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# THE CHARACTERISTICS OF STABILIZATION OF POLYOLEFINS BY ISOCYANATES

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**Abstract**—Infra-red spectroscopic, kinetic, thermodynamic and technological methods have shown that the deactivation of residual unsaturation in polyolefines, as the potentially active centres for decay of macromolecules, produces considerable stabilization. It can be carried out with chemically active compounds such as organic isocyanates and their derivatives.

## INTRODUCTION

Suppression of thermooxidative destruction is practically important as one of the means of increasing the life of a polymer. Destruction of a polymer is known to be governed by its structure. The presence of abnormal structures in polymers, resulting from side-reactions during synthesis, facilitates initiation of destruction processes [1]. Unsaturated vinyl end-groups should be mentioned as active centres having unfavourable effects on polymer stability. Use of chemically active compounds reducing the number of double bonds may result in stabilization. It is of interest to consider the application of isocyanates (IS) having very high reactivity and interacting with almost all compounds containing labile hydrogen atoms as well as with olefin and acetylene derivatives [2].

IS have been shown to be effective modifiers of polyolefin (PO) structure and properties, improving their physico-mechanical, adhesion and rheological properties [3]. i.r. Spectroscopy (Table 1), NMR and TGA have shown the modification to be based on the interaction of IS and PO mainly at vinyl end-groups with the formation of copolymeric products, their side branches containing the oligomeric polyisocyanate fragments [4]. The purpose of the present paper is to study the efficiency and mechanism of IS stabilizing action.

## EXPERIMENTAL

PO of different types and brands have been investigated: high-density polyethylene (PEHD), low-density polyethylene (PELD), ethylene and propylene copolymer (CEP; propylene links: 2, 1%) and polypropylene (PP). Aliphatic and aromatic di- and polyisocyanates, e.g. 2,4-toluylendiisocyanate (TDI), oligourethanes, e.g. diisocyanatourethane (DIDU), and their mixtures were used as modifiers. Such commercial stabilizers as ethyl-4-oxy-3,5-ditertbutylphenylpropionic acid and diethyleneglycol (Phenozan 28) and di-$\beta$-naphthyl-*para*-phenylendiamine (Diaphen-nn) have been used.

The modification has been performed at the processing stage. The kinetics of styrene liquid phase oxidation were studied using a manometric method according to a published procedure [5]. Azobis(isobutyronitrile) was used as initiator ($2.5 \times 10^{-3}$ mol/l; 323 K; oxygen pressure 650 mm Hg).

## RESULTS AND DISCUSSION

While selecting the modification conditions, it was observed that prolonged thermal treatment of the initial PO on the rolls makes them more brittle or flow down the rolls, whereas the modified PO retained their properties (Table 2).

Determination of the oxidation degree of PO, by comparing the absorption band intensity at 1720 cm$^{-1}$ (which corresponds to the carbonyl group) in the spectra before and after the thermooxidative ageing, has confirmed the high stabilizing power of IS (Fig. 1). In the modification of PELD by the mixture of DIDU–Duaphen-nn, the least increase of carbonyl content was noted.

The morphologies of modified and thermooxidized PO samples have been studied. The decrease of the reflection intensity, which indicates the amorphization processes in the material due to the thermal oxidation, is equally present in the initial and as well as the Diaphen-nn stabilized PE (Table 3). The size of crystallites is increased as a result. After ageing, the PO crystallite defects of the second kind, due to the different stresses of distortion of the lattice, are increased. This defect formation is very sensitive to external influences. The crystal structure of the IS modified POs remained unchanged under the same conditions. The attached polyisocyanate fragments, which are the non-crystallizing components, accumulate on the crystallite surface protecting it from destruction by oxidation and are exuded into the amorphous phase during the crystallization.

According to the DTA data, the IS introduced into the polymer brings about a 30–40° displacement of the oxidation peak towards higher temperatures and reduction of the exothermicity of the oxidation (Fig. 2). The activation energy of the destruction calculated by the dynamic methods of TGA (double logarithm, Freeman and Carol), is increased 1.5 to 2-fold. An increase of 30–50° in the thermal destruction temperature occurs.

