

Studies on photocatalytic degradation of polystyrene

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This paper reports the photo degradation of polystyrene (PS) by using zinc oxide (ZnO) as photo catalyst. Virgin PS is not responsive to degradation by ultra violet (UV) light because of the presence of phenyl rings in its repeating units. ZnO acts as an UV absorber and helps in transferring the absorbed energy to various bonds of PS and causes degradation. The concentration of ZnO followed by the dispersion within the PS matrix has been found to be the key as the maximum weight loss of ~16% in 2 h has been obtained with 0.5 wt-% of ZnO. Below and above this concentration, the degradation is clearly low. Addition of a UV sensitive dye has further improved this degradation (up to 18%) owing to synergism with ZnO. The degradation of PS has been further highlighted from infrared spectroscopy, surface analysis, viscosity average molecular weight studies and mechanical properties analysis. A suitable mechanism supporting the UV degradation has also been proposed.

Keywords: Polystyrene, UV degradation, Surface analysis

Introduction

The use of commodity plastics such as polyethylene (PE), polystyrene (PS), polypropylene (PP), poly vinyl chloride (PVC), etc.^{1,2} in our daily life is inevitable owing to their enormous advantages. They are durable and are virtually unaffected by the naturally occurring degrading agents and sources, and therefore generates huge amount of wastes, accumulated in the environment, in their post-application period. For the last 16 years, several attempts have been made for the biodegradation of plastics by dispersing different bio-materials like starch and gelatin,³⁻⁵ although with little success. Rather these experiments are expensive, involve longer experimental time, require substrate specific catalysts and are also really complicated to be implemented commercially. Biopolymers, as is being demanded as the substitute for commodity plastics, are miles away from the target owing to their heavy production cost.⁶⁻⁸ The search for alternatives led the scientists to investigate the photo degradation of the commodity thermoplastics involving energetic agencies of both high radiation such as gamma rays (10^{-4} μm), electron beams (10^{-7} – 10^{-4} μm) and low energy radiations such as ultra violet (UV) light (10^{-2} – 1 μm) in which, the latter is the most convenient for its easy, less complicated and much cleaner technological approach.

During exposure of a polymer to UV radiation, the chromophoric groups present within it absorb the radiation, which are strong enough to cause the cleavage of the covalent bonds. The chromophores may either be

the integral part of the polymer structure or generates *in situ* as impurities such as hydroperoxides or carbonyls formed during storage, processing and weathering. They could also be incorporated as the remnants of the polymerisation catalysts; additives dispersed within the polymer matrix such as pigments, dyes or even antioxidants or the traces of metals from the processing environments, etc.

Ultra violet degradation is preceded by two proposed mechanisms:⁹ photolysis and oxidative reactions. In an inert atmosphere, photolysis is dominated while in presence of air, photo oxidation is the most effective one.

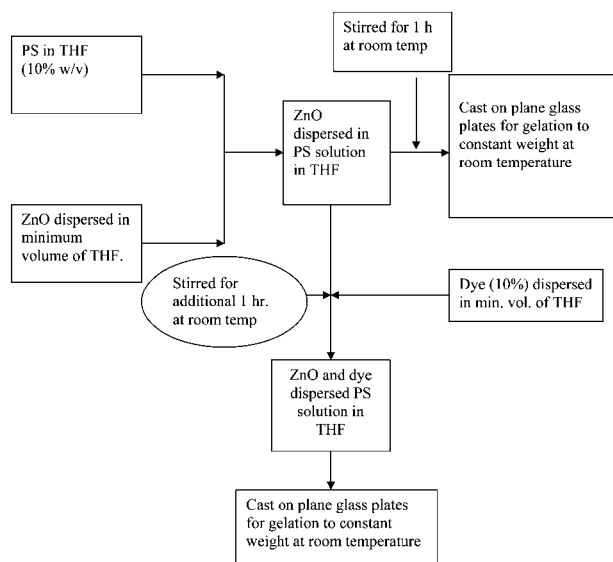
Photo oxidation is principally a free radical based reaction, composing of three different steps. The first step is initiation of the degradation reaction. This is caused by the photolysis of the chromophores present with the system. The second step is the propagation reaction. This is repetitive in nature and several hydro peroxide decomposition mechanisms have been proposed for this step, some of which leads to radicals and/or chain scission^{10,11} and others do not. The third and final step is the termination reaction and it is bimolecular in nature.¹²

Chromophores can act as sensitizers, which are characterised by a filled valence band and empty conduction band.¹³ These can shift the absorption band to either longer or to shorter wavelengths and also sometimes intramolecular energy exchange takes place via transfer of energy from small chromophoric molecules to those on the matrix.

As major fraction of the disposable thermoplastics is non-polar in nature, hence, photo degradation of these plastics requires some external effort in the form of addition of sensitizers. Literatures are available on the

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1 Procedure for preparation of samples

usage of photo sensitizers, such as zinc oxide ZnO),¹⁴ cadmium sulphide (CdS),¹⁵ metallic iron and zinc¹⁶ for rapid degradation of polymer matrices. Among all the photo sensitizers stated above, ZnO has got the biggest advantage of absorbing the longer fraction of the solar spectrum and hence could possibly give the highest efficiency.

