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Effect of Hindered Piperidine Derivatives on Polypropylene Photooxidation

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Summary

The photostabilizing effect of a hindered piperidine derivative was studied in the photooxidation of polypropylene films by following the formation of carbonyl and hydroperoxide groups, as well as the change of concentration of the stabilizer. This additive - the tetramethylpiperidine sebacate - proved to be more effective than hydroxybenzophenone, hydroxybenztriazole or a sulphur containing nickel complex, since no oxidation products were formed after irradiation with 200 Mlxh dose.

Addition of the piperidine derivative together with hydroxybenztriazole or with the organic nickel complex was less effective than with hydroxybenzophenone. In latter case concentration of both stabilizers under irradiation decreased at a slower rate than in the case of separate application. The effect of Cyasorb UV 531 and Tinuvin 770 was additive and the spontaneous rupture of the samples took place only after a long period of irradiation (~ 250 Mlxh).

Introduction

The main features of polyolefin photooxidation are similar to those of thermal oxidation: initiation resulting in radicals followed by oxidation leading to chain scission and to deterioration of physical and mechanical properties. Since polypropylene absorbs light arriving on earth (i.e., above 310 nm) only in a very slight degree, photolysis may occur due to chromofore groups (mainly carbonyls) formed in the polymer during polymerization, processing or storage (HESKINS, GUILLET, 1968; CARLSSON, WILES, 1969). Carbonyls may decompose - depending on conditions - by Norrish I and Norrish II reaction. In course of these processes alkyl and alkoxy radicals, as well as low molecular weight oxygen containing products (e.g. acetone) and olefins are formed. The oxidation of macroradicals leads to the formation of hydroperoxides whose photoinitiated decomposition results in degenerated branching of the kinetic chain. Excited oxygen molecules

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may also be involved in photooxidation by addition to the vinyl groups which also leads to hydroperoxide formation (CICCHETTI, 1970).

Polymers can be protected against photooxidation by application of additives acting by various mechanisms. Substituted o-hydroxybenzophenones and benztriazoles act as UV-absorbers, they prevent excitation of the polymer or impurities by UV light, while sulphur containing organic metal complexes work as quenchers (GUILLORY, COOK, 1973) and - according to other authors - they decompose hydroperoxide groups to non-radical products (CARLSSON, WILES, 1974). Hindered amines do not absorb significantly in the range of UV light arriving on the earth. Their effect cannot be explained by UV-absorption or quenching (SHLIAPINTOKH et al., 1973).

This paper does not deal with the mechanism of hindered piperidine derivatives, rather, it compares their photostabilizing effect with that of some other additives acting as UV-absorber or quencher. Also the efficiency of piperidine derivative in the presence of other stabilizers is briefly described.

Experimental

Materials:

Polymer: Isotactic polypropylene (DAPLEN AT 10) of Petrolchemie A.G.; prepared in laboratory, without additives.

Stabilizers: Commercial, as well as laboratory products.

Cyasorb UV 531 (Cy, Cyanamid product; 2-oxy-4-octyloxybenzophenone)

Tinuvin 326 (Tin 326, Ciba-Geigy product; 2[2-oxy-2-tertiary-butyl-5-methyl-phenyl]-5-chloro-2H-benztriazole)

Ni-DBTC (prepared in our laboratory; nickel dibutyl-dithio-carbamate)

Tinuvin 770 (Tin 770, Ciba-Geigy product; bis-tetramethyl-piperidine sebacate)

TMPS (prepared in our laboratory; bis-tetramethyl-piperidine sebacate).

Stabilizers were added in 1 weight % - relative to the polymer. Samples contained 0,2 weight % Topanol OC antioxidant to avoid oxidation during pressing.

Sample preparation: The stabilizers were mixed with the polymer in benzene solution. After evaporation of the solvent films of about 100 μm thickness were pressed.

Photooxidation was performed in a laboratory-made apparatus, using a Xenon-lamp of 1600 W (TUNGSRAM XHP). The light was focused by elliptic mirrors in a special housing onto the samples mounted on a rotating drum in a thermostate. The daily dose was 2.5-3.5 Mlxh (megalux-hours). This corresponds to 3-5 . 10^{-7} Einstein $s^{-1}cm^{-2}$.

Investigation methods:The concentration of carbonyl groups formed during photooxidation was determined from the integrated intensity of IR band at 1715 cm^{-1}. Concentration change of stabilizer was followed by UV absorption spectra of the additives, on the basis of previous calibration. Wave length: Cy: 327 nm; Tin 326: 354 nm; Ni-DBTC: 328 nm; TMPS: 268 nm. Hydroperoxide concentration was determined by iodometry and by integrated intensity of IR band at 3400 cm^{-1} (LÁSZLÓ-HEDVIG et al.).

