

DISPERSITY OF THE COPOLYMER OF STYRENE AND 2, 2, 6, 6-TETRAMETHYL-4-PIPERIDINYL- METHACRYLATE(PDS) IN POLYPROPYLENE AND ITS INFLUENCE ON PHOTOSTABILIZING ACTION OF PDS*

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ABSTRACT

The morphology of films of PDS/PP blends with various contents of PDS and with PDS of different molecular weights was examined by scanning electron microscopy and the photostability of these films was studied by infrared spectrometry. Experimental results show that PDS is dispersed in PP matrix as spherical globules being in size of the order of $10^{-1}\mu\text{m}$ when content of PDS is in the range of 0.1% to 1%. The phase separation of PDS from PP results in decrease in photostabilizing action of PDS to some extent. It is found that films of PP blended with PDS of different molecular weights show similar morphology and photostabilizing action if the content of PDS is kept constant.

Copolymer of styrene and 2,2,6,6-tetramethyl-4-piperidinyl-methacrylate (PDS) is a new polymeric hindered amine photostabilizer^[1]. For a polymeric stabilizer its compatibility with polymers to be stabilized and dispersity in the stabilized polymers are important. The morphology of blend system of polypropylene (PP) with 5% PDS has been observed by means of microscope by Fan and Hou^[2] and it has been found that PDS is dispersed in PP as separate phase of spherical globules. As a stabilizer PDS is added in polymer in a small amount (usually in the range of 0.1—1%). In such cases the dispersity of PDS in polymer and its influence on photostabilizing action of PDS is thus a topic of technological interest. In present work we examined the morphology of films of PP/PDS blends with various contents of PDS and with PDS of different molecular weights, and the photostability of these films. The influence of the dispersity of PDS in PP on its photostabilizing action was discussed.

Preparation of samples: A mixture of PP powder with PDS and antioxidant Irganox 1010 (the contents of PDS and Irganox 1010 are listed in Table I) was extruded twice by an extruder and cut into grains. The grains thus obtained were pressed into film, 80—90 μm , at 180°C for 1 min, followed by quenching in cold water. PP powder without any commercial additive was supplied by Liao Yang Petroleum Chemical Plant. PDS used with molecular weight 4200 was supplied by Beijing Third Chemical Plant and those with the other molecular weight were prepared in our laboratory.

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Scanning electron microscope observation: Sample films were cleaned many times with dilute nitric acid and distilled water, then dried and coated with a gold layer 200 Å thick by spray coating. The coated films were observed by a scanning electron microscope, Model SEMDX-3A (made by Scientific Instrument Plant, Academia Sinica, Beijing).

Photo-oxidation: The sample films were photo-oxidized in a Weather-Ometer (supplied by Chongqing Test Equipment Plant, Model CS-801). Two 1000 W high-pressure mercury lamps were utilized and a Pyrex glass filter was used to cut out light with wavelength shorter than 2900 Å. Test temperature was $50 \pm 1^\circ\text{C}$. Photo-oxidation product ($>\text{C}=\text{O}$) of PP films was monitored by infra-red spectroscopy using Perkin-Elmer spectrometer Model 180.

Fig. 1 shows the electron micrographs obtained from the pure PP film and PP films with different PDS content. As shown from Figs. 1a, b, the micrograph of PP film containing 0.05% PDS is almost the same as that of pure PP film, and phase separation is not observed. However, when PDS content in PP films is in the range of 0.1% to 1%, the phase separation is obviously observed (Figs. 1c, d, e), and PDS is dispersed in PP as separated spherical globules. This result is similar to that obtained from microscopic observation^[2]. However, in our case the particle size of PDS is about of the order of $10^{-1}\mu\text{m}$, smaller than that given in [2] approximately by an order of magnitude.

