On Reactive Processing of HDPE with 2-Ethylhexyl Acrylate

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SYNOPSIS

Influencing plastic materials by reactive processing of polymer particles, as seen with extrusion processes for example, may be performed in an especially simple way and is described by taking the reactive processing of standard high-density polyethylene (HDPE) plastic material on a twin-screw extruder in the presence of a vinyl monomer as an example. In particular, the investigation deals with the influence of relatively low quantities—if compared with the comonomer portion—of 2-ethylhexyl acrylate on HDPE properties during polymerization. Furthermore, the effect of a powerful chain-transfer agent on the process of reactive processing and on the thermal-oxidative properties of the products made by use of them is shown. Doing this, carbon tetrabromide proved to be an efficient transfer agent. When presenting the properties of the formed extrudates, the mechanical and thermal characteristics and application-related tests, such as those on stress-cracking resistance, is emphasized. The findings of this investigation are discussed on the basis of correlating them to the lamellar thickness of crystallites and the density of tie-molecules. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Influencing the properties of high-density polyethylene (HDPE) mainly gained from slurry-, solution-, and vapor-phase processes is preferably done by varying kind and quantity of the comonomer in addition to changing the molecular weight and its distribution. In recent times, polymerization catalysts based on metallocenes have led to a considerably wider variability and to the standardization of the comonomer structure.[1]

On the other hand, changing the properties of plastic materials by reactive processing of polymer particles (e.g., with extruding processes) seems to be particularly easy if compared with the selective changes of parameters matching the conditions encountered in the process of polymerization.[2-4] Here, mainly the cross-linking reactions and the compatibility of otherwise nonmiscible polymer blend components using organic peroxides are investigated.[5,6]

The selective introduction of branches by grafting reactions, avoiding the lattice defects occurring when peroxides are present, seems to be particularly suitable for influencing the properties. Therefore, the following passages concentrate on the influence of comparatively low quantities of comonomers of 2-ethylhexyl acrylate on these properties, making use of its thermal polymerizability in a twin-screw extruder. The impact of an efficient chain-transfer agent on the process of reactive processing and on the thermal-oxidative properties of the products made by use of it is also investigated.

EXPERIMENTAL

The investigations into reactive extrusions were performed on a twin-screw extruder manufactured by Werner and Pfleiderer (ZSK 30) with a helix diameter of 30 mm and a ratio of screw length/screw diameter L/D of 41. The added monomer or the transfer agent dissolved in it were separately homogenized with polyethylene powder in a mixer and fed into the extruder at a rotational screw speed of 200 rpm and a feeding speed of 10 kg/h. The mean screw temperature was 234°C.

An HDPE with the properties mentioned in Table I was used in the form of a stabilizer-free polyethylene. 2-Ethylhexyl acrylate and carbon tetrabrom-

Table I Properties of HDPE Used

Property	Method	Index
Weight-average molecular weight M_w	SEC[a]	205,000
Density	ISO 1183	0.943 g/cm^3
Degree of branching	FT-IR	0.48 CH$_3$/100 CH$_2$

[a]SEC: size-exclusion chromatography

ide (Fa. Merck KGaA) were used without any further purification.

Determination of the flexural modulus and flexural stress at a peripheral fiber extension of 3.5% was performed according to ISO standard 178 or DIN 53452. Yield stress and yield strain were determined according to ISO 527, the notched Izod impact resistance according to ISO 180, and the ball indentation hardness according to ISO 2039. ISO 1133 and ISO 1183 were used to determine melting index and density. The degrees of branching were determined by Fourier transform infrared (FT-IR) spectrometry.

A modified creep-resistance test[7] was used in analogy to DIN 53449, part 2, to determine the stress-cracking resistance. The test specimens with the dimensions of 110 × 10 × 10 mm were taken from pressing plates sized 300 × 300 × 10 mm and notched. Ethylene glycol was used as medium at a temperature of 80°C and a load of 5 kp.

The Perkin-Elmer differential scanning calorimeter DSC 7 was used to determine the thermal properties according to DIN ISO 3146 at a heating rate of 10 K/min under argon in a repeated run.

The induction times of isothermal oxidation (OIT values) were measured by means of thermogravimetric/differential thermal analysis in anology to EN 728 at a temperature of 150°C and an oxygen flow rate of 400 mL/min.

