

Degradation mechanism and kinetic model for photocatalytic oxidation of PVC–ZnO composite film in presence of a sensitizing dye and UV radiation

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Abstract

White or plastic pollution has become a serious concern to the environmentalists for the last few years. Degradation of waste plastics in conventional incinerators leads to emission of carcinogenic dioxins to the atmosphere. In this work, an attempt has been made for the photocatalytic degradation of polyvinyl chloride (PVC) using ZnO as semi-conductor catalyst in the form of PVC–ZnO composite film. The surface morphology as well as the FTIR spectroscopy of the irradiated film has been critically examined. The degradation was measured by weight loss data and was found to follow a pseudo-first order rate equation. The various parameters studied were loading of the semi-conductor, intensity of UV radiation and presence of Eosin Y as a sensitizing dye. It was observed that dye-sensitization enhanced degradation of PVC to a large extent. A possible mechanism has been suggested and the corresponding rate equation has been modeled for the dye-sensitized rate of degradation. The model has been validated by the experimental data.

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1. Introduction

Development of benign processes for the oxidative degradation of non-biodegradable waste materials has been a challenge for a pretty long time. While advanced oxidation using UV-H₂O₂, UV-O₃ or Fenton's reagent has provided an effective solution for refractory organics, semi-conductor photo-catalysts (such as TiO₂, ZnO, Fe₂O₃, CdS, ZnS, etc.) have proved to be useful for the degradation of refractory organics as well as waste plastics. The electronic structure of a semi-conductor catalyst is characterized by a filled valence band and an empty conduction band. A high-energy radiation in the UV range excites the

atom to eject a valence band electron to the higher energy level of the conduction band leaving a 'hole' behind. In an appropriate environment, a 'hole' may 'react' with a hydroxyl ion in an aqueous solution to yield a hydroxyl radical or a superoxide radical having a high oxidation potential. Among the common semi-conductor catalysts, TiO₂ in the anatase form has been used for many waste degradation applications. But ZnO has a few advantages over its formidable counterpart in terms of a higher quantum efficiency as well as catalytic efficiency. This has been amply demonstrated in a few recent investigations [1–3]. Further, ZnO photo-catalyst has been found to be effective for degradation of polymers and polymer composites as well.

Polyvinyl chloride is a commodity polymer produced in huge quantities. Disposal of the waste polymer is usually done by incineration risking the formation of toxic emission products. The waste polymer sometimes goes for land-filling mixed in municipal solid waste (MSW). The common methods of degradation of polymers and associated chemistry are available in

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Nomenclature

| | |
|-------------|---|
| I | intensity of UV radiation (W/m^2) |
| k | first order rate constant for degradation in Eqs. (16) and (17) (s^{-1}) |
| k' | rate expression obtained in Eq. (18) ($\text{s}^{-1}(\text{kg ZnO/kg PVC})^{-1}(\text{W/kg PVC})^{-1}$) |
| k_1 | rate constant for sensitization ($\text{s}^{-1}(\text{kg ZnO/kg PVC})^{-1}(\text{W/kg PVC})^{-1}(\text{kg Eosin Y/kg PVC})^{-1}$) |
| k_2 | rate constant for excitation of ZnO ($\text{s}^{-1}(\text{kg ZnO/kg PVC})^{-1}(\text{W/kg PVC})^{-1}$) |
| W | weight of PVC film at any time t (kg) |
| W_0 | weight of PVC film at time $t=0$ (kg) |
| [ZnO], [EY] | loading of ZnO and Eosin Y in kg/kg PVC, respectively. |

Greek symbols

| | |
|--------|-------------------------------------|
| ρ | density for PVC (kg/m^3) |
| τ | thickness of PVC film (m) |

