

Chemistry Division, Los Alamos National Laboratory, is gratefully acknowledged for the gift of ^{17}O -enriched water. We are indebted to Dr. Andrew N. MacInnes for assistance with the XPS measurements and Ms. Susan Bradley for the artwork in Figure 10.

Registry No. 6, 137570-63-9; I, 135604-10-3; II (L = THF), 137570-61-7; II (L = 4-MePy), 137570-62-8; AlMe₃, 75-24-1; ^{29}Si ,

14304-87-1; ^{17}O , 13968-48-4; boehmite, 1318-23-6; alumina, 1344-28-1; aluminum silicate, 1335-30-4.

Supplementary Material Available: Full listings of bond lengths and angles, anisotropic thermal parameters, and hydrogen atom parameters (8 pages); tables of calculated and observed structure factors (23 pages). Ordering information is given on any current masthead page.

Proton Spin-Lattice Relaxation in the Rotating Frame Measurements for Some Industrial Polyethylene Composites

A. Natansohn

Department of Chemistry, Queen's University, Kingston, Ontario, K7L 3N6 Canada

Received July 29, 1991. Revised Manuscript Received October 9, 1991

Proton spin-lattice relaxation time in the rotating frame is measured for two polyethylene (PE) samples and a few of their composite materials with CaCO₃ and a cellulosic filler. The composites with poorer impact properties have detectable quantities of monoclinic PE crystals. Each material has a different relaxation behavior. While it is difficult to draw conclusions from the differences in the relaxation of the main signal of PE, the analysis of the amorphous signal relaxation suggests that there are at least two kinds of amorphous domains of PE. The presence of a faster relaxing, higher in proton density and/or mobility, amorphous domain can be associated with improved impact properties of the composite.

Introduction

Since high-resolution solid-state ^{13}C NMR spectroscopy was first proposed in 1976,¹ polyethylene (PE) has probably been one of the most investigated polymers using this method. It is well established now that the two main peaks appearing in the spectrum of almost any PE sample are assignable to the amorphous domains (the broader higher field peak at ca. 31 ppm) and to a mixture of crystalline, amorphous, and maybe "interfacial" domains (the main peak at 32.8 ppm). A considerable effort has been directed to measurement and interpretation of $T_1(\text{C})$ (carbon spin-lattice relaxation time) values. Very recent data are summarized in a review on the subject.²

Apart from $T_1(\text{C})$, the existence of a mixture of crystalline and amorphous domains was proven by measuring some other relaxation parameters. $T_1(\text{H})$ (proton spin-lattice relaxation time) and $T_{1\rho}(\text{H})$ (proton spin-lattice relaxation time in the rotating frame) reflect bulk properties, because protons are abundant spins and the magnetization is easily transmitted within various domains.³ Both parameters were investigated by Packer⁴ and found to be different for different domains within the sample. This was expected, because it is well-known that both these parameters can be used as probes for the phase structure of multiphase systems.³ The use of $T_{1\rho}(\text{H})$ as a probe for polymer blend miscibility was first suggested in 1981.⁵ Another parameter measured in various PE samples is T_{CH} , the cross polarization time. Its value is related to the ease with which magnetization is transmitted from protons to carbons. An inversion-recovery pulse

sequence has been applied by Ritchey et al.⁶ Data for low-density polyethylene, together with data for other polymers, seem to show a correlation with the dynamic storage modulus, an important property for polymers used as materials.⁷ Finally, the last parameter measured on PE is T_{DD} , the time constant for the decay of protonated carbon signals in the absence of cross polarization.⁸

All these parameters indicate the complicated phase structure of various polyethylenes. While every one of them shows different values for crystalline and amorphous regions, in some instances more information can be obtained from the spectra. Biexponential decays were observed for both amorphous and crystalline domains in measuring T_{DD} .⁸ The existence of an intermediary, interfacial layer in PE samples was postulated by Kitamaru et al.,⁹ who analyzed the ^{13}C CP-MAS NMR spectra using a broad resonance at 31.3 ppm assignable to interfacial domains. This finding was recently confirmed by Packer et al.¹⁰ in an indirect way. They used the carbon spectrum to measure $T_{1\rho}(\text{H})$ for every 0.1 ppm within the PE signal. The analysis was performed in terms of a biexponential decay, and a certain region within the main signal was found to have an increased amount of the fast decaying species (amorphous components). This area was assigned to the interfacial domain, in analogy with Kitamaru's results. Another significant publication identified α , β rhombic and monoclinic signals of as-produced PE.¹¹

(1) Schaefer, J.; Stejskal, E. O. *J. Am. Chem. Soc.* 1976, 98, 1031.

(2) Laupretre, F. *Prog. Polym. Sci.* 1990, 15, 425.

(3) VanderHart, D. L. *Makromol. Chem., Macromol. Symp.* 1990, 34, 125.

(4) Packer, K. J.; Pope, J. M.; Yeung, R. R.; Cudby, M. E. A. *J. Polym. Sci., Polym. Phys. Ed.* 1984, 22, 589.