Calculation of Tie-Molecule Density

The density of tie-molecules was calculated by means of the Gaussian[8,9] distribution probability of

end-to-end distances for molecularly uniform chains of polyethylene from the DSC-determined melting temperatures and the resulting lamellar thickness of the crystalline areas.

In contrast to[10] and due to the experimental conditions during the determination of the stress-cracking resistance, only the genuine tie-molecules were used for discussion (i.e., those without considering any possibly entangled or looped structures).

Determination of the crystalline lamellar thickness L_c (in nm) from the melting temperatures T_M was done with adequate accuracy according to the equation of Illers and Hendus[11]:

$$L_c = \frac{0.626 \cdot 414}{414 - T_M} \quad (1)$$

The probability function $p(r)$ of the distribution of end-to-end distances r is given by

$$p(r) = a \cdot r^2 \cdot \exp(-b^2 \cdot r^2) \quad (2)$$

with the following parameters

$$a = \frac{4 \cdot b^3}{\sqrt{\Pi}} \quad (3)$$

and

$$b = \sqrt{\frac{3}{2 \cdot (D \cdot n \cdot l^2)}} \quad (4)$$

Table II Properties of Polymers Made by Use of 2-Ethylhexyl Acrylate

2-Ethylhexyl Acrylate Concentration (weight %)	MFI[a] (190°C, 212 N) (g/10 min)	Degree of Branching (CH$_3$/100 CH$_2$)	OIT (150°C) (min)
0	8.3	0.48	22
0.2	8.4	0.49	22
0.4	8.5	0.53	21
0.6	8.5	0.59	24

[a]MFI: melt flow index

whereby l describes the length of segments, n the number of segments, and D the characteristic relation as measure for the extension of a chain at an undisturbed state.

Length of segment as length of linkage and the respective number of segments as the number of linkages were available from the molecular weight. For the molecular weight, the weight-average molecular weight M_w was found to be an essential reference parameter during investigations of the slow growth of cracks of polyethylene.[9] With polyethylene, these values are $l = 0.154$ and, due to the high molecular weight, $D = 6.87$.[12]

It is assumed that for the occurrence of tie-molecules the end-to-end distance of the random coil is at least $2 L_c + L_a$ with the thickness of the amorphous layer L_a where[13]

$$2L_c + L_a \approx \sqrt{6} \cdot L_c \tag{5}$$

Thus, the density of the tie-molecules P can be derived as follows from the integration of eq. (2) within the range of $\sqrt{6} \cdot L_c$ and ∞:

$$P = \frac{1}{3} \frac{\int_{\sqrt{6} \cdot L_c}^{\infty} r^2 \cdot \exp(-b^2 \cdot r^2) dr}{\int_0^{\infty} r^2 \cdot \exp(-b^2 \cdot r^2) dr} \tag{6}$$

The factor of $\frac{1}{3}$ takes into consideration the negligible probability of the occurrence of tie-molecules in the two other spatial dimensions.[8]

Equation (6) strictly applies to monodisperse systems. As the polymers investigated in this study hardly differ in terms of molecular weight distribution from those already found, we can proceed without further considering this distribution function.[8]

RESULTS AND DISCUSSION

The influence of the monomeric 2-ethylhexyl acrylate during the reactive extrusion of HDPE was investigated in the range of concentration of up to 0.6 weight percent without any free-radical initiators being present.

Table II shows the dependence of melting index and degree of branching as a numeric expression on the relation of FT-IR spectrometric peak areas of the CH_3 and CH_2 signals for the resulting products. It can be seen that the melting index with an enhanced concentration of 2-ethylhexyl acrylate increases only slightly, whereas the degree of branch-

ing increases substantially. Density falls only slightly from an initial value of 0.943 g/cm^3 to a final value of 0.942 g/cm^3. The behavior of the melting index indicates that transfer reactions occurring during extrusion like for example

$$-CH-CH_2-CH_2-CH_2-CH_2-\overset{\cdot}{C}-CH_2-$$
$$\underset{R_1}{|} \qquad\qquad\qquad\qquad \underset{H}{|}$$

$$+ CH_2=CH \rightarrow -CH-CH_2-CH_2$$
$$\underset{R_2}{|} \qquad\quad \underset{R_1}{|}$$

$$\begin{array}{c} H \\ | \\ -CH_2-CH_2-C-CH_2- \\ | \\ CH_2 \\ | \\ \cdot CH \\ | \\ R_2 \end{array}$$

