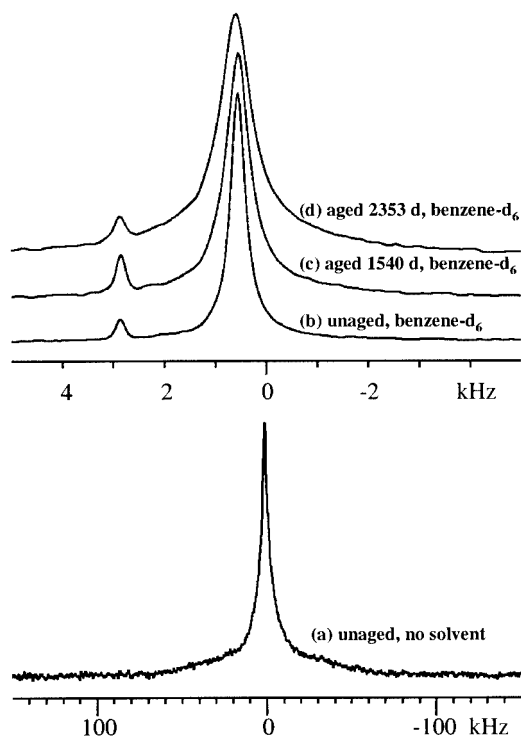


Figure 2 ^1H spectra of unaged and unswollen crosslinked polyethylene cable insulation: (a) spectra of samples swelled in benzene- d_6 at 70°C for 5 min are shown for (b) unaged, (c) aged 1540 days at 110°C , and (d) aged 2353 days. The peak at 2.9 kHz is from benzene.

The ^1H line width of spectra obtained with Hahn echoes remained constant but the peak area monotonically decreased with the delay time. The T_2 relaxation curves for samples swelled in benzene- d_6 are shown in Figure 3. Although the decays are nonexponential, the

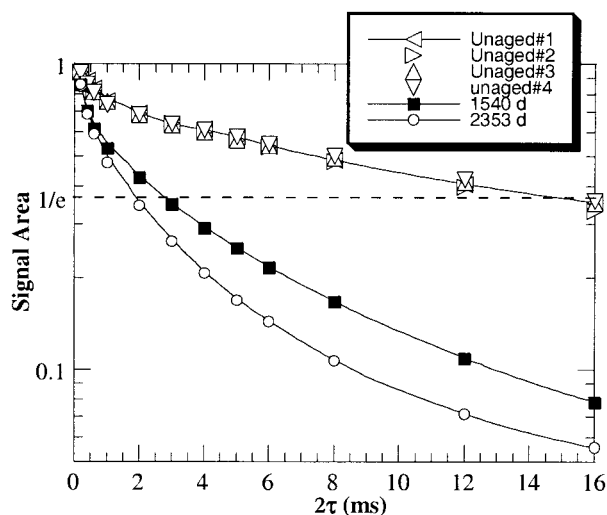


Figure 3 Comparison of ^1H T_2 relaxation curves for unaged cable insulation and samples aged at 110°C . The spectra were obtained after the material was swelled in benzene- d_6 for 5 min at 70°C . The lines are guides for the eye.