As mentioned earlier, commodity thermoplastics such as PE, PP, PS, etc. lack any sort of chromophoric groups and hence are substantially stable in the environment. There are published reports available on the photo degradation of PE,^{17,18} PP^{18,19} and their copolymers¹⁸ and other thermoplastics whereas studies on PS are scanty. Atactic PS, being an important commodity thermoplastic, occupies about 20–22% of the total market on the basis of worldwide consumption. Even though the polymer contains reactive tertiary hydrogen atoms in its repeating units, it is not photodegradable as it forms resonance stabilised free radicals on account of the active participation of the phenyl rings, and therefore poses a critical challenge to the polymer scientists so far as their degradation is concerned. In this regard, the current investigation deals with the photocatalytic degradation of virgin PS using a very simple technique. ZnO, as described earlier possesses wide absorption spectrum compared with other UV sensitizers have been used as the photo catalyst. A dye, Eosine Y, has been tried in conjunction with ZnO in one representative composition in order to investigate the synergistic effect on the degradation phenomena. Different physico-mechanical properties have also been studied for the photo catalytically degraded samples with an attempt to correlate the experimental findings with the mechanistic pathway of the degradation of PS.

Experimental

Materials

Polystyrene (PS, atactic, density 1.050 kg m⁻³ at 25°C, viscosity average molecular weight, $M_v = 2.64 \times 10^4$) was procured from M/S.Science Chem., kolkata, India. Zinc oxide (ZnO, 99% pure), used as the photo degradation catalyst was obtained from Loba Chemie, Mumbai,

India. Eosin Y (it was used without any further modification), the dye of CI no. 45380 and formula weight 691.914 was supplied by Merck India Ltd, Mumbai, India. The solvents, tetrahydrofuran (THF), toluene and the distilled water for conducting the photo degradation experiment, all of laboratory grades, were obtained from indigenous sources.

Sample preparation

The sample preparation technique is demonstrated by the following schematic (Fig. 1).

All the samples were prepared by using solution mixing process as this usually gives better mixing efficiency between the two components widely differ in polarity (PS, ZnO and also the dye) as compared with the melt mixing process. The 10% solutions (w/v) of PS were prepared from THF, ZnO, in different weight proportions (with respect to PS), dispersed in minimum volume of THF was added to the PS solutions and stirred to homogenise for 1 h at room temperature (25°C). The resultant solutions were cast on plane glass plates for gelation under ambient condition. The details of the sample compositions and their designation are enlisted in Table 1. For comparative study, one representative composition with the dye was also prepared with a fixed ZnO concentration. In that case, the dye, dispersed in minimum volume of THF was added to the homogenised PS–ZnO dispersion at room temperature (25°C) and was further stirred for 1 h (Fig. 1). After thorough mixing, the solution was cast on glass plate for gelation till there was no weight variation. Composition of this sample is also included in Table 1.

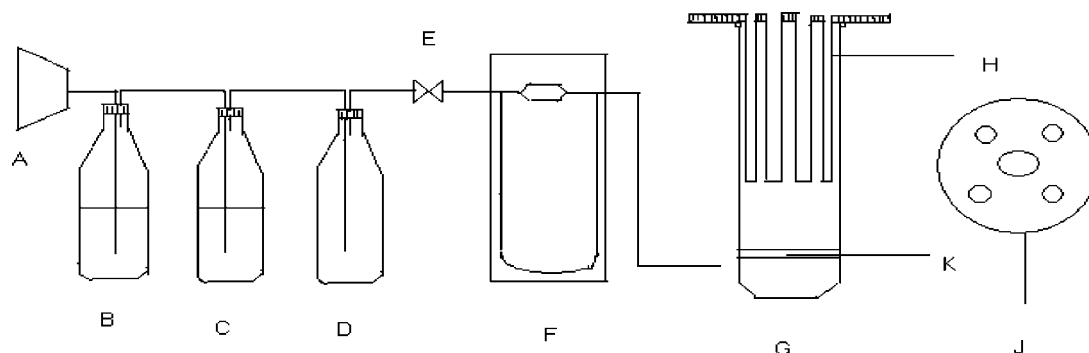
Experimental setup and test procedure

Figure 2 shows a schematic of the experimental setup. The reactor was a borosil glass vessel of 7 in diameter and 12 in length. A stirred glass disk was fitted at a height of 2 in from the bottom to disperse air in the liquid. Four 4 watt UV lamps were inserted within glass tubes fitted in the holes of the Bakelite lid of the reactor. The glass tubes acted as sheaths for the lamps. There was an additional opening in the lid for inserting the sample within the reactor from time to time. Air was supplied to the reactor by calibrated capillary flow meter. An oil trap, a humidifier and demister were fitted between the delivery of the compressor and the reactor.

