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THERMO-OXIDATIVE DEGRADATION OF POLYETHYLENE—III.

THE EFFECT OF TITANIUM DIOXIDE PIGMENTS ON LOW-DENSITY POLYETHYLENE

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Abstract—Low-density polyethylene (LDPE) free from additives and containing 0.1% phenolic antioxidant (4,4'-thio bis (6-tert.butyl-3-methyl)phenol) was mixed with 40% by weight titanium dioxide pigment (TiO_2) in a Brabender Plastograph under a nitrogen blanket. Eight different pigment qualities were used. The mixtures were heated in ultra-pure nitrogen at 315 and 355°, and in air at 150°. Structural changes were studied by gel chromatography, differential scanning calorimetry and gravimetry. Uncoated TiO_2 pigments caused a pronounced yellowing of the LDPE containing antioxidant during the mixing operation. No other structural changes were observed and subsequent heat treatments caused no further yellowing. During heating in ultrapure nitrogen above 300° the pigments exerted only minor influences on the degradation. In the thermo-oxidative degradation at 150° in air, uncoated rutile and anatase pigments promoted degradation while the coated qualities exerted a stabilizing action, increasing with the degree and complexity of the coating.

INTRODUCTION

Previous papers [1, 2] on structural changes of well-defined polyethylenes (PE's) during thermo-oxidative degradation concern additive-free low-density PE (LDPE) and high-density PE (HDPE) heated in air at temperatures below 200°. Degradation at higher temperatures with minor amounts of oxygen have also been performed [3–6]. We intend to include studies of the interaction between PE's and commonly used additives such as antioxidants and pigments.

Although titanium dioxide (TiO_2) pigments are frequently used for PE, there is little information on their effect on PE during processing, especially master-batch production and other types of treatments that may involve thermal or oxidative attack. It is well known however that TiO_2 of the crystalline modification anatase may promote photochemical degradation when used in plastics, fibres and organic coatings. On the other hand, the denser form rutile has a beneficial influence acting solely as a light screen [7]. Akutin [8] found a pronounced increase in induction period for oxygen uptake at 120°. The resin and the pigment were not specified. In another study by Akutin *et al.* [9] i.r. spectra indicated increased amounts of ether and ester groups ascribed to chemical bonds between PE and TiO_2. It has been reported by Solvik *et al.* [10] that yellowing is sometimes observed when TiO_2 pigments are combined with resins containing phenolic antioxidants.

In the present investigation the effect of TiO_2 pigments on the thermo-oxidative degradation of LDPE was studied both in the absence and presence of a phenolic antioxidant. The investigation involved both anatase and rutile pigments representing all the commonly used commercial types.

The structural changes have been studied with gel chromatography (GPC), differential scanning calorimetry (DSC) and gravimetric measurements.

EXPERIMENTAL

Materials

The LDPE resins (Table 1) were kindly supplied by Unifos Kemi AB, Sweden. They are high-pressure products produced in a tubular reactor. Unifos DFDS 6600 has been reported to be free from additives while Unifos 6005 is of the same base resin but contains 0.1% of the phenolic antioxidant 4,4'-thio bis(6-tert.butyl-3-methyl)phenol (Santonox R). Kronos Titan A/S, Norway not only kindly supplied the Kronos TiO_2 pigments (Table 2) but also made

Table 1. Characteristics of samples of investigated LDPE

	Melt index (g/10 min)	Density (kg/m^3)	$\overline{M}_n \cdot 10^{-3}$*	$\overline{M}_w \cdot 10^{-3}$*	$\overline{M}_w/\overline{M}_n$*
Unifos DFDS 6600	0.3	923	19	82	4.3
Unifos DFD 6005 (0.1% Santonox R)	0.3	922	20	98	4.9

* From GPC, based on calibration for linear PE.

Table 2. TiO_2-pigments used

No.	Designation		Type	Treatment (modified with)	TiO_2-content	Density (kg/m^3)
1	(Kronos)	D5	rutile	—	99	4.2
2	(Kronos)	RN45	rutile	Al	95	4.1
3	(Kronos)	RN47	rutile	Al, Si	89	3.7
4	(Kronos)	RNCX	rutile	Al, Si, Zn, organic coating	92.5	4.0
5	(Kronos)	RNCX-P	rutile	Al, Si, Zn, organic coating, silicon oil	92.5	4.0
6	(Kronos)	CL220	rutile	Al, Si, organic coating, silicon oil	92.5	4.1
7	(Finntitan)	RFU	rutile	Zn	98	4.1
8	(Kronos)	A	anatase	—	99	3.9
9	(Kronos)	AV	anatase	Al, Si	96	3.8

No. 6 is produced by the chlorine process [11], all others by the sulphate process [11].
No. 7 is a small crystalline quality all others are of normal crystalline size.
Nos. 1–3 originate from the same TiO_2-batch but have different coatings.

special arrangements so that a series of three pigments with different coatings were prepared from the same batch of rutile. The Finntitan pigment was kindly supplied by Kemira OY, Finland.

