



# Microstructure and thermal behavior of isotropic petroleum pitch based matrix material for carbon carbon composites

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## Abstract

Present work deals with the utilization of petroleum waste in production of engineering material. The microstructure and thermal studies were performed for a new isotropic petroleum pitch based matrix material for carbon fiber reinforced carbon (C/C) composites. This paper is an approach towards exploring an idea to fabricate C/C composite exclusively from petroleum pitch avoiding multiple impregnation steps. Since there is a need of replacing toxic polymers for the same. The idea of using petroleum refinery waste i.e. pitch brightens up. Pitch used was primarily characterized by elemental analysis and Quinoline insoluble content. Work includes stabilization of pitch and a process to convert it into a carbonaceous bulk along with its microstructure and thermal analysis. Advanced characterization techniques like SEM and polarized light microscopy for microstructure analysis and TMA, TGA and DSC for understanding thermal behavior have been carried out. Porosity and density were estimated as well. Bonding between the phases was also observed under SEM for reference sample. This work will be useful for fabrication of C/C composites solely from petroleum pitch in single step carbonization and will give high density without any re-impregnating processes. Hence it is a cost effective approach to fabricate C/C composites.

**Keywords:** Pitch, Composites, Matrix, Microstructure, Thermal behavior.

## Introduction

Carbon composites is a class of materials that have been widely known for its high mechanical, thermal and chemical stability. In case of carbon composites the two phases are independently carbon. The continuous phase is matrix which upon carbonization converts into a bulk graphitic carbon or it can be any other carbonaceous material. Majorly all C/C composites are being fabricated with phenolic resins as a precursor material but during carbonization, heating and cooling rates affect the final physique, texture and microstructure of the sample. Hence working with phenolic resin needs high attention while carbonization. During heat treatment the material shows inconsiderable weight loss, porosity and shrinkage resulting in change in geometry<sup>1</sup>. Looking to these limitations it was thought to use a matrix which can give equivalent properties as phenolics with ease in process ability. Hence isotropic pitch comes into picture as it is a petroleum industry waste. Use of petroleum pitch provides better physical and chemical compatibility<sup>2</sup>. Petroleum pitch can be used as precursor materials for a variety of carbon products, including high thermal conducting C/C composites and other graphitic carbons<sup>3</sup>. Pitch is majorly used as an impregnating material but selective approaches like modifying it in air with or without stirring and controlled oxidation in presence of acids can avail in ease of processing<sup>4</sup>. Pitch is heterocyclic polyaromatic material contains carbon in a major portion. For fabricating C/C composites matrix should have high carbon content and

appreciable flow behavior before solidifying in order to wet reinforcement, this results in better adhesion between the two phases<sup>5</sup>. Further, a matrix should be able to conduct thermal energy hence it is deemed to have high density. Since all thermal properties are structure dependent therefore density is required to be high<sup>6</sup>. Matrix along with the reinforcement must be stable at high temperatures. Isotropic petroleum pitch fulfills almost all these requirements and becomes a strong contender for matrix material in C/C composites.

## Materials and methods

**Materials used and their characteristics:** Low softening point Petroleum pitch was procured from reliance petrochemicals Surat, all the chemicals were obtained from Sigma Aldrich and were 99% pure, PAN based Carbon fiber having intermediate modulus, 6Kspindle was purchased from Toray Japan and was chopped into 3-6mm fiber length manually.

**Petroleum pitch and its characteristics:** Neat Petroleum pitch of low softening point (SP) had characteristics as mentioned in Table-1.

**Table-1:** General Charactersits of Petroleum pitch

Softening Point in °C	Quinoline Insoluble %	Carbon %	Hydrogen %	Char Yield %
106	8	73	8.6	44

**Chemical modification of petroleum pitch:** To improve binding properties, chemical modification of the petroleum pitch was done by taking 50 gram fine powder of petroleum pitch in beaker and constant stirring was carried out along with addition of nitric acid. The reaction was continued for 5 hours at room temperature, Slurry at this point was washed, filtered and dried in an air circulating oven for complete removal of moisture. The powder was finely ground and sieve out from ASTM no 150 to obtain particle size of 106 $\mu$ m consistency. This process was repeated for different concentrations of acid and an array of five powders viz. 15%, 25%, 35%, 45% and 55% concentrated acid treated pitch was obtained. With this treatment the softening point of base pitch was increased up to 200 $^{\circ}$ C.

