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Glassy carbon as a novel mould material for replicative forming of precision glass optics

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Abstract: Replicative forming of precision glass optics has been fast emerging as a rapid, net shape process chain for mobile camera lenses, CD/DVD pickup lenses, microscope objectives, night vision lenses, Fresnel lenses and so on. The process involves moulding a glass gob at high temperatures exceeding the glass transition temperature using a predefined loading and thermal cycle. Typically, the mould material is required to have high strength, low thermal expansion, chemical inertness and anti-adhesion properties, especially at high temperatures. Traditional mould materials, such as, invar or tungsten carbide are difficult to machine which adversely affects the cost of the entire process. In the present work, glassy carbon mould has been developed using p-tolune sulfonic acid (PTSA) cured phenolic resin by a process of carbonization where the composition ratio of phenolic resin and PTSA solution was standardised accompanied by the pyrolysing conditions. Detailed characterisation of the phase evolution, surface compositions, morphology and mechanical parameters of the glassy carbon has been conducted by X-Ray diffraction (XRD) technique, Raman Spectral (RS) analysis, X-ray Photoelectron Spectroscopy (XPS), Field Emission Scanning Electron microscope (FESEM), Energy Dispersive Spectroscopy (EDX) and Nanomechanical testing which reveal an optimal combination of properties of the glassy carbon that makes it an attractive low cost mould material for replicative forming process chain of glass optics fabrication.

Keywords: Phenolic resin, glassy carbon, mould, XRD, FESEM, RS, XPS

1 Introduction: Mass manufactured engineering components with complex shapes are difficult to produce by abrasive machining due to excessive tooling cost, long hours of machining, low productivity and high cost **[1, 2]**. In recent years, due to stiff industrial competition, alternative manufacturing routes with shorter product to market time, low material wastage, less machining operations and high productivity are being critically analysed and evaluated **[3-4]**. Among the alternative manufacturing processes, replicative forming is rapidly emerging as a viable process chain for mass manufacturing of engineering components which yields net shape or nearly net shape products **[5-10]**. The importance and relevance of replicative forming process is highlighted for volume production of precision glass lenses, such as, aspherics, F theta lenses, freeform optics, Fresnel lenses, CD/DVD pickup lenses etc. with complex contours which are in great demand in various technology sectors, such as, consumer electronics, defence, space, automotive, energy generation and so on. The replicative forming process involves moulding a glass gob at high temperatures using a pre-defined loading and unloading schedule. Usually, the mould material is required to have anti adhesion property with respect to glass, low thermal expansion coefficient, high hardness and strength, good chemical stability especially at high temperature

[11-13]. In this context, high hardness and low thermal expansion metallic alloy (e.g., Ni-Based Invar alloy) or hard ceramics (e.g., tungsten carbide) are usually used as mould material due to their favourable thermo-mechanical properties. However, these materials are difficult to machine. They also require application of anti-sticking coating on their surfaces as glasses tend to adhere to these materials under high temperature operations. For both these reasons, the invar or tungsten carbide moulds are expensive which in turn adds to the cost of production of moulded optics [14-15].

Glassy carbon (GC) is an excellent candiate material which can be utilised as a substitute potential mould composition in favour of glass moulding technology due to a combination of favourable properties, such as, excellent thermal stability, very good mechanical strength, low erosion, ultra low thermal expansion, highly stable in chemical assault, and impermeability to fluids and gases [16-19]. In this work, a process for fabricating glassy carbon for replicative forming of glass optics has been reported. The glassy carbon mould material has been characterized for phase, morphology and mechanical properties and exhibit a great deal of promise for successful application as a glass forming mould material with a low cost of production due to a simple process of fabrication with low cost precursors.

1. Experimental

1.1. Instrument used: The XRD measurement was performed by X'pert pro MPD (PANalytical, Netherlands) diffractometer. The X'Celerator is functioning here at 40 kV by utilising Cu K_α radiation. The featured wavelength involved in Cu K_α radiation was 1.54 Å. A step size of 0.1° was used to carry out the XRD measurement. The Raman spectroscopy was obtained using Renishaw inVia Quontor Raman spectrometer (United Kingdom). The excitation wavelength was 514 nm subsequent to an Ar+ laser. The wavenumber range of 200 - 3200 cm^{-1} was examined to perform the experiment. The morphology of the fabricated mould was investigated by FESEM (Supra VP35, Carl Zeiss, Germany). The representative fundamental constituent of the synthesized fabricated glassy carbon block was acquired by the energy dispersive X-ray (EDX) investigation linked with the FESEM. The surface analysis was carried out by ultra high vacuum (10^{-6} < Pa) phi 5000 Versaprobe ll X-ray photoelectron spectroscopy (XPS) from 0 to 1000 eV. The spectral analysis were carried out at 50 W, utilising monochromatic Al source with 200 μm beam diameter with the angle of 45°.The nanomechanical characterization was successfully carried out by Hysitron TI Premier nanoindenter, Bruker, Singapore.

