

## Solid-State NMR Study of Spin Finish of Thermally Treated PAN and PAN/CNT Precursor Fibers

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**ABSTRACT:** Dry-jet wet-spun polyacrylonitrile (PAN) and PAN/carbon nanotubes (CNTs) precursor fibers coated by spin finishes were characterized using the solid-state <sup>1</sup>H nuclear magnetic resonance technique. Series of fiber samples were prepared upon thermal treatment at different temperatures (room temperature to 180°C). Using the Hahn echo sequence, relatively mobile components were identified and the effect of the heat treatment on those components was studied. It was observed that the mobile components are mainly the spin finishes. Heat treatment caused loss of one of the spin finishes (Type B) to a great extent (~80%), whereas the other two spin finishes (Type A and Type C) were more stable. Additional information regarding the change in molecular mobility due to heat treatment was obtained by the spin-lattice relaxation time ( $T_1$ ) analysis. It was found that the presence of CNT affects the  $T_1$  relaxation time of the polymer in the composite fiber, however, that of relatively mobile components remains unaffected. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40734.

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### INTRODUCTION

High-strength, high-modulus carbon fibers are finding increased uses in different applications. Since the last few decades, extensive research studies have been carried out worldwide on the issue relating to the improvement of polyacrylonitrile (PAN)-based carbon fiber properties as PAN is regarded as the most preferred precursor material for the high-strength carbon fibers. To obtain a high-performance carbon fiber, precursor fiber of good quality is a prerequisite. During the processing of multifilament carbon precursor fibers, an essential lubricating composition is deposited on the external surface of the fiber as a coating which is called spin finish. Application of spin finish is one of the important steps to obtain a good quality precursor fiber. It is applied to facilitate the performance, quality, and uniformity of processing. In general, lubricants, emulsifiers, and antistatic agents are three major components of the spin finish; however, it may contain several other components depending on the type and end use of the fiber. In fact the composition and the reasons for the application of the spin finish depend on the specific end uses and as a result, there is no universal spin finish which is used for different fibers. Spin finish also plays a critical role in stabilization during carbon fiber manufacture.<sup>1–5</sup>

Solid-state nuclear magnetic resonance (NMR) can be used to study the thermally stabilized fiber which is a suitable method to obtain insights into the structure, molecular motion, chain dynamics, and intermolecular interactions of the polymeric materials.<sup>6,7</sup> Previously, this technique has been used to study the structural changes of the thermally treated PAN,<sup>8</sup> PAN precursor fiber stabilized at 215°C and above<sup>9</sup> as well as characterizing carbon fiber prepared from PAN.<sup>10</sup> Conversely, low-field NMR is known to be a convenient instrument to measure the spin finish on the fiber. It can differentiate between hydrogens in either the liquid or solid phase of the samples.<sup>5</sup>

In this contribution, we report on thermal treatment of PAN and PAN/carbon nanotubes (CNTs) precursor fibers from room temperature (RT) to 180°C. A detailed analysis is performed using <sup>1</sup>H MAS NMR to investigate the effect of thermal treatment on the fiber. It was demonstrated that this routine NMR spectroscopy can be used as a unique technique to explore different spin finishes in a qualitative as well as quantitative manner which has definite advantages over the conventional Soxhlet method.<sup>4</sup> Especially, our NMR approach is superior in terms of simplicity of the sample preparation, total experimental time,

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**Table I.** PAN and PAN/CNT Composite Fiber Processing Parameters

Sample	Type of precursor fiber	Solution		Spinneret holes diameter ( $\mu\text{m}$ )	Spinning		Drawing		
		Solid content <sup>a</sup> (g/dL)	CNT conc. <sup>b</sup> (wt %)		Coagulation bath		Spin finish <sup>c</sup>		Total draw ratio <sup>e</sup>
					Solvent	Temp. ( $^{\circ}\text{C}$ )	Type	Conc. (wt %) <sup>d</sup>	
1	PAN fiber (control)	11	0	200	MeOH	-50	A	1.5	23.4
2	PAN/CNT composite fiber	10.5	0.5	200	MeOH	RT	B	1	28.8
							C	1.5	
3	PAN/CNT composite fiber	10.5	1	200	MeOH	-50	A	1.5	24.6
							B	0.5	

<sup>a</sup> Of polymer for control solution and polymer + CNT for the composite solution.

<sup>b</sup> CNT concentration with respect to the weight of the polymer.

<sup>c</sup> Applied during postspinning drawing.

<sup>d</sup> Spin finish bath concentration.

<sup>e</sup> Total draw ratio is the spin draw ratio multiplied by the postspin draw ratio.

nondestructive nature of the method, and diverseness of information that can be obtained. Particularly, the relaxation studies could have important implications to quality control efforts within an industrial site with the available low-resolution techniques.

## EXPERIMENTAL

### Materials

PAN polymer with methacrylic acid (MAA) comonomer (4 wt %) was supplied by Japan Exlan (Osaka, Japan). The polymer sample was dried in vacuum at 90°C for 24 h before use. CNT was obtained from Continental Carbon Nanotechnologies (Houston, TX). This CNT is a mixture of few wall (average no. of walls: 2.6) with an average diameter of 3.0 nm and aspect ratio ( $L/D$ ) of  $1040 \pm 50$ . High-performance liquid chromatography (HPLC) grade dimethylformamide (DMF) was purchased from Sigma-Aldrich and used as received. For liquid-state NMR studies, deuterated DMF (DMF- $d_7$ ) was obtained from Sigma-Aldrich. The spin finishes Types A and B were provided by the Matsumoto Yushi-Seiyaku Co., Ltd., Japan and spin finish Type C was obtained from Wacker Chemie AG, Germany.

