



## INTERNATIONAL JOURNAL OF ENGINEERING SCIENCES & RESEARCH TECHNOLOGY

### Effect of HNTs and Organically Modified HNTs on the Properties of PEEK / LCP Blends in Presence of Tungsten Sulphide

Chapal Kumar Das<sup>1\*</sup>, Anirban Maitra<sup>1</sup>, Parthajit Pal<sup>1</sup>, Swindeerjeet Kalra<sup>2</sup>

<sup>\*1</sup>Materials Science Centre, Indian Institute of Technology Kharagpur, Kharagpur 721302, India

<sup>2</sup>Department of Chemistry, Dayanand Anglo-Vedic (D.A-V.) College, Kanpur, India

[chapal12@yahoo.co.in](mailto:chapal12@yahoo.co.in)

#### Abstract

Halloysite nanotube (HNT-OH) was modified organically using N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (APTMS). This modification converts HNT-OH directly to HNT-NH<sub>2</sub> and improves its dispersion in polar polymer matrix. We have also prepared tungsten sulphide powder and introduced it into the Poly Ether Ether Ketone /Liquid Crystalline Polymer blend along with modified Halloysite nanotube (MHNT). All the batches of this nanocomposite were prepared by melt blending. Dispersion of modified HNT in PEEK/LCP matrix was shown by high resolution transmission electron microscopy (HRTEM) and also by field emission scanning electron microscopy (FESEM). FESEM image shows a better fibril formation of LCP phase within PEEK matrix in presence of MHNT. Thermogravimetric analysis shows that the higher thermal stability of PEEK/LCP in presence of modified HNT. Storage modulus, tensile modulus and tensile strength were increased significantly with the incorporation of MHNTs. Tungsten sulphide powder acts as a lubricant here, which increases the high temperature processing properties of the blend.

**Keywords:** APTMS/Chelate/FESEM/HNTs /HRTEM/Nanocomposites.

#### Introduction

Field of polymer blends are growing up very rapidly now a day. These blends have been engineered for the enhancement of mechanical, thermal, electrical, barrier and other specific properties with a very affordable price. Polymer blends containing liquid crystalline polymer (thermotropic/Lyotropic) as one of the component are most attractive area of research recent days. Introduction of LCP to another base polymer system normally increases the processibility of the base polymer with a lesser difficulty in mixing period. It also reduces abrasion during high shear mixing in processing equipments.

Poly (ether ether ketone) (PEEK) is one of the most important engineering thermoplastic which is semicrystalline in nature with an excellent mechanical, thermal properties and chemical resistance properties. According to mechanical characteristics, it has got a high toughness value along with a tensile strength of around 90-110 MPa. These vast and exiting properties of PEEK results its extensive use in various load bearing application such as aerospace, marine sectors [1].

But the processing of PEEK alone is very difficult. It has got a melting temperature of 340°C. So it should

be processed somewhat higher temperature than 350°C and there appear the processing difficulties. To remove these difficulties, thermotropic liquid crystalline polymer has been blended with PEEK that reduces the system viscosity and improves the processability. During processing, the LCP phase forms a fibrillar structure in presence of PEEK matrix, resulting in the formation of self-reinforced composites [2, 7, 11-18].

Halloysite nanotubes (HNTs) have been increasingly used as one dimensional nanofiller in various field of nanocomposite research. Due to its excellent mechanical thermal stability, it is used as nanofiller to fabricate polymer nanocomposites. However, the main challenge is to disperse the polar nanofiller in a nonpolar/less polar polymer matrix uniformly. This paper focuses on the modification of HNTs organically to improve its miscibility and dispersion in PEEK polymer matrix. Organic modification also increases the interfacial interaction between the polymer and nanofiller with a very good stress transfer during mechanical loading and unloading. The surface smoothness was also improved by the addition of MHNTs. [3].

The second motivation was to develop PEEK/LCP/MHNTs nanocomposites and determine

the effect of MHNTs on thermal, mechanical, rheological, morphological characteristics of PEEK/LCP blend system. The effect of WS<sub>2</sub> on the properties of PEEK/LCP blend was also studied. It has been seen that WS<sub>2</sub> further reduces the viscosity and increases the processing characteristics. It further acts as a nanolubricant.

