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Comparison of the photocatalytic degradation of polyvinyl chloride and polystyrene with zinc oxide semiconductor catalyst under tropical sunlight

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ABSTRACT

Composite films have been prepared by dispersing zinc oxide semiconductor particles in the matrix of Polyvinyl chloride (PVC) and Polystyrene (PS). Photocatalytic degradation of the films has been studied under tropical sunlight in presence of air and water. The degradation of the two polymers has been compared. Time-weight loss data have been collected and in both cases, the degradation was observed to follow pseudo first order kinetics. The films were characterized before and after irradiation by SEM and FTIR-ATR to study the surface morphology and the possible degradation products respectively. Increase in zinc oxide loading increased the rate and extent of degradation. A model has been suggested for the degradation reaction and the experimental data fit very well to the kinetic model.

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KEYWORDS

Polyvinyl chloride (PVC);
Polystyrene (PS);
Zinc oxide;
Photocatalytic degradation;
Rate equation.

INTRODUCTION

Polyvinyl Chloride (PVC) is a very popular commodity plastic widely used worldwide as a building material. Polystyrene (PS) or expanded polystyrene (EPS) are generally used as packaging foams and as internals of railway coach. These plastics, being inert and non-biodegradable, do not decompose in landfills when they are disposed as waste. In countries like India, these waste plastics are very often thrown away in the open sewerage or water bodies and as such eventually interfere with the drainage system. The main route to dispose of such wastes has still been incineration, which releases a lot of toxic by-products. The common methods of degradation of polymers and associated chemistry are available in Hamid^[1]. Gotlib et al.^[2] re-

ports an elaborate chemical analysis of the composition of the gases emitted during incineration of PVC. Thermal or catalytic degradation of waste plastics into fuel oil has not yet succeeded into large scale commercial use because the process not only requires a very high temperature, but also asks for a suitable catalyst that can guarantee a narrow distribution of hydrocarbons. Consequently exploration of the new technologies to treat these waste plastic materials is the need of the hour.

Heterogeneous photocatalytic oxidative degradation of plastics is possible in the solid phase using semiconductors in presence of air, water and UV/visible lights under moderate conditions of temperature and pressure. In most of the cases, TiO₂ is the semiconductor used with the plastic in the form of a composite film^[3-6].

However ZnO is comparatively a less explored and cheaper semiconductor though the band-gap energy is nearly the same as that of TiO₂ and it is somewhat more active in the visible region. A few researchers have reported better photocatalytic activity of ZnO compared to TiO₂^[7-9].

The recent reports mentioned above describe the use of Degussa TiO₂ as the photocatalyst for oxidative degradation of both PVC and PS. Cho and Choi^[5] listed a series of reaction as the possible degradation pathways for PVC. Zhang et al.^[10] used tungstophosphoric acid as the photocatalyst irradiated the impregnated films with both UV and visible light to achieve a high degree of degradation. Shang et al.^[11] reported 7% degradation of Cu-phthalocyanine sensitized oxidation of PS-TiO₂ composite film under fluorescent light (310-750nm) radiation in 250 hours. The same authors reported 22% degradation of PS-TiO₂ composite film using UV lamp (254nm) in 150 hours. Solid phase photocatalytic degradation of PS with Fe(II)-phthalocyanine-modified-TiO₂ has been reported by Fa et al.^[12]. They have reported 82% degradation with after 480 h irradiation under 30kW (2mW/cm²) artificial UV radiation and 20% degradation after 12 days irradiation to a solar light of 3.8 mW/cm². In our two previous works^[13,14], we reported dye-sensitized photocatalytic degradation of PVC and the mechanistic model of the same respectively. We obtained about 20% degradation in 2 hours.

