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Diglycidyl Ether of Bisphenol A (DGEBA) Based Epoxy Sizing Agent Induces Surface Polarity in Carbon Fibers†

Indra Neel Pulidindi*

Abstract

Knowledge of the chemical structure and composition of sizing agent is a challenge as its concentration is low varying in the range from ~0.5 wt. % (for PAN based carbon fibers) to ~ 1 wt.% (for pitch based carbon fibers). Moreover, such a knowledge is vital for the design of compatible polymer matrices for the preparation of CFRP's for diverse applications. As a result, the sizing layer that is coated on the carbon fiber surface in the commercial sizing process was separated and isolated from the commercial carbon fibers (NX90, NX100, M55J, T700SC, CCF800H, T800HB) and examined using FT IR spectroscopy. The results revealed that the epoxy resin, namely, the diglycidyl ether of bisphenol A (DGEBA) is the major constituent of the sizing composition. Epoxy sizing with sizing composition, comprising of DGEBA derivative, polysiloxanes and esters, is surmised to improve the compatibility of CFs with resin matrices. In all the carbon CFs examined the sizing composition comprised of DGEBA derivative with poly organosiloxanes. Characteristic bands at 829, 948, 1509 and 1607 cm^{-1} attributable to C-O-C stretching vibration of oxirane, C-O stretching of oxirane, C-C stretching vibration of benzene, and C=C stretching vibration of benzene signify that DGEBA molecule is used in the sizing composition of all the commercial carbon fibers examined. Moreover, the four consecutive bands in the range of 2870-3065 cm^{-1} were observed. These bands were characteristic of CH stretching vibrations of methylene group (~2870 and 2924 cm^{-1}), aromatic CH stretching (~2963 cm^{-1}) and CH stretching of terminal epoxy (~3065 cm^{-1}) groups of DGEBA derivative in the sizing composition. Further insights into the molecular level composition and interaction of the sizing compound with the carbon fiber surface as well as the resin matrix are necessary for developing carbon fiber reinforced composites with desired properties and applications.

†Dedicated to the legendary polymer chemist Professor Xinling Wang, SJTU, for introducing the astounding field of interface of carbon fiber reinforced plastics (CFRPs)

Keywords: Carbon fibers, pitch, polyacrylonitrile, resins, composites, interface, surface functionalization, epoxy sizing, characterization, FT - IR spectroscopy

INTRODUCTION

Carbon fibers (CFs) are non-polar. As a result they are not compatible with the polymer matrices for the production of carbon fiber reinforced composites (CFRCs). However, carbon fibers have several unique features that make them the main loadbearing component in CFRCs [1-4]. So as to make the CFs compatible with plastic matrices resulting in strong interface, surface modification of the CFs is widely used [5]. Among several strategies for inducing polarity onto the surface of CFs, the process of sizing using epoxy resins stands out [6-11].

The commercial carbon fibers available and supplied in the market were all surface modified by the process of sizing. Each of the tows of carbon fibers contain 3000 (3K) -12000 (12K) single

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filaments fibers as shown in Figure 1. Sizing is such a vital process of commercial significance that most of the knowledge of sizing process is a subject of intellectual property rights and such a knowledge is not freely available in open literature. An indepth study on this subject has been made and the results on the characterization of sizing compound and composition used for the surface modification of commercial carbon fibers, both pitch (NX90, NX100) and PAN (M55J, T700SC, CCF800H, T800HB based fibers using FT-IR spectroscopy. The crucial results of the study were systematically summarized.

EXPERIMENTAL

Pitch based carbon fibers (CFs), namely, NX90 and NX100, were procured from Nippon graphite fiber co. Likewise, the polyacrylonitrile (PAN) based CFs 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. The typical procedure for the extraction of the sizing compound from the commercial CFs include refluxing known amount of CFs (2 g) with acetone (100 mL) at 70°C for 6 h. The sizing compound dissolved in acetone solvent was separated, from the residual carbon fibers that were stripped off from the sizing layer of the CFs, by decantation. Then the sizing compound was isolated by evaporation of acetone solvent using roto-evaporator. The sizing compound thus isolated from commercial carbon fibers was thoroughly characterized by FT-IR spectroscopy. Aliquot of the sizing compound was dissolved in minimum amount of acetone. A few drops of sizing compound dissolved in acetone was mixed with KBr dried under IR lamp in a mortar and pestle and thin pellets of KBr with the sizing compound were prepared for FT-IR analysis. The FT-IR spectra of the sizing compound in KBr pellet mode were recorded using a Paragon 1000 FT-IR spectrometer (Perkin Elmer Inc., USA). The spectral range of analysis was 450-4000 cm^{-1} with a resolution of 0.1 cm^{-1}. The spectra were obtained in transmission mode and the number of scans were five.

