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STUDIES OF PHOTODEGRADABLE POLYSTYRENE

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The photodegradation of Polystyrenes containing sensitizers, such as aromatic nitro or quinone compounds, has been investigated. It was found that 1,4-naphthoquinone is the most effective sensitizer for the photodegradation of polystyrene among those tested in this study. The products of the light-irradiated polystyrene were examined by the IR spectroscopy and the thin layer chromatography. It is concluded that the photodegradation of the polystyrene proceeds mainly through the photo-oxidation of polymer.

The amount of consumed plastics is increasing every year and on the other hand junked plastics are turning to be one of the enviromental problems. Adoption of photodegradable plastics will be a useful approach to solve the treatment of waste plastics.

There have been reported two methods to make polymer photodegradable. One is the introduction of photosensitive groups into the polymer molecules. The copolymers with vinyl ketone which is a photosensitive group have been studied by Katoh.[1] The photodegradable plastics announced by Eastman Chemicals[2] seem to be the same type of copolymer containing ketone groups. Another is the addition of sensitizers to the polymer. In this system, light is absorbed by the sensitizer molecule and the absorbed energy is transferred to the polymer molecule which is successfully decomposed by the transferred energy. It has been reported that the addition of aldol-2-naphthyl amine into polyolefines (polyethylene, polypropylene and others) makes plastics photodegradable.[3] Research groups of University of Aston[4] and University of Tront[5] found ultraviolet sensitive materials which were effective to decompose polyolefines.

The light sensitizer type seems to be superior in some points to the copolymerization type because a sensitizer which is effective to a plastic may also be effective to other plastics and it is easy to control the rate of photodegradation by changing sensitiser's consentration.

It is well-known that some of quinone compounds are good sensitizers for the photo-oxidation reaction. Bolland and Cooper[6] studied the photo-oxidation reaction of alcohol by anthraquinone, and found oxidized products, such as aldehyde and peroxides.

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The above oxidation reaction can be applied to the photodegradation process of plastics, because the oxidation will finally cause the destruction of polymer. In this paper, polystyrene is chosen as the representative polymer, and aromatic nitro and quinone compounds are added to the polymer as light sensitizers.

EXPERIMENTAL

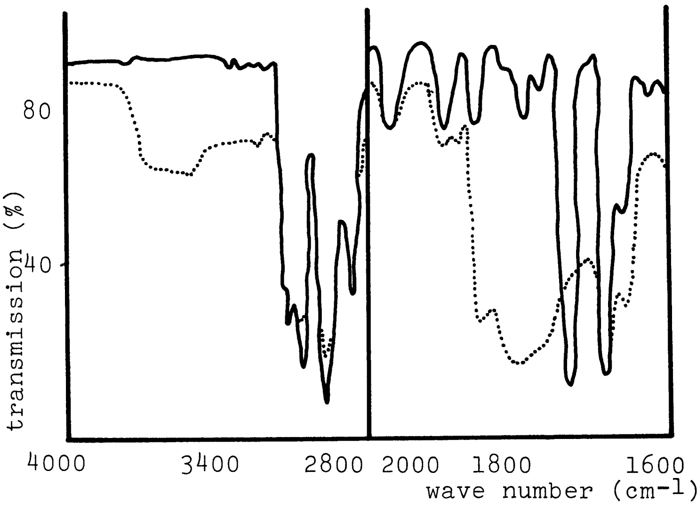
Polystyrene($\bar{P}_n$ = 1600 - 1800) used in the experiment was obtained from Wako Chemicals. Light sensitizers were dissolved into benzene solutions of polystyrene. The solutions were coated on metal plates and then polystyrene films (thickness: 25 - 35 μ) containing sensitizers were obtained after drying.

The films were exposed to a 1 KW Xe lamp at a distance of 30 cm distance. IR spectra of the irradiated films were measured to examine the structural changes of polymer. The photolytic products were analyzed by the thin layer chromatography coated by silica gel (0.2 mm) including fluorescent materials. A mixed solvent of acetone and cyclohexane (1:4) were used for the development of the products. The mechanical strength of the exposed film was tested by using a vibration machine and expressed by a time required for breaking the film completely.

