Tec Nano 2019

Compressive pretreatment of a Novolac Epoxy oligomer to Increase the Electrical Conductivity of Pyrolytic Carbon Therefrom

Saeed Beigi-Boroujeni1, Osamu Katagiri-Tanaka1, Alan Aguirre-Soto[[1]](#footnote-1),\*

1Tecnologico de Monterrey, School of Engineering and Science, Av. Eugenio Garza Sada Sur, Monterrey, 2501, N.L., Mexico.

Abstract

The so-called SU-8 formulation was originally designed as a negative photoresist but has now become the gold standard for the fabrication of carbon microelectromechanical systems (MEMS) mainly due to the electrical conductivity obtained after pyrolysis of the patternable Bis-Phenol A Novolac Epoxy (BPNE) oligomer contained therein. Here, we investigate the possibility of increasing the electrical conductivity by mechanically compressing the uncured oligomer. BPNE sheets were casted, compressed and photo-crosslinked to “freeze” the material in a strained configuration before pyrolysis. The electrical conductivity was estimated using four-point probe measurements. The relative sp2/sp3 content and the degree of crystallinity were determined by Raman and XRD spectroscopy. It was hypothesized that applying compressive loads of up to 2000 kg at 90˚C would suffice to increase the crystallite size and the order of the microstructure by inducing additional alignment of the aromatic segments from the phenolic groups. However, negligible variations in conductivity, sp2 hybridization and crystallinity were observed when compressing BPNE thin sheets as compared to untreated samples, suggesting that higher loads or temperatures may be required to synthesize a glass-like carbon material with a slightly more graphitic character.

[copyright information to be updated in production process]

*Keywords: SU-8 photoresist; Epoxy oligomer; Cationic photopolymerization; Stress-induced graphitization; Pyrolysis; Carbon materials;*

1. Introduction

Carbon materials are uniquely interesting in that from a seemingly simple paradigm, heating organic matter, a broad range of complex structures emerge, each displaying a unique set of properties. It is an epitome of how complexity and diversity arise in Nature from a single building unit with a relatively small set of rules involved in its transformation. Precisely this phenomenon has, somewhat ironically, gained the attention of many trying to find the “ultimate” material, while at the same time making it remarkably difficult to control the precise combination of macroscopic properties of the final material. In general, carbon materials exhibit complexity as a collection of multi-scalar degrees of freedom varying through multi-dimensional continua, where the precise values of in each one combines to yield the unique set of properties we use to characterize the material. Some of the most important features from the molecular to the mesoscale are hybridization, degree of crystallinity, orientation, anisotropy, continuity or discontinuity of the multiscale textures, and porosity. The combination of the intertwined multiscale arrangements has been linked, at least partially, to the broad spectrum of macroscopic characteristics that we utilize to build the profile or fingerprint of the final material. For instance, carbon materials with a range of chemical inertness, electrical conductivity, mechanical strength, optical transparency, and electrochemical stability have been synthesized and employed for various purposes [1–8]. This article focuses its discussion an exemplar material found in between two of the various subsets of materials, namely the so-called glass-like and graphite-like families of carbon materials, often colloquially grouped in the term pyrolytic carbon. We jump between both classes of carbon materials as we investigate the possibility of altering the profile of the typical glass-like material by giving it a slightly more graphitic character.

The relatively high electrical conductivity of pyrolytic carbon materials has made them popular as potential candidates to replace silicon in components for microelectromechanical (MEMS) systems: sensors, batteries, capacitors, and transistors [9–11]. Glass-like carbon materials specifically are attractive from a practical point of view given their characteristic combination of electrochemical stability, redox potentials, thermal resistance and electrical conductivity. Therefore, since the turn of the last Century, a substantial amount of research has been dedicated to the investigation of methods to fine tune the properties of glass-like carbon materials derived from various carbon sources, including synthetic polymers, at reasonable costs to extend the library of carbon materials. Our long-term goal is to synthesize carbon materials with an appropriate set of properties suitable for photo- and photoelectron-chemical catalysis, where one of the most important characteristics is the resistance to strongly oxidizing or reducing environments, while retaining competitive electron transfer rates.

