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Effect of Mechanical Compression Pre-pyrolysis on the Electrical Conductivity of SU-8-derived Carbon Materials

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Abstract

The so-called SU-8 formulation was originally designed as a negative photoresist alternative but has now become the gold standard in the fabrication of micro-electromechanical systems (MEMS) due, in great part, to the electrical conductivity obtained after pyrolyzing the Bis-Phenol A Novolac Epoxy (BPNE) oligomer contained therein. Here, we investigated the possibility of increasing the electrical conductivity by mechanical compression pre-pyrolysis. BPNE sheets were casted, compressed and photo-crosslinked to “freeze” the material in a strained configuration before pyrolysis. The electrical conductivity was then measured using the four-point-probe method. The extent of graphitization and the degree of crystallinity were determined by XRD and Raman Spectroscopy, respectively. Although it was hypothesized that applying compressive load of up to 2000 kg would increase the volume fraction of crystalline domains via π - π stacking of the bis-phenolic core, our results show no significant improvements correlated to the compressive treatment pre-pyrolysis for the conditions used herein.

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1. Introduction

Carbon materials rich in graphitic domains have attracted a great deal of attention in a wide variety of applications thanks to their inertness, high electrical conductivity, stiffness, excellent optical transparency perpendicular to the transmitted light, and electrochemical stability [1–8]. In particular, the high electrical conductivity of carbon materials have made them popular as potential candidates to replace silicon in electronics: sensors, batteries, supercapacitors, and transistors [9–11]. As a result, over the turn of the last Century, a substantial amount of research was dedicated to the investigation of methods to increase the electrical conductivity of carbon materials derived from organic polymer precursors at reasonable costs. From these studies, it is interesting to note that some of the most promising carbon

materials are derived from synthetic organic polymer precursors and through appropriate tuning of the pyrolysis protocol as a function of the macromolecular structure of the precursor.

The pyrolysis of organic polymers has been subject of investigation for the fabrication of carbon materials with the hope to find the ideal combination of polymer and pyrolysis protocol to increase the sp^2 carbon content or simply to learn how to obtain particularly desired carbon allotropes. A myriad of polymer precursors have been tested since the seminal crystallinity studies from the mid-20th Century, where various temperatures and atmospheres, or lack thereof, were analyzed in terms of their impact on the final microstructure of the carbon material [12].

More recently, the so-called SU-8 resin formulation, which was originally developed as a negative UV photoresist that can yield high-transparency coatings after photopolymerization, has turned into one of the most popular precursors for the fabrication of electrically conductive carbon materials with outstanding aspect ratios. Yet, the precise mechanism of how this formulation is capable of achieving such outstanding aspect ratios in the micron scale for carbon micro-electromechanical systems remains unclear. The SU-8 formulation contains an oligomer, Bis-phenol A Novolac Epoxy (BPNE), with a structure based on a number (n) of bisphenol units with $(2n)$ pendant epoxy groups that can undergo cationic polymerization upon production of an acid by an appropriate photoinitiator to produce a highly cross-linked material by ring-opening the epoxy groups. The photoinitiator that is typically found in these formulations is a sulfonium salt, while cyclopentanone is utilized as the solvent to allow fast casting of the oligomer and photoinitiator (Figure 1) [12–14]. Given that in most applications, the cyclopentanone, required to adjust initial viscosity and allow the casting of the precursors oligomer, is mostly evaporated in the casting or electrospinning steps, we will refer to our precursor material as Bis-phenol A Novolac Epoxy (BPNE) considering that the other left-over molecules from the SU-8 formulation are present in relatively low quantities and not expected to greatly affect the properties of the final pyrolyzed materials.

Since carbon materials can vary greatly in the volume fractions of crystalline and amorphous regions, their electronic properties have been documented to change frequently and often dramatically as a function of the precursor and fabrication conditions. Recently, different chemical and physical methods have been applied to increase the extent of graphitization and enhance the electronic and chemical properties of these materials [14–17]. Inspired by these studies, we decided to test the possibility of increasing the electrical conductivity of the carbon materials derived from the pyrolysis of BNPE as a function of the application of a mechanical stress, namely compression, since it is a relatively simple and cost-effective method to increase the crystallinity of polymer precursors before pyrolysis. The latter, given the possibility of going above the melting temperature (T_m) of the uncured epoxy oligomer and using a compressive force to induce the formation of more crystalline domains in the material.