The samples in the form of strips, the width of which were adjustable to pass through the sample holes over the lid of the reactor vessel, were cut out from the solvent cast sample sheets. Those sample strips after immersion in water for one day initially were tied with cotton strings, hung from a glass support and immersed inside the reactor vessel in the distilled water. Immersion of samples in water before the experiment was to allow

Table 1 Composition of samples, wt-%

Sample designation	Polystyrene	Zinc oxide	Dye
PS	100	–	–
PS _{0.1}	100	0.1	–
PS _{0.3}	100	0.3	–
PS _{0.5}	100	0.5	–
PS _{0.5d10}	100	0.5	10% of the ZnO (i.e. 0.05)
PS ₁	100	1	–



A air compressor; B oil separator; C humidifier; D demister; E needle valve; F flow measuring device; G photo reactor; H UV lamp in glass tube; J Sampling port on lid; K sintered glass disk

2 Experimental setup for PCD of PS using ZnO

equilibrium moisture absorption at the surface. The variation in weight owing to degradation was measured by weighing the samples every 30 min interval till there was no weight variation (the surface water was soaked with blotting paper before each weighing measurements) after the commencement of the experiment and the results were expressed as percentage loss in weight from that of their initial values.

Characterisation

Weight loss of degraded samples

The loss in weight owing to degradation was determined by weighing the samples in a standard digital weighing machine (Dhona). The results are expressed in the form of % weight loss against the initial weights of the samples for each and every experiment.

Infra red spectroscopic analysis

The Fourier transform infra red (FTIR) spectroscopic analysis of the samples was carried out in JASCO FTIR spectrophotometer under room temperature using dispersive mode. All the samples were analysed within the wave number region of 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1} . An average of 120 scans had been taken in each case and is reported for analysis.

Atomic force microscopic (AFM) analysis

The surface roughness of the samples was investigated using a digital nanoscope (III) AFM. The area roughness of the samples was determined from the contact mode analysis along the sample surface using a silicon nitride tip.

Determination of molecular weight

The post-experimental viscosity average molecular weight (M_v) of the samples was determined by using a standard Ubbelode viscometer at room temperature. The samples were dissolved in toluene (AR grade, obtained from indigenous source) in concentrations <1% (w/v) and the intrinsic viscosity η was obtained by extrapolating the straight line plot of η_{sp}/c versus c to $c=0$ axis (η_{sp} is the specific viscosity and c is the concentration of the PS in toluene). The viscosity average molecular weight, M_v , was calculated by fitting the η values in the Mark–Howink equation

$$\eta = KM_v^\alpha \quad (1)$$

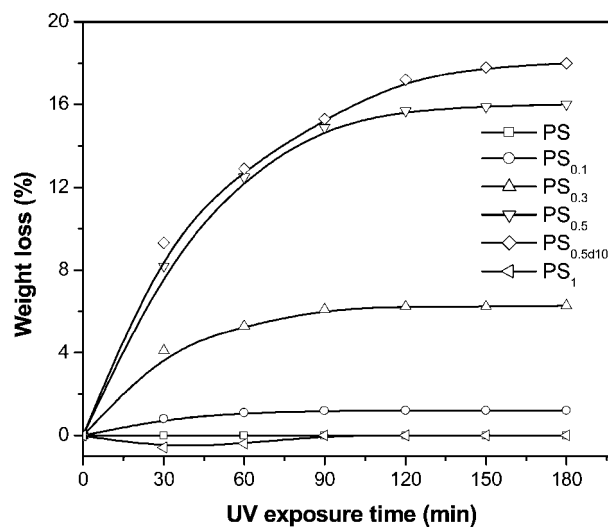
where k and α are the constants. For PS–toluene, system at room temperature, $k=3.7 \times 10^{-4}$ and $\alpha=0.62$ respectively.

Studies on mechanical properties

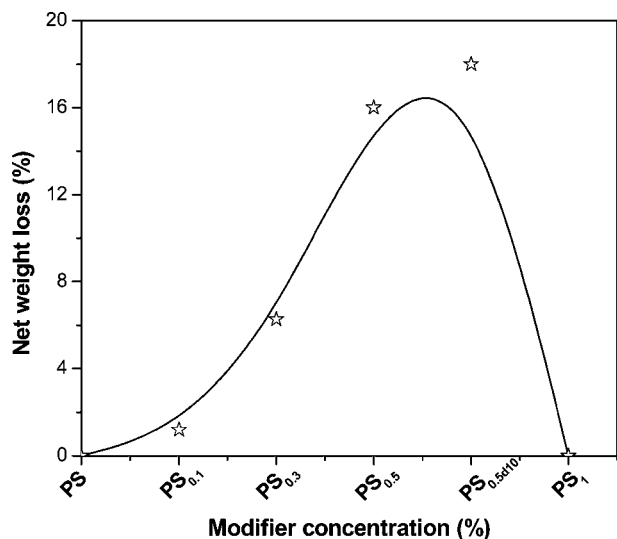
The mechanical properties of the photodegraded samples were determined in a universal tensile testing machine (Blue Star, Germany) with a crosshead speed of 50 mm min^{-1} at room temperature (25°C). The samples were die punched from the strips using an ASTM die C. The results were expressed in the form of tensile strength, elongation at break (%) and the work to break. An average of three tests results has been reported for analysis.

