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Preparation of Polymeric Ultraviolet Absorbers and Their Effects on the Photodegradation of Polyethylene

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SUMMARY

Polymeric ultraviolet absorbers were prepared from 2-hydroxy-4-acryloyloxybenzophenone and 2-hydroxy-4-methacryloyloxybenzophenone and their inhibitive effect for photodegradation of polyethylene were examined by measuring mechanical strength, melt index, carbonyl group, and color difference.

The polymeric ultraviolet absorbers were superior to the same type of ultraviolet absorber with low molecular weight in many properties, but inferior to Tinuvin, a commercial reagent, which has a different molecular structure. Therefore, within the ultraviolet absorbers examined, molecular structure seems to be a more important factor than molecular weight.

EXPERIMENTAL

Preparation of Monomers

2-Hydroxy-4-acryloyloxybenzophenone was prepared according to the previously reported method [21] by the reaction of acrylyl chloride and

2,4-dihydroxybenzophenone. 2-Hydroxy-4-methacryloyloxybenzophenone was similarly prepared by reacting methacrylyl chloride and 2,4-dihydroxybenzophenone.

Polymerization

These monomers gave no homopolymeric materials by the use of such conventional radical initiators as benzoyl peroxide and azobisisoacrylonitrile or by the use of such anionic initiators as grignard reagents and *n*-butyllithium under our experiment conditions. However, the binary catalyst system of metallic salts-dioxane hydroperoxide, which we developed, gave polymeric UV absorbers from these monomers very successfully.

The polymerization conditions and results are given in Table 1. The detailed structure of the polymeric materials obtained will be published elsewhere in the future.

Table 1. Polymerization Conditions and Results^a

Monomer (g)	Co(acac) ₂ (mole/l)	DOX-HPO (mole/l)	Temperature (°C)	Time (hr)	Conversion (%)
BA: 2.0	5×10^{-3}	7.18×10^{-3}	60	10	84.2
BMA: 0.5	5×10^{-3}	5.5×10^{-3}	60	6	63.2

^aSolvent: dioxane, 10 ml. BA: benzophenone acrylate. BMA: benzophenone methacrylate.

INTRODUCTION

Additives such as antioxidant and ultraviolet (UV) absorber evaporate during the molding process or migrate out from plastics on prolonged use [1-6], and this causes unfavorable loss of the inhibitive efficiency for the deterioration of polymers.

Two methods have been considered to overcome this problem. One is to attach UV absorbers permanently or covalently to polymeric materials by introduction of reactive or polymerizable groups such as vinyl or allyl groups to UV absorbers. The other is to prepare polymeric UV absorbers that are less mobile than the conventional low molecular weight compounds [7-21].

This paper describes the preparation of polymeric UV absorbers from 2-hydroxy-4-acryloyloxybenzophenone and 2-hydroxy-4-methacryloyloxybenzophenone, and its inhibitive effects on the photodegradation of polyethylene compared with that of commercial UV absorbers of low molecular weight.

Polymerization was carried out in a glass tube under nitrogen atmosphere. The conditions are shown in Table 1. After polymerization the content of the tube was poured into a large amount of methanol to precipitate the polymer. The polymer obtained was purified by precipitation with the chloroform-methanol system as usual. The purified polymers were dried under vacuum and used for the photodegradation test of polyethylene.

Preparation of Test Specimens and Photodegradation

Polyethylene with a melt index of 0.51 was mixed with commercial UV absorbers or polymeric UV absorbers in a mixer at room temperature for 30 min. The kind and amount of the additives are given in Table 2. The polymers were compression-molded by a 26 ton automatic press under the following conditions: Temperature, 180°C; preheating for 3 min, pressure 110 kg/cm²; and time 4 min, 1 for raising pressure and 3 for pressing.

All films were pressed between Teflon-coated aluminum plates and the resulting effective thickness was 0.35 ± 0.02 mm. Cooling of the films was accomplished by immersing the plates into a water bath at 17 ± 2°C. Rectangular pieces of uniform thickness were cut from each film and used directly for the photodegradation test.

The specimens were placed in a Sunshine Weather-Ometer (Toyo Seiki WESUN-HC type), at a temperature 63 ± 3°C at 50% relative humidity without spray for the desired time.