RESULTS AND DISCUSSIONS

In Fig. 1 IR spectra of polystyrne with 1,4-napthoquinone before and after irradiation are shown. The amount of sensitizer added was 10 weight % with respect to polystyrene. The remarkable changes in the IR spectrum of polystyrene are observed mainly in the region near 3600 cm^{-1} and 1700 cm^{-1}, though the polystyrene without sensitizer shows no change in these regions as is shown in Fig. 2.

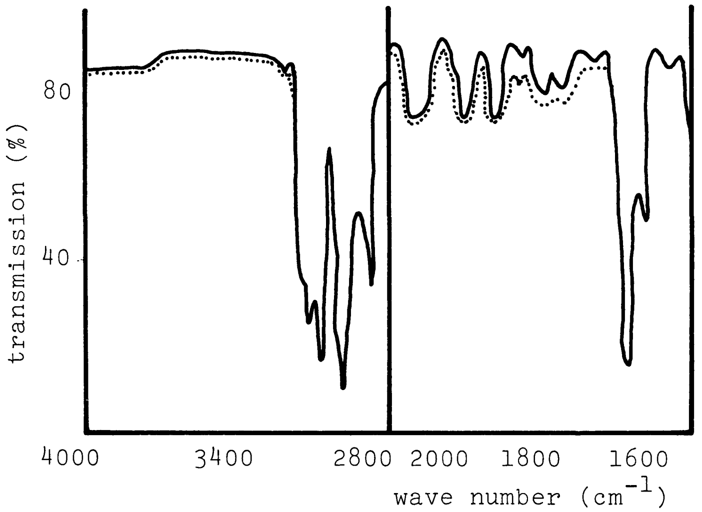
Many weak changes of the IR spectrum other than the above couple of regions are found. This fact indicates that decomposition of polystyrene will give several kinds of products. The appearance of the new bands in the 1700 cm^{-1} region seems to be due to the carboxylic or carbonyl group of the photodecomposition products. The increase of the adsorption band in the 3600 cm^{-1} region suggests the formation of hydroxyl group, which may be attributable to alcohol or carboxylic acid.



—Before irradiation,----Irradiated for 20 hours

Fig. 1. The IR spectra of polystyrene with the addition of 1,4-naphthoquinone (10 weight %) before and after irradiation to light.

The decomposition of the sensitized polystyrene are shown in Fig. 3. Since it was difficult to express the degree of degradation of polystyrene quantitatively, the relative values for the degradation were estimated from the intensities of IR absorptions at 1700 cm^{-1}. It is seen in this figure that 1,2-naphthoquinone is the most effective among four sensitizers. The rate of the degradation of polystyrene increases with increasing concentration of the sensitizer as is shown in Fig. 4. The rate of photo-degradation of the polystyrene film can be controlled by adjusting the sensitizer's concentration.



——Before irradiation,----Irradiated for 20 hours

Fig. 2. The IR spectra of pure polystyrene before and after irradiation to light.

The decomposed products were separated by the thin layer chromatography. The polystyrene film with 10 % 1,2-naphthoquinone exposed to light for 10 hours gives 0 - 0.7 of R_f value while the unexposed polystyrene gives 0.6. The thermally decomposed polystyrene at 200°C for 30 minutes gives 0 - 1 of the value. Therefore, the R_f value for the exposed polystyrene indicates that many kinds of photodecomposed products including low molecular weight's compounds are formed. Since aromatic acids, benzoic acid give 0.25 - 0.4 of R_f value at the same condition as the above, some of photodecomposed products of polystyrene may be acid derivatives.

