

EFFECT OF PHOTO ACCELERATORS ON THE DEGRADATION OF POLYSTYRENE FOAM WASTE

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Abstract

The Polystyrene (PS) foam has been widely used as food packaging and insulators. The former application has been commonly seen as take-away meal boxes. When it reaches the end-users, it would be discarded as municipal solid waste (MSWs). It would readily undergo photodegradation if it was disposed in the open-air dumping. It would take months to be degraded in the natural condition. In the present study, the degradation rate of the PS-foam in open-air dumping and in the artificial exposure, using Standard weatherometer, was investigated. Benzoyl peroxide and AIBN were used as photo accelerators. The concentration of these chemicals varied from 1% to 3% by weight. The decrease in the number average molecular weight of the samples, characterised by GPC technique, was monitored and used to calculate the reaction rate. By using the degradation rate mathematical modelling the order of reaction (b), rate constant (k') and the half-life ($t_{1/2}$) of the photo reactions were obtained. The results showed that the b was increased with the increase of concentration of the accelerators. Likewise, the k' decreased. However, by considering the $t_{1/2}$ it was found that the half life of photo reaction using peroxide as the accelerator slightly decreased when the concentration increased from 1% to 3%. Nevertheless, the value decreased significantly when the AIBN was employed.

Keywords: Polystyrene foam waste, photodegradation, accelerators, mathematical modelling

Introduction

The polystyrene (PS) foam is widely used as food container, especially as the take-away meal boxes. When it reaches the end users, it would be discarded as municipal solid waste (MSWs). A few of them go through the recycling processes. This plastic material is difficult to decompose in the environment. The best known methods for managing the MSWs are recycling, incinerating, landfill and open-air dumping. Each method has a definite limitation in respect of

economic and engineering point of view. Without an environmental awareness, tons of the foam would be left in the open-air environment as a pollutant and would take years to be degraded by the natural causes.

Polymer products can be degraded under the exposure to certain natural environment conditions. Its degradation rate depends largely on the environmental weather and on the generic of polymers. Solar radiation is one of the

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principal factors that have a significant influence on the photodegradation of these materials. The sunlight comprise much of the Ultraviolet (UV) radiation that is responsible for deterioration to the plastic products (Rabek, 1996). The PS foam is degraded when it is exposed to the sunlight and to the artificial light. It is also accelerated by photoinitiators such as ketones, quinones and peroxides (Rabek, 1996; Kaczmarek *et al.*, 2000). However, the degradation reaction is inhibited by photo-crosslinking reaction and the formation of double bonds in the polymer chain. The halogenated compounds found as the polymer additives is evidently observed to accelerate the degradation rate of PS as well (Kenharaj, 2001). In most cases, degradation rate increases when the halogenated flame retardant is incorporated.

It has been found that the foam was easily degraded by photo irradiation which is the reaction mechanism controlled by the environmental exposure (Mustafa *et al.*, 1993; Jellinek *et al.*, 1983). Under the sunlight, it was commonly degraded by chain scission. The degradation rate was influenced by photoinitiators, or accelerators, polymer additives and temperature, 10°C increasing in temperature under UV-light exposure would double the reaction rate (Torikai *et al.*, 1995).

In this work, the degradation of the PS foam by photo reaction was carried out in both natural open-air and in standard accelerated chamber. Photo accelerators, benzoyl peroxide and AIBN, were employed to accelerate the photodegradation progression. The main aim of the present work was to investigate the effect of type and concentration of the photo accelerators on the degradation rate of PS foam in both under natural sunlight and artificial conditions. The mathematical modelling was also employed to evaluate the reaction rate parameters.

Materials and Methods

Materials

The PS foam used in this study was directly obtained from the unused commercial meal boxes. It had the initial number average molecular weight (\bar{M}_n) and molecular weight

distribution (MWD or DP), characterised by GPC using PS as the standard reference, of 132,000 g/mole and 1.9, respectively. The rectangular specimens with the approximate dimension of 10 cm × 15 cm were manually cut using the sharp knife cutter.

Benzoyl peroxide and AIBN as the accelerators were supplied by Mark Schuchardt™ and were used as received. Prior to apply the accelerator onto the surface of specimen, it was dissolved in Ethyl Alcohol with the final concentration of 10% w/v. The solution was gently applied onto the surface of the sample by brushing and then completely dried by using warm air drier. The process was repeated until the required accumulative percentage of the weight of the accelerator (w/w), 1, 2 and 3% of the accelerator on the surface of the foam sample, was obtained.

