Production of a self-adhering mesophase powder from anthracene oil for low pressure forming of graphite artefacts

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Abstract

The objective of the investigation was to produce a high mesophase content pitch from low cost anthracene oil without the use of catalysts. The pitch product was then used to produce graphitic artefacts using only a low pressure (5 MPa) forming step followed by carbonization and graphitization at a comparatively high heating rate.

The heat treatment times and temperatures were varied across a wide range but only material treated at 475 ºC produced a significant amount of mesophase. Furthermore only one pitch material resulted in a successful moulding which could be carbonized and graphitized. This pitch contained a significant portion (~ 8 wt%) of light material, which results in melting and flow behaviour during pressing, rather than sintering, if it is removed the material can no longer be successfully pressed.

Due to the high mesophase content of the pitch a high density (1720 $kg.m^{-3}$), highly graphitic artefact with minimal deformation during heat treatment is produced. The graphite product demonstrates grain separation but still results in a reasonable flexural strength of 4.5 MPa which may be improved further by re-impregnation depending on the requirement. This combined with its excellent purity and high yield make it a good candidate for nuclear applications.

Keywords: anthracene oil; nuclear graphite; low pressure moulding.

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1. Introduction

High density and high strength artefacts of carbon and graphite are widely used in advanced modern technologies. They are indispensable for applications in nuclear reactors, electrical contacting, drilling, semiconductor production and for use as inert crucibles for chemicals [1]. Traditionally these materials are manufactured through a multi-step process using two primary components namely, pulverized petroleum coke and coal tar pitch. The coke filler is blended with the pitch as a binder and is either moulded by cold isostatic pressing or formed by extrusion [2]. This is followed by a slow baking step to avoid cracking and deformation. The green artefacts are then machined if necessary followed by carbonization, graphitization, slow cooling and machining into the final shape. This process often results in low density material of insufficient strength, hence baking and impregnation steps are repeated. The overall process can take up to several weeks or even months depending on the required final properties [3]. In addition, significant material losses are incurred during the machining steps which are difficult to re-use, especially in the case of the graphitized material.

For this reason alternative production routes [4, 5] have been developed which in some cases use self-sintering carbonaceous grains for binderless moulding [6-10]. Mesocarbon microbeads (MCMBs) have been extensively explored as a precursor for such high density and high strength artefacts [11-19]. However, the production of MCMBs is also a multi-step process which involves the thermal treatment of a precursor to develop the microbeads followed by a tedious solvent extraction step that uses expensive and dangerous aromatic solvents such as pyridine. The overall yield of MCMBs from the starting material is very low, even specialized high yield techniques using coalescence inhibitors are only capable of yields less than 50 vol% [20]. Further losses are then incurred during the carbonization and graphitization steps. This material has recently become quite scarce in the market place and because of all these factors it currently has a very high cost [21]. In addition, to produce the green artefacts from MCMBs very high pressures (>100 MPa) are required for the cold pressing step [12, 17, 18]. This further adds to the capital and production costs of MCMB based carbon and graphite products.

Anthracene oil (AO) is a heavy distillate fraction from coal-tar distillation. It has the significant benefit for nuclear applications that it contains no inorganic

contaminants which could influence its moderation performance. The boiling range is typically between 250 and 370 ºC and it is mainly composed of polycyclic aromatic hydrocarbons (PAHs) making it an ideal precursor for mesophase production [22, 23]. A low cost source of AO is available locally and preliminary indications are that it is suitable for the production of a high mesophase content pitch. The aim of this research is to develop a high yield, low cost method for the rapid production of high strength graphite artefacts.

Traditionally catalysts such as $AlCl_3$ are used to convert anthracene oil to mesophase pitch, however this metal would have to be removed for certain applications. The closed porosity developed in most synthetic graphite materials makes this very difficult and costly. The first objective of this investigation is to determine whether a suitable heat treatment procedure can be developed to produce a mesophase pitch from AO without the use of catalysts. This will reduce cost and negate the need to remove the catalyst later if the product is to be used in certain specialized applications such as the fabrication of nuclear materials. The second objective is to ascertain whether this pitch can be used to produce graphitic artefacts using only a low pressure (5 MPa) forming step followed by carbonization and graphitization at a comparatively high heating rate of 10 $^{o}C.min^{-1}$.

