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New Insight into the Composition and Structure of Sizing Agent from NMR Spectroscopy

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Abstract

Sized carbon fibers (CFs) are of commercial significance as they form the main load bearing component in the advanced materials, namely, the carbon fiber reinforced plastics (CFRPs). Much of the knoweldge of sizing composition and the process of sizing is a subject of intellectual property rights owing to its commercial relevant. In this original research aticle, deeper insights into the structure and composition of the sizing agent used for the surface modification of commercial cabron fibers (NX90, NX100, CFF800, T800HB, T700SC and M55J) were obtained using ^{1}H, ^{13}C, ^{29}Si and heteronuclear single quantum coherance (HSQC) NMR spectroscopic analysis. NMR analysis of the sizing compound extracted from the sized crabon fibers revealed that indeed a dimer of diglycidyl ether of biphenol A, DGEBA, (trade name, E51) is used in the sizing composition for making the fiber compatible with the polymer matrices so as to increase the interfacial strength via improved chemical bonding. The distinguishing feature between the ^{1}H NMR spectra feature of the monomer of DGEBA and the dimer of DGEBA (E51) is the relative intensities of the signals from the aliphatic (methyl protons) and the aromatic protons. In the ase of the DGEBA monomer the intesity of the signal correspodning to the methyl prtonts (6H, S at 1.65 ppm) is slightly higher than the signals from that of the aromatic protons (H-5, m, 4H, 7.2 ppm; 6.8, H-4, m, 4H, 6.8 ppm).

Keywords: Sizing agent, carbon fibers, carbon fiber reinforced plastics, CFRPs, E51, DGEBA dimer, crown ethers, organo siloxanes, PDMS, HDMS, NX90, NX100, CFF800, T800HB, T700SC, M55J

INTRODUCTION

In sharp contrast, in the case of the DGEBA dimer, the intesity of the signal corresponding to the mehtyl protons (12H-f, s at 1.67 ppm) is almost double or even higher than the intesnity of the signal corresponding to the aromatic protons (H-e, m, 8H, 7.18 ppm; H-d, m, 8H, 6.89 ppm; the alphabets used for coding different protons in the chemical structure of the dimer of DGEBA correspond to the protons in different chemical environment). Such a demarcation between the monomer of DGEBA and the dimer of DGEBA is not perceptible from FT-IR analysis, though the FT-IR analysis of the sizing compounds isolated from the carbon fibers celarly pointed to the presence of the DGEBA derivative in the sizing composition. From the ^{1}H NMR anaysis of the zising compound isolated from the selected commecial carbon fibers, it is deduced that the sizng composition used for the surface modificato of cabro fibers is the dimer of DGEBA (commercial trade name, E51). Thus E51 is a promising sizing composition for inducing surface polarity into the cabron fibers and making them compatible with the polymer matrices resulting in potential carbon fiber reinfoced composit3es with a strong interface yield good mechanical properties. Such an interpretatio nis further substantiated by the ^{13}C NMR analysis as well. Apart from the dimer of DGEBA, the sizing

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composition also contained an unusual ether, namely, the 18-crown-6 ether complex with a sharp singlet at 3.53 ppm corresponding to the methylene protons. It is common practice by polymer chemists to use crown ethers as disersant in sizing composition. Moreover, the methylene protons of the 18 crown-6-ether, an integral compound in the sizing composition, should not be mistaken with the protons of the expoxy sizing in the epoxy resin homologues (for instance, diglycidyl bis disulfide carbon ether of bisphenol, which too gives a characterstic peak at 3.6 ppm). This is because, the FT-IR analysis of the sizing compounds clearly pointed to the dimer of DGEBA and not to the presence of diglycidyl bis disulfide carbon fether of biosphenol A. This is one of the classical exdamples that demonstrates the cross verification of the presence of a certain compound in the analyte by more than one analytical tool to avoid committing a mistake. Another vital observation of the ^{1}H and ^{13}C NMR spectra of the sizing compounds isolated from the commercial carbon fibers is the presnece of a signal close to 0 ppm. It is well know that the standard used for NMR studies, namely, the tetra methyl silane (TMS) resonates at 0 ppm. However, the signal around 0 ppm in the ^{1}H and ^{13}C NMR should not be confused with that of the TMS. To further inestigate the origin of this signal close to 0 ppm in the ^{1}H and ^{13}C NMR, ^{29}Si NMR of the sizing compounds were recorded. As surmised, a signal in the range of - 110 to - 111 ppm characteristic of the prsence of organosilicone ($Si-CH_3$) type compound in the sizing composition is discovered. Usually, the methyl protons of CH_3-Si-O groups present in polydimethyl siloxanes (PDMS) and hexamethyl disiloxanes (HMDS) are responsible for the peaks observed at 0.18 ppm and 0.1 ppm in the ^{1}H NMR sepctrum of the sizing compound Such organosiloxane compounds serve as a protective surface film and prevent the sizing compound (dimer of DGEBA) from undergoing undesirable reactions like the hydroglysis, cyclization and polymerization. In addition to preenting the unwanted side reactions, the organo silicone compounds in the sizing composition serves as anti-foaming agents and structure shaping agents.

A web of science search with the keywords, namely, sizing agent, gives 1,08, 103 results. However, the results reduce by three orders of magnitude to only 41, when the search keywords include CFRP in addition to sizing agent [1-10]. It doesn't mean that only two papers deal with CFRP and the utility of sizing agents in the advanced materials, namely the carbon fiber reinforced plastics (CFRPs) is under-utilized. The subject of sizing agent and its chemical composition when used in CFRPs has been the subject of intellectual property rights owing to the commercial significance of the process of sizing as well as the structure and composition of the sizing agents. Such a deduction is further substantiated by the research results from google scholar (20, 500 results) and google patents (more than 1, 00, 000) with the same search keywords, namely, sizing agent and CFRPs. However, it is up to the data bases, namely, the web of science and the google scholar to sort out the discrepancies in the numbers 2 and 20, 500 with the same keywords, namely, "sizing agent and CFRPs".

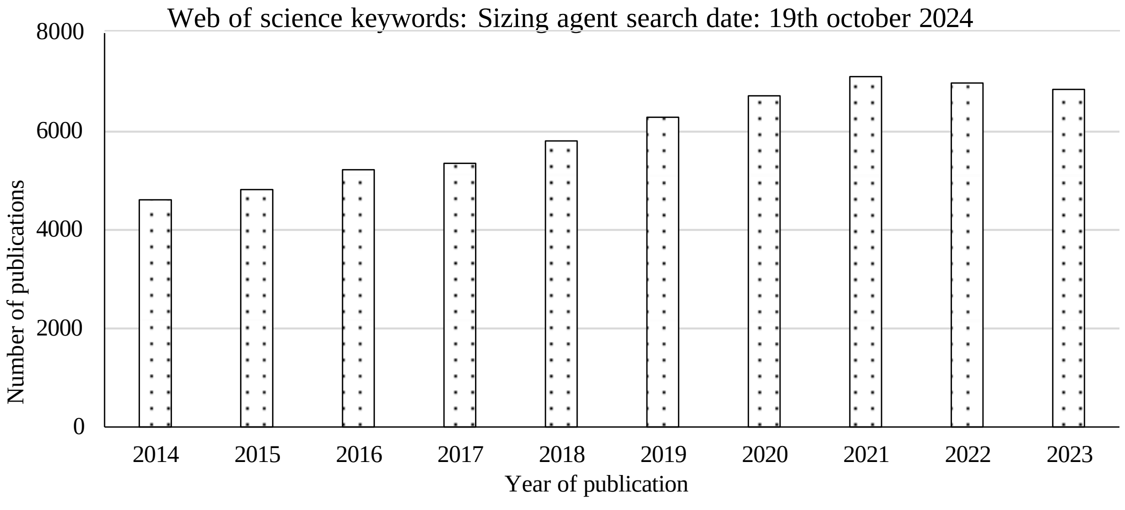

Figure 1. Advance in the research and development (R & D) activity of "sizing agent" during the past decade (2014-2023).

A steady advance in the field of "sizing agent" during the past decade (2014-2023) can be noticed from the bar-diagram shown in Figure 1 that depicts the change in number of publications as a function of year of publication. With the advent of the advanced materials like the carbon fiber reinforced composites as metal substitute in the field of infrastructure, aeronautics, astronautics, geonautics, aquanautics, sports and space exploration, the applications of sizing agents is surmised to grow at a rapid pace compared to the conventional trend observed during the past decade. As mentioned earlier, much of the knowledge of sizing composition and the sizing agents is of the domain of intellectual property rights owing to its commercial significance [11-20].

Sizing agent is used for imparting polarity onto the carbon fibers. As a result the sized carbon fibers become more compatible to be composited with a variety of polymer matrices [21, 22]. The presence of sizing layer on the surface of the carbon fibers results in the formation of strong interface between the main load bearing component of the CFRPs, namely, the carbon fibers, and the polymer matrix. Such strong interfaced is needed for the best mechanical properties (interfacial shear strength, IFSS and the interlaminar shear strength, ILSS) increasing the utility of the CFRP's many a fold.

The central aspect of this original research article is to examine the structure and composition of the sizing compound used for the surface modification of the commercial carbon fibers, through the commercial sizing process. With this objective commercial carbon fibers, namely, the pitch based (NX90, NX100) and the polyacrylonitrile (PAN) based (CFF800, T800HB and T700 SC) chosen as a representative example were examined using NMR spectroscopy. As a result of the study it was found that all the CFs examined were surface modified using epoxy sizing agent containing the (diglycidyl ether of biphenol A) DGEBA dimer (E51). Moreover, in addition to the major sizing compound E51, the sizing composition also contained unusual compounds based on organo silicone that are mean for forming a surface protective layer on the CFs as well as to foam formation suppressors during the process of sizing as well as subsequent use of the sized fibers for forming composites with polymer matrices.