Some of the most promising carbon materials have been derived from synthetic organic polymer precursors and through appropriate tuning of the pyrolysis protocol as a function of the molecular structure of the carbon source. As a result, the pyrolysis of synthetic organic polymers has been the subject of investigation for the fabrication of carbon materials with the hope to find the ideal combination of polymer and fabrication protocol/conditions to control all the molecular to mesoscale features that dictate the profile of the final carbon material, e.g. unique combination of carbon allotrope content, crystallite size and order of the crystalline domains appropriate to yield a more graphite-like or glass-like material. 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, where analyzed in terms of their impact on the final microstructure of the carbon material [12]. Since then, it is generally agreed upon that the molecular structure of the polymer appears to be the most important factor in determining the profile of the final carbon material. However, the importance of other variables, such as crosslink density, sample dimensions, thermal treatment curve and type of ‘pre-treatment’, which refers to any strategy followed to alter the mesoscale structure of the polymer before pyrolysis. It is important to note that the profile of properties of the final carbon material must justify the pyrolysis of the often-expensive synthetic polymers, which often already have outstanding properties of their own. For instance, in the pursuit of a material for heterogeneous photoelectrocatalysis, most synthetic organic polymers will either lack in their redox potentials or in their resistance to solvents and strongly oxidizing environments.

It has been known for some time that phenolic resins are an excellent candidate for the fabrication of glass-like carbon. Specifically, the so-called SU-8 formulation, originally developed as a negative UV photoresist that can yield thermosetting materials often used for coatings with high transparency 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 behind why and how this formulation can form carbon materials with their unique set of properties remains unclear. The SU-8 formulation remains bound to patents, which complicates its analysis. From what can be discerned from the available information, it contains an oligomer, Bis-phenol A Novolac Epoxy (BPNE), with a structure based on a number (n) of bisphenol units with (2n) pendant epoxide groups that can undergo cationic polymerization upon production of an acid by an appropriate initiator, activated by either thermal or electromagnetic energy, to produce a highly crosslinked material by ring-opening the epoxide groups. Most often, the photoinitiator (PI) found in these formulations is a sulfonium salt, e.g. triarylsulfonium hexafluoroantimonate salt, where cyclopentanone is utilized as the highly volatile solvent suitable for fast casting of the oligomer/PI/salts mixture (Figure 1) [12–14]. The cyclopentanone, required to adjust the initial viscosity and facilitate manipulation of the solid-state oligomer, is mostly evaporated in the casting or electrospinning steps. Therefore, we will refer to our carbon source material as simply Bis-phenol A Novolac Epoxy (BPNE), considering that the other left-over molecules from the SU-8 formulation, PI and salt additives, are present in relatively low quantities and not expected to greatly affect the properties of the final pyrolytic carbon materials.

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 material. The study showed that the structures shrank about 70% of their original size. Canton et al. [14] deposited BPNE fibers over BPNE posts to form monolithic microstructures, where the shrinkage and elongation of suspended BPNE fibers during pyrolysis appears to influence the final electrical properties. As the walls shrink during pyrolysis, shrinkage-induced internal forces seem to result in the elongation of the suspended fibers. Evidence appears to suggest that the electrical conductivity increases when fibers are elongated and stretched as their diameter decreases due to internal forces during free-volume loss [14]. These observations guided us in stipulating that one could increase the graphitization in BPNE-derived carbon materials by straining the uncured BPNE just before crosslinking the multifunctional epoxide into the thermosetting polymer network to be pyrolyzed. However, it can be reasonably expected that proving this hypothesis on the suspended nanowires fabricated by Cardenas-Benitez and coworkers will be a remarkable experimental challenge considering the dimensions and the precision that one must have in order to controllably stress the precursor material at such scales. This sparked the present proof-of-concept investigation into the possibility of enhancing the electrical conductivity of millimetric “thin” sheets of BPNE by compressing the casted and uncured BPNE resin before photo-crosslinking and pyrolysis; where the desired long-term goal is to retain the chemical resistance of the glassy-like while slightly improving its electrochemical performance.