Results and discussion

Figure 3 shows the plots of an increase in percentage weight loss against the UV exposure time for the virgin PS and different ZnO and dye modified PS samples. The virgin PS has shown virtually no weight variation even after an UV exposure for 180 min within aerated water. This is quite anticipated as the phenyl rings in the repeating units of PS forms resonance stabilised radicals, already mentioned. Addition of 0.1 wt-%ZnO in $\text{PS}_{0.1}$ has definitely increased the weight loss of the composite and this trend gradually increases with increasing ZnO concentrations up to 0.5 wt-% with respect to PS. In fact the weight loss has further increased and also in slightly greater rate with the dye mixed 0.5 wt-%ZnO containing sample. The degradation phenomenon in all the cases has shown an exponential behaviour, i.e. a sharp



3 Variation in weight (%) with time of exposure in UV light for virgin PS and modified samples



4 Plots of net weight loss against modifier concentrations for virgin and modified PS samples

increase initially, which after some time gradually levels off. Beyond the ZnO concentration of 0.5 wt-% with respect to PS, a drastic change in the degradation behaviour has taken place as the sample containing 1% weight of ZnO hardly shows any weight loss under the experimental conditions.

Figure 4 summarises this phenomenon quite nicely. It shows the maximum weight loss of the samples that could be derived from different modifier concentrations (the data points are collected from Fig. 2). A maximum of 16% weight loss is recorded with 0.5 wt-% ZnO concentration and this is found to be the optimum under the present circumstances. Addition of dye has slightly improved this degradation as is observed from both these figures (Fig. 3 and 4). The rate of degradation is marginally higher for PS_{0.5d10} than that of PS_{0.5}

(Fig. 3) and the net weight loss also increases up to 18% (Fig. 4).

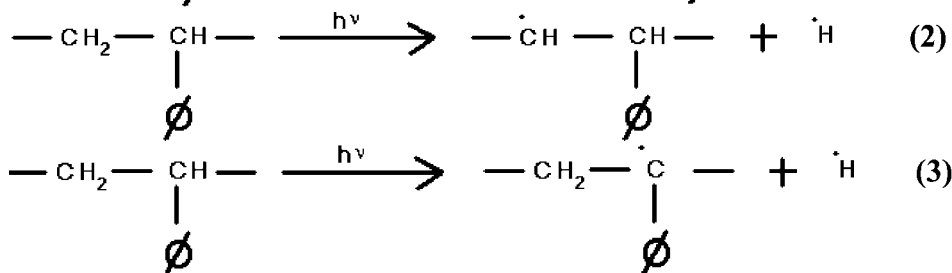
A mechanistic pathway could be framed to interpret the degradation phenomena. ZnO, which acts as a UV absorber, transmits the absorbed energy to the C–C and C–H bonds of the PS molecules. As this energy is greater than that of the dissociation energies of these bonds, they undergo cleavage. Following are the possible cleavage reactions that occur within the system (Fig. 5).

Occurrence of Photo-Fries rearrangement in this system is virtually out of possibility owing to presence of sufficient oxygen in the reaction vessel and therefore has been consciously avoided.

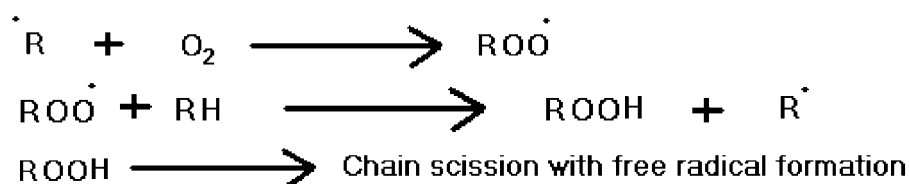
Radicals associated with the benzene rings (reactions (1) and (3)) are expected to be stable owing to resonance. The other radicals may further react with oxygen to form several oxygen containing groups – COOH, –OH, –OOH, etc. by the following mechanisms (Fig. 6).²⁰

Association of oxygen with the radical formed in reaction (1) (CH₂) could be the most useful member in effecting the degradation of the polymer as it could give rise to the cleavage of the main chains by discarding any recombination reaction. These oxygenated groups in part are lost from the surface mainly in the form of carbon dioxide (CO₂).⁹ Loss of water is also probable depending on the concentrations of hydroxide and hydroperoxide groups on the surface. Release of CO₂ owing to degradation of PS has been traced by checking the pH of the water in the reaction vessel after completion of the experiment. One such measurement for PS_{0.5} shows the drop in pH from 6.8 to 6.2 and supports the authors' speculation.

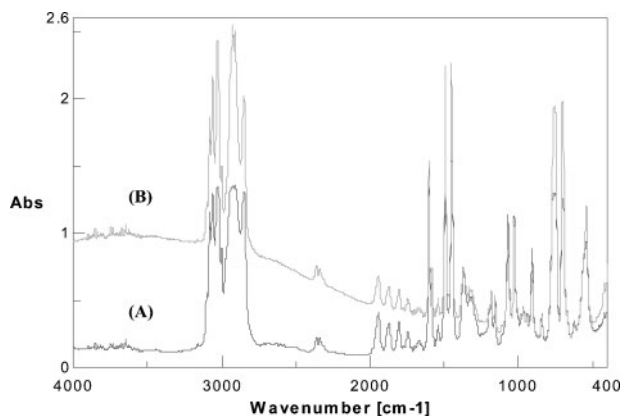
The most important point in this mechanism is the dispersion of ZnO within the PS matrix. The better the dispersion of ZnO, the more polymer macrochains would absorb over the metal oxide and the greater would be the chances of chain cleavage reactions by



