

# INFLUENCE OF INTERFACE ON CRYSTALLINE PARAMETERS, COEFFICIENT OF THERMAL EXPANSION AND ELECTRICAL CONDUCTIVITY IN CARBON-CARBON COMPOSITES

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## Introduction

Carbonization of phenolic resin as such results in formation of non graphitizable carbon with glass like texture [1]. However, in carbon-carbon composites, matrix derived from phenolic resin gets influenced by shrinkage and thermal stresses generated during the carbonization and graphitisation process in these composites [2,3]. In addition to influencing the structure of the matrix, these stresses may, under certain conditions, affect structure of the fiber [4]. In the earlier study, composites prepared using three type of PAN based carbon fibers possessing different surface characteristics were found to make the different of type interactions with resol type phenolic resin. High strength carbon fiber composites developed columnar type texture where the fiber matrix interactions were strongest and laminar type texture was observed in case of high modulus carbon fiber composites where fiber matrix interaction are weakest [5,6]. The present investigation was undertaken to understand how the different type of interfaces influence the development of crystalline parameters, coefficient of thermal expansion and electrical conductivity in carbon-carbon composites.

## Experimental

In the present investigation three different types of PAN based carbon fibers possessing different physico-mechanical properties and surface characteristics were used as reinforcements and Resol type phenolic resin as matrix precursor. Unidirectional polymer composites were prepared by wet winding and match mold die technique keeping same fiber volume ( $45 \pm 2\%$ ) in all the three type of composites. The composites prepared from three different type of carbon fibers are coded as;

- A. High strength carbon fiber composites
- B. Intermediate carbon fiber composites
- C. High modulus carbon fiber composites.

The polymer composites were heat treated at 1000,1400, 1800, 2200 and 2600 °C under inert atmosphere. These heat treated composites as such and their powdered

counterparts ( after grinding the UD composites into a fine powder) were characterized for crystalline parameters by X-ray diffraction technique by mixing the high purity silicon powder as inner standard [7]. The average interlayer spacing  $d_{002}$  was determined by Bragg's angle of diffraction and by Bragg's equation;

$$n \lambda = 2D \sin \theta ,$$

where, n is the order of diffraction,

$\lambda$  is the wave length of radiation used

$\theta$  is angle of diffraction.

The crystallite size (L) was calculated using Scherrer equation [8];

$$L = K\lambda / \beta \cos \theta$$

where,  $\beta$  is full width at half- maximum peak height, K is correction factor,  $\lambda$  is the wave length of Cu K $\alpha$  radiation( 1.5418 Å) used.

The crystallite size along the c-axis was calculated from half maximum width of 002 and 004 diffraction coded as Lc 002 and Lc 004 where the correction factor K=0.98, and along a-axis by 110 diffraction coded as La110 where the correction factor K= 1.84. The correction for the peak broadening due to equipment was made by referring to silicon.

The heat treated composites were characterized for coefficient of thermal expansion measured by TMA in the temperature range 50-950°C under inert atmosphere. The electrical conductivity of all three type of heat treated composites were measured by four probe method.

## Results and Discussion

### Crystalline Parameters

#### Interlayer spacing with HTT of composites

Figure 1a, shows variation in interlayer spacing with stages of heat treatment temperature of composites A, B and C. At 1000°C, the interlayer spacing is of the same order in composites A and B, whereas composite C shows marginally lower value, which may be due to

contribution of interlayer spacing value from high modulus carbon fiber. With further heat treatment to higher temperature, d-spacing is found to increase instead of decreasing as is usually observed in carbon [9,10]. However, after reaching maximum value in between 1800-2200°C, there is a sudden substantial drop in d-spacing in all the composites. The sudden and substantial drop in interlayer spacing (from 2200 to 2600 °C) is thought to be due to relaxation of thermally induced stresses generated during heat treatment [11,12]. At 2600°C, composite A shows minimum d spacing, which infact is due to contribution from both fiber and the matrix. Normally, one would have expected composite C to show minimum d spacing (at 2600°C). Surprisingly, the value of interlayer spacing in composite C is almost same as at 1000°C. The observation confirms that the changes in interlayer spacing of the composites upon heat treatment may depend on the type of fiber-matrix interactions established at polymer stage.

