

## Effect of Carbon Black on Time Dependence of the Melt Flow Index\*

H. P. SCHREIBER and A. RUDIN, *Central Research Laboratory, Canadian Industries Limited, McMasterville, Quebec, Canada*

### Synopsis

Time dependence in the melt indexing of polyolefins stabilized against thermally induced changes is well known, the prevalent effect being an increase in melt index toward a steady-state value. The melt index of polyethylenes compounded with carbon black has been found to decrease, in some cases radically, although oxygen uptake data show no evidence of thermal instability. The melt index-time plot can be restored to its normal shape by adding excess quantities of a standard thioether antioxidant. Data are rationalized by assuming that polyethylene adsorbs on the available pigment surface, forming a crosslink network. The thioether antioxidant, however, may adsorb preferentially, thereby restoring the normal response of the polymer to forces resulting in its capillary extrusion. The results emphasize the contribution of chain orientation effects to the time dependence of melt index.

### INTRODUCTION

The well-known<sup>1</sup> tendency of thermoplastics like polyethylene to undergo oxidative changes when exposed to elevated temperature has resulted in the widespread use of organic inhibitors (e.g., diamines, thioethers, hindered phenols, etc.) which confer considerable thermal stability to melts of these materials. Nevertheless, it has been shown that the melt viscosity of these thermoplastics is time-dependent under apparently invariant extrusion conditions, the predominant effect being a gradual decrease in the melt viscosity. The effect was discussed in detail<sup>2</sup> with reference to the important ASTM melt flow index (MFI) determination.<sup>3</sup> The two predominant contributions to a time-dependent increase in MFI were identified<sup>2</sup> as an increase in the effective pressure drop across the capillary as the melt reservoir drains, and an effective decrease in melt viscosity as the polymer chains orient parallel to the direction of applied force.

In many applications, polyethylene is compounded with 2-3% carbon black; this in itself acts as a fair antioxidant<sup>4</sup> in addition to effectively protecting the polymer against ultraviolet radiation. The synergistic effects of carbon black and some organic thermal stabilizers (e.g., thioethers) have also been well established.<sup>4,5</sup> In the course of studying the

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time effects in melt indexing of polyethylenes compounded with carbon blacks, patterns of behavior have been found which differ distinctly from those established earlier for unpigmented polyethylene melts.<sup>2</sup> The present paper reports on these unexpected behavior patterns and attempts to draw some inference as to the underlying causes.

### EXPERIMENTAL METHODS

Four high-pressure polyethylenes (HPPE) were used in this work. All had nominal melt flow index values near 0.2 g./10 min., and further molecular characteristics are provided in Table I. With one exception, noted in the text, the carbon black was a widely used G. L. Cabot Co. channel black (Monarch 74), with a B.E.T. surface area of 330 m.<sup>2</sup>/g. and a volatile content reported by the supplier to be 5%. A commercial thioether antioxidant, 4,4'-thiobis(3-methyl-6-*tert*-butyl phenol) (Monsanto Chemical Co.) was employed and all compounding of materials was done on an electrically heated roll mill operating at about 160°C.

TABLE I  
Some Molecular Properties of Test Polyethylenes

Polymer	$\bar{M}_w \times 10^{-5}$ <sup>a</sup>	CH <sub>3</sub> /1000 C	MFI <sup>b</sup>
HPPE-A	12.3	18.5	0.16
HPPE-B	4.10	21.0	0.24
HPPE-C	6.50	—	0.22
HPPE-D	4.95	—	0.24

<sup>a</sup> Light scattering in 1-chloronaphthalene solutions.

<sup>b</sup> Compounds with 0.1% antioxidant, ASTM D 1238, condition E.