Compounding

The compounding was performed in a Brabender Plastograph®, type PL 35, kindly put at our disposal by Forshaga AB, Sweden. The mixing chamber volume was 60 ml and the oil bath temperature 160°. Mixtures containing 40% by weight of TiO_2 were prepared by charging under nitrogen and mixing for 10 min at 90 rpm. This treatment resulted in a temperature increase to 180° in the mass. As a control of the dispersion, minor amounts of each sample were dissolved in 1,2,4-trichloro-benzene (TCB) and studied by light microscopy.

The samples (20 × 40 mm) were cut from 0.7 mm thick films moulded in a multistep procedure at 140° between reinforced polytetrafluoroethylene films.

Heat treatment

The samples were placed on thoroughly cleaned [3] microscope cover glasses. Heating was performed in a tubular oven in ultrapure nitrogen (0.0003% O_2) at 315° for 24 min or at 355° for 90 min; for further details see Ref. [3]. Other samples were heated in an air oven with forced circulation at 150 ± 2° for 2 and 5 hr.

Gel chromatography

Details of the GPC-analysis have been given previously [1, 4]. A Waters Associates GPC Model 200 operating at 135° with TCB as solvent was used. The column combination consisted of five Styragel^R columns with permeabilities ranging from 10^3 to 10^7 Å, giving good separation in the molecular weight (MW) range of interest. Great difficulties were encountered in the preparation of test solutions free from TiO_2. Low pressure and frequent replacement of asbestos filters were necessary. In spite of this only a minor amount of TiO_2 free solutions were obtained for each sample and so it was not possible to supplement the GPC-analysis with viscometric determinations. No corrections for long-chain branching could therefore be performed in the manner used in our previous investigations. In calculating molecular weight distributions (MWD) and MW averages, the calibration curve for linear PE was therefore employed using Drott's computer program [3].

Weight measurement

The samples ($\sim$0.5 g) were weighed before and after heat treatment on a Mettler analytical balance S-6 to better than ±0.01 mg. The weight changes reported refer to the original amount of PE in the samples. A correction has been made for the moisture content in TiO_2 ranging from 0.1 to 1.6% for the actual experimental conditions.

Differential scanning calorimetry

Melting behaviour and degree of crystallinity were determined with a Perkin–Elmer DSC-1 differential scanning calorimeter. The heating rate was 8°/min, the sample size 12.0 mg, and the runs were performed in nitrogen. Before analysis, all samples were given the same thermal pretreatment by heating to 150° and cooling to room temperature in a controlled manner in the apparatus. In the determination of crystalline content, n-$C_{32}H_{66}$ was utilized as a 100% crystalline calibration material according to common practice [14]. T_m is taken as the temperature at the peak maximum.

RESULTS AND DISCUSSION

The method for preparing the chosen pigmented compounds involved longer processing times at a higher temperature than used in full scale masterbatching operations. In spite of this, no changes in MWD or the DSC-thermograms could be detected.

However, both under a nitrogen blanket and in air, the TiO_2 pigments 1, 7 and 8 (Table 2) caused pronounced yellowing of Unifos DFD 6005. With Unifos DFDS 6600, no discolouration was observed. As pointed out by Solvik *et al.* [10], the yellowing is thus connected with the use of a phenolic antioxidant. From our investigation, it is obvious that only the uncoated samples of TiO_2 cause the discolouration. It should be noticed that the Zn-addition to TiO_2, e.g. in pigment No. 7, is not a surface coating but exerts a photostabilizing action, being an integral part of the crystal lattice. No further yellowing was observed either in the thermal or in the thermo-oxidative degradations discussed below.