In case of composites A, B and C, heat treated to 1000°C, strong thermal stresses develop on the fiber-matrix interface, and these stresses go on increasing upto 1800-2200°C as evidenced by increase in value of d-spacing. This increase is more glaring in composite A, since the fiber matrix interactions are strongest than in composites B and C. With increasing HTT, the severity of the residual stresses increases and is maximum in between temperature 1800-2200°C where one finds the highest value of interlayer spacing. Hence, with increase in the heat treatment temperature of the composites, interlayer spacing increases upto 2200°C. The increased interlayer spacing is attributed primarily to the stacking disorder and resultant attenuation of weak vander waal bonding between layers.

Figure 1b, shows the changes in interlayer spacing of powdered composites. In this case the different heat treated composites were ground to fine powder and crystalline parameter studied as above by XRD. The changes in interlayer spacing show completely opposite trend upto 2200°C (as compared to the one observed in figure 1a) and thereafter shows a sudden fall. Also the final d spacing values particularly in composites A and B are much lower ( 3.38 Å as against 3.42 Å for composite C) as compared to value of d-spacing of as such composites (figure 1a). This could be due to stress relaxation at the interface during grinding process.

In carbon fiber reinforced carbon matrix composites, due to the shrinkage of matrix during composites fabrication and thermal contraction, mismatch between fiber and matrix during cooling near the end of composites fabrication, the fiber surface in a composites develop residual stresses. These stresses may affect the structure of the fiber as well as matrix and lead to the degradation of mechanical properties of composites. The severity of these

stresses depends upon the bonding nature of fiber-matrix interactions established at polymer stage. On grinding of such composites into powder, frozen stresses present (i.e. fiber matrix interface) gets released and as a result the interlayer spacing increases. With increasing the heat treatment temperature, the frozen stresses (shrinkage and thermal stresses) increase continuously in composites and decrease on grinding accordingly. Hence, the interlayer spacing trend with stages of heat treatment temperature is different in as such composites and its powdered counterparts.

### **Lc 004 with HTT of composites**

Figure 2 (a and b) shows the variation in Lc ( 004) with stages of heat treatment of as such composites and their powdered counterparts. At 1000°C (figure 2a), the value of Lc (004) is 22 Å in composites A and B while in composite C it is around 35 Å as expected. On increasing the heat treatment temperature, the Lc (004) increases gradually in composites A and B upto 2200°C. Above 2200°C the Lc(004) in composites A and B increases more sharply from 30-32 Å to 42-45 Å, while in composite C it increases gradually upto 2600°C. Finally all the composites exhibit same value of Lc at 2600°C. The sudden change in the value of Lc in composites A and B is due to generation of stacking order. Figure 2b shows the variation in Lc (004) of powdered composites. The value of Lc (004) increases in same pattern as observed in figure 2a with higher value of Lc upto 2200°C. Above 2200°C the Lc increases suddenly in case of composites A and B, exhibiting a value of 105 -110 Å in composites A and B while in composites C it is 55 Å only. This increase in the value of Lc (in composites A and B) is due to the relaxation of thermally induced stresses and microcrystalline strain between the layers as a result higher value of Lc in case of powdered composites is observed.

### **La 110 with HTT of composites**

Figure 3 (a and b) show changes in La ( 110) with heat treatment of as such composites and their powder counterparts. At 1000°C (figure 3a), the value of La (110) is 28-33 Å in composites A and B while in composite C it is around 35 Å as expected. On increasing the heat treatment temperature the La (110) increases moderately in all the composites A, B and C and attain the value in between 45-55 Å at 2600°C. The increase in the value of La with heat treatment is due to crystallite growth and decrease in grain boundaries. Figure3 b shows the variation in La (110) of powdered composites. The value of La (110) increases in the same pattern as observed in figure 3a

upto 2200°C. Above 2200°C the  $L_a$  increases suddenly in all the composites and exhibit the values 55 Å in composite C, 85 Å in composites A and 105 Å in case of composites B. This increase in the value of  $L_a$  is due to the relaxation of thermally induced stresses and microcrystalline strain from the distorted crystallites. The difference in the values of  $L_a$  in case of the three composites are due to different level of the stresses generated in these composites which in turn depends on severity of fiber matrix interactions established at polymer stage.

### **Coefficient of Thermal Expansion with Stages of HTT of Composites**

In case of carbon-carbon composites, Coefficient of Thermal Expansion (CTE) parallel to the fiber axis is dominated by the fiber thermal expansion[13]. In transverse direction, however, the CTE contribution from the matrix material is significant as well as it would depend upon the type of fibers and their surface characteristics. Therefore in the present study CTE measurement were carried out in transverse direction of composites only.