Hamid [4]. Gotlib et al. [5] reports an elaborate chemical analysis of the composition of the gases emitted during incineration of PVC. The emission contains polychlorinated dibenzodioxines and dibenzofurans besides a host of other highly toxic substances whose dioxine equivalent is also reported. The toxic hazards and related technological issues have been discussed by Wey et al. [6], Besombes et al. [7], McKay [8] and Wey et al. [9] among others. The present day emphasis is on developing the technology to prevent generation of toxic emission rather than cleaning the emission. Photocatalytic degradation of polymers such as PVC or even chlorine-less polymer such as polyethylene (PE) has been an area of intense investigation in the recent years [10,11]. It may not be immediately competitive, but its technological potential is well recognized [10]. A few recent reports [11,12–14] describe the use of Degussa TiO_2 as the photo-catalyst for oxidative degradation of PVC. Cho and Choi [13] listed a series of reaction as the possible degradation pathways. Zhang et al. [15] used tungsto-phosphoric acid as the photo-catalyst irradiated the impregnated films with both UV

and visible light to achieve a high degree of degradation. In the present work we have been able to achieve partial degradation of PVC films using ZnO photo-catalyst and oxygen of air in an aqueous medium in presence of UV radiation. Eosin Y has been used as a dye-sensitizer which functions like a promoter in conventional catalysis. Such a sensitizer has an even lower band energy gap than a semi-conductor. On excitation, it generates a singlet electron, which in turn excites a semi-conductor atom leading to the formation of an electron–hole pair. A mechanistic pathway of the degradation reaction has been suggested and a rate equation has been developed. The degradation data could be fitted satisfactorily in the rate model and the rate parameters have been calculated.

2. Materials and methods

The polymer: PVC beads received from Reliance Industries Limited, India; trade name—Reon, grade 67-01; k -value— 67 ± 1 ; free from plasticizers (Table 1)

The sensitizer: Eosin Y; CI number 45380; formula weight—691.914; λ_{max} —516 nm.

The semi-conductor catalyst: ZnO, GR grade, LOBA Chemie, India; mean particle size—146.7 nm (*Zeta Plus*, Brookhaven Instrument Corporation); BET surface area— $3.23 \text{ m}^2/\text{g}$.

Solvent: cyclohexanone, SRL India; boiling range—154–156 °C.

Preparation of the PVC film: A solution of the polymer in cyclohexanone (1×10^{-3} kg polymer in 50×10^{-3} kg solvent) with requisite quantities of ZnO and Eosin Y was sonicated for 30 min to prepare a uniform suspension. The loading of ZnO varied from 0 to 0.3 g per gram of the polymer, and the maximum loading of the sensitizer was 20%. The film was made by casting the liquid on a stainless steel tray. The average film thickness was 100 μm .

3. Experimental

Photo-degradation experiments were carried out in a borosil glass reactor filled with water. Both the substrate PVC film and the UV source were kept immersed in water. The film was placed

Table 1
Specification of the PVC powder used (Reon from RIL, India), grade 67-01

| Property | Test method | Unit | Description |
|---------------------------|--|------------------------------|-----------------|
| k -Value | BFG 893 (1% in cyclohexanone at 30 °C) | % max | 67 ± 1 |
| Heat loss | BFG 362-H | % max | 0.3 |
| Particle size | BFG 812-H | % max | |
| Retained on 40 mesh | | | Traces |
| Retained on 60 mesh | | | 10 |
| Retained on 140 mesh | | | 25 |
| Porosity (DOP adsorption) | BFG 1094-A | ml/g | 0.19–0.25 |
| Bulk density | BFG 690-Fab | g/ml | 0.56 ± 0.03 |
| Residual VCM content | BFG 1005-F | ppm max | 1 |
| Dark resin count | BFG 1064 | No max | 4 |
| Fish eye count | BFG 909-G | No max | 20 |
| Flow time | BFG 692-E | S max | 25 |
| Electrical conductivity | ASTM D-1755 (method 14) | Micromhos cm^{-1} g | <6 |

in close proximity (within 12 mm) and direct view of the UV lamp to ensure maximum irradiation. Details of the experimental set up were described elsewhere [16]. Oxygen was supplied by sparging air in the reactor. Four 4 W and one 6 W UV lamps were used in separate experiments for irradiation. The loss of weight of the film was accurately measured from time to time (Satorius Model BT224S, 0.1 mg accuracy) to monitor the progress of degradation.

4. Results and discussions

The weight loss of the PVC film or the extent of its degradation is predictably a function of the process variables—namely the loading of the photo-catalyst, the concentration of the dye-sensitizer, and the intensity of the UV radiation. The rate of air sparging was maintained sufficiently high.