The heat treatment time and temperature of the AO was gradually increased until mesophase formation was observed. These materials were then pressed to determine if shaping was possible. Finally the samples were carbonized and graphitized. The flexural strength, extent of graphitization, density and overall yield was determined for the materials which successfully withstood all processing steps. The proposed approach is quite unique in several respects, firstly is the use of the industrial by-product anthracene oil without the addition of a catalyst under comparatively high pressure to achieve conversion. This is not a pure starting material such as naphthalene or anthracene used in prior investigations [20, 22]. Conventionally graphite is produced via a multi-step process including the use of very high pressure moulding (in the case of MCMBs) as well as multiple mixing, baking and re-impregnation steps. In the current investigation only a single low pressure pressing step is used followed by rapid heating to high temperature. If successful the procedure can significantly cut down on processing time and cost. The final product has the

potential for a wide variety of applications including use as fuel spheres in next generation nuclear reactors.

2. Experimental

The AO used in this investigation is produced by Arcelor Mittal (South Africa) as a by-product of coke manufacturing from coal. The AO was characterized during a previous study [24] but its main properties are summarized here. The oil has a slightly lower than expected boiling range of between 200 and 250 ºC and a carbon to hydrogen ratio of around 1.6. The primary components were confirmed as phenanthrene, anthracene, fluoranthene, pyrene and acenaphthene using gas chromatography – mass spectrometry (GC-MS). The as-received material is a liquid at room temperature and has a zero carbon yield when heated under atmospheric pressure, as demonstrated by thermo-gravimetric analysis (TGA). The material also has a zero ash content and zero quinoline insoluble content (QI), making it an ideal starting material for producing extremely high purity graphitic products.

For the reasons mentioned in the introduction a high pressure (2 MPa), catalyst-free, thermal treatment procedure was chosen. The as-received AO (60 g) was placed in a reactor vessel which was sealed and pressurized using pure nitrogen. The heat treatment times and temperatures were varied across a wide range as reported in Table 1.

Table 1: Pitch production tests

Experiment	Temperature (^{o}C)	Heat treatment time (min)
1	350	117
2	400	125
3	420	90
4	420	130
5	440	120
6	440	135
7	475	50
8	475	70
9	475	80
10	475	90
11	475	110
12	475	120
13	475	180
14	490	120

Only the pitch materials treated at 475 ºC (Exp. 7 – 13) produced a significant amount of mesophase. Beyond this temperature an infusible solid was produced which could not be sintered. The pitch materials containing mesophase were milled for 6 hours in MRC Scientific Ball Mill with alumina spheres at a rotational speed of 350 RPM. The milled samples were then sieved to obtain a particle size fraction of less than 250 μm.

The samples were characterised using several techniques. Polarised light microscopy (Leica DM 2500) was performed on the samples to determine their mesophase content through image analysis. To determine the carbon yield and thermal behaviour of the produced pitch thermo-gravimetric analysis (TA Instruments SDT Q600 TGA) was used. The softening and glass transition points of the samples were measured using thermo-mechanical analysis (TA Instruments Q400 TMA) and dynamic-mechanical analysis (Perkin Elmer 8000 DMA) respectively.

The pitch materials from experiments 7 to 13 were all pressed in a Vertex Hydraulic Press at 5 MPa applied pressure. For the pressing 5 g of pitch powder was loaded into a rectangular mould (4 cm x 1 cm), the pressure was applied and the sample was then heated to the desired temperature. Several heating rates, soak temperatures and soak times were explored for each mesophase containing pitch, as detailed in Table 2.

Table 2: Pitch pressing tests

Experiment	Temperature (^{o}C)	Heating rate (^{o}C.min^{-1})	Pressing time (min)
1	250	7	180
2	300	7	60
3	300	7	180
4	350	7	60
5	350	7	180
6	400	7	60
7	400	7	180
8	450	7	30
9	450	7	60
10	450	7	90
11	450	7	120
12	450	7	180
13	480	7	30
14	450	2.5	30

Test bars which could be successfully pressed and maintained their shape after removal from the mould were then carbonized (1500 ºC) and graphitized in a TTI furnace (Model: 1000-2560-FP20) up to 2700 ºC at a heating rate of 10 ºC.min^{-1} under pure helium purge. To confirm the extent of graphitization the bars were characterized using a PANalytical X-pert Pro powder diffractometer (XRD) with variable divergence and receiving slits coupled to an X'celerator detector using iron-filtered cobalt Kα radiation. Electron microscopy (Zeiss Ultra Plus 55 High Resolution Field Emission Gun SEM) was used to investigate the microstructures of the different materials. Test bar flexural strength was determined using a custom built single cantilever testing rig. The setup was validated using test bars of Grade 6250 extruded graphite (Le Carbone). The sample mass and volume was measured after each step in order to calculate product yields and bulk densities. The skeletal densities of the samples were measured using a helium pycnometer (Micromeritics AccuPyc II 1340).

