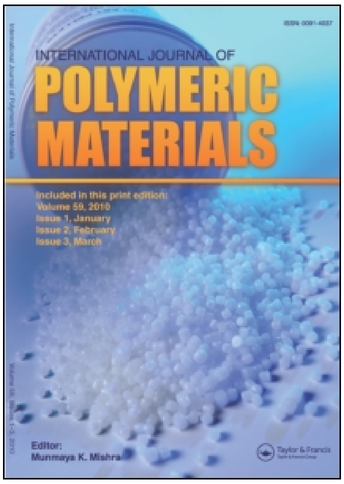

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Kinetic Model of Polymer Degradation Occurring during Extrusion Process

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Chemical transformations occurring during melt processing of polymers such as polyethylene are described in terms of kinetics of relevant reactions. A model is developed which takes into consideration; chemical, thermal, and mechanical effects, autocatalitic reactions, as well as the role of inhibitors. The calculated predictions are verified with the experimental data. The results are used to make recommendations for the improvements of the melt extrusion process.

KEY WORDS Polymer melt processing, extrusion, polyethylene, degradation mechanisms, stabilization, oxydation, mathematical model.

INTRODUCTION

Investigations and numerical representation of chemical transformation mechanisms occurring during polymers' processing have recently been the focus of numerous studies. In this paper a model is presented describing the interrelation of mechanical destruction and thermal oxidation phenomena during PE extrusion. This model permits one to determine changes in molecular weight, the amounts of reaced oxygen and the quantities of accumulated peroxide together with the amount of the inhibitor consumed during extrusion. These parameters have a significant effect on physical and mechanical properties of polymers and allow one to assess the lifetime of finished products under operating conditions.

RESULTS AND DISCUSSION

Polymer processing is usually accompanied by numerous chemical reactions which result in transformations leading to considerable changes in physical and mechanical properties of polymeric materials resulting in reduced lifetimes of finished products.

The chemical aspect of this problem is difficult to model. Relevant chemical reactions take place at relatively high temperatues. During extrusion processing, the thermal, mechanical and autocatalitic reactions occur involving free radicals, ions, ionic pairs etc. occur simultaneously. The current knowledge of chemistry of polymer degradation does not yet describe satisfactorily the complicated kinetics of degradation process. Practical needs, however, require mathematical models which can address these changes occurring in polymer materials.[1] The existing models do not take into account chemical transformations in the polymer backbone. These transformations are influenced by the specific reaction conditions and in turn determine the changes in polymer structure. It is clear that in such cases the possibilities of extrapolating beyond the investigated conditions are very limited.

In this paper we try to describe transformations in polymers during processing by examining the kinetics of relevant reactions. The objective was to improve the quality of the decomposition model representing the mechanical and thermal oxidation transformations occurring during the processing at shear rates of $10-10^2$ $\sec^{-1}$, temperatures of 180–250°C and in presence of oxygen. As an example, the behavior of regular PE during extrusion has been studied.

The degradation is manifested through the formation of alkyl $R^{\bullet}$ radicals which interact with oxygen to form peroxide $RO_2^{\bullet}$. The formation of $RO^{\bullet}$ radical will eventually lead to breakage of macromolecular links and decreases of molecular weight. The molecular weight is the most important parameter which should be used to optimize the processing conditions.

The technique of determining the molecular weight during polymer's processing is described and verified in Reference 2.

According to the scheme of macromolecule transformation given in Figure 1 there are two reasons for the decrease of molecular weight: isomerization process leading to breakage of alkyl radical $R^{\bullet}$ (Reaction $2_d^{RO\bullet}$) and decomposition of alcoxyl radical $RO^{\bullet}$ (Reaction $2_d^{RO\bullet}$). The increase of molecular weight is achieved through the joining of $R^{\bullet}$ radical to the double bond (Reaction $2_i^{R\bullet}$). These three processes

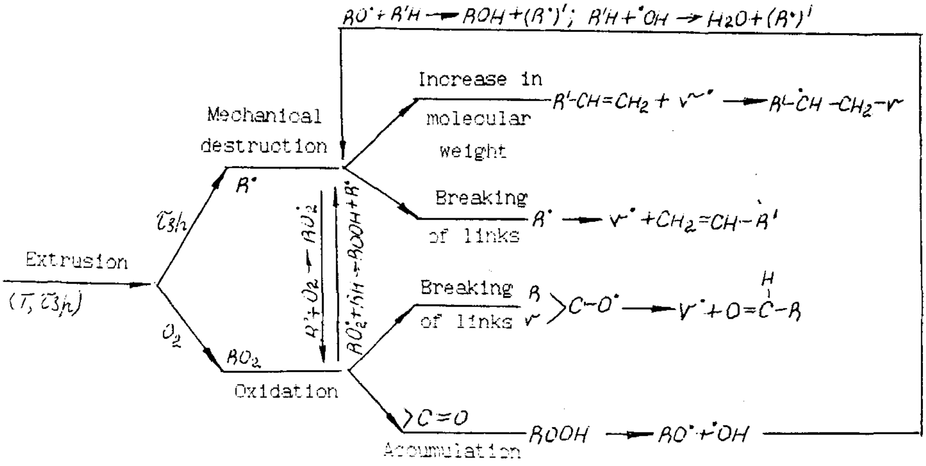


FIGURE 1 Changes in macromolecules occurring during polymer processing.

take place simultaneously and rival each other. There are two more reactions causing mechanically-initiated bond breakage (Reaction 0 and Reaction 4). They produce certain impact on the size of macromolecules but may be neglected because their reaction rates are of the same magnitude while their directions are opposite.