**Thermal treatment of petroleum pitch:** Desired amount of pitch was ground coarsely and calcined in limited supply of zero air at 450 $^{\circ}$ C temperature; Stainless steel container having pitch was put in a muffle furnace under controlled heat in zero air environment and soaked for 4 hours. Powder obtained after completion of heat treatment was ground in ball mill for 8 hours and sieve out from ASTM 150. This was called partial coke and it showed 92.7% chars yield and 98.4% Quinoline Insoluble content. Precautions were taken to prevent formation of 100% coke.

**Fabrication of matrix pallets:** Binder pitch and thermally treated pitch were both ground separately for minimum 8 hours to achieve consistent texture and required particle size (106  $\mu$ m) at room temperature. 40 grams of thermally modified pitch was taken in a container and 10% of binder pitch was weighed and mixed well together with thermally modified pitch i.e. partial coke, 10 such samples were obtained and one neat pitch without any binder was taken under study. Mixture was further put in a mill to mix well for 1 hour. This mixture was then put in a properly lubricated mild steel die and pressed under a hydraulic press at pressure of 240 Kg/cm<sup>2</sup> and temperature of 220 $^{\circ}$ C. Hold time under these conditions was kept for 1 hour. The system was allowed to cool at room temperature and a green pallet was removed carefully. Figure-1 shows green pallets and Figure-2 represents setup for preparing matrix pallets.



Figure-1: Green Matrix pallets

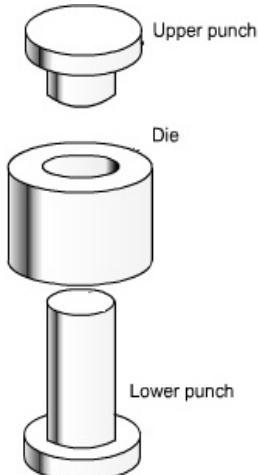


Figure-2: Die Setup for Fabricating Matrix Pallets

**Fabrication of a reference pallet with carbon fiber for bonding studies:** This paper focuses on the thermal behavior and microstructure imaging of petroleum pitch based matrix. But it was necessary to study bonding behavior between matrix and reinforcement so a single pallet having 20% heat treated chopped carbon fibers, 10% HNO<sub>3</sub> treated binder with 55% concentration of acid was taken as this ratio showed lower porosity and high density. Green composite was prepared as mentioned above.

**Carbonization:** Carbonization of green pallets was performed in a muffle furnace with CHINO PID temperature controller; all the heat treatments were performed in a controlled inert atmosphere of nitrogen. Gas flow was maintained via flow meter to 0.5 LMP. Table-2 shows heating and cooling rates of a sample along with a complete cyclic steps. The carbonization processes took around 80 hours to complete.

Table-2: Representing HTT program

Step	Temperature Range ( $^{\circ}$ C)	Heating/Cooling rates (X $^{\circ}$ C/min)	Soaking time (h)
1	30-250	80	nil
2	250-1000	20	nil
3	1000	soaking	4
4	1000-250	20	nil
5	250-30	80	nil

**Sample preparation for polarized light optical microscopy:** Small flat piece of samples were cut from pallets. Epoxy resin with hardener was poured on the samples in a mold and allowed to cure. Cast was removed from the mold and polished with micro grit SiC paper in an automatic polisher. All these samples were polished to obtain clean reflecting surface.

**Characterization:** Soxhlet extraction method was used to find out QI content of pitch until clear solution was obtained in the Soxhlet funnel. Softening point of pitch was obtained from hand operated Ring and Ball apparatus.

TGA was performed on PerkinElmer Pyris1 TGA, TMA was performed on Mettler Toledo TMA. Elemental analysis was performed on Perkin Elmer PE 2400 CHNS/O, density was found out using Mettler Toledo AG204 bench top density meter, polarised light optical microscope of Leica made and HITACHI S3000 N SEM were used to obtain micrographs.

## Results and discussion

**Scanning electron microscopy and polarized light optical microscopy:** SEM and optical microscopy were used to image microstructure and bonding of fibers with the matrix, Petroleum pitch based matrix is isotropic and shows higher mechanical properties over anisotropic matrix. Isotropic nature is concluded by the use of polarizer, while turning on the polarizer in optical microscope, an anisotropic content is seen only in a minuet fraction in Figure-3 while matrix majorly dominates by isotropic fraction which is darker in shade in Figures-3 and 4. Figure-5 shows some porosity as these are clearly observed in a micrograph; this is incorporated because of the presence of volatiles in binder. Figure 6 on the other hand shows microstructure and bonding of matrix-reinforcement. It shows that chopped fiber were completely wet and are adhered to the matrix.