Others have used the idea of mechanically compressing the polymer precursors before pyrolysis to increase the crystallinity of the final carbon material and thus the electrical conductivity. Ghazinejad et al. [17] investigated the effect of compression and tension on the degree of graphitization and molecular alignment of poly-acrylonitrile (PAN) fibers. An electrospinning process was used to unwind and orient the molecular chains via electrohydrodynamic forces in far-field electrospinning with and without carbon nanotubes as templating agents. The stabilized PAN fibers were then pyrolyzed for samples with and without the mechanical strain in compression and tension modes, where thermal crosslinking was employed to lock the polymer into a network configuration. Their results show that with the correct combination of thermal crosslinking and mechanical stress, the previously “un-graphitizable” PAN can be converted into a carbon material with a significant sp^2 -hybridized carbon content and good electrical conductivity via a stress-induced route. The latter motivated the present investigation of the possibility of enhancing the electrical conductivity of other materials, i.e. Bis-Phenol A Novolac Epoxy, with a combination of photo-crosslinking and compression to increase its electrical conductivity after pyrolysis beyond the current limits.

Cardenas-Benitez et al. [12] proposed that mechanical forces during the pyrolysis of photocured BPNE-derived structures, evidence by their shrinkage, contribute towards increasing the electrical conductivity of the final carbon materials. The study showed that the structures shrank about 70% of their original size. The shrinkage and elongation of suspended BPNE fibers during pyrolysis influenced the resulting electrical properties [14]. Canton et al. [14]

deposited BPNE fibers over BPNE posts to form monolithic micro-structure. As the walls shrink during pyrolysis, shrinkage-induced internal forces result in the elongation of the suspended fibers. Evidence appears to suggest that the electrical conductivity increased when fibers were elongated/stretched with a decrease of their diameter [14]. These observations additionally guided us in stipulating that one could increase the crystallinity of BPNE-derived carbon materials by compressing them before pyrolysis. However, it is reasonable to expect that proving this hypothesis through a compressive mechanical test for the previously used suspended nanowires will be a remarkable experimental challenge considering the dimensions and the precision that one must have in straining the material.

