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Research paper



Biomorphic Silicon Carbide from Malaysian Hardwood

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Abstract

Porous silicon carbide with mimicking the original microstructure of wood are prepared by pyrolysis and subsequently impregnated with silicon by silicon melt infiltration. The infiltration process was performed at 1500 °C for 3 hours holding times in inert atmosphere. Two types of wood were used as precursor which is Kapur and dark red Meranti.The morphology of resulting porous SiC have been investigated using scanning electron microscope (SEM/EDX) and X-ray diffraction (XRD) analysis. The density of the samples was characterized by Archimedes methods. The excess of silicon was removed by etching with the mixture of hydrofluoric and nitric acid. The flexural strength was tested by the three-point flexural method at room temperature.It has been shown that the final SiC for both precursors have similar density. The existence of SiC was proved by the XRD result, whereas EDX analysis of silicon content revealed that the formation of silicon carbide in dark red Meranti is higher than that of Kapur. The flexural strength and modulus of dark red Meranti samples were much higher than those of the kapur samples because of higher formation of silicon carbide in dark red Meranti.

Keywords: *biomorphic SiC, Kapur, dark red Meranti, infiltration, flexure strength*

1. Introduction

Wood waste is one of the most urgent because almost all of them were brought into the landfill of household waste. The major source of wood waste comes from commercial and residential activities. The construction and demolition of old building generate a significant amount of solid waste. It includes sawdust or wood scrap from sawmill and furniture factory, landscaping, lumber mills as well as branches or tree removed from the orchard. The large amount of wood waste will sent to the landfill and end up with open burning. According to Zuni ,the estimated of solid waste in Malaysia in 2020 is 9 092 611 tons per year. As at present, landfill is the only method used for disposal solid waste in Malaysia and most of landfill sites are open dumping area [2][3]. These will contribute to the air pollution and other environmental problem. Considering wood based industry as one of the Malaysian's industry sources, this sector produces a significant environmental impact because these residues are totally wasted. This problem initiates the development of wood waste into the useful materials. Conversion of wood into biomorphic silicon carbide is one of the interesting research and potential solution because the availability and low cost of wood source thus reduced the processing cost.

Porous silicon carbide is one of the promising materials for high temperature applications due to its excellent strength, hardness and oxidation resistance. The use of natural materials such as wood, coconut, papers, bamboo as a biotemplate material have received more attention in the last decade[4][5]. The abundant, renewable, less expensive and environmentally friendly are the factors where wood was chosen as a precursor. In addition, the resultant silicon carbide inherits microstructure of original wood. This unique property can be used in varied applications including catalyst, liquid and gas separation, filters and catalyst support and automotive industry. The increasing demand in silicon carbide based natural materials or ecoceramic has attracted much interest many researchers in the field of biomorphic silicon carbide.

Wood is a solid material derived from woody plant which can be classified into hardwood and softwood. Hardwood composed of cellulose, hemicelllulose and lignin [6]. The existent of these three components forms an insoluble network, which is difficult to be separated. The only simple way to convert lignocellulosic materials is by pyrolysis. During pyrolysis, these three components decomposed into amorphous carbon which maintained their original wood structure. Pyrolysis temperature that are commonly applies is in the range of 500-900 °C[7][8].

A number of research have been done on converting woods into silicon carbide with different kinds of typical Mediterranean species such as pine ,Birch[10],beech [11], eucaplitus[12] and oak [13].Different approaches were developed for conversion of woods into SiC ceramic. The basic process for the formation of porous SiC is by transforming wood into carbon template and subsequently reacting this template with silicon. This has been carried out by liquid silicon infiltration [15] or by soaking cabon template into ethanol solution of tetraethoxysilane [$Si(OC_2H_5)_4$ [13] or SiO gas infiltration [16]. However, silicon melts infiltration methods has the best methods since the resulted sic have good mechanical properties [17].

The objective of this study is to evaluate the mechanical properties of silicon carbide from Malaysian species which is dark red Meranti (*Shorea spp*) and Kapur (*Dryobalanop spp*). This species were classified as light hardwood and medium hardwood respectively, and the classification of Malaysian Timber Industry is based on their wood density. Medium hardwood is extensively used for the production of furniture, cabinet and kitchen unit[18]. Kapur and dark red Meranti was converted into SiC by infiltration of molten silicon into carbon perform, which was fabricated from

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pyrolysis process.The infiltration was performed at 3 hours holding time in order prolong the formation of silicon carbide.