3. Results

Only the AO samples heat treated at a temperature of 475 ºC produced a pitch with a significant amount of mesophase. The result is to be expected from prior investigations; however the use of high pressure in the absence of a catalyst has led to the unique pressing behaviour as will be clear later. The fact that no mesophase is formed below 475 ºC even for very long soak times indicates that a certain minimum temperature is required for the polycondensation reaction to proceed to any noticeable extent. On the other hand, the transition occurs in a very narrow temperature range since higher temperatures simply resulted in an infusible coke material. The properties of these mesophase pitches are reported in Table 3.

Table 3: Mesophase pitch properties

Treatment time (min)	T_G (^oC)	T_S (^oC)	Carbon Yield (%)	Mesophase content (%)	C:H ratio
50	48	101	56	8	1.92
70	67	123	58	27	-
80	100	150	72	37	-
90	105	201	85	89	3.86
110	117	350	89	100	-
120	120	400	92	100	-
180*	114	194	89	45	2.46

*Loading increased to 350g

As expected, both the glass transition temperature (T_G) and the softening temperature (T_S) increase with a prolonged heat treatment time as can be seen from Figure 1.

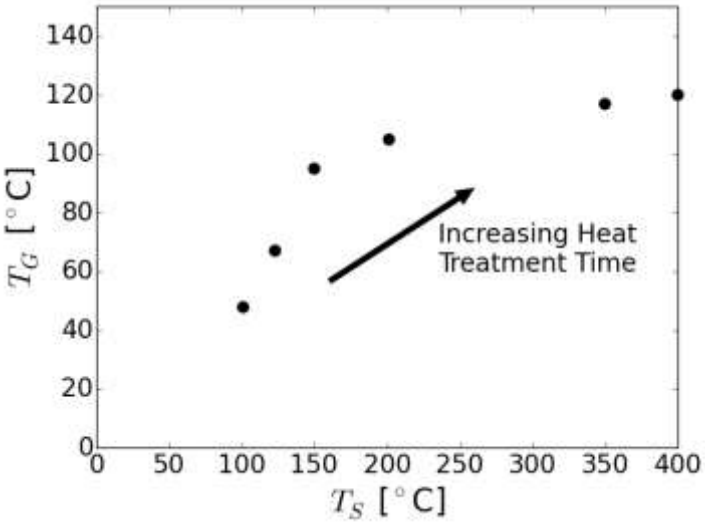

Fig. 1: Softening and glass transition temperature progressions with heat treatment

It is interesting to note that the softening point shows a rapid increase relative to the glass transition temperature beyond 90 min treatment time. Based on the optical analysis these materials are fully converted to mesophase and have begun the transition into an infusible semi-coke. The gradual development of the mesophase is demonstrated in Figure 2.