Physical Tests

Tensile Strength. Tensile strength of the specimens was made by a Tensilon All Mighty Tensile Strength Tester (Toyo Sokuki UT, M-1 5000). The retention of tensile strength was calculated by

$$F = F_t/F_0 \times 100$$

where F = retention of tensile strength (%) (for yield, elongation, breaking); F_t = tensile strength after exposure; and F_0 = tensile strength of the original specimen.

Table 2. Description of Samples^a

Sample No.	UV absorber
1	None
2	Uvinul-400 ^b (0.02 phr) ^c
3	Poly-BA (0.02 phr)
4	Poly-BMA (0.02 phr)
5	OPS ^d (0.05 phr)
6	Tinuvin 327 ^e (0.02 phr)

^aEach sample contains BHT (4-hydroxy-3,5-di-tert-butyltoluene; 0.05 phr) and DSTDT (distearylthiodipropionate; 0.05 phr).

^bUvinul 400: 2,4-dihydroxybenzophenone.

^cPHR: parts per hundred resin.

^dOPS: p-octoxyphenyl salicylate.

^eTinuvin 327: 2-(2'-hydroxy-3',5'-di-tert-butylphenyl)-5-chlorobenzotriazol.

Melt Index. Melt indexes were measured according to ASTM under the following conditions: Sample, ca. 4 g; load, 2.160 kg; preheating, 6 min; temperature, 190°C. The melt index was given as effluent weight, g/10 min.

Ball Impact Test. Ball impact test was made by a Ball Impact Tester (Long Corp., U.S.A.) at an impact speed of 50 m/sec. The impact energy was calculated according to

$$\text{impact energy} = \frac{1}{2} MD^2 \left[\left(\frac{1}{T_1^2} - \frac{1}{T_2^2} \right) - \frac{1}{T_{1A}^2} + \frac{1}{T_{2A}^2} \right]$$

where D = distance between phototubes (cm), M = mass of ball, T_1 = time detected by Phototube 1 with sample, T_2 = time detected by Phototube 2 with sample, T_{1A} = time detected by Phototube 1 without sample, and T_{2A} = time detected by Phototube 2 without sample. T_{1A} and T_{2A} are correction terms of air resistance. Thus, the final equation used for the calculation of impact strength was

$$\text{impact strength} = 2.0395 \times 10^8 W [(1/T_1^2 - 1/T_2^2) - (1/T_{1A}^2 - 1/T_{2A}^2)] \text{ (kg cm)}$$

where W = weight of ball (g), and T = time (μsec).

Color Difference. Color difference was measured by an Automatic Color and Color Difference Meter (Toyo Rika Corp., AU-CH-1), and estimated according to the following equation (ASTM-D-1365-55T)

$$\Delta ab = (aL^2 + bL^2)^{1/2}$$

where aL = color value for red-green direction after certain exposure time, and bL = color value for yellow-blue direction after a certain exposure time.

RESULTS AND DISCUSSION

Mechanical Strength

Retention of strength determined by a ball impact strength test was plotted against exposure time and is shown in Fig. 1. As shown, retention

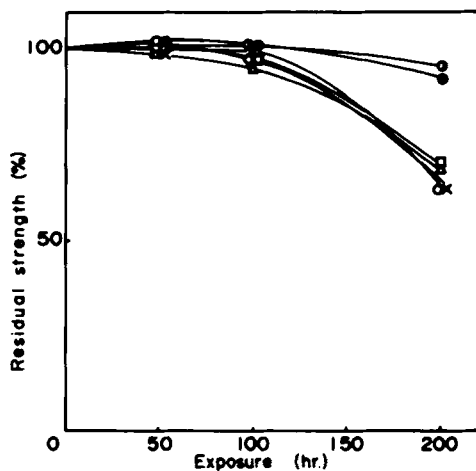


Fig. 1. Residual strength vs. exposure time. ○: No. 1. ×: No. 2. △: No. 3. □: No. 4. ●: No. 5. ◐: No. 6.