2. Methodology

2.1. Materials and Methods

Dark red Meranti and Kapur were selected as a precursor to fabricate SiC ceramic. The wood sample was first prepared by cutting into rectangular shape of 100 mm x 25 mm x 20 mm. Then, the sample was oven dried for 24 hours at 110 °C to remove the moisture. The woods sample was then pyrolyzed in a tube furnace with an argon flow.

Two stages of heating were done to avoid cracking of samples. The first stage involved a heating to 500°C at 1°C/min for 30 minutes. The second stage involved a heating to 850 °C with 2 °C/min and held for 1 hour. The pyrolyzed wood was then packed in excess silicon powders and heated up to 1500 °C for 1 to 5 hours holding times. Finally, Chemical etching with a solution of hydrofluoric (HF) and Nitric Acid (HNO) was used to remove excess silicon. Fig. 1 summarizes the processing scheme of manufacturing silicon carbide from wood.

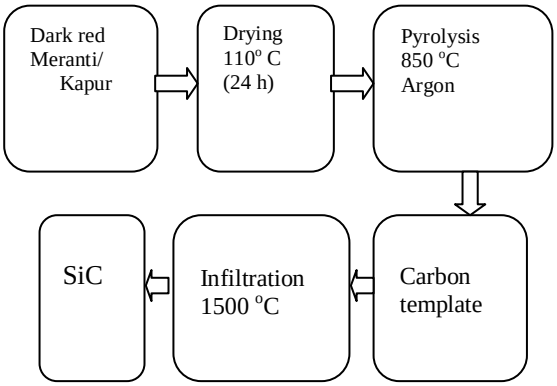

Fig. 1: Processing methods of manufacturing silicon carbide from wood

2.2 Characterization

Thermogravimetric analysis was performed by a thermal analyzer (Model Netzsch TG 209 F3) under flowing nitrogen gas at flow-rate of 100ml min^{-1} with heating rate of 10 °C min^{-1} from room temperature to 1000 °C. Alumina powders was used as a reference sample to determine the mass loss during pyrolysis. Density was measured by Archimedes method (ASTM C373-88) whereas Scanning Electron Microscope (SEM-Hitachi S-2500) operated at 20kV and 20mA was used for microstructure analysis. The phase composition was determined by X-ray Diffraction (XRD) on a RigakuUltima III) X-ray diffractometer using Cu Kα radiation produced at 35kV and 20mA and Energy-dispersive X-ray spectroscopy (EDX) with a detector attached to the same SEM .Three point flexural strength were performed using ASTM -C1161 configuration B with inner 20 mm and 40 mm outer span with a 1 mm/min crosshead speed.

3 Results and Discussion

3.1. Silicon Carbide Formation

Wood structure were pyrolyzed in argon atmosphere to obtain solid carbon perform. During pyrolysis, there are some shrinkage and weight loss occur on the dimension of wood which is about 60-70% of its volume and its depends on the variation of pore size, orientation as well as different percentage of wood compositions [5][19]. Decomposition of organic polymers in wood structures known as celluloce, hemicelluloses and lignin lead to the shrinkage and weight loss that left behind the only carbon structure.

The infiltration of carbon preform with liquid silicon involves packing of carbon preform in excess silicon powders and heating up to above melting temperatures of silicon. The conversion of carbon into silicon carbide can be expressed as

$$C(solid) + Si\ (liquid) \rightarrow SiC(solid) \quad (1)$$

During infiltration, some carbon preform was converted into SiC by filling up the pore with liquid silicon and few pores were not completely filled. The formation of SiC were from capillary effect and reactive wetting. The driving forces from both factor sled to the infiltration of silicon into small and large pores followed by reaction of carbon with liquid Si. The formations of SiC layer occur very fast which was less than 2 seconds. The primary layer of SiC occurred at the surface of the pore structure. The existence of excess Si in the sample can be removed by leaching process with hydrofluoric acid and nitric acid according to:

$$3Si + 12HF + 4HNO_3 \rightarrow 3SiF_4 + 4NO + 8H_2O \quad (2)$$

$$SiO_2\ (s) + 6HF(l) \rightarrow H_2\ SiF_6(l) + 2H_2O(l) \quad (3)$$

The final resulted SiC composed of crystalline SiC and unreacted carbon.