Since PVC is prone to slow degradation on exposure to UV radiation, we measured the photolysis of the film in the absence of the catalyst and the sensitizer. The weight loss was not detectable over a period of several hours. However, in presence of the dye-sensitizer alone, about 5% degradation could be achieved over a period of 2 h. With the addition of ZnO, the fractional weight loss reached a maximum of 20%. Further addition of the photo-catalyst caused a reduction in weight loss (Figs. 1 and 2). This is due to the blanketing effect of the ZnO particles at a higher loading. Zhang et al. [15] reported a degradation of up to 70% of a PVC film impregnated with tungsto-phosphoric acid and irradiated with visible light over a period of 250 h.

The primary objective of this study being modeling of the rate of dye-sensitized photo-degradation of PVC, the effect of the concentration of Eosin Y was measured in separate experiments. Interestingly, increased loading of the sensitizer was found to have similar effects as that of the photo-catalyst. The fractional degradation reached a maximum of 20% on addition of 2×10^{-4} kg of the dye in 1×10^{-3} kg of the polymer. With a higher dose of the dye (3×10^{-4} kg), a blanketing effect, that partially prevents photons from reaching the catalyst par-

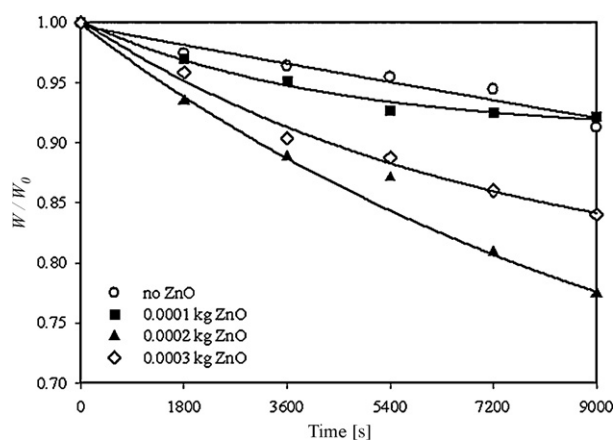


Fig. 1. Effect of ZnO loading on the dye-sensitized photocatalytic degradation of PVC film [casting solution: PVC 1×10^{-3} kg, cyclohexanone solvent 50×10^{-3} kg, Eosin Y dye 0.2×10^{-3} kg, UV radiation 16 W and temperature 40°C].

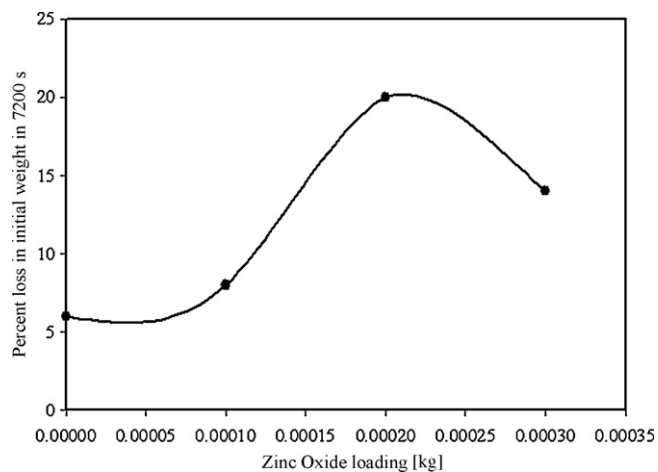


Fig. 2. Limiting loading of ZnO semi-conductor [casting solution: PVC 1×10^{-3} kg, cyclohexanone solvent 50×10^{-3} kg, Eosin Y dye 0.2×10^{-3} kg, UV radiation 16 W and temperature 40°C].

ticles, occurs as in the case of ZnO. Thus at a higher dye concentration, much of the sensitizer and the catalyst within the film remains unutilized or underutilized causing a reduction in degradation. The influence of the UV irradiation is shown in Fig. 3. The average estimated optical intensity in the photo-reactor (measured with Advantest TQ 8214 digital optical power meter) was varied in the range of 1.05×10^{-3} W/m² with one 6 W lamp to 1.92×10^{-3} W/m² when four 4 W lamps were used.

