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Synthesis and Antibacterial Application of Nanosized Polyethylene oxide - Iodine Complex by Solid - Vapor Reaction

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ABSTRACT

An eco-friendly reaction between polyethylene oxide (PEO) and iodine vapor has been studied on microslide. Growth kinetics was studied by measuring an increase in weight of the material as a function of time and found to increase non- linearly. Random distribution of iodine in the complex was observed by SEM-EDS studied. UV-visible absorption spectroscopy revealed a new peak at ~ 300 nm due to interaction of iodine with the polymer. Powder x-ray diffraction (XRD) patterns of the reactant and reactant product were compared. Both were found different. Crystallite size of the complex was calculated by using Debye Scherrer formula and found in the range 20-30 nm. The complex was thermally less stable than the reactant. An enhancement in the electrical conductivity was observed on complexation with iodine. SEM results also showed morphological change on complexation. TEM studies revealed the formation of nanosized (<10 nm) complex, in agreement with XRD results. Antibacterial application of the complex was investigated on blood agar containing gram negative bacteria *E. coli* and no bacterial growth was observed in its presence. It is found to be highly effective against the bacteria *E. coli*.

Keywords: Poly ethylene oxide, solid-vapor reaction, antibacterial application

I. INTRODUCTION

Much attention has been given to the development of synthetic routes to hybrid materials composed of organic and inorganic components [1,2]**.** Organic-inorganic hybrids are presenting novel properties usually not exhibited by either of the component materials. Surfaces containing polyethylene oxide are interesting biomaterial because they exhibit low degrees of protein absorption and cell adhesion. Solid state reactions provide the synthesis, structure and properties of the solid phase materials which have commercial and industrial importance. The understanding and control of chemical reaction at interface (solid/ gas, liquid/gas and solid/ liquid) are central to many modern technology and environmental phenomena. Avnir etal [3-5] have reported that the surfaces of most materials are fractal on molecular scale. Several iodination reactions in the solid state have been investigated in the past by Rastogi etal [6-8] and Agrawal etal [9]. Molecular iodine plays a vital role in polymer science. A unique feature of molecular iodine is its ability to bind to polymeric materials. Molecular iodine is an inexpensive, easily available and environmentally benign catalyst [10]. Halogenation is an integral part of organic reactions that involve the use of molecular iodine. It is extended to pharmaceutical and medical applications, disinfection, catalysts, doping agent for polymers and stabilizers, germicidal activities. However, halogenation of polymers was confined mainly to chlorination and bromination. Molecular iodine reacts easily with electron rich molecules via a charge transfer mechanism to form charge transfer complexes. Ignatova etal [11] have reported the preparation of poly (ethylene oxide) / polyvinyl pyrrolidone) - iodine complex and its application as antimicrobial wound dressing material. Iodine sorption by polyurethane and melamine – formaldehyde foams was studied by Wang etal [12] and antimicrobial activity of polymer coated

with iodine complex polyvinyl was reported by Kristinsson etal [13].

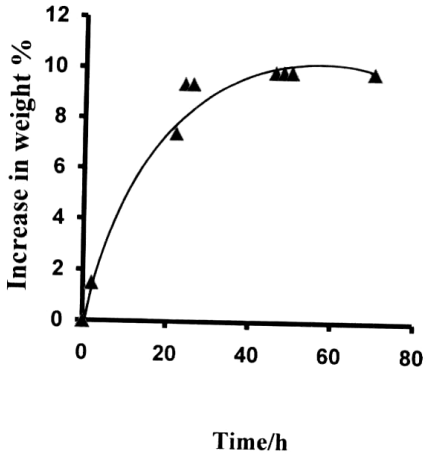
In this communication we report synthesis of nanosized polyethylene oxide – iodine complex by solid vapor reaction on microslides. The main objective of this investigation is to investigate the interaction of iodine vapor with a non-ionic water soluble biocompatible polyethylene oxide to form a nanosized polyethylene oxide – iodine complex by solid - vapor reactions on microslides. Kinetics of the reaction will be studied by measuring increase in weight of the material as a function of time. The reaction product will be characterized by powder x-ray diffraction, UV-visible spectroscopy, SEM, TEM, SEM-EDS and electrical conductivity measurements. Antibacterial activity will be studied on blood agar culture plate containing gram negative bacteria *E. coli*.