## Materials and methods

### Materials and Procedure:

The polymer used here was PEEK, whose industrial trade name is Victrex 380G, was supplied by ICI. The thermotropic liquid crystalline polymer was Vectra B 950, a copolymer based on 6-hydroxy-2-naphthoic acid (60%), aminophenol (20%) and Terephthalic acid (20%), obtained from Ticona (USA). The chemical structure of Vectra B is shown in Figure 1.

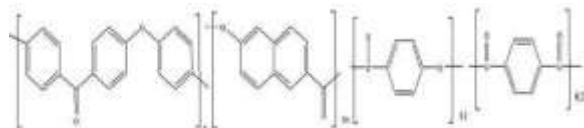


Figure 1: The chemical structure of Vectra B.

Halloysite nanotubes were obtained from Sigma-Aldrich (Germany) as powder form. N-(2-aminoethyl)-aminopropyltrimethoxy silane (APTMS) (Z6020, DOW Corning Corporation Midland, MI) was used as received without further purification. Hexadecyl amine and carbon di-sulphide and Tungsten oxide were obtained from Sigma-Aldrich (Germany).

### Preparation of Tungsten Sulphide:

In this procedure Tungsten oxide (W<sub>18</sub>O<sub>49</sub>) (20 mg) and hexadecylamine (1gm) were added to a 50 ml three necked round bottom flask equipped with a condenser and under inert gas atmosphere. The mixture was heated to around 100°C to remove water and then again heated to 250°C. After incorporation of carbon disulphide in the reaction mixture, the system is again heated to 350 °C. The initial light blue color solution was eventually become brownish. It reveals the formation of tungsten oxide.

### Preparation of modified HNTs (chemical modification):

HNT was modified by using N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (APTMS). Surface modification of Halloysite nanotube was done by the following way. At first, 6 ml of APTMS was dissolved in 150 ml of toluene. Then 2.0 g of the HNTs was added to the mixture and the resulting

suspension was dispersed ultrasonically for 30 min. The sonicated suspension was then refluxed at 100 °C for 20 h. The obtained powder was filtered and rinsed six times with fresh toluene to remove excess APTMS and then dried at 80°C temperature under vacuum for overnight. The powder was named as MHNTs [8, 9, 19-20].

### Preparation of Nanocomposites:

Before mixing, PEEK and LCP was dried in vacuum at 65°C and HNTs (both unmodified and modified) at 250°C for 10 hours. A sigma high-temperature internal mixture (Brabender) equipped with two Sigma type counter rotating rotors was used for the preparation of PEEK / LCP /HNTs/ WS<sub>2</sub> nanocomposites, at a temperature of 350°C with a rotor speed of 100 rpm. The formulations for the nanocomposite preparation were given in Table 1. After mixing, the composites were compression molded at 330°C and under a constant pressure of 15 MPa for 15 minutes and allowed to cool to room temperature under the same pressure.

Table 1: Sample codes and formulations for the nanocomposites

Sample code	PEEK	LCP	HNT (Wt. %)	MHNT (Wt. %)	WS <sub>2</sub> (Wt. %)
PL	70	30	-	-	-
PLH	70	30	1	-	-
PLM	70	30	-	1	-
PLHW	70	30	1	-	1
PLMW	70	30	-	1	1

## Characterization

**High Resolution Transmission Electron Microscopy (HRTEM).** High-resolution transmission electron microscopy (HR-TEM, JEOL 2100) analysis was performed on HNT, MHNTs and MHNTs / WS<sub>2</sub> filled samples, microtomed at room temperature, to observe the dispersion of nanofillers in the blend system at an accelerating voltage of 120 kV.

**Field Emission Scanning Electron Microscopy (FESEM).** A Carl Zeiss-SUPRA 40 FESEM with an accelerating voltage of 5 kV was employed to observe the surface morphology of the tensile fractured nanocomposites. A thin layer of gold was

sputtered on the fracture surface of the specimens for electrical conductivity.

**Thermogravimetric Analysis (TGA).** Thermo gravimetric analysis curves were recorded with a DuPont 2100 thermogravimetric analyzer. The TGA measurements were conducted with a heating rate of 10°C/ min under nitrogen atmosphere from 50 to 700°C.

**Dynamic Mechanical Thermal Analysis (DMTA).** Dynamic Mechanical analysis was performed for the nanocomposite samples using TA Instrument (DMA 2980 model) in single cantilever bending mode. The storage modulus ( $E'$ ), loss modulus ( $E''$ ), and  $\tan \delta$  were measured at a frequency of 1Hz from room temperature to 250°C and a heating rate of 5°C/ min.