4.1. Physical characterization of the film

Although fractional weight loss is a direct and lumped measure of degradation of a film, examination of a partially degraded film was very important to have an insight into the phenomenon. SEM pictures (JEOL 5200) of the original and the partially degraded films at different stages are shown in Fig. 4. A fresh film has a smooth appearance except for a few microscopic air

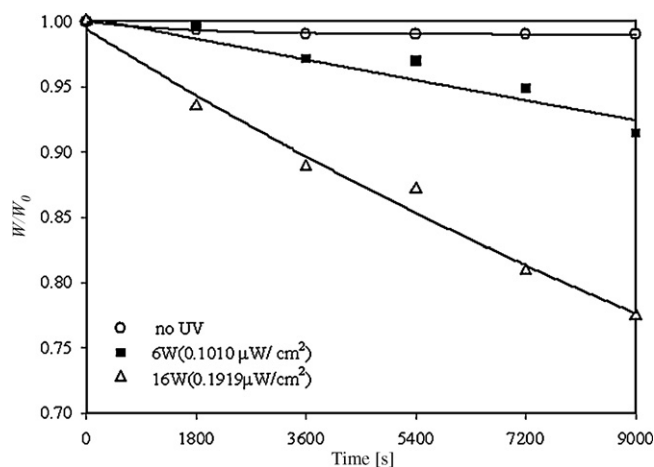


Fig. 3. Effect of intensity of UV radiation on the dye-sensitized photocatalytic degradation of PVC film [casting solution: PVC 1×10^{-3} kg, cyclohexanone solvent 50×10^{-3} kg, Eosin Y dye 0.2×10^{-3} kg, ZnO loading 0.2×10^{-3} kg and temperature 40°C].