II. METHODS AND MATERIAL

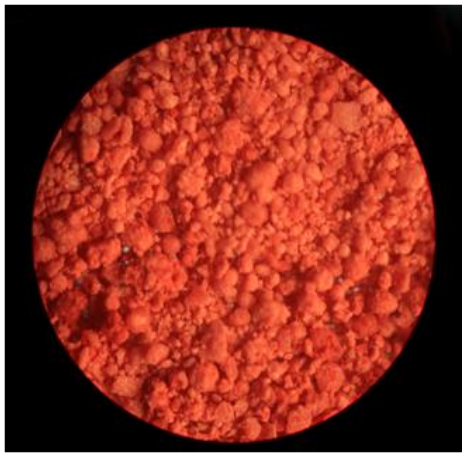
Polyethylene oxide MW 1,00,000 (Alfa Ae Sar), iodine, peptone (s d fine –chem. limited , India), nutrient agar (Qualigens) were used as such

1. Synthesis and measurements

Reaction between non-ionic polyethylene oxide and iodine was studied by solid – vapor reaction on a micro slide. Polyethylene oxide was powdered and a solid thin film was prepared on the slide. It was pressed by another glass plate to make the surface uniform. The upper plate was then removed and put in a glass desiccator containing solid iodine in such a way that iodine crystal might not come in contact with the slide. As soon as the iodine vapor comes in contact with the surface of polyethylene oxide, reaction started. Kinetics of the reaction between solid polyethylene oxide and iodine vapor was studied by measuring the weight of material on the micro slide. Percent increase in weight was plotted as a function of time as shown in **Figure.** 1(a). At the end of the reaction, microphotograph of the product was taken and shown in **Figure.** 1(b). Reaction between 1% aqueous PEO and iodine vapor was also studied on a microslide. 1 mL PEO solution was spread over the microslide and put in the iodine chamber. Micrograph was taken and shown in **Figure.** 1(c).



(a)



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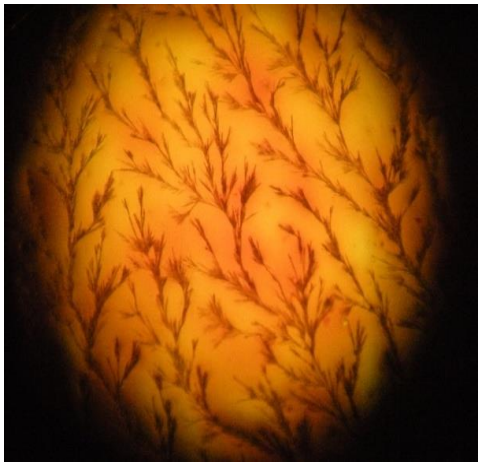
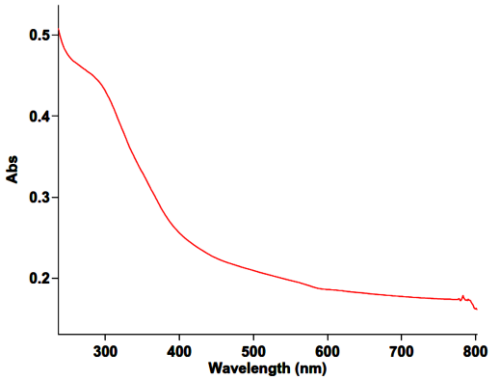


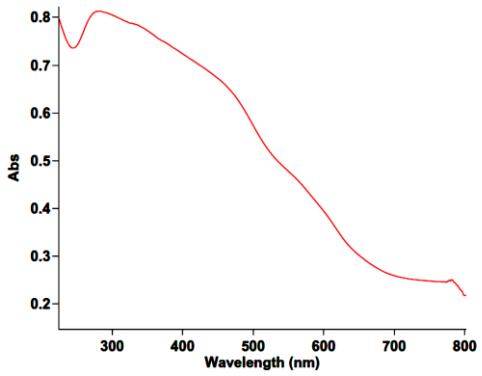
(c)

Figure. 1. (a) Plot of % increase in weight as a function of time at 25.0 ± 0.1ºC and (b, c) microphotographs of reaction product obtained in the solid vapor reaction and 1% aqueous polyethylene oxide solution with iodine vapor respectively.