Figure 4 shows the variation in CTE in transverse direction of composites A, B and C with heat treatment. At 1000°C the CTE in case of all three composites is of the same order with composite C showing little higher value. The lower thermal expansion in case of composite A is a clear manifestation of presence of strong boundary restraint and anisotropic contraction of individual constituent i.e. fiber and matrix.. With increasing the heat treatment temperature CTE in all the three composites registers a gradual increase upto almost 2000°C, which is attributed to marginal improvements in the matrix crystallinity.

Above 2000°C sharp increase in the value CTE is registered in all three composites. However, in case of composites A it registers a maximum value of rise and minimum incase of composite C. The sudden increase in CTE above 2000°C is due to onset of stress graphitisation. Stress graphitisation would clearly depend upon the degree of frozen stresses in the composites. These stresses would be maximum in case of composite A while minimum in case of composite C. This explains why composite A shows maximum rise while composites C minimum rise in CTE values between temperature 2000 °C and 2600°C. This indicates that in composite C it is the presence of strong intercrystalline bonds, which prevent the full strain free c-axis due to minimum graphitisation.

### **Electrical Conductivity With Stages of HTT of Composites**

The electrical conductivity mainly depends upon the mean free path of charge carriers and in carbon material it would

depend upon the degree of graphitisation and crystallite size. Figure 5 shows variation in electrical conductivity ( $\sigma$ ) with heat treatment temperature of the composites. At 1000°C,  $\sigma$  is nearly same in all the three composites. With increasing the heat treatment temperature upto around 2200°C,  $\sigma$  increases moderately in all the composites while composite C maintains a slightly higher value. The marginal improvement upto 2200 °C is attributed to improvement in matrix crystallinity. Above 2200°C,  $\sigma$  registers sharp increase in all three composites. However, in case of composites A it registers a rise from  $8 \times 10^2$  /ohm.cm (2200°C) to  $16 \times 10^2$  /ohm.cm (2600°) while it improves from  $\sim 7.5 \times 10^2$  /ohm.cm(2200°C) to  $11 \times 10^2$  /ohm.cm (at 2600 °C) only in case of composite C, while in case composite C value  $\sigma$  during whole range of temperature is in between composites A and C  $\sigma$  value. The sudden increase in  $\sigma$  above 2200°C is due to onset of stress graphitisation. Stress graphitisation (as the name suggests) would clearly depend upon the degree of frozen stresses in the composites i.e. upon fiber matrix interactions. It is already explained in earlier section, in case of composite A strongest interaction are developed while weakest in case of composite C. Therefore, stresses would be maximum in case of composite A while minimum in case of composite C. This explains why composites A shows maximum rise while composites C minimum rise in  $\sigma$  values between temperature 2200 °C and 2600°C.