The standard ASTM apparatus for MFI determination was used,<sup>3</sup> all melts being extruded at 190°C. under the standard load of 2160 g. Consecutive extrudate cuts were taken up to a maximum of 60 min. flow time, which corresponded to draining less than half the total amount of polymer present in the melt indexer reservoir. This minimized the effect of increasing pressure at the die entry, an effect known to influence the throughput rate in some thermoplastic materials.<sup>2</sup> To study weight changes in various compounds, polyethylenes were pelletized and exposed for selected periods to circulating air in an oven set at 150°C. In some cases the carbon black used had previously been evacuated to a residual pressure of 10<sup>-5</sup> torr. at 200°C. or had been heated to 800°C. for 30 min. in a nitrogen stream.

To support this work, it was desirable to investigate some aspects of the adsorption properties of the carbon black for polyethylene and antioxidant. The procedure here followed established techniques for adsorption studies from polymer solutions.<sup>6</sup> Polymer and antioxidant were mixed with carbon black in such proportion as always to provide 33 m.<sup>2</sup> of surface per gram of polymer. The mixture was equilibrated in reagent grade *p*-

xylene at 80°C. ( $\pm 0.5$ ) (the lowest convenient temperature at which clear solutions of polyethylene could be prepared), by continuously tumbling, for 12 hr., sealed ultracentrifuge sample cells mounted on a rotating bar within a constant temperature oil bath. The cells were then transferred to a Spinco ultracentrifuge with hot stage attachment and centrifuged at 80°C. and 10<sup>4</sup> rpm for 15 min. The clear supernatant solution was then decanted, the residual polyethylene precipitated with methanol, and analyzed gravimetrically. Residual antioxidant was estimated by ultraviolet absorption intensity. For the latter purpose a calibration curve of ultraviolet spectrum versus antioxidant concentration in *p*-xylene had previously been obtained.

## RESULTS AND DISCUSSION

### Survey of Experimental Data

The principal experimental findings discussed in this work are illustrated by the results for sample HPPE-A in Figure 1. Consecutive extrusion rate measurements at 190°C. were converted to nominal MFI and plotted against the time elapsed from the moment of applying the standard load to the polymer melt. The curve for uncompounded polymer shows distinct evidence of oxidative crosslinking, while the incorporation of 0.1% antioxidant results in a curve which is characteristic of melt index/time plots for polyethylenes of this general viscosity.<sup>2</sup> Since only a relatively small

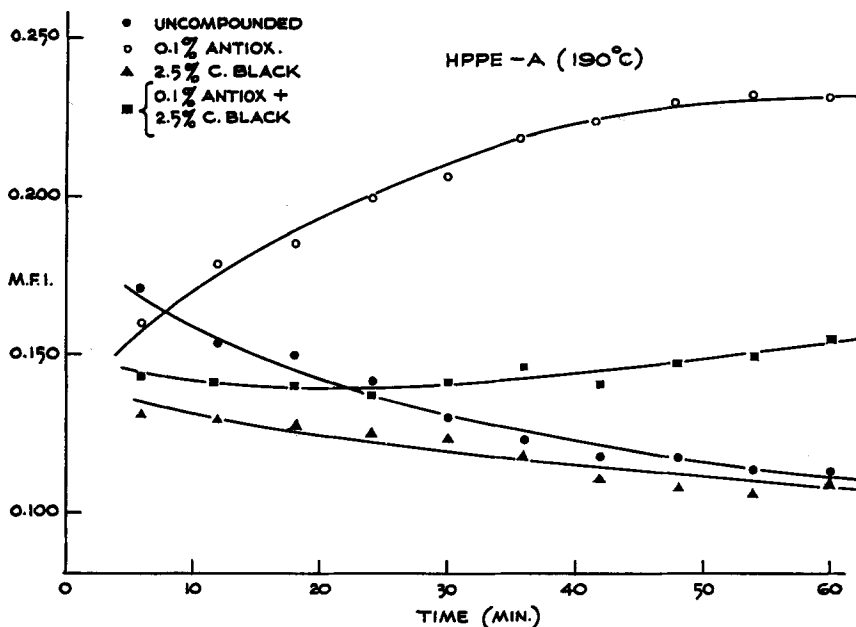


Fig. 1. Effect of carbon black and thioether antioxidant on MFI-time plot of HPPE.