1.2. Materials used: Phenolic no bake resin (Coolset 1001) was used as base material for glassy carbon mould. Super-saturated solution of para toluene sulphonic acid (PTSA) was used as curing agent. Both the solutions were collected from Hindusthan Chemicals private limited, Kolkata, India.

1.3. Fabrication of glassy carbon mould: In order to replicate an aspheric shape of a glass composition, at first, a mould is required. The mould should be the inverse replica of the ultimate aspheric shape of the lens. Here, an aluminum master mould with the inverse replica of the final aspheric shape of the lens was prepared by a highly accurate diamond machining procedure. To fabricate GC mould, a replicated template of polydimethylsiloxane (PDMS) was fabricated by utilising the previously shaped aluminium master mould. Afterwards, precursor having a combination of 99.5 vol. % phenolic resin and 0.5 vol. % p-toluensulfonic acid (PTSA) monohydrate were poured on the PDMS template. To obtain an aspheric structured GC mould with very good surface quality, the removal of micro air bubbles produced during the resin-curing agent integration procedure, is the major subject. During a beginning experimental run, an exothermic reaction occurred due to the rapid curing process and increasing internal stress blocked the gas escape path. To defeat this issue, a three-step curing procedure was employed in the total fabrication process. Firstly, the curing procedure was carried out at 30 ºC for 120 hours under atmospheric pressure. The next curing procedure was completed at 140 °C in

a muffle furnace. The rate of increment of temperature was 0.1 °C/min with a holding time of 60 min for each 10 °C of temperature raise.

On completion of the basic two-step curing procedure of phenolic precursor, finally, the carbonization was conducted in furnace under continuous nitrogen purging at a highest temperature of 1200 °C to achieve the GC mould. In view of the fact that, a natural size and shape transform was happened during carbonization procedure of PTSA cured phenolic resin because of the heat decomposition. The profile modification percentage was calculated and an enlarged shape of the final aspherical lens was furnished. The precisely calculated reduction percentage was 25.2 % which is added at the time of PDMS replication, PTSA cured phenolic resin duplication and carbonization procedure and an additional 25.2 % enlarged cavity was applied at the time of manufacturing of master mould. To reduce the imperfections like crack, pore, warpage, distortion etc. in GC mould, the effects of temperature history in curing, given amount of curing agent and carbonization process was optimized **[20-22]**. The process flow [shown in Figure (1)] is summarized below,

- Positive shaped PDMS template was fabricated by using a negative shaped master mould.
- Negative shaped phenolic resin template was fabricated by using previously fabricated positive shaped PDMS mould.
- Template was sintered at N_2 atmosphere at 1200 °C at slow heating rate and held for several hours.

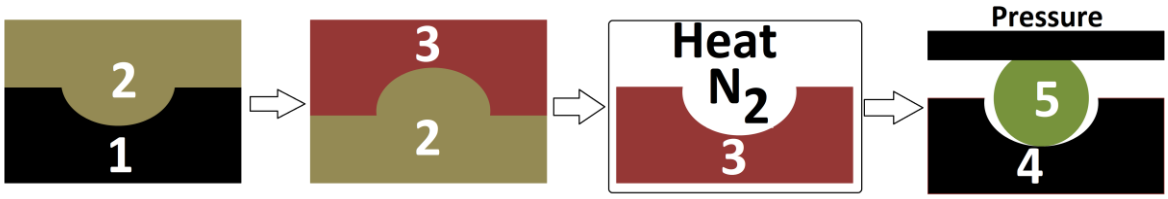

Figure (1). Schematic flowchart for aspherical glass lens fabrication using glassy carbon mould. Indications: Tungsten carbide master mould (1); PDMS replication (2); Phenolic mixture (3); Cured resin after carbonization process (4) and Glass precursor (5).