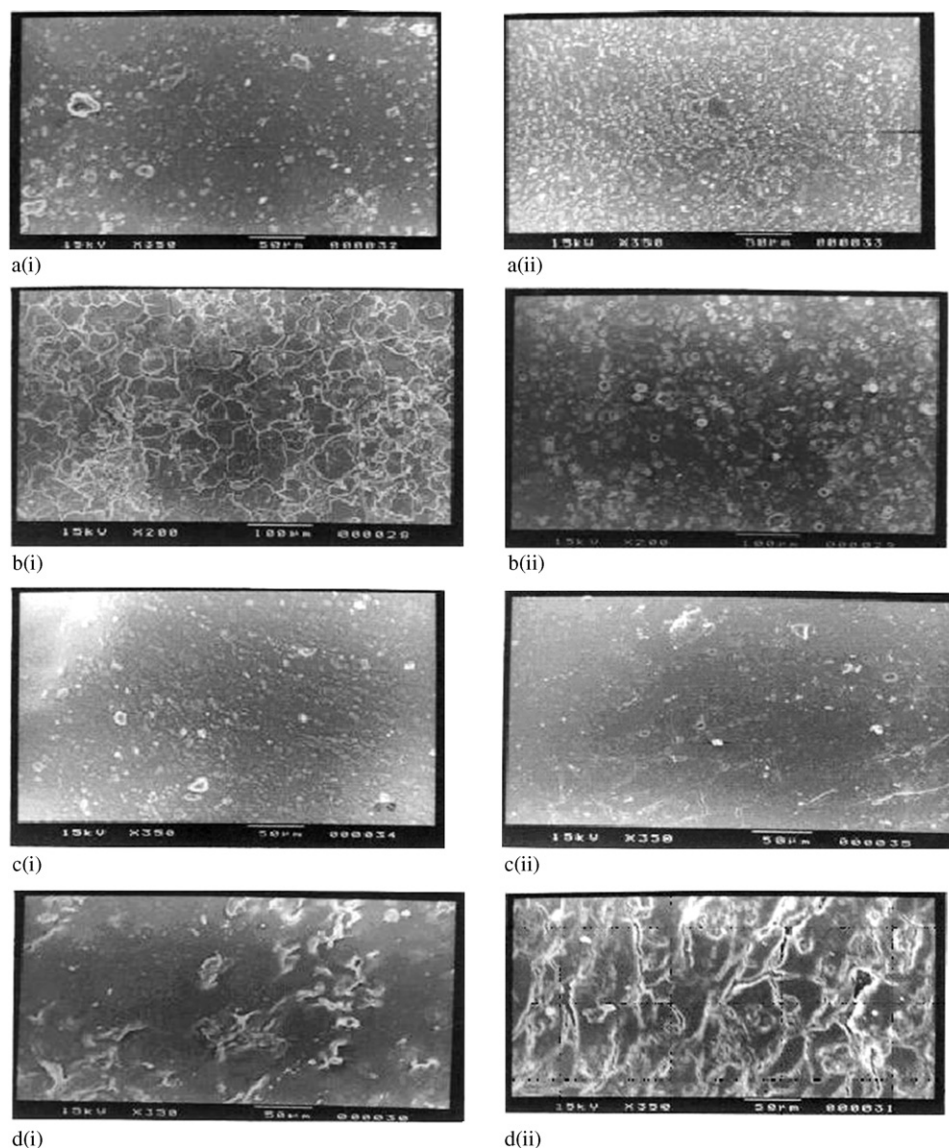


Fig. 4. SEM pictures of various PVC films before and after irradiation for 2.5 h. (a) PVC films before (i) and after (ii) irradiation. (b) PVC–ZnO–Eosin Y composite film before (i) and after (ii) irradiation. (c) PVC–Eosin Y composite film before (i) and after (ii) irradiation. (d) PVC–ZnO composite film before (i) and after (ii) irradiation.

pockets formed during casting. The progress of degradation and how it is influenced by the photo-catalyst and the sensitizer are discernible in the pictures. There is a clear change in the surface morphology. A partially degraded PVC–ZnO–Eosin Y composite film shows a cauliflower-like surface pattern (Fig. 4b(ii)) that changes to a serrated pattern with numerous pinholes with progress of irradiation in presence of aeration.

Degradation is expected to involve attack of the highly oxidizing free radicals on the polymer chains with the formation of different end-groups. This was established by FTIR spectroscopy conducted in the ATR mode (*Jasco FTIR-670 Plus*). Fig. 5(a) shows typical spectra of the composite film before and after irradiation. Absorption peaks appear in the ranges of $600\text{--}800\text{ cm}^{-1}$, $3400\text{--}3500\text{ cm}^{-1}$ and also around 695 cm^{-1} , 1100 cm^{-1} , 1600 cm^{-1} , 1700 cm^{-1} and 1770 cm^{-1} . The peaks around $3400\text{--}3500\text{ cm}^{-1}$ represent surface hydroxyl groups with

typical polymeric association. The one around 1100 cm^{-1} is also indicative of primary alcohol O–H bending. It is well established that a surface-bound hydroxyl group behaves as ‘surface zincanol’ ($\text{ZnO}\cdots\text{OH}^\bullet$), which is ultimately responsible for the degradation [1].

The peak around 695 cm^{-1} is due to C–Cl bond stretching, the intensity of which decreases after irradiation indicating cleavage of the PVC basic structure, at least partially. This facilitates the degradation process. A peak around 1600 cm^{-1} with a considerable fractional transmittance (44%) clearly suggests the formation of carboxylic acid groups as a result of attack by the oxidizing radicals. The presence of carbonyl groups (especially aldehyde, a precursor of carboxylic acid) is indicated by the absorption maxima around 1700 cm^{-1} and 2858 cm^{-1} . An absorption maximum around 1768 cm^{-1} is due to the presence of carbonates, perhaps an intermediate. A cluster of less intense