Open-air Exposure

The samples with and without accelerator coated were exposed to the natural sunlight by attaching onto the standard exposure rack in according to the ASTM D 1435-85 at the annual average temperature of 27°C. The specimens were left to expose under the natural condition for a period of 180 days starting from September 1999 to February 2000. In order to follow up the degradation rate, the specimen was randomly taken on a weekly basis by cutting a tiny piece of sample with approximately 3 mm. in depth from the upper surface of specimen using sharp knife cutter. At least 6 sampling sites from a different test specimen were obtained for each sampling point. Consequently, they were dissolved in THF and then clarified by using microfiltration through the 0.5 µm PTFE filter. Finally, the \bar{M}_n and the MWD were analysed by GPC technique using HPLC grade THF as an eluent.

Artificial Weathering Exposure

Standard Weatherometer, S3000, manufactured by Atlas Electric Devices Co. was employed to carry out the artificial weathering trial. The instrument mainly consisted of a boro-borosilicate inner filter, the Xenon arc lamp, compressed air system and the deionized water used for cooling the system and as well as

spraying water as the artificial rain. The lamp system was used to generate the continuous UV light at 340 nm. The irradiation power of the lamp was constantly controlled at 0.5 W/m², which is equivalent to the UV energy dosage on the sample surface of 1.8 kJ/(m².h). Based on the meteorological data of Maung district, Nakhon Ratchasima as shown in Table 1 and from the calculation, approximately the total of 1,440 hours irradiation time would equal to a year of solar radiation energy obtained by the sunlight in this region (Kenharaj, 2001). The artificial test conditions are presented in Table 2. The lowest stable controlled test temperature in the chamber for this equipment was 65°C. The controlled values of the relative humidity, spraying cycle and the irradiation intensity in the chamber were 68%, every 2 minute and 0.5 W/m², respectively. The speed of the sample holder was rotated at 1 rpm. The samples were constantly collected by using the hole puncher with an approximate diameter of 0.5 cm. They were consequently turned inside out for homogenously exposed for both surface every 120 hours of the testing cycle. The \bar{M}_n of the degraded samples were followed up in the similar manner as described in the natural exposure.

Results and Discussion

Open-air Exposure

Figure 1 shows the plots of molecular weight (\bar{M}_n) and the MWD of neat PS and 1% Benzoyl peroxide coated PS sample obtained

Table 1. Meteorological data of Maung district, Nakhon Ratchasima.

Meteorological data	Average value (per year)
Temperature (°C) ^a	27.3
Relative humidity (%) ^a	68.1
Rainfall (mm) ^a	85
Total solar radiation (MJ/m ²) ^b	5,058

^a Data collected from January 1997 to 1998

^b Data collected from January 1996 to 1998

from the GPC with the exposure time, respectively. The molecular weight exponentially decreased from 132,000 g/mole to approximately 20,000 g/mole and the MWD slowly increased from 1.9 to about 5, within 180 days of the exposure time. From the curve, the results also suggested that there were two steps of molecular weight reduction. The first step was for the first 45 days where the chain reduction was dramatically declined. Then, it remained almost the same for a period of 80 days. After that the chain again decreased to 20,000 g/mole. At the final stage, the samples were very brittle and finally broken into tiny pieces by external natural forces such as wind and rainfall. Considering the changes in MWD , we could see there was a slightly increased in the first step of degradation. However, notable increase in MWD was observed at the last stage of deterioration. From the results obtained, the hypothesis for photodegradation of the PS foam could be pronounced that the initial degradation mechanism of the PS chain would be half chain scission mechanism. Accordingly, the molar mass of the polymer chain was exponentially decreased. However, this degradation phenomenon would not significantly affect to the MWD . As the result, it was not considerably distorted. Also by applying the mathematical modelling as shown below;

$$-\frac{d\bar{X}_n}{dt} = k[C]^a[\bar{X}_n]^b \tag{1}$$

$$-\frac{d\bar{X}_n}{dt} = k'[\bar{X}_n]^b \tag{2}$$

where $-\frac{d\bar{X}_n}{dt}$ = the reduction rate of the average chain length (\bar{X}_n) of the PS-foam (day⁻¹)

C = the concentration of the accelerator or additive (% wt)

t = the exposure time (days)

k = degradation rate constant

k' = overall rate constant = $k[C]^a$

and a and b = order of degradation reaction with respect to accelerator and average chain length of the foam, respectively

For the free radical addition polymerisation of PS, at a steady state condition, where the concentration of free radical was constant, was predetermined. Therefore, the photodegradation of this polymer, which underwent depolymerisation reaction, and the concentration of the radical was also assumed constant. The order of degradation reaction (b), the overall rate constant, (k'), and the half-life ($t_{1/2}$), which is the time for the chain length degraded into half, can be computed. They were shown in Table 2 (Kenharaj, 2001). The order of reactions, a and b , were 1.58 and 1.75, and the half life were 119 days and 84 days, for neat PS and the peroxide coated PS, respectively. These two numeric figures indicated that peroxide can be used to accelerate the photodegradation for the PS foam. When only for the half-life was considered, it suggested that the reaction rate almost doubled when only 1% of peroxide was incorporated onto the surface of PS foam.