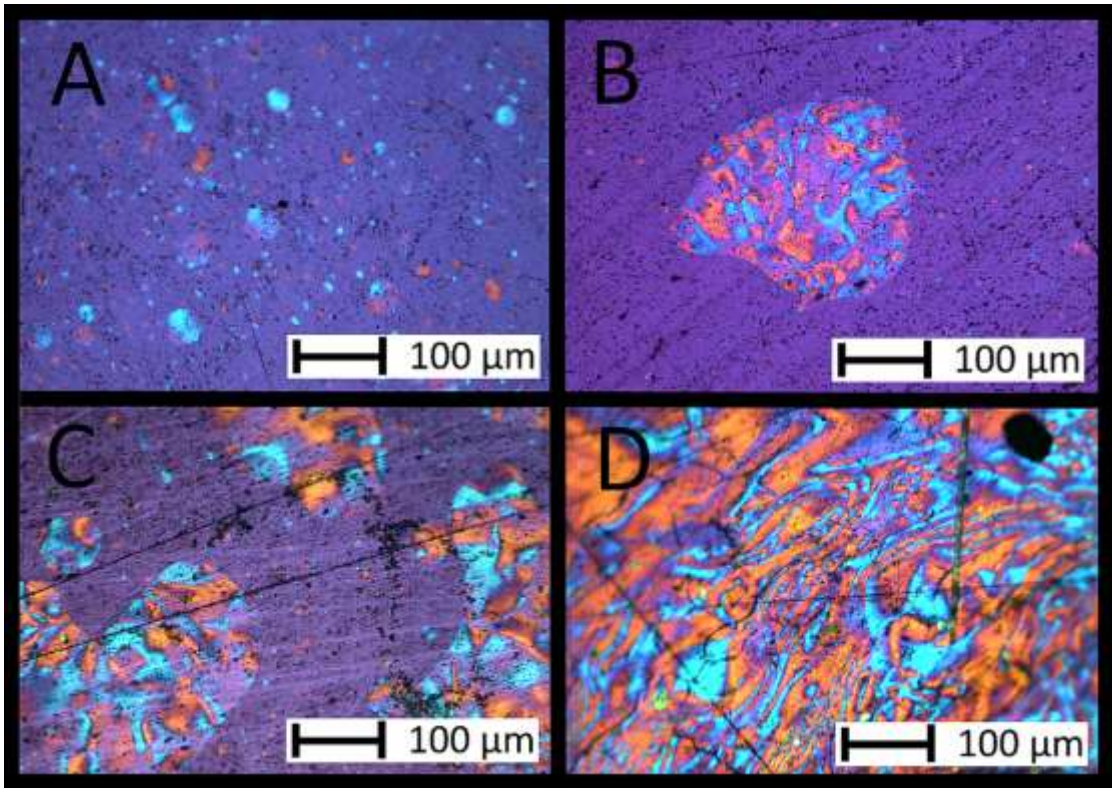

Fig. 2: Polarized light images of pitch heat treated for (A) 50 (B) 70 (C) 80 and (D) 90 min at 475 ºC

The 90 minute material exhibited a high carbon to hydrogen (C:H) ratio of 3.86, indicating a very high degree of aromaticity. In an effort to increase the amount of material available for pressing, the reactor loading was increased to 350 g from 60 g and the heat treatment time extended to 180 min. This produced a somewhat anomalous result as can be seen from Table 3. The sample has a lower than expected T_S, T_G, mesophase content and C:H ratio given its increased heat treatment time. It is expected that reaction kinetics may account for this observed difference. The larger amount of AO requires a longer time to fully convert to mesophase. However, the temperature is high enough so that the material which has been converted is mesophase of the same character as produced at low loading. This can be seen from the optical image of the material shown in Figure 3.

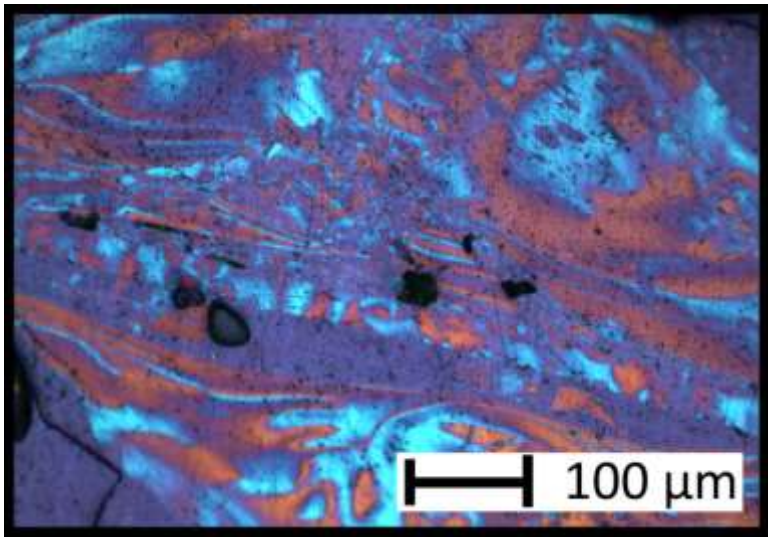

Fig. 3: Polarized light image of pitch (350g) heat treated for 180 min at 475 ºC

Thus instead of producing a material which is somewhere in between isotropic pitch and mesophase (such as that produced at low loading for 110 min), a mixture of the two is formed. This can be seen from a comparison of the TGA results for the different heat treated materials, as given in Figure 4.