It was envisaged that if solar energy could be employed, the photocatalytic degradation process would be the most economical one. India is a tropical country and the daily average solar energy incident over India varies from 4 to 7 kWh/m² with about 2300 - 3200 sunshine hours per year, depending upon location^[15,16]. It is thus especially desirable that environmental remediation problems in a tropical country like India may be addressed economically with the help of solar energy rather than employing a relatively costly power generated from fossil fuel. Robert et al summarized the various aspects of water detoxification using solar photocatalysis^[17]. Reports are available for oxidative degradation of dye pollutants using solar radiation^[18] and reduction of heavy metals using solar photocatalysis^[19]. However reports on solar photocatalytic degradation of plastics are not much.

In the present work, we aimed at degradation of PVC and PS under solar radiation (in the month of March in east coast of India where average intensity of radiation within the period of experiment remains at about 59klux) in presence of air and water with ZnO dispersed in the polymer matrix. There are two reasons for choosing such experimental conditions. Photocatalytic oxidation requires oxygen and water for generation of hydroxyl radical and when thrown into water bodies, the waste plastics are exposed to the ambient conditions. The work is under progress and in this report we would like to point out the comparative degradation of the two polymer-semiconductor composites with otherwise same experimental conditions.

EXPERIMENTAL

The polymers

PVC beads received from Reliance Industries Limited, India; trade name – Reon, grade 67-01; *k*-value - 67±1; free from plasticizers. Details have been given elsewhere^[13]. Polystyrene beads are from Haldia Petrochemicals Ltd. Molecular weight range is 4000-15000.

The semiconductor catalyst

ZnO, GR grade, LOBA Chemie, India; mean particle size - 146.7 nm (Zeta Plus, Brookhaven Instrument Corporation); BET surface area - 3.23 m²/g.

Solvent

Cyclohexanone, SRL India; boiling range 154 to 156°C.

Preparation of polymer-ZnO composite films

A solution of the polymer in cyclohexanone (3 g polymer in 150 g solvent) with requisite quantities of ZnO was sonicated for 30 min to prepare a uniform suspension. For dissolving polystyrene beads, the polymer-solvent mixture was heated to 50°C. The film was made by casting the liquid on a borosil tray in case of PVC and on aluminium foil in case of PS. The average film thickness was 100 µm for PVC and 80-350µm for PS, measured by Mituyido digital micrometer IP 65. The average size of sample was 2.5cm × 5.5 cm.

Experimental set up and procedure

Figure 1 shows the set up for the solar experiments.

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Here the samples have been placed horizontally so that solar radiation can directly hit the sample through the quartz top - plate. Oxygen was supplied by sparging air in the water-filled reactor. The optical intensity of solar radiation was measured using a digital lux meter (Metriavi series 1300). The data in the photometric unit (klux) however has been alternatively reported in the radiometric unit (W/m^2) using empirical conversion factors provided by Thimijan and Heins (1983)^[20]. The

intensity was approximately constant at 59klux ($237.18 \text{ W}/\text{m}^2$) within the period of experiment. Air was bubbled through the water in the reactor for supplying oxygen.

Most of the experiments were repeated at least twice and the standard deviation was within 3%.

The loss of weight of the film was accurately measured from time to time (Sartorius Model BT224S, 0.1 mg accuracy) to monitor the progress of degradation.