In our previous investigations, heating above 300° in nitrogen containing small amounts of oxygen was used to reveal the tendencies to degradation in high-speed extruders. Heating at 315° for 24 min (Fig. 1) resulted in the same changes in MWD as found previously for this resin [4], i.e. a domination of molecular enlargement reactions. Although present to 40% by weight the TiO_2 samples showed slight effects only. Heating at 355° for 90 min resulted in a considerable shift of MWD towards lower MW in accordance with previous findings [4]. In this case too,

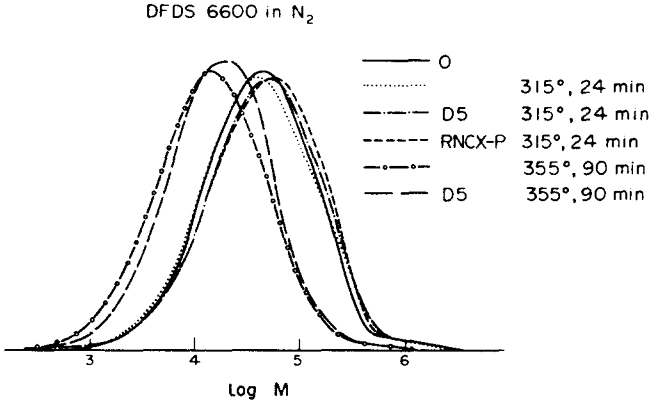

Fig. 1. MWD for unstabilized LDPE heated in nitrogen at 315 and 355° with and without titanium dioxide pigments.

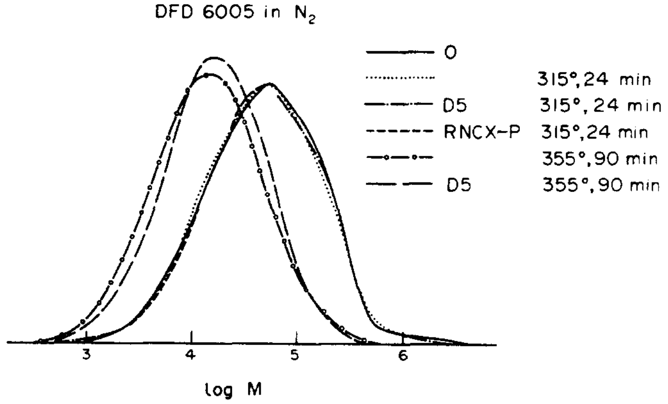

Fig. 2. MWD for stabilized LDPE heated in nitrogen at 315 and 355° with and without titanium dioxide pigments.

the TiO_2 samples exerted only a minor influence on the degradation. The uncoated rutile pigment No. 1 had the largest effect causing a somewhat smaller shift of the MWD.

At 355° the antioxidant in Unifos DFD 6005 showed no effect (Fig. 2); at 315° it had a preventive effect on the changes in MWD.

The antioxidant was also very effective in the thermo-oxidative degradation at 150° in air. No changes in MWD and DSC-thermograms were observed either for the unpigmented resin or for the TiO_2 mixtures with Unifos DFD 6005.

The unstabilized unpigmented LDPE, however, underwent a considerable shift of MWD (Fig. 3) towards lower MW in accordance with previous findings [1]. Changes in crystalline melting behaviour are also revealed by the thermograms in Fig. 4. It is further shown that different samples of TiO_2 affect the thermo-oxidative degradation to quite different degrees. The uncoated rutile No. 1 promoted the degradation (Fig. 3) while the coated qualities from the same rutile batch exerted a stabilizing action increasing with degree and complexity of the coating. This effect is less pronounced after the longer degradation time (5 hr). The thermograms (Fig. 4) also demonstrate the difference between coated and uncoated rutile. This difference is still pronounced after 5 hr. The weight changes (Fig. 5) also demonstrate the same general order between the rutile pigments. The weight loss

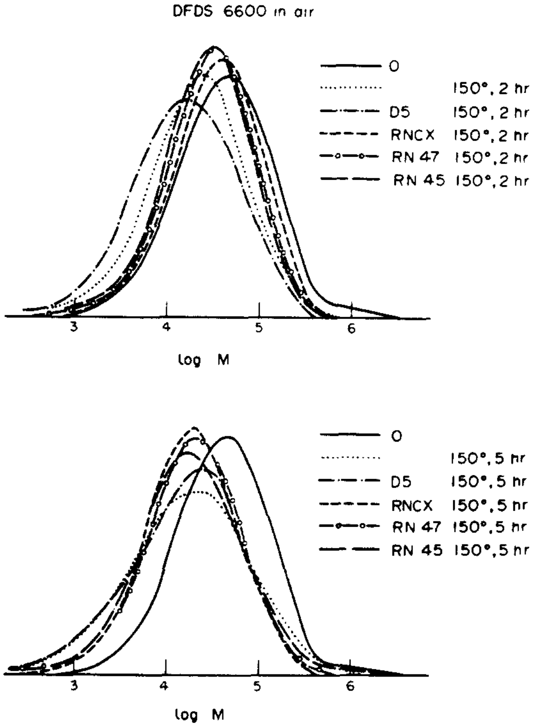

Fig. 3. MWD for unstabilized LDPE, with and without rutile pigments, heated in air at 150° for 2 and 5 hr.