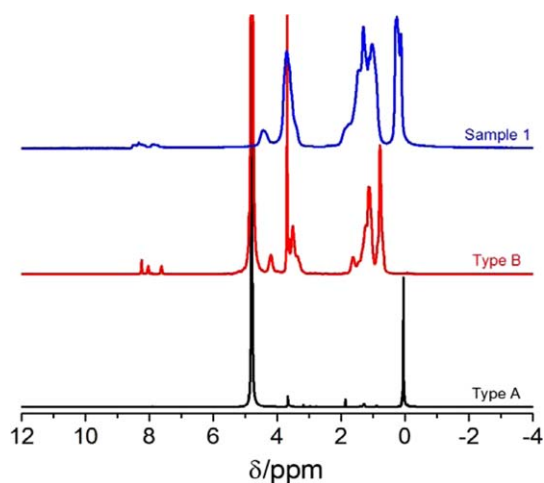
### Method

The PAN and PAN/CNT composite solutions were prepared following the procedure described elsewhere.<sup>11</sup> Table I compares the compositions and conditions used for fiber spinning and drawing. Approximately 60 mg of control and composite fiber samples were thermally treated using a vacuum oven (constant vacuum level: 25 inHg) at 80, 110, 130, 150, 160, 170, and 180°C for 24 h. All the thermally treated fiber samples were kept in the desiccator at RT before NMR experiments.

NMR Experiments were performed on fiber samples using a Bruker DSX-300 solid-state NMR spectrometer (Bruker Biospin, Rheinstetten/Germany), operating at a magnetic field of 7.05 T ( $^1\text{H}$  frequency of 300 MHz). The experiments were carried out

using a magic angle spinning (MAS) probe at RT (298 K). About 50 mg of sample was packed into a 4 mm regular zirconia rotor (80  $\mu\text{L}$  volume) with a Kel-F® cap. The temperature at the sample position was measured with an external thermocouple. No background signal was obtained from the rotor or cap.  $^1\text{H}$  MAS NMR spectra were recorded using the Hahn echo sequence ( $\pi/2_z\text{-}\tau\text{-}\pi_y\text{-}\tau\text{-Acq}$ )<sup>12</sup> with a time delay,  $\tau = 175 \mu\text{s}$  and  $\pi/2$  pulse length of 5  $\mu\text{s}$  at a spinning speed of 10 kHz. Typically 512 scans were acquired per experiment. The delay  $\tau$  and  $\pi/2$  pulse length in the Hahn echo sequence were set such that only a slow decaying or relatively mobile component was observed as shown in Supporting Information Figure S1.

The spin-lattice or longitudinal ( $T_1$ ) relaxation time was measured at a nonspinning condition using the conventional saturation recovery<sup>13</sup> experiment. The 90° excitation pulse length was 5  $\mu\text{s}$ . For a given sample, 34 different relaxation delays from 0.1 ms to 30 s were measured with 8 scans each. To make a quantitative analysis of the spectra corresponding to individual relaxation delay, the DMFIT program<sup>14</sup> was used. Utilization of this program allows the spectra to be fitted to Lorentzian and Gaussian components. It was found that individual spectrum can be fitted satisfactorily using a Gaussian function characterizing the solid-like component (named as the “broad component” in the subsequent discussion) and a Lorentzian function for the narrow line corresponding to the mobile components of the sample<sup>15</sup> as can be seen in Supporting Information Figure S2. A selective spin-lattice relaxation analysis for the relaxation functions of the solid-like and mobile components has shown that the respective recovery function is a single exponential for the broad component and can be fitted with eq. (1). The behavior is complicated for mobile component and the selective analysis of the spin-lattice relaxation of the mobile fraction may be described by a bi-exponential spin-lattice relaxation function (named as the “narrow component 1” and “narrow component 2,” respectively, in the subsequent discussion) as given in eq. (2).



**Figure 1.** Isotropic region of  $^1\text{H}$  high-resolution spectra of liquid spin finish Types A and B measured at  $^1\text{H}$  frequency of 400 MHz at RT and  $^1\text{H}$  MAS spectra of Sample 1 measured at  $^1\text{H}$  frequency of 300 MHz at RT using Hahn echo with an echo time  $\tau = 175 \mu\text{s}$ . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

$$S_1(t) = A_{\text{broad}} \{1 - \exp(-t/T_{1,\text{broad}})\} + C_1 \quad (1)$$

$$S_2(t) = A_{\text{narrow 1}} \{1 - \exp(-t/T_{1,\text{narrow 1}})\} + A_{\text{narrow 2}} \{1 - \exp(-t/T_{1,\text{narrow 2}})\} + C_2 \quad (2)$$

where  $A$  is the amplitude of the corresponding exponential and  $C$  is a constant. To keep the analysis simple, in this study, the influence of cross relaxation is not taken into account.

Further  $^1\text{H}$  NMR spectra on spin finishes were obtained on a Bruker AV3 400 high-resolution spectrometer operating at a static magnetic field of 9.4 T ( $^1\text{H}$  frequency of 400 MHz) at RT. Infrared spectra were obtained on Spectrum One spectrometer (Perkin Elmer) by collecting 64 scans at a resolution of  $2 \text{ cm}^{-1}$ . Spectra were measured using KBr discs prepared with the fiber samples. Thermogravimetry (TGA) was carried out using a TGA Q500, TA Instruments, with temperature accuracy and temperature reproducibility of  $\pm 0.5^\circ\text{C}$ . The samples were introduced into an open platinum pan and were heated at a constant heating rate of  $1^\circ\text{C}/\text{min}$  from 35 to  $200^\circ\text{C}$  under nitrogen atmosphere.

