# SYNTHESIS OF CERAMER MATRIX FOR DEVELOPMENT OF CARBON-CARBON COMPOSITES

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## Introduction

Carbon-carbon composites are prepared   using high strength carbon fibers and phenolic resin or similar thermosetting resin as precursor for carbon matrix.  High strength PAN based carbon fibers make strong interactions with resin matrix  at polymer stage.  During pyrolysis of these composites because of  the significant shrinkage of polymer matrix,   carbon fibers get damaged. Also due to large difference in strain to failure of high strength carbon fibers (1.5%) and carbonized matrix  (0.5%) derived from  phenolic resin. These composites therefore tend to give poor mechanical properties [1-5],

Full potential of carbon fibers is not in the composites.

In order to overcome above mentioned drawbacks of  carbon-carbon composites prepared from high strength carbon fibers and phenolic resin matrix it was thought to ;

- Modify the matrix to reduce the adhesion  between
  polymer matrix and carbon fibers

- To increase the  strain to failure of  matrix comparable
  to  that  carbon  fibers.

To achieve above mentioned objectives, the  resorcinol-formaldehyde resin was modified by introducing  silica network in it. The  hybrid  material prepared  from  a mixture of  resorcinol-formaldehyde (organic) and a ceramic i.e. silica  (inorganic) is known as 'ceramer'. The ceramer was  synthesized by sol-gel process[6-7].   Such hybrid material (ceramer)   can exhibit   optimum combination of  properties  coming  from  the  two components e.g. ductility and low density coming from the organic component and low thermal expansion, high temperature  resistance,  higher  mechanical properties coming from inorganic components.   The objectives of the present investigation was   to synthesis  the ceramer matrix through sol-gel process and reinforce it with high strength carbon fibers which upon pyrolysis should give high performance carbon-carbon composites.

## Experimental

### Synthesis of ceramer

The  resorcinol-formaldehyde \ silica hybrid known as ceramer was  synthesized by sol-gel process[6-7].  The tetraethoxysilane (TEOS) and  dimethyl diethoxysilane (DMDEOS)  was used as  source of silica. The mixture of   resorcinol  formaldehyde  and  TEOS  as  well  as resorcinol formaldehyde and DMDEOS was taken in different molar ratios  to get in different percentage of silicon by weight in ceramer matrix in the carbonized stage. The sodium carbonate was used as a   basic catalyst. The  formaldehyde solution used for synthesis of ceramer  consists of formaldehyde ( H-CHO) 37-41 % weight/ volume, methanol 14 % weight/ volume   rest being water. Therefore, there was no need of  using another   solvent for hydrolysis and polycondensation reaction.  The different ceramers prepared  by using two

alkoxide as silica source were cured at 150°C and characterized for their structural analysis by FTIR. The coefficient of thermal expansion and thermal stability of cured ceramer was measured by Mettler Thermal Analysis system TA-4000.

## Preparation & characterization of composites

Unidirectional polymer composites were prepared using PAN based T-300 carbon fibers as reinforcement and pure resorcinol formaldehyde resin and ceramer as matrix precursor. The polymer composites were prepared using wet winding and match mould die technique keeping $50 \pm 2$ % fiber volume. The polymer composites were heat treated at 1000°C and 1450°C respectively in inert atmosphere. The polymer and heat treated composites were characterized for mechanical properties on Instron universal testing machine model 4411 as per ASTM D-790-80. The ceramers prepared from the different silicon sources and also from composites prepared from same ceramers were coded as ;

C1- Resorcinol formaldehyde resin matrix composites

C2- 7% Silicon from TEOS source ceramer composites

C3-15 % Silicon from TEOS source ceramer composites

C4-10% Silicon from DMDEOS source ceramer composites

C5-20% Silicon from DMDEOS source ceramer composites

## Result and Discussion

### FTIR studies

Figure 1 shows FTIR spectra of uncured and cured ceramer resin . In case of uncured ceramer ( curve c), the absorption peaks at 466 and 790 cm$^{-1}$ are due to the Si-O-Si asymmetric stretching vibration and symmetric bending vibration respectively [8,9]. The strong peak at

around 880cm$^{-1}$ is associated with Si-OH groups[10]. The absorption peak at 1091 cm$^{-1}$ is associated with CH$_2$-O-Si network. Peak around 1200 cm$^{-1}$ is of C-H stretching vibration of aromatic ortho para substitution. The peak at 1441 cm$^{-1}$ is associated with CH$_2$ stretching vibrations. The strong peak at 1614 cm$^{-1}$ corresponds to C-C stretching mode of aromatic carbon. The broad absorption band at 3364 cm$^{-1}$ is characteristic of OH stretching vibrations. It is observed from the FTIR results that functional groups present in the ceramer are polar in nature. While in case of cured spectra (curve b) the Si-OH, CH$_2$-O-Si peaks and OH band shifted to higher wave number. The appearance of peaks at higher wave number is due to polycondensation reaction taking place at higher temperatures.