Fibers are oriented in arbitrary directions; this provides maximum interaction of fibers with continuous phase which results in better adhesion. Fibers in the Figures-6 are completely covered with matrix and some are brighter as shown in Figure-4 because they have highly oriented graphitic structure which reflects the light with high intensity.

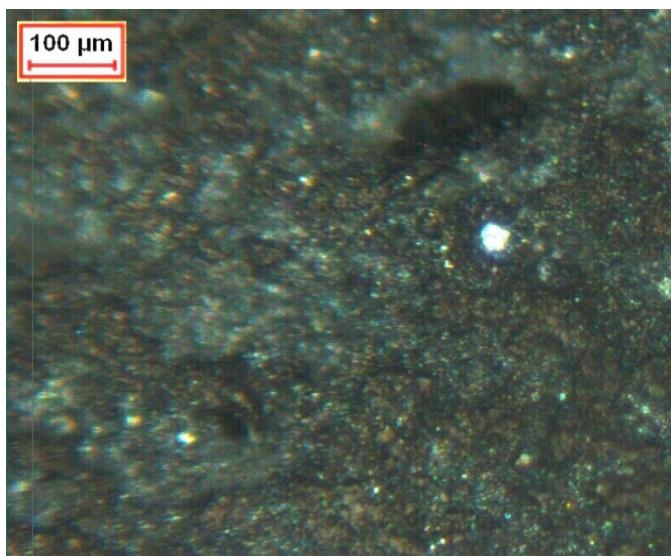


Figure 3: POL Optical micrograph of carbonized Matrix

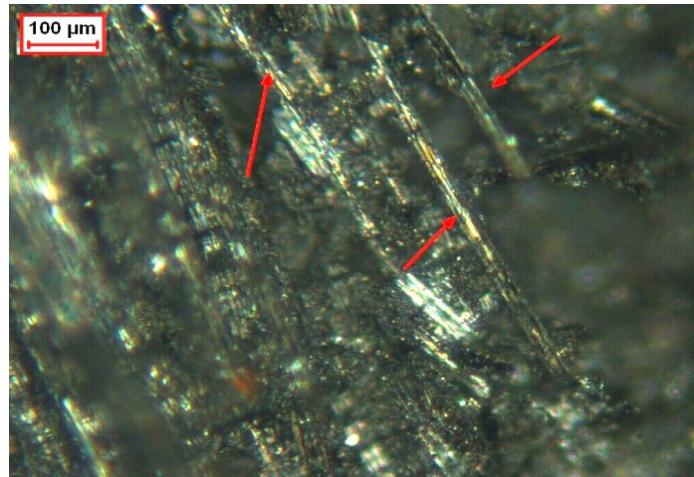


Figure 4: POL Optical micrograph of matrix and fiber

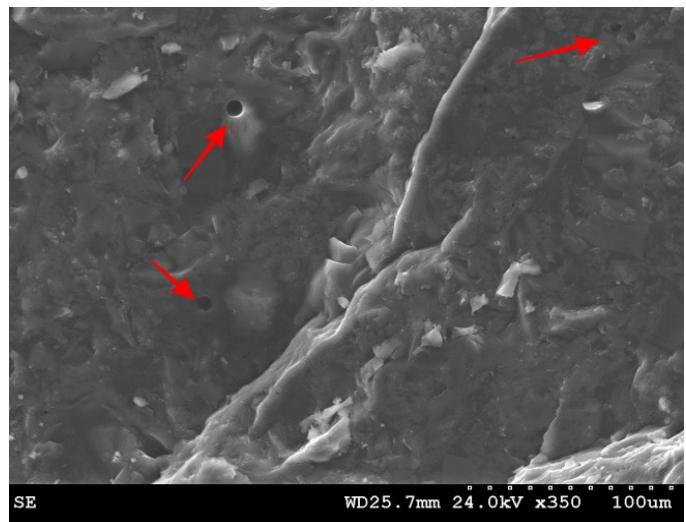


Figure 5: SEM Micrograph of Matrix Showing some Porosity

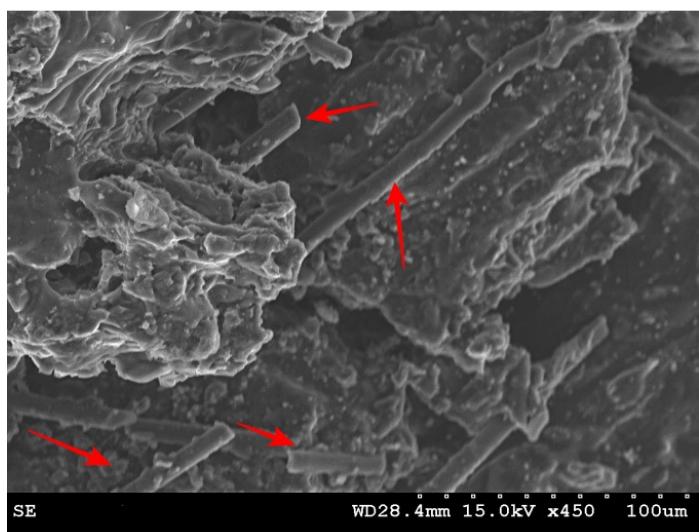


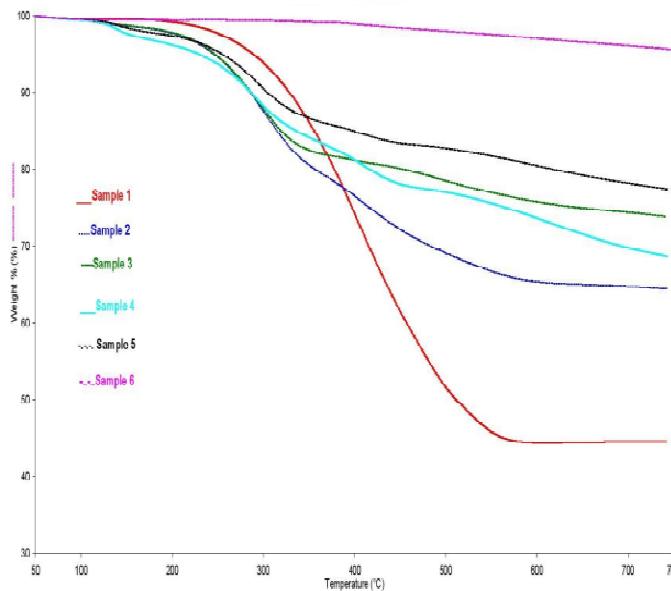
Figure 6: SEM of C/C Composite Representing Fiber Matrix Interface

**Elemental analysis of chemically modified pitches and effects of modification:** CHN is an important technique used to determine carbon and hydrogen content in a pitch, Table-3 shows that with an increase in concentration of acid in modification process, there is