Various chemical and physical methods have been reported to produce carbon materials with higher graphitic character by purposely altering the morphology of the polymer before pyrolysis [14–17]. Specifically, the idea of mechanically compressing the polymer precursors pre-pyrolysis to increase the crystallinity of the carbon material therefrom, and thus the electrical conductivity was successfully employed by Ghazinejad and coworkers [17]. In that case, the effect of compression and tension on the degree of graphitization and molecular alignment of poly-acrylonitrile (PAN) fibers was investigated. The forces involved in the electrospinning process plus carbon nanotubes as templating agents were used to orient the molecular chains. Then, thermal crosslinking was employed to lock the polymer into a network configuration with higher crystallinity under the mechanical stress. The stabilized PAN fibers were pyrolyzed for samples with and without the mechanical strain. Their results showed that, with the combination of thermal crosslinking and mechanical stress, the previously “non-graphitizable” PAN can be converted into a graphitic carbon material with a noticeably higher sp2-hybridized carbon content and good electrical conductivity via a stress-induced route. Compression appears to result in carbon materials with higher conductivity than samples that were crosslinked under tension. This study guided us into testing the possibility of increasing the electrical conductivity of the carbon materials derived from the pyrolysis of BNPE by applying a relatively simple mechanical pretreatment, namely isothermal compression close to melting, since it is a relatively straight-forward and cost-effective modification to the standard protocol. The latter may be reasonably expected to increase the crystallinity of the macromolecular carbon source before pyrolysis; given the possibility of inducing the formation of more crystalline domains in the carbon source by going above the melting temperature (Tm) of the uncured Novolac resin and using a compressive force to favor π-π stacking of the phenolic groups.

Additional insights supporting our hypothesis are those observed in the variations of the electrical conductivity of carbon electrodes upon the application of mechanical stresses, proposed to be due to an increase in the alignment of the polymer linear segments within the fibers, i.e. similar templating mechanism as that of the electrospinning with carbon nanotubes and graphene sheets[18,19]. The electrical conductivity of carbon electrodes increased after pyrolysis, as the precursor polymer chains align within the fibers yielding carbon structures with higher crystallinity as a result of the internal mechanical stresses that develop during pyrolysis. The use of carbon nanotubes, for instance, [16,17,20] in combination with the hydro-electromechanical forces from the electrospinning process also appears to result in the alignment of polymer chains, leading to the production of carbon fibers with superior electrical conductivity; which is now a classical example of the use of the templating mechanism to align polymer chains along the flow axis [21].

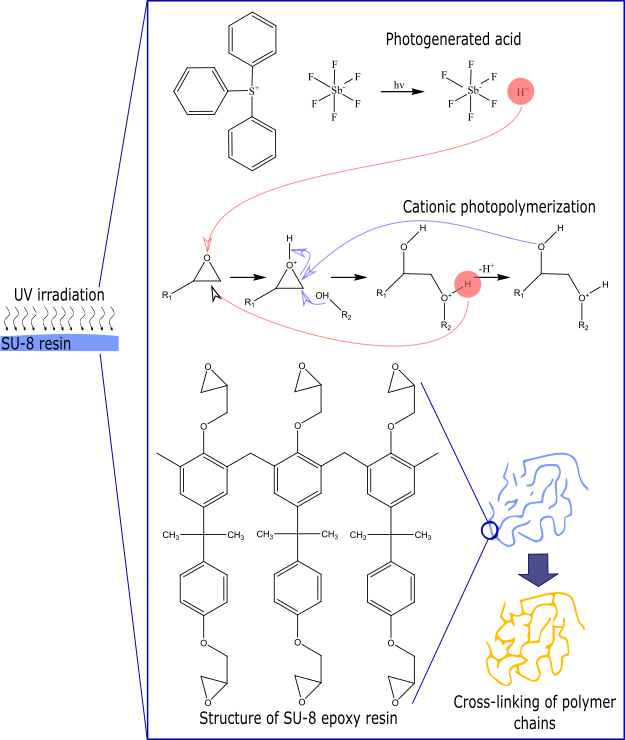


Figure 1. Cationic photo-crosslinking of Bis-phenol A Novolac Epoxy contained in the SU-8 formulation upon exposure to 365 nm light.

Here, we investigated if the electrical conductivity of the carbon materials formed after pyrolysis of the photo-crosslinked Bis-phenol A Novolac epoxy oligomer can be increased by mechanically compressing BPNE sheets before the photo-crosslinking and pyrolysis steps. The aim of this article is to evaluate whether there is a significant correlation between mechanical pretreatment and the final electrical conductivity of BPNE-derived carbon materials fabricated from macroscopic thin sheets of BPNE. From a practical point of view, the overarching goal is to find methods to produce carbon materials from patternable polymer precursors that yield materials of higher electrical conductivity and mechanical strength by matching the fabrication conditions to the particular organic polymer selected and to its molecular structure. The present study serves as a first attempt to demonstrate if a relatively simple modification to the standard MEMS fabrication method, such as mechanical compression of the epoxy resin before photo-crosslinking and pyrolysis, can be reliably used to produce higher conductivity materials, and to obtain insights into the uniqueness of the BPNE chemistry for the fabrication of MEMS. The general goal is to gain insights into structure/synthesis/properties relationships that guide the fabrication of novel materials with a unique set of properties based on their combination of features from the molecular to the nanoscopic to the microscopic scales. An additional long-term goal in this endeavor is expanding the portfolio of applications of electrically impractical thermosetting photopolymers by developing methods to fabricate patternable conductive carbon materials from them with geometries spanning multiple scales.