## RESULTS AND DISCUSSION

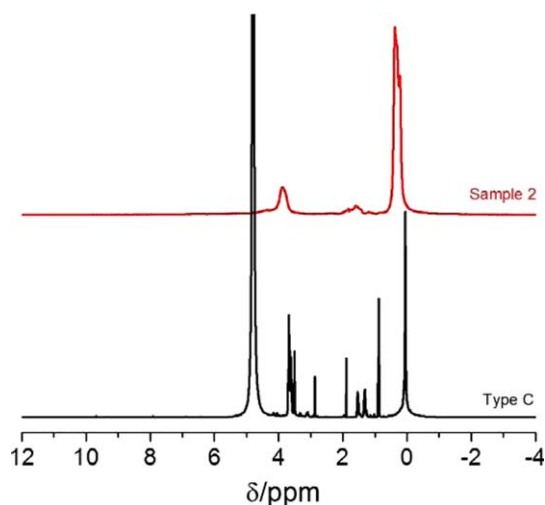
### Results from Spectroscopic $^1\text{H}$ MAS Experiments

Figure 1 shows the solid-state  $^1\text{H}$  MAS spectra of Sample 1 acquired at a spinning rate of 10 kHz along with the spectra of spin finish Types A and B obtained from the high-resolution NMR using deuterated DMF as a solvent. As explained in the Experimental section, the delay  $\tau$  and  $\pi/2$  pulse length in the Hahn echo sequence were set such that only the mobile components can be observed in the  $^1\text{H}$  MAS spectra. It was found that dried PAN powder does not show any significant peak in its  $^1\text{H}$  MAS spectra (data not shown) suggesting the absence of any mobile component in the sample. On the contrary, the fiber Sample 1 shows several peaks at a chemical shift of 0.5, 0.7–2, 3.5, 4.3, and 7.5–9 ppm revealing the signature of the mobile

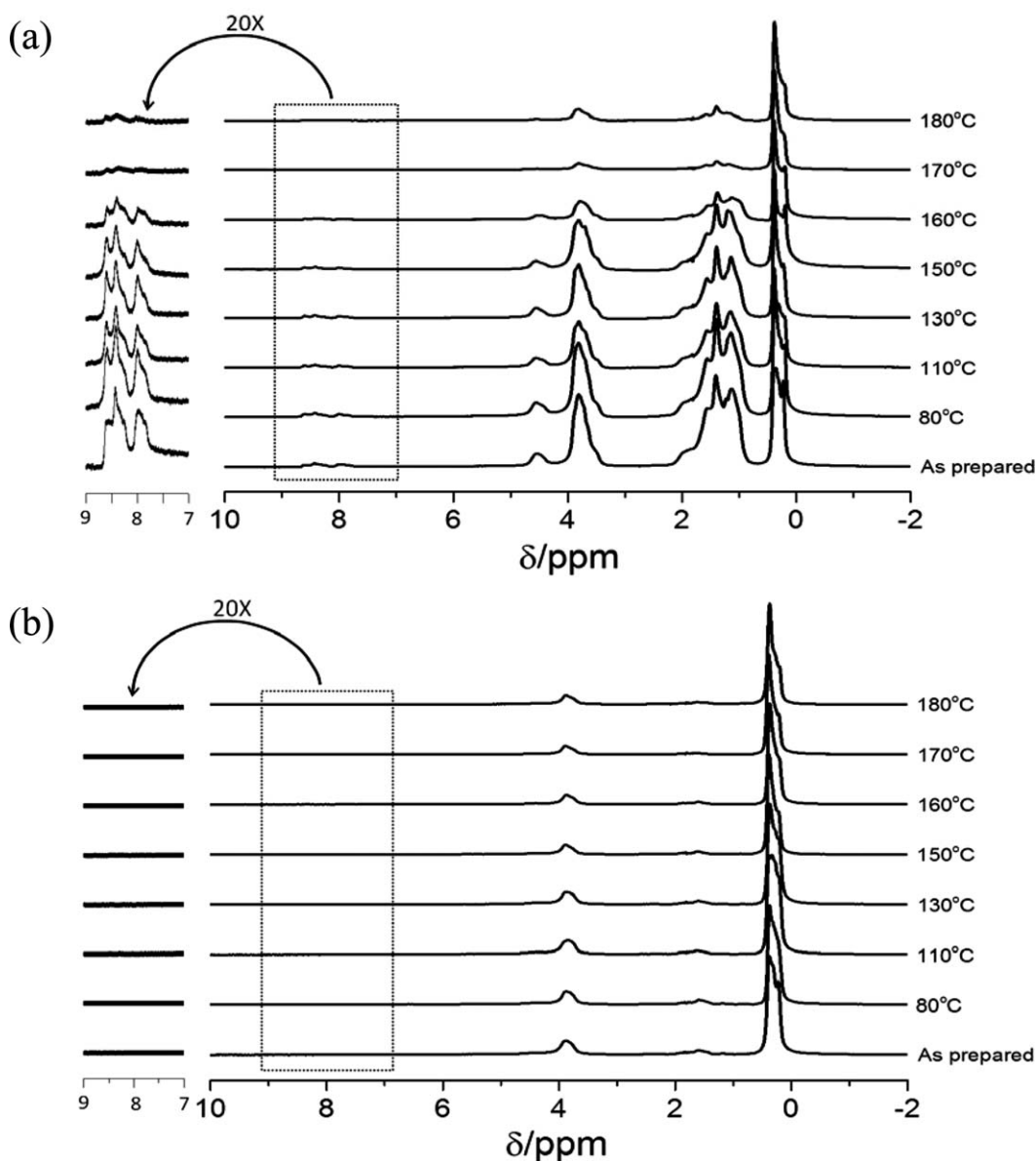
components. Note that the fiber samples under investigation contain PAN polymer, CNT, spin finishes, and possibly residual solvent (DMF). In general, DMF shows a chemical shift at 8.1 ppm for the  $-\text{CH}$  group, 2.93 and 2.73 ppm for the  $-\text{CH}_3$  groups, respectively. Conversely, the spin finishes (Types A and B in the Sample 1) are the mixture of different low molecular weight molecules. To assign the signals obtained for the fiber, high-resolution spectra of Types A and B spin finishes were carried out as shown in Figure 1. Each of these spectra shows a peak at 4.8 ppm which is due to the presence of water molecule in the spin finish emulsions. Comparing remaining signals of the spin finishes with the signals observed for the fiber sample, it is found that the peak at 0.5 ppm of the Sample 1 arises from the Type A spin finish whereas resonance lines appear at around 0.7–2, 3.2–3.8, and 4.2 ppm are due to the Type B spin finish. From Figure 1, it is also evident that there are three individual small peaks in Type B spin finish at the chemical shift region from 7.5 to 9 ppm which are absent in Type A spin finish. Note that Type B spin finish might have some poorly soluble components in DMF which could be the source of the wider line widths compared to that of Type A spin finish.