(5) Stejskal, E. O.; Schaefer, J.; Sefcik, M. D.; McKay, R. A. *Macromolecules* 1981, 14, 275.

(6) Parker, A. A.; Marcinko, J. J.; Shieh, Y. T.; Shields, C.; Hedrick, D. P.; Ritchey, W. M. *Polym. Bull.* 1989, 21, 229.

(7) Parker, A. A.; Marcinko, J. J.; Shieh, Y. T.; Hedrick, D. P.; Ritchey, W. W. *J. Appl. Polym. Sci.* 1990, 40, 1717.

(8) Cholli, A. L.; Ritchey, W. M.; Koening, J. L.; Veeman, W. S. *Spectrosc. Lett.* 1988, 21, 519.

(9) Kitamaru, R.; Horii, F.; Murayama, K. *Macromolecules* 1986, 19, 636.

(10) Packer, K. J.; Poplett, I. J. F.; Taylor, M. J.; Vickers, M. E.; Whittaker, A. K.; Williams, K. P. *J. Makromol. Chem., Macromol. Symp.* 1990, 34, 161.

(11) Jarrett, W. L.; Mathias, L. J.; Porter, R. S. *Macromolecules* 1990, 23, 5164.

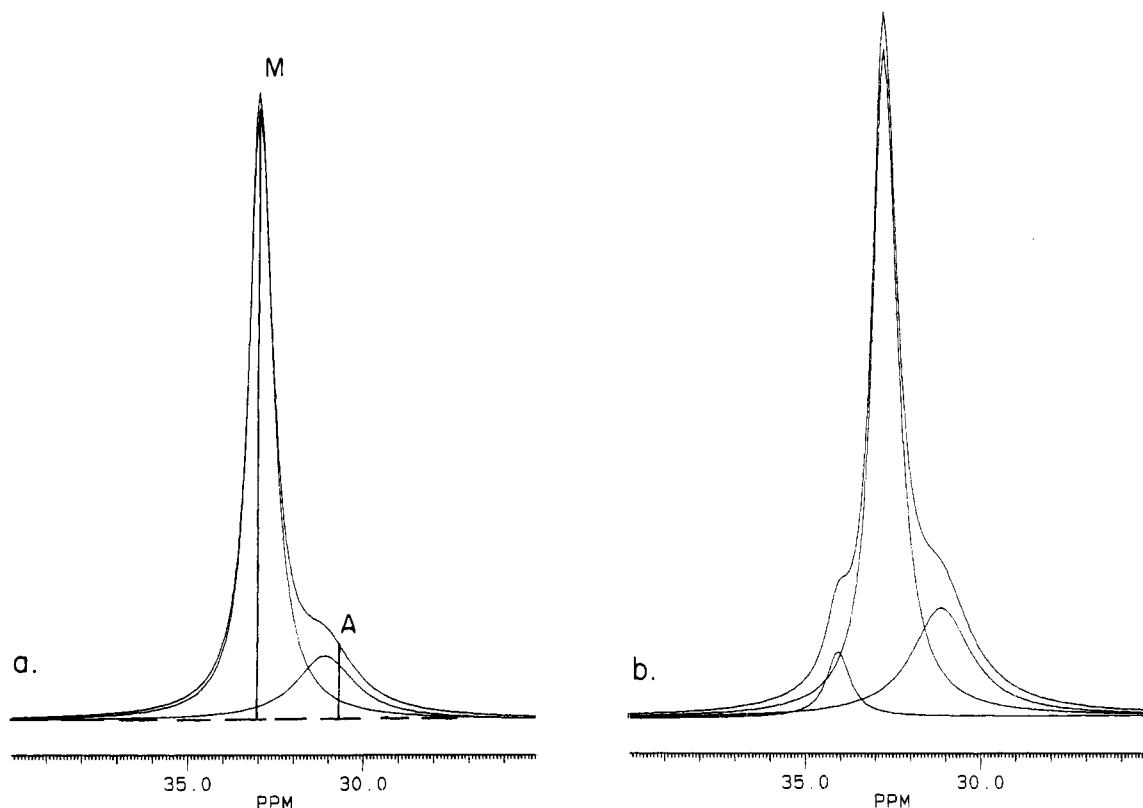


Figure 1. (a) Spectrum of sample PE1 at 13-ms contact time, its deconvolution into main and amorphous signals and the chemical shift at which the amorphous signal height was measured. (b) Spectrum of sample PE1C2 and its deconvolution into monoclinic, main, and amorphous signals.

Monoclinic crystals of PE are not a common occurrence; however, in certain conditions they are kinetically produced and stable. Their presence can be identified easily by NMR, because they resonate at a lower field (34.2 ppm). Finally, probably the most promising, and still to be explored, development in the recent literature is the measurement of spin diffusion rates between amorphous and crystalline domains.¹² This method clearly proves the existence of an interfacial layer in between these domains.