Quantitative representation of the autooxidation of the polymer melt at various oxygen concentrations and in presence of an inhibitor seems to be an important aspect of the entire problem. The basic data required for such calculations is reported in References 3–5.

During the first phases of the model development, the number of elementary steps can be limited. The diffusion problems that might happen during polymer mixing and processing can be neglected.

The kinetics of chemical transformations is the following:

0. $R^{\cdot}—CH_2—CH_2—R'' \xrightarrow[T,\ \tau_{igb}]{W_0} R'CH_2^{\cdot} + {}^{\cdot}CH_2R''$ Breaking of carbon chain-initiation

1. $R^{\cdot} + O_2 \xrightarrow{K_1} RO_2^{\cdot}$

Developing of kinetic chain

2. $RO_2^{\cdot} + RH \xrightarrow{K_2} ROOH + R^{\cdot}$

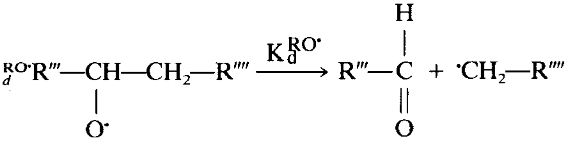
3. $ROOH \xrightarrow{K_3} RO^{\cdot} + {}^{\cdot}OH$ Branching of kinetic chain

2. ${}^{R^{\cdot}}R^{\cdot} + R'H \xrightarrow{K_2^{R^{\cdot}}} RH + (R')^{\cdot}$

2. ${}^{RO^{\cdot}}RO^{\cdot} + RH \xrightarrow{K_2^{RO^{\cdot}}} ROH + R^{\cdot}$ Developing of kinetic chain

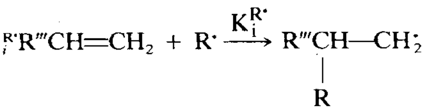
2. ${}^{\cdot OH}HO^{\cdot} + RH \xrightarrow{K_2^{\cdot OH}} H_2O + R^{\cdot}$

Breaking of carbon chain

2. 

$${}_{d}^{RO^{\cdot}}R'''—\underset{\displaystyle O^{\cdot}}{\underset{|}{CH}}—CH_2—R'''' \xrightarrow{K_d^{RO^{\cdot}}} R'''—\overset{\displaystyle H}{\overset{|}{\underset{\displaystyle O}{\underset{\|}{C}}}} + {}^{\cdot}CH_2—R''''$$

2. ${}_{d}^{R^{\cdot}}R'''CH_2—{}^{\cdot}CH—CH_2—R'''' \xrightarrow{K_d^{R^{\cdot}}} R'''CH{=}CH_2 + {}^{\cdot}CH—R''''$

2. 

$${}_{i}^{R^{\cdot}}R'''CH{=}CH_2 + R^{\cdot} \xrightarrow{K_i^{R^{\cdot}}} R'''\underset{\displaystyle R}{\underset{|}{CH}}—CH_2^{\cdot}$$

Developing of carbon chain

4. $R^{\cdot} + R^{\cdot} \xrightarrow{K_4} R{-}R$

5. $RO_2^{\cdot} + R^{\cdot} \xrightarrow{K_5} ROOR$ Breaking of kinetic chain

6. $RO_2^{\cdot} + RO_2^{\cdot} \xrightarrow{K_6}$ Alcohol + ketone + oxygen

7. $RO_2^{\cdot} + TnH \xrightarrow{K_7} ROOH + Tn^{\cdot}$ Transfer of kinetic chain

8. $RO_2^{\cdot} + Tn^{\cdot} \xrightarrow{K_8}$ Molecular product Breaking of kinetic chain

10′. $Tn^{\cdot} + RH \xrightarrow{K'_{10}}$ Molecular product + $R^{\cdot}$ Transfer of kinetic chain

10″. $TnO_2^{\cdot} + RH \xrightarrow{K''_{10}} TnOOH + R^{\cdot}$

11. $Tn^{\cdot} + O_2 \xrightarrow{K_{11}} TnO_2^{\cdot}$

The above combination of elementary steps should be regarded as an approximation to the real chemical process. For example, Reaction 3 is one of the many reactions relating to the mechanism of peroxides decomposition. It is known that peroxides can decompose through a bimolecular process which involves another peroxide group, "C—H" bond or free radicals. Besides, the peroxide decomposition constant can depend upon the nature of adjacent functional group, i.e. hydroxyl, carbonyl or carboxyl. The decision of limiting the number of steps may appear arbitrary. However, the authors used their own experimental data showing that at high oxidation temperatures the number of elementary steps to describe this complex process should not be large. Because under such conditions the reactions having highest activation energies prevail. The above indicated kinetic scheme permits one to formulate a system of differential equations representing polymer oxidation, the amounts of inhibitor consumed and the changes of molecular weight. The intermediate calculations will be omitted and we shall present only the final expressions describing the kinetics of changes in concentrations of major oxidation products. For convenience, the time differentiation is replaced by the differentiation against length (l) of the extruder screw.