EXPERIMENTAL

The carbon fibers, namely NX90 and NX100 (pitch derived) were procured from Nippon graphite fiber co. CFs, namely, T700SC, CCF800H, T800HB (polyacrylonitrile, PAN, derived) were purchased from Toray Ltd. Acetone used for isolating the sizing compound from the surface of the commercial carbon fibers were obtained from Sinpharm chemical reagent co. Ltd., All the materials obtained were used as received. Typical procedure adoped for isolating the sizing compound from the commercial carbon fibers is reported elsewhere [4]. NMR (^{1}H, ^{13}C, ^{29}Si, HSQC) spectroscopic analysis of the sizing agent isolated using acetone reflexion from the commercial carbon fibers (both pitch and PAN based) was carried out using a 500 MHz Bruker NMR measuring instrument. D_2O was used as a solvent. Typical sample for NMR analysis was prepared by taking 400 μL of the analyte (sizing compound extracted from the commercial carbon fibers dissolved in minimum amount of acetone) in an NMR tube and by adding 200 μL of $CDCl_3$ as solvent and a 50 μL of THF (used as an internal standard for the quantification of the sizing compound).

RESULTS AND DISCUSSION

Determination of structure of sizing compound using ^{1}H, ^{13}C and ^{29}Si NMR

The structure and composition of the sizing agent used for the modification of the surface modification of cabron fibers were systematically studied using ^{1}H, ^{13}C, ^{29}Si and HSQC NMR spectroscopic analysis. NMR analysis of the sizing compound isolated from the commercial carbon fibers, namely, revealed that indeed a dimer of DGEBA (trade name, E51) is used in the sizing composition. The strucutre of E51 is shown in the inset of the ^{1}H NMR spectrum of the sizing compound isolated from the carbon fiber NX90 (Figure 2). The NMR result is no way a contradiction to the FT-IR analysis of the sizing compund [4], but substantiates the findings from NMR analysis in addition to providing a more clear insights. The differene in the structure of monomer of DGEBA and the dimer of DGEBA (E51) is perceptible from NMR while it is not so from FT-IR spectroscopy where in the presence of the monomer of DGEBA is observed in the sizing compound isolated from different commercial carbon fibers, including the NX90, as in the present case. The ^{1}H NMR spectra of the sizing compound isolated from other carbon fibers, namely, NX100, T700SC, CCF800H, T800HB were shown in Figures 3 to 6 respectively.

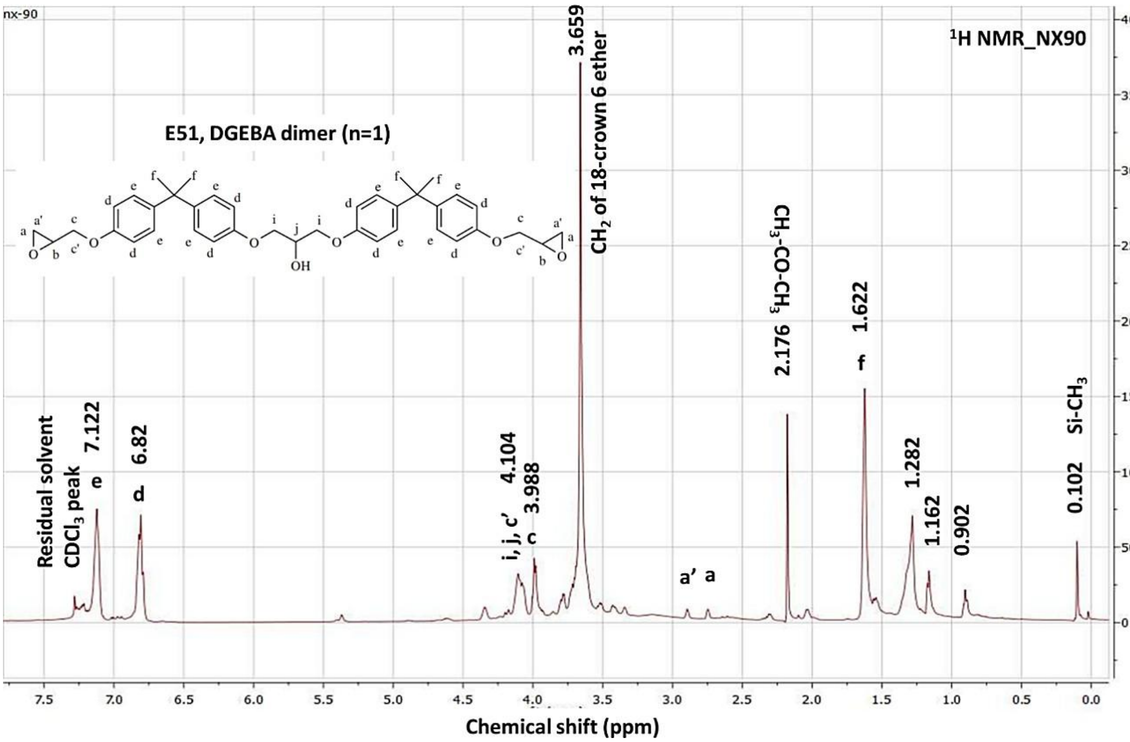

Figure 2. ^{1}H-NMR spectrum of sizing agent extracted from carbon fibers NX90.

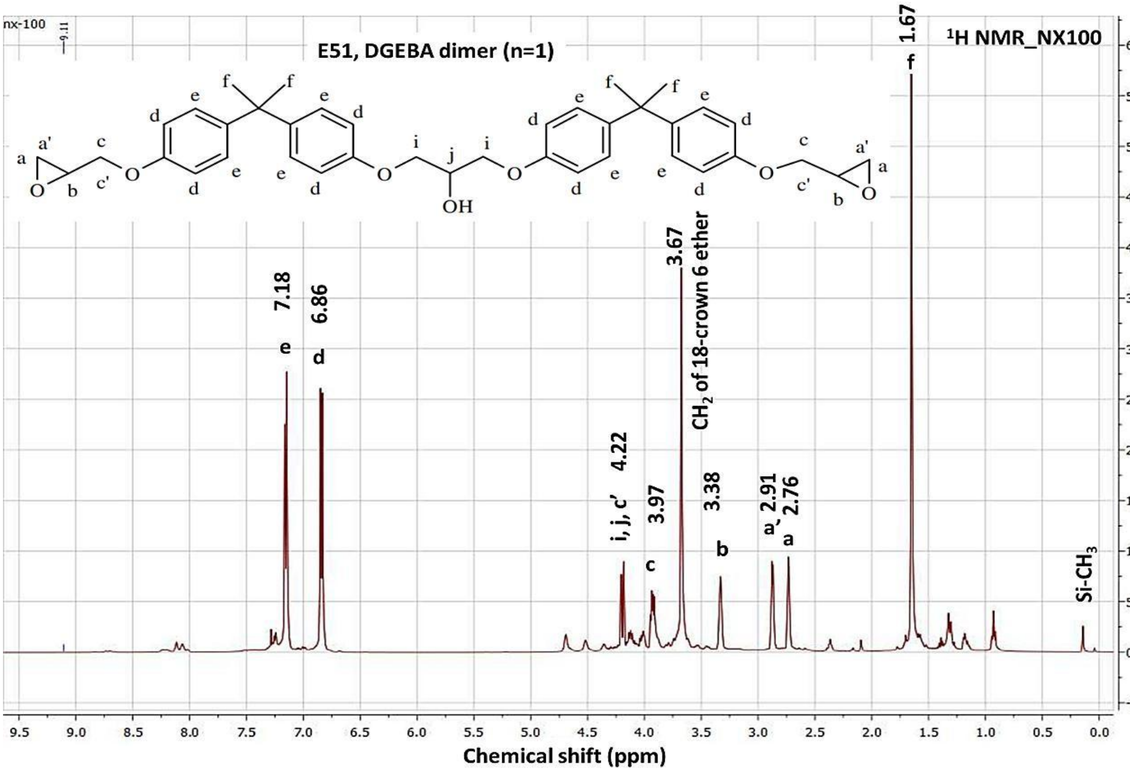

Figure 3. ^{1}H-NMR spectrum of sizing agent extracted from carbon fibers NX100.

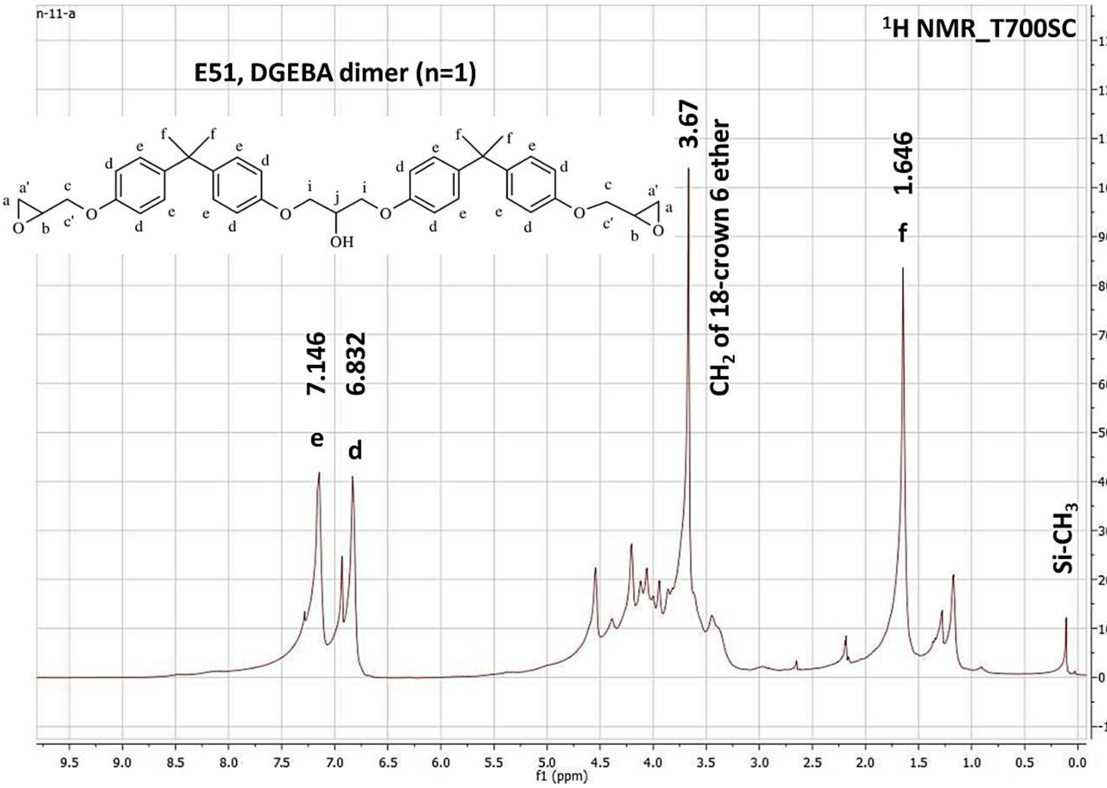

Figure 4. ^{1}H-NMR spectrum of sizing agent extracted from carbon fibers T700SC.