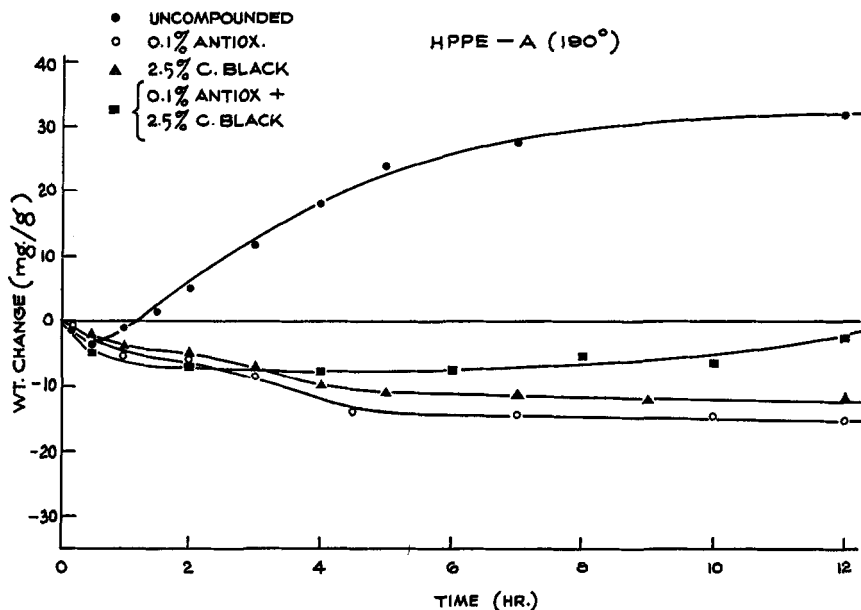


Fig. 2. Weight changes in variously compounded HPPE due to air exposure at 150°C.

fraction of the polymer in the reservoir was extruded in the experimental time, the substantial increase in MFI is chiefly attributable to orientation effects leading to decreased melt viscosity.<sup>7</sup> The apparent leveling off in MFI at a value of about 0.230 is also consistent with the chain orientation hypothesis. Surprisingly, the channel black compound has a melt flow versus time pattern which strongly resembles the uncompounded polymer, in spite of the fact that the presence of carbon black should provide substantial thermal stability to the melt.<sup>1,4,5</sup> The combined synergistic mixture of channel black and thioether antioxidant<sup>4,8</sup> in polyethylene produces a curve which, while intermediate between the extremes of behavior in Figure 1, nevertheless more closely resembles the behavior of the carbon black compound and the uncompounded material. Unless unsuspected thermal instability effects are operative, therefore, the data indicate that the presence of carbon black in the polyethylene compound strongly reduces the response of the melt to orientational forces, at least in a relatively low shear stress field.

The question of thermal stability in the compounds discussed above is resolved by the data shown in Figure 2. The materials were exposed to air at 150°C. and the weight change per gram of compound plotted versus exposure time. The experiments were terminated after 12 hr. when the uncompounded sample became discolored. In this sample the initial small weight loss can be ascribed to the loss of volatiles from the polyethylene. Following about 30 min. exposure, however, a marked weight gain is noted. This is presumably due to oxygen absorption accompanying

the free-radical mechanism of polyethylene oxidation.<sup>9</sup> In the other samples the only effect noticed was the slight weight loss, again, presumably, due to the loss of volatiles. Samples of HPPE-A, other than the uncompounded material, may therefore be regarded as "thermally stable" from this conventional point of view.

In another high-temperature exposure experiment the samples withdrawn from the oven were melt-indexed according to the standard procedure in order to compare the weight changes with changes in the nominal MFI of the sample. The data are summarized in Table II. The weight change results closely follow the patterns established in Figure 2. The systematic increase in weight and decrease in MFI of the uncompounded

TABLE II  
Weight and MFI Changes Due to Heat Treatment of HPPE-A at 150°C.

