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SYNTHESIS OF (SiC based) CERAMIC MATRIX COMPOSITE VIA A POLYMER PRECURSOR ROUTE

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Abstract

Vinyl Triethoxysilane (VTEOS) which was stimulated by stannous 2-ethyl-hexanoate catalyst was polymerized to form polymer precursors consisting of polysiloxane structures $(-Si(R_1R_2)-0-)_n$ with and without the presence of $Al(N0_3)_3$. The precursor could produce SiC based ceramic matrix composite when heated to high temperatures. TGA analysis up to 550°C showed weight loss approximately 28% and 56% in VTEOS and $A1(NO_3)_3$/VTEOS samples respectively. Weight loss of $A1(NO_3)_3$/VTEOS sample became rapid (46%) after heating from 200°C to 300°C. XRD analysis showed the formation of $SiC\text{-}Al_2O_3$ composite at 1200°C from $A1(NO_3)_3$/VTEOS sample whereas VTEOS sample produced SiO_2 phase at the same temperature. Pyrolyzed (1200°C) precursor pellets shrank approximately 21%.

1.0 INTRODUCTION

Ceramics processing is conventionally carried out by means of plastic forming, powder pressing, and slip casting. These methods require a direct manipulation of ceramic raw materials and also need a very complex processing control to produce a good quality dense ceramic body. The problems which need to be monitored are cracks, moisture, shrinkage, porosity during fabrication, drying and firing of ceramic body.

Researchers have developed processes and found a novel method in producing ceramic bodies. Ceramics derived from polymer precursors have recently been introduced in industry especially for SiC fiber industries. These ceramics possess attractive features that exhibit a unique approach in ceramic processing especially for ceramic matrix composites. The fabrication of ceramic bodies from polymer precursors offers some advantages and potential to overcome conventional ceramic processing. Baldus et. al. (1992) state the advantages of the method as follows:

i) Suitable for plastic forming technology
ii) No sintering aids and binders applied
iii) Pure precursors serve metastable solid phases
iv) Requiring low heat treatment (around 1000°C)

The development of ceramic products derived from polymer precursors started in 1960 by Aiger and Herbert (1960) and Chantrell and Popper (1965), when they reported non-oxide ceramics production. The early polyorganosilicon compounds for ceramic products were polysilazane, polysilane and polycarbosilane where Winter et. al. (1974) successfully produced high performance SiC/Si3N4 ceramic fibre. Then, Japanese researchers Yajima et. al. (1987) developed a polycarbosilane polymer that is suitable for SiC based fibre. As a result, many scientists worked on new polymers to synthesize such polymer precursors.

The flow chart of the pyrolysis process is as follows :

Organosilicon **Precursors** → Rearrangement **cross-linking** → Pre-ceramic **Polymer pyrolysis** → Ceramic **product**

Synthesized polymer precursors are dried and pyrolyzed in a furnace for polymer-ceramic conversion. During the pyrolysis process, the changes in the polymer are simply illustrated as shown in the flow chart above. The polymer will decompose and the rearrangement of the structure occurs as the temperature increases. Finally, some ceramic phases are formed at a temperature of around 1000°C which is considered as forming a ceramic matrix composite system.

2.0 METHODOLOGY

2.1 Materials

The materials used in the experiment were vinyl triethoxysilane (VTEOS) (Fluka Chemika), distilled water, ethanol (Fluka Chemika), stannos 2-ethyl hexanoate (Sigma), aluminum nitrate (Fluka Chemika) and ammonium (Fluka Chemika).

2.2 Preparation

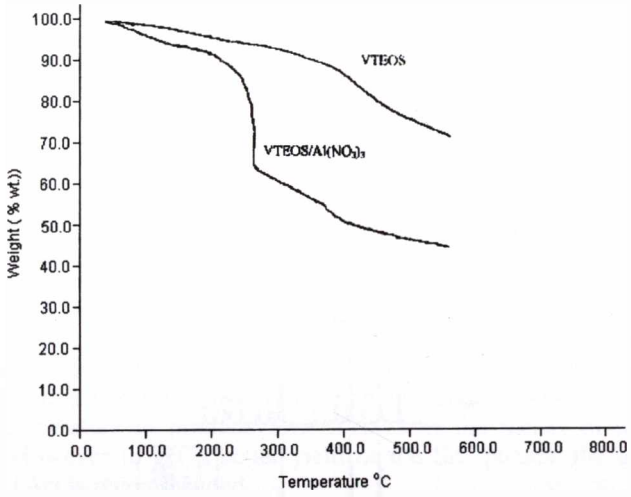
Polymer gel precursor was prepared by adding distilled water, ethanol and vinyl triethoxysilane liquid in a beaker in the presence of a catalyst (stannous 2-ethyl-hexanoate). The solution was continuously stirred until the polymer gel formed. The gel was then washed with ethanol, filtered and dried. Finally a dry, white polymer precursor powder was produced for ceramic derivation. Repeating the same method, A1(NO3)3 was added to the sample during mixing with a weight ratio of A1(NO3)3 to the monomer of 3:2. The pH of the solution was determined by dropping ammonium solution slowly into the solution during stirring until pH9 was obtained. The gel was then washed with distilled water, followed by ethanol, and continued drying.

2.3 Instrumentation

The samples were pyrolyzed at 800°C, 1200°C, 1300°C and 1450°C (each for 5 hours with 10°C/min. heating rate) in an electrical tube furnace (Carbolite CWF-J300). The weight loss of the sample up to 600°C was observed by TG (Perkin-Elmer TGA7) analysis and phases of pyrolyzed samples were identified by XRD (Phillips PW1729) analysis. The dried precursors were also compacted into pellets (10mm diameter, at 4 tones load) and heated up to 1200°C (10°C/min. heating rate, 5 hours) to determine the shrinkage of the sintered body.