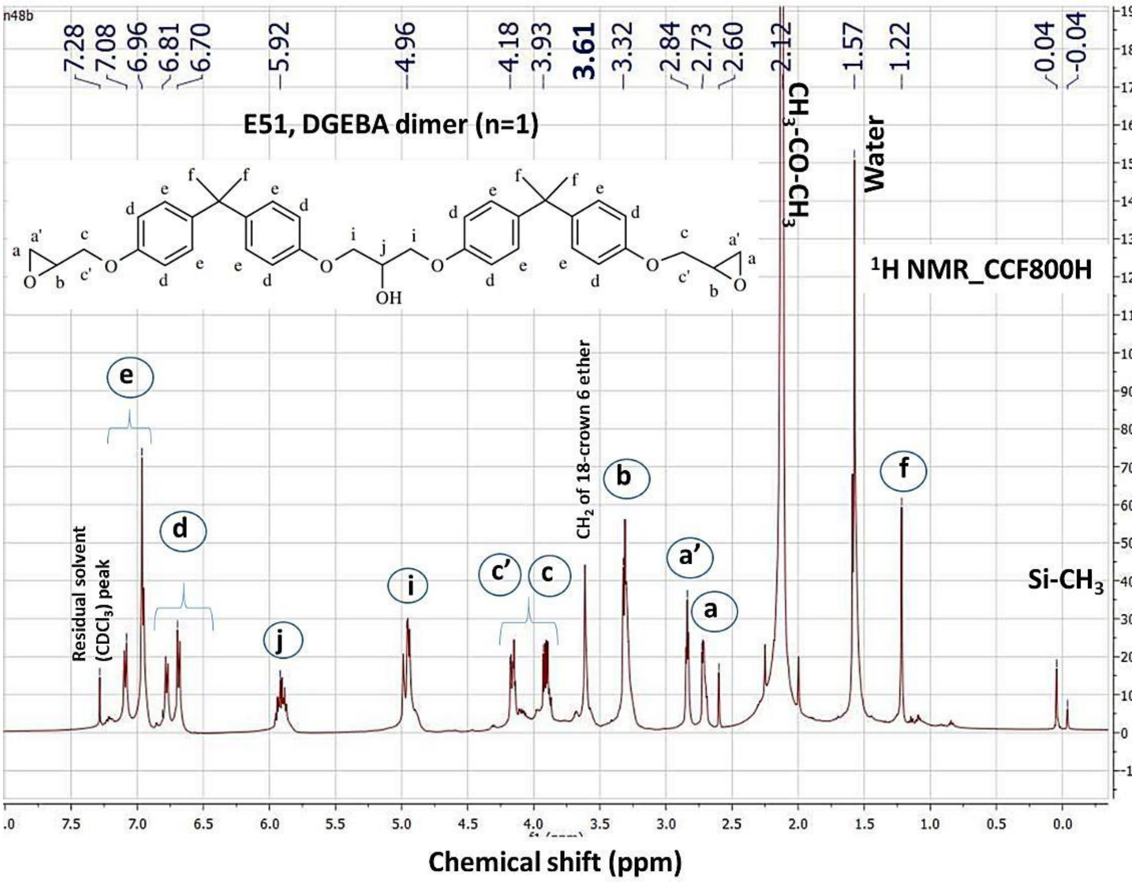

Figure 5. ^{1}H-NMR spectrum of sizing agent extracted from carbon fibers CCF800H

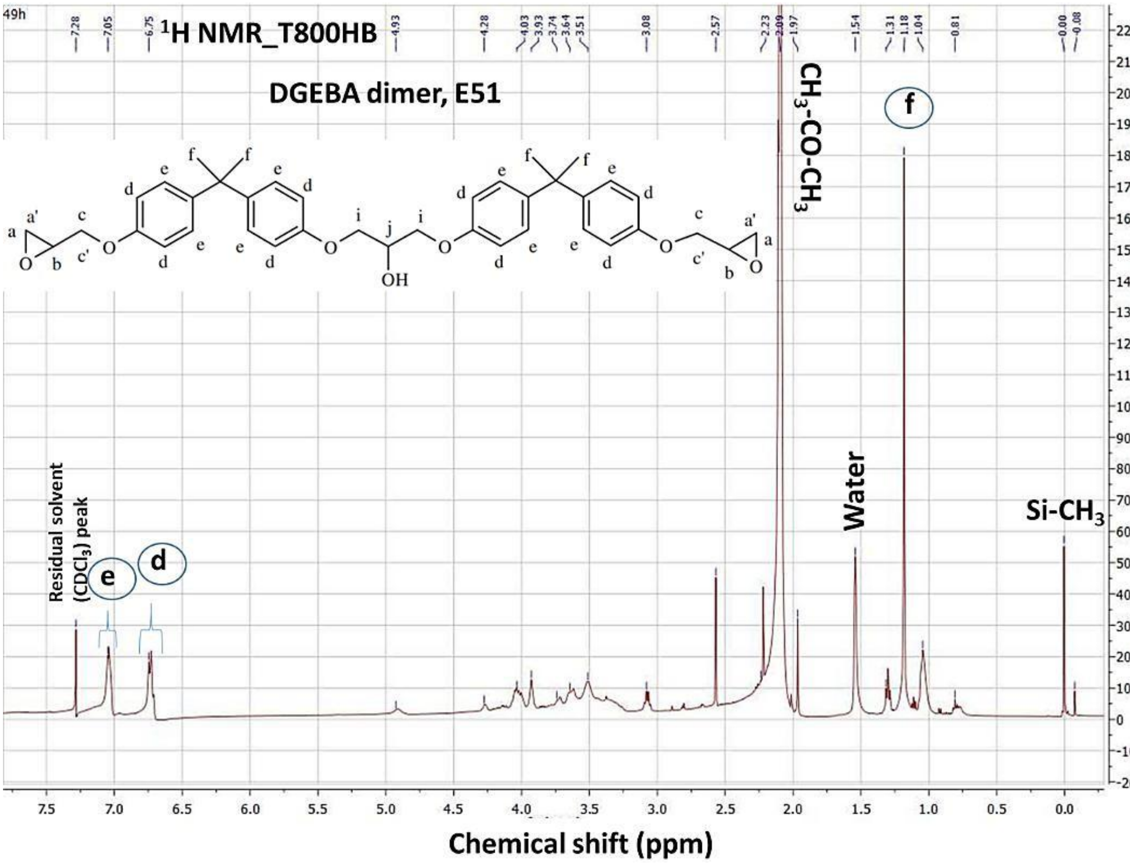

Figure 6. ^{1}H-NMR spectrum of sizing agent extracted from carbon fibers T800HB.

Lui et al., reported on the the ^{1}H and ^{13}C NMR spectrum of the monomer of DGEBA [23]. Likewise, Schaefer and Simat et al., reported on the NMR (^{1}H and ^{13}C) NMR spectral features of the dimer of DGEBA (commercial trade name E51) [24]. For ready reference the 1H NMR spectrum of E51 is shown in Figure 7. Discussion of the ^{1}H NMR spectral features of the siing compound extrated from commercial carbon fibers(Figures 2-6), is elaborated in the specific instance of sizing compound isolated from NX100 (Figure 3) as this particular carbon fiber is very special owing to its very high degree of crystallinity [22]. Characteristic spectral data deduced from ^{1}H NMR spectrum of the sizing compound isolated from NX100 (Figure 3) [^{1}H-NMR (500 MHz; $CDCl_3$): 7.18 (H-e, m, 8H), 6.86 (H-d, m, 8H), 4.22 (H-j, m, 1H), (H-i, m, 4H), (H-c', dd, 2H), 3.97 (H-c, dd, 2H), 3.38 (H-b, m, 2H), 2.91 (H-a', dd, 2H), 2.77 (H-a, dd, 2H), 1.67 (H-f, s, 12H) ppm] correlate to the structure of the dimer of DGEBA (chemical structure with protons in different chemical environments are alphabated as shown in the inset (Figure 3). The ^{1}H NMR spectrum of the sizing compound from NX100 natches well with the ^{1}H NMR spectrum of E51 implying that the molecule in question, namely, the sizing agent mainly comprises of E51 (the dimer of DGEBA) (Figure 7). The interpretation agrees well with the report from Schaefer and Simat [24]. Similar spectral features are observed in the ^{1}H NMR spectra of the sizing compound isolated from the carbon fibers NX90 (Figure 2**)**, and also in the ^{1}H NMR spectra of the sizing compound extrated from the PAN based carbon fibers (T700SC, CCF800H, and T800HB) (Figures 4-6) indicating that the sizing compound used for the surface mofidication of all the carbon fibers studied is the dimer of DGEBA (E51). The striking difference between the spectral features of the monomer of DGEBA [23] and the dimer of DGEBA (Figure 7) is the relative intensities of the the signals from the aliphatic (methyl protons) and the aromatic protons. In the case of DGEBA monomer the intensity of the single corresponding to methyl protons (6H, S) at 1.65 ppm is slightly higher than the signals of the aromatic protons [7.2 (H-5, m, 4H), 6.8 (H-4, m, 4H)] [23]. On the contratry, in the case of the dimer of DGEBA the intensity of the signal corresponding to methyl protons (12H, S) at 1.67 ppm is almost double or even higher compared to the intenity of the signal corresponding to aromatic protons [7.18 (H-e, m, 8H), 6.86 (H-d, m, 8H)]. Such a fine distinction of the sturcture of the monomer of DGEBA and the dimer of DGEBE is not persceptible in FT-IR analysis though FT-IR analysis unequivocally indicated that the compound under test is DGEBA derivative [24].