Experimental results and discussion

In a previous paper it was shown, that in the case of Cy, Tin 326 and Ni-DBTC the concentration of carbonyl and hydroperoxide groups increases after an induction period depending on the quality and quantity of the stabilizers (BÁLINT et al., 1976). After the induction period the formation rate does not depend on the stabilizer because by the end of the induction period the additive has decomposed or transformed into inactive products. The changes in stabilizer concentration and carbonyl formation are different for the various additives, e.g. the amount of Cy decreases linearly and slow carbonyl formation is observable during the induction period. Ni-DBTC transformation is initially fast, then decelerates, and a UV band characteristic of the stabilizer disappears before the end of the induction period. The decrease in concentration of Tin 326 is initially slow, and at the end of the induction period a considerable amount of stabilizer is still present in the system.

In the presence of TMPS (and Tin 770) carbonyl and hydroperoxide formation cannot be observed during irradiation even after a dose of 210 Mlxh (Fig.1.). At this stage the stabilizer is almost completely transformed and the sample broke. The effectiveness of hindered piperidine derivatives can be explained by their radical scavenging ability (SHLIAPINTOKH et al., 1975).

There are some references in the literature to the possibility of synergism when stabilizers working by different mechanisms are added jointly to the polymer (BONKOWSKI, 1969; SAVIDES, 1973). In our experience, however, substituted hydroxybenztriazole, which is known as a UV-absorber, did not give any synergistic effect when added together with hindered piperidine derivative. Neither did stability improve in the simultaneous application of Ni-DBTC, which is assumed to act as a quencher and a hydroperoxide decomposer, and a hindered piperidine derivative. The decreased effectiveness as compared to the stabilizing effect when additives were applied alone can be explained by a chemical reaction assumed to occur between the stabilizers.

In the case of simultaneous addition of Tin 770 and Tin 326 both stabilizers decompose somewhat faster than when added separately. This behavior may be attributed

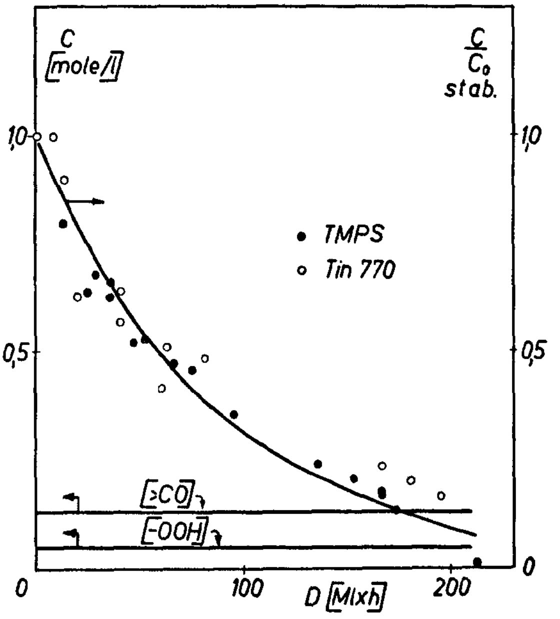

Fig.1. Photooxidation of PP films containing 1 w % Tin 770 or TMPS: change of concentration of carbonyl [=CO] and hydroperoxide [-OOH] groups, as well as stabilizer concentration during irradiation

to the fact, that Tin 326 is capable to react with carbonyls (PÁC et al., 1975) ; this reaction may occur also with the carbonyl groups present in Tin 770.

A similar change in stabilizer concentration can be observed in the case of joint addition of Tin 770 and Ni-DBTC, and a possible explanation for this may be that Ni-DBTC reacts with radicals (GERVITS et al., 1976). Since during irradiation piperidine sebacate produces radicals presumably participating in stabilization, a radical scavenger present in the system may accept active radicals and thus decrease efficiency.

Another possible explanation is given for this antagonistic effect by Scott and coworker (CHAKRABORTY, SCOTT, 1978), who presume the necessity of the presence of hydroperoxides to form nitroxy radical from the piperidine derivative. Thus, the presence of hydroperoxide decomposer lowers the possibility of radical formation from piperidine derivatives which therefore cannot exert its stabilizing effect.

Finally, it can be assumed that radicals effective for stabilizing can form by the interaction of UV-light and piperidine derivative. A quencher in the system may accept the excitation energy from the piperidine derivative and thus its stabilizing efficiency may decrease.