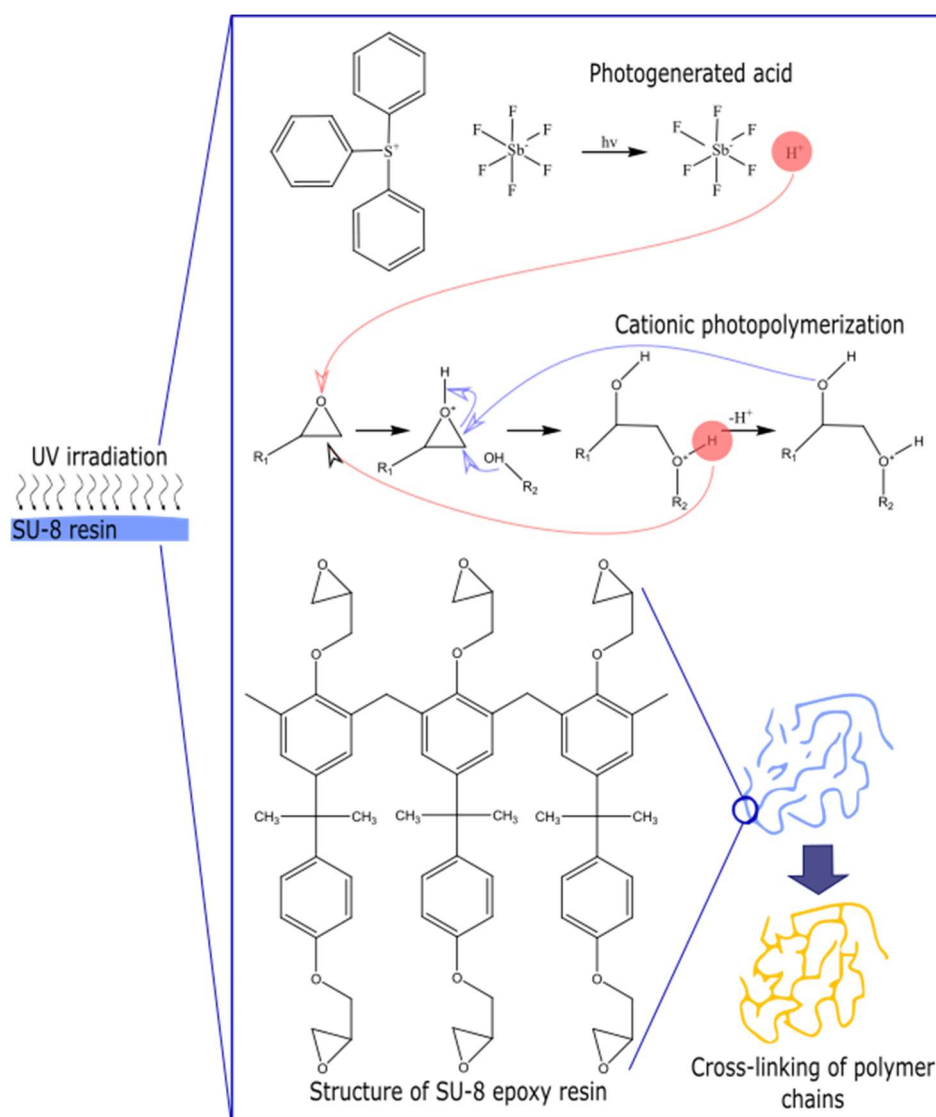


Fig. 1. Cationic photo-crosslinking of Bis-phenol A Novolac Epoxy contained in the SU-8 formulation upon exposure to 365 nm light.

On the other hand, the electrical conductivity of carbon electrodes has been shown to improve with the application of mechanical stress and proposed to be due to the alignment of the polymer linear segments within the fibers, i.e. a type of templating mechanism. Recent studies showed that the electrical conductivity of carbon electrodes is enhanced after pyrolysis, as the precursor polymer chains align within the fibers yielding carbon structures with enhanced quality and crystallinity as a result of the internal mechanical stresses that develop during pyrolysis [18,19]. The use of carbon

nanotubes, for instance, [16,17,20] in combination with hydro-electromechanical strain via electrospinning processes, resulted in the alignment of polymer chains, that lead to the production of carbon fibers with superior electrical conductivity, which is now a classical example of the use of a templating mechanism to align polymer chains along an axis [21].

Here, we aimed at investigating if the electrical conductivity of the carbon materials formed after pyrolysis of photo-cross-linked Bis-phenol A Novolac Epoxy oligomer can be increased by mechanically compressing BPNE sheets before photo-crosslinking and pyrolysis. The aim of this paper is to evaluate whether the correlation between mechanical straining and final electrical conductivity of BPNE-derived carbon materials can be proven on such macroscopic sheets. The overarching goal is to find methods to produce carbon materials from polymer precursors yielding higher electrical conductivity and mechanical strength by matching the fabrication conditions to the particular organic polymer selected and its molecular structure. The present study serves as a first attempt to demonstrate if mechanical compression and photo-crosslinking of the epoxy oligomers before pyrolysis can be reliably used to produce higher conductivity materials for sensors and electromechanical devices.