2. Results and discussion

An investigation was performed with respect to the density, apparent porosity, weight reduction, and shrinkage value found in the aspherical shaped glassy carbon mould on the basis of carbonization condition. Before sintering, the density of the PTSA cured Phenolic resin green aspheric shape was found to be 1.48 g/cm^3, whereas it reduced to 1.21 g/cm^3 at 1200 °C. The trend and values are good compared with the literature value **[23]**. The weight reduction is ascribed to the removal of unreacted resin along with volatile contents. X-ray diffraction technique (XRD) was used to confirm the presence of amorphous phase of carbon, whereas, Raman Spectroscopy confirmed the amorphous phase of carbon is nothing but the glassy carbon. FESEM structural investigation was carried out to explore the surface quality and the microstructure of the fabricated mould. EDX and XPS were engaged to confirm the phase purity of aspheric glassy carbon mould. Satisfactory and valuable mechanical strength have been found by measuring mechanical properties.

2.1. XRD analysis: To investigate the presence of amorphous phase of carbon, XRD analysis has been employed in the scan range from 2θ of 10° to 90° with a step size of 0.1°. At ambient conditions and larger angles, the XRD pattern shown in Figure (2) clearly shows the amorphous first diffraction peak (2θ = 23.63°), the second distinct peak (2θ = 43.67°) and the third peak (2θ = 78.72°) originated from inter- or interlayer distances of its fullerene related fragments. The origins of these three peaks are

comparable to the (002), (100), and (110) peaks of graphite, except that these are much broader than the corresponding crystalline peaks in graphite. These peak positions and their broadening response in width and shape confirm that our synthesised glassy carbon material was typically amorphous in nature **[24-25]**.

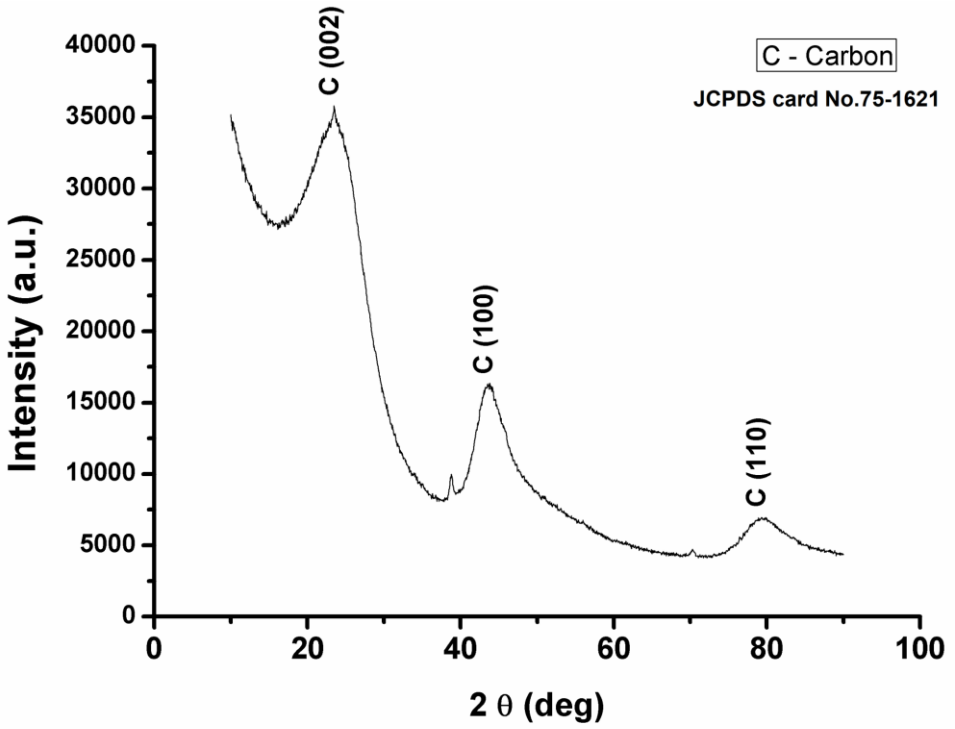

Figure (2). XRD pattern of fabricated glassy carbon mould.