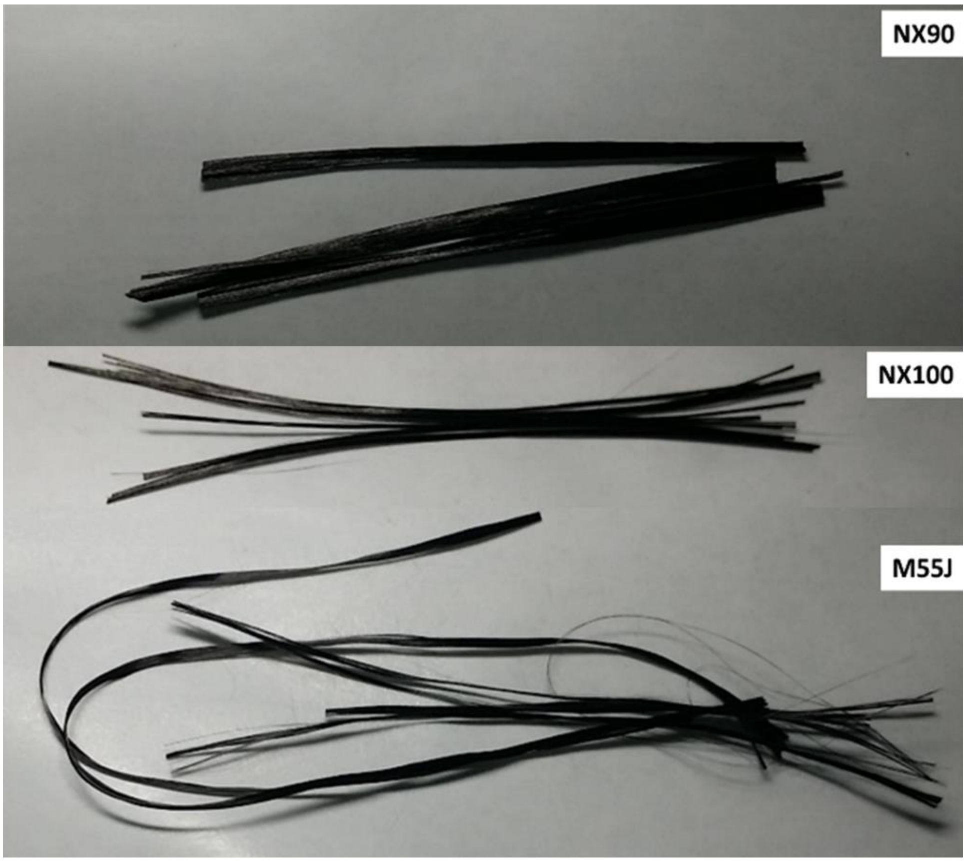

Figure 1. Digital photgraph of the commercial carbon fiber tows: pitch based (NX90, NX100) and polyacrylonitrile (PAN) based (M55J).

RESULTS AND DISCUSSION

Determination of Surface Functionality of the Sizing Compound Using FT-IR Spectroscopy

The FT-IR spectra of the sizing compound isolated from the carbon fibers, namely, NX90, NX100, M55J, T700SC, CCF800H, T800HB, were shown in Figures 2-7 respectively. Each of the characteristic bands were assigned to specific functional groups pointing out to the sizing compound namely, diglycidyl ether of bisphenol A (DGEBA) derivative along with the corresponding wave number values.

Irrespective of the supplier of carbon fibers and the type of the carbon fibers, whether pitch based (NX90, NX100) or PAN (M55J, T700SC, CCF800H, T800HB) based, all the fibers comprise of the DGEBA type epoxy polymer (EP) used in the sizing compound for the surface modification of carbon fibers and to generate the required polarity and oxygen functionality on the carbon fibers. In the FT-IR spectra of sizing compound isolated from carbon fibers shown in Figures 2-7 each of bands were attributed to the specific vibrations of the bond in the structure of diglycidyl ether of bisphenol A (DGEBA). Finger print bands in FT-IR spectrum of the sizing compound from NX90 shown in Figure 2 is discussed here. The bands at 829, 948, 1509 and 1607 cm^{-1} corresponding to C-O-C stretching vibration of oxirane, C-O stretching of oxirane, C-C stretching vibration of benzene, and C=C stretching vibration of benzene) of the DGEBA molecule. In addition, the four consecutive bands in the range of 2870-3065 cm^{-1} were attributed to the CH stretching vibrations of methylene group (~2870 and 2924 cm^{-1}), aromatic CH stretching (~2963 cm^{-1}) and CH stretching of terminal epoxy (~3065 cm^{-1}) signifying the presence of DGEBA derivative in the sizing composition (Figure 2). Similar spectral features were observed in all the sizing compounds isolated from other carbon fibers, namely, NX100, M55J, T700SC, CCF800H, T800HB, as well indicating that the unique compound in the sizing composition is DGEBA derivative (Figures 3-7). González et al., compiled an elegant book chapter on "Applications of FT-IR on Epoxy Resins - Identification, Monitoring the Curing Process, Phase Separation and Water Uptake" that serves as an excellent guidance for researchers characterizing polymer compounds, in general, and DGEBA derivatives, in particular, using FT-IR [12]. For comparison the FT-IR spectrum of the commercial DGEBA samples and its hydrogenated derivative are shown in Figure 8 [12]. The assignment of each of the bands to a specific bond vibration in the structure of DGEBA is shown in Table 1.