5 Different cleavage reactions in PS–ZnO system on exposure to UV



6 Combination of O₂ with different hydrocarbon macro radicals (R)

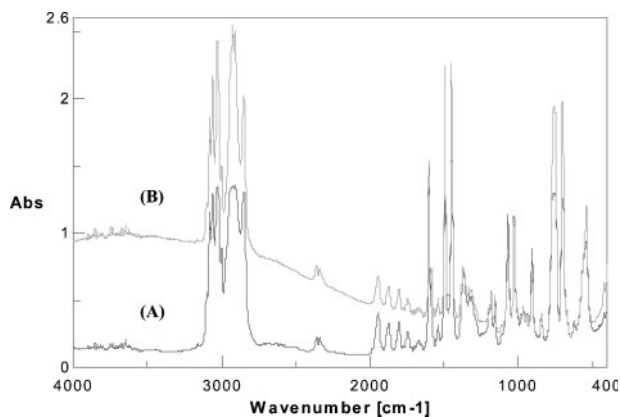


7 Fourier transform infra red spectra of A pure PS and B 0.5 wt-%ZnO loaded PS compound before photocatalytic degradation

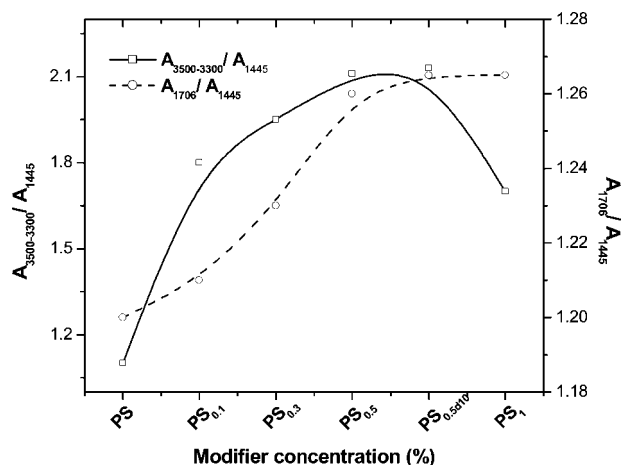
efficient energy transfer to the matrix. As Figs. 3 and 4 indicate, the net weight loss of the system increases till to 0.5 wt-% of ZnO concentration, it suggests that the dispersion of ZnO up to this point is fairly good. Beyond this concentration, there is a clear case of aggregation of ZnO, which reduces the average surface area for interaction with PS and hence the efficiency of degradation is also low. Addition of the dye brings about a synergistic effect, as it can also act as an UV absorber and is also compatible with the organic polymer matrix to give better dispersion.

Oxidation of the polymer owing to photo degradation is confirmed from the infrared spectroscopic analysis of the samples. Figures 7 and 8 show the representative FTIR spectra of virgin PS and PS_{0.5} arbitrarily stacked before and after degradation respectively. The principal absorption peaks associated with PS are the vibrations of C–H stretching at 2850–2960 cm⁻¹ and the series of peaks within the range of 1500–2000 cm⁻¹ corresponding to various C–H and C–C vibrations of the benzene rings.

Figure 9 shows the plots the ratio of the peak areas for C=O (1706 cm⁻¹) and –OH (3300–3500 cm⁻¹) vibrations, against the peak areas corresponding to C–H bending peak at 1445 cm⁻¹, against different sample compositions. The absorbance corresponding to the C=O vibrations in the degraded samples interferes with that of the different C–C and C–H vibrations of benzene