## Thermo-mechanical analysis

Figure 2 shows the TGA curve of cured resorcinol formaldehyde (RF) resin and the ceramer. From the TGA curve of cured RF resin it is observed that, broadly , there are two regions of weight loss. First region upto 550°C, weight loss is much steeper and thereafter it slows down. On the other hand , in case of the ceramer, weight loss starts at 350°C and continues upto 750°C at the same rate as in the case of RF resin. This is due to formation of oxygen silicon linkages in the ceramer which are thermally stable. There is further transformation in to carbon oxygen silica and silcon-carbon linkages as a result of evolution of reaction products at higher temperature.. Beyond 750°C, rate of weight loss slows down. It is significant to note that the weight loss in ceramer gets restricted to ~10 % (upto 550°C) only as compared to 25 % observed in case of RF resin. The TG curve also suggests that the ceramer resin synthesized from resorcinol-formaldehyde and TEOS is thermally stable upto about 350°C and gives higher yield

than resorcinol-formaldehyde resin. The TG analysis of all other ceramer samples is presented in table 1.

**Table 1: TG analysis of resin**

| Ceramer Code | Wt. loss start Temperature °C | % Weight Loss at 1000°C |
|---|---|---|
| C1 | 200 | 40 |
| C2 | 300 | 36 |
| C3 | 250 | 34 |
| C4 | 290 | 35 |
| C5 | 250 | 34 |

**Table 2: Chemical analysis of ceramers**

| Ceramer Code | Actual % of Si in ceramer |
|---|---|
| C1 | 00 |
| C2 | 7.0 |
| C3 | 14.5 |
| C4 | 9.9 |
| C5 | 21.00 |

Table 2 gives the total amount of Si present in different ceramer matrices. The % Si was explained from the residue of the cured ceramer heated in air at 1000 °C.

Figure 3 shows the relative variation of thermal expansion coefficient (CTE) as a function of temperature for cured matrix C1 and C3 matrix. The curves indicate two matrices behave quite differently. With increasing temperature, CTE of C1 increases moderately upto 150 °C and thereafter it increases sharply upto 350°C. However, in case of ceramer, the CTE increases moderately upto 180°C and then flatten up. The contrasting behaviour has been attributed to orientation of the resorcinol formaldehyde chains between the silica domains, which is expected to occur only if the silica and

resorcinol-formaldehyde component exist in co-continuos phases [11]. The lower value of CTE in ceramer is further attributed to overall reduction in free volume by formation of a rigid network in the ceramer or tight silica network relative to resorcinol-formaldehyde components [6].

Low value of CTE in case of ceramer should be conducive for making better carbon-carbon composites.

## Mechanical Properties

Figure 4 shows flexural strength of composites at different stages of processing. At 150°C ( i.e. polymer stage) the value of flexural strength is maximum in case of composites C1 as compared to ceramer matrix composites. The higher value of flexural strength in C1 composite is due to stronger fiber matrix interactions resulting in high stress transfer capability . In case of the ceramer matrix composites (C2 -C5), lower value of flexural strength at polymer stage is due to presence of silica in ceramer matrix which weakens the fiber matrix interactions [12]. However, upon carbonization (at 1000°C), the flexural strength of composites C1 decreases to large extent while in case of ceramer matrix composites i.e. C2 and C3 the extent of decrease is lower comparatively. In case of composite C1 as explained earlier, the shrinkage stresses developed during carbonization lead to matrix micro-cracking [1,4] which upon application of external load, even at small stress levels, is able to propagate the cracks through fibers without any deviation at the interface. As a consequence the mechanical properties of composites are poor. In case of ceramer matrix composites the matrix micro-cracking is controlled by the comparatively lower shrinkage of the matrix during carbonization and also formation of three dimensional silica network around the carbon fibers, even though there is strong fiber matrix interaction.