Figure 2 shows the solid-state  $^1\text{H}$  MAS spectra of Sample 2 acquired at a spinning rate of 10 kHz along with the spectra of spin finish Type C obtained from the high-resolution NMR using deuterated DMF as a solvent. Sample 2 has less number of peaks (at 0.5, 1.5, and 4 ppm) compared to that of Sample 1 which can be assigned, similarly as explained above, using the high-resolution spectra of Type C spin finish.

Type A spin finish shows few small peaks between 0.5 and 4 ppm which cannot be seen in the fiber spectra in Figure 1. These peaks could be either coinciding with the broader peak of Type B spin finish (e.g., peaks at 1.5 and 3.8 ppm) or disappear because of the less stable components in the spin finish which evaporate during drying of the fiber in the course of precursor



**Figure 2.** Isotropic region of  $^1\text{H}$  high-resolution spectra of liquid spin finish Type C measured at  $^1\text{H}$  frequency of 400 MHz at RT and  $^1\text{H}$  MAS spectra of Sample 2 measured at  $^1\text{H}$  frequency of 300 MHz at RT using Hahn echo with an echo time  $\tau = 175 \mu\text{s}$ . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

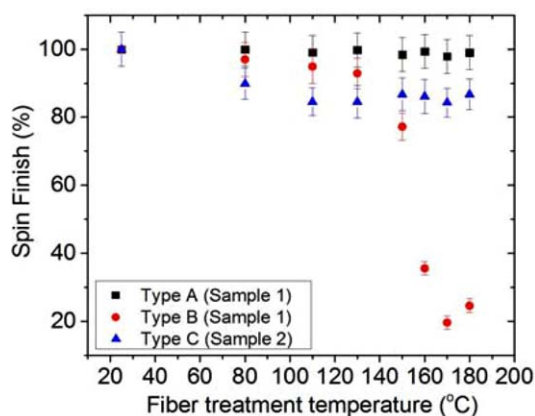


**Figure 3.**  $^1\text{H}$  MAS spectra of thermally treated (a) Sample 1 and (b) Sample 2. Sample treatment temperatures are listed on the right side. The spectra were obtained at RT at a  $^1\text{H}$  frequency of 300 MHz using Hahn echo with an echo time  $\tau = 175 \mu\text{s}$ .

fiber production. In Figure 2, similar behavior can be observed in case of Type C spin finish in Sample 2. Obviously, in a typical high-resolution (liquid-state NMR) spectrum the resonance lines are narrow, clearly revealing their complex structure comparing to the broad peaks in a solid-state NMR as can be seen in Figures 1 and 2.

Figure 3 summarizes the  $^1\text{H}$  spectra of the Sample 1 and Sample 2 after 24 h of heat treatment at different temperatures. Comparing the peak corresponding to the spin finish Type A at 0.5 ppm to the remaining peaks in Figure 3(a), it can be seen that the intensity of the peaks corresponding to the spin finish Type B at 0.7–2, 3.2–3.8, 4.2, and 7.5–9 ppm decreases significantly with increasing the treatment temperature, whereas little change in peaks from Type A spin finish is observed. The fiber

treated at 170°C shows two peaks at 0.5 and 3.8 ppm due to the presence of Type A spin finish and two more peaks at 0.7–2 and 7–9 ppm which are representing the signal from the remaining Type B spin finish. In case of peak at 0.5 ppm, there is a small reduction of intensity during the heat treatment which could be due to the removal of less thermally stable components from the Type A spin finish. As stated before, the fiber can also contain DMF as a residual solvent which has a boiling temperature of 154°C and it would disappear from the sample while treated at 160°C. However, NMR data are inconclusive to verify the presence of DMF as the peak corresponding to at 8.1 ppm would coincide with the peak of Type B spin finish and the intensity of the other two peaks at 2.93 and 2.73 ppm would be sufficiently short to detect at current experimental condition if the amount of residual DMF is low in the sample.



**Figure 4.** Percent of Types A and B spin finishes in the Sample 1 and Type C spin finish in the Sample 2 as calculated independently from Figure 3. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

To explore the effect of presence of CNT on the NMR spectra, Sample 3 (PAN/CNT composite fiber in which spin finishes Types A and B were used) was introduced and NMR spectra were obtained after heat treatment of the fiber samples at 110, 150, and 170°C, respectively. The experimental results are shown in Supporting Information Figure S3. These samples show similar peak assignments for the Types A and B spin finishes similar to that of Sample 1 as well as the reduction of spin finish Type B due to heat treatment. Note that the ratio of spin finish Type B to Type A in the as prepared Sample 3 is slightly less as compared to that of Sample 1 which could be due to the effect of different spin finish bath concentration (see Table I).