2.2. Raman Spectroscopy

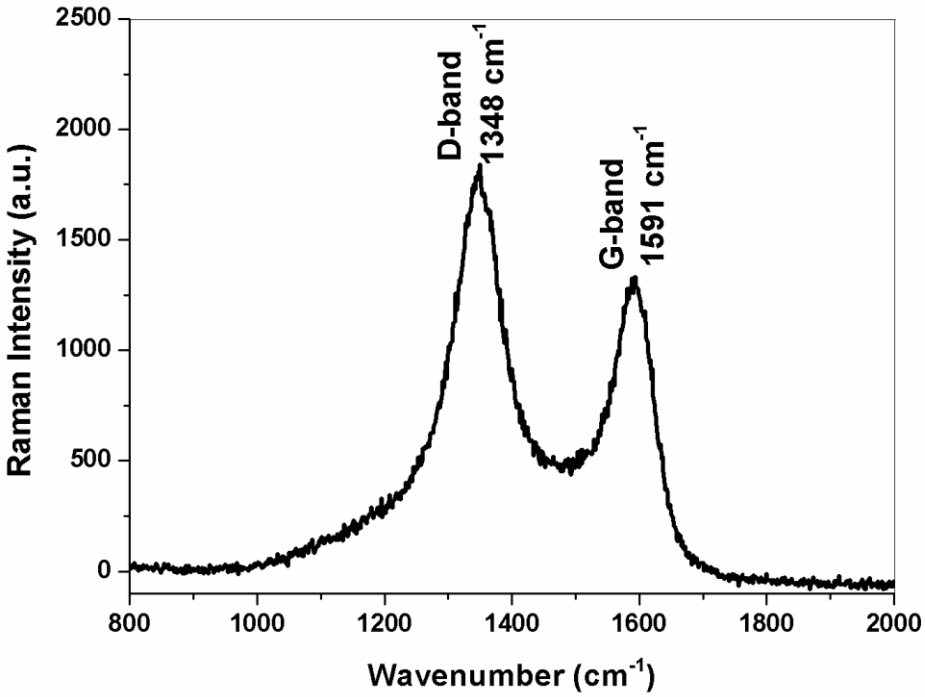

Figure (3). Raman spectra of fabricated glassy carbon mould.

The phase evolution of the GC solid block has been examined through Raman spectroscopy. Figure (3) shows Raman spectra of the aspheric GC mould material fabricated at CSIR-CGCRI under ambient circumstances. From the above spectral analysis it has been seen that, peaks around 1350 cm^{-1} and 1590 cm^{-1} are the two prominent featured peaks associated with the major carbon D and G bands, correspondingly. From the literature it can be found that that carbon based materials having disordered sp2 carbon bonds is mainly responsible for these peaks. The structural disorder can be measured by the Tuinstra–Koenig model. According to this model, the ratio of the intensities of these bands (I_D/I_G) was employed to determine the structural disorder. The I_D/I_G ratio was then calculated to be 1.4 which is the strong evidence of glassy carbon **[26-30]**.