Sample	Time in oven, hr.	$\Delta$ MFI	$\Delta w$ , mg./g.
Uncompounded	1	-0.118	-2.9
	2	-0.165	+4.9
	4	-0.191	+18.1
	7	-0.211	+25.1
	12	-0.221	+32.2
With 0.1% antioxidant	1	+0.017	-5.3
	2	+0.019	-7.8
	4	+0.014	-9.0
	7	+0.008	-13.3
	12	+0.010	-14.0
With 2.5% carbon black	1	-0.017	-3.4
	2	-0.068	-5.0
	4	-0.069	-9.6
	7	-0.057	-10.1
	12	-0.057	-11.8
With 0.1% anti-oxidant + 2.5% carbon black	1	+0.026	-5.7
	2	-0.011	-8.5
	4	-0.036	-7.0
	7	-0.027	-6.5
	12	-0.019	-1.0

sample is in sharp contrast with the behavior of the black compound where the decreased MFI has no counterpart in weight increment.

The results in Figure 3 for HPPE-B serve a twofold purpose. First, they indicate that the unexpected MFI decrease in carbon black compounds is not confined to the earlier polymer sample and, second, they suggest that the interference of carbon black in polymer chain orientation during the viscosity measurement is connected with the nature of the filler surface. Evacuating at 200°C. or heating the black at 800°C. prior to compounding has a definite influence on the MFI-time plots, which now more closely resemble the shape of those for clear polymer-antioxidant compounds. Evacuation at 200°C. is reported to have little influence on

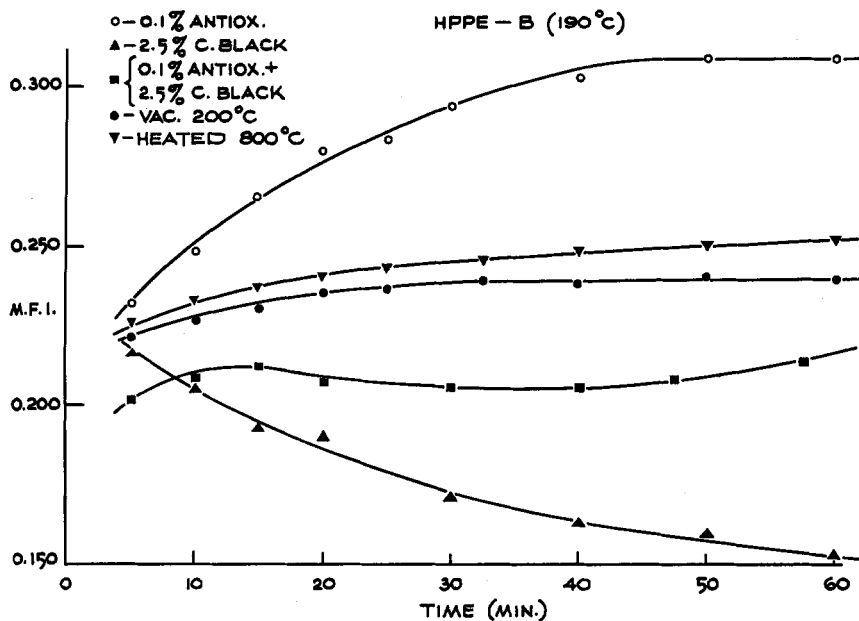


Fig. 3. Effect of pretreating carbon black on MFI-time plots of HPPE compounds.

antioxidant effectiveness as such,<sup>4</sup> but it could result in the removal of weakly adsorbed molecules and the decomposition of radicals whose presence influences polymer-carbon black contacts. Treatment at high temperatures in the absence of oxygen is known to remove oxygen-containing groups from the carbon surface,<sup>4</sup> and this again could influence the polyethylene-antioxidant-surface interaction balance.