$R_1 = $ alkyl $R_2 = -COOCH_2CH(C_2H_5)C_4H_9$

preferably lead to grafting and polymerization reactions, whereas a sharp decrease of the melting indices occurs in the case of the cross-linking reaction of HDPE with trimethylol propantriacrylate initiated by peroxides.[14] Preferably, the transfer reactions should be mainly carried out via the HDPE methylene groups that show a slightly lower transfer constant and transfer reactivity as compared with those reached with methine groups during prototype tests for ethylene vinyl acetate copolymers with various vinyl monomers[15] but show an essentially higher degree of concentration. This is confirmed by calculations for LDPE at 200°C.[16]

Regarding the mechanical properties of the extrudates obtained from the 2-ethylhexyl acrylate the results of the bending test are shown in Figure 1. It can be seen that the flexural modulus and the flexural stress fall at 3.5% peripheral-fiber extension with increasing concentrations of 2-ethylhexyl acrylate. The measuring results of the tensile test are summarized in Figure 2. It can be seen that an increased quantity of 2-ethylhexyl acrylate added before reactive processing also leads to a lower yield stress, whereas the yield strain increases. This decreasing rigidity of the extrudates at increasing monomer concentrations also indicates—if compared to reference 14—a negligible proportion of cross-linking reactions during reactive processing.

The toughness properties of the polymers obtained in the extruder are illustrated in Figure 3. The Izod impact strength increases at +20°C and at −20°C with higher concentrations of 2-ethylhexyl acrylate.
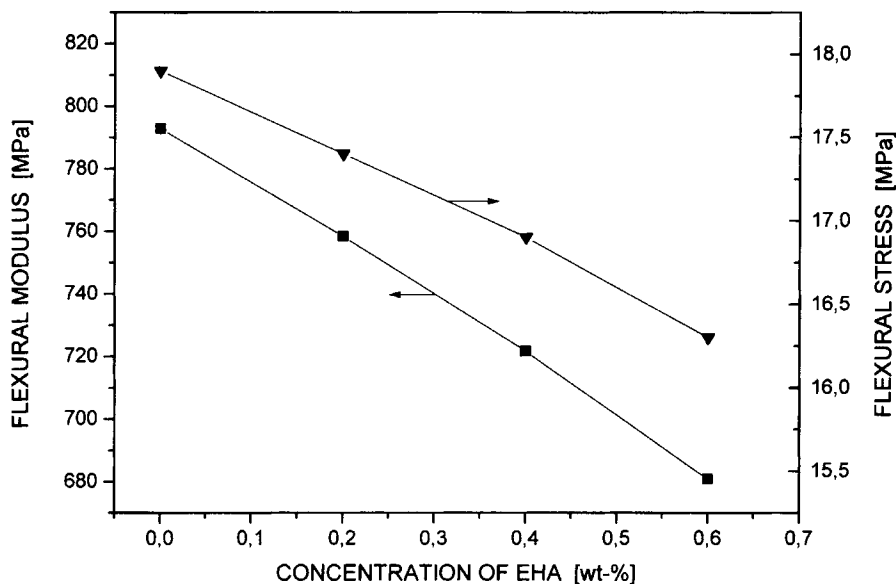
Figure 1 Dependence of flexural modulus and flexural stress at 3.5% peripheral fiber extension on the 2-ethylhexyl acrylate (EHA) concentration.