It is to be noticed that a particular band absent in the typical FT-IR spectrum of the commercial DGEBA standard is appearing in the FT-IR spectra of all the sizing compounds isolated from both pitch and PAN based carbon fibers, though of varying intenisty, ie, a band at ~1720 cm^{-1} (Figures 2-7). The band at ~1720 cm^{-1} is for sure not related to the structure of DGEBA. However, it is common practise that epoxy resins of DGEBA are cured using esters like castor oil maleate that are used under the curing conditions: 1 h at 80°C, 1 h at 100°C, 1 h at 120°C, 1 h at 150°C and 3 h post curing at 180°C using TEBAC – triethyl benzyl ammonium chloride (TEBAC) as a catalyst. The role of such curing agent like maleate is to reduce the brittleness of epoxy resin by acting as plasticizers and diluents [13]. Not only the presence of the band at ~1720 cm^{-1} but also the relative intensity of this band compared to the band at 830 cm^{-1} corresponding to the C-O-C stretching of epoxy gives valuable information on the properties of the carbon material. As can be noticed in the instrace of pitch based fibers NX90 and NX100, the intensity of band at ~1720 cm^{-1} is lower (Figures 2 and 3) compared to the band at 830 cm^{-1} where as this is the opposite in the case of PAN based fibers (Figsures 4-7). This imply that that amount of the curing agent (maleate) as diluent and plasticizer is lower in the case of pitch based fibers compared to PAN based fibers. This is one of the reasons for the brittleness of the pitch based fibers. As a result the handling and isolation of single fibers of NX90 and NX100 is difficult compared to the PAN based fibers (M55J, T700SC, CCF800H, T800HB). It is recommended that the production process of pitch based carbon fibers is so modified that the amount of the ester compound used in the curing agent/the diluent and plasticizer for reducing the brittleness of epoxy resin should be increased and kept at a level on a par with PAN based fibers. An example of the epoxy resin cured with maleate ester as curing agent, meant for reducing the brittleness of the epoxy resin, containing a sharp intense band at ~1720 cm^{-1} corresponding to the C=O stretching of the ester groups, in addition to the regular bands typial of the structure of the DGEBA is reported by Rosu and coworkers [13].