Artificial Weathering Exposure

From the previous publication (Meekum and Kenharaj, 2002), by using the statistical analysis, ANOVA, it was found that the degradation data obtained from the artificial accelerated weathering exposure was intimately corresponded to those arisen from the open-air degradation. Consequently, by employing the artificial test condition, more generic type of accelerators and the effect of its concentration can be investigated. The plot of \bar{M}_n and MWD of the degraded products with the exposure time of PS foam without accelerator and also with 1%, 2% and 3% benzoyl peroxide in the artificial weathering chamber was shown in Figure 2. Closely related to those observed in the natural sunlight exposure, the \bar{M}_n of the foam samples were continuously and exponentially decreased with the exposure time. The final molecular weight of the polymer was reduced to around 8,000 g/mole. At the end of the exposure time, the specimen became brittle and eventually felt into tiny pieces caused by the force of the spraying water. Considering the trend of MWD change, we could see that it was yet again similar to that found in the natural exposure except that it increased more constantly than the

Table 2. The model values of b , k' and $t_{1/2}$ of the PS-foam in both open-air and accelerated exposure conditions.

Sample	Order of reaction (b) ^a	Rate const. (k') [*]	Half life ($t_{1/2}$) ^{**}
Open-air exposure:			
• neat PS-foam	1.58	3.51×10^{-4}	119
• PS-foam + 1% Peroxide	1.75	1.29×10^{-4}	84
Accelerated exposure:			
• neat PS-foam	1.78	1.95×10^{-5}	441
• PS-foam + 1% Peroxide	1.82	1.82×10^{-5}	348
• PS-foam + 2% Peroxide	1.91	8.91×10^{-6}	359
• PS-foam + 3% Peroxide	1.95	6.92×10^{-6}	343
• PS-foam + 1% AIBN	1.96	8.32×10^{-6}	264
• PS-foam + 2% AIBN	2.02	6.17×10^{-6}	228
• PS-foam + 3% AIBN	2.28	1.78×10^{-6}	119

^a obtained from the plot using equation (2)

^{*} Unit of k' are day⁻¹ and hour⁻¹ for open-air and accelerated exposure, respectively

^{**} Unit of $t_{1/2}$ is days and hours for open-air and accelerated exposure, respectively

previous observation. These results indicated that the random chain scission was more favored when directly exposed to the high-energy radiation. It might also be due to the fact that there was no seasonal fluctuation in the artificial chamber when compared with the natural contacts. Again by using the mathematical modelling as described above, it was found that the degradation rate was a function of the concentration the peroxide accelerator. Within the experimental errors, the rate constants (k'),

order of reaction (b) and also the half-life ($t_{1/2}$) of reaction derived from the model was summarised in Table 2. The $t_{1/2}$ decreased from 441 days to 343 days when 3% of peroxide were incorporated into the specimen. The results also showed that the reaction rate improved slightly by an increase in the accelerator concentration from 1% to 3%.

Figure 3 also illustrates the effect of AIBN concentration on the photodegradation rate of the PS-foam. The result showed the similar trend as

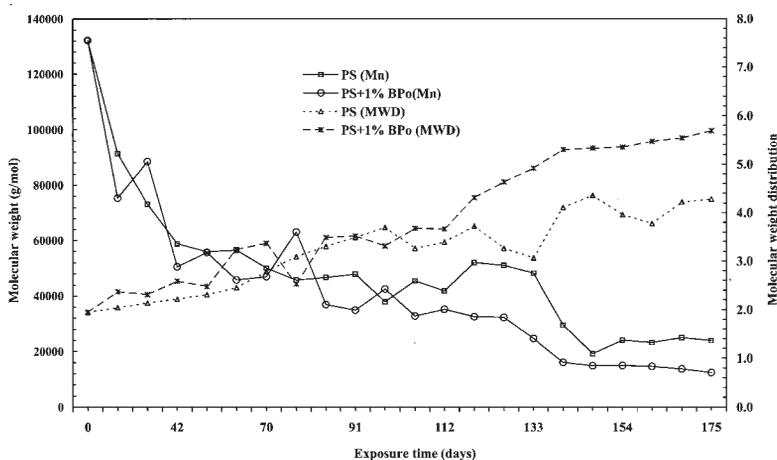


Figure 1. The \bar{M}_n and MWD of degraded (\square) neat PS foam and (\circ) 1%, peroxide coated PS foam under open-air exposure.