In our laboratory, proton $T_{1\rho}$ is being measured in various systems and correlated to the phase structure for monophasic and phase-separated blends¹³ and for industrially useful composites.¹⁴ This paper presents the results of T_1 (H) measurements for a series of PE composites generously provided by Du Pont Canada. The purpose of our investigation was to compare the same PE as used in a few composites and to draw some conclusions about differences encountered. Table I summarizes all previous $T_{1\rho}$ (H) data found in the literature for PE. As a general rule, each sample in Table I has at least two values of $T_{1\rho}$ (H), assigned mainly to the crystalline phase and to the amorphous phase protons.

Experimental Section

The PE and composite samples were prepared and processed at the Du Pont Research Centre, Kingston, Canada, following proprietary procedures. Melting of these samples was monitored

Table I. $T_{1\rho}$ (H) Values for Various Polyethylenes

PE	proton freq corresponding to magn field		$T_{1\rho}$ (H), ms	ref
	main, MHz	spin-locking, kHz		
low-density single-crystal	100	57	30	5, 6
	60	40	59.4	4
			13.1	4
high-density	60	40	1.4	4
			190	4
			23.1	4
linear	60	64	3.5	4
			33	15
branched	60	64	12	15
			5.9	15
highly branched	200	70	3.7	15
			8.7	16
linear low-density	300	53	4.0	16
			19	10
			2.6	10

on a Mettler differential scanning calorimeter (DSC) operating with a TA-3000 processor. Two PE samples were provided for comparison with the composites. PE1 is a pure polyethylene, and PE1C1 and PE1C2 are two composites of PE1 with CaCO_3 . PE1C1 has "good" impact properties, while PE1C2 has "bad" impact properties. PE2 is a maleic anhydride grafted polyethylene, and PE2C1 and PE2C2 are its composites with a cellulosic material. Again, one of the composite samples (PE2C1) has better impact properties than the other (PE2C2). The NMR spectra were obtained on a Bruker CXP-200 spectrometer. The samples were packed as powders in the spinners. The pulse sequence used was a standard cross polarization sequence with variable contact time.⁵ This pulse sequence can be used with reliable results even at relatively long contact times, as was verified for poly(*N*-vinylcarbazole) in a previous paper.¹⁷ The delay between pulses was 10 s, the proton 90° pulse was $3.7 \mu\text{s}$ (i.e., the

(12) Schmidt-Rohr, K.; Clauss, J.; Blumich, B.; Spiess, H. W. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* 1990, 31, 172.

(13) Simmons, A.; Natansohn, A. *Macromolecules* 1991, 24, 3651.

(14) Natansohn, A.; Lacasse, M.; Banu, D.; Feldman, D. *J. Appl. Polym. Sci.* 1990, 40, 899. Feldman, D.; Banu, D.; Natansohn, A.; Wang, J. *J. Appl. Polym. Sci.* 1991, 42, 1537.

(15) Schroter, B.; Posern, A. *Makromol. Chem., Rapid Commun.* 1982, 3, 623.

(16) Perez, E.; VanderHart, D. L.; Crist, Jr., B.; Howard, P. R. *Macromolecules* 1987, 20, 78.

(17) Natansohn, A. *Macromolecules* 1991, 24, 1662.

Table II. Percentages of the Areas of PE Signal Measured at 4-ms Contact Time

sample	amorphous (31 ppm)	orthorhombic (32.8 ppm)	monoclinic (34 ppm)
PE1	32	68	
PE1C1	31	69	
PE1C2	38	55	7
PE2	42	58	
PE2C1	30	70	
PE2C2	25	71	4

spin lock field frequency was 67 kHz), and the contact varied between 0.25 and 100 ms. Spinning was performed at ca. 4 kHz, and no spinning sidebands were observed. Typically, 8 scans were enough to obtain a very good spectrum, but the experiments were repeated with 32 scans with no observable change. To check for signals other than $-\text{CH}_2-$, 400 scans were run for some samples. In the conditions employed here, there was no clear separation of the amorphous and main resonances in PE. Consequently, the intensities of these resonances were measured in two ways. First, the signals were deconvoluted into the main peak (32.8 ppm with a width of 41 Hz) and an amorphous peak (31 ppm, width 110 Hz). The program used was GLNFFIT, supplied by Bruker. No attempt was made to include the "interfacial" region. The \ln (integrated intensity) values of these peaks were plotted as a function of the contact time. The error of such deconvolution could exceed 7%, so an alternative method was used for all samples, similar to that suggested by Packer.¹⁰ The intensity of the signals were approximated by the heights. Things are pretty simple for the very intense main signal, which has no interference from the amorphous components. Figure 1a shows that, when the height was measured on the high-field side of the amorphous peak, it paralleled the deconvoluted amorphous signal and could be approximated with its intensity. Comparison of the decays of the signals measured by deconvolution and by height showed a very good fit. The advantage of using height instead of deconvolution is related to the much better precision of measurement of the height for a well-phased spectrum. The error in this last case is estimated at ca. 2–3%. Another factor to be mentioned is that, as the amorphous signal relaxes faster than the main signal, the precision of the height measurement as compared to the precision of the area measurement improves markedly with increasing contact times. The only sample with a higher error in measuring heights of the amorphous peak was PE2, and comments on this will be found in the Results and Discussion. Figure 1b shows a spectrum which presents a clear monoclinic peak at 34 ppm (width 41 Hz) and its deconvolution.