However, with increasing the silicon percentage in ceramer matrix during synthesis, the flexural strength in these composite decreases because of large amount of porosity which is created in the matrix and also due to more strong cross links between fibre and the matrix. On further heat treatment of these samples at 1450°C, due the to presence of silicon in ceramer matrix, strong bond with carbon are formed via formation of Si-O-C and Si-C. Consequently significant improvement in flexural strength is observed in C2,C3,C4 and C5 composites . On the contrary, the flexural strength of in composite C1 decreases further. In case of C1 composites the cracks developed during carbonization in the matrix may get enlarged which ultimately dominate the flexural strength of the composites. The larger improvement in the value of flexural strength in case of composites C2 and C3 may also be attributed to the intrinsic characteristic of the ceramer matrix i.e. better ductility as well as the mechanical properties( flexural strength and flexural modulus). It is evident from fig. 6 showing load - displacement bahaviour of the composites C2 and C3 . These composites fracture at a strain level which is much higher than that of composites C1.

The flexural strength of composites C4 and C5 is lower as compared to C2 and C3 mainly because of the presence of comparatively higher porosity as evident of their density values shown in table-3. Flexural modulus of these composites are compared in figure 5. At polymer stage, the contribution of matrix to flexural modulus of the composites is negligible because the fiber

**Table 3: Bulk Density of 1450°C heat treated Composites**

| Composites Code | Bulk Porosity (g/cm$^3$ ) |
| --- | --- |
| C1 | 1.33 |
| C2 | 1.36 |
| C3 | 1.30 |
| C4 | 1.34 |
| C5 | 1.25 |

modulus is always much greater than the matrix modulus. Therefore, in all the composites flexural modulus ranges between 95 GPa for composite C1 to 110 GPa for ceramer based composites. With increase in heat treatment temperature, flexural modulus of C1 composite decreases while in case of ceramer matrix composite it increases and attain the value of 120 GPa in C2 composites heat treated to 1450°C. The decrease in the flexural modulus in case of C1 composites is due to the large difference in strain to failure of carbon fiber and carbonized matrix as a result the carbon fiber modulus is not exploited in these composites. The increases in flexural modulus in case of ceramer matrix (C2) composites is due to the intrinsic characteristics of ceramers.

Figure 6 shows load -displacement curves of the composite heat treated at 1000°C and 1450°C respectively. In case of C1 composites, fracture is nearly pure tensile mode (Figure 6 a and b) while ceramer matrix based composites heat treated at 1000°C fracture is only tensile cum shear mode while after HTT to 1450°C the fracture behaviour becomes tensile cum shear with initial micro-cracking.

## Conclusion

A ceramer matrix, synthesized through sol-gel process from a mixtures of resorcinol formaldehyde and different alkoxide source of silica, showed that ceramer was network of Si-O-Si , Si-O-CH2 and Si-OH type groups linked with benzene ring. The ceramers possessing different amount of silicon exhibits varying temperature of thermal stability and it is stable upto

300°C. The ceramer matrix exhibits lower thermal expansion as compared to pure resorcinol formaldehyde resin due to the presence of silica and resorcinol formaldehyde in co-continuos phase. The composites prepared from ceramer matrix shows lower values of mechanical properties at polymer stage due to weak fiber matrix interactions as compared to resorcinol formaldehyde resin matrix composites. However, after HTT at 1450°C these shows large improvement in the mechancial properties e.g. flexural strength is improved by a factor of two whereas flexural modulus is increased by 40 %.