As can be seen from the Table 1 below, density of raw kapur is higher than of raw dark red meranti as kapur is classified in group medium hardwood instead of light hardwood for dark red meranti. Carbonization of wood by pyrolysis process will remove the moisture and also organic polymer content in original wood structure thus reduced the density of pyrolyzed carbon. The final resulted SiC from both wood precursors did not show a significant difference between them. Despite kapur having high density,the final resulted SiC almost similar to that dark red meranti which is 0.81 and 0.858 respectively. As the density of the resulted SiC is linear proportional to the density of pyrolyzed carbon[20][21].The formation of SiC from carbon perform not only dependent on density of carbon preform but also the porosity and the microstructure, such as anisotropic orientation and diameter of the tracheidal pore structures [22] .

Table 1: Density of original, pyrolyzed and resulted siC for kapur and dark red meranti precursor

Density g/cm^3	Kapur	Dark red meranti
Raw	0.819	0.778
Pyrolyzed	0.671	0.583
SiC	0.891	0.858

3.2. TGA

Fig.2 and Fig.3 shows the TG and DTG analysis curves of kapur, dark red meranti in Argon atmosphere flow rate of 110ml/min and 10°C/min heating rate.Generally, the mechanism in the conversion of wood into carbon is quite similar to all three kinds of wood. However, some differences may exist due to differences in cell wall structure of different wood samples [15]. The TG curves show that the major decomposition of woods happened dramatically in a range of temperature from 275 °C to 475 °C.The maximum mass loss rate of Kapur is at temperature of 345 ,lower than of dark red Meranti which is at 360 °C . At the end of pyrolysis process, the total residual mass left of Kapur and dark red Meranti 25.32% and 13.27% and 4.82% respectively. The differences in the inherent structures and chemical nature of the three components in each type of wood possibly account for the different in total mass residual left. The variation of the weight loss was related to differences in the types of chemical compounds, especially more weight loss occurred with the lower lignin content[23].

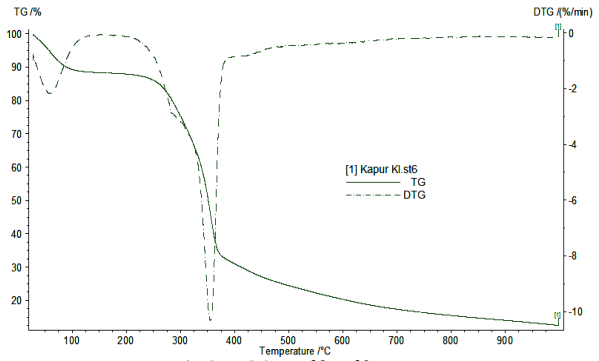

Fig 2: TGA profile of kapur

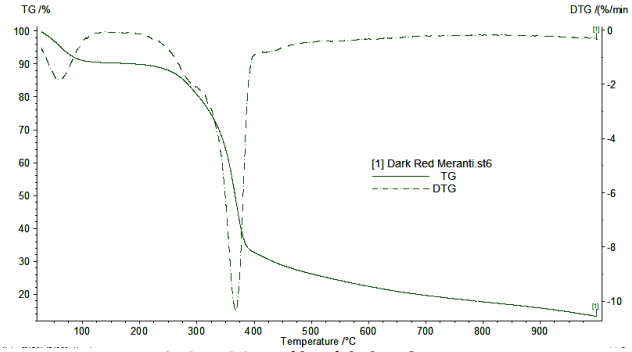

Fig.3: TGA profile of dark red Meranti

The temperature above 600°C was the stage where the graphitic carbon forming, which is necessary for infiltration process [24].Generally, the mechanism in the conversion of wood into carbon is quite similar to other kinds of wood. However, some differences may exist due to differences in cell wall structure of different wood samples [21].

3.3. SEM

The microstructure from carbon perform for kapur and dark red meranti obtained by pyrolysis process are shown in Fig.4 (a and b) respectively. It can be seen that the capillaries inside the solid framework of carbon template as the structure of the original wood template was retained.