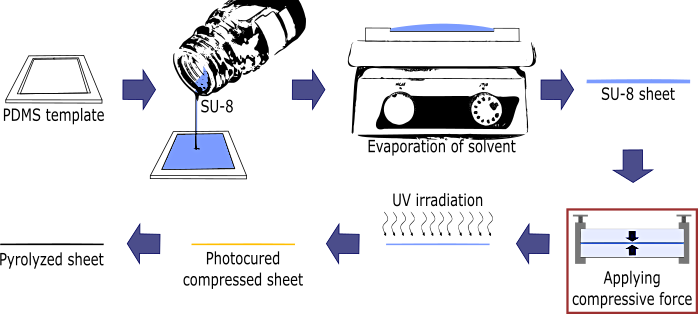


Figure 2. Modified procedure for the fabrication of carbon materials derived from SU-8 with addition of a mechanical pretreatment step where the uncured oligomer is isothermally compressed before photopolymerization.

1. Materials and Methods
   1. Casting, compressive pre-treatment, photo-crosslinking and pyrolysis of thin sheets of Bis-phenol A Novolac Epoxy

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, Dow Chemical Company, USA) was purchased and used without any modification and according to the manufacturer instructions to fabricate molds for the casting of the SU-8 thin sheets.

Control samples were fabricated without applying the mechanical compressive force and without exposure to the UV light for comparison. Compressed samples were fabricated according to the steps described in Figure 2. The SU-8 2100 formulation was casted and utilized after evaporation of the cyclopentanone by increasing the temperature to 75 °C for 4h using a standard hot-plate. For the case of the mechanically pre-treated samples, the pre-heated SU-8 sheets were compressed by quickly applying a constant load of up to 2000 kg for 30 minutes to yield a maximum compressive stress of around 50 MPa isothermally at 90˚C. The compressed samples were immediately thereafter exposed to 365 nm light in a UV chamber (DYMAX 2000-EC equipped with a halogen bulb with an intensity of approximately 105 mW/cm2) for 60 seconds.

Photo-polymerized samples with and without the compression step were subsequently pyrolyzed at 1000 °C under N2 atmosphere. The samples were pyrolyzed in a furnace (PEO 601, ATV Technologie GmbH, Germany) according to the following temperature profile: (1) the temperature was increased from room temperature to 300°C at a heating rate of 30°C/min, (2) temperature was kept at 300 °C for 3hours, (3) the temperature was ramped to 900°C at 10°C/min and kept for 1hour, and (4) the temperature was brought back to room temperature at 30°C/min. This protocol was based on the standing procedure to fabricate MEMS from the photolithography of photoresist formulations such as SU-8 and expecting to obtain optimal properties in the pyrolytic carbon material with these temperatures and heating rates.

* 1. 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 Kα 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 µm2 tiles.

* 1. Electrical conductivity measurements

The conductivity of samples was measured using the four-point-probe method. Four electrical probes were placed in contact with the surface of the casted thin sheets. The current is applied through the sample from the outer two probes and the voltage drop is measured by the inner two probes [22]. In very thin samples, the resistivity is calculated using the following equation (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 between 0 and 1.5 amperes.

1. 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 estimating the conductivity using the four-point probe technique for all the BPNE sheets with and without compression. We obtained values for the resistivity of around 18 (Fig. 3) for the pyrolyzed sheets both with and without compression before pyrolysis. Our values are decently comparable to previously reported values for carbon materials derived from the pyrolysis of BPNE with different geometries. For example, Pramanick et al[23], reported that the resistivity of pyrolyzed SU-8 samples oscillated around 37 once a temperature of 900 is reached in the pyrolysis protocol. Therefore, our measurements appear to give reasonable values despite the sample geometry utilized herein and the surface roughness that was obtained in the pyrolyzed sheets due to the compression. These results give a conductivity of around 5,500 S/m, which is relatively low compared to other pyrolyzed organic polymer precursors and previously reported values for BPNE-derived carbon materials [12]. However, discrepancies may stem from inaccuracies in the electrical conductivity measurements depending on the geometry and size of the final carbon material; where the exact magnitude of the conductivity is not the central focus of this study, but rather the relatively change caused by the mechanical pretreatment.