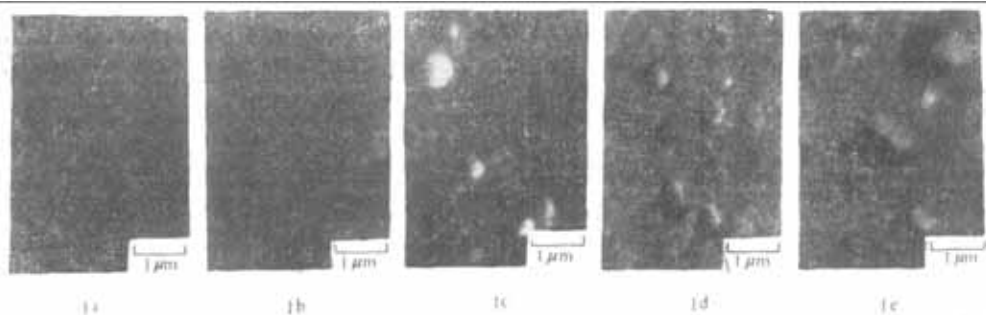


Fig. 1 Electron micrographs of PP film and PP films with different contents of PDS
PDS content (%): (a) 0; (b) 0.05; (c) 0.1; (d) 0.3; (e) 1.
Multiplying power: 10000.

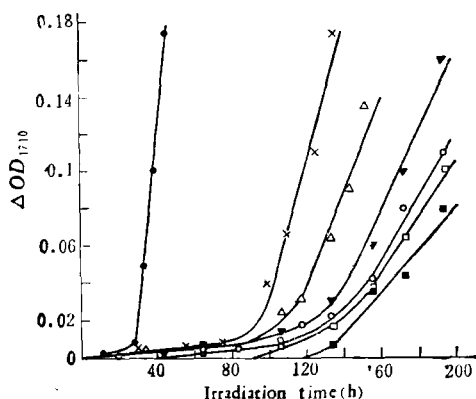


Fig. 2 Formation of carbonyl (1710cm^{-1}) during photo-oxidation of PP films with different contents of PDS:
PDS content (%): 0(●); 0.05(×); 0.1(△); 0.3(▼); 0.5(○); 0.7(□); 1(■).

Fig. 2 shows the kinetic curves of the formation of carbonyl group during photo-oxidation for PP films with various PDS contents. Taking the time when increment of optical density of infrared absorption of carbonyl $\Delta O.D_{1710}$ reaches 0.02 as the induction period, we obtained the values shown in the fourth column of Table 1. The times to embrittlement of these films are also listed in Table 1 (column 5). From comparison the values of induction periods with times to embrittlement it can be seen that they correspond with each other. The change of induction periods of PP films with the change of PDS content is shown in Fig. 3.

Table 1 Photostability of PP films with various contents of PDS and with PDS of different molecular weights

Sample	PDS content* (wt%)	Molecular weight of PDS	Induction period of photo-oxidation (h)	Time to embrit- tlement (h)
0	0	—	30	42
1	0.05	4200	94	107
2	0.1	4200	106	126
3	0.3	4200	122	173
4	0.5	4200	132	182
5	0.7	4200	136	182
6	1	4200	146	193
8	0.1	5600	106	133
9	0.1	17500	87	107
10	0.1	12000	94	126
11	0.1	8000	108	133
12	0.1	3240	108	133

* Except for 0# film in each sample film Irganox 1010 is added (0.05%) to protect PP from thermal oxidation in processing.