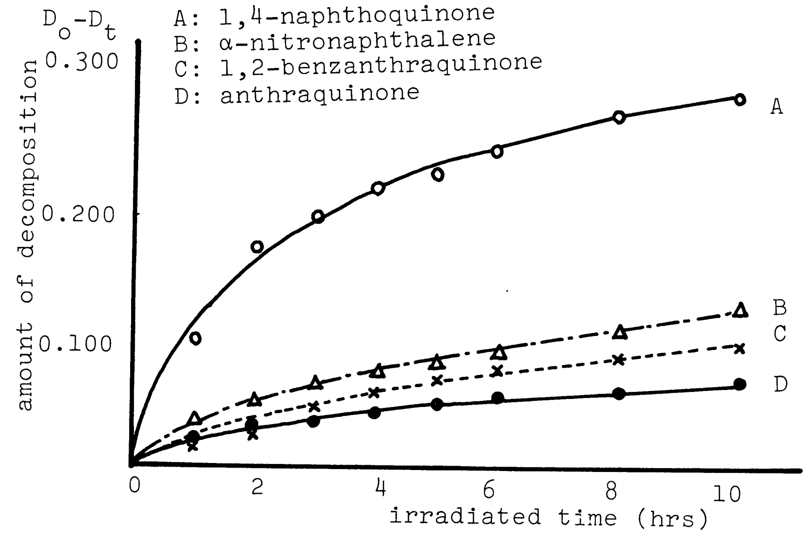


Fig. 3. The degradation of polystyrene with various sensitizers (10 weight % with respect to polystyrene)

The formation of acid derivatives indicates that the sensitized photo-oxidation takes places during the destruction process of polystyrene. Trozzolo[7] explained the photodecomposition of polystyrene by the singlet oxygen mechanism. The singlet oxygen might play an important role in the photo-oxidation of polystyrene but it is difficult to clarify the entire photodegradation mechanism from the results obtained here. One can only conclude that the degradation of polystyrene is caused by the sensitized photo-oxidation. Further experiments are required to determine the complete reaction scheme.

The mechanical strenth of the irradiated polystyrene film was tested by the vibrational method. The results are shown in Table 1. It is seen in this table

Table 1. Destruction time of the exposed polystyrenes

Sample	Concentration of 1,4-naphthoquinone	Irradiated time	Destruction time	Relative ratio of destruction
1	8 %	20 hrs	12 sec	1
2	8	10	21	1.8
3	none	10	1160	97
4	8	none	960	80
5	none	none	2300	192

that the irradiated polystyrene containing 1,4-naphthoquinone has much shorter destruction time, comparing with the non-irradiated polystyrene, while the irradiated polystyrene without sensitizer has not so different value from the pure polystyrene. The exposed polystyrene with the sensitizer shows a weak mechanical strength. It can easily be destructed to powder after 20 hours of exposure.

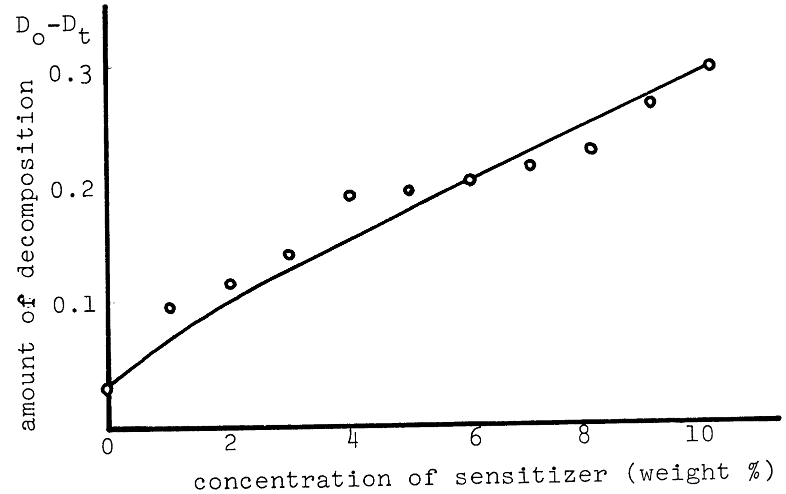


Fig. 4. The effect of sensitizer's concentration on the photodegradation of polystyrene (sensitizer used: 1,4-naphthoquinone).

The IR spectrum of the exposed polystyrene suggests that polystyrene is decomposed to oxidezed compounds and that photo-oxidation reaction proceeds during the exposure of the sensitized polystyrene. Polystyrenes containing sensitizers such as naphthoquinone, anthraquinone and nitro-naphthalene are found to be good photodegradable plastics. Since the sensitizers act as the photo-oxidation initiator for the decomposition, the same kind of sensitizer will be effective to the photo-oxidized degradation of several plastics other than polystyrene.

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