In spite of differences between the natures of the oxidations of the POs due to their chemical difference, one can deduce that IS have a specific stabilizing effect; in contrast to commercial antioxidants, they not only increase the induction period for thermal oxidation but also cause a sharp reduc-

Table 1. Contents of unsaturated and carbonyl groups in the initial and modified PE using 2.0% by wt TDI

| | *Groups for 1000 C-atoms* | | | | | |
|---|---|---|---|---|---|---|
| | PELD | | PEHD | | PEMD | |
| Type of link | Initial | Mod. | Initial | Mod. | Initial | Mod. |
| $R_1R_2C=CH_2$ (888 cm$^{-1}$) | 0.0355 | 0.036 | 0.0818 | 0.0776 | 0.025 | 0.028 |
| $R_1CH=CH_2$ (909 cm$^{-1}$) | 0.0420 | 0.028 | 0.1610 | 0.0780 | 0.140 | 0.084 |
| $-C=C-$ (965 cm$^{-1}$) | 0.0540 | 0.051 | 0.0689 | 0.0687 | 0.059 | 0.057 |
| $R_1R_2C=0$ (1720 cm$^{-1}$) | 0.0330 | 0.052 | 0.0300 | 0.0640 | 0.024 | 0.056 |

Table 2. Change of the properties of POs initiated and modified by TDI dimer (0.5% by wt) during rolling

| | Initial polyolefins | | | | Modified polyolefins | | | |
|---|---|---|---|---|---|---|---|---|
| Time of rolling (min) | Destructive stress (MPa) | IFM (g/10 min) | tg $\delta$ $\times 10^4$ | Relative elongation (%) | Destructive stress (MPa) | IFM (g/10 min) | tg $\delta$ $\times 10^4$ | Relative elongation (%) |
| | | | | *Polypropylene, t = 448 K* | | | | |
| 0 | 40.31 | 1.89 | 5.2 | 86.4 | 40.70 | 2.093 | 5.6 | 177.6 |
| 20 | | Destroyed | | | 43.21 | 8.00 | 5.5 | 105.6 |
| | | Destroyed | | | 41.18 | 12.68 | 5.1 | 92.0 |
| | | | | *Copolymer of ethylene with propylene, t = 418 K* | | | | |
| 0 | 35.60 | 0.410 | 1.2 | 848.0 | 29.02 | 0.630 | 1.9 | 895.0 |
| 20 | 27.94 | 0.577 | 1.6 | 834.0 | 27.13 | 0.543 | 1.8 | 856.0 |
| 40 | 25.18 | 0.760 | 3.1 | 849.0 | 25.45 | 0.533 | 1.8 | 892.0 |
| | | | | *Polyethylene of high density, t = 418 K* | | | | |
| 0 | 29.04 | 0.435 | 1.7 | 830.0 | 27.57 | 0.588 | 5.7 | 816.0 |
| 20 | 31.43 | 0.536 | 1.7 | 809.0 | 30.49 | 0.306 | 3.2 | 785.0 |
| 40 | 30.15 | 1.108 | 2.3 | 554.0 | 28.11 | 0.369 | 2.7 | 823.5 |

tion of the rate of interaction of the POs with oxygen. The IS nature does not greatly affect the oxidation kinetics, the differences in rate being insignificant.

The inhibition of the oxidation is increased with increase of IS content in the polymer, and the highest values occur at 1–2% by wt (Fig. 3). The fall of oxidation rate can be explained not only by the deactivation of the residual terminal double bonds