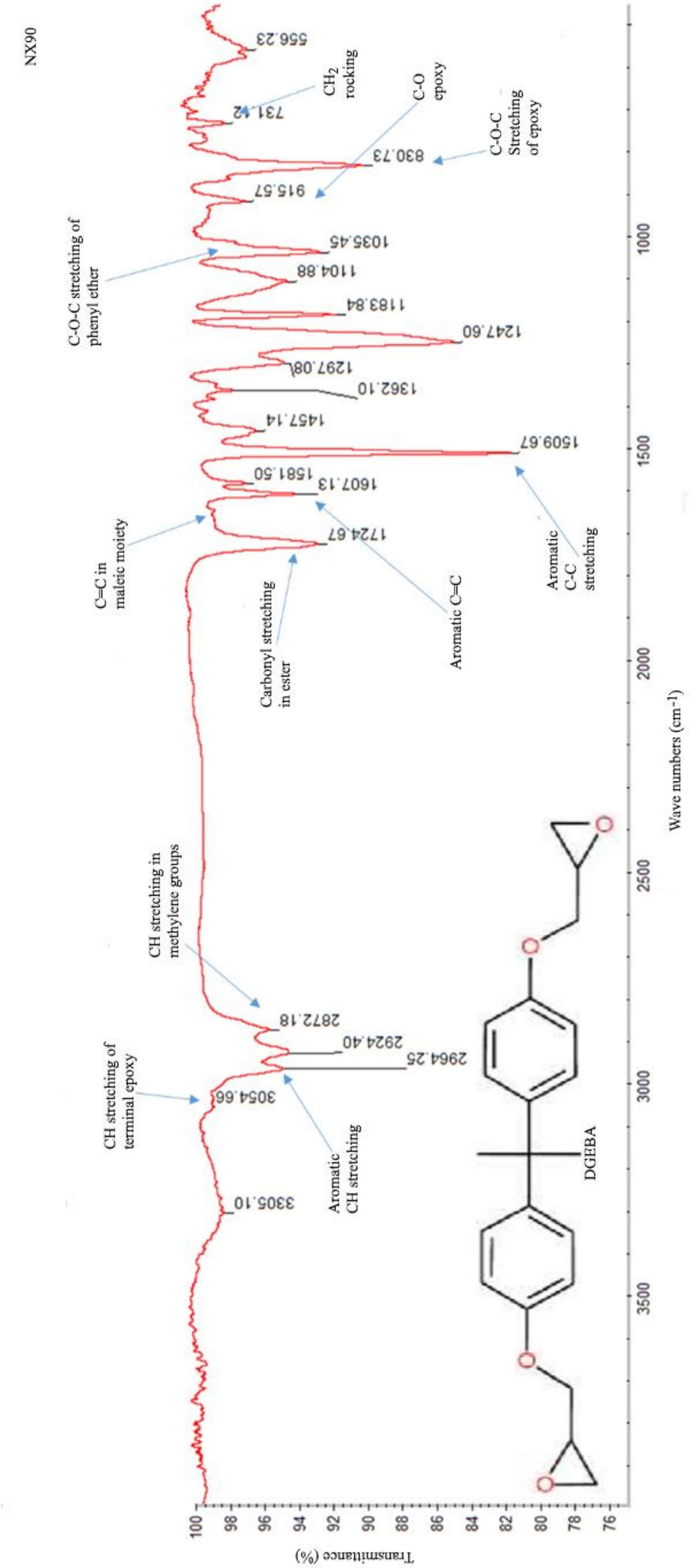

Figure 2. FT-IR spectrum of sizing agent extracted from carbon fibers NX90.

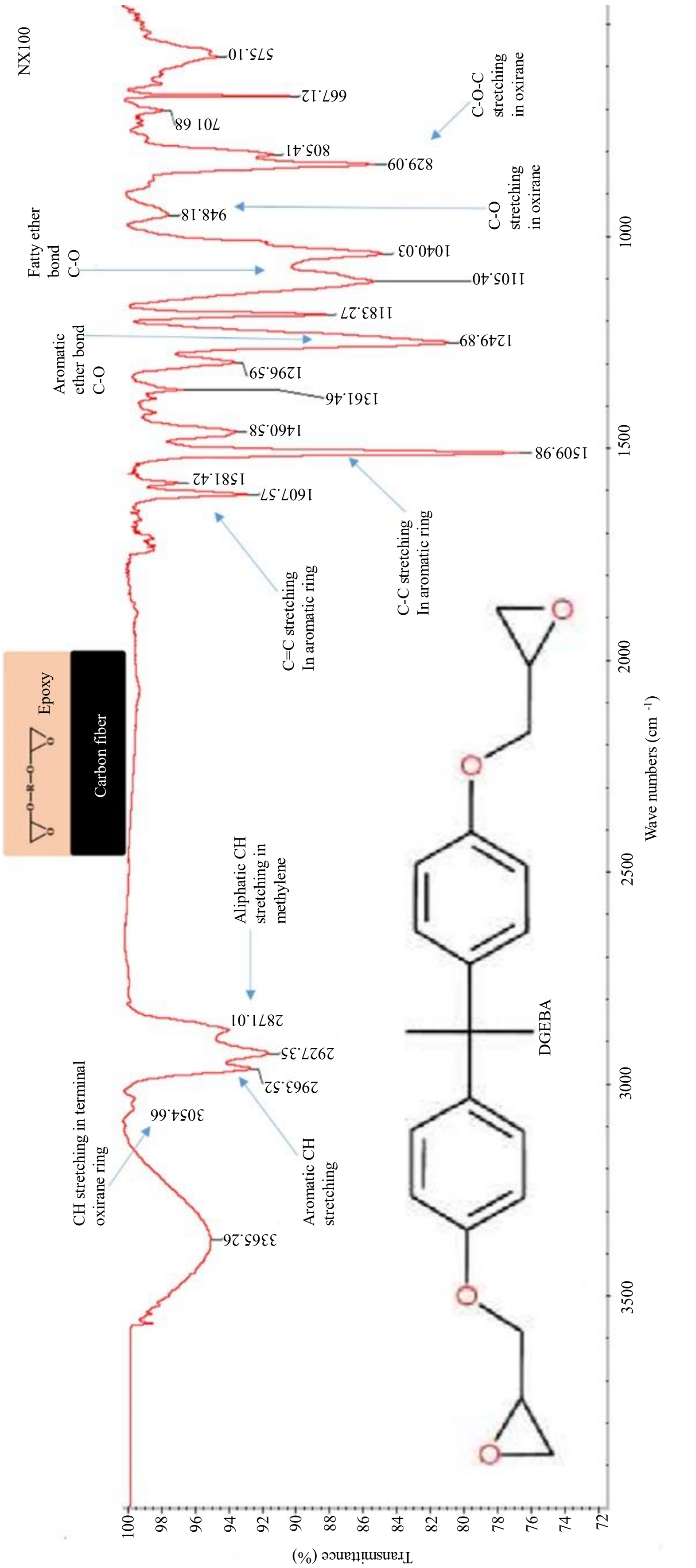

Figure 3. FT-IR spectrum of sizing agent extracted from carbon fibers NX100.