8 Fourier transform infra red spectra of A pure PS and B 0.5 wt-% ZnO loaded PS compound after UV degradation



9 Plots of ratio of peak areas against modifier concentrations for PS and different modified samples

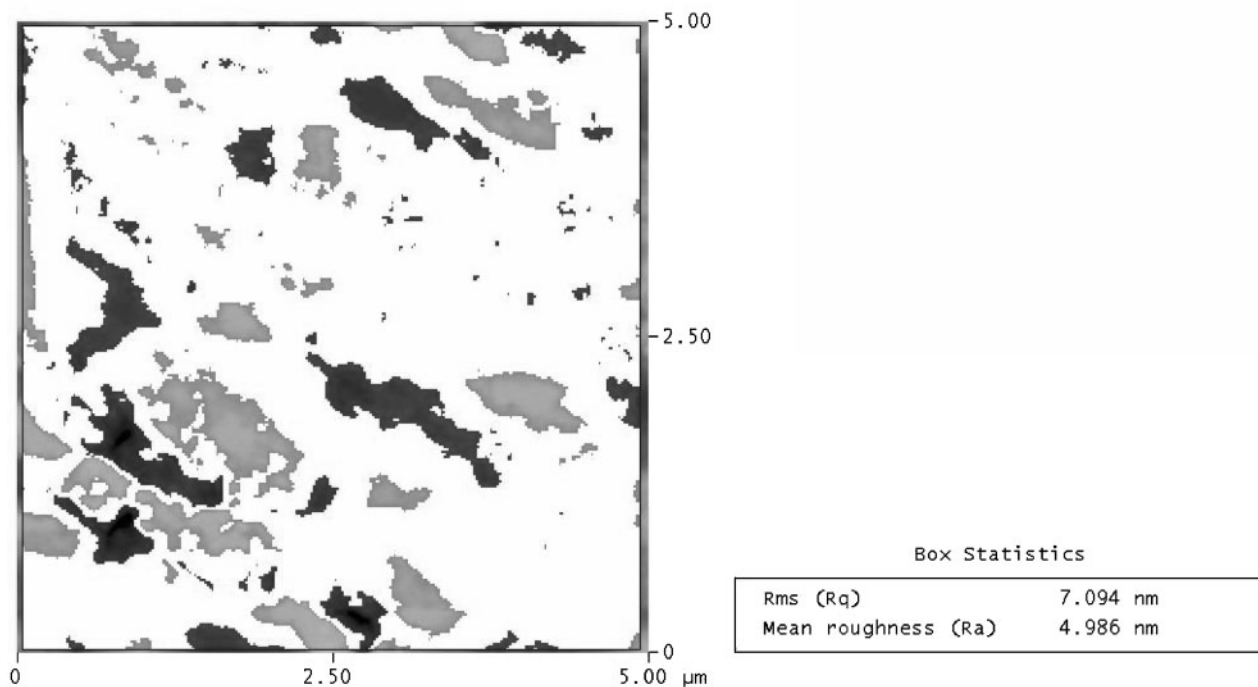
rings in the virgin PS. with increasing concentration of ZnO, both the values increase, which indicates the existence of higher concentrations of the oxygenated groups on PS surface, generated owing to photo oxidation. Moreover, it implies relative oxidation of the samples against the UV exposure. At 1% of ZnO concentration, the concentration of C=O remains almost unchanged while that for OH shows a slight down fall, implying good parity with the earlier observations. On addition of dye at 0.5 wt-%ZnO concentration, the data points on the figure (Fig. 10) has slightly gone up from that of PS_{0.5}, which confirms the synergism in degradation assisted by generating more polar groups over PS along with ZnO.

Modification of the sample surfaces owing to catalytic photo degradation is investigated using AFM. Figures 10–12 compare the representative area roughness analysis data of virgin PS, PS_{0.5} before and PS_{0.5} after degradation (Figs. 10–12) respectively. The root mean square (RMS) roughness of PS as determined from the contact mode AFM analysis records a value of ~7 nm, which on addition of 0.5 wt-% of ZnO increases to 14 nm. This is quite understandable, as ZnO, being an inorganic oxide, has got substantial differences in surface energy from that of PS and hence tends to migrate more towards the surface. The same sample on photo catalytic degradation has become ~7 times rougher, recording a RMS roughness value of 101 nm. This complies with the earlier observations by Ochs *et al.* on roughening of organic coatings owing to UV degradation.²¹ The possible reason being the loss of oxidised materials (mainly as CO₂) from the surface on UV exposure.

The loss of materials in the form of CO₂ and H₂O preceding the cleavage of the main chain of PS is nicely reflected through the viscosity average molecular weight (M_v) measurements of the degraded samples. All the samples have been redissolved in toluene and the molecular weights are determined by studying their relative viscosities at different solution concentrations and subsequent fitting of the data in equation (1). The results are plotted in Fig. 13. The redissolution of the degraded samples in toluene also implies the fact that there has been negligible crosslink formation within the samples on UV exposure.