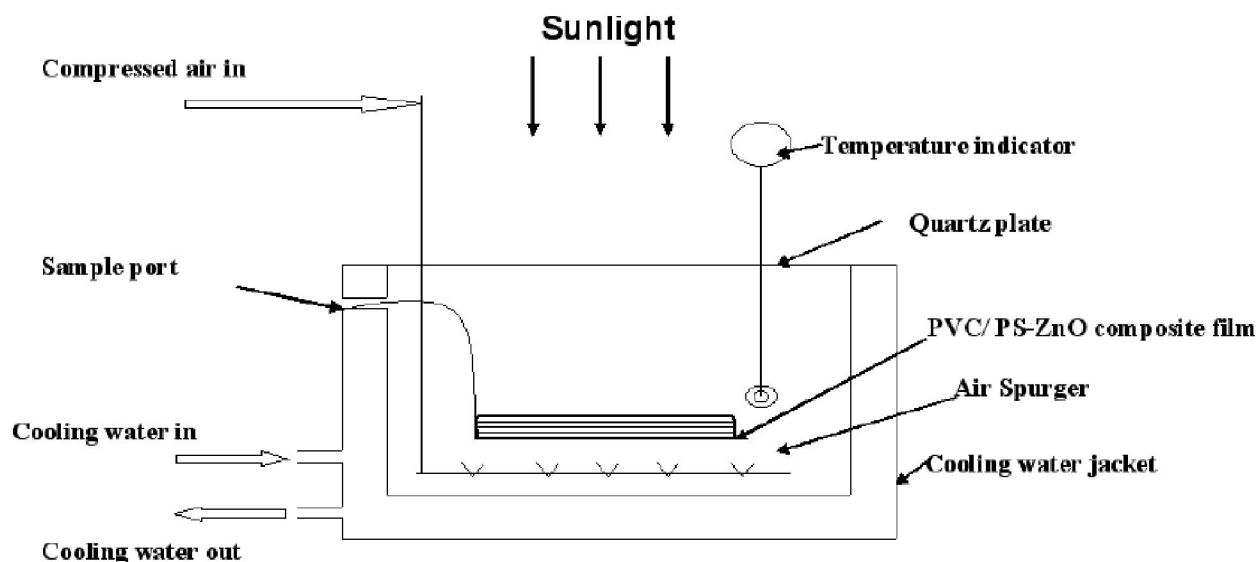


Figure 1 : Experimental set-up for the solar photocatalytic degradation of polymer composite film

RESULTS AND DISCUSSIONS

Characterization of the polymer-ZnO composite films

Figures 2a(i) and (ii) shows the surface morphology of the PVC-ZnO composite film before and after irradiation and figure 2b(i) and (ii) shows the same for

the PS-ZnO composite film. PVC-ZnO film was observed to develop puckered parallel channels after irradiation. After irradiation, PS-ZnO film had developed very few pin-holes. But grossly, the PS-ZnO composite film has undergone negligible morphological change on solar irradiation. The basic surface characteristics of the two composite films are different due to their different chemical and structural properties.

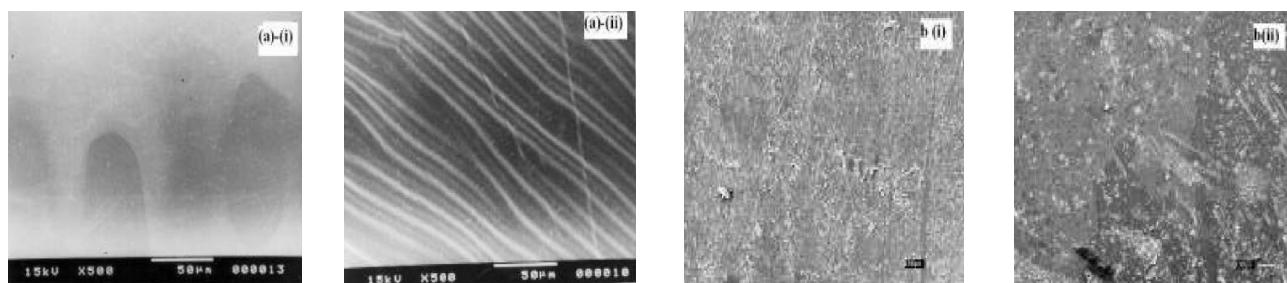


Figure 2 : Scanning electron micrograph for (a) PVC-ZnO film (i) before (ii) after irradiation (b) PS-ZnO film (i) before (ii) after irradiation

Figures 3a shows the FTIR-ATR spectra for the unexposed and exposed PVC-ZnO composite film.