In contrast to the ^{1}H NMR spectra of the sizing compound from the pitch based fibers (NX90 and NX100), in the ^{1}H NMR spectra of the sizing compound from PAN based T700SC (Figure 4), not all peaks corresponding to all the protons in the different chemical environments in the structure of the sizing compound, namely, the dimer of DGEBE, are visible. However, from the presence of signals of methyl protons “f” and aromatic protons “e” and “d” and from their relative intensities it is deduced that the structure of the sizing compound in this case too is the dimer of DGEBA. As will be dealt, in the subsequent section, the quantification of the sizing compound showed that the amount of sizing agent in T700SC (0.32 wt.%) is nearly 2-3 times lower compared to the amount of sizing compound in the pitch based fibers, namely, NX90 (0.96 wt.%) and NX100 (0.67 wt.%). Since the amount of sizing is lower than 0.5 wt.% in the carbon fibers T700SC, the peaks corresponding to all the protons, in different chemical environments in the structure of the dimer of DGEBA are not of perceptible intensity. As a consequence only those protons of the aromatic ring and methyl protons are clearly observed (Figure 4). Similar arguments hold good for the ^{1}H NMR of the sizing compound isolated from the carbon fibers, T800HB (Figure 6).

Though the ^{1}H NMR spectral features of the sizing compound isolated from the carbon fibers CCF800H (Figure 5) is similar to that of the sizing compound from other carbon fibers namely, NX90, NX100, T700SC (Figures 2, 3 and 4) and T800HB (Figure 6) and to that of the standard E51 spectral features (Figure 7), there is a perceptible and striking distinguishing feature pertaining to the resolution of the signal corresponding to the protons “j” “i” and “c”. These three protons resonate at three different chemical shift values in the case of T800HB while these three protons appear at a single chemical shift value in all other instances. This indicate that the relative binding of the sizing compound is through the hydroxyl group in the vicinity of the chemical environments of the protons “I” and “j” leading to the shift of the signals corresponding to these protons to down field due to deshielding effect. Thus valuable information on the site of binding of the epoxy sizing compound to the carbon fiber surface during the process of sizing can also be deduced from the ^{1}H NMR spectra (Figure 6).

The ^{1}H NMR spectral features of the sizing compound from T800HB (Figure 6), is similar to that of the sizing compound isolated from other carbon fibers, namely, NX90, NX100, T700SC, CCF800 (Figure 2-5) in all aspects except the absence of peak at ~3.6 ppm. The peak at ~3.6 ppm is not present in the ^{1}H NMR spectrum of the standard sample of the dimer of DGEBA (E51) making it clear that this peak is not arising from the compound, namely dimer of DGEBA used as sizing compound for the surface modification of carbon fibers (NX90, NX100, T700SC, CCF800, T700SC). However, it is a common practice is the production of carbon fibers to use 18-crown-6-ether as dispersing agent [25]. Such a dispersing agent of 18-crown-6-ether is used in the sizing composition of NX90, NX100, T700SC, CCF800HB (Figures 2-5) but not in T800HB. However absence of signal at ~3.6 ppm in the ^{1}H NMR spectrum of T800HB should be taken with a pinch of salt as no sanctity is attached with this material compared to other commercial carbon fibers. Since the sizing amount expected is typically less than 0.5 wt. %, there is a chance that the signal might have been missed and it is recommended that the experiment with T800HB is repeated with higher amounts of sizing compound before concluding that the crown ether is not used in the sizing composition of T800HB. Thus the signal at 3.6 ppm in the case of the sizing compound from NX90, NX100, T700SC, CCF800HB is attributed to the use of 18-crown-6-ether in the sizing composition [25]. Use of such crown ethers also facilitates the initiation of cationic polymerization of epoxy compounds [26]. Vidil et al., reported on the ^{1}H NMR spectrum of the 18-crown-6-ether complex (BF_4^- 4-chloroanilinium 18-crown-6-complex) with the methylene protons of the crown ether resonating at 3.53 ppm [26]. The signal of the methylene protons of crown ether used as dispersant should not be mistaken with the protons of the epoxy ring in epoxy resin homologues like diglycidyl bis disulfide carbon ether of bisphenol A, which too resonate at 3.6 ppm [27].

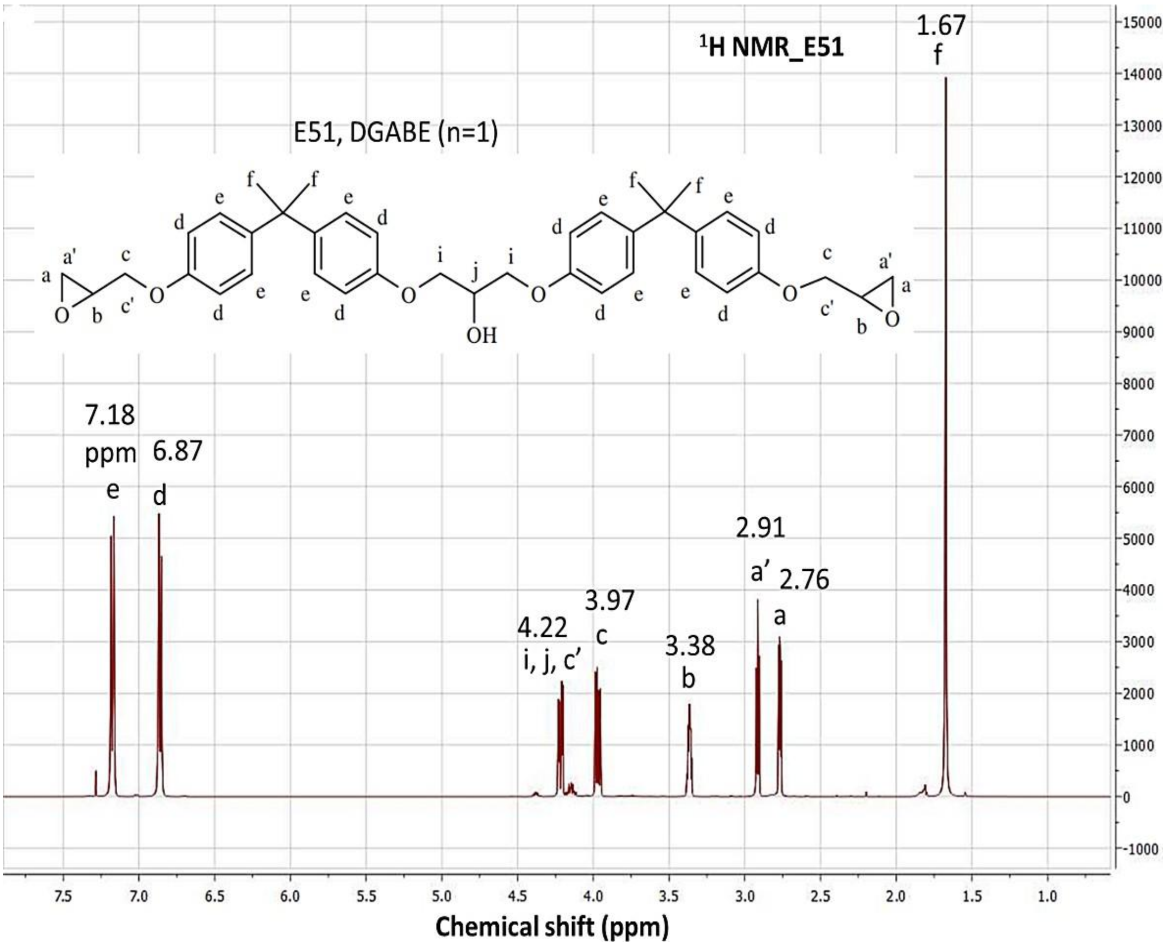

Figure 7. ^{1}H-NMR spectrum of dimer of diglycidyl ether of bisphenol A, DGEBA dimer, (E51) (This result is generously shared by Dr Chongchong Yang, SJTU, Shanghai).

^{13}C NMR spectra of the sizing compound isolated from the carbon fibers NX90, NX100, CCC800H and T800HB were shown in Figures 8-11 respectively. Each of the signals were assigned to specific carbon nuclie of the dimer of DGEBA (E51). For comparison the ^{13}C NMR spectra of DGEBA and the dimer of DGEBA were shown in Figure 12 and Figure 13 respectively. In the monomer DGEBE, the carbon nuclie present in nine different chemical environments resonate and nine different chemical shift values and as a result nine signals are observed (Figure 12). Likewise, in the dimer of DGEBA (E51), the fifteen carbon nuclie in nine different chemical environments yield nine singnals (Figure 13-17). As can be observed the ^{13}C NMR of the monomer DGEBA as well as the dimer have so similar spectral featues that distinguishing the monomer and dimer becomes difficult. However, since ^{1}H NMR studies clearly revealed that the structure of sizing compount is the dimer of DGEBA, and as the ^{13}C NMR spectral features of the sizing compounds from the carbon fibers NX90, NX100, CCC800H and T800HB matched well with the standard spectra of both the monomer and dimer of DGEBA, it is concluded that the structure of the sizzing compound using for the surface modification of these fibers is indeed the dimer and not the simple monomer of DGEBE. Moreover, all the fifteen carbon nuclei in the different chemical environments in the structure of the sizing compound from the carbon fibers NX90, NX100, CCC800H and T800HB could be assigned to the each of the signals in the respective ^{13}C NMR spectra (Figures 8-11).