**Mechanical Properties Study.** The tensile tests were carried out on dumb-bell-shaped samples using a Hounsfield HS 10 KS (universal testing machine); at room temperature with a gauge length of 35mm and crosshead speed of 5mm/min. Tensile values reported here were an average of the results for tests run on at least four specimens.

**Rheology.** Rheology study was carried out in a Capillary Rheometer (Smart RHEO 1000,CEAST) at 360°C, at different shear rates, to investigate the effect of LCP, HNTs, MHNTs and WS<sub>2</sub> on viscosity of PEEK/LCP blend.

## Results and discussions

### Field Emission Scanning Electron Microscopy (FESEM):

Surface morphology of the samples was observed by FESEM and the respective micrographs are shown in figure 2. From the first micrograph in figure 2(a), it was clear that the blend partner PEEK and LCP were not miscible in nature. Whereas from figure 2(b), after addition of HNTs the globular domain of LCP tends to form fibril shape but till few globules were present which were totally absent in case of modified HNTs incorporated nanocomposite; figure 2(c). This fibrillation further increases on incorporation of WS<sub>2</sub> in presence of modified HNTs. Here WS<sub>2</sub> takes the interfacial position between the polymer layers and also acts as lubricating agent. So slippage of polymer layers was observed in presence of WS<sub>2</sub> for PLW nanocomposite, figure 2d [23].

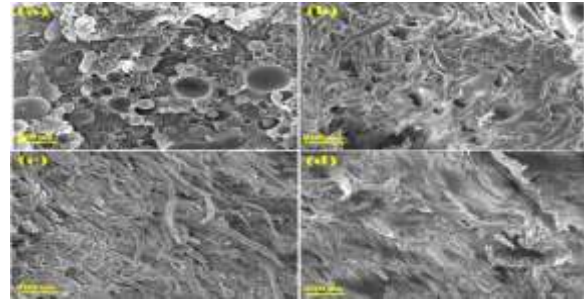


Figure 2: FESEM images of (a) PL and (b) PLH (c) PLM (d) PLMW.

### High resolution transmission electron microscopy (TEM):

Figure 3 shows the TEM micrographs, where the figure 3(a), 3(b), 3(c) represents the PLH, PLMH and PLW nanocomposites respectively. Agglomeration of nanofillers was observed in PLH nanocomposite, as HNTs were not able to overcome their Vander Waal force of attraction, but this interaction was got ridded when it was modified with APTMS. Hence a good dispersion of HNTs was observed in 3(b) micrograph [24]. Almost same thing was observed when WS<sub>2</sub> were employed along with modified HNTs. Figure 3(c) shows that WS<sub>2</sub> were present along with HNTs and they dispersed properly in the polymer matrix.

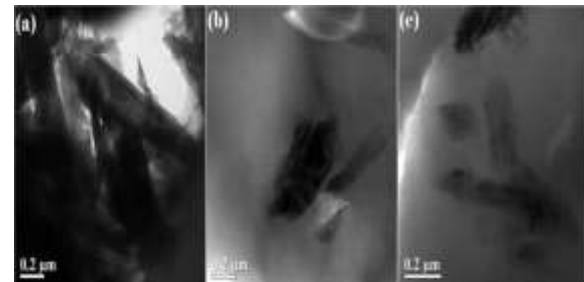


Figure 3: HR-TEM image of (a) PLH and (b) PLMH (c) PLW.

The probable reason for the WS<sub>2</sub> to remain with the HNTs could be the coordination bond. In modified HNTs, the surface contains some organic functional groups which have N atoms. Those N atoms can donate its lone pair to tungsten atom of WS<sub>2</sub> and create a chelate complex (fig-4) fulfilling its coordination number.