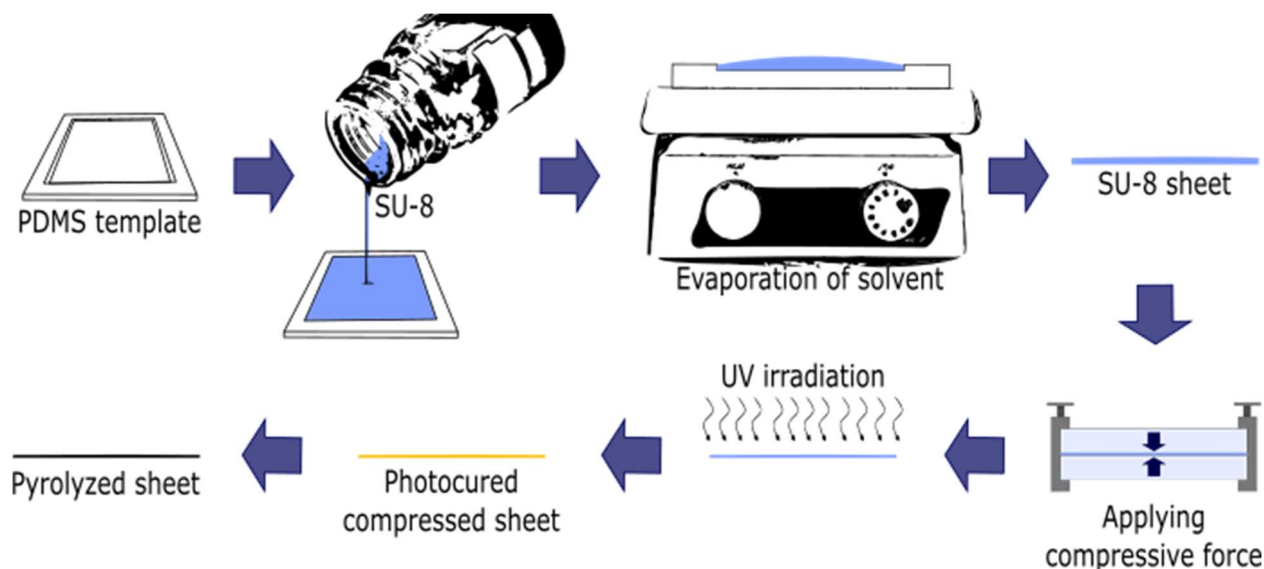


Fig. 2. Schematic diagram of the fabrication process for samples

2. Materials and Methods

2.1. Bis-phenol A Novolac Epoxy sheets casting, photo-crosslinking and pyrolysis

The SU-8 2100 formulation was purchased from MicroChem Corp. (now Kayaku Advanced Materials, Westborough, MA, USA) and used as received according to the thin sheet casting protocol below. A poly-dimethyl siloxane (PDMS) soft-lithography kit (Sylgard 184, Sigma Aldrich) was purchased and used without any modification and according to the manufacturer instructions to fabricate molds for the casting of the SU-8 sheets.

Compressed samples were fabricated according to the steps described in Figure 2. The SU-8 2100 formulation was casted and its solvent evaporated by increasing the temperature to 75 °C for 4h using a standard hot-plate. The pre-heated SU-8 sheets were compressed by applying a constant load of up to 2000 kg for 30 min to yield a maximum compressive stress of around 50 MPa. The compressed samples were immediately exposed 365 nm light in a UV chamber (DYMAX 2000-EC equipped with a halogen bulb with an intensity of approximately 105 mW/cm²). Photo-polymerized samples with and without the compression step were subsequently pyrolyzed at 1000 °C under N₂

atmosphere. Control samples were fabricated without applying the mechanical compressive force and without exposure to the UV light for comparison.

The samples were pyrolyzed in a furnace (PEO 601, ATV Technologie GmbH, Germany) according to the following temperature profile: (I) the temperature was increased from room temperature to 300°C at a heating rate of 30°C/min. It stayed at 300 °C for 3hours and then, the temperature was ramped to 900°C at 10°C/min and stayed for 1hour. Finally, it was cooled down to room temperature at 30°C/min.

2.2. XRD and Raman spectroscopy

X-ray diffraction (XRD) patterns were obtained for all samples recording over a 2θ in the range of 5-55° using a spectrometer (Miniflex 600, Rigaku, USA) equipped with the Cu K α radiation source.

Analysis of the sp²-hybridized carbon content was carried out using a Raman spectrometer (Bruker, USA) equipped with a 532 nm laser. The Raman maps and the averaged Raman spectra were collected across 25 μm^2 tiles.

2.3. Electrical conductivity measurements

The conductivity of samples was measured using a four-point-probe. In this method four probes are placed in contact with the sheet sample surface. The current is applied through the sample from the outer two probes and thereby the voltage drop is measured by the inner two probes [22]. In very thin samples, the resistivity is calculated using the following equation (1):

$$\rho = \frac{\pi t}{\ln(2)} \frac{V}{I} \quad (1)$$

Where, V is the voltage, I is the applied current, and t is the thickness of the thin sample sheet. The thickness was adjusted to 0.5 mm for all samples. The control samples were casted in a different mold to yield a comparable thickness. The other samples were casted in different molds with higher thickness (1.5 mm) and after applying compressive force, the thickness turned to 0.5 mm. The current was changed from 0 to 1.5 amperes.