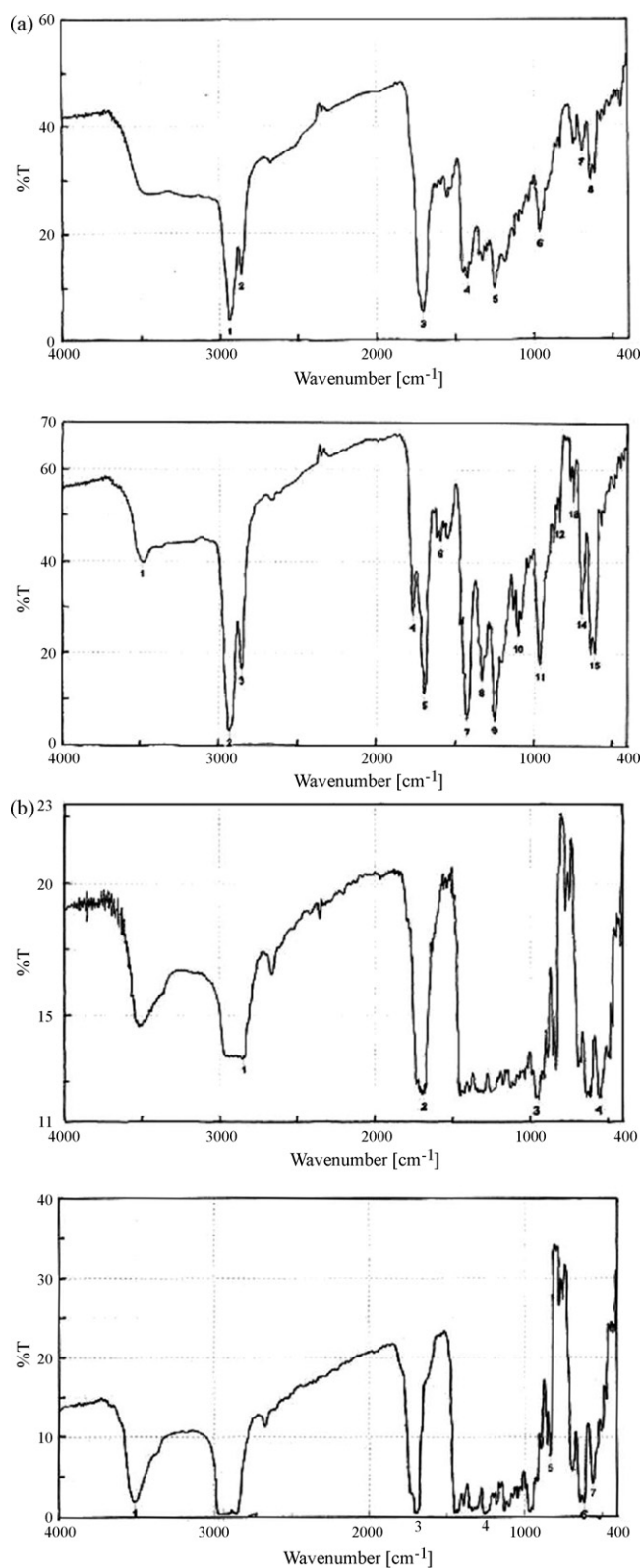


Fig. 5. FTIR spectrograph for PVC+ZnO+EY and PVC+ZnO composite films before and after irradiation, respectively.

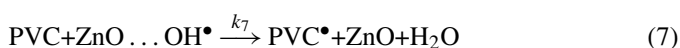
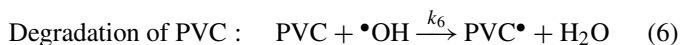
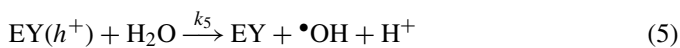
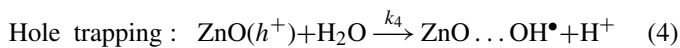
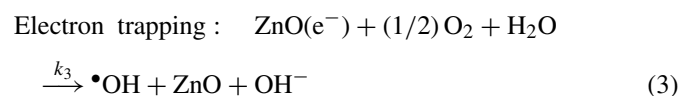
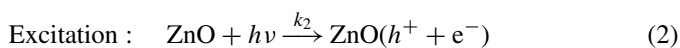
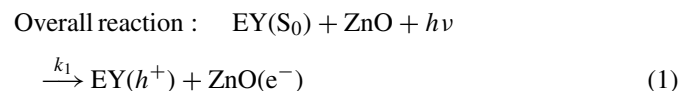
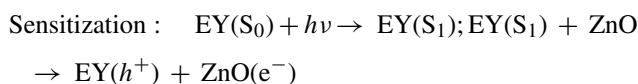
peaks is also indicative of diverse groups generated by photocatalytic cleavage.

4.2. Degradation mechanism and kinetic model

In the presence of a dye-sensitizer there are two pathways of formation of the hydroxyl and the superoxide radicals. While ZnO particles absorb UV radiation to generate electron-hole pairs directly, an irradiated sensitizer, Eosin Y in this case, produces an electron in the excited singlet (S_1) state and a hole in the (S_0) state. A charge separation takes place at the interface between ZnO and Eosin Y. If, on the other hand, ZnO is optically excited, hole injection from the valence band of ZnO to the ground state of Eosin Y is thermodynamically permitted. The dissociation of the free electrons and holes can occur at the interface. This reduces the possibility of their recombination and ensures a higher charge separation efficiency and better photooxidation capacity for the composites [14].