We observed 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 mechanical compression. Attention was paid to make the BPNE sheets of approximately the same final thickness for both sets of samples. 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 surface roughness and irregularities in the BPNE thin sheets after pyrolysis lead to poor precision in the four-point-probe measurements. Therefore, we decided to further investigated whether variations in the structure of the samples can be detected through the analytical methods discussed below and confirm the absence of a statistically significant effect of the compressive pre-treatment on the properties of BPNE-derived carbon materials.

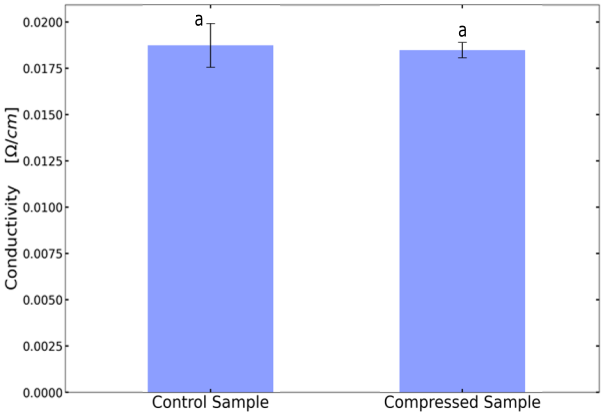


Figure 3. Average resistivity of pyrolyzed Bis-phenol A Novolac Epoxy thin sheets with and without the compressive pre-treatment obtained from the four-point-probe method (p > 0.05 ANOVA) a.

Given the suspicion that the four-point probe method may not be ideal to quantify small variations in electrical conductivity in the 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 E2g bands, respectively. The G (E2g) peak arises from the stretching motion of the sp2-hybridized carbon-carbon bond in graphitic materials and D peak corresponds to the disorder structure. The intensity ratio of D peak to G peak and the breadth of the two bands are used for the relative determination of the degree of graphitization. Hence, the higher the D to G ratio, the lower the alignment of graphitic planes is, thereby lowering the degree of graphitization in the carbon structure [24]. As it can be seen in Figure 4, the intensity of the peaks is the same, yielding an 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 (PAN) with carbon nanotubes as templating agents yielded an 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, which may be related to mechanical properties of the starting polymer before the mechanical treatment.

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 discussed above, which are associated to graphitic domains, and observed that in both cases the surface appears to be highly uniform in terms of its carbon allotropes. 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 and appear to be further indicating that indeed higher temperatures and mechanical loads may be required to induce a higher degree of alignment of the phenolic segments within the material before crosslinking and thus a higher degree of graphitization in the final carbon material.