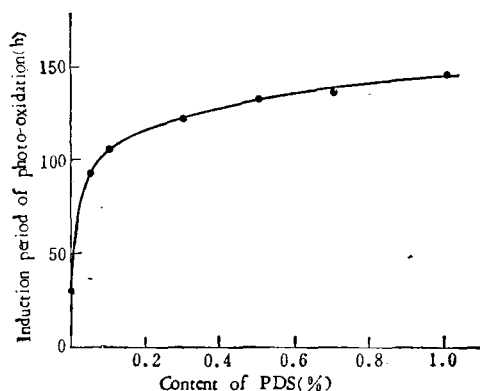


Fig. 3 Effect of PDS content on photostability of PP films with PDS

There exists obvious correlation between the experimental results related to photostabilizing action and dispersity of PDS in PP. Thus, when PDS content is 0.05%, the phase separation is not observed from the electron micrograph. Correspondingly, stabilizing effectiveness of PDS seems the highest in this case. Adding 0.05% PDS to PP leads the induction period to increase from 30 h to 94 h (the increment of induction period is 64 h) (Table 1). When PDS content is 0.1%, there appears clear phase-separation. Since part of piperidine groups active for stabilization is surrounded within the center of PDS spherical particles and thus protected from contacting with PP, the stabilizing effectiveness of PDS would decrease. Experimental result shows that when PDS content increases from 0.05% to 0.1% (increment is 0.05%), the increment of induction period is only 12 h. Stabilizing effectiveness obviously decreases indeed in this case. When PDS content is in the range of 0.1%—1% dispersity of PDS in PP is not so different from each other (Figs. 1c, d, e) and the PDS particle size is about of the same order, the particle number would increase with the increased content so that the photostabilizing effect would correspondingly increase. As shown in Fig. 3, the photostabilizing effect indeed increases gradually with PDS content increase in this range. However, the inhomogeneity of PDS particle size and distribution will increase with the further increase of PDS content. In fact, as shown in [2], when PDS content is 5%, the particle size of PDS reaches several micrometer. Therefore, the tendency of photostabilizing action to increase with the increase of PDS content should gradually decrease. From our experimental data it is shown that the photostability of PP fibers containing PDS 1.5% and 1.0% respectively is nearly the same. In present work since the dispersity of PDS is nearly similar in the range of PDS content from 0.1% to 1%, increase of PDS content can lead to some rise of the stabilizing action, but the tendency of stabilizing action to increase gradually becomes less (Fig. 3). It is easy to see that further increase of PDS content over that range have no significant value for promoting the photostabilizing action. From the above-mentioned result we can obtain some conclusion interesting for practice that the optimum amount of PDS added to the polymer is several tenth of 1 percent.

From electron microscope observation it is found that films containing PDS of the same content (0.1%) but with different molecular weights show similar morphology (similar to that shown in Fig. 1c). It means that in the range of molecular weights used in our experiments (3240—17500), the molecular weight difference does not lead to great change in the dispersity of PDS.

Fig. 4 shows the formation of carbonyl during photo-oxidation of PP films containing PDS with various molecular weights. The values of induction periods and times to embrittlement for these films are listed in Table 1. It can be seen that only for films with PDS of molecular weight 17500 and 12000 the photo-oxidation rates are a little higher, but for others the photo-oxidation rates are the same. Apparently, this result coincides with that of morphology observation.

It must be noted that these experimental results are obtained when molecular weight of PDS is changed in a rather small range. If the change of molecular weight is over this range, there might be other situation. It is needed, therefore, to study the influence of molecular weight in a larger range of change.

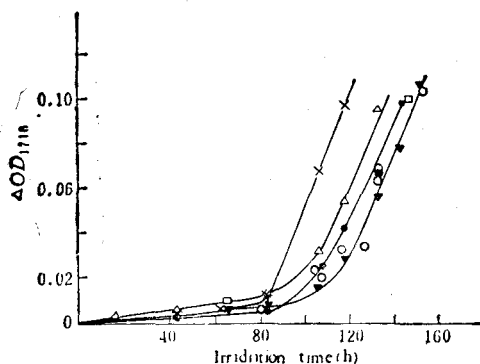


Fig. 4 Formation of carbonyl (1710 cm^{-1}) during photo-oxidation of PP films containing PDS with different molecular weights
Molecular weight of PDS: 4200 (□); 5600 (●); 17500 (×); 12000 (△); 8000 (▼); 3240 (○). Content of PDS: 0.1%.

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