2.3. Microstructural analysis by FESEM:

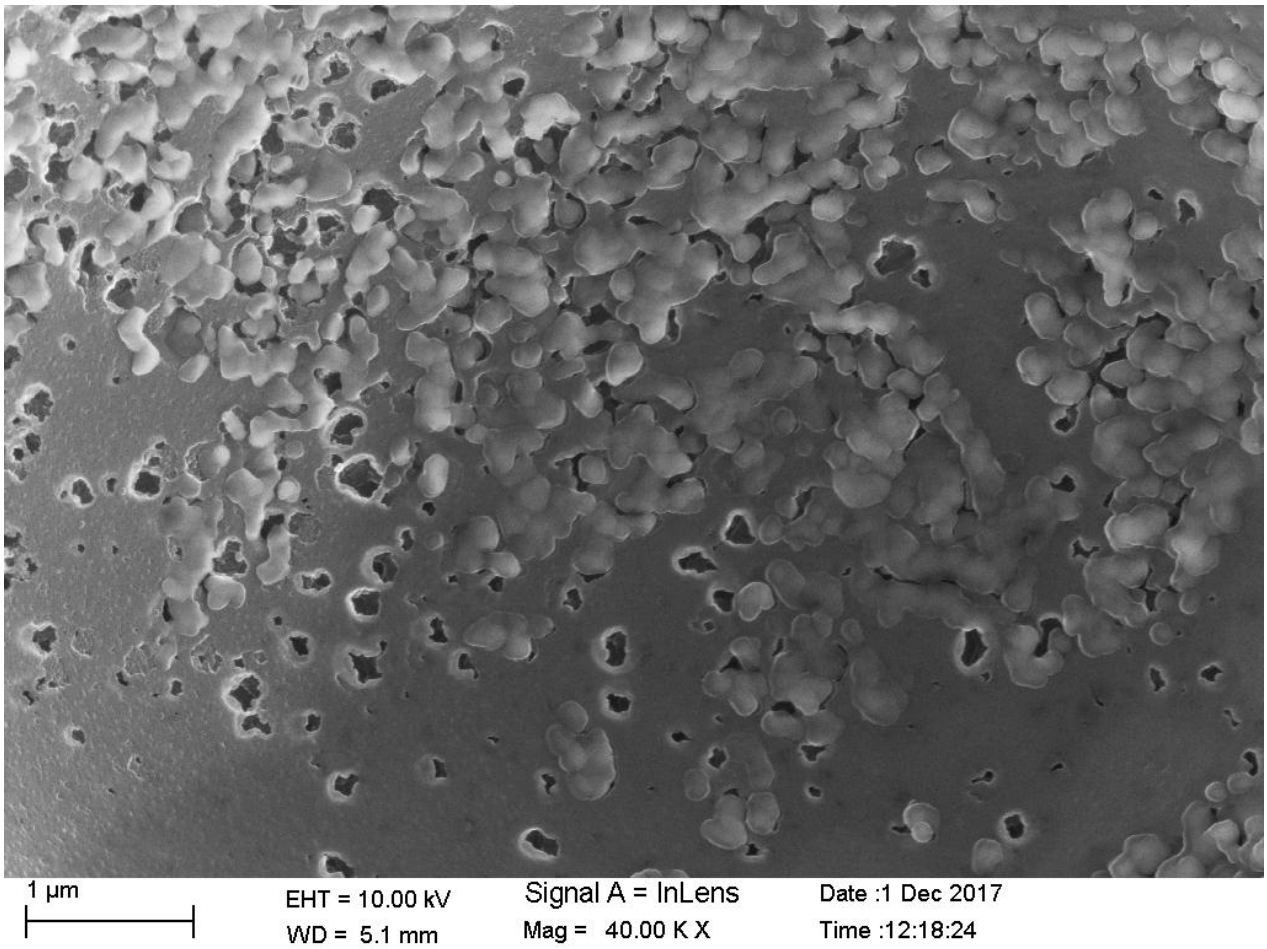

Figure (4). Microstructure and surface quality analysis by FESEM of glassy carbon mould material.

Figure (4) shows FESEM image of the microstructure and surface of our fabricated glassy carbon block. From the microstructural overview, on the uppermost plane some dimples and pores have been experienced. These are mainly as a result of outgassing of the volatile content presented in the matrix, at the time of caronization process at high temperature under nitrogen atmosphere. High magnification image reveals porous structure, very shallow and closed pores of sub-micron size. Form the critical microstructural investigation it may be concluded that the surface machining of approximately 1 micron will lead to sufficiently smooth surface for moulding application.