The shape of the MFI-time plot of a black-containing compound is strongly dependent on the concentration of thioether antioxidant, as shown in Figure 4, for HPPE-C. Once again the clear compound with 0.1% thioether provides the control from which the black compound deviates most seriously. Increasing the antioxidant concentration up to 3% leads, progressively, to a closer approximation of the control curve both in general shape and in the actual MFI level. Using the MFI for the control resin at any flow time as a reference value, and plotting the difference in melt index level ( $\Delta$ MFI) at any flow time versus antioxidant concentration (above about 0.5%) results in good straight lines having a common abscissa value and slopes which depend on the flow time. The plot is shown in Figure 5 for HPPE-D; nearly identical lines were generated by the data for HPPE-C in Figure 4. In this manner it was feasible to estimate the antioxidant concentration required to overcome the interfering effect of Monarch 74 carbon black and restore the original flow time response of high-pressure polyethylenes in the shear field of the melt index apparatus. For HPPE-C the required antioxidant concentration was found to be  $6.0 \pm 0.5\%$ , and a nearly identical value of about 5.8% was found for

HPPE-D. To test the validity of this estimate, a compound of HPPE-C, containing 2.5% Monarch 74 and 6% antioxidant was prepared and evaluated. As shown in Figure 4, this compound does indeed duplicate the MFI-time curve of the control, clear HPPE-C compound for all practical

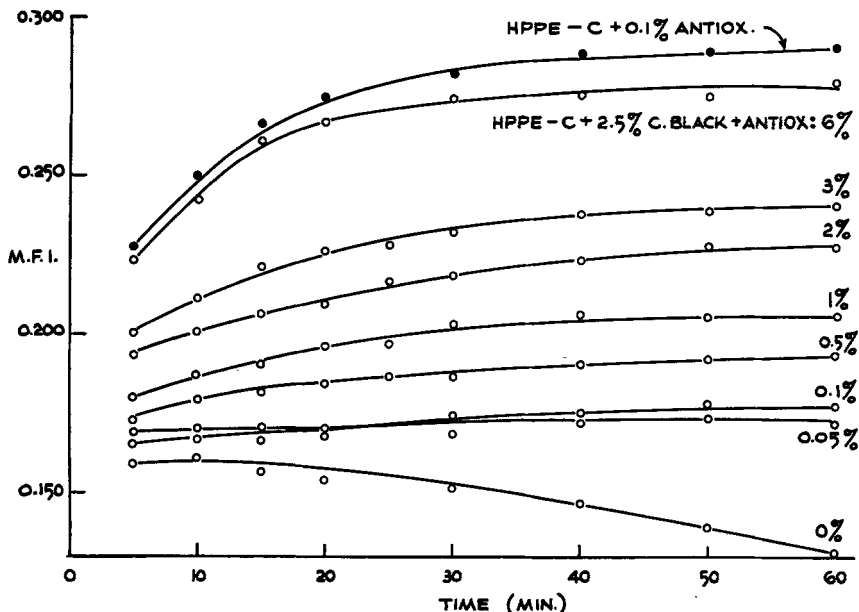


Fig. 4. Change in MFI-time plots for HPPE with varying amounts of thioether added.