A set of reactions in presence of water molecules and dissolved oxygen follow leading to the formation of several active oxygen species such as superoxide anion, singlet oxygen, hydroperoxyl radical besides hydroxyl radical [12]. The main active species, OH^\bullet , free or adsorbed on the catalyst surface, designated as active 'zincanol ($\text{ZnO} \dots \text{OH}^\bullet$)', may attack PVC to produce PVC^\bullet radical [1,17]. It was assumed that rate of formation of PVC^\bullet is proportional to the rate of degradation of PVC. Because of the low energies involved, dyes of a wide variety of structures can sensitize the formation of singlet oxygen via the dye triplet state. Sensitizers, such as Eosin Y, operate primarily through singlet oxygen in such photodynamic reactions [18].

Based on the above observations and on the sequence of reactions in TiO_2 -photo-catalyzed degradation of PVC suggested by Cho and Choi [13], we propose the following mechanistic pathways and 'reactions':



The total rate of degradation of the polymer can be expressed as

$$d \frac{[PVC^\bullet]}{dt} = k_6[PVC][OH^\bullet] + k_7[PVC][ZnO \dots OH^\bullet] \quad (8)$$

The hydroxyl radicals are generated by reactions (3) and (5) and consumed by reaction (6), i.e.,

$$d \frac{[OH^\bullet]}{dt} = k_3[ZnO(e^-)[O_2]^{1/2} + k_5[EY(h^+)] - k_6[PVC][OH^\bullet] \quad (9)$$

Assuming the net rate of formation of the radical to be zero at pseudo-steady state [19],

$$k_6[PVC][OH^\bullet] = k_3[ZnO(e^-)[O_2]^{1/2} + k_5[EY(h^+)] \quad (10)$$

We will make use of pseudo-steady approximation to find out expressions for $[ZnO(e^-)]$, $[EY(h^+)]$, and $[ZnO \dots OH^\bullet]$ in terms of measurable quantities with a view to arriving at a useful rate equation. Equating the rates of formation and consumption of $EY(h^+)$ from Eqs. (1) and (5),

$$k_5[EY(h^+)] = k_1[EY][ZnO][I_{UV}] \quad (11)$$

Use Eqs. (3), (1) and (2) to obtain the pseudo-steady state concentration of $[ZnO(e^-)]$.

$$k_3[ZnO(e^-)[O_2]^{1/2} = k_1[EY][ZnO][I_{UV}] + k_2[ZnO][I_{UV}] \quad (12)$$

Similarly, the pseudo-steady state concentration of the zincanol radical can be obtained from Eqs. (7), (4) and (2).

$$k_7[ZnO \dots OH^\bullet][PVC] = k_4[ZnO(h^+)] = k_2[ZnO][I_{UV}] \quad (13)$$

From Eqs. (8) and (10)–(13),

$$d \frac{[PVC^\bullet]}{dt} = k_1[EY][ZnO][I_{UV}] + k_2[ZnO][I_{UV}] + k_1[EY][ZnO][I_{UV}] + k_2[ZnO][I_{UV}] = 2k_1[EY][ZnO][I_{UV}] + 2k_2[ZnO][I_{UV}] \quad (14)$$

If I_f is the flux of UV radiation (W/m^2), W the mass of the PVC film of density ρ and thickness l , the intensity of UV radiation can be expressed as

$$[I_{UV}] = \frac{I_f W}{\rho l} \quad (15)$$

The rate of degradation of the polymer can now be expressed in the following form as a first order process in the mass of undegraded polymer (W), the rate constant being a function of the concentrations of the photo-catalyst (ZnO), the sensitizer (EY) and the intensity of the UV radiation (I_f).

$$\frac{-dW}{dt} = \frac{d[PVC^\bullet]}{dt} = kW \quad (16)$$

where

$$k = 2[ZnO] \left(\frac{I_f}{\rho l} \right) (k_1[EY] + k_2) \quad (17)$$

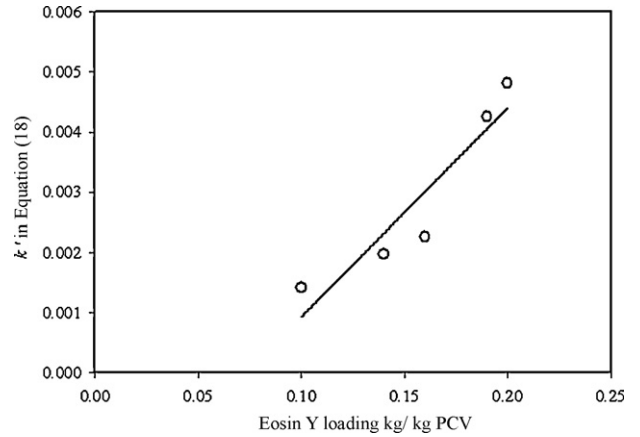


Fig. 6. Determination of rate constants in Eq. (18).