The  $^1\text{H}$  MAS spectra of the heat treated Sample 2 are shown in Figure 3(b). Type C spin finish was used during drawing for this fiber, corresponding to the peaks at 0.5 and 3.8 ppm. A small change in intensity in 0.5 ppm peak reveals the loss of a part of the Type C spin finish throughout the heat treatment. The results suggest that Type C spin finish is less stable than the spin finish Type A but more stable than Type B under the present experimental condition. Moreover, the shape and position of the peaks of the Sample 2 treated at 180°C are comparable to those of the Sample 1 treated at the same temperature [Figure 3(a)]. Note that the NMR data do not show the characteristic peaks at 8.1, 2.93, and 2.73 ppm of the residual DMF solvent in the composite fiber samples [Figure 3(b)].

As shown in Figure 4, an estimation of the percent of Types A and B spin finishes were obtained for the as prepared and treated Sample 1 from the integration of the NMR absolute peak area from Figure 3(a) and calibrated using the respective sample weight used during the experiment. The same calculation was carried out to obtain the percent of Type C spin finish from the NMR absolute peak area in Figure 3(b). Figure 4 shows that the percent of spin finish A remains mostly unchanged in the fiber Sample 1, whereas, there is a  $\sim 80\%$  reduction of the spin finish Type B due to the heat treatment. This clarifies the fact that the components of spin finish Type B are thermally less stable as compared to that of spin finish Type

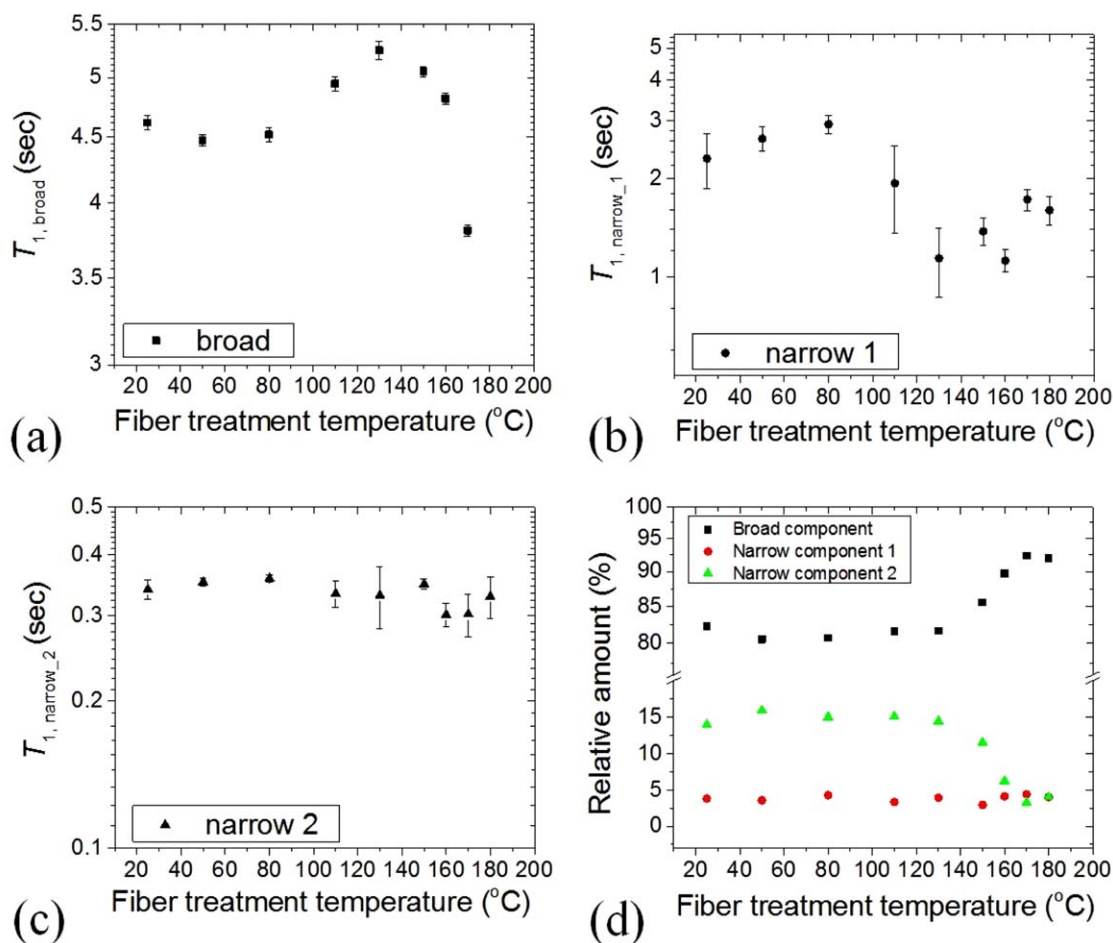
A in Sample 1. Conversely, it was found that there is  $\sim 15\%$  loss of Type C spin finish in Sample 2 due to the heat treatment as can be seen in Figure 4. It should be also noted that, based on the peak integration analysis [Figure 3(a)], the spin finishes on fiber 1 of Sample 1 (as prepared) are associated with relative amounts of 3:7, corresponding to the ratio protons in the spin-finishes A and B, respectively. However, the proton ratio does not necessarily represent the relative amounts of the two spin finishes in the sample.

Note that Soxhlet method can be used to determine the amount of spin finish applied to the fiber. Dried Sample 1 was treated using the solvent methyl ethyl ketone at about 70°C for 2 h in the Soxhlet apparatus to remove the spin finishes and dried afterward. The  $^1\text{H}$  NMR MAS spectra of the treated sample as obtained from the above described method showed complete removal of spin finish Type B, however, there was hardly any loss of spin finish Type A (data not shown). Thus,  $^1\text{H}$  NMR MAS study, as proposed in this work, could be used as a suitable tool to check the presence of any of the remaining spin finishes in the fiber sample if the Soxhlet method is used for the quantitative analysis. This will provide more precise calculation of the amount of spin finish in the fiber.