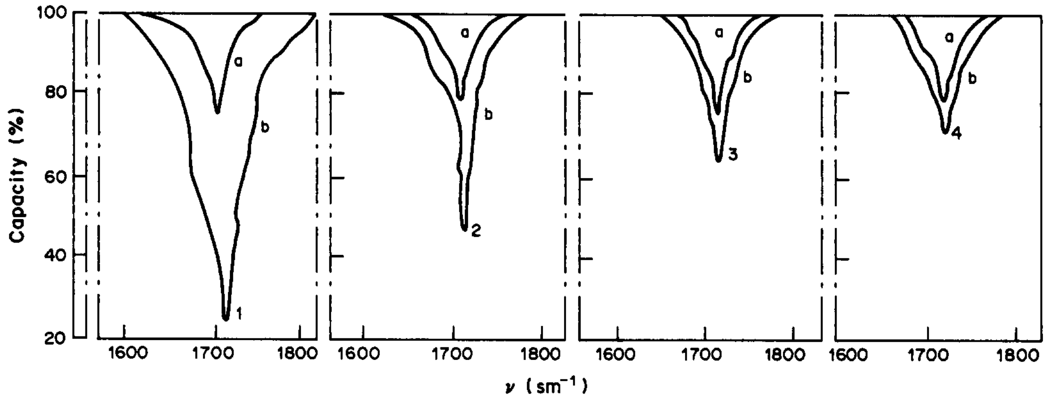

Fig. 1. Absorption band for group >CO in i.r.-spectra PELD initial (1); and modified 0.1% by wt of Diaphen-nn (2); 2.0% by wt DIDU (3); and by the mixture of 2.0 by wt DIDU with 0.075% by wt of Diaphen-nn (4), before (a) and after (b) 4 hr of static thermo-oxidative ageing.

Table 3. X-ray structural analysis data for initial and modified PELD before and after 4 hr of static thermooxidative ageing $t = 473$ K

| | Crystallinity degree (%) | | Crystallite size | | *Defects (%)* | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | First kind | | Second kind | |
| Modifier | Before | After | Before | After | Before | After | Before | After |
| — | 40 | 33 | 270 | 295 | 3.90 | 3.76 | 3.13 | 4.79 |
| 0.1% by wt Diaphen-nn | 44 | 38 | 230 | 270 | 4.42 | 3.94 | 2.72 | 4.31 |
| 1.0% by wt dimer TDI | 35 | 34 | 250 | 280 | 4.23 | 3.80 | 2.80 | 3.91 |
| 1.0% by wt DIDU | 38 | — | 250 | — | 3.62 | — | 2.71 | — |
| 2.0% by wt DIDU | 37 | 35 | 240 | 275 | 4.27 | 3.88 | 2.91 | 4.01 |
| 2.0% by wt DIDU+ 0.075% by wt Diaphen-nn | 45 | 44 | 240 | 250 | 3.98 | 4.18 | 2.70 | 2.52 |

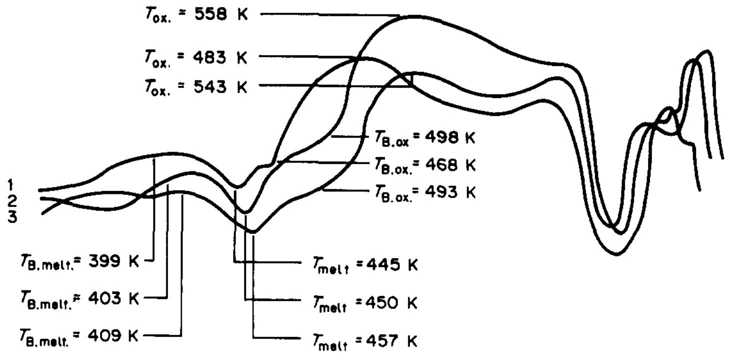

Fig. 2. Heat thermograms of initial PP (1); and modified PP 1.0% by wt DIDU (2); 1.0% by wt 4,4$^1$-diphenylmethanediisocyanate (3).

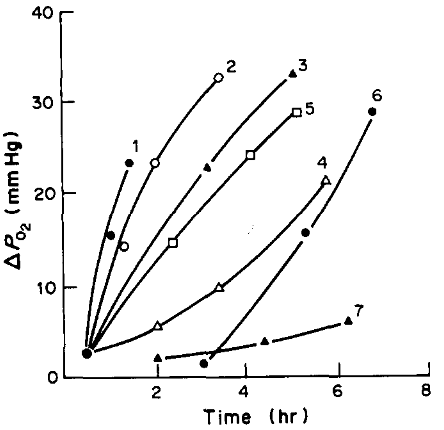

Fig. 3. Kinetic curves of autooxidation PELD initial (1); and dimer modified TDI 0.25% by wt (2); 0.5% by wt (3); 0.1% by wt (4); 1.0% by wt DIDU (5); 0.1% by wt of Diaphen-nn (6); by the mixture of 0.05% by wt Diaphen-nn and 2.0% by wt of DIDU (7).

but also by the decreasing of yield and accumulation of peroxide radicals and hydroperoxide groups in the sample which would be responsible for the oxidation.

Model experiments [5] have confirmed that isocyanates do not break the kinetic chains of oxidation, interacting with peroxide radicals. The curves in Fig. 4 amply illustrate the absence of noticeable changes in the kinetics of styrene oxidation by addition of IS. Moreover small additions of IS (0.1–0.5% by wt) do not inhibit but catalyse the process of initiated styrene oxidation, the liberation of gases taking place.