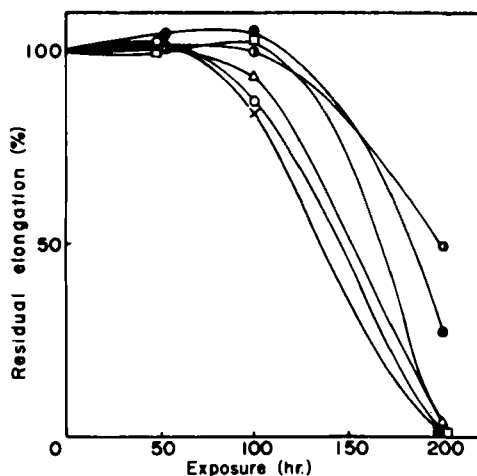


Fig. 2. Residual elongation vs. exposure time. ○: No. 1. ×: No. 2. △: No. 3. □: No. 4. ●: No. 5. ◐: No. 6.

strength does not change until 100 hr of exposure in each sample, but at 200 hr exposure appreciable differences are observed among the samples. Mechanical strength of Samples 1, 2, 3, and 4 drop markedly at 200 hr exposure and Samples 5 and 6 retain most of their original strength. However, polymeric UV absorbers (Nos. 3 and 4) show slightly higher retention strength than do Nos. 1 and 2.

Retention elongation was plotted against exposure time, as shown in Fig. 2. As shown, elongation drops extremely at 200 hr exposure. Nos. 1, 2, 3, and 4 lost almost all of their original elongation, but Nos. 5 and 6 possess ca. half of their original elongation. At 50 hr exposure no appreciable difference is observed among the samples, and at 100 hr exposure Nos. 1 and 2 show slightly lower elongation.

Similar results were obtained in yield and breaking strength.

Melt Index

Melt index was plotted against exposure time and is shown in Fig. 3. In general, melt index indicates the initial cross-linking of polymer which causes the decrease in fluidity of polymer and the successive main chain cleavage by photodegradation. Thus, polymeric materials with less change in melt index are considered to be stable for photodegradation. With respect to this principle, the melt index

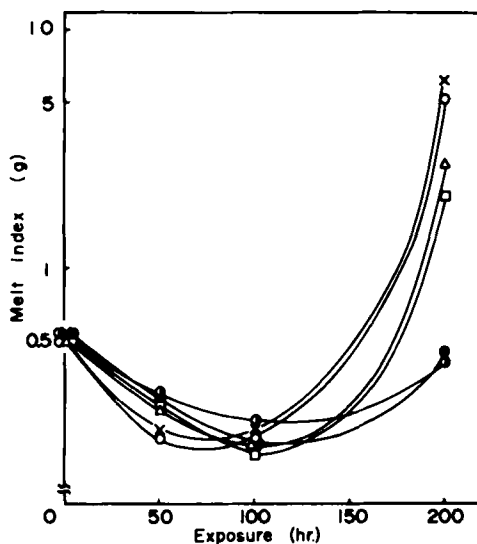


Fig. 3. Melt index vs. exposure time. ○: No. 1. X: No. 2. △: No. 3. □: No. 4. ●: No. 5. ◐: No. 6.

shown in Fig. 3 illustrates the chemical reaction which occurs differently among the samples. According to Fig. 3, the change of melt index seems to be divided into three groups: Nos. 1 and 2, Nos. 3 and 4, and Nos. 5 and 6 in the following stable order:

$$\text{Nos. 5 and 6} > \text{Nos. 3 and 4} > \text{Nos. 1 and 2}$$

At 50 hr exposure, the decrease in the melt index of Nos. 1 and 2 is larger than that of the other samples. At 100 hr exposure most of the samples show minimum values and the remarkable difference among them is unobservable. However, a drastic change occurs at 200 hr exposure. Namely, Nos. 1 and 2 show the highest melt index, indicating the occurrence of a number of main chain cleavages between 100 and 200 hr. The samples containing polymeric UV absorbers also increase the melt index; however, the values are lower than those of Nos. 1 and 2 samples. Melt indexes of Nos. 5 and 6 are much lower than those of the other samples; in other words, they are more stable to photodegradation than the other samples.