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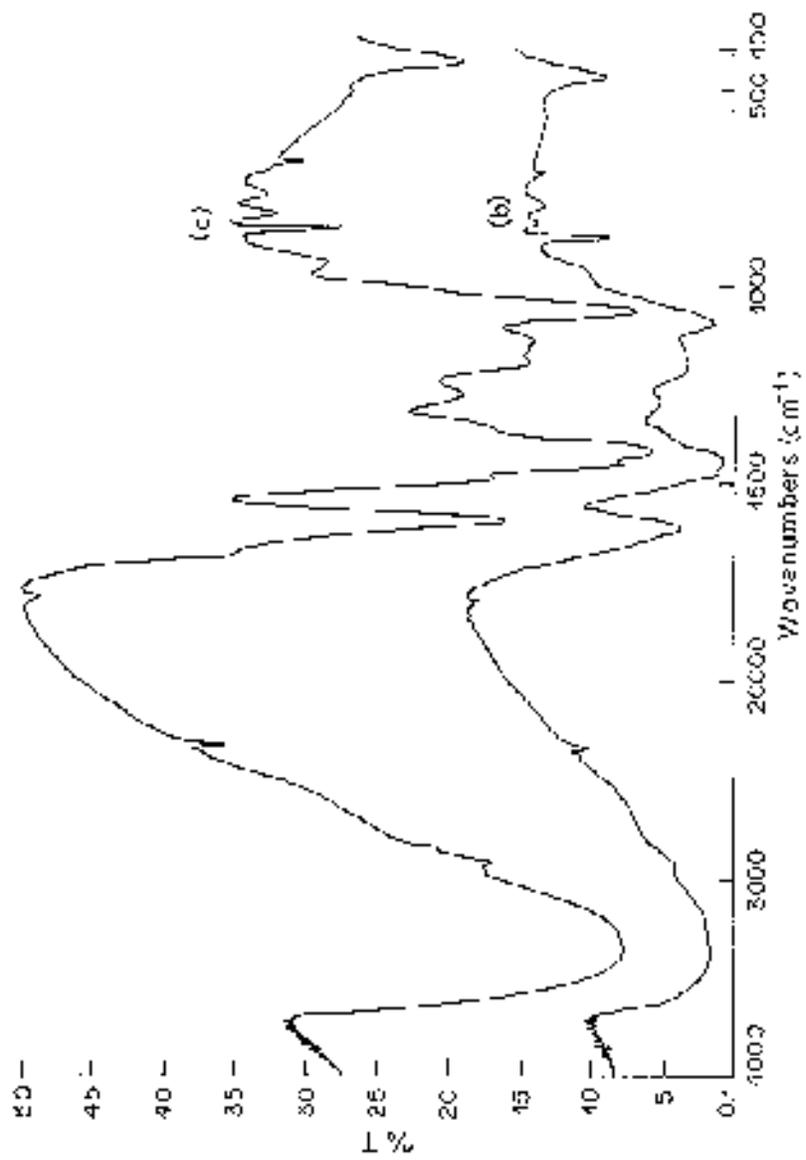
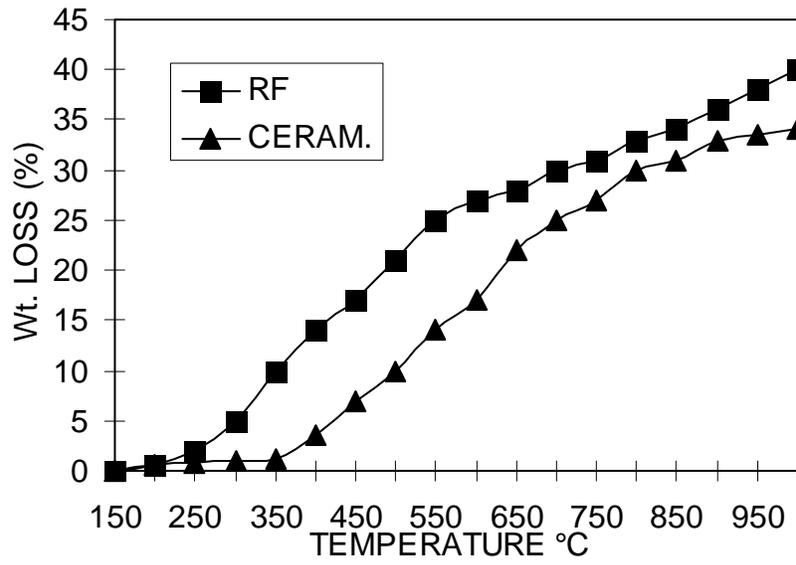Figure 1: FTIR spectra of (c) uncured and (b) cured ceramer resin.