As shown in Figure 4, the indentation hardness decreases with increased toughness of the extrudates and increase of the quantity of 2-ethylhexyl acrylate. However, if cross-linking reactions at HDPE occur, this effect runs into the opposite direction.[14]

The findings of the examinations of the stress-cracking resistance at 80°C and a load of 5 kp of the polymers made by use of 2-ethylhexyl acrylate are also shown in Figure 4. It can be seen that the stress-cracking resistance is substantially increased at an increased concentration of 2-ethylhexyl ac-

rylate. As the observation of the slow crack growth of polyethylene at room temperature took the number of tie-molecules as the essential factor of influence on the failure behavior into consideration,[8,17] the following discourse also tries to establish a correlation between the case of the medium-induced stress-cracking resistance of HDPE at an increased temperature (80°C) and the number of tie-molecules. Then, the density of the tie-molecules P for the different concentrations of the HDPE samples made by use of 2-ethylhexyl acrylate are calculated
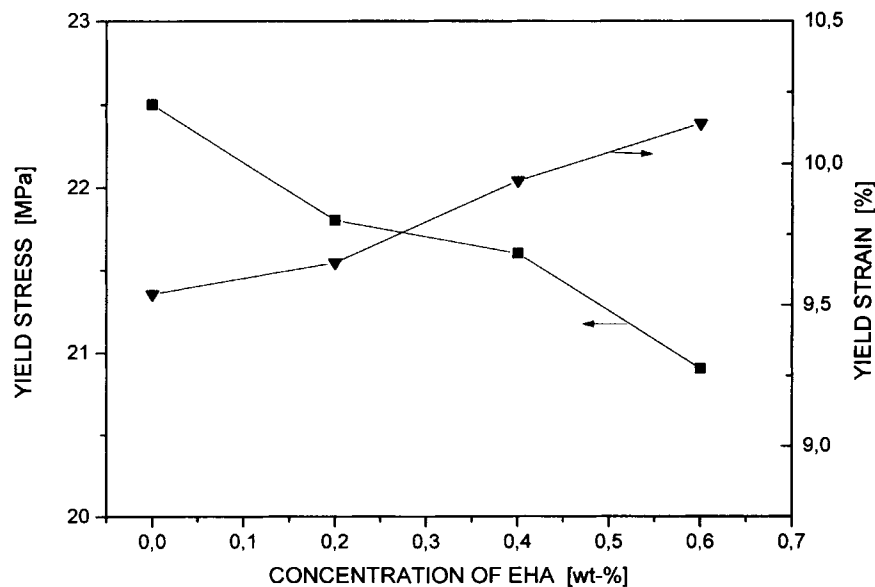
Figure 2 Correlation between yield stress and yield strain during tensile test and concentration of 2-ethylhexyl acrylate (EHA).
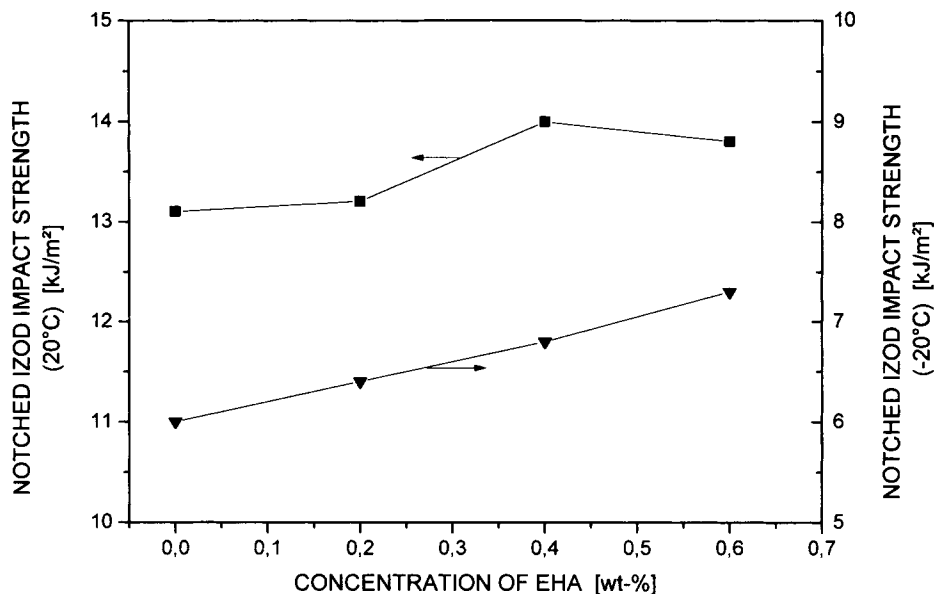
Figure 3 Influence of 2-ethylhexyl acrylate (EHA) quantity on the toughness of extrudates at +20°C and −20°C.

using the structural parameters according to the abovementioned formula and shown in Figure 5. As, on the one hand, there is no substantial change of molecular weight caused by a significantly different melting behavior in comparison with the initial HDPE to be observed and, on the other hand, the concentration of the 2-ethylhexyl acrylate added and the negligible amount of cross-linking reactions have been evidenced by the properties, the change of molecular weight was neglected for these calculations.