Results and Discussion

The maleic anhydride grafted PE (PE2) must contain very small amounts of grafted maleic anhydride, because even hundreds of scans do not reveal significant signals in the carbonyl region. The melting endotherm in the DSC scan gives a crystallinity of ca. 57%, which is lower than that calculated for the other PE sample (PE1, crystallinity of ca. 65%). Grafting is supposed to introduce disorder; hence, it is not surprising that it decreases the crystallinity. Although not a perfect method to measure the crystallinity, the areas under the main and amorphous peaks could also be used as an estimate. Table II presents the percentages for all samples when the spectrum was obtained with a contact time of 4 ms. It is preferable to use a contact time on the decreasing side of the intensity of the signal, but differences in the decay rates make this method not quite quantitative. The estimated crystallinities for the two samples compare well with the percentages obtained by DSC.

It is interesting to note in Table II that the overall percentage of crystallinity does not seem to be important in terms of the impact properties. PE1C2 (the "bad" sample) has a higher amorphous component than PE or PE1C1, while for the other system PE2C2 (the "bad" sample) has the highest crystallinity. PE2 has the highest

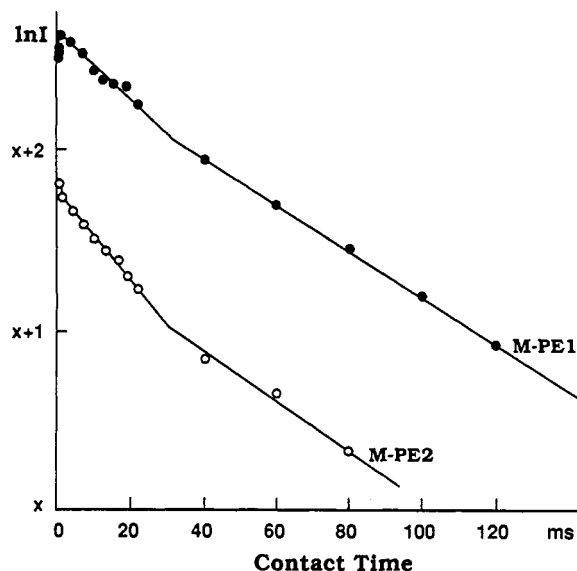


Figure 2. Plot of \ln (magnetization) as a function of contact time for the main signal of PE in PE1 and PE2. The vertical axis is shifted to provide for good separation between the two samples.

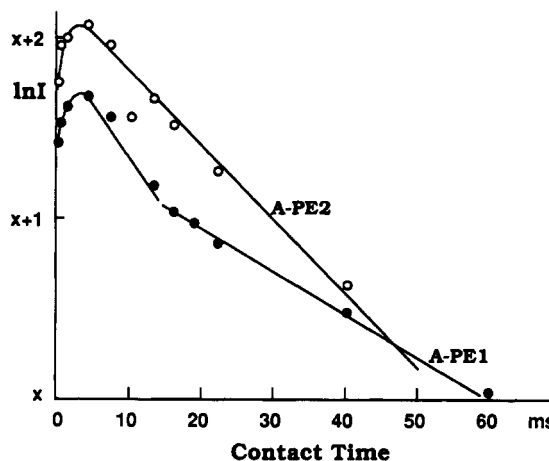


Figure 3. Decay of the amorphous signal intensity as a function of contact time for PE1 and PE2. The vertical axis is shifted arbitrarily. For PE1 the intensity is measured as height, for PE2 as area of the deconvoluted signal.

proportion of amorphous domains of all the samples analyzed. At such low crystallinity, the amorphous peak starts to have a rather significant effect in the overall PE signal. This is the explanation for a higher error in measuring $T_{1\rho}(\text{H})$ using peak heights for this sample. Probably the most significant result in Table II is the amount of monoclinic PE crystals in various samples. Processing which generates composites with poor impact strength is also producing a certain amount of monoclinic PE; hence, one can conclude that there is some connection between these two.

The effects of grafting on the relaxation behavior of the protons in the main peak are presented in Figure 2. As expected, the relaxation of the main signal (M) is not exponential. The main signal is a combination of carbons in at least two phases, consequently the protons will relax through various mechanisms and at various rates. However, the decay in the two curves can be approximated by a biexponential. Such an analysis generates a faster relaxing portion and a slower relaxing portion of M. For both samples, the faster relaxing portion has a time constant of 13 ms and accounts for ca. 34% of the signal. The main difference is in the slower relaxing component, which generates a $T_{1\rho}(\text{H})$ of 78 ms for PE1 and 85 ms for PE2.