These results indicate that the efficiency of the UV absorbers for the

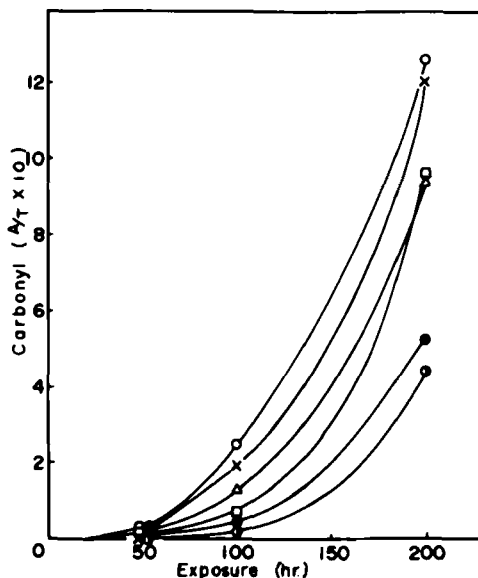


Fig. 4. Carbonyl (1725 cm^{-1}) vs. exposure time. ○: No. 1. X: No. 2. △: No. 3. □: No. 4. ●: No. 5. ◐: No. 6. A: intensity at 1725 cm^{-1} .

inhibition of the photodegradation of polymers is primarily dependent on the structure of the absorbers. Second, it is dependent on the molecular weight of the absorbers, and higher molecular weight compounds are more effective than lower molecular weight compounds.

Carbonyl Group

The optical sensitivity at 1725 cm^{-1} was plotted against exposure time and is shown in Fig. 4. The carbonyl group is a good parameter to estimate the chemical change in polymeric material during the oxidative degradation of polymers, and the absorption spectra of the carbonyl region increases with the formation of oxygenated groups.

As shown in Fig. 4, the carbonyl group increases with increasing exposure time, and the samples can be divided into three groups: the first group (Nos. 1 and 2), which is very accessible to oxidation and gives a higher carbonyl content, the second group (Nos. 3 and 4), and the third group (Nos. 5 and 6), which is stable and gives a lower carbonyl content. The order of chemical change estimated by carbonyl group is consistent with that of melt index, i.e., polymeric UV absorbers are more effective than

the same type of UV absorbers with low molecular weight, but are less effective than other types of absorbers, Tinuvin and OPS.

Color Difference

The change of color difference during the photodegradation is shown in Fig. 5. For an UV absorber, it is naturally desirable that the compounds have a light original color and do not change the color during the photoirradiation. As shown in Fig. 5, polymeric UV absorbers (Nos. 3 and 4) are more favorable than No. 2 (Uvinul-400) and No. 5 (OPS).

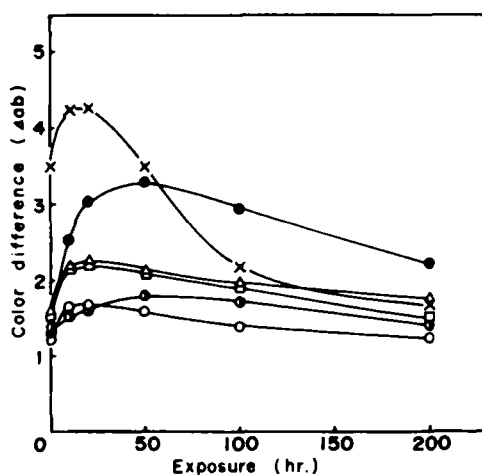


Fig. 5. Color difference vs. exposure time. ○: No. 1. X: No. 2. Δ: No. 3. □: No. 4. ●: No. 5. ◐: No. 6.

Various factors must be considered in the evaluation of UV absorbers for photodegradation of polymeric materials, for example, heat and photostability, ability to absorb UV, compatibility with polymer, volatilization properties at molding temperature, migration properties for prolonged storage or usage, and coloring properties. Therefore it seems rational to evaluate the UV absorbers examined in this experiment from two points of view: molecular weight and structure of UV absorbers.

With respect to molecular weight, as previously mentioned, physical and chemical tests indicate that polymeric UV absorbers (Nos. 3 and 4) are superior to Uvinul-400 (No. 2) with low molecular weight, i.e., higher mechanical strength (see Figs. 1 and 2), lower melt index changes (see Fig. 3), lower carbonyl formation (see Fig. 4), and less color difference

(see Fig. 5). These favorable properties, observed in polymeric UV absorbers, obviously seem to be given by higher molecular weight affecting the factors mentioned above. However, polymeric UV absorbers are inferior to commercial Tinuvin in many properties.

Therefore, within the UV absorbers examined, the efficiency of UV absorbers for the inhibition of photodegradation of polymers is primarily dependent on the type or structure, and secondly on the molecular weight.

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