3. Results and discussion

Since, the electrical conductivity is well known to correlate with the extent of graphitization and it is our target property, we began by measuring the conductivity using the four-point probe method for all the BPNE sheets with and without compression. We measured a resistivity of around 0.018 Ω/cm (Fig. 3) for the pyrolyzed sheets both with and without compression before pyrolysis. Our values are very close to the previously reported values for other pyrolyzed geometries of the same carbon materials. Pramanick et al[1], reported that the resistivity of pyrolyzed SU-8-derived samples oscillated around 5-10 Ω/cm once a maximum temperature of 700 or higher is reached in the pyrolysis protocol. Therefore, our measurements appeared to give reasonable values despite the sample geometry and the surface roughness that were obtained in the pyrolyzed sheets. These results give a conductivity of around 53 S/cm, which is relatively low compared to other pyrolyzed organic polymer precursors and even BPNE samples of different geometries [12].

We observe a negligible difference in the resistivity values for the samples that were compressed before photo-crosslinking as compared to the samples that were photo-crosslinked and pyrolyzed without the mechanical compression. Attention was paid to make the BPNE sheets of approximately the same thickness for both sets of samples, 1.5 mm. At least three samples were tested for every group. This result appears to indicate that there is no increase in electrical conductivity correlated to the use of compression before pyrolysis. However, it is possible that rugosity and irregular shapes of the samples after pyrolysis lead to poor precision in the four-point-probe

measurements. Therefore, we decided to further characterize the variations in the structure of the samples through the analytical methods discussed below to obtain additional evidence confirming the lack of correlation between compression and electrical properties.

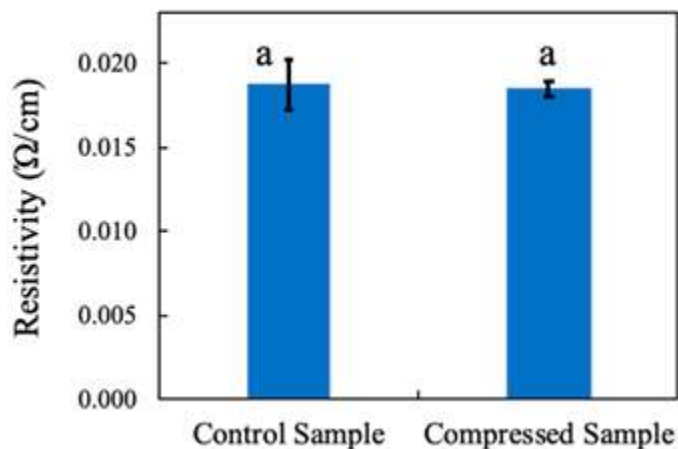


Fig. 3. Average resistivity of pyrolyzed Bis-phenol A Novolac Epoxy casted into thin sheets with and without compression ($p > 0.05$ ANOVA).

Given our hypothesis and the suspicion that the four-point probe method may not be ideal to quantify small variations in electrical conductivity in pyrolyzed thin sheets that were obtained in this study, we investigated the Raman spectra of the pyrolyzed samples. The uniformity of graphite crystallites can be evaluated by Raman Spectroscopy. Figure 4 shows the average Raman spectra of different samples. There are two characteristic peaks at ~ 1367 and ~ 1600 cm^{-1} assigned to the D and G bands, respectively. The G peak arises from the stretching motion of the sp^2 -hybridized carbon-carbon bond in graphitic materials and D peak corresponds to the disorder structure. The intensity ratio of D peak to G peak is used for evaluation the degree of graphitization. Hence, the higher the D to G ratio is related to the lower alignment of graphitic planes and thereby lower degree of graphitization in the carbon structure [23]. As it can be seen in Figure 4, the intensity of the peaks is the same, yielding a ID/IG ratio that is close to 1, coinciding with the graphite crystallite size and the degree of disorder obtained previously for pyrolyzed organic polymers. In comparison, compressive stress treatment of poly-acrylonitrile with carbon nanotubes as templating agents yielded a ID/IG ratio of 0.69 [17]. Most importantly, we observe that the mechanical compressive treatment does not appear to have a significant effect on the microstructure of the pyrolyzed sheets with and without compression.