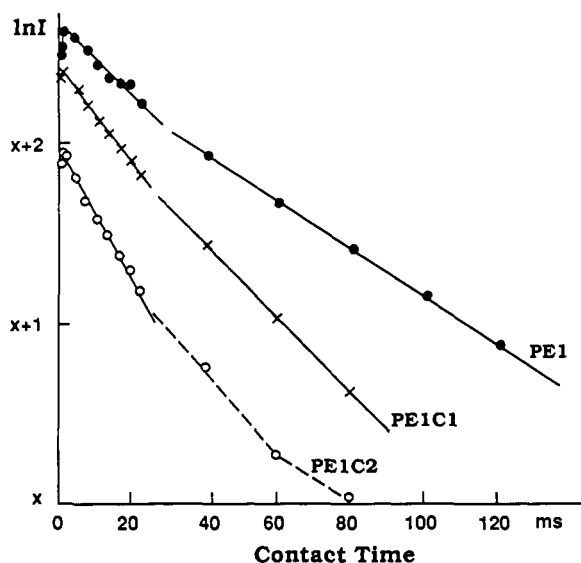


Figure 4. Intensities of the main signals of PE1 and its composites: PE1C1 and PE1C2 as a function of contact time. The vertical axis is shifted arbitrarily.

These are not significant differences, especially considering that in crystalline samples some spin-spin relaxation mechanism must be present.

Figure 3 shows a similar analysis of the amorphous signal (A) of the two PE samples. The nonexponential decay of A-PE1 is somewhat surprising, because unlike the main signal, the amorphous signal is supposed to correspond only to carbons belonging to an amorphous phase. Packer et al.¹⁰ also analyzed the decay of this part of the signal in terms of two exponentials; however, the proportion of the slower decaying signal was rather low at this chemical shift. A nonexponential decay can be explained in two ways. First and the most obvious is that amorphous portions of the sample are distributed within phases which have slightly different proton densities. The second explanation is related to the fact that at room temperature PE is above its T_g , and polymers above their T_g usually have different relaxation behavior for protons attached to different carbons in the molecule.¹⁸ This happens mainly due to the high mobility above T_g . In the case of PE, however, all carbons and protons belong to methylene groups, so this second explanation reduces to the first one: there must be some parts of the amorphous PE which are more mobile than others, and they will presumably be in separated phases. The nonexponential decay can be analyzed by a biexponential, as suggested by the straight lines in Figure 3. The results of this analysis indicate that about 45% of the amorphous part of PE1 is found in faster relaxing domains ($T_{1\rho}(H) = 6$ ms), while the rest of the amorphous part relaxes with a time constant of 42 ms. The grafted PE sample, however, shows an exponential decay for all the amorphous signal with the relaxation time constant close to the relaxation time constant of the slower relaxing domains of PE1 ($T_{1\rho}(H) = 40$ ms). The grafting appears to have as an effect a homogenization of the amorphous domains of PE. All amorphous methylene groups now belong to the domains of lower proton density and/or reduced mobility.

The effect of compounding PE with CaCO_3 on the decay of the main signal is illustrated in Figure 4. As expected, the differences between PE1, PE1C1, and PE1C2 are not very important. The decay of the main signal in PE1C1

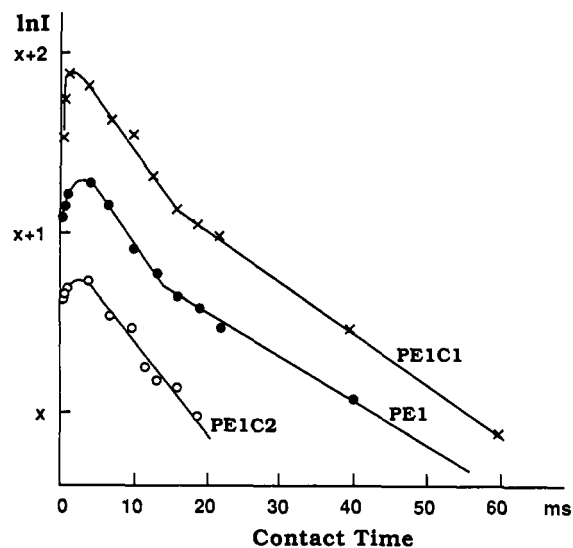


Figure 5. Magnetization decay for the amorphous peaks of PE1, PE1C1, and PE1C2. The vertical axis is shifted arbitrarily.

can be analyzed in a similar manner to that of PE1, i.e., by a biexponential curve. Comparing the curves for PE1 and PE1C1, the amount of CH_2 groups resonating in the faster relaxing domains is smaller in PE1C1 (ca. 19% compared to ca. 34%), but the relaxation time constant for both is identical (13 ms). The slower relaxing domain is slower in PE1 (78 ms) than in the "good" composite (50 ms). The "bad" composite, PE1C2, cannot be analyzed by a biexponential decay, and consequently no percentages or time constants were calculated. Its relaxation is not very different from the other two samples, only the curvature of the decay is more pronounced.