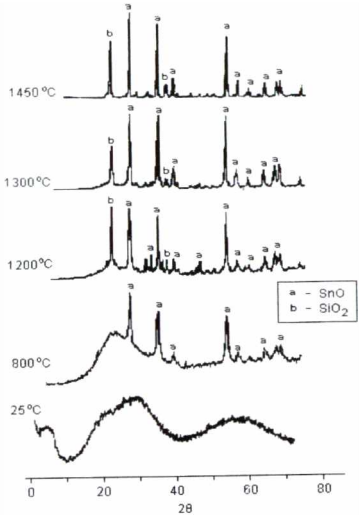
3.0 RESULTS AND DISCUSSION

TG analysis of the samples was performed up to 550°C as shown in Figure 1. The sample weight loss ended at a temperature of around 500°C.



The analysis proved that VTEOS and A1(NO3)3/VTEOS samples lost approximately 28% and 56% of the total sample weight respectively. According to Lipowitz (1991), at 100°C to 200°C, both samples indicated the evolution of alcohol, water and volatile substances. Between 200°C to 400°C, a rapid loss of the A1(NO3)3/VTEOS samples (36%) weight was claimed as a result of the decomposition of the Si-H, Si-C and C-H bonds (Hurwitz et. al. 1993). As the decomposition proceeded, the rearrangement of the structure also occurred after 400°C. As Lipowitz stated, it is estimated that the decomposition of the two samples will be completed at 800°C. At this stage the conversion of polymer-ceramic phases will start to occur by rearrangement of the structure. This illustrated that the pyrolysis temperature of the polymer precursor could be started at 800°C.

Figure 2a : XRD analysis of VTEOS sample at 25∞C, 800∞C, 1200∞C, 1300∞C and 1450∞C (at the same intensity scale).



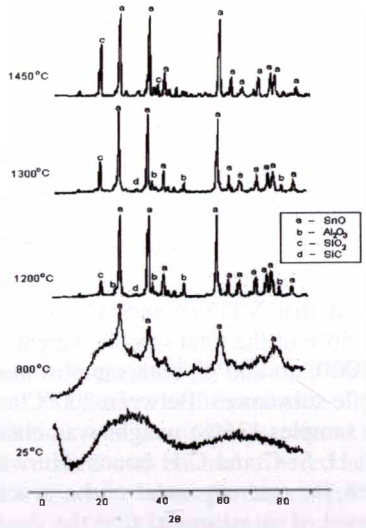


Figure 2b : XRD analysis of VTEOS/Al(NO3)3 sample at 25∞C. 800∞C, 1200∞C, 1300∞C and 1450∞C (at the same intensity scale).

Figure 2 shows the XRD results of the pyrolysis of both samples at 800°C, 1200°C, 1300°C and 1450°C. The XRD analysis indicates major peaks of impurity (SnO) at each sintering temperature, which resulted from the use of the catalyst. The presence of SiC and A12O3 phases however, could still be analyzed where some small peaks of the phases are seen clearly. SiO2 and C peaks are seen clearly at 1200°C in the VTEOS sample. As the temperature increased up to 1450°C, it did not show much change in the sample. Nevertheless in the existence of filler, SiC and A12O3 peaks could be detected at 1200°C. At 1300°C, SiC seemed to be unstable and easily to form SiO2 phase. The increase of the temperature has made A12O3 unstable and is associated with SiO2 to form sillimanite.

Table 1: Ceramic products of the polymer precursors derived ceramic after pyrolysis

Sample	800°C	1200°C	1300°C	1450°C
VTEOS	amorphous	SiO2,, C	SiO2, SiO2.xH2O	SiO2, C
A1(NO3)3/VTEOS	amorphous	A12O3, SiC	Al2O3 ,SiO2, SiO2.xH2O	SiO2, Al2SiO5 , C

Table 1 shows XRD analysis on the samples where the transition of polymer-ceramic phases can be observed. At 800°C, the samples were in amorphous form. As the temperature increased to 1200°C, A12O3 and SiC phases were detected. The SiC phases would be decomposed at above 1300°C above and oxidized to form Si02. The temperature of 1200°C is an optimum pyrolysis temperature to produce SiC- A12O3 as the matrix of the ceramic composite. However to get a better yield of the SiC phases, the use of inert atmosphere (Ar) is recommended.

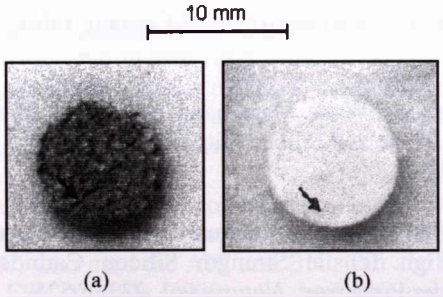


Figure 3 : Pellets of (a) VTEOS and (b) VTEOS/Al(NO3)3 samples which were sintered at 1200∞C (arrows show cracks in the pellets).

After undergoing heat treatment at 1200°C the pellets showed 21% shrinkage and some cracks (Figure 3). This could be due to the presence of impurity (SnO), and might also result from the difference of the thermal coefficient of the existing phases (A12O3 and SiC). However the pellets could still retain their initial shapes after heating.

4.0 CONCLUSION

The chemical mixture of aluminum nitrate (A1(NO3)3) and monomer vinyl triethoxysilane (VTEOS) has shown a potential for deriving ceramic matrix composite (SiO2- A12O3 and SiC- A12O3) through the polymer precursor route process. The combination of the chemicals produced alumina and silicon carbide phases after undergoing a precursor synthesizing and pyrolysis process at 1200°C. The SiC phase could still somehow be maintained above 1200°C by means of inert atmosphere.

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