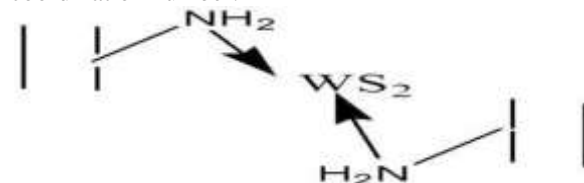
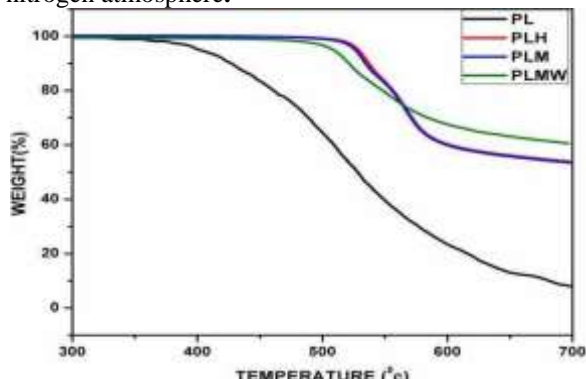


Figure-4 Probable structure of the chelate complex

**Thermogravimetric Analysis:**

To observe the effect of HNTs, MWNTs and WS<sub>2</sub> on the thermal properties of PEEK/LCP blend system; TGA was performed for the nanocomposites with same loading of the fillers and WS<sub>2</sub>.

Figure 5 shows the TGA weight (%) loss curve for the pure blend system and nanocomposites in nitrogen atmosphere.



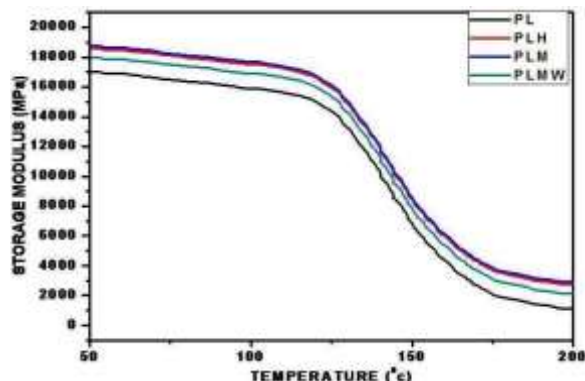
**Figure 5: TGA curves of PEEK/LCP/MHNTs/WS<sub>2</sub> nanocomposites**

All the nanocomposites show higher thermal stability as compared to the pure PEEK/LCP blend system without fillers. The onset degradation temperature of pure PEEK/LCP blend without filler was found to be 398°C (at 5.5% weight loss) which abruptly increases to 520°C (at 2% weight loss) with the incorporation of 1wt% HNTs [1]. The onset degradation temperature for MHNTs nanocomposites shows almost similar value as compared to HNT nanocomposites. The introduction of HNTs/MHNTs definitely reduces the chain flexibility and interchain slippage of the polymer matrix by imposing huge numbers of obstruction sites which reduces the thermal vibration of the C–C bond [21]. So the nanocomposites require much higher thermal energy for the degradation of the polymer chain which increases their thermal stability.

Presence of WS<sub>2</sub> along with MHNTs shows another important characteristic. In presence of WS<sub>2</sub> the thermal onset degradation temperature reduces to 470°C with 2% weight loss. The reason for these can be concluded that WS<sub>2</sub> was acting as a lubricant which again increases the flexibility and chain mobility of PEEK to some extent.

**Dynamic Mechanical Thermal Analysis (DMTA):**

Figures 6(a) and 6(b) represent the DMTA results. Figure 6(a) shows the variation of storage modulus with temperature for PEEK/LCP blend and its composites with MHNTs and WS<sub>2</sub>.

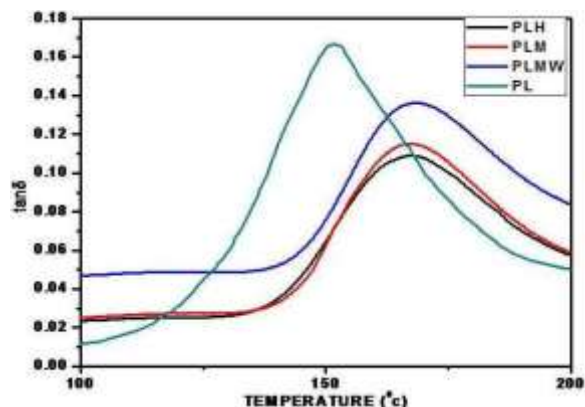


**Figure 6(a) shows the variation of storage modulus as a function of temperature**

The storage modulus curve shows an increase in stiffness of MHNTs nanocomposites with the incorporation of MHNTs into the PEEK/LCP blend, both below and above the glass transition temperature (around 143°C). The storage modulus for pure PEEK/LCP blend (PL) is the lowest compared to others [1]. The increase in storage modulus value to a higher zone for the MHNTs filled nanocomposites is attributed to the decrease in the polymer chain mobility. Also MHNTs act as a cross-linking site in between the LCP polymer chain and PEEK polymer matrix (which increases the stiffness of the nanocomposites).