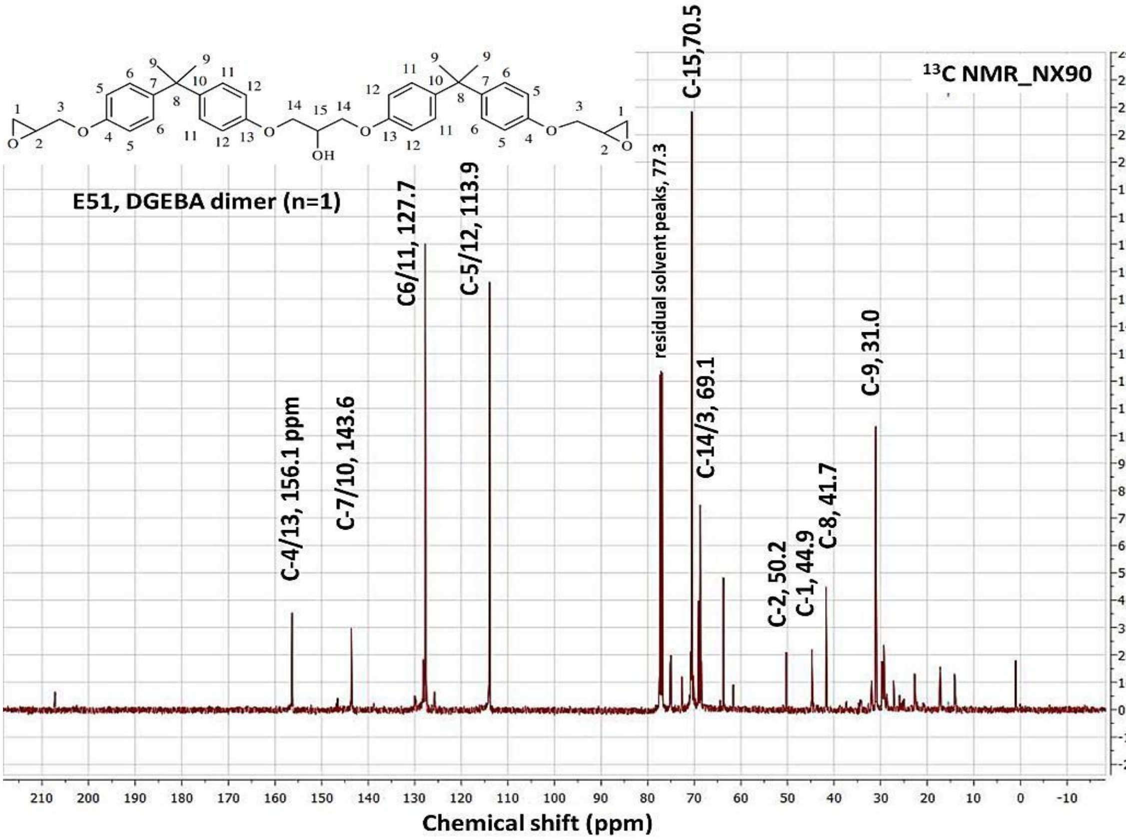

Figure 8. ^{13}C-NMR spectrum of sizing agent extracted from carbon fibers NX90.

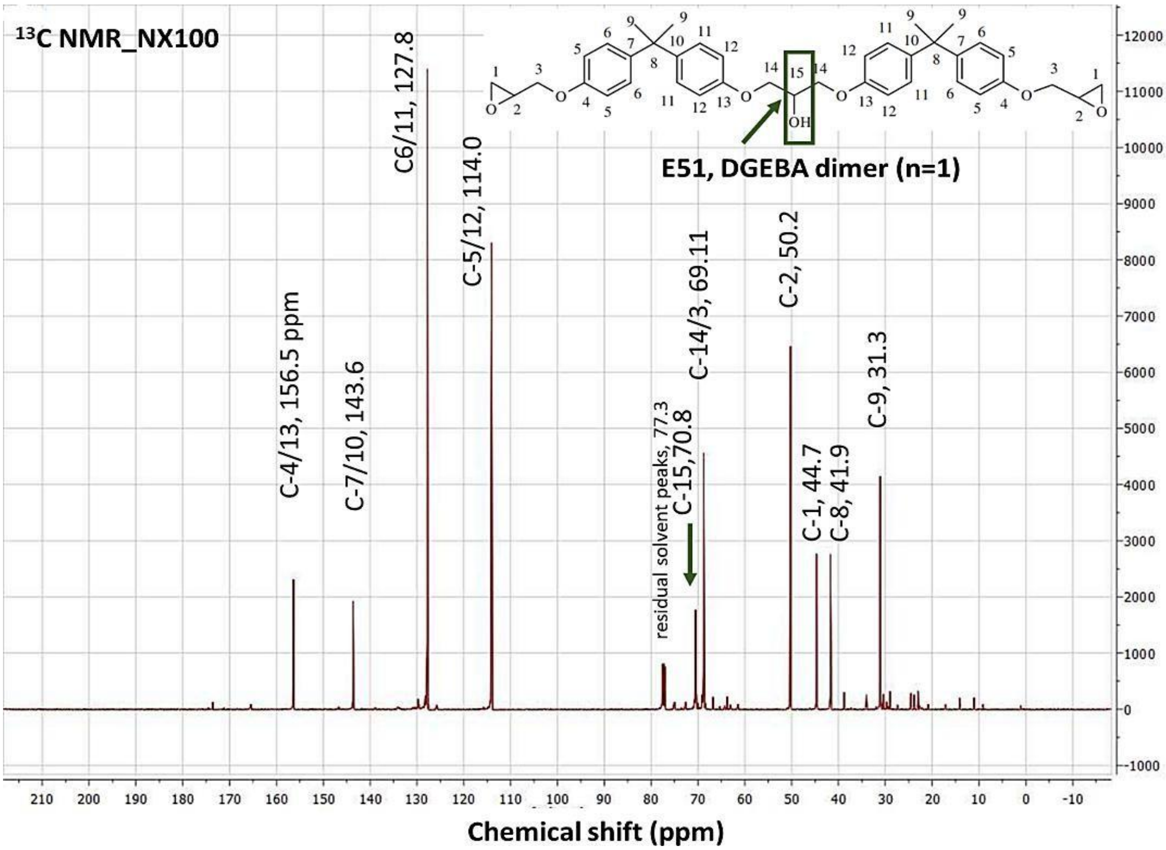

Figure 9. ^{13}C-NMR spectrum of sizing agent extracted from carbon fibers NX100.

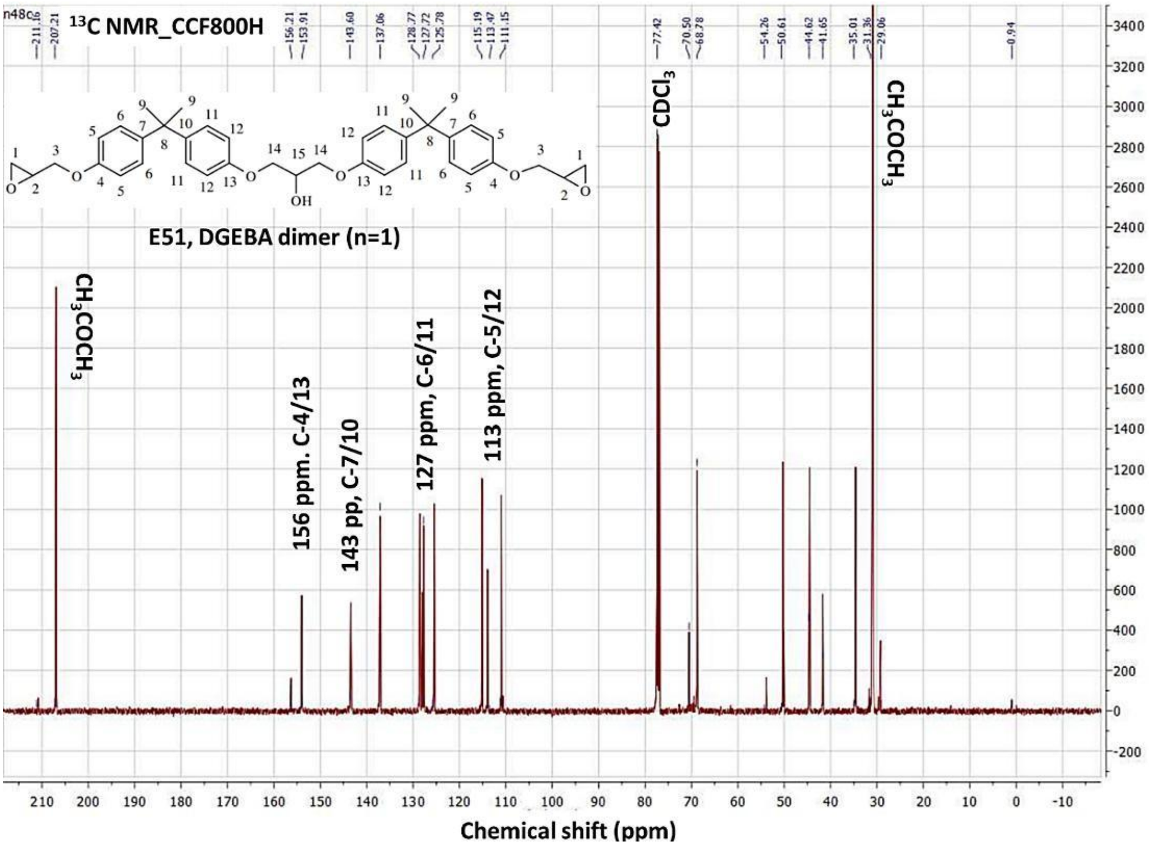

Figure 10. ^{13}C-NMR spectrum of sizing agent extracted from carbon fibers CCF800H.