UV –visible spectra of solid polyethylene oxide and its reaction product with iodine vapor were taken using UV151109A-02 from SAIF Cochi. Results are shown in **Figure.** 2.



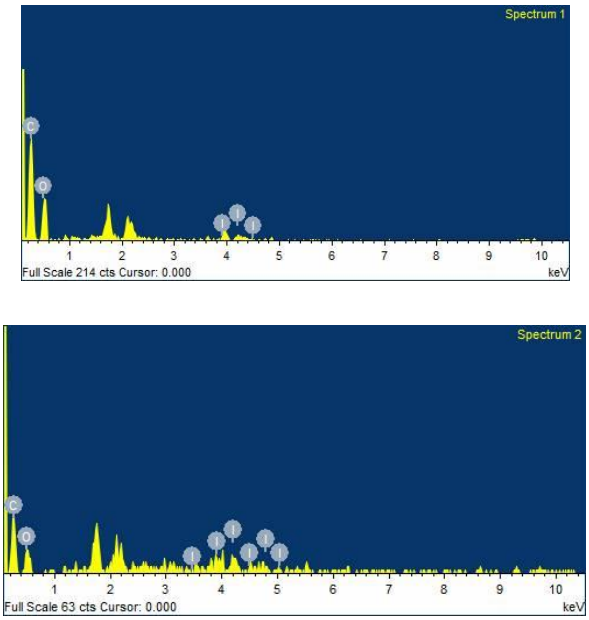
(a)



(b)

Figure. 2. UV-visible spectra of (a) polyethylene and (b) its reaction product with I_2vapour.

SEM-EDS studies of the reaction product were carried out using EDS model 5-ADD0048 at the resolution 5.9 KeV from central Instrument Facility, IIT BHU. Results are shown in **Figure.** 3 and recorded in Table 1.



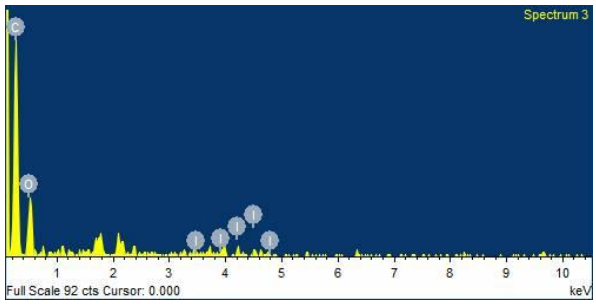
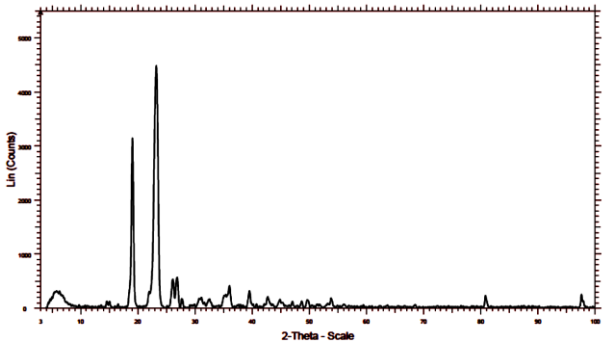


Figure. 3. SEM-EDS images and the corresponding spectrum of polyethylene &I_2reaction product.

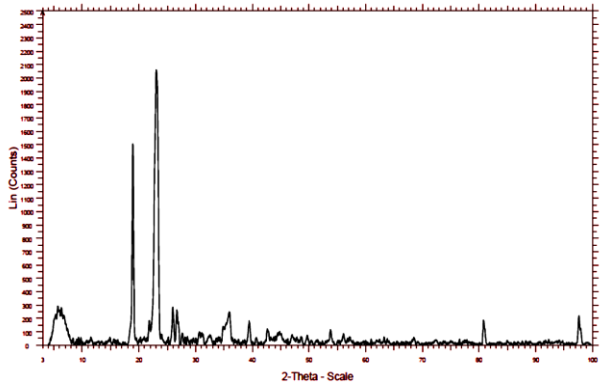
Table 1. SEM – EDS data for polyethylene oxide-iodine reaction product.