Figure 5 illustrates that the density of the tie-molecules rises significantly with increasing the concentration of 2-ethylhexyl acrylate. This is proof of a correlation between the stress-cracking resistance and the density of the tie-molecules in so far as an increase of the stress-cracking resistance of HDPE has to be attributed to the addition of 2-ethylhexyl acrylate to the polymer structure.

It should be possible to modify the influence of 2-ethylhexyl acrylate during the reactive extrusion
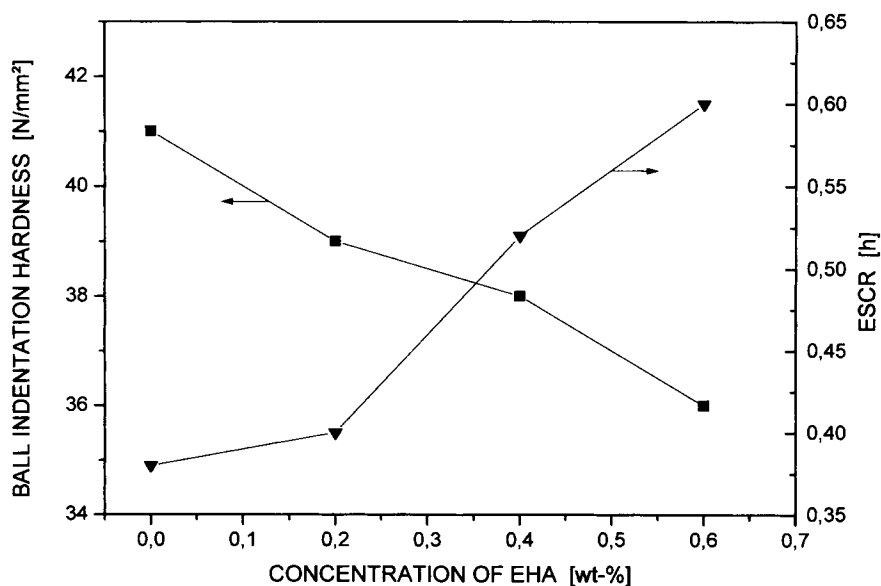
Figure 4 Dependence of ball indentation hardness and stress-cracking resistance (ESCR, 80°C, 5 kp) on the concentration of 2-ethylhexyl acrylate (EHA).
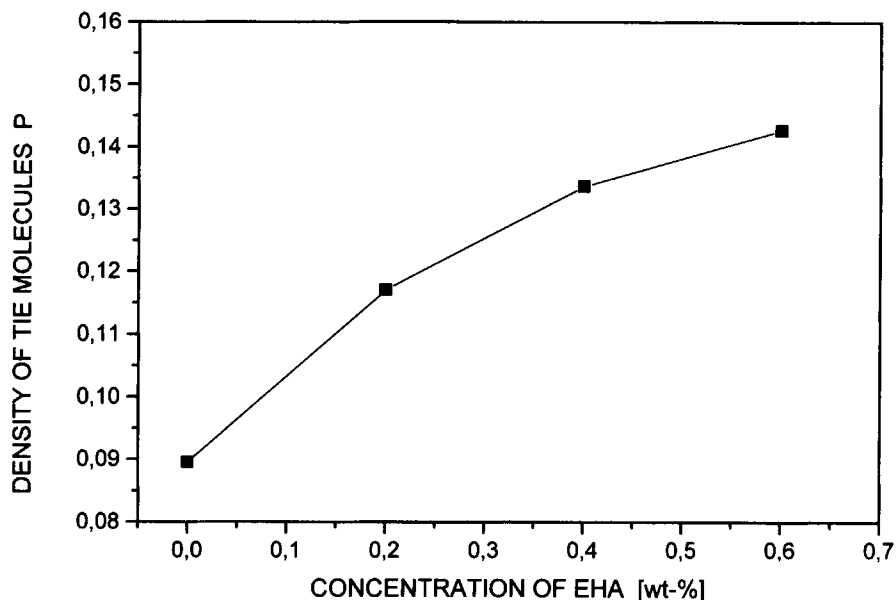
Figure 5   Influence of the quantity of 2-ethylhexyl acrylate (EHA) on tie-molecule density P.