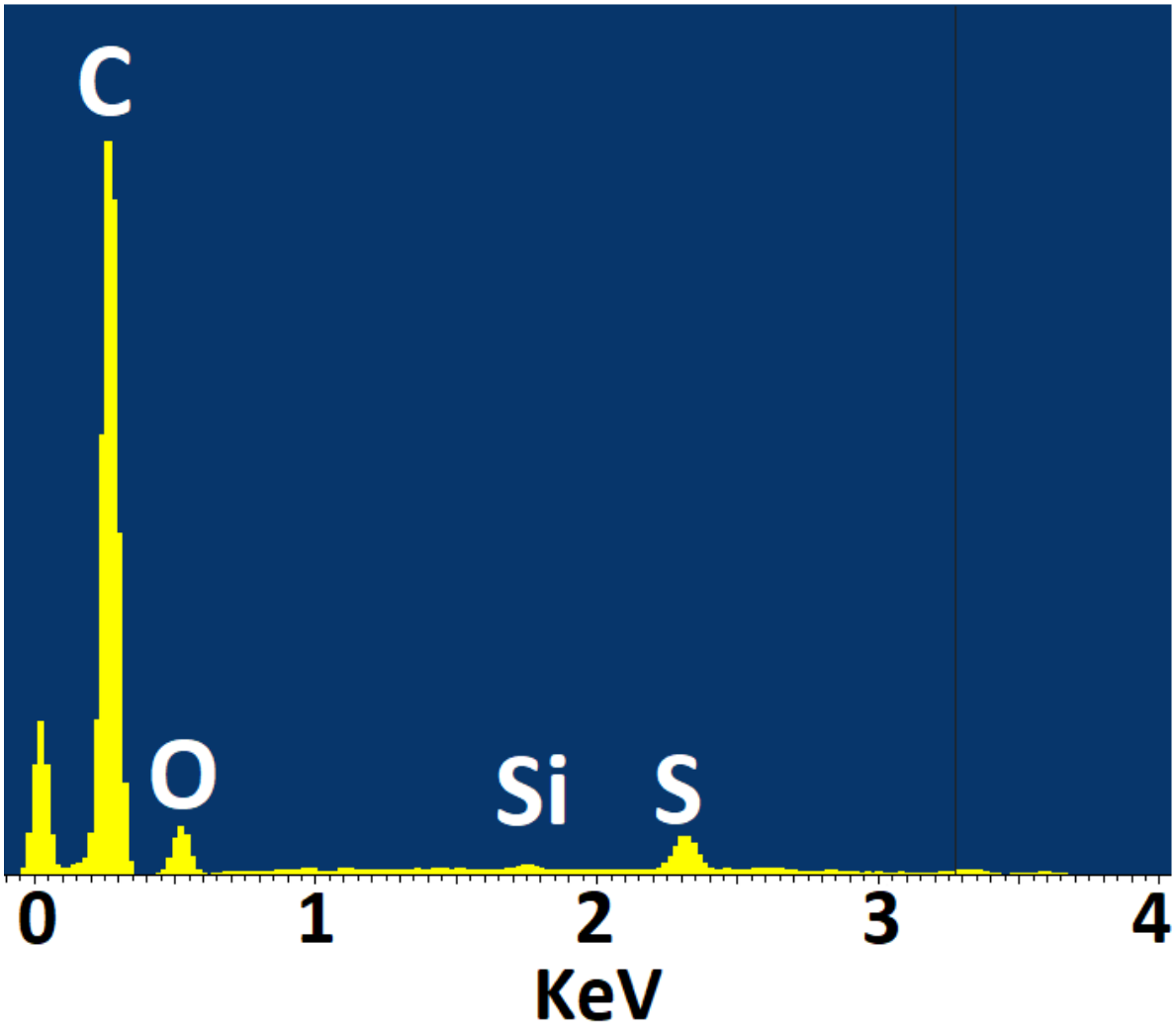

Figure (5). Elemental composition analysis by EDX spectra for glassy carbon mould material.

The elemental composition of the glassy carbon block is shown in figure (5). The atomic compositions of the fabricated cabon material primarily composed of carbon (~82 %) and oxygen (~ 9 %). The unwanted presence of sulpher (up to 8 %) and silicon (~1 % each) peak basically comes from the para-tolunesulfonic acid and PDMS master mould.

2.4. X-ray photoelectron spectroscopy (XPS) analysis: The compositional investigation of the solid glassy carbon fabricated at high temperature (1200 °C) was conducted by XPS. Figure (6) demonstrates the XPS spectrum obtained from the upper surface of the solid glassy carbon block. The presence of sulphar and silicon can be attributed to the curing agent (PTSA) which was introduced to accelerate the polymerization process into the resin precursor to a complete cured solid block and master mould of PDMS respectively.