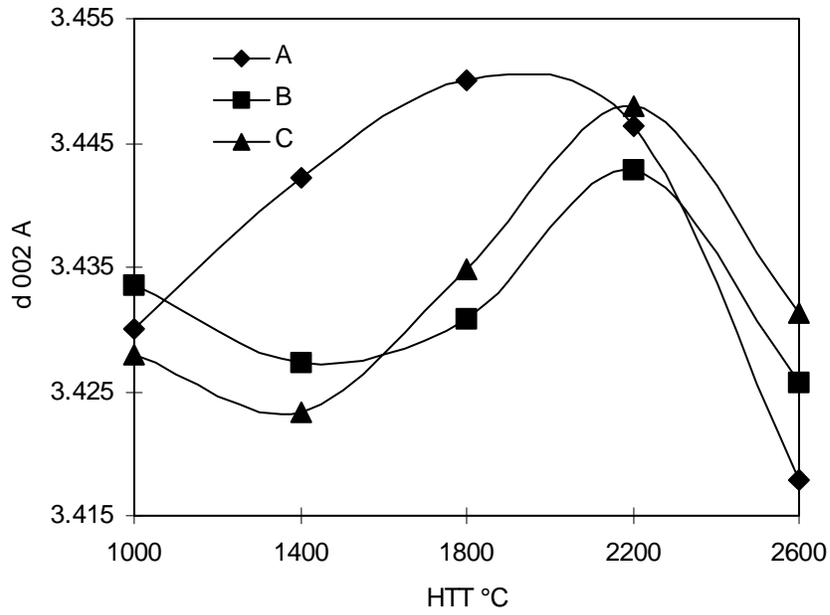
### **Conclusions**

1. It has been observed for the first time that d spacing in composites increases with HTT upto 2200°C which is contrary to the general belief that the d-spacing in carbon materials decreases upon heat treatment temperature from 1000°C onwards. However, powdered samples of these composites show entirely different behaviour. The d-spacing in all the composites decreases gradually upto 2200°C and suddenly falls thereafter.
2. It is also observed that crystallite dimensions ( $L_a$  and  $L_c$ ) of powdered composites increases upto 2200°C in the same pattern as in 'as such' composites but above 2200° it increases suddenly.
3. The Coefficient of thermal expansion and electrical conductivity is found to strongly depend upon the fiber matrix interactions and matrix structure.

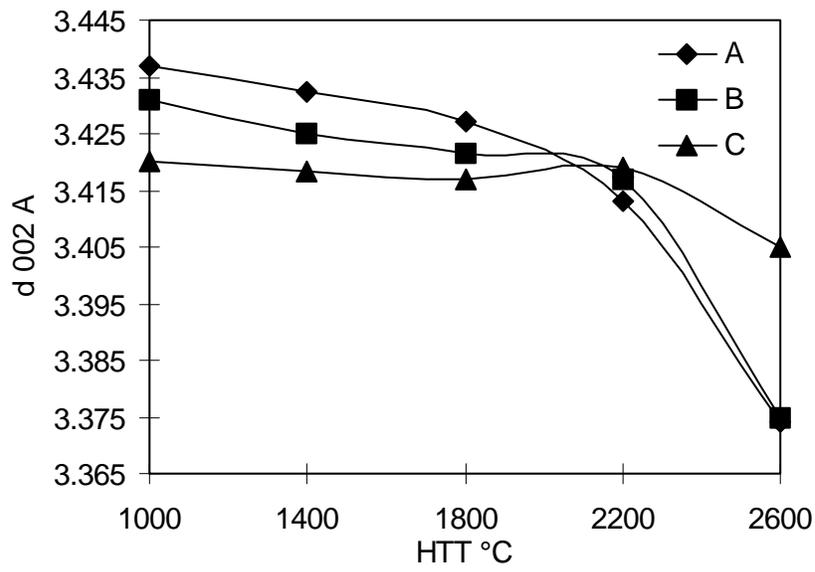
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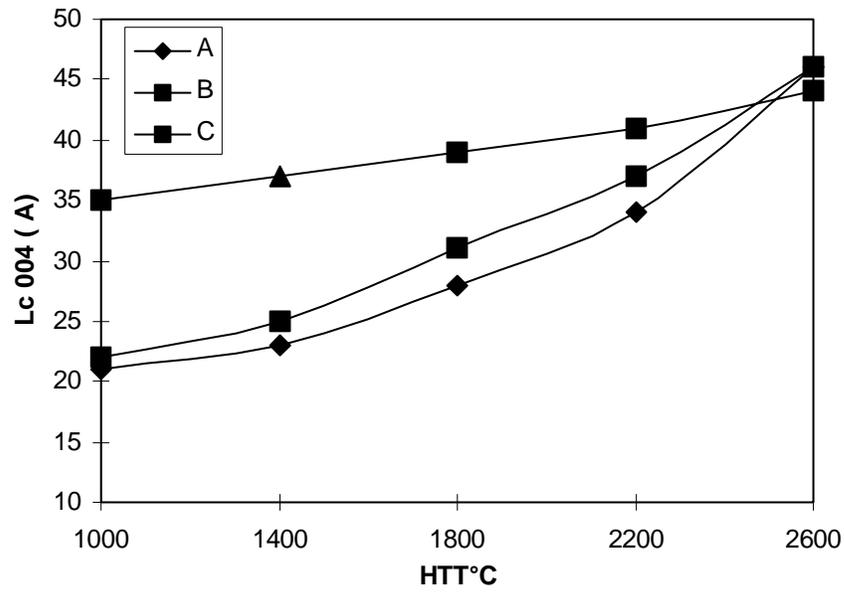


(a)