Furthermore, the 2D maps from the Raman spectroscopy analysis of pyrolyzed BPNE-derived sheets with and without compression is depicted in Figure 4. We focused on the same bands associated to graphitic domains and observed that in both cases the surface appears to be highly uniform. These results suggest that there is a significantly uniform graphitization microstructures in both cases and that the surface is smooth at least microscopically in the cross-section area analyzed on the pyrolyzed sheets. These observations agree with the seemingly constant electrical conductivity that we quantified with the four-point probe method.

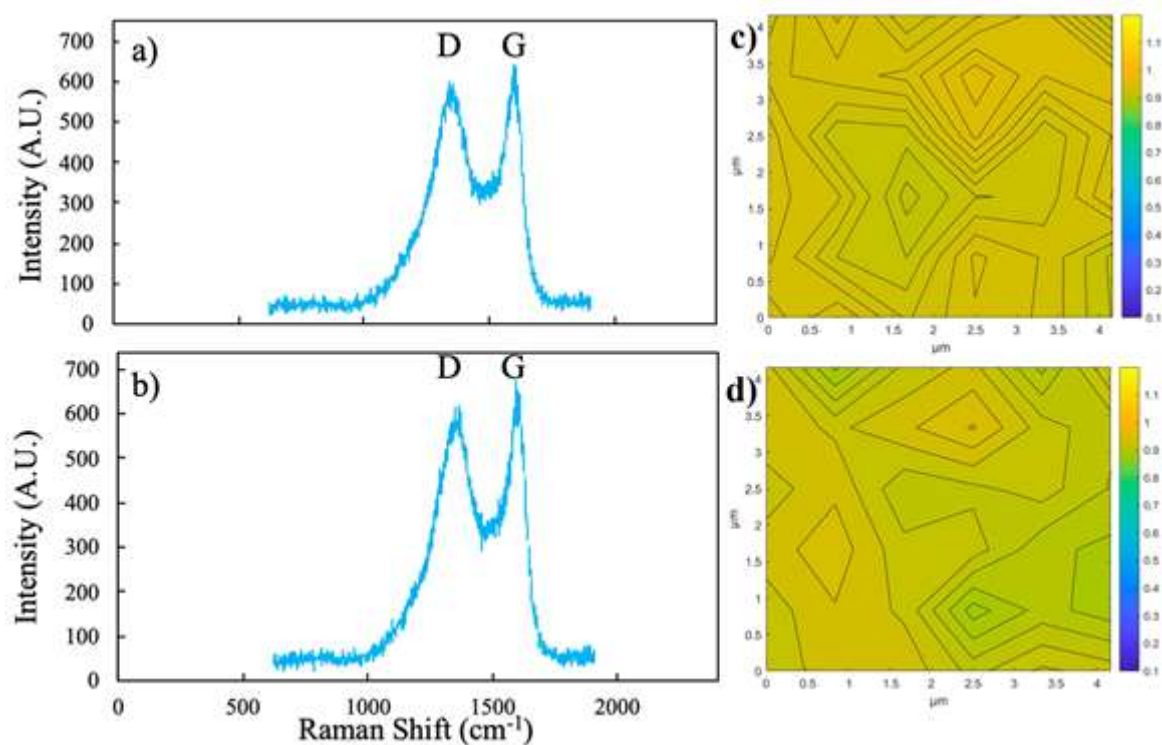


Figure 4: Analysis of carbon content in pyrolyzed Bis-phenol A Novolac Epoxy sheets a) without and b) with compression before pyrolysis. 2D Raman analysis of the pyrolyzed films c) without compression and d) with compression.

In order to obtain a confirmation for the lack of correlation between the compression and the properties of the pyrolyzed BPNE-derived sheets, as per the resistivity measurements and the Raman spectroscopy analysis, we employed X-ray diffraction (XRD) spectroscopy to try to discern if there were any variations present between the two groups of samples, in terms of crystallinity. The results are shown in Figure 5. Two broad diffraction peaks can be observed in both the samples, in 22° and 55° . The broad bands at 22° and 55° are related to (002) plane and (100) plane respectively [24]. The broadness of these peaks appears to be correlated with poor stacking of graphene layers in (002) and (100) plane. This is similar to previous XRD spectra of similar glassy-carbon materials, where the mesoscale structure resembles that of semi-crystalline organic polymer networks. Most importantly, we observe no noticeable differences between the XRD spectra for the BPNE-derived sheets with and without compression. Thus, we can establish that this third evidence further supports the lack of contribution of the compressive stress of the BPNE thin sheets on their microstructure and on the electrical properties stemming therefrom.