Unexpected inhibition of oxidation has been obtained when investigating the initiated oxidation of styrene with added IS in the presence of triethylamine; the IS anion acts as a polymerization catalyst (Fig. 4). The IS homo- and copolymerization processes with unsaturated compounds during the anionic catalysis are likely to occur [2].

A study has been made of the possibility of IS interacting with cumyl hydroperoxide, to study the possibility of IS destroying the reagent which

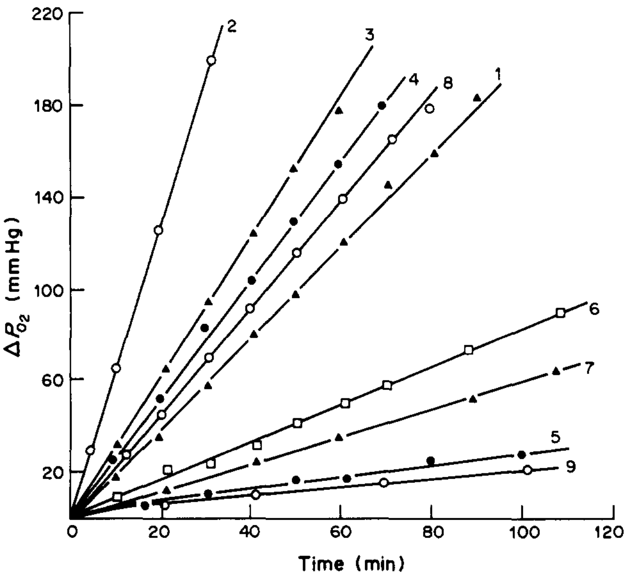

Fig. 4. Kinetic curves of the initiated oxidation of styrene without additions (1); with the addition of TDI $1.0 \times 10^{-3}$ mol/l (2); $2.5 \times 10^{-3}$ mol/l (3); $5.0 \times 10^{-3}$ mol/l (4); $5.0 \times 10^{-2}$ mol/l TDI and 20% TEA (5); $5.0 \times 10^{-2}$ mol/l TDI and 2% TEA (6); $2.5 \times 10^{-4}$ mol/l of Phenozan 28 (7); $2.5 \times 10^{-4}$ mol/l of dimer TDI (8); of mixture of Phenozan 22 and TDI dimer (1:1) (9).

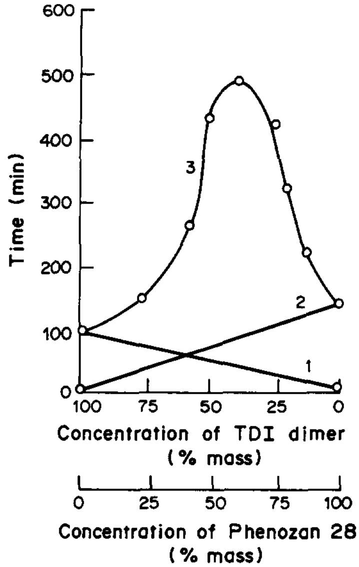

Fig. 5. The dependence of the induction period for oxidation of PP upon the mixture composition of TDI dimer and Phenozan 28 at $10^{-2}$ mol/l (3), as well as the concentration of the mixture components: TDI dimer (1), Phenozan 28 (2). Temperature = 473 K, initial oxygen pressure = 250 mm Hg.

branches the kinetic oxidation chain. The steadiness of the semi-wave height on the polarogramm for 4 hr indicated that there is no effect.

The model reactions have shown that the stabilizing effect of IS does not fit the traditional mechanisms and confirmed the conclusion about their deactivating influence on the residual double bonds in the polymer, as the centres for the destruction decay.

It should be noted that in certain cases the use of IS mixtures and antioxidants results in synergistic effects (Figs 3–5). The data show significant differences in the behaviours of commercial antioxidants and IS in the polymer. The former act mainly as reagents which do not influence the nature of the polymer or its properties. They prevent, however, for a time the development of thermooxidative destruction in the polymer. The commercial stabilizers investigated by us are unable to protect effectively a polymer at higher temperatures. The IS chemically combined with macromolecules result in a new polymer material having a whole range of valuable properties, notably thermostability.

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