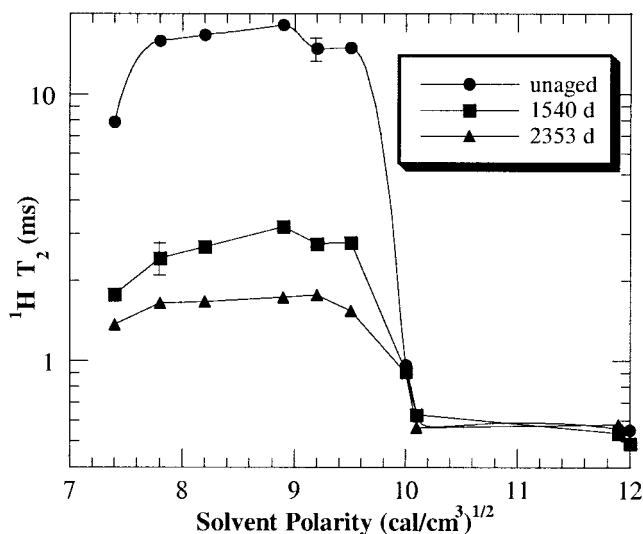


Figure 4 Dependence of ^1H T_2 relaxation constant on solvent polarity constant. All spectra were acquired at 70°C . The T_2 value of the nonexponential decay is arbitrarily defined as $I_{2\tau} = I_0/e$. The two symbols with error bars represent the 95% confidence interval based on four replicate experiments.

curves for aged samples lie below the unaged values at all echo times. As seen in the decay plot, the selection of $I_{2\tau} = I_0/e$ as the criterion for determining T_2 achieves superior accuracy and precision for quantifying the degree of degradation. The technique also has excellent reproducibility. Relaxation curves for four unaged insulation samples swelled in benzene- d_6 showed the 95% confidence intervals to be 14.8 ± 0.8 ms. The uncertainty under other conditions was also determined from four replicate experiments: 2.4 ± 0.4 ms for 1540-day insulation swelled in methyl cyclohexane- d_{14} and 0.58 ± 0.02 ms for 2353-day insulation swelled in acetonitrile- d_3 .

A good solvent is necessary to achieve optimal separation of the T_2 values for unaged and aged material. All solvents with polarities in the range of $7.8 < \delta < 9.5$ are effective solvents for both aged and unaged samples. The T_2 value of the swelled unaged insulation at 70°C was near 15 ms for all solvents in this polarity range, as shown in Figure 4. The maximum observed value was 18.1 ms for insulation in toluene- d_8 . The relaxation constant of aged materials in the solvents also reached plateau values in the same polarity range and again reached a maximal value in toluene- d_8 . Thus, all solvents in this range are approximately equal for quantifying polymer degradation. Poor solvents with polarities outside the optimal region are not as suitable for quantifying degradation because the differences between aged and unaged materials are decreased. Solvents more polar than chlorobenzene, $\delta > 9.5$, were all poor solvents for the insulation and the value of T_2 decreases precipitously to 0.9 ms for unaged insulation in nitrobenzene. For

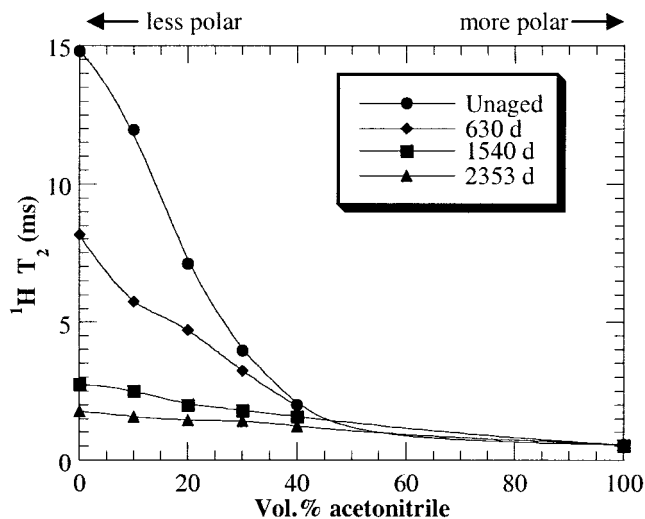


Figure 5 ^1H T_2 of unaged and aged cable insulation at 110°C swelled in benzene- d_6 and acetonitrile- d_3 mixtures. All samples showed similar trends. Lines are guides for the eye.

even more polar solvents, T_2 decreases to 0.5 ms, which is equal to the value obtained for dry samples.