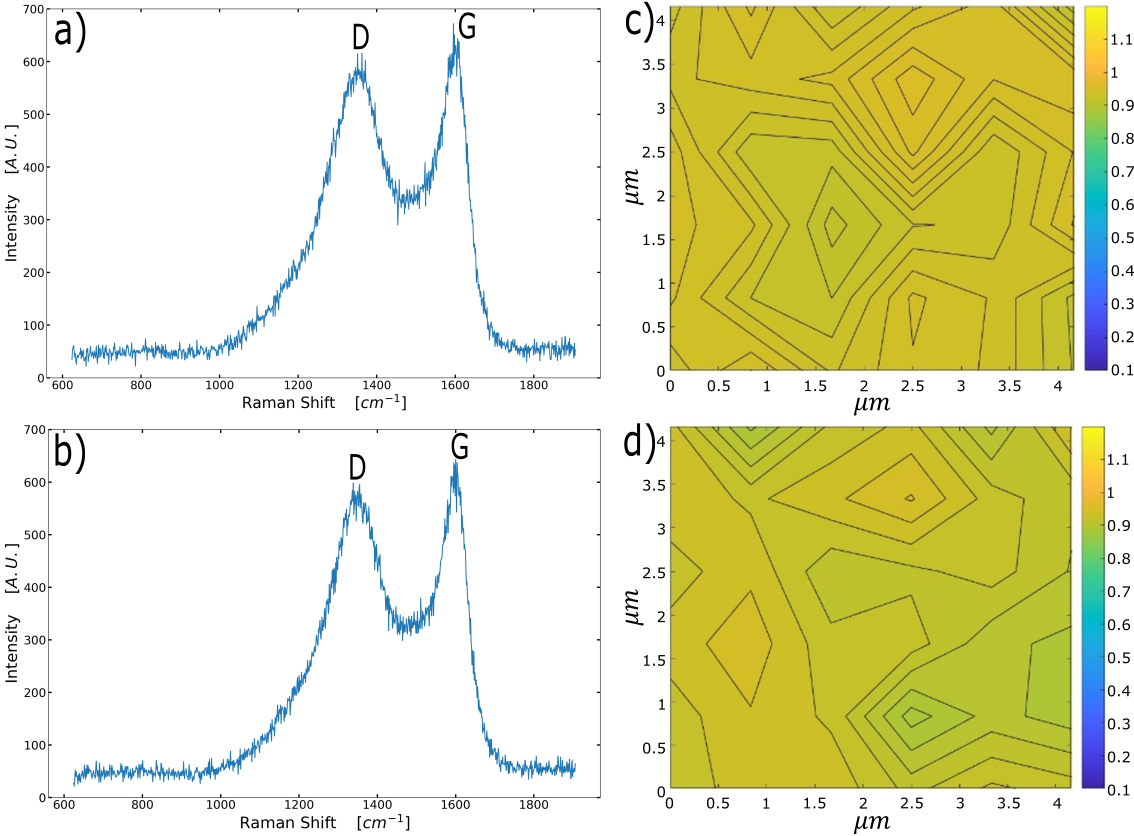


Figure 4. Analysis of carbon content in pyrolyzed Bis-phenol A Novolac Epoxy sheets a) without and b) with compression before pyrolysis. 2D Raman analysis of the pyrolyzed films c) without compression and d) with compression.

In order to obtain additional 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 sets of samples, in terms of their 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 [25]. The broadness of these peaks appears to be correlated with poor stacking of the graphene layers in the (002) and (100) planes. This is similar to previous XRD spectra of similar glass-like 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 the compression pre-treatment. Thus, we can establish that this third evidence further supports the lack of contribution of the compressive force imposed on the uncured BPNE thin sheets on the microstructure and the electrical conductivity of the final carbon materials produced therefrom.

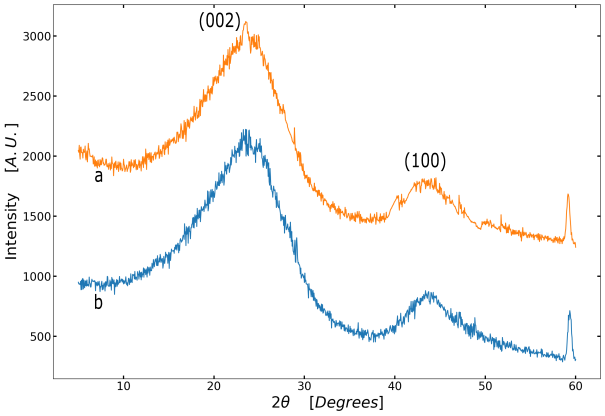


Figure 5. Crystallinity of Bis-phenol A Novolac Epoxy thin sheets a) without and b) with compression before pyrolysis from their X-Ray diffraction (XRD) patterns.

Although mechanical stresses had been successfully employed to increase the crystallinity of PAN and therefore the extent of graphitization and conductivity of the final carbon materials produced after pyrolysis [17], it appears that in the case of BPNE the highly-strained configuration and orientation of graphite crystallites within the relatively amorphous crosslinked carbon network make it difficult to induce further alignment in these materials, at least at the temperature and force utilized in this initial study. This may indicate that if the electrical conductivity of BPNE-derived carbon materials can be enhanced at all, higher temperatures and pressures will most likely be required. 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, it can be hypothesized that for that case the stress per unit mass must have been greater than the ones reached in this study; the latter stemming from the shrinkage stresses induced by the gasification of the ether linkages in the phenolic groups within the polymer network. Therefore, it is suggested to further explore the validity of this hypothesis by carefully designing experiments were 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. In the present study, the temperature was kept at 90˚C during the mechanical pretreatment given that the uncured BPNE samples begin deforming and flowing at slightly higher temperatures; therefore, making it difficult to control the sample geometry.