Peak Surface Area Summit Zero Crossing Stopband Execute Cursor

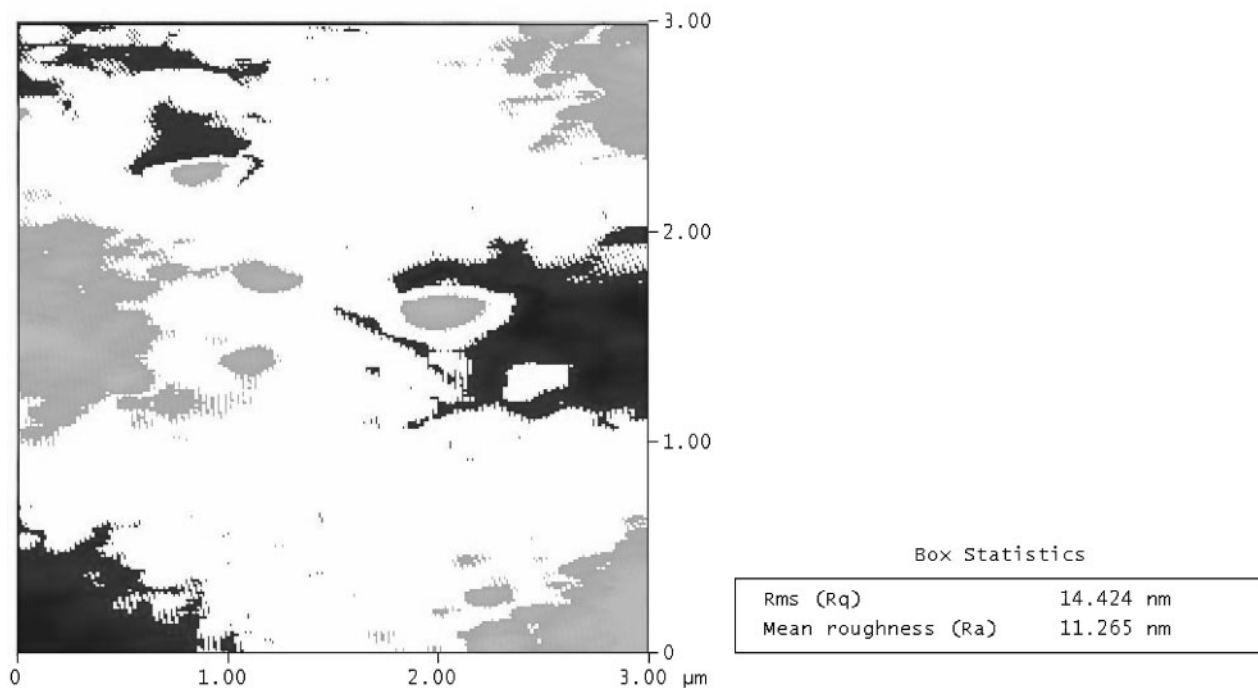
Roughness Analysis



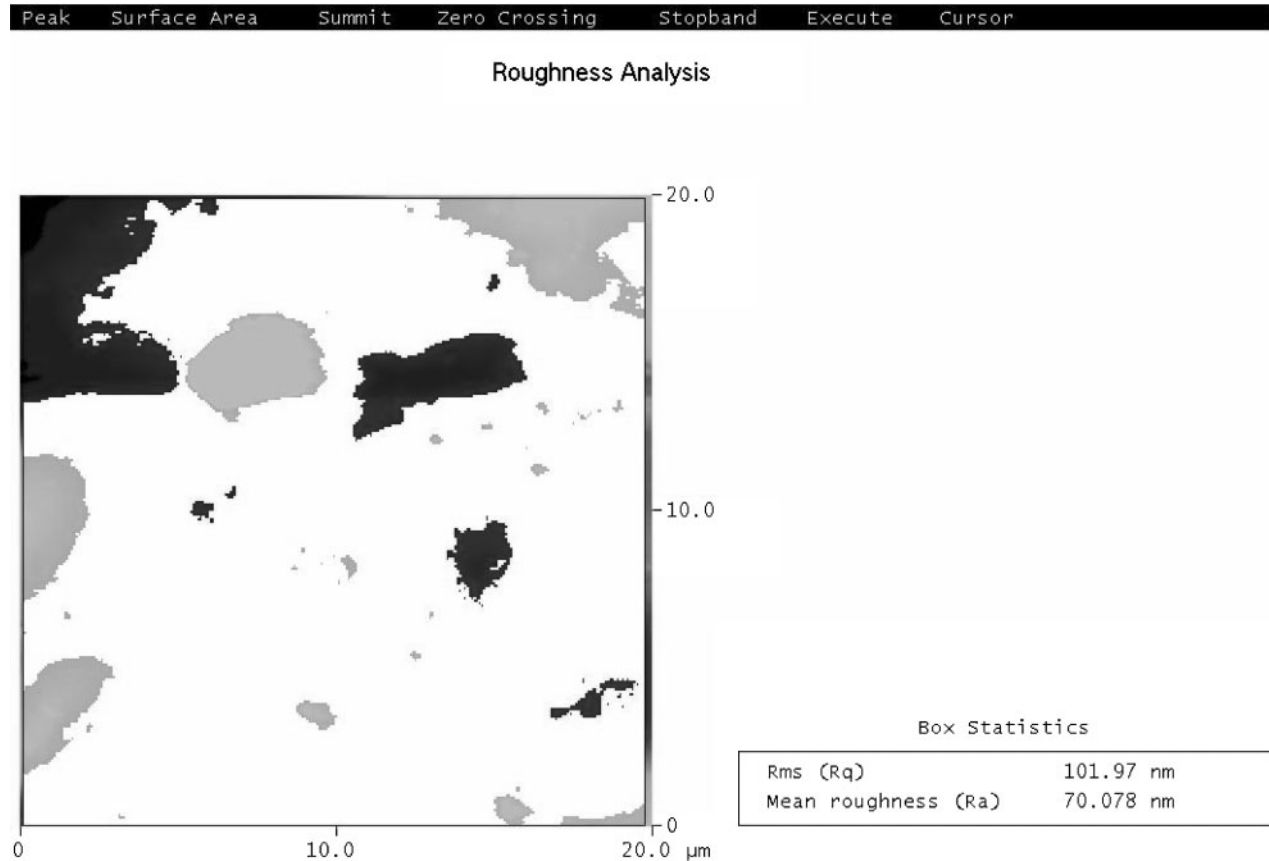
10 Atomic force microscopic roughness analysis of pure PS strip before degradation

Peak Surface Area Summit Zero Crossing Stopband Execute Cursor

Roughness Analysis



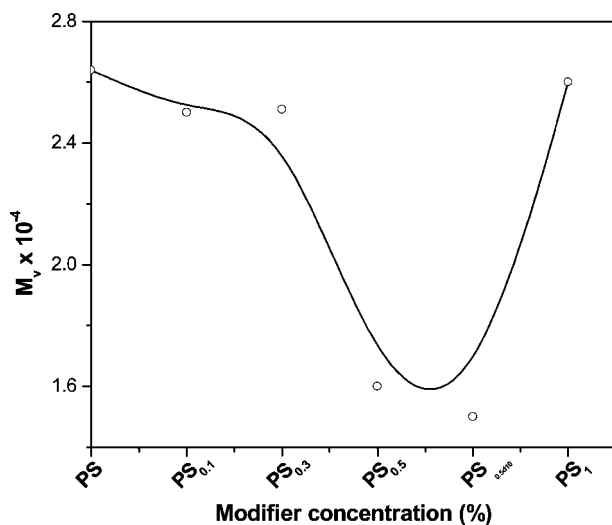
11 Atomic force microscopic roughness analysis of 0.5 wt-% ZnO containing PS sample before degradation