a major change in many properties and composition. Chemical treatment with strong acid like  $\text{HNO}_3$  oxidizes carbon and increases the carbon yield as confirmed from CHN along with char value and quinoline insoluble fraction. All these changes or rather increments were observed because of the reason that acid treatment results into formation of solid bulk carbon in a pitch which is generally stable and also insoluble in quinoline.

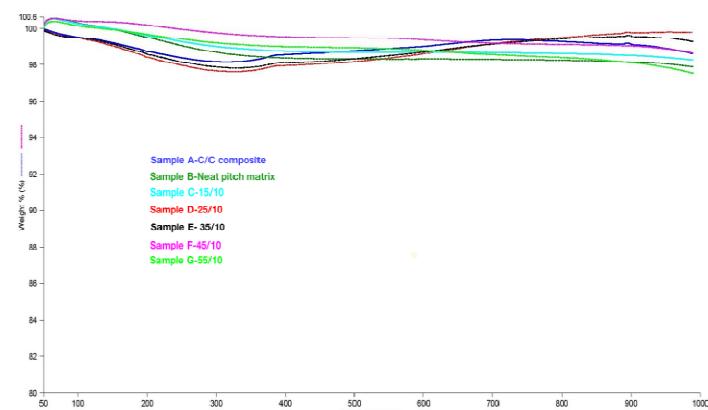
**Table-3:** CHN Analysis Along with Char Content from TGA

Pitch treated with given concentration of acid %	Quinoline Insoluble fraction %	Carbon %	Hydrogen%	Char yield from TGA %
15	8.5	77.50	3.64	66
25	8.9	78.63	3.64	72
35	9.4	88.71	4.47	76
45	10.7	90.58	4.31	78
55	11.5	91.67	3.27	80

**Thermal gravimetric analysis:** TGA study reveals physical stability of pitch at elevated temperature; Figure-7 shows an overlay of chemically modified pitches. Figure-8 represents temperature to weight relation of the final matrix at  $1000^{\circ}\text{C}$  after carbonization.