The decrease in storage modulus of PLW nanocomposites than the PLM nanocomposites can be described that, the WS<sub>2</sub> acts as a lubricating agent which decreases the polymer chain rigidity and increases the polymer chain flexibility to some extent as compared to PLM.

The tan δ curve for the PEEK/LCP blend and nanocomposites is shown in Figure 6(b).



**Figure 6(b) shows the tan δ curve for the PEEK/LCP blend and nanocomposites**

As can be seen the glass transition temperature ( $T_g$ ) shifts to the higher value with the incorporation of MHNTs. The pure blend system shows a  $T_g$  of 151°C, which increases to 168°C for PLH and 161°C PLM nanocomposites, respectively. The increase in  $T_g$  can be concluded as to the immobilize action of MWNTs at high temperature.

With the incorporation of  $WS_2$ , the  $\tan \delta$  peak decreases as compared to the other nanocomposite system which suggests improved damping behavior of these nanocomposites with minimum heat buildup. The  $WS_2$  acts as lubricant here [15].

#### Mechanical Properties:

Tensile tests were performed for the compression molded samples to study the effect of introduction of HNTs, MHNTs and  $WS_2$  into the PEEK/LCP blend system.

The results of tensile tests were summarized in Table 2.

Table 2: Mechanical properties of nanocomposites

Sample code	Tensile Strength (MPa)	Elongation at Break (%)	Young's Modulus (GPa)
PL	75.8	22.4	6.1
PLH	87.3	8.2	8.2
PLM	87.9	8.8	8.1
PLMW	82.6	10.4	7.6

As we can see from the results Table-2, the young's moduli of the nanocomposites are somewhat greater than the PEEK/LCP blend. The Young modulus value of the PEEK/LCP blend was found to be 6.1 GPa and it is increased to 8.2 GPa due to the incorporation of 1 wt% of HNTs into the system.

The young modulus for MHNTs filled samples shows almost same value with HNT filled samples. For tungsten sulphide filled samples the young modulus decreases to some extent.

The tensile strength value of HNTs and MHNTs filled samples has been increased by 15.17% and 15.96 % respectively as compared to pure blend system. But the addition of  $WS_2$  again decreases the tensile strength as compared to HNTs and MHNTs filled samples.

The percentage of elongation value obtained for pure PEEK/LCP blend was 22.4, which decreases to 8.2 and 8.8 % for HNTs and MHNTs filled samples.

This might be due to increasing the rigidity and chain stiffness of the polymer chain. Addition of  $WS_2$  again

increases the elongation at break value as compared to HNTs and MHNTs filled samples. These may be due to increasing the chain flexibility to some extent.

#### Rheology:

Figure 7 shows the viscosity of PL/HNTs/MHNTs nanocomposites as a function of shear rate

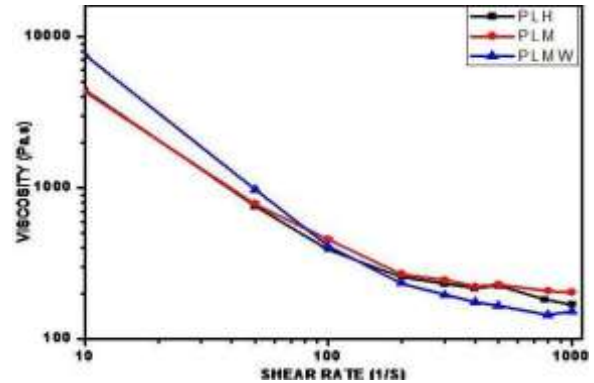


Figure 7: Variation of Viscosity with Shear rate.

The reduction of viscosity of PEEK/ LCP blend compared to PL/HNTs/MHNTs nanocomposites is mainly due to the ease of interfacial chain slippage between the two polymers. Blending LCP (30%) with PEEK increases the processability of PEEK at higher temperature. As from FESEM image (fig-2) we can draw some conclusion here that LCP forms fibrils at higher shear rate in presence of PEEK matrix, which enhances the chain slippage. So at higher shear rate region oriented structure of LCP make it easier to slide past each other which reduce the viscosity [22].