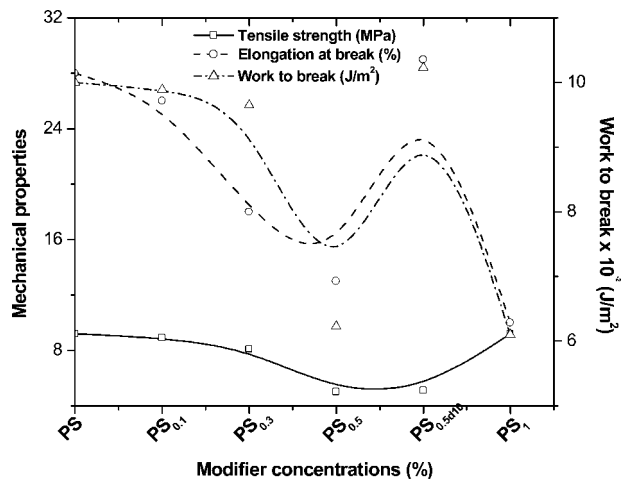
12 Atomic force microscopic roughness analysis for 0.5 wt-%ZnO containing PS sample after degradation

Pure PS has shown almost no weight loss owing to degradation and hence its molecular weight remains unchanged (2.64×10^4 as read from Fig. 13 is the same as that being reported in the experimental section for the undegraded PS). For 0.1 and 0.3 wt-%ZnO containing PS samples, the net weight losses are slightly greater (Fig. 4) and hence the corresponding M_v values are reduced accordingly. The maximum drop in M_v is obtained with 0.5 wt-%ZnO containing PS sample (Fig. 13). PS_{0.5} has shown the highest loss in weight,

which, as explained earlier, has been due to the simultaneous loss of some CO₂ and H₂O resulting in the degradation of the main chains and therefore records the minimum molecular weight value. On loading the dye, the molecular weight has further gone down (Fig. 13) owing to even more cleavage reaction of the main chains than that occurs in the previous case. At 1% ZnO concentration, the sample has exhibited almost no weight loss on exposure to UV within the experimental conditions probably owing to the lack of dispersion of ZnO within the PS matrix and hence exhibits almost no drop in the molecular weight values (Fig. 13).



13 Plots of post-degradation viscosity average molecular weight versus modifier concentrations for virgin PS and modified samples



14 Plots of variation in mechanical properties after degradation for virgin PS and modified samples

The drop in molecular weight poses detrimental effects on mechanical properties of the samples and these results are illustrated in Fig. 14. The variation in tensile strength for the different modified samples of PS is almost similar to that of the previously shown molecular weight curve (Fig. 13). The samples, which elucidate lesser extent of degradation, register higher tensile strength and the reverse phenomenon takes place for the cases with higher extent of degradation. The elongation at break (%) values show sharp drop with increasing weight loss of the samples. This is possibly due to two combined effects: increasing brittleness on account of catalytic photo oxidation and the increase in relative volume fraction of the ZnO particles owing to loss of organic matrix, which acts as flaws and causes early failure of the samples. The dye containing sample fails much early owing to similar reasons as well. Accordingly, the work required to break the samples calculated from the area under the tensile stress-strain curves varies inversely with that of the degradation phenomenon, i.e. the greater the photo degradation, the lesser the strength and elongation, and hence the lower the energy necessary to cause failure of the samples.

Summary and conclusions

The present investigation elucidates a very simple technique for the photo oxidative degradation of atactic PS films. Polystyrene, a non-degradable thermoplastic, has been modified with ZnO, which acts as a photo catalyst by transferring absorbed energy from the UV source to different bonds of the matrix hydrocarbon and ultimately leads to photo oxidative degradation of the same. A plausible mechanism leading to photo oxidation has also been suggested. There has been a net weight loss of 16% in only 2 h, recorded for PS on modification with ZnO, which increases up to 18% with the help of dye.

Interestingly, the photo degradation of PS has been greatly affected by the concentration of ZnO, dispersed within the PS matrix by solution mixing technique. In fact, beyond 0.5 wt-% of ZnO concentration, the rate of photo degradation has been slowed down significantly owing to poor dispersion of ZnO within the PS matrix and thereby leading to inferior PS-ZnO interaction.

The presence of several oxygenated groups, indicated from the FTIR spectroscopic analysis, modifies the PS surface. The sample becomes rougher after the degradation, as is being quantified through AFM analysis. The direct evidence of the main chain cleavage of PS has been obtained from the viscosity average molecular weight data, which actually decreases with increasing extent of photo degradation with different ZnO concentrations. The mechanical properties also become inferior on higher extent of degradation compared with those where the extent of degradation is low.

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