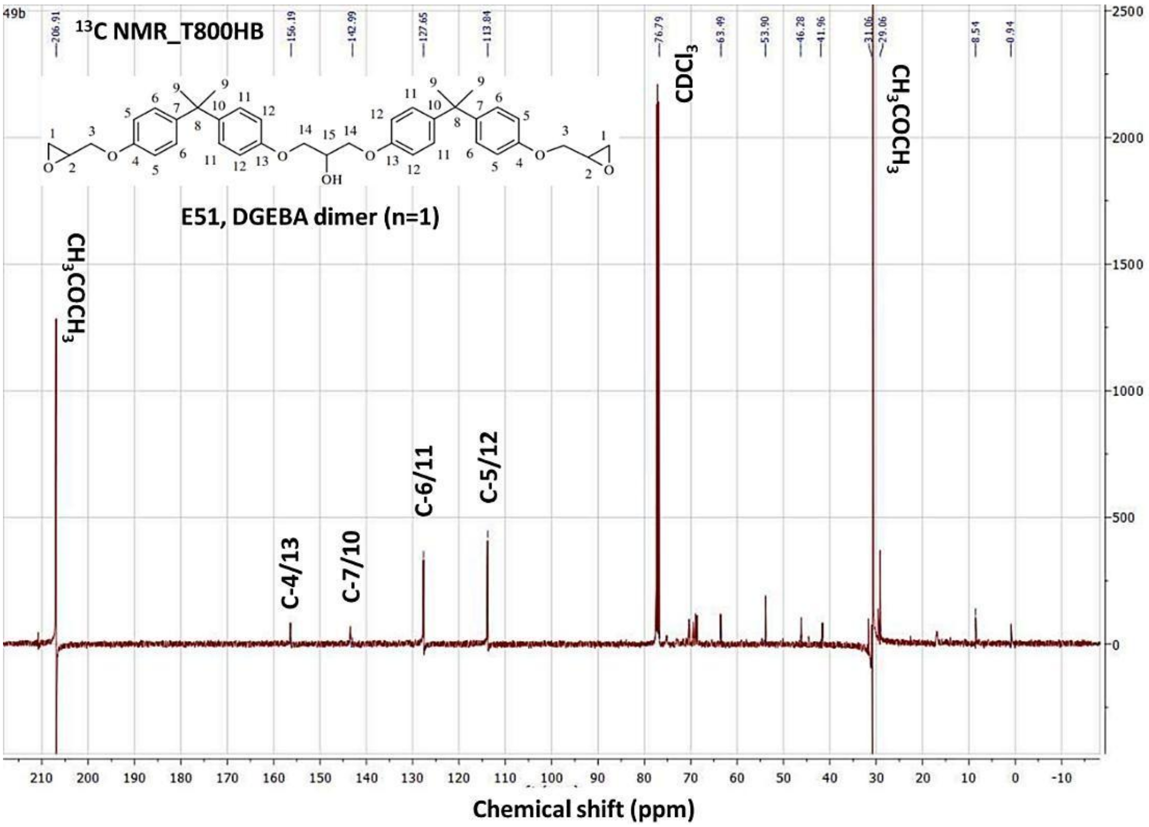

Figure 11. ^{13}C-NMR spectrum of sizing agent extracted from carbon fibers T800HB.

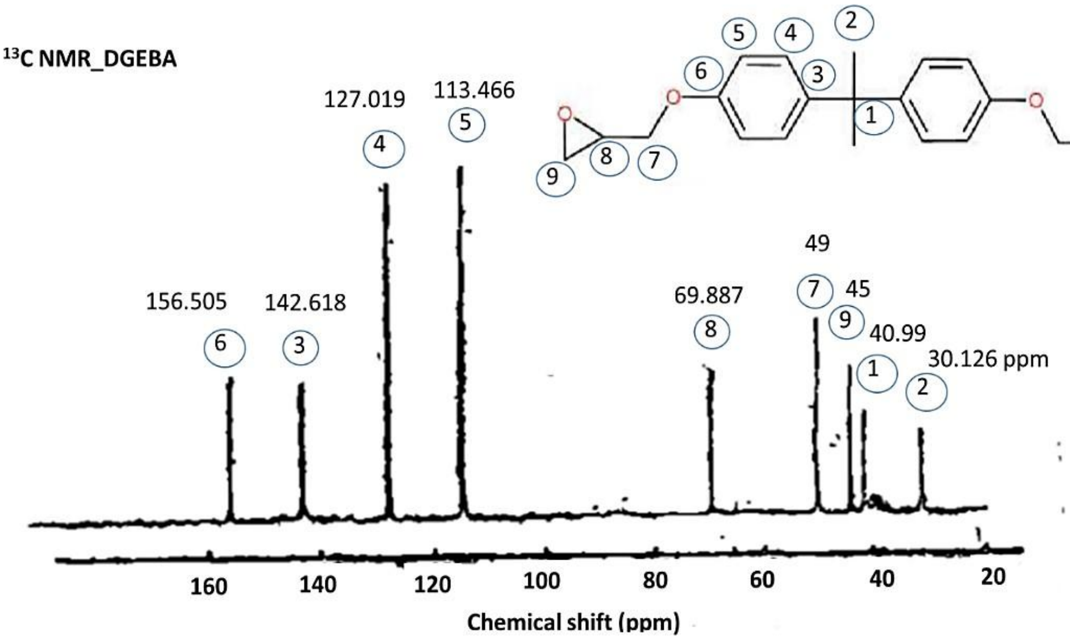

Figure 12. ^{13}C NMR spectrum of DGEBA [28].

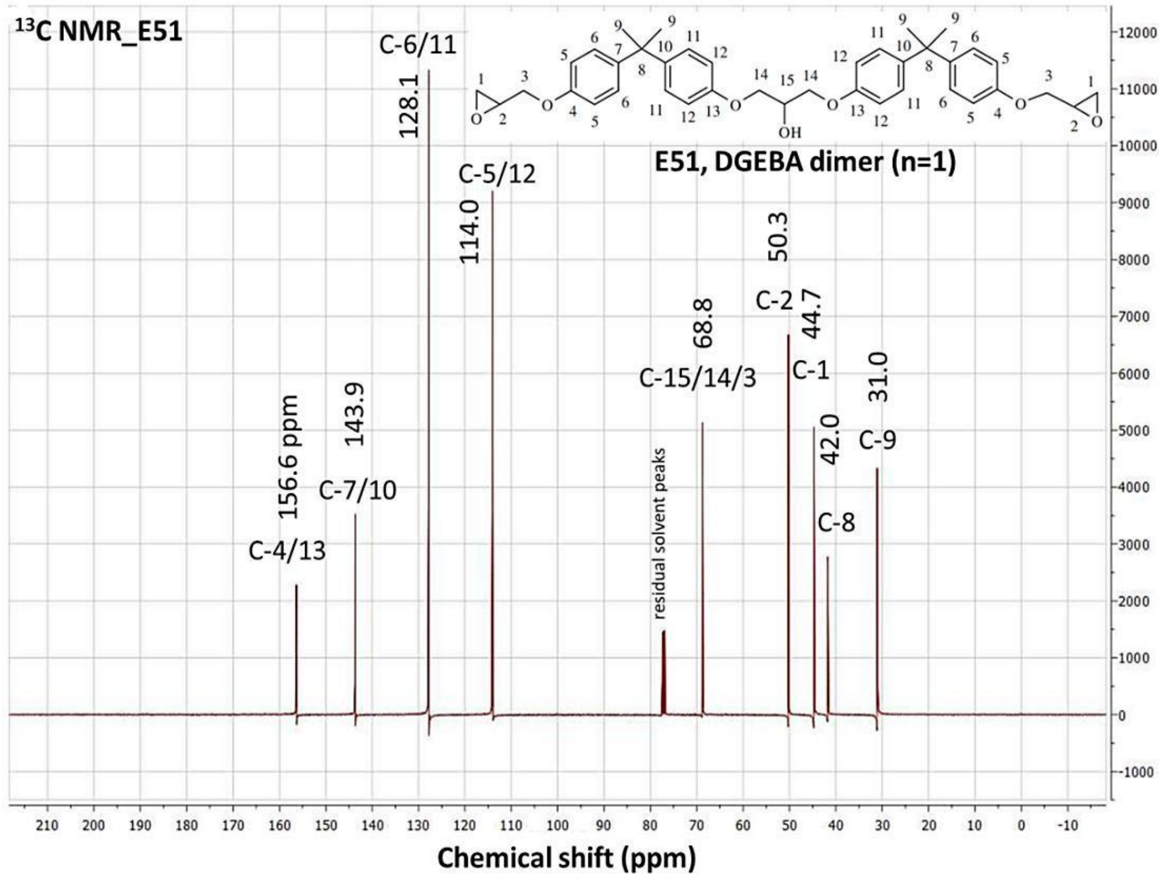

Figure 13. ^{13}C NMR spectrum of E51 (dimer of DGEBA) [This result is generously shared by Dr Chongchong Yang, SJTU, Shanghai].

Apart from ^{1}H and ^{13}C NMR, the structure of the sizing compound isolated from NX90 was further characterized by heteronuclear single quantum coherence (HSQC) NMR. The HSQC NMR spectrum of the sizing compound isolated from NX90 is shown in Figure 14.