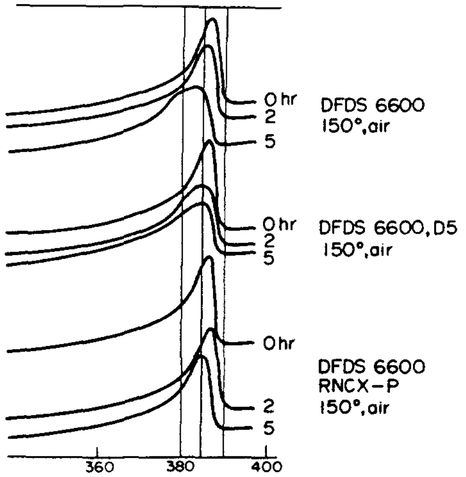

Fig. 4. DSC-thermograms for unstabilized LDPE without pigment, with uncoated rutile, and with the most coated rutile, heated in air at 150°.

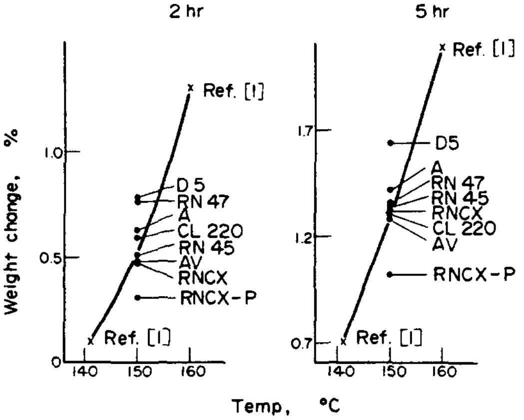

Fig. 5. Weight changes of unstabilized LDPE containing different titanium dioxide pigments and unpigmented LDPE according to Ref. [1].

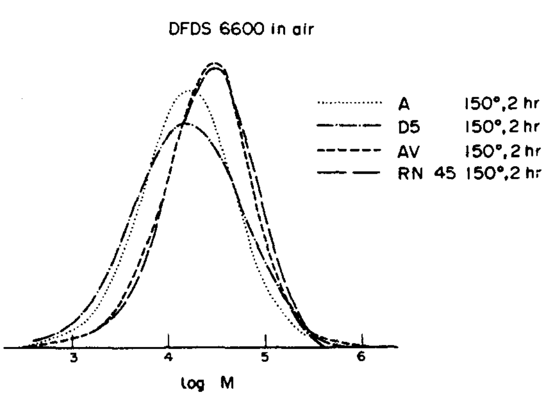

Fig. 6. MWD for unstabilized LDPE containing uncoated and similarly coated rutile and anatase pigments, after heating in air at 150° for 2 hr.

for the unpigmented LDPE is in good agreement with previous values [1].

The increased degradation observed with the uncoated pigment should reflect an increased hydroperoxide decomposition promoted by the TiO_2 surface.

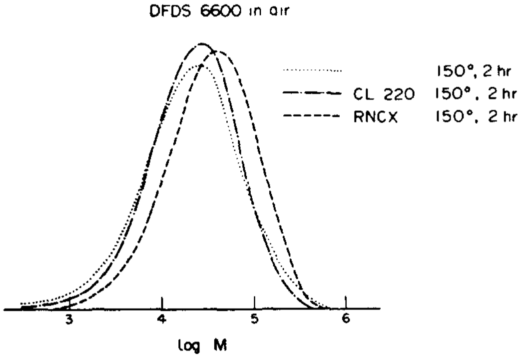

Fig. 7. MWD for unstabilized LDPE heated in air at 150° for 2 hr without pigment and with similarly coated rutiles obtained by the chlorine and the sulphate processes.

The coating not only inactivates the surface but may also function as a trap for radicals and oxygenated degradation products, thus improving the stability of the system. This ability should be gradually lost during degradation due to saturation of the surface of the coating, so accounting for the decreased stabilization ability after 5 hr.

As judged from MWD (Fig. 6) the uncoated anatase pigment is less active as degradation promoter than the rutile pigment, contrary to the behaviour of photochemical degradations. Figure 6 also clearly shows that the differences between these pigments are cancelled by the coating.

Compared with the results presented above, the distributions in Fig. 7 illustrate rather unexpected behaviour. The multicoated rutile No. 6 (Table 2) obtained by the chlorine process is much less stabilizing than the rutile No. 4 (Table 2) obtained by the sulphate process and coated in a similar way. One reason for this difference could be an inferior coating.

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