The peaks around 3400 cm^{-1} present in the exposed PVC film represent surface hydroxyl groups with typi-

cal polymeric association. Intensity of peak around $1650\text{--}1700\text{ cm}^{-1}$, indicating alkene-linkage of PVC, decreases from unexposed to exposed film. This suggests breakage of the double bond present in the PVC. A new peak around 1200 cm^{-1} suggests carboxylic acid. Peaks within $800\text{ to }1000\text{ cm}^{-1}$ indicate carbonyl group (aldehyde or ketone). Figure 3b shows the FTIR-ATR spectra for unexposed and exposed PS-ZnO film. Characteristic peaks of PS were obtained at 695 cm^{-1} , $\sim 1493\text{ cm}^{-1}$, $\sim 3000\text{ cm}^{-1}$ and at $\sim 3500\text{ cm}^{-1}$ in both exposed and unexposed films. These are indicative of aromatic compounds with alkyl/ alkane

side chain. Intensities of all the mentioned peaks were found to decrease by 50% on an average after irradiation. Peak at $\sim 1170\text{ cm}^{-1}$ indicates a helical structure of the PS chain; decrease in its intensity suggests the straightening of the chain. A few new peaks appeared after irradiation in the range $800\text{--}1000\text{ cm}^{-1}$, which are indicative of side-chain aromatic aldehydes. A new peak at around 1385 cm^{-1} suggests generation of aryl carboxylic acid. Peak at $\sim 3734\text{ cm}^{-1}$ indicates presence of free --OH group. All these observations suggest oxidative breakage of PVC-ZnO and PS-ZnO composite films by solar radiation.

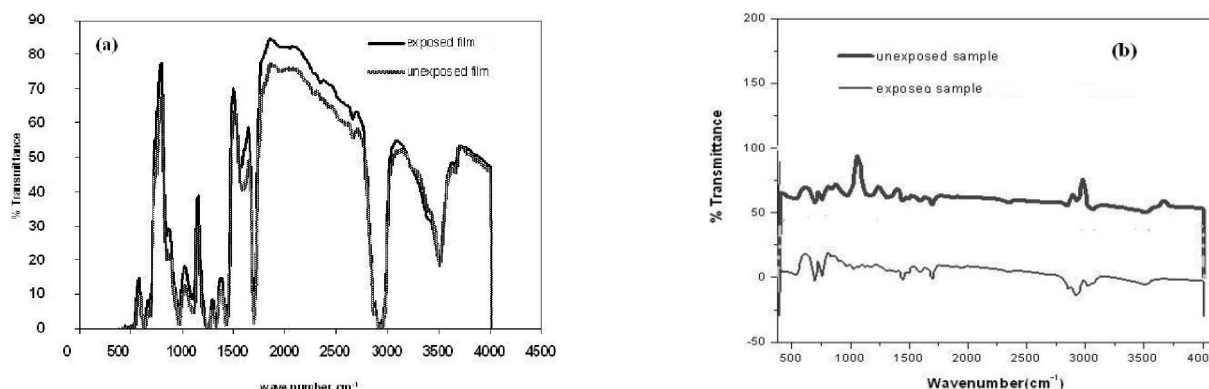


Figure 3 : FTIR-ATR spectra for (a) PVC-ZnO film before and after irradiation (b) PS-ZnO film before and after irradiation

Photocatalytic degradation

Time-weight loss data for the photocatalytic degradation of the two polymers with different semiconductor loadings have been collected. The kinetics of degradation for both the polymers is pseudo-first order. Figure 4 shows that the loss of weight is exponen-

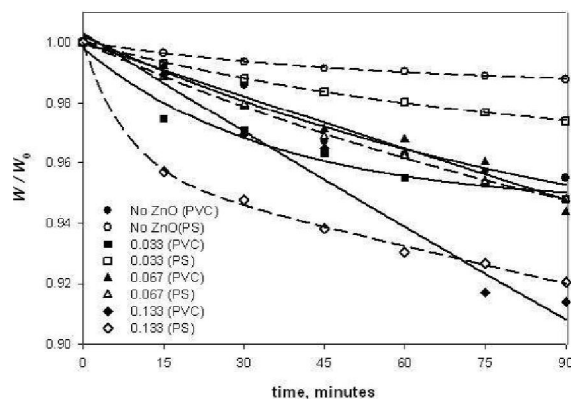


Figure 4 : Time-weight loss plot for photocatalytic degradation of PVC-ZnO composite film (—) and PS-ZnO composite film (—) under solar radiation at different ZnO loading. [Casting solution 3g polymer in 150g cyclohexanone, solar radiation 59 klux (237.18 W/m^2), temperature 31°C]