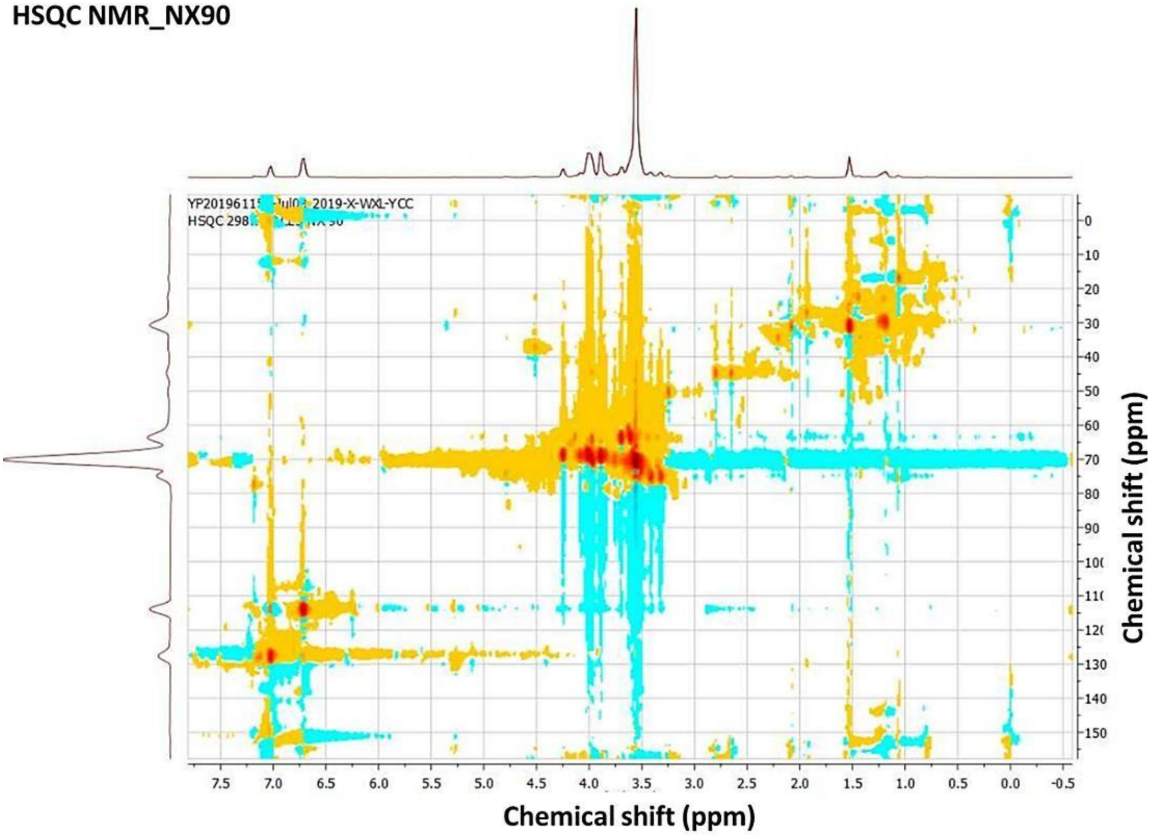

Figure 14. HSQC spectrum of the sizing compound isolated from NX90.

It is note worthy that in the in all the ^{1}H NMR (Figures 2-6) as well as the ^{13}C NMR spectra (Figure 8-11) of the sizing compound isolated from carbon, there is a characteristic signal close to 0 ppm. Usually the standard used for NMR studies, tetramethyl silane (TMS) resonates at 0 ppm. This gives a clue that the observed signal at 0 ppm in all the ^{1}H and ^{13}C NMR spectra of sizing compounds isolated from various carbon fibers contains some kind of organo siloxane compound. Infact, Mojsiewicz-Pienkowska et al., observed such signals close to 0 ppm, in the range of 0.1 to 0.2 ppm, while dealing with the ^{1}H NMR spectra of polymethylsiloxane compounds present in wine and edible oils. Figure 12 The methyl protons of CH_3-Si-O groups present in polydimethylsiloxanes (PDMS) and hexamethyldisiloxane (HMDS) exibited peaks at chemical shift values of 0.18 and 0.1 ppm respectively. Usually, such siloxane compounds like polydimethylsiloxanes (PDMS) and hexamethyldisiloxanes (HMDS) are used in food-prossessing industry as structure shaping agents for food additive applications. Such siloxanes form protective surface film preventing changes caused by undesirable reactions like hydrolysis, polymerization and cyclization. Such compouds are also used to suppress foam formation as anti-foaming agents [29]. Thus the presence of signal around 0 ppm in the ^{1}H NMR spectra of the sizing compounds (Figures 2-6) hint to the use of polydimethylsiloxane type compounds in the sizing composition to form protective layer over the carbon fiber surface. Indeed, the sizing compound isolated contained traces of oil agent (that will be a subject of discussion in the next communication) where in the organo silicone compound are used in the production of caron fibers. Use of organo silicone compounds appears to be inevitable for both sizing composition as well as the oil agent compostion. However, the stucture of the organosilicone compound in sizing composition is simpler than that in oil agent composition. To know more of the origin of the signal near 0 ppm, ^{29}Si NMR studies were carried out. The ^{29}Si NMR spectra of the sizing compound isolated from the carbon fibers, namely, CCF800H and T800HB were shown in Figure 15 and Figure 16 respectively. A single in the range of ~ - 110-111 ppm, indeed prove that the hypothesis of the presence of organo-silicone type compound in the sizing compostion is true. Organo-slicone compounds with Si-CH_3 type functionality are present in the sizing composition. Leonardelli et al., attributed to the peak at ~ -110 ppm to the siloxane, $[Si(O_{0.5})_4]$ type Q_4 units while analyzing the extent of presence on hydroxyl groups on silica surface [30]. Further studies in this direction comprise of a detailed characterization of the oil agent used in sizing composition by various spectroscopic methods. Such a study forms a separate communication.

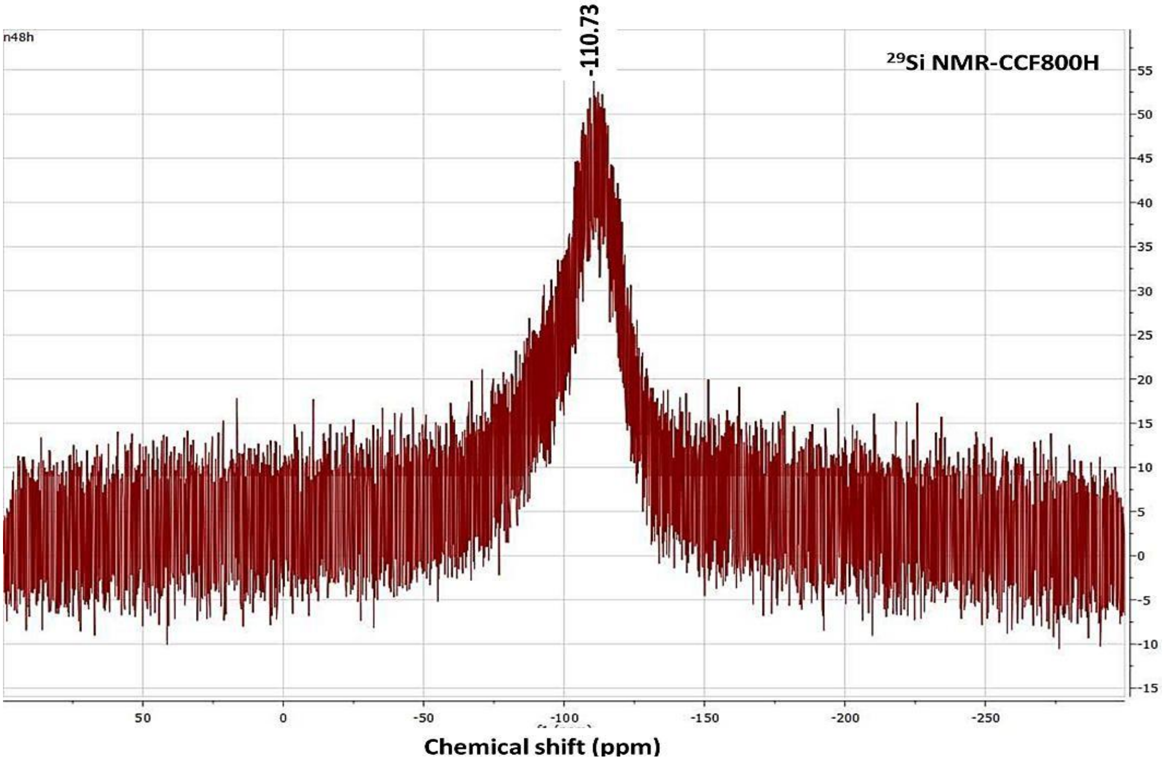

Figure 15. ^{29}Si NMR spectrum of CCF800H.

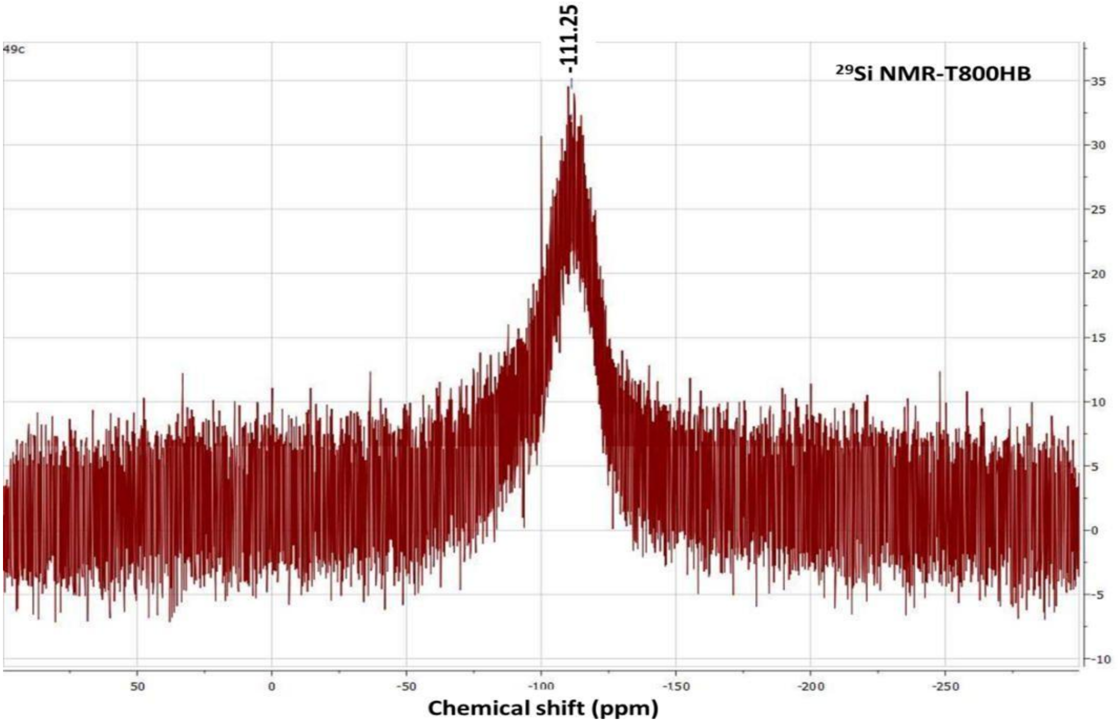

Figure 16. ^{29}Si NMR spectrum of T800HB.