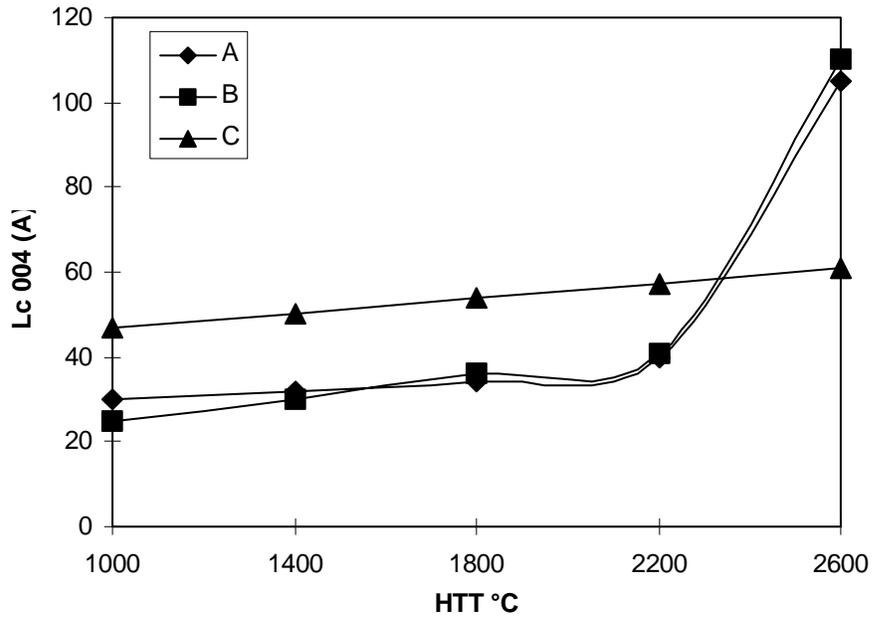


(b)

Figure1: Variation in interlayer spacing (a) as such composites  
(b) powdered composites with stages of heat treatment temperature

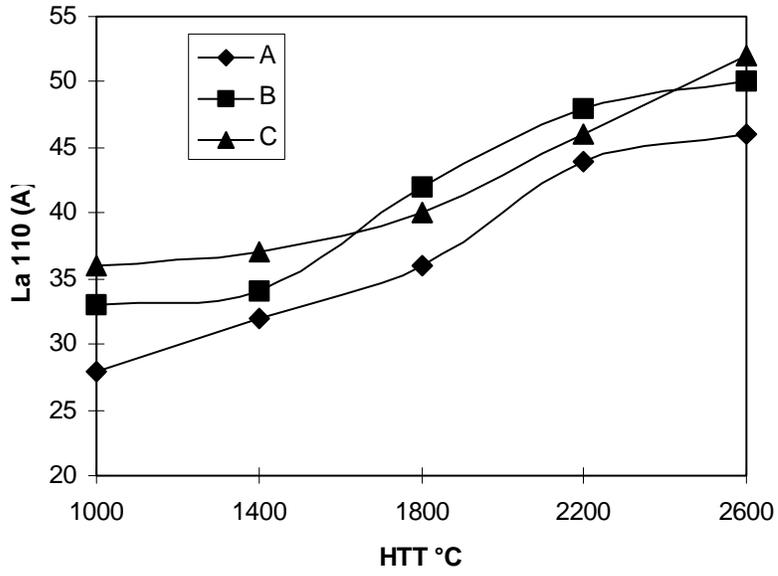


(a)

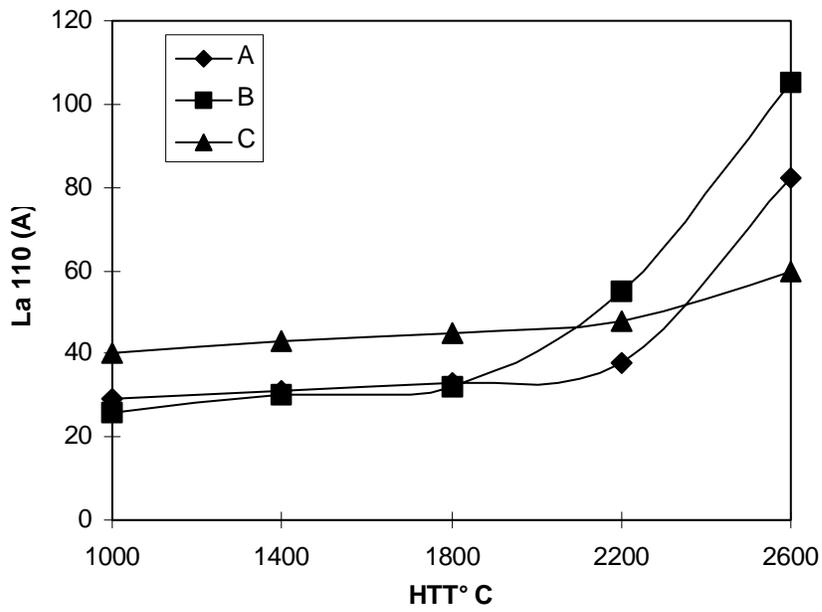


(b)