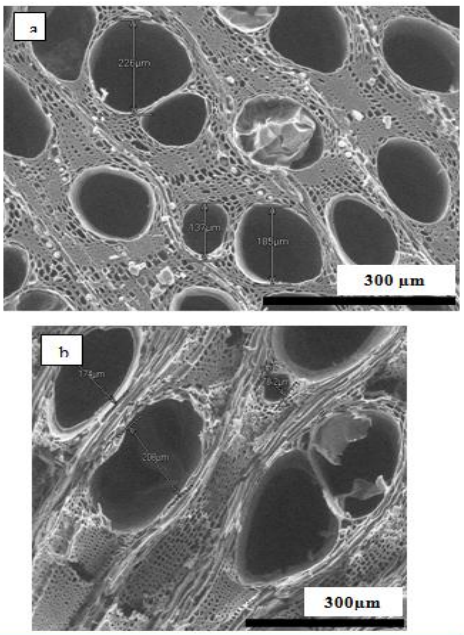

Fig 4: SEM micrograph of pyrolized wood from (a) Kapur and (b) dark red Meranti

Different kinds of woods will have a different shapes and sizes of pores. Kapur has two kind of pore structure which is small and large pore. Its pore sizes is approximately between 150µm-230µm. Dark red Meranti however has majority large pore structure with some smaller pores. Their pore sizes are between 70µm to 370µm.

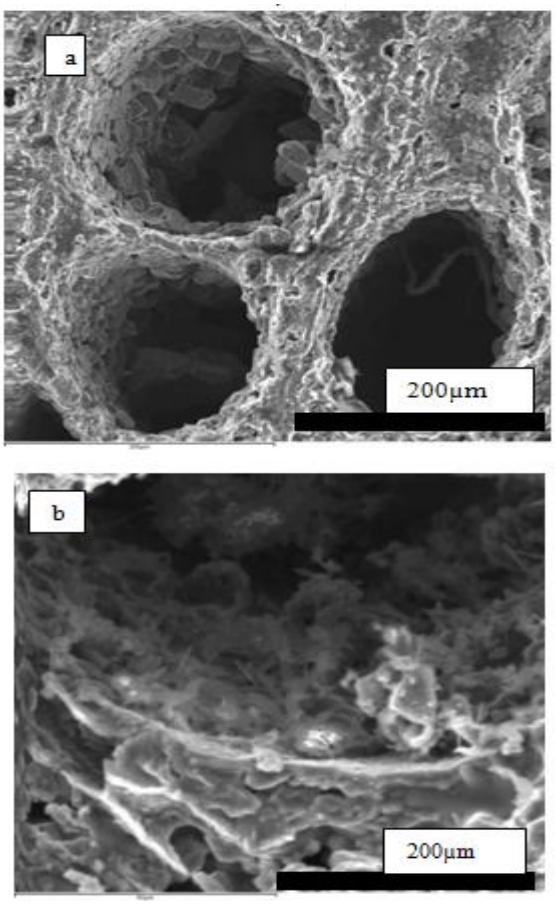

Fig. 5: SEM micrograph of Sic from (a) Kapur and (b) dark red Meranti

These open structures in the initial carbon preform helps in the conversion of carbon to SiC by facilitating Si vapors to pass into and through the pores and to react with the carbon.

The SEM images of resulted porous SiC are shown in Figure 3(a-b). It can be seen that the structure of the original wood template was retained. The formation of crystalline Si at the surface and pore walls are clearly visible. The resulted SiC filled some pores and covered up the whole surface and few of SiC formed and filled at pore wall. However, there are some of pore does not filled by molten silicon. This is because the capillary effect is higher in smaller pores. The liquid silicon from the larger pore was extracted into small pores until the pressure equilibrium is reached [11] as can be seen in Figure 2(d).

The infiltration of Si through pore can be shown in the elemental mapping as shown in Fig`6. The green colour is corresponding to silicon while red colour is corresponding to carbon element. It can be observed that the green colour which correspond to silicon are more in the pore walls which prove that the formation of silicon carbide occur in the pore structure .It is also evident how the SiC phase mimics the precursor microstructure.