	Spectrum 1		Spectrum 2		Spectrum 3	
Element	Weight %	Atomic %	Weight %	Atomic %	Weight %	Atomic %
C K	57.46	66.84	72.85	82.63	62.77	71.10
O K	37.31	32.58	19.42	16.53	33.52	28.50
I K	5.23	0.58	7.73	0.83	3.71	0.40
Totals	100.00		100.00		100.00	

Powder x-ray diffraction patterns of polyethylene oxide and its complex with iodine were taken in the 2θ range 3-100º. Results are shown in **Figure.** 4 and recorded in Table 2.



(a)



(b)

Figure. 4. Powder x-ray diffraction patterns of (a) polyethylene and (b) the reaction product.

Table 2. Powder X- ray diffraction data for Polyethylene oxide – iodine complex

2θ (degree)	FWHM (degree)	Raw area (cps x degree)	Crystallite size (nm)
80.888	0.422	1.196	20.46
22.963	0.750	27.47	28.66
18.821	0.284	8.785	28
39.405	0.368	1.2	35.68
26.616	0.491	1.973	21.80
25.891	0.312	1.782	28.04

SEM and TEM images of the reaction product were taken using Scanning Electron Microscope (Model JSM-7600F) and Philips Transmission Electron Microscope (Model CM 200) respectively. Results are shown in Figs. 5 and 6.

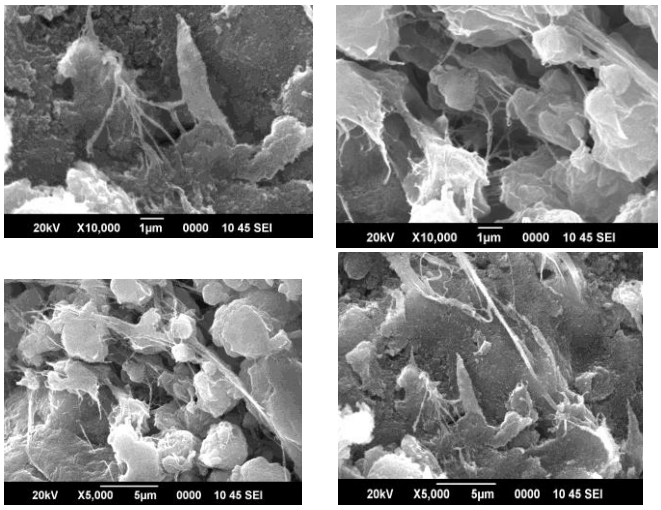
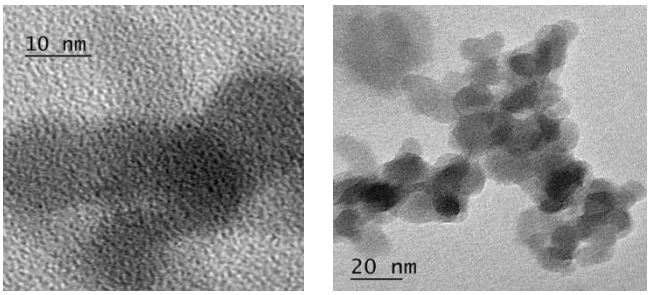


Figure. 5. SEM images of polyethylene oxide and the reaction product.



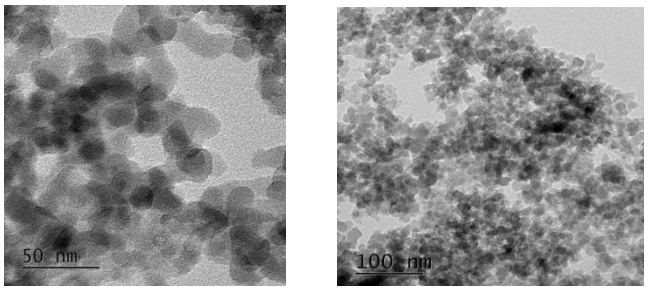


Figure. 6. TEM images of the reaction product.