Figure 7 shows the effect of introduction of HNTs in the PEEK/LCP blend (PLH). Presence of HNT increases the viscosity of the blend at higher shear rate region.

Introduction of MHNTs in the PEEK/LCP blend (PLH) also increases the viscosity of the blend compared to PL/HNTs at higher shear rate region. This is an evidence of strong interfacial interaction between the HNTs and polymer matrix due to the presence of organic modification at the surface of HNTs.

Introduction of  $WS_2$  in the PEEK/LCP blend (PLW) decreases the viscosity of the blend compared to PL/HNTs and PL/MHNTs nanocomposites at high shear rate region. This clearly indicates that  $WS_2$  acting as a lubricating agent which help to decrease the viscosity in the higher shear rate region.

So, we can conclude that  $WS_2$  probably positioned at the interfacial boundary. HRTEM images (fig-3) also reveal that  $WS_2$  positioned at the surfaces of MHNTs that makes ease of processing.

#### Conclusion

PEEK/LCP/MHNTs and PEEK/LCP/MWHNT/ $WS_2$  nanocomposites were prepared by melt blending process.

Rheology Characteristics shows that WS<sub>2</sub> in presence of MHNTs act as a lubricating agent which reduces the viscosity of PL/MHNTs/WS<sub>2</sub> as compared to the PLM nanocomposites. Modification of HNTs by large chain APTMS, shows a very good dispersion of the nanofiller in the PEEK/LCP blend. Hence the interfacial adhesion and the ability to transfer the stress between the filler and the matrix are enhanced. In the blend system, as showed by HR-TEM, The fibrillation of LCP occurs in presence of MHNTs. It is a very good evidence for the better processibility of PEEK in presence of LCP and WS<sub>2</sub> at higher temperature.

### Acknowledgments

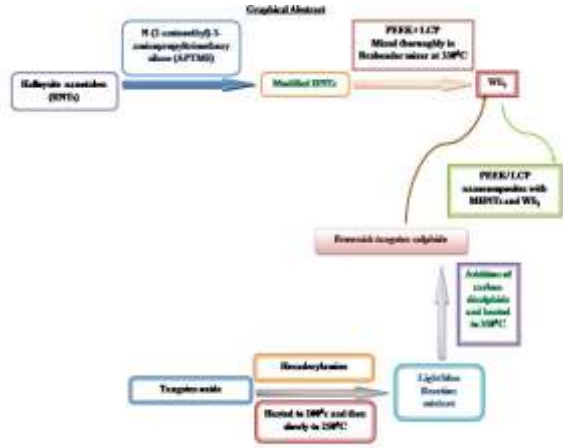
This work was supported by the Indian Institute of technology Kharagpur. West Bengal - 721302, India. I must thank to my research supervisor, all the co-workers and colleges for their great contributions for the studies covered in this paper: Professor C.K.Das as a research supervisor (Materials Science Center, Indian Institute of Technology, Kharagpur 721302, India), Swinderjeetsingh Kalra, (Department of Chemistry, Dayanand Anglo-Vedic (D.A.V.) College, Kanpur, India).

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**Author Bibliography**

	<b>Parthajit Pal (Second author)</b> Research scholar (IIT Kharagpur) M.Tech (Materials Science and Engineering). Email: <a href="mailto:pal.p85@gmail.com">pal.p85@gmail.com</a>
	<b>Swinderjeet Singh Kalra (Third Author)</b> Department of Chemistry, D. A-V College Kanpur 208001, India E-mail: <a href="mailto:sskdav@rediffmail.com">sskdav@rediffmail.com</a>

	<b>Prof. Dr. Chapal Kumar Das. (Corresponding author)</b> PhD (IIT Kharagpur). Professor in Materials Science centre, IIT Kharagpur. Kharagpur-721302, West Bengal. My PG teaching and industrial research experience is of 42 years. I have also published more than 300 papers in journals/books of repute and presented 40 papers in national and international conferences. Email: <a href="mailto:chapal12@yahoo.co.in">chapal12@yahoo.co.in</a>
	<b>Anirban Maitra (First author)</b> Research scholar (IIT Kharagpur) B.Sc(Cheistry), M.Tech (Materials Science and Engineering). Email: 1. <a href="mailto:anirbanm1212@gmail.com">anirbanm1212@gmail.com</a> 2. <a href="mailto:rajumaitra1234@gmail.com">rajumaitra1234@gmail.com</a>