**Figure-7:** TGA of Chemically Modified Pitch and Partial Coke



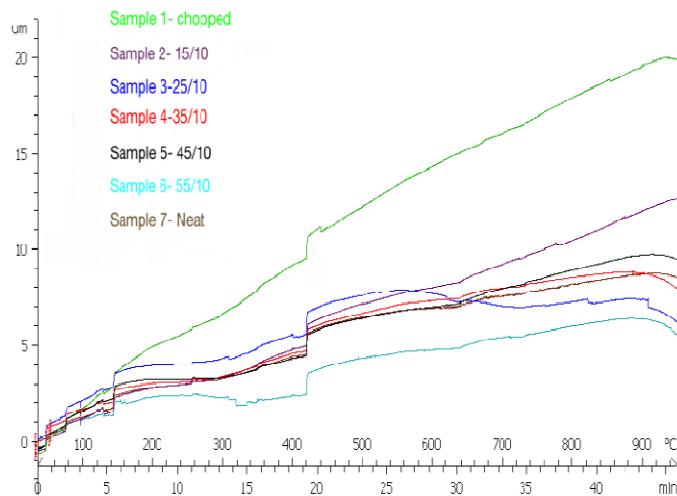
**Figure-8:** TGA of Carbonized Matrix

Chemical modification brought about major changes in thermal properties of pitch samples, sample 1 is a neat pitch. From Figure-7 it is seen that it has very low char yield which is 45%. Sample 2-5 are chemically modified i.e. with  $\text{HNO}_3$  for 4-5 hours, this method results in the increment of char yield as seen in an above plot. Sample 5 was treated with 55% concentrated acid and has 82% char yield and sample 2 was treated with 15% concentrated acid and has 65% char yield. It is seen that the charring increases as the concentration of the acid increases. For a C/C composites, polymer or any other carbonaceous precursor material must have high char yield. The top most curve i.e. sample 6 is of thermally modified pitch in zero air. This sample was analyzed till  $1000^{\circ}\text{C}$ . Thermal modification brings about the maximum char yield. For this sample char yield is 92% at  $1000^{\circ}\text{C}$ . Figure 8 is TGA of matrix after carbonization along with a C/C composite sample and neat pitch matrix, it reveals that all samples are highly stable at higher temperature and do not show any significant weight loss, hence matrix is stable and maintains its physique at elevated temperatures after carbonization process.

**Thermo mechanical analysis:** To study dimensional changes of carbonized pitch matrix at  $1000^{\circ}\text{C}$  TMA was carried out. Figure-9 shows that there is a minor change in dimension of samples, which is in a range of  $0\text{-}20\mu\text{m}$ . Sample 1 which is a reference composite having 20% chopped fibers shows maximum dimensional change, this could be attributed to the fact that the fibers have their own thermal expansion coefficient and it adds with the matrix giving maximum change in the dimension. Sample 7 is a matrix with 55%  $\text{HNO}_3$  treated binder and it shows minimum change. Sample 2 is the one with 15%  $\text{HNO}_3$  binder and it shows second higher value of change in dimensions. Hence from this plot it is clear that as the acid treatment concentration of binder increases the dimensional expansion decreases. From this study sample 7 showed the best results for fabrication of C/C composites. Table-4 shows Coefficient of Thermal Expansion (CTE) of matrix and composite samples obtained from TMA instrument. All the samples were analyzed for the change in position of sample on Y axis.

**Table-4:** Coefficient of Thermal expansion

Sample No	Sample Type	Coefficient of thermal expansion, ppm/K
1	Neat	25.44
2	Reference composite	32.16
3	15/10	26.4
4	25/10	25.44
5	35/10	20.19
6	45/10	19.42
7	55/10	18.09



**Figure-9:** TMA Analysis of Carbonized Matrix

**Density:** Bulk density was calculated by taking weight and dimensions of samples. Simultaneously these samples were analyzed with Mettler Toledo AG204 benchtop density meter. For this analysis two samples were taken under observation, one cubical and another irregular in shape. These samples were dried in a hot air circulating oven for 4 hours. Theoretical and practical densities show slight variation which was under acceptable range, this is because of the fact that water has high cohesion and surface tension hence it may not be absorbed completely in meso pores, this gives errors or imprecise values of volume displaced. Table-5 shows theoretical and practical densities of all the samples. Where 15, 25, 35.... are concentrations of acid used while 2 and 10s are the weight percentage of binder used to fabricate matrix pallets with partial coke.