of HDPE by adding a soluble nonperoxidic agent acting as the medium of chain transfer. For this purpose, carbon tetrabromide was selected as a highly effective chain-transfer agent[18] and investigated at concentrations of 0.6 weight percent in relation to the 2-ethylhexyl acrylate used. The concentration of the 2-ethylhexyl acrylate was kept constant in relation to the HDPE (i.e., at 0.4 weight percent).

Table III illustrates that the use of carbon tetrabromide did not result in a significant change of the melting index. On the other hand, the notched impact resistance could be increased by the use of carbon tetrabromide, especially at lower temperatures. This is shown in Figure 6, which also shows the dependence of stress-cracking resistance at 80°C and a load of 5 kp on the concentration of carbon tetrabromide in 2-ethylhexyl acrylate. We can see a sig-

nificant increase in stress-cracking resistance at higher carbon tetrabromide concentrations. From Table III we can conclude that the ball indentation hardness further decreases with an increasing amount of carbon tetrabromide if compared with that extent obtained with the use of 2-ethylhexyl acrylate.

Comparing these results with those obtained without using carbon tetrabromide indicates that an active chain-transfer agent could essentially increase the efficiency of 2-ethylhexyl acrylate in terms of the modifying properties of HDPE. The induction time of the isothermal oxidation (OIT) of HDPE proved to be a useful index for the characterization of a change of the thermal-oxidative properties of HDPE. In Table II, these induction times are given for the products modified with 2-ethylhexyl acrylate, and Table III shows these times for the polymers

Table III   Properties of Polymers Made Additionally with Carbon Tetrabromide as Chain-Transfer Agent

Carbon Tetrabromide Concentration in 2-Ethylhexyl Acrylate (weight %)	MFI (190°C, 212 N) (g/10 min)	Ball Indentation Hardness (N/mm²)	OIT (150°C) (min)
0	8.5	38	21
0.1	8.5	37	23
0.6	8.6	36	22

Proportion of 2-ethylhexyl acrylate: 0.4 weight percent in relation to HDPE.
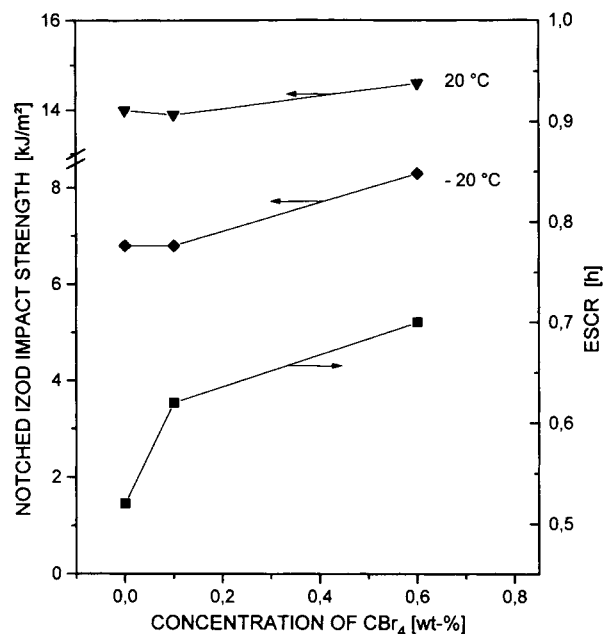MFI: melt flow index

Figure 6 Dependence of notched impact resistance of extrudates at +20°C and −20°C and stress-cracking resistance (ESCR, 80°C, 5 kp) on the concentration of carbon tetrabromide in 2-ethylhexyl acrylate (concentration of 2-ethylhexyl acrylate: 0.4 weight % related to HDPE).

formed additionally with carbon tetrabromide. It can be seen that neither the integration of a monomeric 2-ethylhexyl acrylate nor that of carbon tetrabromide as chain-transfer agent caused a negative change of the thermal-oxidative properties of the polyethylenes subjected to reactive extrusion.

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