There are greater effects of mixing in the amorphous peak decay. Figure 5 compares the decays of the amorphous peaks for PE1, PE1C1, and PE1C2. Again, the "good" composite is rather similar to PE. The differences are similar to what was described before. The amount of fast relaxing methylene is reduced in the composite (ca. 37% compared to ca. 45%), and the relaxation time constant is somewhat reduced (35 ms from 42 ms). Both PE1 and PE1C1 have two domains of amorphous PE. This is not the case for the "bad" composite (PE1C2), which can be described by a single-exponential decay with an intermediate value of $T_{1\rho}(H)$ (20 ms). Here, the mixing of CaCO_3 seems to have homogenized the amorphous regions, all of them having now a similar proton density or mobility.

As expected, there is no "communication" between PE and the filler. The filler is completely transparent in the CP-MAS NMR experiment, not possessing any protons to generate magnetization. Any physical interaction between the two components of the composite would allow some magnetization to be transmitted from the abundant protons of PE to the carbons of CaCO_3 . This would translate into a signal observable for the filler. Such a signal has not been observed even after hundreds of scans at long contact times.

Unlike the composites with CaCO_3 , the composites containing a cellulosic filler exhibit signals of the filler around 70–80 ppm, as shown in Figure 6. The effect of this addition to the relaxation of the PE main signal is illustrated in Figure 7. Surprisingly, both composites have a relaxation pattern which can be described by a single exponential. The relaxation is faster in the "good" composite ($T_{1\rho}(H)$ is 50 ms for PE2C1 and 85 ms for PE2C2). The component which was relaxing with a 13-ms time constant in PE2 does not exist in any of the two composite samples. The most interesting effect of mixing PE with

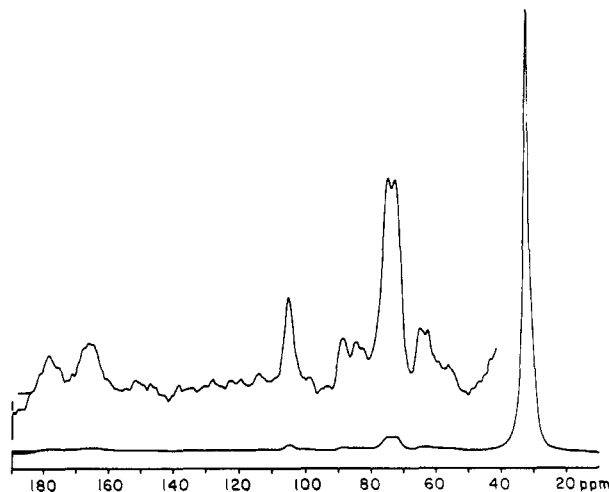


Figure 6. CP-MAS NMR spectrum of PE2C1 recorded with a contact time of 1 ms.

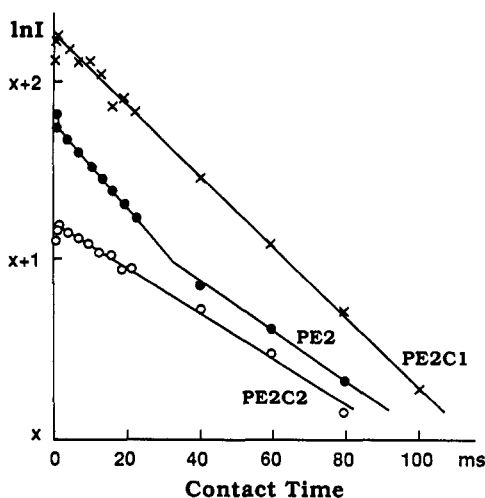


Figure 7. Magnetization decay for the main peak of PE2, PE2C1, and PE2C2. The vertical axis is shifted arbitrarily.

a cellulosic filler is on the amorphous peak decay, presented in Figure 8. In this case, the mixing conditions employed to generate the "bad" composite do not seem to have affected the relaxation behavior of the amorphous peak. The amorphous domains in PE2 and PE2C2 appear to be somewhat similar ($T_{1\rho}(H)$ for PE2 is 30 ms and for PE2C2 is longer, 42 ms). However, the amorphous domains of PE2C1, the "good" composite, appear to be very similar to PE1 and to a lesser extent to PE1C1. There are two kinds of amorphous domains. One is relaxing with a time constant of 6 ms and contains ca. 45% of the amorphous methylene groups; the other is relaxing with a time constant of 42 ms. As for the cellulosic filler, all its signals are relaxing with a $T_{1\rho}(H)$ of 10 ms, in both composites or in the spectra of the pure cellulosic filler. One example is given in Figure 8. Obviously, these composites also have no communication between the components. A summary of all relaxation data is provided in Table III. The last column in Table III, $\langle T_{1\rho}(H) \rangle$, has been obtained by measuring the initial slope of the decay curve, and it reflects the weighted average relaxation rate of the amorphous protons, regardless of how many amorphous domains may or may not be present. The PE composites with CaCO_3 do not show any marked differences in $\langle T_{1\rho}(H) \rangle$; the slight increase in the "bad" composite is just above the measurement error. The PE composites with the cellulosic material, however, show the same trend as the deconvoluted values, i.e., the "bad"