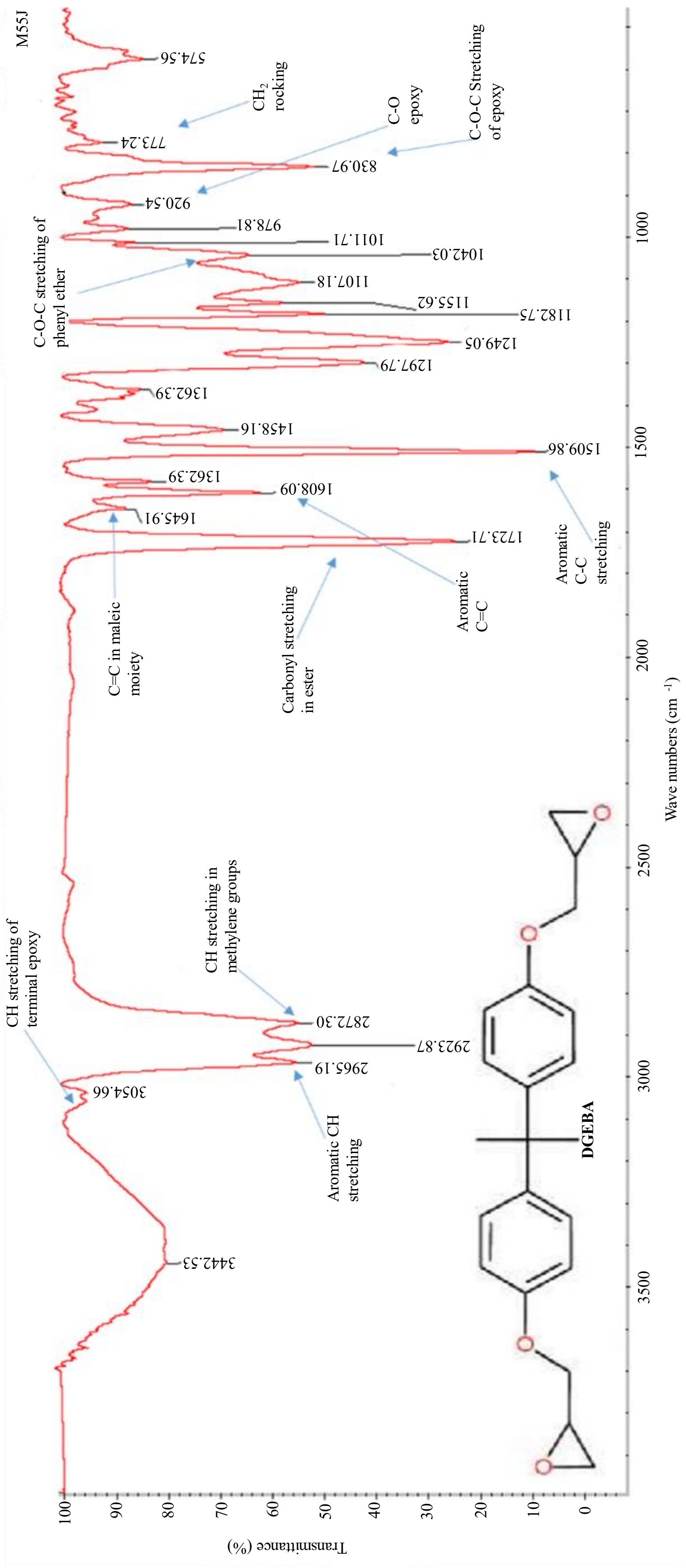

Figure 4. FT-IR spectrum of sizing agent extracted from carbon fibers M55J.