|  |  |  |
| --- | --- | --- |
| Characteristics of chitosan | Bonding Strength (kPa) | Ref. |
| HMW 76% | 14.1 | [40] |
| LMW 77% | 10.9 | [40] |
| LMW 91% | 12.8 | [40] |
| MMW 77% | 24.7 | [38] |
| MMW 78% | 21 | [34] |
| MMW 80% | 15.6 | [40] |
| MMW 80% + Porous | 13.8 | [43] |
| MMW 85% | 17 | [36] |
| MMW 78% (90%) OC 85% (10%) | 22 | [34] |
| MMW 78% (90%) OC 85% (10%) + Porous | 22.5 | [34] |
| MMW 80% (70%) OC 85% (30%) | 14.5 | [43] |
| MMW 80% (70%) OC 85% (30%) + Porous | 14 | [43] |
| MMW 80% (90%) OC 85% (10%) | 13.4 | [43] |
| MMW 80% (90%) OC 85% (10%) + Porous | 12.4 | [43] |
| MMW 78% (90%) OC 85% (10%) + L-DOPA | 24 | [34] |
| MMW 78% (90%) OC 85% (10%) + L-DOPA + Porous | 30 | [34] |
| MMW 80% + OFM | 23 | [33] |
| MMW 15% + Lysozymes | 15 | [41] |

1. Conclusion

In this study, we tested the hypothesis that the structure 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 of the electrical macroscopic properties with the compression pretreatment. 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 the addition mechanical or other types of treatments before pyrolysis. The latter was at least demonstrated to be unfeasible with the fabrication process used herein. However, it appears that if mechanical deformation resulting from the pyrolysis of the phenolic epoxide precursors takes part in the previously documented increase in electrical conductivity due to internal stresses from the pyrolysis itself, the stresses therein must be considerable higher to induce in the alignment of the phenolic cores and induce a higher degree of order through π-π stacking and a carbon material with higher electrical conductivity. The goal is that this study serves as starting point in the search of relatively low-cost methods to obtain carbon materials with more suitable electrical conductivity for MEMS and sensors derived from organic polymer precursors that can be easily patterned into functional geometries.

Acknowledgements

We thank Prof. Dr. Marcelo Videa for use of the XRD spectrometer and Dr. Sunny Holmberg for help with the Raman spectroscopy measurements of the pyrolyzed BPNE sheets. We thank Dr. Arnoldo Sanchez for guidance with the four-point-probe method. We thank the support of a China-Tec from Tecnologico de Monterrey seed-fund for the development of 2D photosensitive materials.

# Nomenclature

BPNE Bis-phenol A Novolac Epoxy

PDMS Poly-dimethylsiloxane

PAN Poly-acrylonitrile

MEMS Microelectromechanical systems

XRD X-ray diffraction

UV Ultraviolet

References

[1] R.L. McCreery, Advanced Carbon Electrode Materials for Molecular Electrochemistry, Chem. Rev. 108 (2008) 2646–2687.

[2] A.K. Geim, Random Walk to Graphene (Nobel Lecture), Angew. Chemie Int. Ed. 50 (2011) 6966–6985.

[3] M.J. Allen, V.C. Tung, R.B. Kaner, Honeycomb Carbon: A Review of Graphene, Chem. Rev. 110 (2010) 132–145.

[4] Y. Zhu, S. Murali, W. Cai, X. Li, J.W. Suk, J.R. Potts, R.S. Ruoff, Graphene and Graphene Oxide: Synthesis, Properties, and Applications, Adv. Mater. 22 (2010) 3906–3924.

[5] M.. Katsnelson, A.. Geim, Electron scattering on microscopic corrugations in graphene, Philos. Trans. R. Soc. A Math. Phys. Eng. Sci. 366 (2008) 195–204.

[6] D. Li, R.B. Kaner, MATERIALS SCIENCE: Graphene-Based Materials, Science (80-. ). 320 (2008) 1170–1171.

[7] A.K. Geim, K.S. Novoselov, The rise of graphene, Nat. Mater. 6 (2007) 183–191.

[8] A.K. Geim, Graphene: Status and Prospects, Science (80-. ). 324 (2009) 1530–1534.

[9] H.C. Schniepp, J.-L. Li, M.J. McAllister, H. Sai, M. Herrera-Alonso, D.H. Adamson, R.K. Prud’homme, R. Car, D.A. Saville, I.A. Aksay, Functionalized Single Graphene Sheets Derived from Splitting Graphite Oxide, J. Phys. Chem. B. 110 (2006) 8535–8539.

[10] H.C. Schniepp, K.N. Kudin, J.-L. Li, R.K. Prud’homme, R. Car, D.A. Saville, I.A. Aksay, Bending Properties of Single Functionalized Graphene Sheets Probed by Atomic Force Microscopy, ACS Nano. 2 (2008) 2577–2584.