Thermogravimetry (TG) and derivative thermogravimetry (DTG) results for solid PEO and its complex with iodine were obtained from STIC Cochin and results are shown in **Figure.** 7.

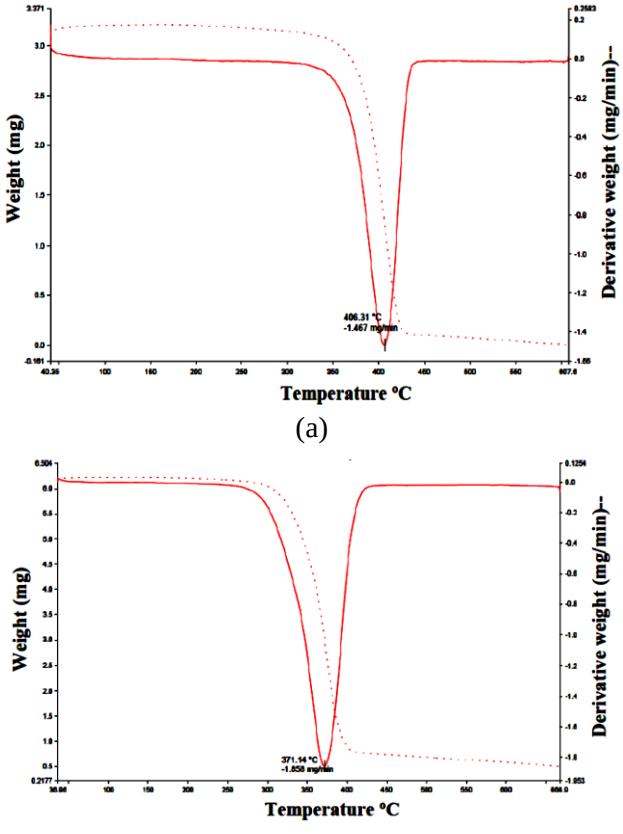


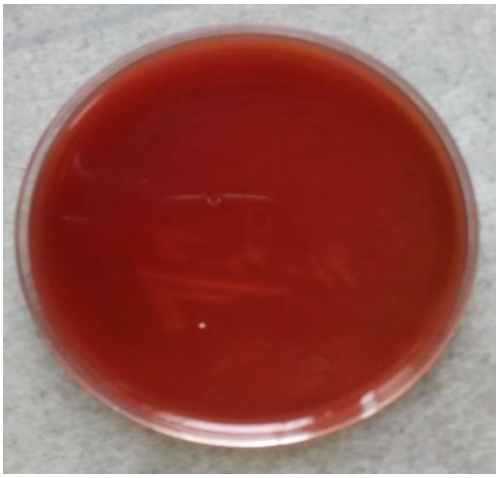
Figure. 7. TG/DTG curves for (a) polyethylene oxide and (b) the reaction product.

2. Antibacterial studies

Antibacterial activity of polyethylene oxide and polyethylene oxide -iodine complex was investigated on blood agar culture plate. Gram negative bacteria *E. coli* was selected for this study. The medium used was nutrient agar (28g/L) enriched with 10% sheep blood (blood agar medium). 15 mL of nutrient medium was poured in a disposable sterilized Petridis (90 mm

diameter) and kept at room temperature for solidification. Moist surface of the culture plate was dried in an incubator maintained at 37±0.1°C for about an hour. Experimental technique as described earlier by Das etal [14] was employed. About 0.1 mL of bacterial culture was inoculated into 2mL of peptone water containing an equal amount of polyethylene oxide and polyethylene oxide-iodine composite separately and incubated for 3 hours. A loop full of this culture broth having bacteria *E. coli* in lag phase was inoculated on the surface of the culture plate and incubated at 37±0.1 °C for 24 hrs. In order to check the reproducibility, three plates of each sample were simultaneously prepared. Growth patterns of *E. coli* on the blood agar surface are shown in **Figure.** 8. Bacterial count was measured in each case using Sonar (India) colony counter machine.