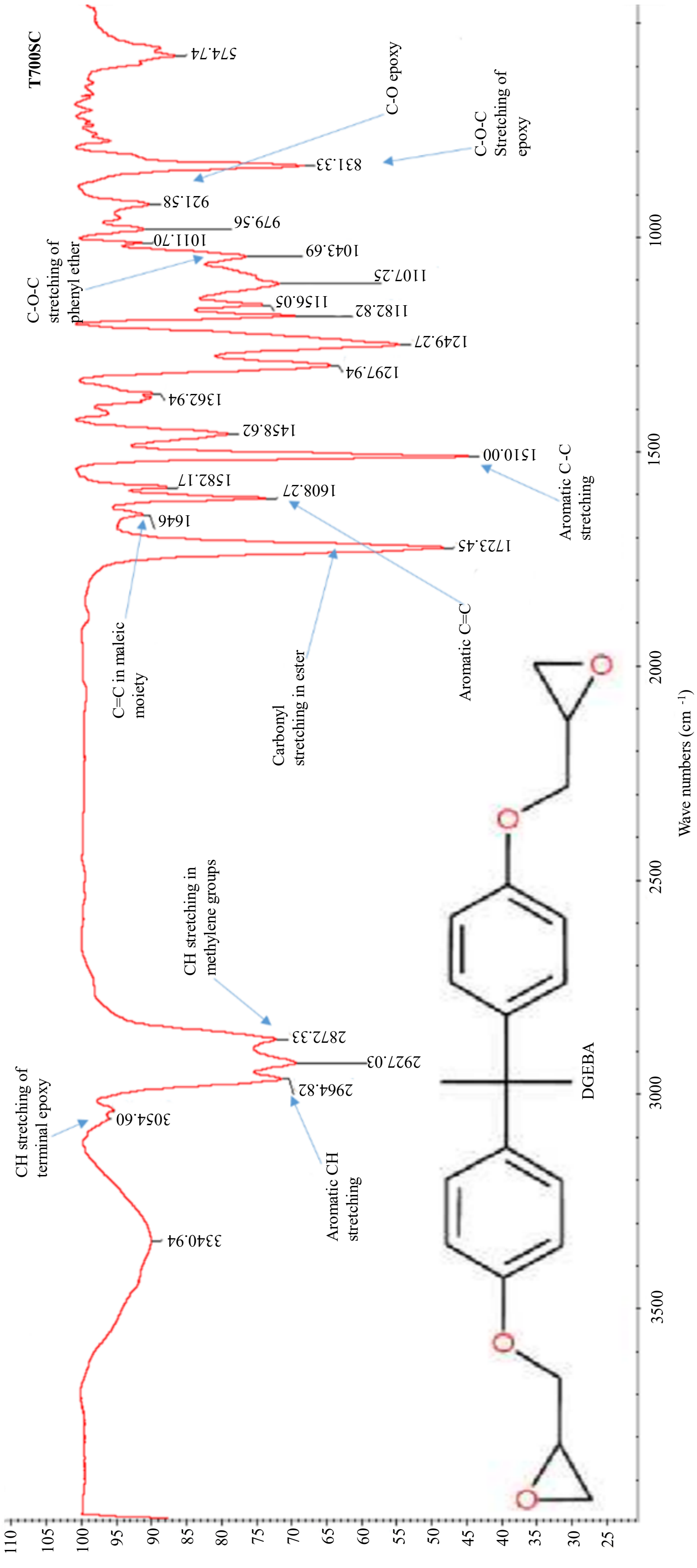

Figure 5. FT-IR spectrum of sizing agent extracted from carbon fibers T700SC.