[11] M.F. El-Kady, V. Strong, S. Dubin, R.B. Kaner, Laser Scribing of High-Performance and Flexible Graphene-Based Electrochemical Capacitors, Science (80-. ). 335 (2012) 1326–1330.

[12] B. Cardenas-Benitez, C. Eschenbaum, D. Mager, J.G. Korvink, M.J. Madou, U. Lemmer, I. De Leon, S.O. Martinez-Chapa, Pyrolysis-induced shrinking of three-dimensional structures fabricated by two-photon polymerization: experiment and theoretical model, Microsystems Nanoeng. 5 (2019).

[13] B.Y. Park, L. Taherabadi, C. Wang, J. Zoval, M.J. Madou, Electrical Properties and Shrinkage of Carbonized Photoresist Films and the Implications for Carbon Microelectromechanical Systems Devices in Conductive Media, J. Electrochem. Soc. 152 (2005) J136.

[14] G. Canton, T. Do, L. Kulinsky, M. Madou, Improved conductivity of suspended carbon fibers through integration of C-MEMS and Electro-Mechanical Spinning technologies, Carbon N. Y. 71 (2014) 338–342.

[15] N. Liu, K. Kim, H.Y. Jeong, P.C. Hsu, Y. Cui, Z. Bao, Effect of Chemical Structure on Polymer-Templated Growth of Graphitic Nanoribbons, ACS Nano. 9 (2015) 9043–9049.

[16] A. Allaoui, S.V. Hoa, M.D. Pugh, The electronic transport properties and microstructure of carbon nanofiber/epoxy composites, Compos. Sci. Technol. 68 (2008) 410–416.

[17] M. Ghazinejad, S. Holmberg, O. Pilloni, L. Oropeza-Ramos, M. Madou, Graphitizing Non-graphitizable Carbons by Stress-induced Routes, Sci. Rep. 7 (2017) 16551.

[18] T. Maitra, S. Sharma, A. Srivastava, Y.K. Cho, M. Madou, A. Sharma, Improved graphitization and electrical conductivity of suspended carbon nanofibers derived from carbon nanotube/polyacrylonitrile composites by directed electrospinning, Carbon N. Y. 50 (2012) 1753–1761.

[19] D. Mattia, M.P. Rossi, B.M. Kim, G. Korneva, H.H. Bau, Y. Gogotsi, Effect of Graphitization on the Wettability and Electrical Conductivity of CVD-Carbon Nanotubes and Films, J. Phys. Chem. B. 110 (2006) 9850–9855.

[20] S. Holmberg, M. Ghazinejad, E. Cho, D. George, B. Pollack, A. Perebikovsky, R. Ragan, M. Madou, Stress-activated pyrolytic carbon nanofibers for electrochemical platforms, Electrochim. Acta. 290 (2018) 639–648.

[21] M. Yoonessi, J.R. Gaier, M. Sahimi, T.L. Daulton, R.B. Kaner, M.A. Meador, Fabrication of Graphene–Polyimide Nanocomposites with Superior Electrical Conductivity, ACS Appl. Mater. Interfaces. 9 (2017) 43230–43238.

[22] B. Xue, Y. Zou, Y. Yang, A photochemical approach for preparing graphene and fabrication of SU-8/graphene composite conductive micropatterns, Mater. Des. 132 (2017) 505–511.

[23] Pramanick B, Vazquez-Pinon M, Torres-Castro A, Martinez-Chapaa SO, Madou M. Effect of pyrolysis process parameters on electrical, physical, chemical and electro-chemical properties of SU-8-derived carbon structures fabricated using the C-MEMS process. Materials Today: Proceedings 5 (2018) 9669-82.

[24] Y.M. Hassan, C. Caviglia, S. Hemanth, D.M.A. Mackenzie, T.S. Alstrøm, D.H. Petersen, S.S. Keller, High temperature SU-8 pyrolysis for fabrication of carbon electrodes, J. Anal. Appl. Pyrolysis. 125 (2017) 91–99.

[25] S. Mamidi, M. Kakunuri, C.S. Sharma, Fabrication of SU-8 Derived Three-Dimensional Carbon Microelectrodes as High Capacity Anodes for Lithium-Ion Batteries, ECS Trans. 85 (2018) 21–27.

1. \* Corresponding author. Tel.: +52 1 81 11706549.

   *E-mail address:* alan.aguirre@tec.mx [↑](#footnote-ref-1)