tial in both the cases. The rate constants are given in TABLE 1. It was observed that the extent and rate of solar photodegradation without semiconductor is different for the two polymers owing to the different molecular structure of the two, but when semiconductors are present in the polymer matrix, the extent and rate of photocatalytic degradation of the two polymers are more or less the same. In other words, it may be concluded that the rate of OH^\cdot radical attack and generation of the unstable polymer free radical is independent of the polymeric structure. If the intensity of solar radiation remains unaltered, the degradation increases with increase

TABLE 1 : Pseudo first order rate constants for photocatalytic degradation of PVC and PS

| PVC-ZnO film | | | | PS-ZnO film | | | |
|------------------------|----------------------|---|----------------|------------------------|----------------------|---|----------------|
| ZnO loading, kg/kg PVC | k, min^{-1} | k', $\text{kg}/(\text{m}^2 \cdot \text{klux} \cdot \text{s})$ | R ² | ZnO loading, kg/kg PVC | k, min^{-1} | k', $\text{kg}/(\text{m}^2 \cdot \text{klux} \cdot \text{s})$ | R ² |
| 0.000 | 0.0006 | 2.2E-08 | 0.9447 | 0.000 | 0.00024 | 4.70E-09 | 0.9642 |
| 0.033 | 0.0007 | 2.57E-08 | 0.9109 | 0.033 | 0.0003 | 3.08E-08 | 0.9609 |
| 0.067 | 0.0007 | 2.57E-08 | 0.9724 | 0.067 | 0.0006 | 6.17E-08 | 0.9857 |
| 0.134 | 0.0011 | 4.04E-08 | 0.9773 | 0.134 | 0.0012 | 1.23E-07 | 0.8431 |

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in the semiconductor loading due to increase in the active catalytic sites. Figure 5 shows the relative degradation of the two polymers with different ZnO loading.

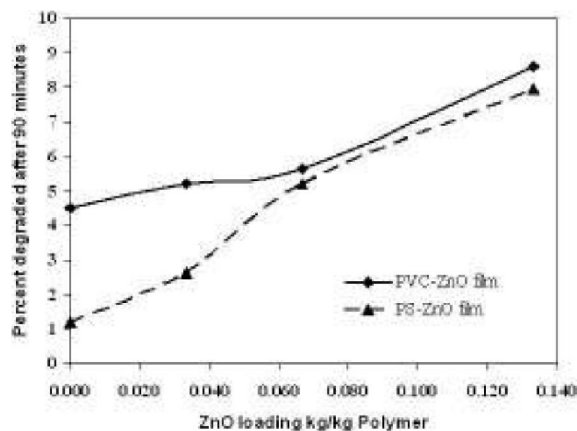
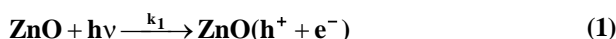


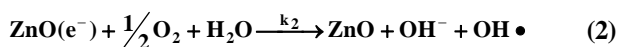
Figure 5 : Comparative degradation of PVC-ZnO and PS-ZnO film

Proposed mechanism and rate equation

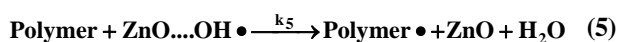
Solar energy, which contains both UV and visible light, excites the semiconductor surface to generate hole-electron pair:



In presence of air (oxygen) and water, trapping of this hole and electron generates hydroxyl radical:



This active species, OH \bullet radical, free or surface-bound, attacks the polymer matrix:



In addition, polymers are attacked by solar radiation only and are photodegraded:



In all cases it was assumed that rate of generation of polymer free radical out of a stable polymer molecule, is proportional to the rate of degradation of the polymer. Therefore the rate of degradation becomes:

$$\frac{d}{dt}[\text{Polymer}\bullet] = k_4[\text{Polymer}][\text{OH}\bullet] + k_5[\text{Polymer}][\text{ZnO}\dots\text{OH}\bullet] + k_6[\text{Polymer}][I_{UV}] \quad (7)$$

With respect to the loss in weight, the rate of degradation is a pseudo first order one:

$$-\frac{dW}{dt} = d[\text{Polymer}\bullet]/dt = kW \quad (8)$$

Applying pseudo steady state concept for the generation of OH \bullet , ZnO...OH \bullet , ZnO(h $^+$) and ZnO(e $^-$)^[21], we get:

$$-\frac{dW}{dt} = 2k_1[\text{ZnO}][I_{UV}] + k_6[I_{UV}] \quad (9)$$

If I_r is the flux of solar radiation in klux, W is the mass of the polymer film of density and thickness l, the intensity of UV radiation per unit area of the sample (I_{UV}) can be expressed as,

$$[I_{UV}] = I_r W / \rho l \quad (10)$$

Combining eq. (8), (9) and (10), we get:

$$k = \frac{I_r}{\rho l} \cdot \{2k_1[\text{ZnO}] + k_6\} \text{ and } k' = 2k_1[\text{ZnO}] + k_6 \quad (11)$$

$$\text{where } k' = \frac{k}{\left(\frac{I_r}{\rho l}\right)}$$

If experimentally obtained values of k' are plotted against ZnO loading, values of k_1 and k_6 can be obtained from the slope and intercept of the plot. Density of PS has been taken as 1040 kg/m 3 and that for PVC has been taken as 1300 kg/m 3 . Average thickness of PVC films was measured as 100 μ m and for PS, the average thickness varied from 80 μ m (with no ZnO) to 350 μ m (with ZnO).

The model has been tested with a few preliminary experimental data, the plot of which has been shown in Figure 6a and b for PS and PVC respectively. The fitting were fairly good, the regression coefficient being 0.9995 for PS and 0.8929 for PVC. The values of k_1 and k_6 for PS obtained from the model are 4.5×10^{-7} kg. m $^{-2}$. klux $^{-1}$.s $^{-1}$. (kg ZnO/kg PS) $^{-1}$ [1.115×10^{-7} kg. m $^{-2}$. (W.m $^{-2}$) $^{-1}$.s $^{-1}$. (kg ZnO/kg PS) $^{-1}$] and 4×10^{-9} kg. m $^{-2}$. klux $^{-1}$.s $^{-1}$ [1×10^{-9} kg. m $^{-2}$. (W.m $^{-2}$) $^{-1}$.s $^{-1}$] respectively. For PVC, k_1 and k_6 were calculated as Values of k_1 and k_6 are 1.0×10^{-7} kg. m $^{-2}$. klux $^{-1}$.s $^{-1}$. (kg ZnO/kg PVC) $^{-1}$ [0.2477×10^{-7} kg. m $^{-2}$. (W/m 2) $^{-1}$.s $^{-1}$. (kg ZnO/kg PVC) $^{-1}$] and 2×10^{-8} kg. m $^{-2}$. klux $^{-1}$.s $^{-1}$ [0.4954×10^{-8} kg. m $^{-2}$. (W/m 2) $^{-1}$.s $^{-1}$]. It may be noted that from the model, the rate constant for photolysis, k_6 , is calculated to be less in case of PS compared to PVC. This supports the fact that PS is more resistant towards solar photodegradation.