#### Results from Static $^1\text{H}$ $T_1$ Relaxation Experiments

The  $^1\text{H}$   $T_1$  relaxation times of different components of the PAN powders and fiber samples were measured to understand the change in molecular mobility of different components of the samples. Note that the assignment of the relative components in the  $T_1$  relaxation study could be different than that of  $^1\text{H}$  MAS spectra where only the relatively mobile components were selected for study.

PAN homopolymer powder has a  $T_1$  relaxation time of  $2.4 \pm 0.4$  s obtained from a single component, whereas PAN-co-MAA powder shows two individual components having  $T_1$  relaxation time of  $3.4 \pm 0.1$  s and  $2.6 \pm 0.2$  s, respectively, obtained from the corresponding  $\sim 93\%$  of Gaussian (broad) and  $\sim 7\%$  of Lorentzian (narrow) relative components, respectively. To assign the corresponding components, it is to be noted that the amorphous phase of the PAN polymer would be in rigid glassy state at RT as the glass transition temperature of PAN is  $\sim 85^\circ\text{C}$ . In that case, the relaxation time difference between the crystalline and amorphous phases of PAN becomes small as discussed by Herbert et al.<sup>16</sup>. Thus, the broad component could be attributed to the crystalline and glassy amorphous phases averaging the  $T_1$  due to spin diffusion. Conversely, relatively mobile components ( $\sim 7\%$ ) show a significantly shorter  $T_1$  relaxation time of 2.6 s. As noted in the experimental section, in a PAN copolymer containing about 4% MAA as a comonomer,  $\sim 92.3\%$  protons from the PAN molecule containing three protons in the repeating unit and  $\sim 7.7\%$  protons from the MAA molecule containing six protons in each molecule contribute to the NMR signal. A similar distribution of relative weights of the short as well as long components can be seen from the experimental values of PAN powder  $T_1$  relaxation time measurement. This might suggest that the narrow components in PAN powder could be caused by the MAA comonomer molecules. This, however, is not expected if MAA



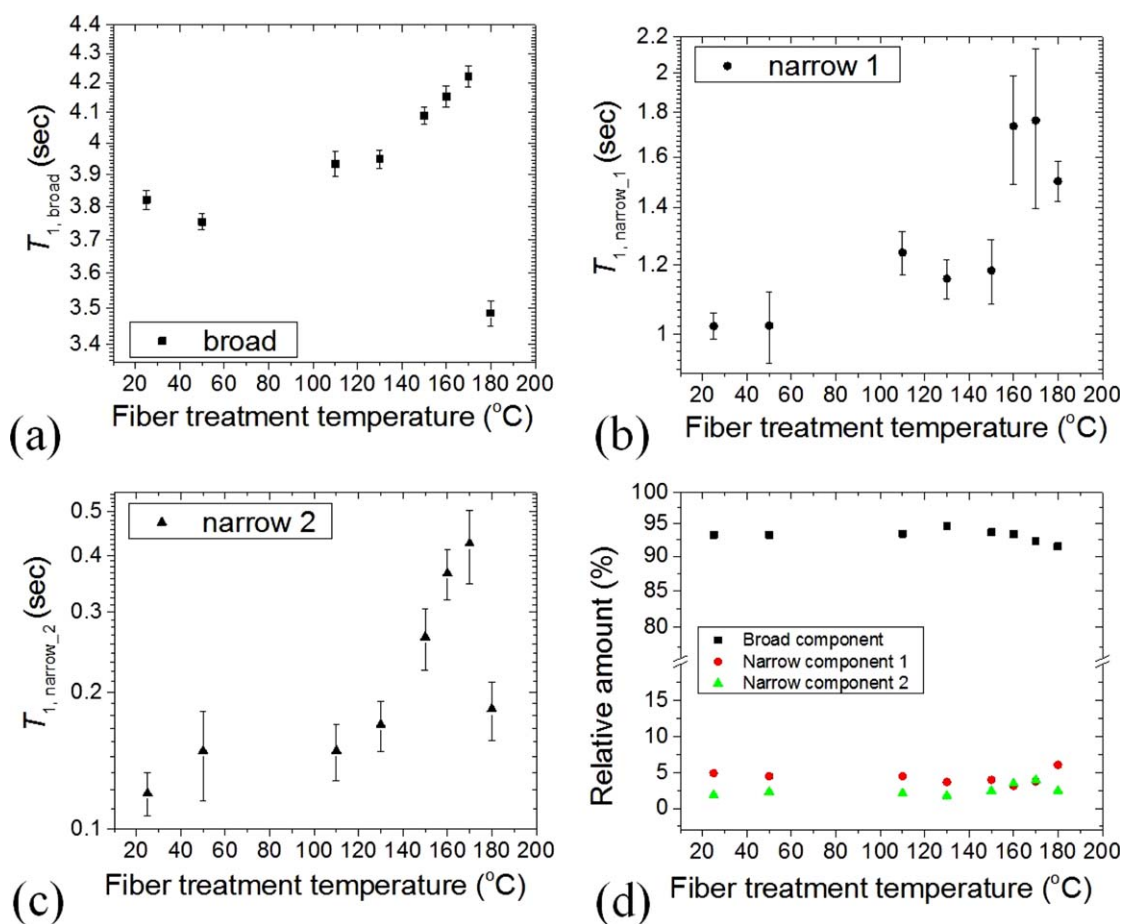
**Figure 5.**  $^1\text{H}$  spin-lattice relaxation times ( $T_1$ ) of the (a) broad component, (b) and (c) narrow components of the thermally treated Sample 1 in the temperature range from RT to 180°C. The experiments were carried out at RT. (d) Calculated percent of relative components in Sample 1 for the analysis shown in (a), (b), and (c). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

is incorporated as comonomers into the rigid PAN polymer. Gupta and Singhal<sup>17</sup> suggested that the comonomer units exist in the crystalline phase only above a critical concentration which is 25 mol % for methacrylonitrile (MAN) and 12 mol % for methyl methacrylate (MAA) in PAN-co-MAN and PAN-co-MAA, respectively. It is, therefore, reasonable to also speculate that the MAA comonomer could be available mostly in the polymer amorphous phase with the possibility of short comonomer containing sequence which will allow more flexible conformation.