Quantification of sizing using gravimetry, thermogravimetric analysis (TGA) and ^{1}H NMR

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^{1}H NMR and ^{13}C NMR studies provided valuable information on the structural details of the sizing composition used for the surface modification of carbon fibers NX90, NX100, T700SC, CCC800H and T800HB. To achieve more information from the ^{1}H NMR on the amount of sizing agent used for the surface modification of carbon fibers, quantitiative studies on the estimation of sizing amount were made using ^{1}H NMR. Tetrahydro furan was used as internal standard for such quantification of the sizing compound, namely dimer of DGEBA. The amount of sizing compound used for the surface modificaiton of caborn fibers estimated using ^{1}H NMR was found be less than 1 % in the case of pitch based caron fibers, namely, NX90 (0.96 wt.%) and NX100 (0.67 wt. %). In the case of PAN based fibers the sizing amount is even lower. The sizing amount used for the surface modification of the PAN based cabron fibers, namely, M55J and T700SC were 0.23 wt.% and amd 0.32 wt.% respectively. The values of the sizing amount deduced from ^{1}H NMR studies were compared by the values determined by other methods, namely, gravimetry and thermogravimetry and the results were summarized in Table 1. Usually, in an industrial process for the production of carbon fibers, typically, < 1 wt.% of sizing compound is used for the surface modificaiotn. This is the very reason that it is indeed very challenging to gain knowledge into the structure and composition of size that is a very cruitical surface modificaiton process that enhances the compatibility of carbon fibers with the resin matrix leading to stronger adhesion strength at the interface. A comparison of various methods for the estimation of sizing compound revelas that ^{1}H NMR based analytical technique facilitates obtaing values closure to that of the real values of the sizing amount, namely, < 1 wt.%. As expected the sizing amount in pitch based fibers is nearly, 2-3 times higher than that of the PAN based fibers. This is the very reason why handling (isolating single filaments of pitch based fibers for characterization) is much more tedious and time taking process than that of handling and working with PAN based fibers. ^{1}H NMR is an elegant method for the quantification of sizing amount.

Table 1. Quantification of sizing amount by gravimetry, thermogravimetric analysis (TGA) and ^{1}H NMR

Carbon Fibers	**Amount of sizing agent (Wt.%)**		
	Gravimetry	**Thermogravimetry***	**^{1}H NMR**
NX90	3.84	2.32	0.96
NX100	2.26	0.96	0.67
M55J	0.27	1.24	0.23
T700SC	1.35	-	0.32
CCF800H	1.64	-	-
T800HB	1.6	-	-

**Data on the Sizing amounts deduced from TGA were geneously provided by Dr Chongchong Yang, SJTU, Shanghai.*
“-“ This data could not be generated; further experimentation is required

Method of estimation of sizing amount in the carbon fibers using ^{1}H NMR

The methodology adapted for the quantification of sizing amount that was used in the surface modificaiton of cabron fibers is described below in the specific example of the carbon fibers NX100. Typcial process of ^{1}H NMR sample preparation compries of taking 400 μL analyte (sizing agent dissolved in solvent acetone) and 200 μL solvent ($CDCl_3$) and 50 μL internal standard (THF). The ^{1}H NMR resulting from such sample composition is shown in Figure 17.

The method comprises of comparing the integral area of the ^{1}H NMR signal of aromatic ring protons (16H, S, 6.8-7.2 ppm) of DGEBA dimer to that of the area of the signal from the protons (4H, S, 3.08 ppm) of THF. Typical composition of analyzte for the quantification of sizing compound comrpise of taking 400 μL analyte (sizing agent dissolved in solvent acetone) and 200 μL solvent ($CDCl_3$) with 50 μL internal standard (THF).

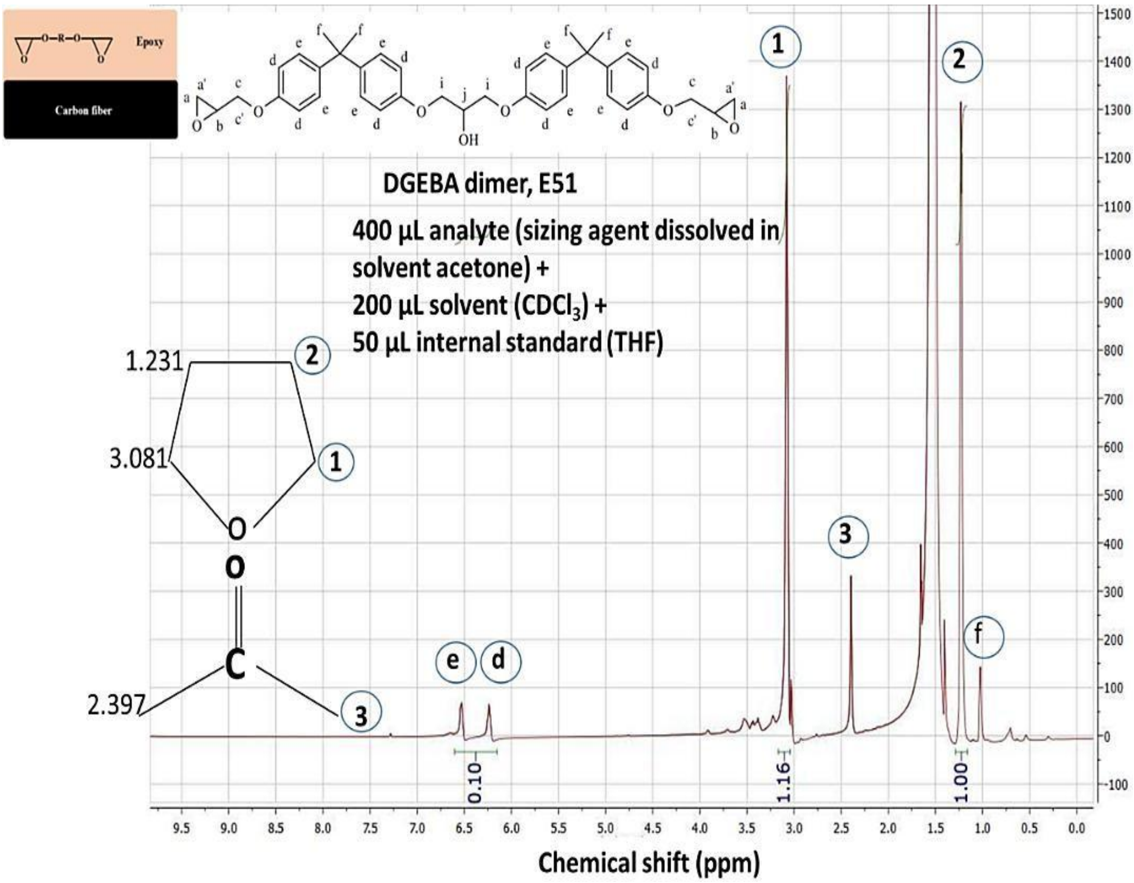

Figure 17. Quantification of sizing amount in the carbon fibers NX100 using ^{1}H NMR.

The ratio of relative peak areas of the standard THF and the analyte are related to the relative amounts of THF and the analyte be the following equation (4) [31]:

$$\frac{\textbf{Moles of THF}}{\textbf{Moles of analyte}} = \frac{\frac{\textbf{Area under the peak of THF}}{\textbf{no. of protons}}}{\frac{\textbf{Area under the peak of sizing agent}}{\textbf{no. of protons}}} \cdots \quad (4)$$

Mol. wt. of THF = 72.11 g/mol
Density of THF = 0.887 g/mL
Moles of THF in 50 µL = 6.1503 x 10^{-4}

$$\frac{6.1503 \text{ x } 10^{-4}}{Moles\ of\ analyte} = \frac{\frac{1.00}{4}}{\frac{0.10}{16}} = \frac{0.25}{0.00625}$$

Moles of analyte = 0.1537 x 10^{-4}

Wt. of analyte (sizing agent), g in 0.4 mL = 0.1537 × 10^{-4} × 340.41286 (molecular wt. of DGEBA) = 52.32 × 10^{-4} g.

Wt. of analyte (sizing agent), g in 2.5 mL (total volume of analyte) = 52.32 x 10^{-4} x 2.5/0.4 = 0.033 g

Wt. % of sizing agent in carbon fibers = (wt. of sizing agent / total wt. of carbon fibers) x 100

= (0.033/4.826) x 100 = 0.68 wt%

Thus a potential analytical method based on ^{1}H NMR is applied to the estimation of sizing amount used for the surface modificaiton of carbon fibers.

CONCLUSION

The commercial carbon fibers (CF's) characterized in the present study, namely, NX90, NX100, T700SC, CCF800H, and T800HB were surface modified by epoxy (EP) based sizing agent, analogous to the dimer of DGEBA (commercial trade name E51). In addition NMR spectroscopic analysis revealed the presence of organo siloxane compounds like polydimethylsiloxanes (PDMS) and hexamethyldisiloxanes (HMDS) in the sizing composition. Use of crown ethers in the sizing composition is unambiguously established using NMR spectroscopy. Such crown ethers perform the role of dispersant as well as complex solvent mixtures and also as initiators for cationic polymerization of epoxy monomers used for the surface modification in the sizing composition. ^{1}H NMR is proved to be a better technique for the quantification of sizing amount used for the surface modification of CF's compared to either gravimetry or thermogravimetry. The amount of sizing compound in PAN based fibers is typically < 0.5 wt. % while the same is in the range of 0.5 to 1 wt. % in pitch based fibers. Thus, designing of the sizing composition is a Chemistry marvel, comprising, in the present instance, of the dimer of DGEBA, 18 crown 6 ether, and the organo silicone compounds, analogous to those present in the commercial composition, namely, E51. Thus NMR spectroscopy in fusion with FT-IR, LC-MS, MALDI-TOF, offers finer details into the characterisation of the sizing composition. Apart from being a potential quantification tool for the determination of the sizing composition used for the surface functionalization of commercial carbon fibers, NMR is a reliable measuring instrument for the quantification of sizing compound. It was found that the sizing compound used for the surface modification of pitch based fibers (NX90, 0.96 wt.%; NX 100, 0.67 wt. %) is nearly 2-3 times higher than that used for the surface sizing of PAN based carbon fibers (M55J, 0.23 wt.%; T700 SC, 0.32 wt.%).

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Dedication

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