Figure 2: TGA curve of cured resorcinol formaldehyde (RF) resin and the ceramer
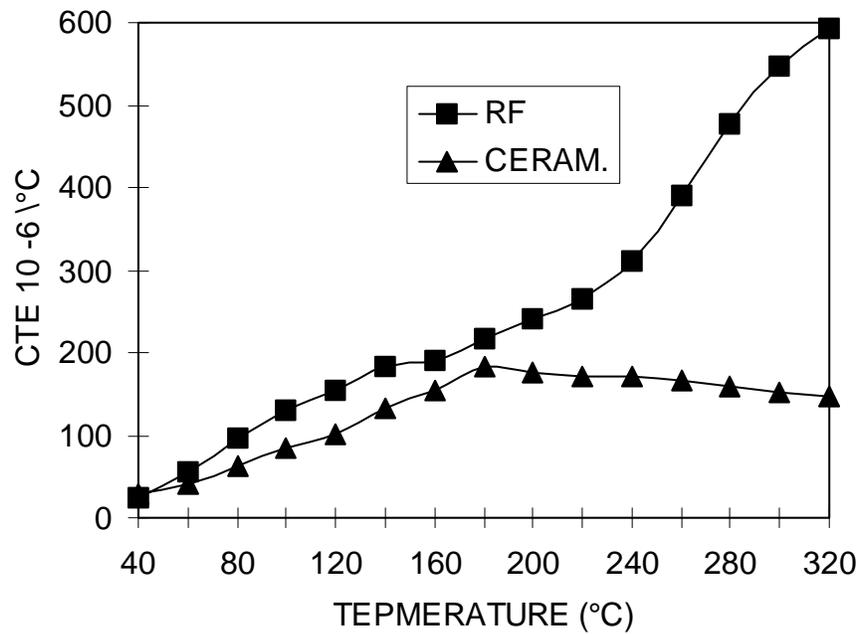


Figure 3: Relative variation of thermal expansion coefficient (CTE) as
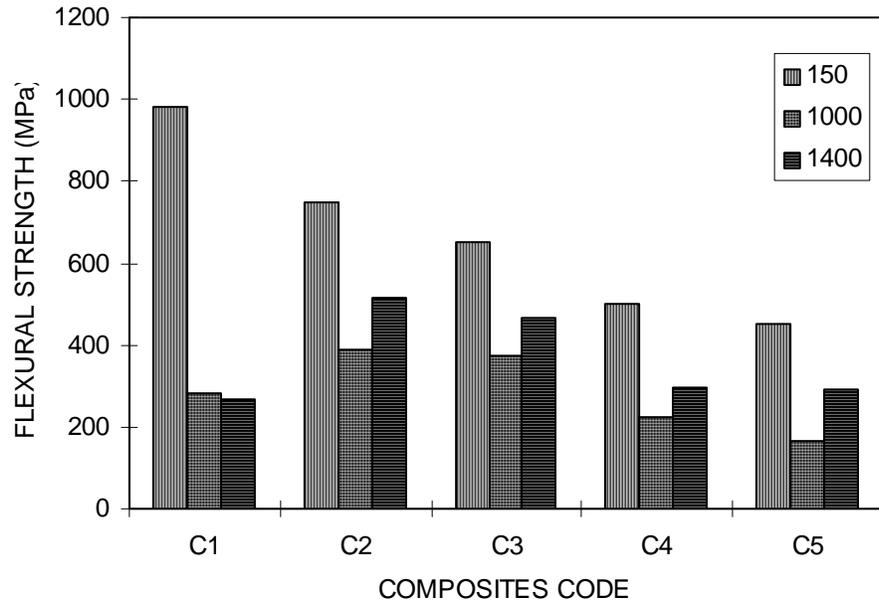a function of temperature for cured RF and ceramer matrix

Figure 4: Flexural strength of composites at different stages of processing
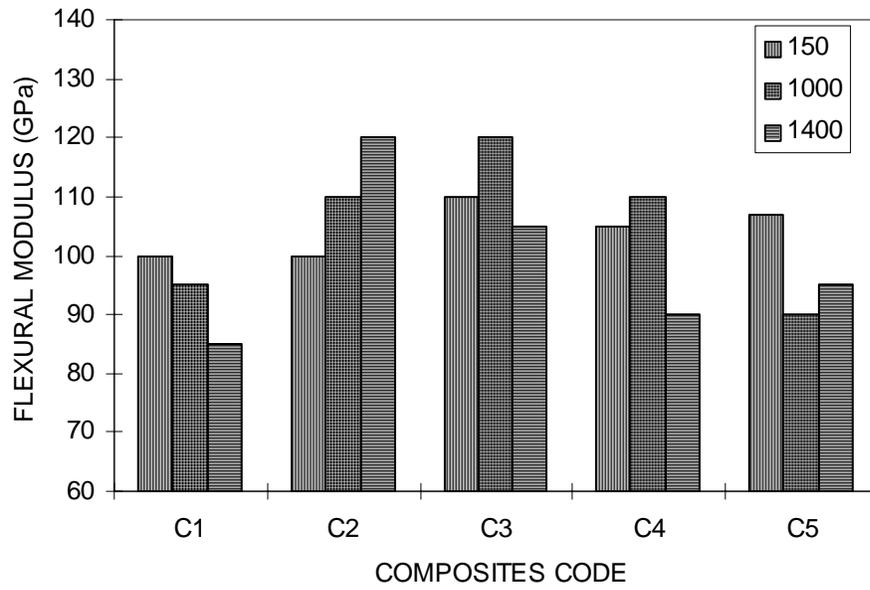