Carbon carbon composites and its matrix are expected to be highly dense. Density and mechanical properties along with

microstructure are in co-relation, generally higher the density higher is the mechanical properties. Carbon materials are known for their high thermal conduction, in such materials the heat flux must be flowing continuous and unhindered, hence density of such materials are desired to be high in order to entertain phonon-phonon or phonon-defect interactions which are primarily responsible for thermal conduction. Since low density materials have air sac and air being bad conductor of heat decreases the net conduction of a material due to discontinuous bulk form. The stabilized matrix material showed acceptable density in the range of 1.5-1.8 g/cc.

**Table-5:** Bulk and Practical Densities of Carbonized Matrix

Sample	Bulk density g/cc	Practical density g/cc	Practical density of irregular sample piece g/cc
Neat	1.30	1.49	1.51
15/2	1.47	1.58	1.59
15/10	1.57	1.67	1.63
25/2	1.44	1.47	1.40
25/10	1.48	1.66	1.62
35/2	1.45	1.60	1.61
35/10	1.53	1.68	1.67
45/2	1.57	1.62	1.62
45/10	1.54	1.65	1.68
55/2	1.56	1.72	1.75
55/10	1.55	1.78	1.76

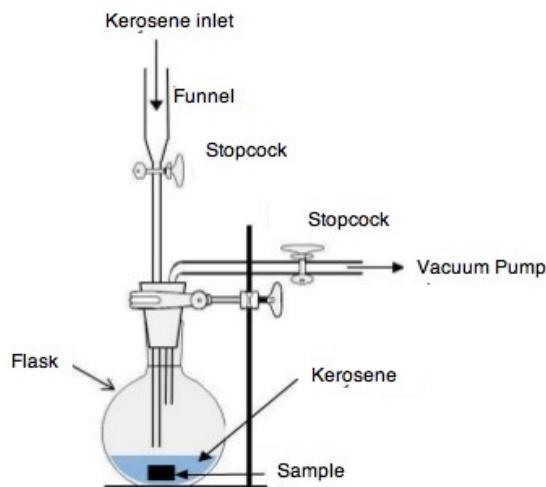
**Porosity:** For calculating porosity, kerosene porosity method under vacuum was implemented as mentioned in literature. Porosities were calculated by using formula shown below. Porosity is an inborn nature of any material, it can either be incorporated or it comes automatically while processing. Pitch has large amount of volatiles which brings about porosity while the green pallets undergo carbonization. Setup is shown in Figure-10.

$$P = \frac{W_i - W_f}{D \cdot V} \cdot 100$$

Where: P is porosity in percentage,  $W_i$  is initial weight of sample,  $W_f$  is final weight of sample, D is density of kerosene (0.81 g/cc), V is the volume of a sample.

**Table-6:** Porosities of Carbonized Matrix

Sr no	Sample	Porosity %
1	Neat	18
2	15/2	14.64
3	15/10	9.5
4	25/2	11.2
5	25/10	8.2
6	35/2	11.7
7	35/10	8.6
8	45/2	10.3
9	45/10	7.8
10	55/2	9.31
11	55/10	7.3



**Figure-10:** Kerosene Porosity Setup

## Conclusion

The work concludes that controlled modification of petroleum pitch with acid and calcination along with proper selection of ratio of binder to partial coke gives higher thermo physical stability and properties. Hence there is a high chance of replacing toxic resins as a matrix material for C/C composites. Pitches have high char yield and are easily available over phenolic or novolac resins. This work will allow cutting the cost in production of such materials. From this study C/C composite was fabricated with 55% acid treated binder and thermally modified pitch i.e. partial coke as this gives best favorable results in bonding. Microstructure of these carbonized pallets show uniform distribution of fibers and matrix. Bonding between the two phases was quite satisfactory as seen from SEM micrographs. Fibers were all observed to be bonded and completely wet in the matrix. This gives an ease in fabrication of high performance carbon carbon composites solely made from petroleum pitch without reimpregnation process.

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