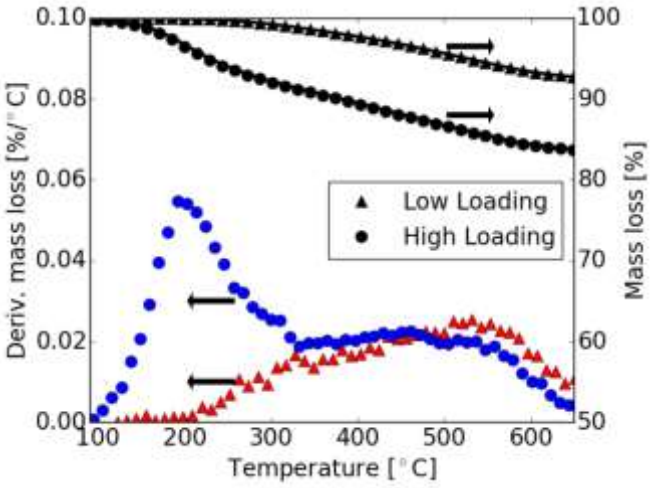

Fig. 4: Mass loss and derivative curves for high and low reactor loadings

The high loading material has a clear mass loss peak at around 220 ºC, indicative of a low molecular weight component. This is in the boiling range expected for the as-received AO. Thus this is a light fraction of material (~ 8 wt%) which has not yet undergone full polycondensation to produce mesophase. There is however also a prolonged mass loss region between 325 and 550 ºC. This corresponds with the region where the very high mesophase content, low loading material undergoes mass loss.

This indicates with good certainty that the compositions, or at least molecular weights, of this fraction of the two materials are very similar. Thus the high reactor loading causes a partial conversion of the AO to mesophase whilst leaving a fraction of unconverted or only partially converted light material. This light fraction is thought to be significant in enabling successful pressing as will be demonstrated soon.

Of all the pitch materials produced and all the pressing methods explored, only one combination succeeded in producing an intact green bar: mesophase pitch produced at 475 ºC heat treated for 180 min (high loading), combined with a slow heating rate of 2.5 ºC.min^{-1} under 5 MPa pressure to a final temperature of 450 ºC with a soak time of 30 min. This sample was then carbonized and graphitized, the associated changes in skeletal and bulk densities are given below in Table 4.

Table 4: Properties of reference, green, carbonized and graphitized bars

Sample	Bulk density (kg.m^{-3})	Skeletal density (kg.m^{-3})	Flexural Strength (MPa)
Green	1290	1480	2.0
Carbonized	1600	1980	6.3
Graphitized	1720	2190	4.5
Ref. 6250 Graphite	1670	-	11

The reference material measurements have an error of less than 10% compared to the expected value of 12 MPa [3], which serves to validate the strength measurement. To confirm the graphitic nature of the samples, the XRD diffractograms of the test bars are illustrated in Figure 5.

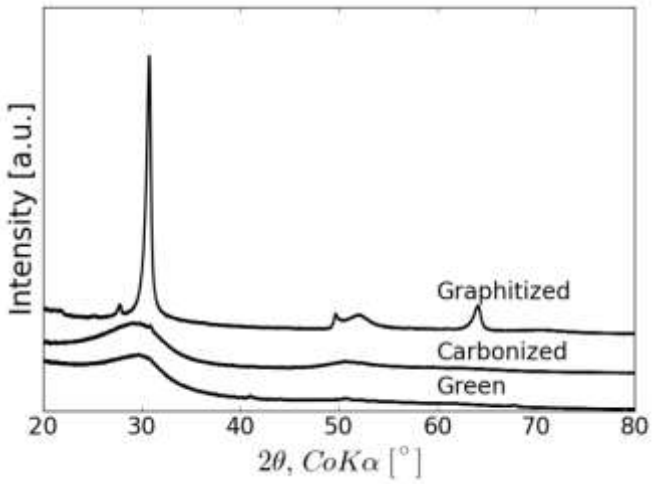

Fig. 5: XRD diffractograms for green, carbonized and graphitized bars

The graphitized bar clearly shows the characteristic d_{002} graphite reflection at 30.9º (CoKα) along with the (100) and (110) peaks at around 50º. This confirms the highly graphitic nature of the final product. This is supported by the skeletal density measurement of the graphitized material at 2.19 $g.cm^{-3}$ which is very close to the theoretically expected density for perfect graphite of 2.26 $g.cm^{-3}$. The microstructure of the material was closely examined using electron microscopy and the typical layered structure of graphite is clearly visible in Figure 6.