Figure1: Variation in Lc (004) (a) as such composites (b) powdered composites with stages of heat treatment temperature



(a)



(b)

Figure 3: Variation in La (110) (a) as such composites (b) powdered composites with stages of heat treatment temperature

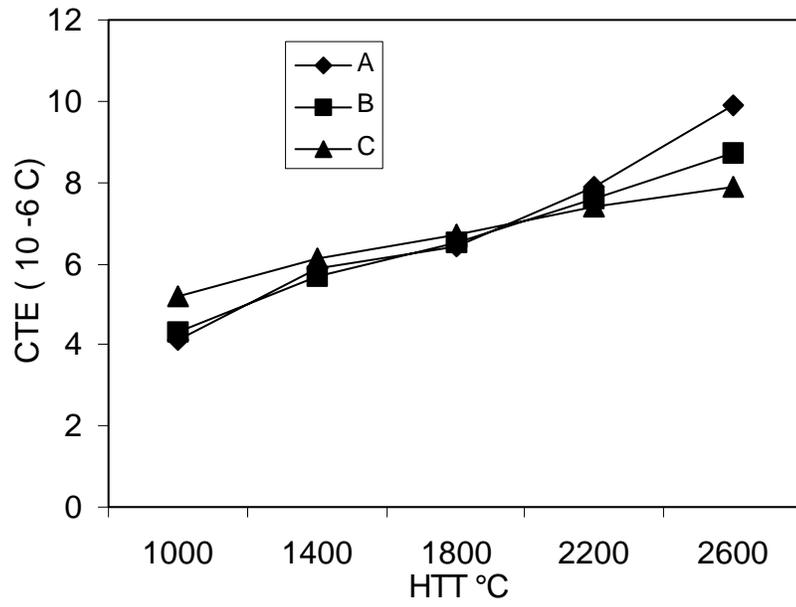


Figure 4: Variation in CTE in transverse direction in composites with stages of heat treatment temperature.

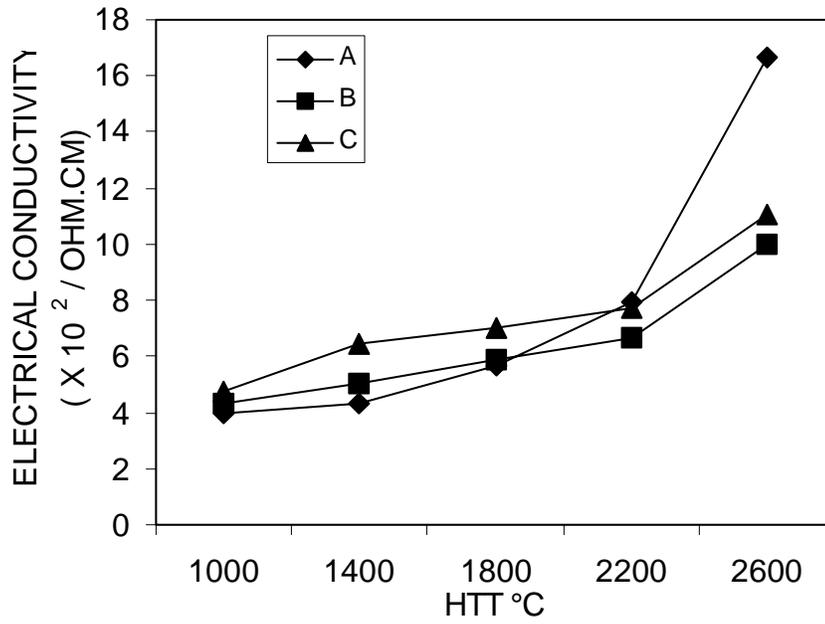


Figure 5: Variation in electrical conductivity with stages heat treatment temperature of composites.