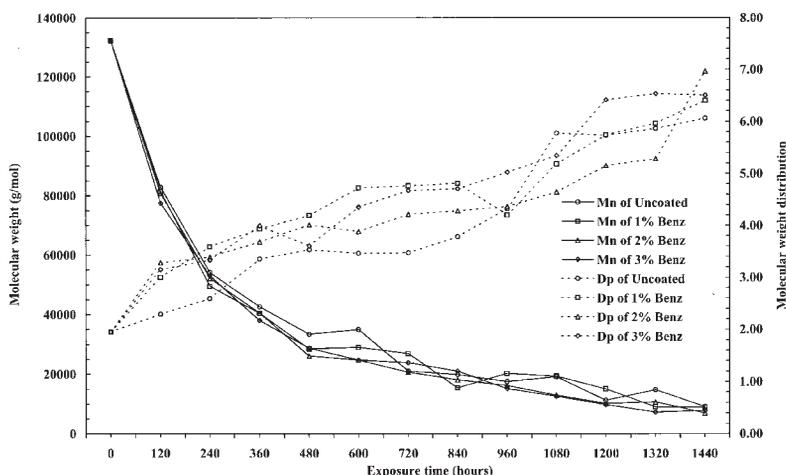


Figure 2. The \bar{M}_n and MWD of degraded (\circ) neat PS foam, (\square) 1%, (\triangle) 2% and (\diamond) 3% peroxide coated PS foam under artificial weathering exposure time.

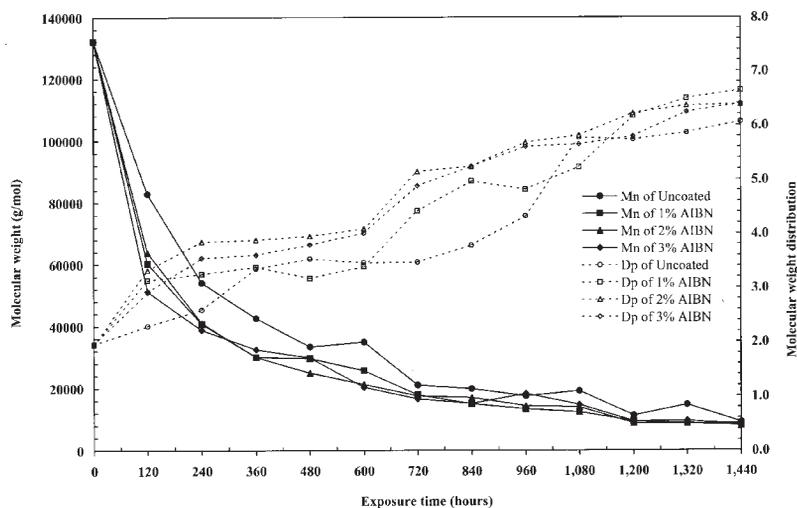


Figure 3. The \bar{M}_n and MWD of degraded (○) neat PS foam, (□) 1%, (△) 2% and (◇) 3% AIBN coated PS foam under artificial weathering exposure.

indicated in the deterioration rate using peroxide as the accelerator. Accordingly, the similar explanation would be appropriate. However, with the close observation on the order of the degradation reaction (b), the rate constant (k') and also the half-life ($t_{1/2}$) were obtained and summarised in Table 2. When the value of $t_{1/2}$ was considered, it was seen that the AIBN was a more effective photo accelerator than was the peroxide. By incorporating the AIBN up to 3%, the $t_{1/2}$ of the chain degradation decreased more than twofold, i.e., it decreased from 441 days to 119 days.

Conclusion

PS foam was exponentially degraded by the photo reaction under the open-air natural sunlight within 6 months. It also rapidly deteriorated in the accelerated chamber. Accelerators, benzoyl peroxide and AIBN can be used to enhance the degradation process in both experimental conditions.

By using the mathematical model to resolve the reaction rate parameters such as the order of reaction, the rate constant and the half-life of chain degradation, the results indicated that the degradation rate of PS-foam

depended on the generic types and also the concentration of the accelerators. From the data obtained in this study, the degradation rate increased with an increase of the accelerator concentration. It was also found that AIBN was a more effective photo accelerator than was benzoyl peroxide.

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