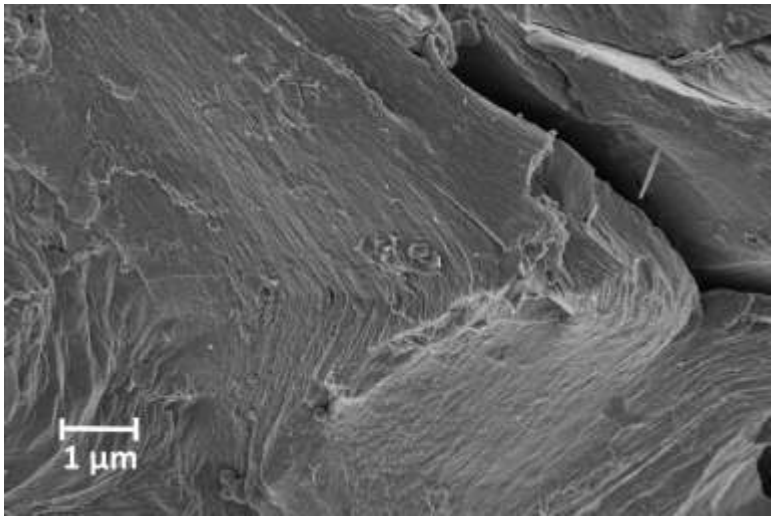

Fig. 6: SEM image of layered structure in graphitized material

When the sample is examined at slightly lower magnification grain separation and the resulting porosity can be observed as in Figure 7.

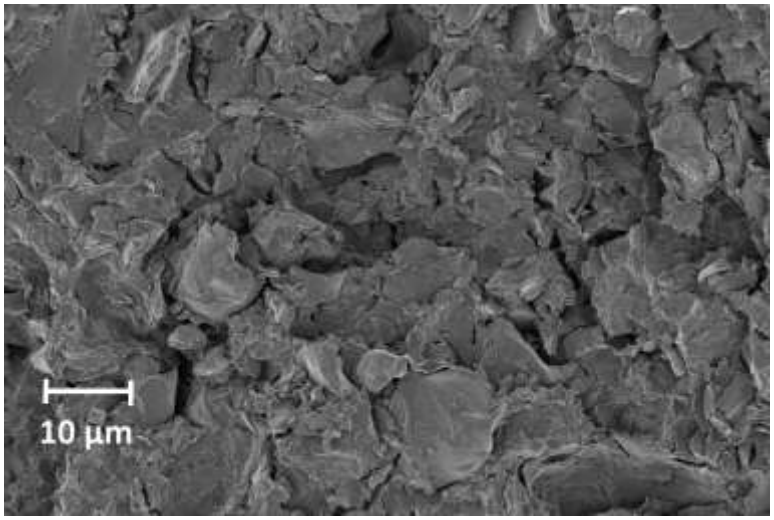

Fig. 7: SEM image of grain separation in graphitized material

It appears that initially the structures were very well bonded together, but upon high temperature heat treatment some bond sections delaminate due to shrinkage as can be seen in Figure 8.

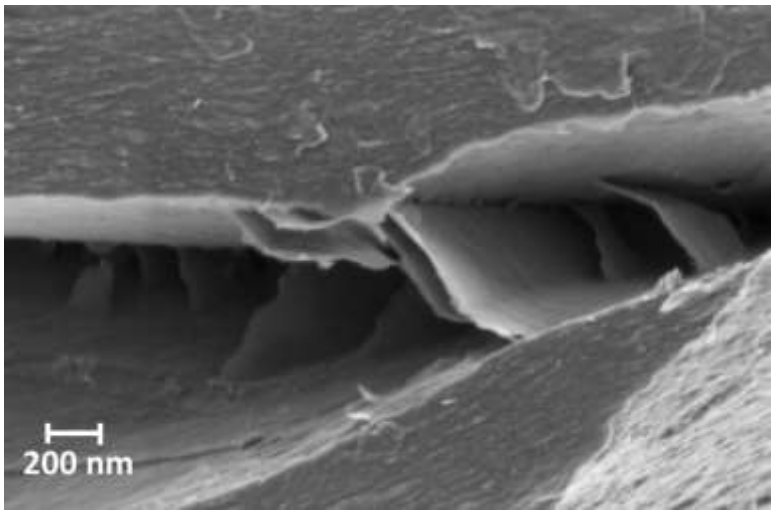

Fig. 8: SEM image of bond delamination

The green material supports this statement as a highly coalesced and intact microstructure is visible in Figure 9.