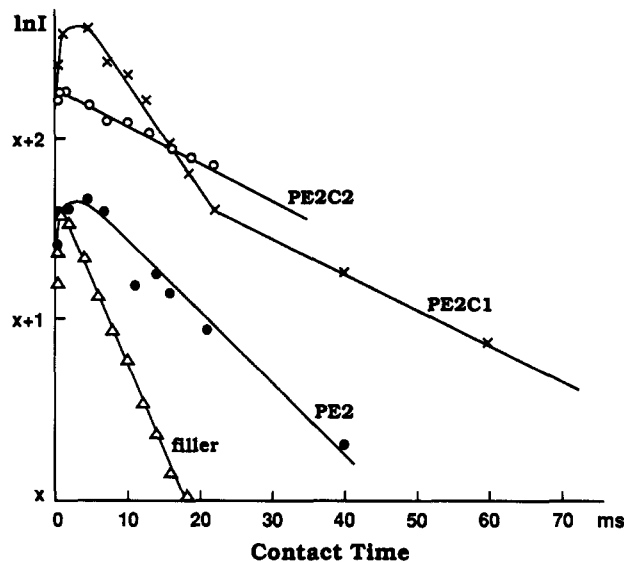


Figure 8. Magnetization decay for the amorphous peak of PE2, PE2C1, and PE2C2. Also presented is the decay of one peak belonging to the cellulosic filler. The vertical axis is shifted arbitrarily. The PE2 peak intensity is measured as the area of the deconvoluted signal; all other peak intensities are measured as heights.

Table III. Summary of $T_{1\rho}(H)$ Measurements

sample	main peak $T_{1\rho}(H)$, ms		amorphous peak $T_{1\rho}(H)$, ms		$\langle T_{1\rho}(H) \rangle^b$
	fast (amt)	slow (amt)	fast (amt)	slow (amt)	
PE1	13 (34%)	78 (66%)	6 (45%)	42 (55%)	15
PE1C1	13 (19%)	50 (81%)	6 (37%)	35 (63%)	18
PE1C2			20 (100%)		20
PE2	13 (34%)	85 (66%)	30 ^a (100%)		30 ^a
PE2C1		50 (100%)	6 (45%)	43 (55%)	18
PE2C2		85 (100%)		42 (100%)	42

^a This value was calculated with the curve deconvolution procedure, because the sample contains a high proportion of the amorphous signal.
^b The error in $T_{1\rho}(H)$ calculation is estimated at $\pm 10\%$.

composite relaxes much slower than either PE2 or the "good" composite.

It is difficult, if not impossible, to try to draw any conclusions from the changes in relaxation of the main peak. The crystalline part of it, which may involve some spin-spin relaxation mechanisms, together with the well-known fact that more than one phase of PE resonates there, makes any interpretation doubtful. The amorphous peak relaxation, however, seems to suggest some general observations. In both types of composites, the filler is completely separated and noncommunicating with the PE. Within the PE domains, there are some instances in which the amorphous PE belongs to two types of domains, and presumably they are separated by crystalline domains and/or by the filler. The two kinds of amorphous domains, at least for the samples analyzed here, show a very similar pattern of relaxation ($T_{1\rho}(H)$ is 6 ms for the faster relaxing domain and ca. 40 ms for the slower relaxing domain). There are many factors which affect the value of $T_{1\rho}(H)$ in polymers. If one discounts differences in spin diffusion (polyethylene is extremely rich in protons in either crystalline or amorphous domains) the two main remaining factors are the motion at the spin-locking frequency and the interproton distance (proton density). Some of our $T_{1\rho}(C)$ studies on different polymers indicate that motion may play just a minor role in proton relaxation,¹⁹ while proton density may be more important in systems rich in protons. If one considers the proton density as the dom-

(19) Simmons, A.; Natansohn, A. *Polym. Mater. Sci. Eng.* 1991, 65, 158; also manuscript in preparation.

inant factor in the relaxation of the amorphous domains, then the faster relaxing domains reflect an increased proton density and could be compared to a dispersed rubbery phase within more rigid domains. Their presence, not surprisingly, seems to favor improved impact properties. If one disregards the biexponential decay of the amorphous peak and concentrates only on the average value of $T_{1\rho}(\text{H})$, this conclusion is not so obvious for the PE1 composites but still valid for the PE2 composite series.

The analysis of just a few samples is not enough to confirm these suggestions or to determine which is the decisive factor: the presence of monoclinic crystals, the differences in amorphous relaxation, or both. But the initial results definitely warrant a more systematic study of the correlations of $T_{1\rho}(\text{H})$ values in various PE samples with some of the mechanical properties. Filler content and processing parameters will have to be varied, and their effect on the $T_{1\rho}(\text{H})$ will have to be quantified. Indirect results could be obtained on the phase structure of the PE

components in its composites.

The results presented here also show that $T_{1\rho}(\text{H})$ is a parameter which may offer valuable information in multicomponent materials. Its use as a probe for blend miscibility is well established. It also gives information on nonbonding interactions, interfacial communication,¹³ and, as demonstrated here, on formation of different amorphous domains in polyethylene composites under different processing procedures.