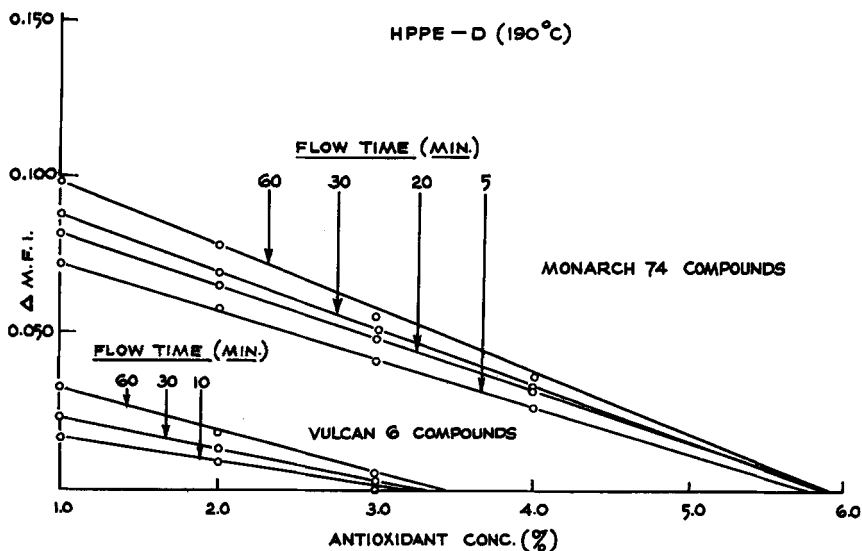


Fig. 5. Estimate of thioether concentration needed to overcome effect of carbon black on MFI-time plot.

purposes. On the assumption, noted earlier, that the carbon black surface is an important factor in this phenomenology, the experiment with HPPE-D was repeated replacing the channel black with a relatively neutral furnace black (G. L. Cabot Inc. Vulcan 6, with a measured B.E.T. surface area of 135 m.<sup>2</sup>/g. and a volatile content reported to be less than 1%). As shown in Figure 5, a real, though considerably less severe, decrease in MFI with flow time is experienced when the furnace black is incorporated, and the antioxidant concentration needed to overcome the interfering effect of this black is reduced to about 3.2%.

### Interpretation of Results

The experimental data are not sufficiently detailed to permit decisive conclusions being reached and the interpretation presented here is therefore regarded only as a working hypothesis.

The view has already been justified that in the cases reported, the upward drift in MFI of clear polyethylene-antioxidant compounds is due primarily to orientation of polymer chains under the influence of the shear field acting in the melt indexer. The addition of carbon black to polyethylene confers chemical stability much as the thioether does, but it is suggested that chain orientation is hindered either because some polyethylene chains adsorb or actually crosslink on the carbon black surface. The crosslinking step is, of course, not a novel suggestion,<sup>9-11</sup> and the presence of free radicals, peroxides, etc. in the carbon black surface capable of initiating the reaction has been reported on numerous occasions. The considerably reduced effect of "neutral" furnace black as compared with channel black on the MFI-time curve of HPPE-D (Fig. 5) lends credence to the crosslinking concept. Similarly, evacuation and heat treatment of carbon black, both of which can be expected to remove adsorbates capable of initiating polyethylene-carbon black crosslinking mechanisms, reduce the influence of the filler on the MFI-time plot, although the effectiveness of these treatments is relatively slight (Fig. 3). This, however, could be due to the procedure followed which necessitated some exposure of the pyrolyzed or evacuated blacks to air at elevated temperatures during compounding of the polymer. To some extent, the effects of prior treatment may have been undone by this procedure.

The thioether antioxidant may be assumed to compete with the polymer for adsorption sites and, specifically, for active adsorbates capable of initiating crosslinking steps. This would account for data of the type shown in Figure 4, assuming that the thioether-carbon black interaction is the preferred one. Increasing the available thioether then would lead to a displacement of adsorbed polymer, and to a reduction in the number of adsorption sites capable of initiating the polymer-filler crosslinking reaction. As a result a partial restoration of the flow index-time plot would be explained. The apparent saturation value of antioxidant necessary to effectively eliminate the effects of polymer-filler crosslinks would be ex-



pected to depend on the nature of the filler surface as shown by the results of Figure 5 and as intimated by the effects of pretreating the carbon black samples (Fig. 3).

In the context of this interpretation a brief study of some aspects of the adsorption properties of Monarch 74 channel black for HPPE and thioether antioxidant was carried out. The pertinent results are given in Table III. There are obvious objections to the use of these adsorption data in terms of the present discussion. The data are too scanty to provide a conclusive picture of the relative adsorption tendencies of the black for the competing adsorbates, and, furthermore, the compromise temperature at which the adsorption experiment was carried out is considerably below the temperatures of melt flow studies. Nevertheless, the contentions introduced in this discussion appear to be corroborated by the data in Table III. The amounts of residual antioxidant in solutions equilibrated

TABLE III  
Comparison of Apparent PE and Thioether Adsorption:  
HPPE-A on Monarch 74 Black at 80°C.