It is concluded that the pore size is one of the important factor for optimum infiltration to occur. If pore diameter is too small, the SiC formed at the surface could block and restricted further infiltration process inside the pore walls. Otherwise too large pore could leave unreacted carbon as SiC not fully converted [25].Therefore, the pore size should be ideal for optimum reaction to occur. Besides, another factor that could be considered in Si infiltration included contact angle and surface tension [26].

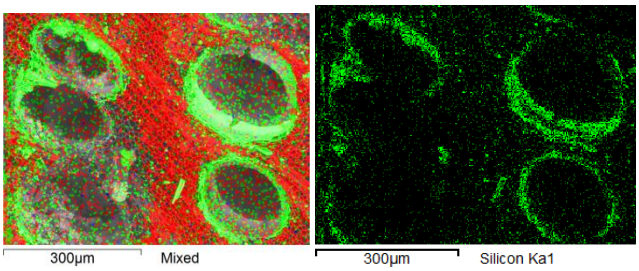

Fig6: Elemental maping of silicon carbide (a) silicon (green) and carbon(red) element (b) silicon element (green)

3.4. XRD

Fig.7 shows the XRD patterns of carbon preform and resulting SiC. It can be seen that carbon is amorphous with a broad peaks at around 22° and 44°suggesting that both pyrolyzed kapur and dark red meranti are amorphous. The major crystalline phase is SiC at 2θ= 35.6°,41.4°,59.9°and 75.5°.It is apparent that the intensity of the XRD peaks corresponding to kapur is significantly higher than peaks correspond to SiC derived Dark red meranti. the peaks correspond to carbon amorphous clearly disappeared. High intensity in SiC derived kapur shows the samples has high crystall structure and this in agreement with SEM in Fig.5 (a).There is no detectable residual silicon peak which as residue Si was remove away by etching process [27].

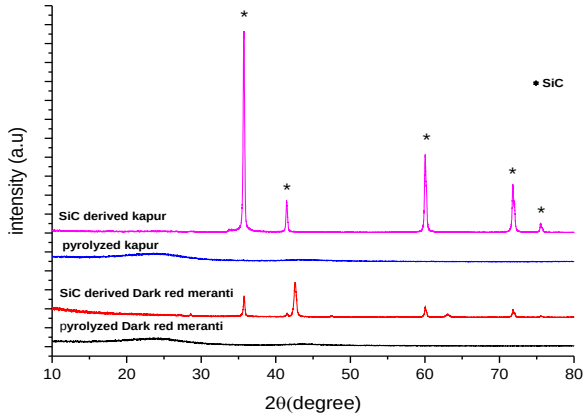

Fig7: XRD pettern of pyrolized carbon and resulting siC at 3 hours holding time

3.5. Mechanical Properties

Mechanical properties (flexural strength,and Young's modulus) of biomorphic SiCs were determined using three- point flexural tests at room temperature. The fracture surfaces of the SiC were found to be flat and smooth, characteristic of brittle fracture. It was found that the flexural strength of SiC derived dark red meranti is higher than SiC derived kapur. The higher flexural strength and modulus values of the infiltrated dark red meranti preform are most likely attributable to the presence of a greater amount of SiC phase as the Si content is 48.93 w.t%, and a lesser amount of Si in SiC derived kapur which is 44.98 w.t%. The mechanical properties of the wood derived biomorphic SiC composites not only depend on he density but also the porosity and the microstructure, such as anisotropic orientation and diameter of the tracheidal pore structures [22] .

Table 2: Mechanical properties of SiC derived Kapur and dark red Meranti

SiC	Flexural strength (MPa)	Elastic modulus (GPa)
Kapur	33.33	20.83
Dark red Meranti	53.03	32.63

4. Conclusion

Biomorphic SiC ceramics have been successfully pre-pared using silicon melt infiltration method using two types of precursor;kapur from medium hard wood and dark red meranti from light hard wood. The resulting porous microstructure mimics the original wood microstructure and is made up of a SiC network filled with Si. SEM micrograph reveals that the formation if SiC are mostly occur in the pore walls of wood structure. Dark red Meranti show a high flexural strength compared to Kapur which is 53.33 MPa, indicating that the formation of silicon carbide in wood structure not only depends on the original wood density as the final density for both precursor almost similar.

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