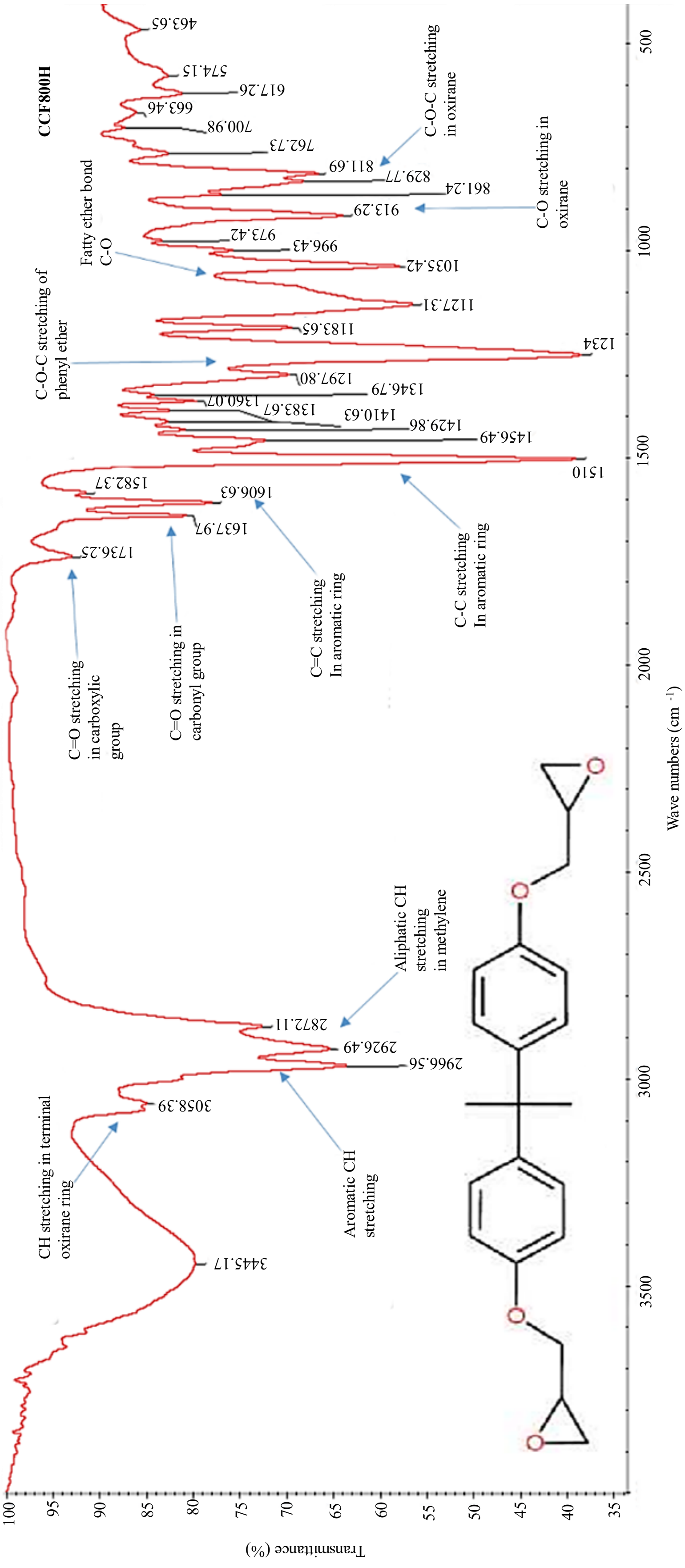

Figure 6. FT-IR spectrum of sizing agent extracted from carbon fibers CCF800H.