The  $T_1$  values of broad (solid like) and two narrow (relatively mobile) components of Sample 1 are plotted in Figure 5 as a function of fiber treatment temperature. It can be seen that the  $T_{1, \text{broad}}$  value in the fiber (4.6 s) is higher than that of the PAN powder (3.4 s) which could be due to the enhanced rigidity of the polymer chains due to fiber structure development through crystallization and molecular orientation as a result of drawing during the course of fiber processing. It is observed that, for the broad component, the  $T_1$  relaxation time shows a gradual increase until reaching a maximum when treated at 130°C and then starts to decrease. There is a sudden drop of the  $T_1$  value due to heat treatment at 170°C. It is to be noted that in the

temperature range 180–300°C, the stabilization reaction occurs in the PAN precursor fiber which is an intermediate step for the conversion of precursor fiber to the carbon fiber.<sup>3</sup> Thus, decrease of  $T_1$  value at high temperature could represent a change in the polymer structure due to the onset of cyclization.

As stated in the experimental section, there are two types of narrow components observed in Sample 1. The  $T_{1, \text{narrow}_1}$  value starts to drop while heating above 80°C. Conversely, the  $T_{1, \text{narrow}_2}$  value does not show any significant change due to heat treatment. In case of Sample 1, the mobile components could be the spin finish Types A and B, residual DMF as well as the mobile component observed in the PAN powder. It is found that the relatively mobile components in Sample 1 show significantly different  $T_1$  values of 2.3 and 0.34 s for the narrow 1 and narrow 2 components, respectively. To identify the individual spin finish,  $^1\text{H}$  MAS spectra were acquired at two different conditions: (a) relaxation delay (10 s)  $\approx 5 T_1$  and (b) relaxation delay (0.1 s)  $\ll 5 T_1$  of the narrow 1 component. As can be seen in Supporting Information Figure S4, signal of Type A spin finish is reduced significantly at condition (b) which confirms that spin finish Type A is one of the contributors in the signal of narrow 1 component. The other contributor would be the



**Figure 6.**  $^1\text{H}$  spin-lattice relaxation times ( $T_1$ ) of the (a) broad component, (b) and (c) narrow components of the thermally treated Sample 2 in the temperature range from RT to 180  $^{\circ}\text{C}$ . The experiments were carried out at RT. (d) Calculated percent of relative components in Sample 2 for the analysis shown in (a), (b), and (c). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

narrow component which shows similar relaxation time as observed in the PAN powder. Consequently, narrow 2 component is attributed to the spin finish Type B.

The  $T_1$  relative narrow components, as calculated<sup>18</sup> from the values obtained from the fitting of eqs. (1) and (2), reveal that the narrow 2 component in Sample 1 decreases with the increase of treatment temperature, whereas that of narrow 1 component remains constant as can be seen in Figure 5(d). This further supports our findings from Section A: during heat treatment Type B spin finish shows significant loss of its

components, whereas Type A remains stable [Figure 3(a)]. It is also to be noted that relaxation time of Type B spin finish remains the same inside the error limit [Figure 5(b)] throughout the heat treatment, although the relative amount (%) is decreased as can be seen in Figure 5(d).

Figure 6 shows the  $T_1$  relaxation times of broad and narrow components of Sample 2 after heat treatment in the range from RT to 180  $^{\circ}\text{C}$ . Comparing Figures 5 and 6, it is found that the  $T_1$  values of all of the components in the Sample 2 are shorter than that of the Sample 1. It is known that existence of a

**Table II.**  $T_1$  and % of Relative Components in Sample 3 (Containing Type A and B Spin Finishes) in the as Prepared and Heat Treated Fiber

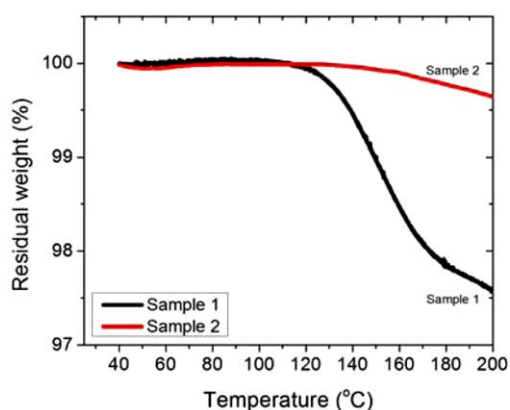
Heat treatment temperature	Broad component		Narrow 1 component		Narrow 2 component	
	$T_1$ (s)	Relative amount (%)	$T_1$ (s)	Relative amount (%)	$T_1$ (s)	Relative amount (%)
As prepared	2.9 ± 0.1	87.3	1.8 ± 0.1	4.4	0.3 ± 0.01	8.3
110 $^{\circ}\text{C}$	3.8 ± 0.1	91.8	2.5 ± 0.2	3.7	0.3 ± 0.02	4.5
150 $^{\circ}\text{C}$	3.7 ± 0.1	92.5	2.2 ± 0.1	3.8	0.3 ± 0.02	3.7
170 $^{\circ}\text{C}$	3.7 ± 0.1	93.5	1.8 ± 0.1	3.8	0.2 ± 0.03	2.7

paramagnetic component within a polymer will lead to a significant reduction of the  $T_1$  value.<sup>19,20</sup> In this study, the catalytic content in the CNT was 1.2 wt % (measured by TGA) which could be a source of paramagnetic impurities and a possible reason of significantly shortened  $T_1$  value. Another factor which could affect the conducting areas within the polymer is the ring current induced in the CNT. However, it can be predicted that the relaxation time of narrow 2 component, which could be assigned to the spin finish Type C, will have a minimum effect as the spin finish is applied on the outer surface of the fiber. In case of Sample 2, the  $T_{1, \text{broad}}$  values gradually increase with the increase of the heat treatment temperature until 170°C and sharply drop at 180°C which could be due to starting of the cyclization reaction as discussed above.