These observations imply that the polymer polarity does not significantly increase after oxidative degradation. If a change occurred, there might be polar solvents that were effective solvents for aged material but poor solvents for unaged samples. Thus, aged samples might exhibit longer relaxation constants than those of unaged samples. Mixtures of benzene- d_6 ($\delta = 9.2$) and acetonitrile- d_3 ($\delta = 11.9$) provided access to an important polarity range to further support the hypothesis of unchanging polymer polarity. The T_2 values observed for samples swelled in the binary solvent system are shown in Figure 5. The mixtures are all moderate or poor solvents for both aged and unaged solvents. The T_2 relaxation constants for all insulation samples decreased approximately linearly with an increasing concentration of acetonitrile- d_3 . At all acetonitrile concentrations, more highly aged samples exhibited shorter relaxation constants. The change of polymer polarity appears to be insignificant during aging.

On the basis of a high degree of swelling and low cost, benzene- d_6 was selected as the standard solvent for further investigations. The measured T_2 values for cable insulation thermally aged at 100, 110, 125, and 152°C are shown in Figure 6. The curves for thermally aged insulation show a large decrease in relaxation constants as the material becomes more degraded. The measurements for irradiated samples are also shown in the graph but show different trends. The samples have a significant initial change in T_2 value, but T_2 only slowly decreases during extensive irradiation. The lack of change might be related to the observation that the gel content exhibits only small variations after irradiation.³

The T_2 relaxation constants were compared with the ultimate elongation values (Fig. 7). If the material

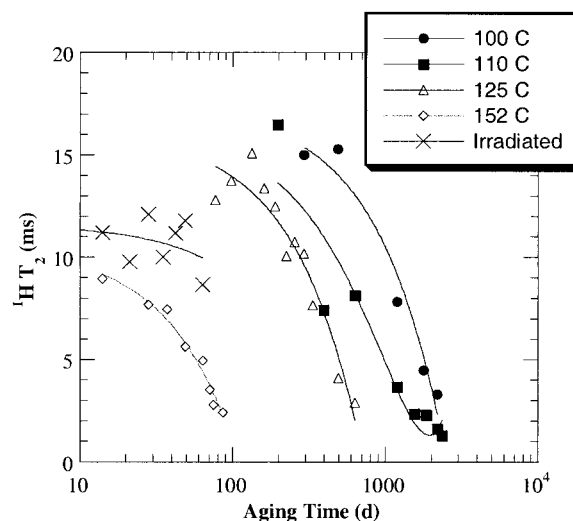


Figure 6 Dependence of ^1H T_2 on aging time. Irradiated samples were subjected to 200 Gy/h at 22°C .

obeyed time-temperature superposition,¹ accelerated aging would result in identical changes to all material properties. Comparison of any two properties should fall along the same curve regardless of aging conditions. The samples aged at 100 and 110°C follow a similar curve, suggesting a relationship between increased crosslink density in the NMR experiments and loss of mechanical strength. The overlap of curves also suggests that time-temperature superposition may be applicable for cable insulation aging below 110°C . When the ultimate elongation for a material aged at these lower temperatures is approximately half the initial value ($\sim 150\%$), the T_2 value has decreased by a

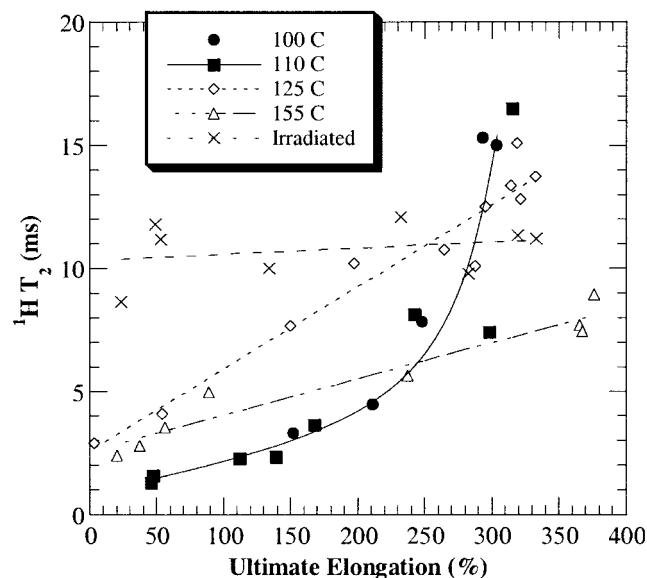


Figure 7 Correlation of ^1H T_2 and ultimate elongation for thermal aging at the indicated temperatures and for 22°C gamma-irradiated at 200 Gy/h .