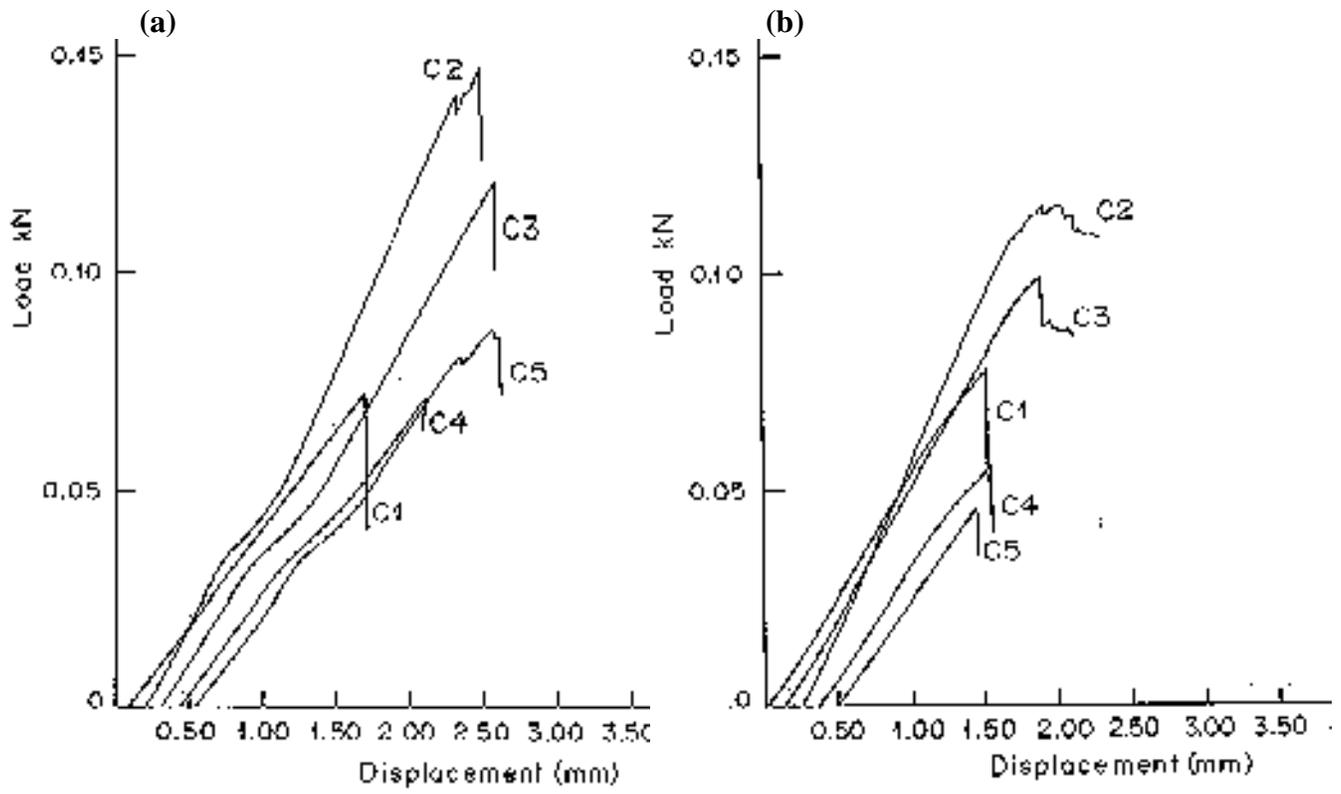Figure 5: Flexural modulus of composites at different stages of processing

Figure 6: Load -Displacement curve of  (a)1000°C and (b)1450°C.