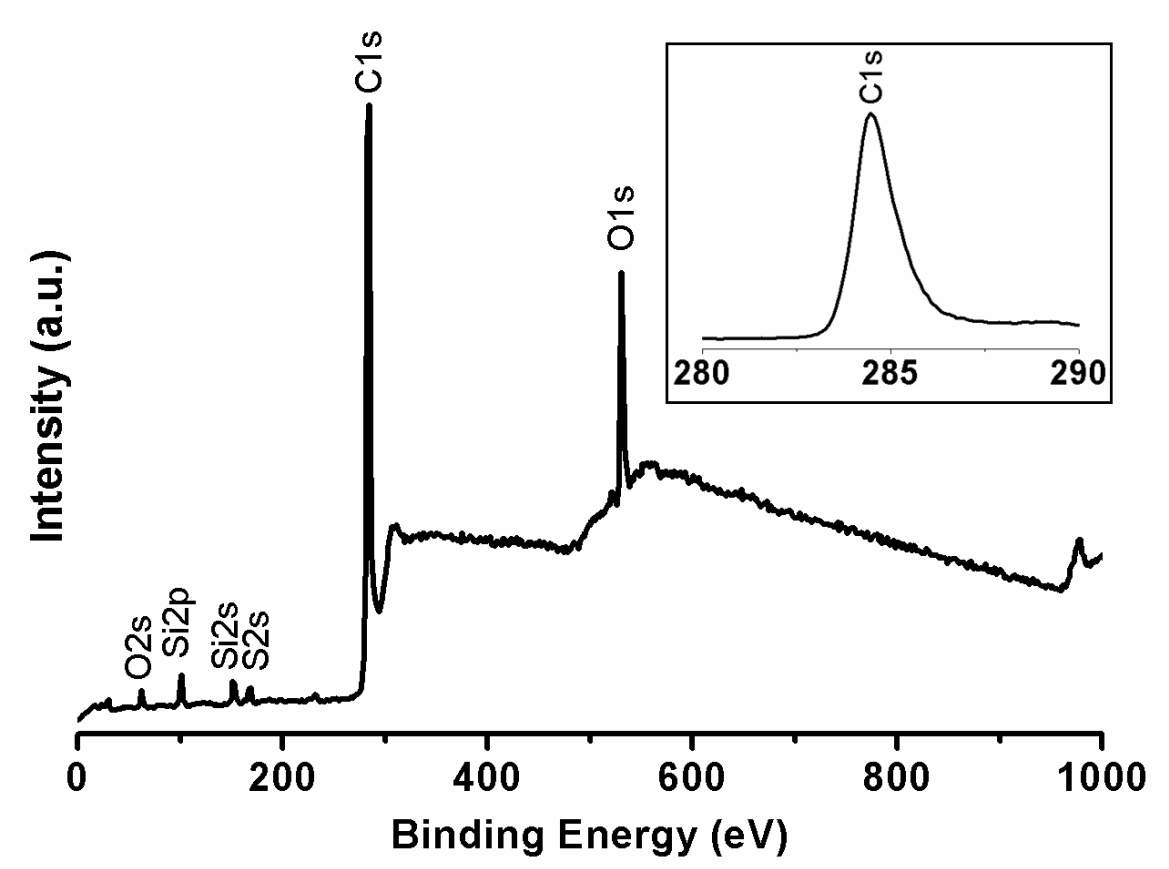

Figure (6). XPS analysis of glassy carbon mould material.

2.5. Nanomechanical characterization and comparison: Nano-indentation with sharp pyramidal indenters was used to determine the reduced Young's modulus (Er) and hardness (GPa) of the material. A highly polished surface was used to conduct the measurement. The properties of the material are presented in Table 1 and are found in good concurrence with the commercial glassy carbon material **[31-32]**. Indentation tests were conducted with Hysitron TI Premier nanoindenter, shown in Figure (7). Indentation tests were performed with a Berkovich indenter tip at 8000 - 10000 μN.

Table (1). Nanomechanical parameters of glassy carbon material synthesized in this study vis-a-vis commercial glassy carbon material

	Load 8000 uN	**Load 10000 uN**	**Commercial Glassy Carbon* (For comparision)**
Reduced Young's modulus (Er) (GPa)	23.5	22.78	35
Hardness (GPa)	4.19	4.11	2.25
Density (gms/cc)	1.21		1.42