Acknowledgment. The contributions of Dr. Graham White and the research team at Du Pont Canada in the form of samples and helpful discussions are gratefully acknowledged. Also appreciated is the spectrometer time offered by Du Pont Canada for running these experiments. Partial financial assistance from NSERC Canada is acknowledged as well.

Registry No. Polyethylene, 9002-88-4; calcium carbonate, 471-34-1; cellulose, 9004-34-6.

Influence of Oxygen on the Stability of Zr_4Sn

Young-Uk Kwon and John D. Corbett*

Department of Chemistry and Ames Laboratory—DOE,¹ Iowa State University, Ames, Iowa 50011

Received August 12, 1991. Revised Manuscript Received November 12, 1991

Contradictions regarding the stability of Zr_4Sn have been resolved in terms of the effects of oxygen (and perhaps other) impurities. The phase is stable at 800–1050 °C (at least) and has the composition $\text{Zr}_{4.0-4.2}\text{Sn}$, but the decomposition $3\text{Zr}_4\text{Sn} \xrightarrow{\text{O}_2} \alpha\text{-Zr}(\text{Sn}_2\text{O}) + \text{Zr}_5\text{Sn}_3$ is driven by the solution of oxygen in the metal. Even trace amounts give three-phase products, such as on the surface of substantially all arc-melted and annealed samples of Zr_4Sn , and the decomposition is complete at 1050 °C in the presence of ≥ 3 at. % oxygen. The separate and combined effects of tin and oxygen solutes on the lattice constants of $\alpha\text{-Zr}$ support the conclusions. The effect of oxygen (Fe, etc.) impurities on the solidus composition for $\alpha\text{-Zr}(\text{Sn})\text{-Zr}_4\text{Sn}$ may be responsible for some literature differences.

Introduction

During a recent study of the $\text{Zr}_5\text{Sn}_3\text{-Zr}_5\text{Sn}_4$ portion of the Zr–Sn system, our interest was also drawn to the Zr_4Sn region.² Reports on this phase have been contradictory as regards its composition, structure, and stability. Our investigations at that time supported the conclusion of a critical evaluation of the literature,³ that the composition is near Zr_4Sn (as originally assigned⁴), and that the structure is the cubic A15 (Cr_3Si) type. The compound appears to be a line phase at 1000 °C judging from its lattice constants. Other assignments of a Zr_3Sn composition⁵⁻⁷ were evidently only nominal and based on the structure type. However, our studies also showed that additional, very weak diffraction lines were regularly observed in the

Guinier powder pattern of Zr_4Sn that required a doubling of the unit cell ($a = 11.252 \text{ \AA}$). Although the responsible superstructure has not been established, a predominantly substitutional ordering of the excess zirconium seems probable.

The stability properties of Zr_4Sn are more problematical. Some investigators have reported that Zr_4Sn is stable only at high temperatures,^{6,8,9} while one early study did not find this compound at all.¹⁰ A marginal stability has been suggested.³ Our earlier work² indicated that complete conversion to Zr_4Sn was difficult to achieve, and some partial decomposition seemed to occur on equilibration at 820 °C. Although $\text{Zr}(\text{Fe,Ni,Cr})_2$ compounds have been well identified as precipitates in zircalloys ($\sim 98\% \text{ Zr}$, 1.2–1.7% Sn, 0.2–0.5% Fe, Ni, Cr, ...), the precipitation of Zr_4Sn from these alloys has never been seen¹¹⁻¹⁴ even though the ac-

(1) The Ames Laboratory—DOE is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This research was supported by the Office of Basic Energy Sciences, Materials Sciences Division.

(2) Kwon, Y.-U.; Corbett, J. D. *Chem. Mater.* 1990, 2, 27.

(3) Abriata, J. P.; Bolcich, J. C.; Arias, D. *Bull. Alloy Phase Diagrams* 1983, 4, 147.

(4) McPherson, D. J.; Hansen, M. *Trans. Am. Soc. Met.* 1953, 45, 915.

(5) Gran, G.; Andersson, S. *Acta Chem. Scand.* 1960, 14, 956.

(6) Rossteutscher, W.; Schubert, K. *Z. Metallkd.* 1965, 56, 815.

(7) Naik, U.; Banerjee, S. *Trans. Indian Inst. Met.* 1978, 31, 318.

(8) Schubert, K.; Anantharaman, T. R.; Ata, H. O. K.; Meissner, H. G.; Pötzschke, M.; Rossteutscher, W.; Stolz, E. *Naturwissenschaften* 1960, 47, 512.

(9) Luo, H. L.; Vielhaber, E.; Corenzwit, E. *Z. Phys.* 1970, 230, 443.

(10) Nowotny, H.; Schachner, H. *Monatsh. Chem.* 1953, 84, 169.

(11) Speich, G. R.; Kulin, S. A. *Zirconium and Zirconium Alloys*; American Society of Metals: Metals Park, OH, 1953; p 200.

(12) Vander Sande, J. B.; Bement, A. L. *J. Nucl. Mater.* 1974, 52, 115.

(13) Vitikainen, E.; Nenonen, P. *J. Nucl. Mater.* 1978, 78, 362.