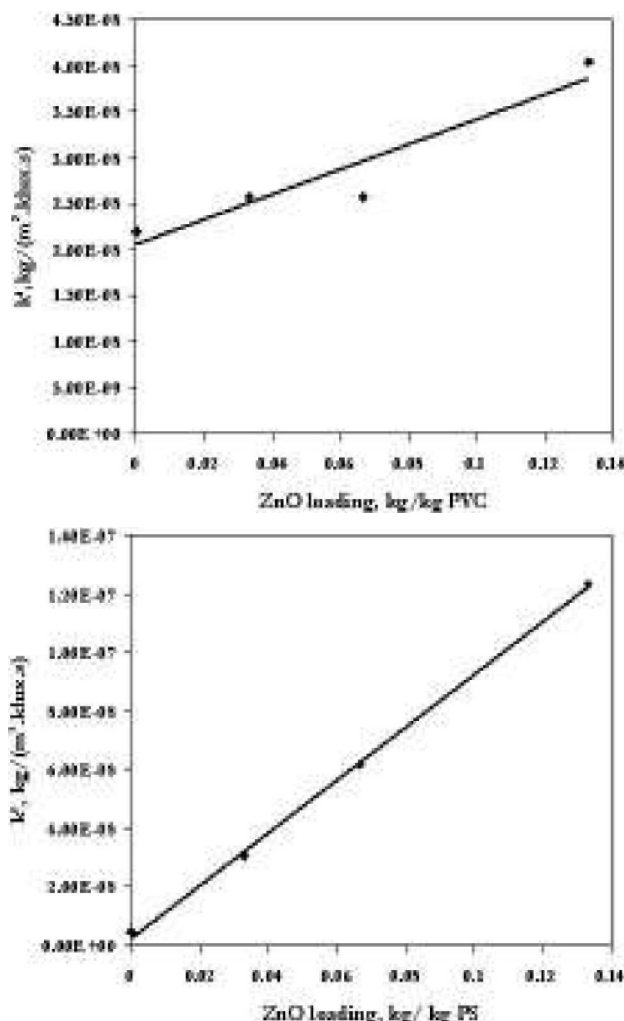


Figure 6 : Data fitting in Eqn (11) for (a) PVC-ZnO and (b) PS-ZnO

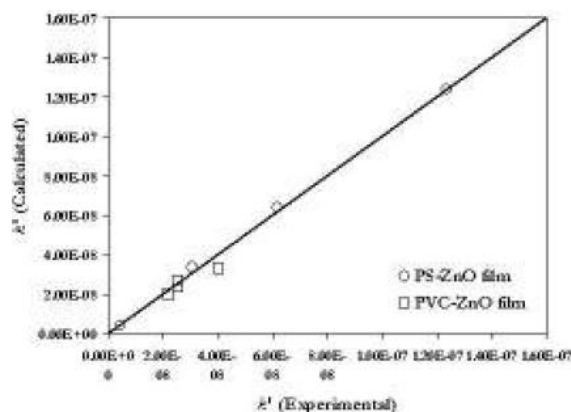


Figure 7 : Parity diagram for the experimental and calculated values of the pseudo-first order rate constants

Moreover, the rate constant for photogeneration of hole-electron pair, k_1 , is higher in case of PS than in case of PVC. Since PS is more transparent^[22] compared to PVC, sunlight penetrated PS film better than

PVC film and hence photoexcitation of embedded ZnO catalyst was better for PS-ZnO composite film. The corresponding parity diagram for the experimental and calculated values of the pseudo-first order rate constant for the two polymers are shown in figure 7. They are in good agreement, especially, the data for PS fit better. The work is, however, under progress are some more experimental data will be fitted into the model equation.

CONCLUSION

A comparative study has been made on the photocatalytic degradation of PVC-ZnO and PS-ZnO composite films under tropical sunlight in presence of air and water. Under otherwise same experimental conditions of 59 klux solar radiation, 0.13 kg / kg ZnO loading and ambient temperature, 7.9% of the original weight of PS-ZnO film and 8.6% of the original weight of PVC-ZnO film was degraded in 90 minutes. SEM suggests considerable change in surface morphology and FTIR-ATR indicates presence of expected oxidation products. A possible mechanism has been suggested and a kinetic model has been proposed. The experimental data fitted pretty well to the model. However, the work is still under progress and the model will be validated with more data in future. The degradation will be carried out with waste polymers as well.

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