* www.mwi-inc.com/wp-content/uploads/2014/10/propglassycarbon.pdf

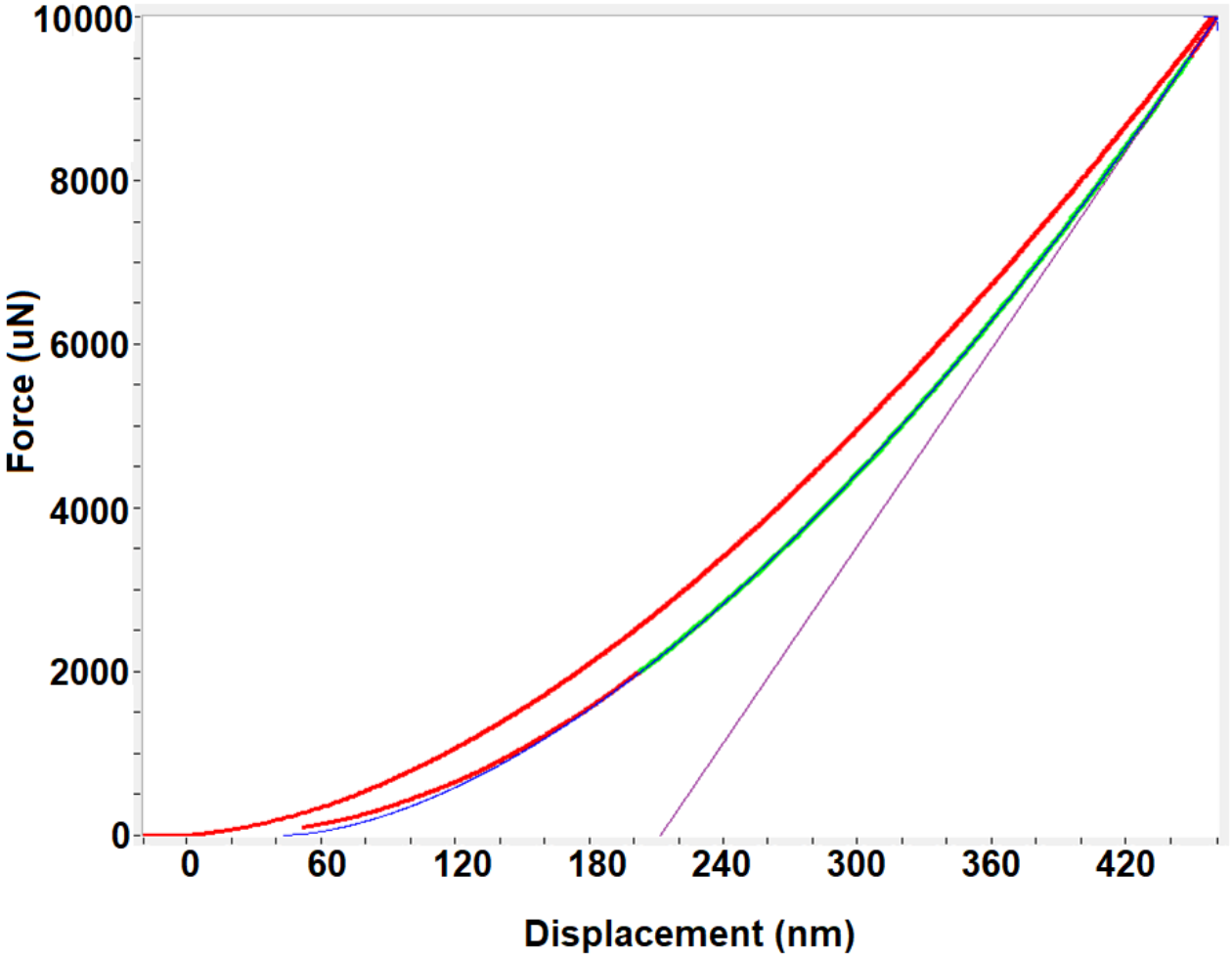

Figure (7). Hardness testing fabricated glassy carbon block by nanoindentation.

3. Conclusions: A method to fabricate ultra high precision glassy carbon mould has been investigated by replicating p-tolune sulfonic acid (PTSA) cured phenolic resin followed by high temperature carbonization process at nitrogen atmosphere. To enhance the excellency of the surface properties of the glassy carbon mould, composition ratio of the phenolic resin and PTSA solution was standardized together with the thermal treatment factors as well as carbonization procedures. XRD and RS were used to confirm the phase evolution of glassy carbon; FESEM was used to investigate the surface quality and the microstructure of the fabricated mould. EDX and XPS confirmed the phase purity of glassy carbon. Satisfactory elastic modulus and appreciable hardness values have been found by measuring mechanical properties. Thus this low cost, non-sticky, nontoxic, simply fabricated glassy carbon mould with required hardness values and good surface quality can be used to perform the highly précised moulding application for various optical components and an alternative for traditional WC or Inver mould as well as a promising candidate for mass manufacturing industries.

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