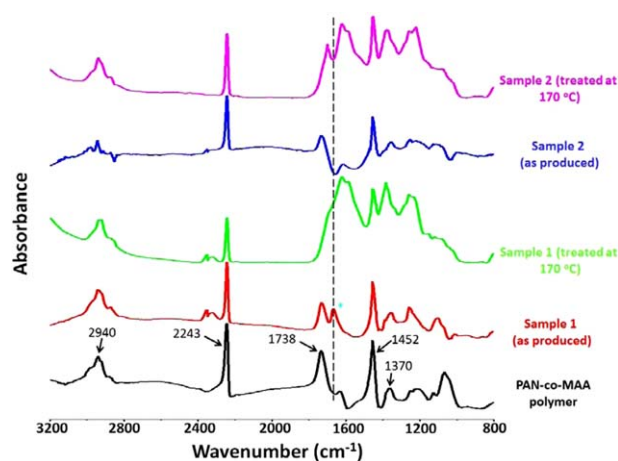
To understand the role of CNT on the relaxation behavior, the relaxation time of different components in Sample 3 were studied and summarized in Table II. It can be seen that  $T_{1, \text{broad}}$  values of Sample 3 are the lowest compared to that of Samples 1 and 2. These samples contain the highest amount of CNT compared to the other samples (see Table I) and the paramagnetic components present in the CNT might explain the observed results as discussed above. Moreover,  $T_{1, \text{narrow 1}}$  values of Sample 3 show similar values and tendency with the heat treatment as the Sample 1 where CNT was not used during the fiber processing. This suggests that the contribution of the spin finish Type A dominates in the relaxation of narrow 1 component. Relaxation time of the narrow 2 component representing spin finish Type B in Sample 3 is  $\sim 0.3$  s as can be seen in Table II. This result is comparable to the relaxation time of the spin finish Type B in the Sample 1 [Figure 5(c)]. This is a strong indication that the presence of CNT does not affect the relaxation time of the spin finish unlike to that of the polymer chain.

### Results from TGA and FTIR Experiments

Figure 7 shows the TGA of Samples 1 and 2. It can be seen that the fiber Sample 2 containing spin finish Type C shows relatively less % of volatile components removal from the sample compared to that of Sample 1 containing spin finishes Types A and B in the temperature range 120–170°C. These results further support the quantitative analysis of the spin finishes as pre-



**Figure 7.** TGA weight loss curves of Samples 1 and 2 measured at a heating rate of 1°C/min in nitrogen. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 8.** FTIR spectra of PAN-co-MAA powder, Sample 1 and Sample 2. The vertical line corresponds to the 1668  $\text{cm}^{-1}$  peak for the DMF carbonyl group. The curves are vertically shifted for clear comparison. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

sented in the NMR studies which demonstrated that the removal of Type B spin finish in the heat treated fibers follows the similar pattern in this temperature range. The volatile components also could contain the residual solvent DMF which can be investigated using the FTIR spectroscopy.

The IR spectra of the PAN powder, as prepared and thermally treated PAN (Sample 1) and PAN/CNT (Sample 2) fibers, are shown in Figure 8. All the samples show the characteristic band of  $-\text{CH}_2$  group at 2940  $\text{cm}^{-1}$  ( $\nu_{\text{C-H}}$ ) and 1452  $\text{cm}^{-1}$  ( $\delta_{\text{C-H}}$ ), the band of the nitrile group at 2243  $\text{cm}^{-1}$  and the band of  $-\text{CH}$  group at 1370  $\text{cm}^{-1}$  in the polymer chain. Another strong band appears at 1738  $\text{cm}^{-1}$  which may be attributed to the carbonyl group stretching from the acid comonomer.<sup>21–23</sup>

The presence of residual DMF can be evaluated by the band of the carbonyl group at 1668  $\text{cm}^{-1}$ .<sup>24</sup> From the Figure 8, it is clear that only the as prepared Sample 1 shows the residual DMF, and there is no residual DMF in the PAN fiber treated at 170°C. Note that residual DMF peak could not be differentiated in the NMR data obtained in Sample 1 [Figure 3(a)] because of its low concentration in the fiber and peak overlapping with that of the spin finish. Figure 8 demonstrates that Sample 2 does not contain any residual DMF in its structure which is in good agreement with the  $^1\text{H}$  NMR study [Figure 3(b)].

### CONCLUSIONS

Heat treatment of PAN and PAN/CNT composite fibers was carried out in the temperature range of RT to 180°C. Solid-state NMR was used to study the control and composite fibers at RT. The relatively mobile components in the fiber were detected from the NMR spectra using the Hahn echo sequence.  $^1\text{H}$  MAS NMR study of Sample 1 PAN control fiber clearly indicated that spin finish Type A is thermally stable, whereas Type B loses  $\sim 80\%$  of its weight because of the heat treatment. Type C, the spin finish used in the composite fiber Sample 2, shows  $\sim 15\%$  loss of its weight due to heat treatment. With this technique, it was possible to detect the signal of two different spin finishes



applied in a single fiber as well as their relative amounts in the fiber. From the FTIR it was found that small amount of DMF is present in the as prepared PAN control fiber. The analysis of spin-lattice relaxation time ( $T_1$ ) presented evidence on different molecular dynamics of the fiber components at different temperatures. The molecular mobility determined by the  $T_1$  relaxation time could be one of the most important parameters to study the effect of spin finish and its thermal degradation on the resulting carbon fiber properties. However, the presence of CNT in the composite fiber affects the  $T_1$  relaxation time due to the catalytic impurities in the CNT.

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