In case of the joint applications the only composition which exhibited enhanced efficiency proved to be Tin 770 with Cy. Carbonyl and hydroperoxide concentration, as well as stabilizer concentration changes can be seen in Fig.2., in the case of a sample containing 1 w % Tin 770 and 1 w % Cy. The change in concentration in the presence of Cy alone is also shown in the figure (dotted line).

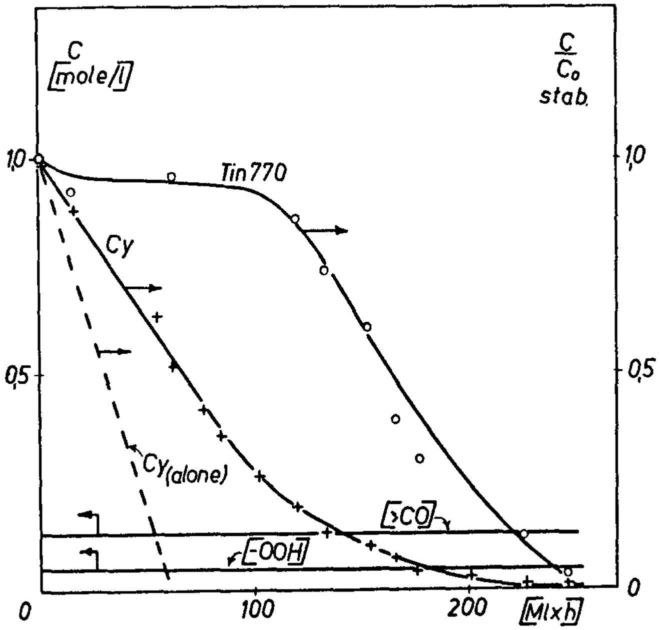

Fig.2. Concentration of carbonyl[=CO] and hydroperoxide [-OOH] groups, as well as change in concentration of stabilizers in the presence of 1 w % Tin 770 and 1 w % Cy during irradiation

The shapes of the curves indicate that during the first period of irradiation the UV-absorption effect of Cy delays oxidation. Decrease in Tin 770 concentration accelerates when - upon the decomposition of Cy - radical formation on the polymer chain commences. On the other hand, Cy decompostion is somewhat slower than when applied alone (dotted line in Fig.2.), thus, Tin 770 seems to retard its photodecomposition.

Spontaneous rupture of the samples took place at ~ 250 Mlxh dose showing a superposition of effects of the piperidine derivative and hydroxybenzophenone added simultaneously to the polymer.

References

BÁLINT, G., KELEN, T., REHÁK, Á. and TÜDŐS, F.: React. Kin. Cat. Letters 4, 467 (1976)

BONKOWSKI, J.E.: Text. Res. 39, 243 (1969)

CARLSSON, D.J. and WILES, D.M.: Macromol. 2, 587 (1969)

CARLSSON, D.J. and WILES, D.M.: J. Polym. Sci., Polym. Chem. Ed. 12, 2217 (1974)

CHAKRABORTY, K.B. and SCOTT, G.: Chem. and Ind. 237, (1978)

CICCHETTI, O.: Adv. Polym. Sci. 7, 70 (1970)

GERVITS, L.L., ZOLOTOVA, N.V. and DENISOV, E.T.: Vysokomol. Soed. Kratk. Soob. A18, 408 (1976)

GUILLORY, J.P. and COOK, C.F.: J. Polym. Sci., Polym. Chem. Ed. 11, 1927 (1973)

HESKINS, M. and GUILLET, J.E.: Macromol. 1, 97 (1968)

LÁSZLÓ-HEDVIG, S., IRING, M., BÁLINT, G., KELEN, T. and TÜDŐS, F.: IUPAC Macromol. Symp. on Long-Term Properties of Polymers, Stockholm, 1976; J. Appl. Polym. Sci., in press

PÁC, J., SEDLAR, J., PETRUJ, J. and PARIZEK, M.: Plaste u. Kaut. 22, 724 (1975)

SAVIDES, C.: SPE J. 29, 38 (1973)

SHLIAPINTOKH, V.A., BISTRITSKAIA, E.V., SHAPIRO, A.B., SMIRNOV, L.N. and ROZANTSEV, E.G.: Izv. Akad. Nauk. SSSR, Ser. Khim. 1915 (1973)

SHLIAPINTOKH, V.A., IVANOV, V.B., KHVOSTACH, O.M., SHAPIRO, A.B. and ROZANTSEV, E.G.: Dokl. Akad. Nauk. SSSR, Ser. Khim. 225, 1132 (1975)

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