or,

$$\frac{k}{2[ZnO](I_f/\rho l)} = k' = k_1[EY] + k_2 \quad (18)$$

The ‘lumped’ rate parameter, k , can be calculated from the experimental weight loss data for given values of the parameters in a particular run. Thickness of the film was estimated by SEM and the average thickness of 100×10^{-6} m was used in the calculations. Density of the PVC was estimated as 1300 kg m^{-3} [12]. Following Eq. (18), a plot of k' calculated from the experimentally determined values of k against the corresponding loadings of the dye-sensitizer, is expected to be linear. Such a plot of the lumped rate constant, k , is shown in Fig. 6. The calculated values of the model rate constants are: $k_1 = 3.47 \times 10^{-2} \text{ s}^{-1}(\text{kg ZnO per kg PVC})^{-1}(\text{W/kg PVC})^{-1}(\text{kg Eosin Y per kg PVC})^{-1}$ and $k_2 = -2.5 \times 10^{-3} \text{ s}^{-1}(\text{kg ZnO per kg PVC})^{-1}(\text{W/kg PVC})^{-1}$. It is apparent from the rate constant values that the rate of sensitization is larger than the rate of semi-conductor excitation. In fact a negative value of k_2 indicates a hole–electron recombination in case of ZnO excitation with UV radiation in absence of a dye-sensitizer. In other words, sensitization, instead of semi-conductor excitation, enhances the rate of PVC degradation by a large extent. A parity diagram for the experimental and the cal-

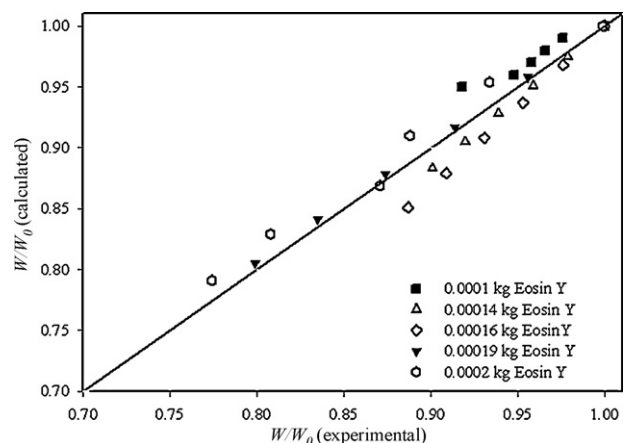


Fig. 7. Parity diagram indicating the experimental and calculated weight loss data in the photocatalytic degradation of PVC films with different dye loading.

culated values of the fractional weight loss data (Fig. 7) shows a good agreement between the two.

5. Conclusions

The photocatalytic degradation of polymer composites consisting of PVC, ZnO and Eosin Y dye-sensitizer has been studied under the influence of UV radiation at 356 nm. The dye-sensitized degradation is influenced by the amount of semi-conductor, intensity of UV radiation and the amount of dye present. Besides carbon dioxide, the possible degradation products have aldehyde, ketone and carboxylic acid functional groups. The degradation kinetics was studied by monitoring the loss in weight from time to time and it was found that the rate followed a pseudo-first order kinetic model with respect to the loss in the net weight of PVC. Compared to the other studies referred to before, the time required for 20% weight loss is substantially small (2 h) in the present study. A model for the degradation kinetics has been developed. It shows that the loading of Eosin Y sensitizer enhances the degradation in a particular range when the intensity of UV radiation and loading of semi-conductor are kept constant. The potential of use of a sensitizer together with the photo-catalyst deserves more attention to enhance the feasibility of the technique. Use of solar radiation for photo-degradation is likely to be a practical step to commercially exploit this technique.

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