(a)



(b)

Figure. 8. Growth patterns of *E. coli* on the surface of blood agar containing polyethylene oxide (a) and its polyethylene oxide – iodine complex at 37.0 ± 0.1 ºC (b).

III. RESULTS AND DISCUSSION

An eco- friendly reaction between solid polyethylene oxide and iodine vapor was studied on microslides. It is a solvent free reaction which allows the reactants to chemically react in the absence of any solvent. Iodine treatment changed the color of polyethylene oxide from colorless to light brown reaction product as shown in **Figure.** 1b. UV- visible spectra of solid polyethylene oxide and its iodine complex are shown in **Figure.** 2. The product exhibited an absorption peak at ~ 300 nm [**Figure.** 2b] which was not observed in the spectrum of polyethylene oxide [**Figure.** 2a]. The colour change is due to the interaction of polyethylene oxide with iodine. It may be assumed to have the iodine randomly distributed among its ether oxygen. The random distribution of iodine in the complex is indicated in SEM-EDS spectra as shown in **Figure.** 3 and recorded in Table 1. Growth kinetics of the reaction was monitored by measuring the increase in weight of polyethylene oxide as a function of time. Percent increase in weight of the material was plotted as a function of time as shown in **Figure.** 1a. It is found to increase non-linearly. It increased first sharply then attained almost a constant value. % iodine uptake was calculated by using a relationship and found to be ~ 10 % .

$$\%\ I_2\ \text{uptake} = \frac{\text{Increase in weight of the PEO}}{\text{Original weight of PEO}} \times 100$$

Powder x-ray diffraction patterns of polyethylene oxide and its iodine complex are shown in **Figure.** 4 and data are recorded in Table 2. Results revealed that both the materials were different. Structural behavior was studied by SEM. Results shown in **Figure.** 5, also indicated that both have different morphologies.

The crystallite size (t) of the reaction product was calculated using Debye Scherrer formula

$$t = \frac{0.9\lambda}{\beta cos\theta} . \frac{360}{2\pi}\ \text{Å}$$

where λ = wave length of x-ray radiation
ß = full width at half maximum
θ = Bragg's angle

The average crystallite size was found in the range 20 - 30 nm. TEM results are shown in **Figure.** 6. The size of the reaction product lies in the nano size range (< 10

nm). It is in agreement with the XRD results. Thermograms of PEO and its complex with iodine are shown in **Figure.** 7. DTG results showed a remarkable difference in its thermal stability. PEO and its complex showed peaks in DTG curves at 406.31 and 371.14 ºC respectively. It is evident that PEO is thermally more stable than its iodine complex. DTA results showed an endotherm at 410 ºC with ΔH = 105.2221 J/g in case of PEO which was absent in its iodine complex.

Electrical conductivity of 1% aqueous solutions of PEO and its complex was measured with the help of a conductivity meter. Electrical conductivity of polyethylene oxide – iodine complex was found 4.28 x 10^{-4} S/cm, higher than that of PEO (3.88 S/cm). An enhancement in the conductivity value is due to interaction of iodine with the polymer. Reaction between 1% aqueous solution of PEO and iodine was also studied on microslides for comparison. A fractal like geometry was observed in this case. Microphotographs was taken and shown in **Figure.** 1c. Antibacterial activity of polyethylene oxide and its complex with iodine on gram negative bacteria *E. coli* was investigated on blood agar plates. Results are shown in Figure 8. It is observed that the polyethylene – oxide complex completely inhibited the growth of *E. coli.*

IV. CONCLUSION

1. Nanosized polyethylene oxide – iodine complex was synthesized by solid – vapor reaction.
2. A light brown reaction product was obtained. Kinetics of the reaction was studied by measuring an increase in weight of the material on the microslide.
3. The reaction product was characterized by powder x-ray diffraction, UV-visible spectroscopy, SEM and TEM studies.
4. XRD and TEM studies revealed the formation of nanosized complex.
5. SEM-EDS results revealed random distribution of iodine in the complex.
6. The complex is found to be highly effective against the bacteria *E. coli*.
7. Upon complexation several new findings such as colour formation, antibacterial activity and electrical conductivity enhancement were observed.

V. ACKNOWLEDGEMENTS

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