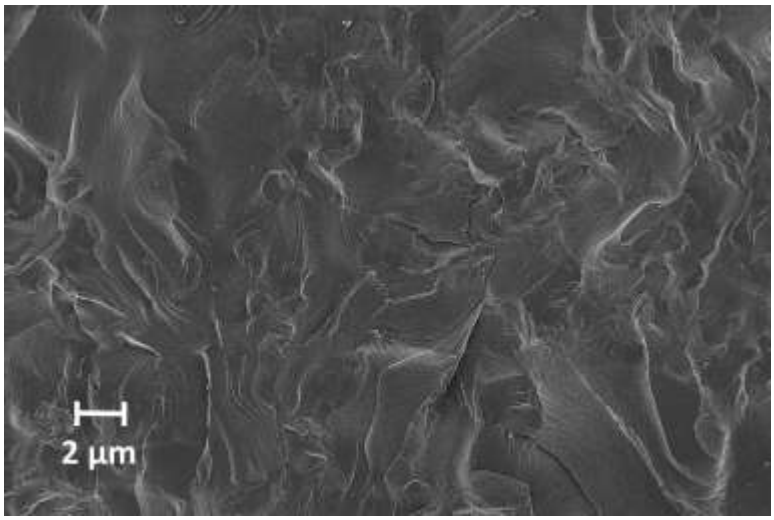

Fig. 9: SEM image of highly coalesced structure in green material

The structure is more indicative of a molten state during pressing as opposed to a sintered material where only limited coalescence is expected. This demonstrates the role of the light fraction in binding together the mesophase pitch grains. This produces a very fine grained material as can be seen from Figure 10.

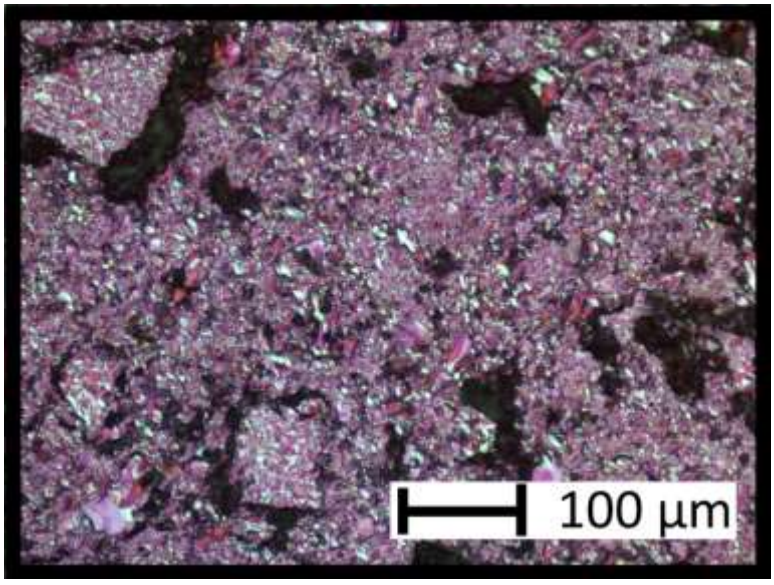

Fig. 10: Polarized light image of graphitized specimen

Due to these factors a highly isotropic material is produced. Strength measurements were repeated three times for each treatment and the average is reported in Table 4. The flexural strengths of all three samples are quite low compared to industrial grade graphite (~60% less). This is to be expected given the single step production procedure. Normally a coke would be graphitized and then bound together with a suitable pitch and baked, followed by several re-impregnation/baking steps as required and then carbonization. For the material under consideration here, only a single pressing step is used followed immediately by carbonization without any baking or re-impregnation. As can be seen in Figure 7 and 8 significant grain separation and bond delamination occurs during the heat treatment, this porosity is probably the main cause of the low strength. That being said, there may be room for improvement by modifying the pitch properties before pressing or by using a re-impregnation step. Overall the behaviour is as expected with the carbonized material showing the highest strength followed by the graphitized material and the green having the lowest strength. While the porosity may have led to a compromise in strength it has a beneficial effect during carbonization as will be seen next. The dimensional changes during heat treatment have been quantified in Table 5.