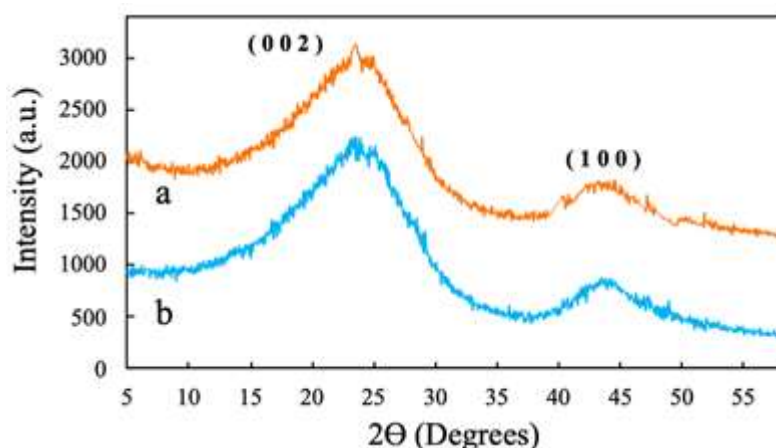


Figure 5: Crystallinity analysis of Bis-phenol A Novolac Epoxy thin sheets a) without and b) with compression before pyrolysis from their X-Ray diffraction (XRD) patterns.

Although mechanical stresses had been successfully employed to increase the crystallinity, conductivity and graphitization of polymers like poly-acrylonitrile [17], it seems that the complicated microscopic configuration and orientation of graphite crystallites within a relatively amorphous crosslinked carbon network make it difficult to induce further alignment in these materials. This may indicate that if the electrical conductivity of BPNE-derived carbonaceous materials can be enhanced at all, this will require higher temperatures and pressures to have an effect in the microstructure after pyrolysis. It is still possible that the previously observed increase in the electrical conductivity of suspended nanowires is related, at least in part, to the mechanical stresses that develop during pyrolysis. However, in this case, it can be hypothesized that the stress per unit mass must then be higher than the ones reached in this study, especially as a result of the shrinkage from the gasification of the ether linkages within the precursor polymer network. Therefore, it is suggested to further explore the validity of this hypothesis by carefully designing experiments where mechanical stresses are applied on other types of geometries and sizes of casted BPNE samples that are more susceptible to the application of higher compressive or tensile forces before photo-crosslinking.

4. Conclusion

In this study, we tested the hypothesis that the microstructure and the electrical conductivity of carbon materials derived from the pyrolysis of Bis-phenol A Novolac Epoxy can be increased by mechanical compression pre-pyrolysis using millimeter scale thin sheets. First, measurements of the resistivity indicated that there is a negligible variation correlated with compression. Then, Raman spectroscopy and XRD supported the finding that there does not seem to be any significant variations in the graphitic crystallite size and order, or in the crystallinity between the samples with and without compression of up to 50 MPa, respectively. We cannot conclude from this study if the electrical properties of BPNE-derived carbon materials can be at all enhanced by modifying the fabrication protocol with mechanical forces. The latter was at least not possible with the fabrication process used herein. However, it appears that if mechanical deformation resulting from the pyrolysis of bis-phenolic epoxy precursors takes part in the previously documented increase in electrical conductivity with internal stresses, the stresses therein must be considerable higher to result in the alignment of the phenolic cores and induce a higher degree of order through π - π stacking that may lead a higher-conductivity glass-like carbon material. The goal is that this study serves as starting point in the search of relatively low-cost methods to obtain high-electrical-conductivity carbon materials from organic polymer precursors that can be easily patterned.

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Nomenclature

BPNE	Bis-phenol A Novolac Epoxy
PDMS	Poly-dimethylsiloxane
PAN	Poly-acrylonitrile
MEMS	Micro-electromechanical systems
XRD	X-ray diffraction
UV	Ultraviolet

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