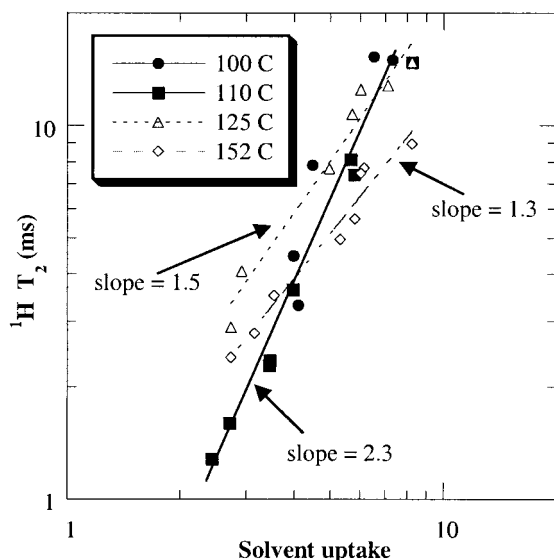


Figure 8 Correlation of $^1\text{H } T_2$ and solvent-uptake factor (defined as the final solvent + polymer weight divided by the original polymer weight). Power-law fits of the data are also shown in the graph.

factor of five from the initial value of 15 to 3 ms. The large change makes NMR a sensitive technique to follow thermal degradation.

The insulation samples thermally aged above the 119°C melting point do not follow the same curve as that of the lower-temperature thermally aged materials. This change highlights the danger of extrapolating accelerated aging data obtained above a phase transition. Therefore, extreme caution must be used when studying the accelerated degradation of semicrystalline materials. NMR condition monitoring must rely on curves of samples aged below the peak melting temperature.

Data for irradiated samples, also shown in Figure 7, indicate another limitation of the NMR technique for monitoring aging. There is little correlation between $^1\text{H } T_2$ relaxation constants and ultimate elongation. This observation for the irradiated material is not surprising because the damage mechanism is fundamentally different. Gel content measurements demonstrated that, at room temperature, radiation of the crosslinked cable insulation results in chain scission.³ After 9 weeks of irradiation, the gel content had decreased from an initial value of 57% to a final value of 51%.

The T_2 values of the thermally aged samples were correlated with the solvent-uptake values obtained in refluxing *p*-xylene (Fig. 8). Both measurements are related to the crosslink density and thus should show similar behavior. Since the results for materials aged at 100 and 110°C are reasonably similar, one line was drawn for these data. A power-law fit of the data had a slope of 2.3. The samples aged above the peak melt-

ing point had very different correlations to the solvent-uptake values, with the power-law slopes decreasing to 1.5 for the 125°C samples and 1.3 for the 152°C samples. Theoretical interpretation of the power-law fit is nontrivial and will depend on the method used to extract T_2 .¹¹ No attempt was made in this study to explain these observations.

CONCLUSIONS

NMR measurement of $^1\text{H } T_2$ represents a promising approach for characterizing the thermal aging for this particular cable-insulation material and has potential for studying other crosslinked polymer systems. The analysis is quick and reproducible and requires only little of the sample (potentially micrograms). A solvent with a solubility parameter within ± 0.8 of the polymer's effective polarity must be selected. Solvents that are either too polar or nonpolar do not effectively swell the insulation and thus do not provide large separation in T_2 values between unaged and aged samples. Below the main peak of the crystalline melting region, polymer aging appears to obey reasonable time-temperature superposition where T_2 can be correlated with the experimental ultimate elongation data. However, no correlation between T_2 and ultimate elongation was found for the irradiated samples.

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