Composition (in xylene solution)	Adsorption	
	HPPE-A mg. $\times$ $10^2/m.^2$ surface	Residual thioether in soln., %
1% PE	24.2	—
1% PE + 0.2% antioxidant	16.9	~7
1% PE + 0.5% antioxidant	13.3	~18
3% PE	66.7	—
3% PE + 0.2% antioxidant	47.5	~11
3% PE + 0.5% antioxidant	40.0	~21

with carbon black are very small, while, in contrast, the quantity of polyethylene adsorbed on the available surface decreases with an increase in the amount of available antioxidant. A preferential antioxidant-surface site interaction is therefore indicated.

## CONCLUSIONS

The presence of carbon blacks in thermally stabilized compounds of high-pressure polyethylene strongly influences the melt index time plot of the polymer. Polyethylene appears to adsorb on the carbon black surface and thereby effectively crosslink, resulting in a decreasing melt flow index. Thioether antioxidant is either preferentially adsorbed or combines with active adsorbates in the filler surface to counteract the polymer adsorption or crosslinking tendencies. When this antioxidant is added in sufficient quantity, the normal increase in melt flow index with extrusion time is observed. The critical amount of antioxidant required to counteract the effects of carbon black depends on the nature of the carbon black surface and can be estimated from the melt flow index versus time plot. Further

study into the adsorption properties of various carbon blacks for polymer-antioxidant mixtures appears needed to fully resolve present observations. These, while shedding interesting light on polymer-stabilizer-filler interactions in no way invalidate the empirical usefulness of the melt index measurement.

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### Résumé

La dépendance en fonction du temps du point de fusion de polyoléfines stabilisées contre des changements dus à la température est bien connue, l'effet principal étant un accroissement de point de fusion jusqu'à atteindre une valeur stationnaire. Le point de fusion des polyéthylènes contenant du noir de carbone diminuait dans certains cas de façon très prononcée bien que les résultats d'absorption d'oxygène ne manifestent pas d'instabilité thermique. Les diagrammes indices de fusion en fonction du temps peuvent être retrouvés dans leur forme normale en ajoutant des quantités en excès d'antioxydant standard à base de thioéther. Des résultats sont rationalisés en admettant que le polyéthylène adsorbe à la surface des pigments, donnant lieu à un réseau ponté. L'antioxydant thioéther, toutefois, peut adsorber préférentiellement cet oxygène et ainsi restaurer la réponse normale du polymère aux forces résultant de son trusion capillaire. Les résultats soulignent la contribution des effets d'orientation de chaîne à la dépendance en fonction du temps du point de fusion.

### Zusammenfassung

Zeiteffekte bei der Schmelzindexbestimmung an Polyolefinen, die gegen thermisch induzierte Veränderungen stabilisiert wurden, sind wohl bekannt; vorwiegend besteht der Effekt in einem Ansteigen des Schmelzindex gegen einen stationären Wert. Es wurde gefunden, dass der Schmelzindex von Polyäthylen-Russmischungen absinkt, und zwar in manchen Fällen radikal, obgleich Versuche über die Sauerstoffaufnahme keine Hinweise auf eine thermische Instabilität liefern. Das Schmelzindex-Zeitdiagramm kann durch Zusatz eines Überschusses eines Standard-Thioätherantioxydants wieder auf seine normale Gestalt gebracht werden. Es wird angenommen, dass Polyäthylen an die zu-

gängliche Pigmentoberfläche unter Bildung einer vernetzten Struktur adsorbiert wird. Das Thioätherantioxydans könnte jedoch präferentiell adsorbiert werden und dadurch das normale Verhalten des Polymeren gegen die Kräfte wiederherstellen, die zu seiner Kapillarextrusion führen. Die Ergebnisse lassen die Wichtigkeit des Be trages von Ketten-orientierungseffekten zur Zeitabhängigkeit des Schmelzindex erkennen.

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