Table 5: Dimensional change and yield

Sample	% change in mass	% change in volume	Overall Yield (wt%)
Green (during pressing)	-16.2	-	83.8
Carbonized	-8.7	-26.7	76.5
Graphitized	-2.7	-9.4	74.4

Despite the reduction in volume during the high temperature heat treatment steps, the bars retained their shape very well with no noticeable warping or cracking, despite the high heating rate. The reason is the fairly porous structure which allows the evolved gases to escape without damage to the structure. This demonstrates that the material and method may be suitable for near net shape manufacturing of graphite artefacts. Unfortunately the strength is very disappointing when compared to typical values achieved for MCMB based materials (~200 MPa). Nonetheless, it is of the same order of magnitude as the extruded graphite reference material, as is the bulk density. This indicates that the method is suitable for producing nuclear grade fuel spheres, since their typical strength is around 10 MPa [25]. However, for structural components and other high load applications the strength will have to be improved. The overall yield however is excellent with almost 75% of the original AO being retained during the entire transformation to graphite. This is significantly higher than the overall yield for MCMB's which is expected to be in the range of 40%.

To substantiate the hypothesis that the light fraction is required for successful pressing, a sample of the high load material was "dried" at low temperature (~200 ^{o}C). This involved heating the material to temperature in a vessel open to atmospheric conditions and soaking for two hours. The TGA of the resulting material is shown in Figure 10, along with the original, un-"dried" material.

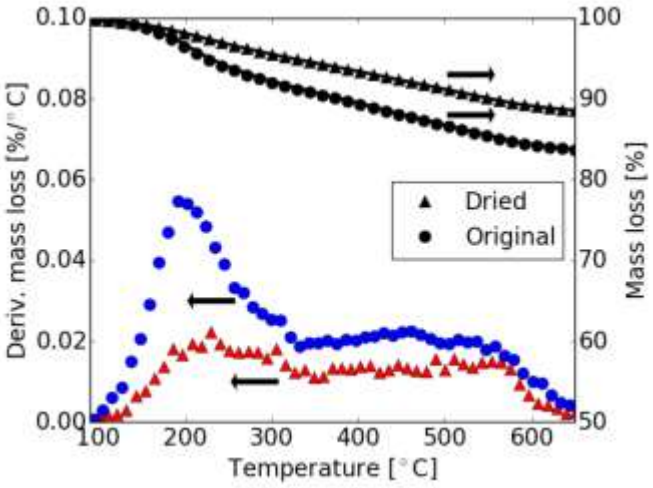

Fig. 11: Mass loss and derivative curves for original and dried material

It is clear that there is a large reduction in the amount of the light component or unconverted anthracene oil present. The resultant product could no longer be successfully pressed, similar to the high mesophase content material produced at low reactor loading. This confirms that the light fraction is required to successfully produce a self-adhering mesophase powder from anthracene oil.

4. Conclusions and recommendations

Anthracene oil is a heavy distillate fraction from coal-tar distillation. A low cost source of AO is available as an alternative to expensive MCMBs for producing pressed graphite artefacts. The objective of this investigation was to determine if a high mesophase content pitch could be produced from AO without the use of catalysts. The pitch product was then investigated for it suitability to be used to produce graphitic artefacts using only a low pressure (5 MPa) forming step followed by carbonization and graphitization at a high heating rate of 10 ^{o}C.min^{-1}.

The heat treatment times and temperatures were varied across a wide range but only the pitch materials treated at 475 ^{o}C produced a significant amount of mesophase. Several heating rates, soak temperatures and soak times were explored for each mesophase containing pitch during pressing. However, only one pitch resulted in a successful moulding which could be carbonized and graphitized. The successful pitch was produced during a high reactor loading and contained a significant portion (~ 8 wt%) of a light fraction, presumably unconverted or only slightly modified AO.

Based on visual inspection it can be confirmed that this light fraction results in melting and flow behaviour during pressing, rather than the sintering traditionally observed for MCMBs. If this fraction is removed the material can no longer be successfully pressed.

Due to the high mesophase content of the pitch it does produce a high density (1720 $kg.m^{-3}$), highly graphitic artefact. The sample does undergo significant shrinkage during carbonization and graphitization but retains its shape and structural integrity, indicating that it may be suitable for near net shape manufacturing of graphite artefacts. The material demonstrates grain separation during heat treatment with some delamination of the graphitic structure, which results in a low flexural strength of 4.5 MPa, compared to MCMB artefacts. This does however compare well to traditional extruded graphite for structural components and pressed fuel spheres, which in combination with its purity make it very attractive for nuclear applications.

Future work will focus on improving the strength of the AO based graphite artefacts by exploring the influence of different combinations of light and heavy fractions and re-impregnation.

Acknowledgements

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