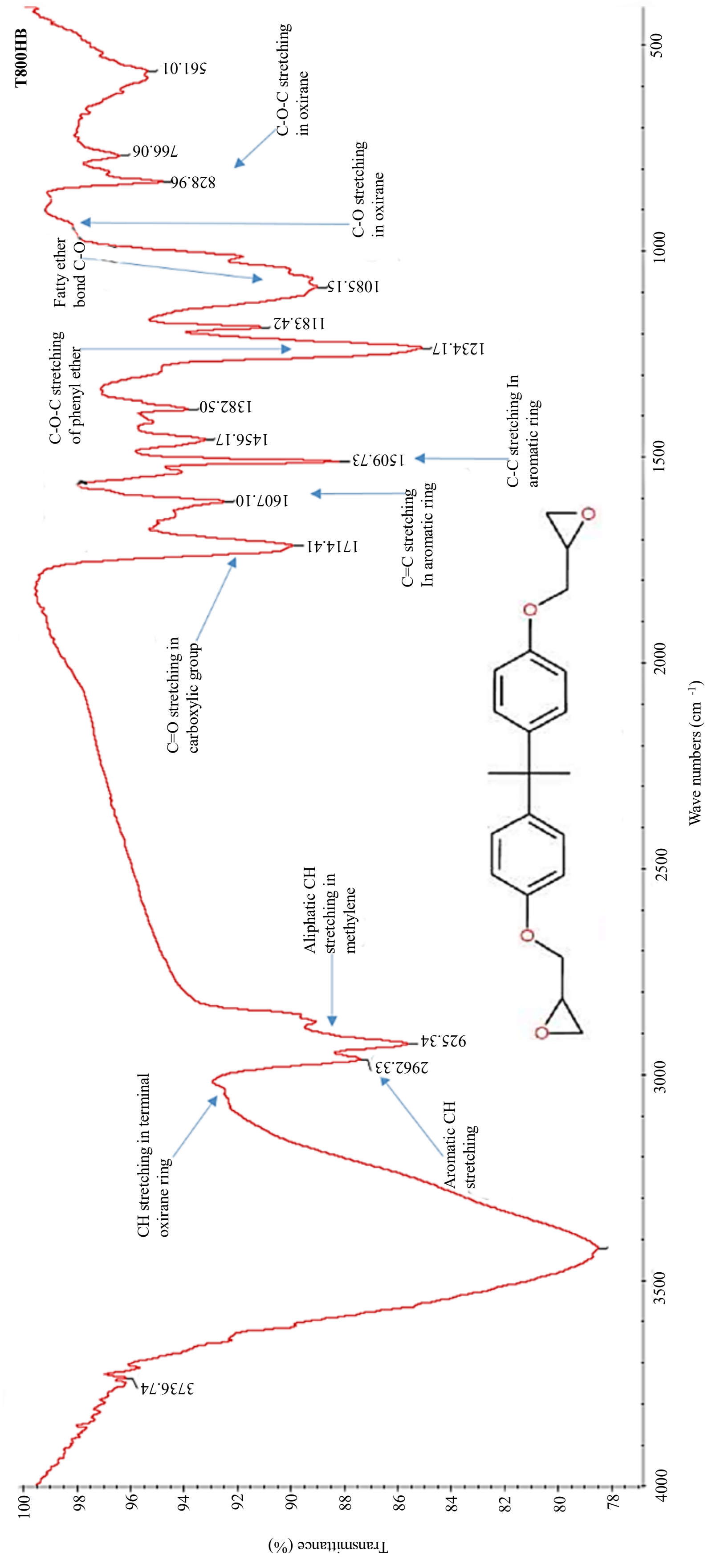

Figure 7. FT-IR spectrum of sizing agent extracted from carbon fibers T800HB.

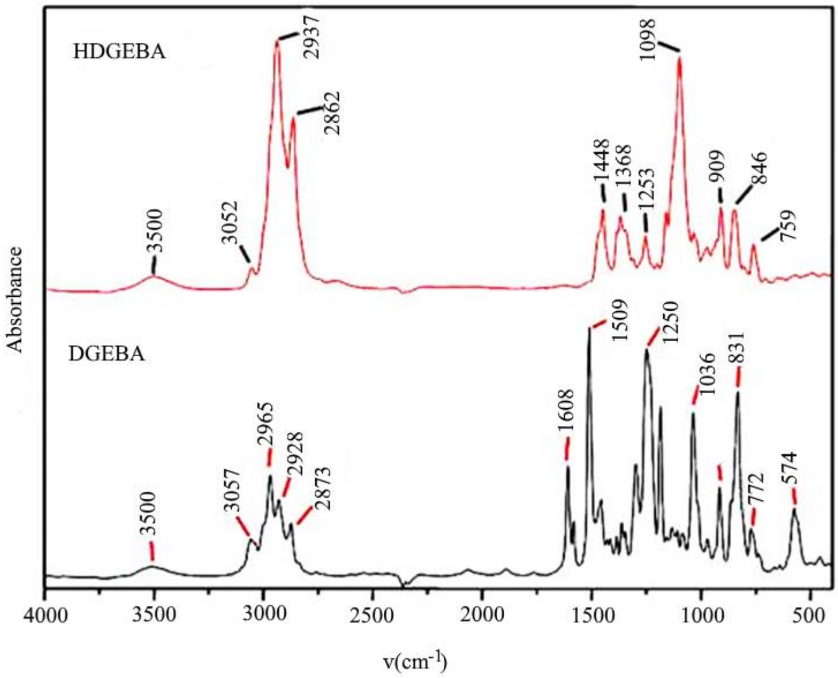

Figure 8. FT-IR spectrum of (a) diglycidyl ether of bisphenol A (DGEBA) and (b) its hydrogenated derivative (HDGEBA) [Adapted with permission from reference 12].

Table 1. Assignment of FT-IR bands to specific bond vibrations of diglycidyl ether of bisphenol A (DGEBA) in the sizing composition [12].

Band position (cm^{-1})	Assignment
~3057	Stretching of C-H of the oxirane ring
2965-2873	Stretching of C-H of CH_2 and CH aromatic and aliphatic
1608	Stretching of C=C of aromatic rings
1509	Stretching of C-C of aromatic rings
1036	Stretching of C-O-C of aromatic rings ethers
915	Stretching of C-O of oxirane group
831	Stretching of C-O-C of oxirange group
772	Rock CH_2

Thus epoxy sizing composition with DGEBA derivative, as well as an ester compound used as either a diluent or curing agent to reduce the brittleness of the DGEBA sizing layer is used for inducing surface polarity into the carbon (both pitch based and PAN based) fibers. Such a sizing composition is surmised to form strong interface leading to improved interfacial shear strength and other vital interfacial properties.

CONCLUSION

The potential of FT-IR spectroscopy is judiciously used to probe the chemical composition of the sizing layer of the commercial carbon fibers. The presence of diglycidyl ether of bisphenol A (DGEBA) derivative as a ubiquitous sizing compound in all the carbon fibers studied is established from the FT-IR analysis of the sizing compound isolated from the commercial carbon fibers (NX90, NX100, M55J, T700SC, CCF800H, T800HB). An in depth analysis into the structure and molecular level bonding of the sizing compound with the carbon fibers as well as the resin matrix is being probed using NMR analysis which will be subject of the next communication. Knowledge of the chemical composition, structure and interaction of the sizing compounds with the carbon fiber surface as well as the resin matrix at the interface is crucial for designing carbon fiber reinforced composites with desired properties and application.

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