$$-\frac{d[O_2]}{dl} = V^{-1}\left[(K_2RH + K_7[TnH]) \sqrt{\frac{K_3[ROOH] + W_0}{K_6\left(\frac{K_7 \cdot K_8[TnH]}{K_6 \cdot K_{10}RH} + 1\right)}} \Bigg/ \left(1 + \frac{K_2RH\sqrt{K_4}}{\sqrt{K_6} \cdot K_1[O_2]}\right) + K_3[ROOH]\right] \quad (1)$$

$$\frac{d[\mathrm{ROOH}]}{dl} = V^{-1}\left[(\mathrm{K_2RH} + \mathrm{K_7[TnH]})\cdot\sqrt{\frac{\mathrm{K_3[ROOH]} + W_0}{\mathrm{K_6}\left(\frac{\mathrm{K_7\cdot K_8[TnH]}}{\mathrm{K_6\cdot K_{10}RH}} + 1\right)}}\Bigg/\left(1 + \frac{\mathrm{K_2RH}\sqrt{\mathrm{K_4}}}{\sqrt{\mathrm{K_6}}\cdot\mathrm{K_1}\cdot[\mathrm{O_2}]}\right) - \mathrm{K_3[ROOH]}\right] \quad (2)$$

$$-\frac{d[\mathrm{TnH}]}{dl} = V^{-1}\left(\frac{\mathrm{K_7[TnH]}\cdot\sqrt{\mathrm{K_3[ROOH]} + W_0}}{\sqrt{\mathrm{K_6}\left(\frac{\mathrm{K_7\cdot K_8[TnH]}}{\mathrm{K_6\cdot K_{10}RH}} + 1\right)}}\Bigg/\left(1 + \frac{\mathrm{K_2RH}\sqrt{\mathrm{K_4}}}{\sqrt{\mathrm{K_6}}\cdot\mathrm{K_1[O_2]}}\right)\right) \quad (3)$$

where, V = linear speed of melt flow in the extruder barrel (or its projection on the extruder length); $(\mathrm{K_7\cdot K_8[J_nH]})/(\mathrm{K_6\cdot K_{10}RH}) + 1)$ = parameter which takes into account the amount of inhibitor consumed in bond breakage; $(\mathrm{K_2RH}\sqrt{\mathrm{K_4}})/(\sqrt{\mathrm{K_6}}\cdot \mathrm{K_1[O_2]}) + 1)$ = parameter which takes into account $\mathrm{R}^\cdot$ to $\mathrm{RO}_2^\cdot$ relationship and the effect of $\mathrm{R}^\cdot$ radical on chain breakage; $\mathrm{K_{10}} = \mathrm{K'_{10}} + \mathrm{K''_{10}/O_2}$ = parameter which takes into account the reaction of chain development caused by both alkyl $\mathrm{J'_n}$ and peroxide $\mathrm{J_nO_2^\cdot}$ inhibitor radicals.

The solution of these equations allows us to obtain concentration profiles for oxygen, peroxide and the inhibitor (along the extruder's length).

It should be noted that W_0 parameter, being the function of temperature and shear rate, can also vary with length but for the first approximation its mean value will be considered as a constant.

The calculations of alkyl $\mathrm{R}^\cdot$ radical, alcoxyl $\mathrm{RO}^\cdot$ radical concentrations, and increases of polymer chain do not present difficulties:

$$[\mathrm{RO_2^\cdot}] \approx \frac{\sqrt{\mathrm{K_3[ROOH]} + W_0}}{\sqrt{\mathrm{K_6}\left(\frac{\mathrm{K_7\cdot K_8[TnH]}}{\mathrm{K_6\cdot K_{10}\cdot RH}} + 1\right)}\left(1 + \frac{\mathrm{K_2RH}\sqrt{\mathrm{K_4}}}{\sqrt{\mathrm{K_6}}\cdot\mathrm{K_1[O_2]}}\right)} \quad (4)$$

$$[\mathrm{R^\cdot}] = \frac{\mathrm{K_2[RH]}}{\mathrm{K_1[O_2]}}[\mathrm{RO_2^\cdot}] \quad (5)$$

$$[\mathrm{RO^\cdot}] = \frac{\mathrm{K_3[ROOH]}}{\mathrm{K}_d + \mathrm{K}_d^{\mathrm{RO^\cdot}}[\mathrm{RH}]} \quad (6)$$

In this case, the change in molecular weight resulting from specific conditions of the extrusion process can be represented as the result of degradation reactions ($2_d^{R^\cdot}$ and $2_d^{RO^\cdot}$) and the increase in chain length ($2_i^{R^\cdot}$).

$$\frac{dn}{dt} = (K_d^{R^\cdot} - K_i^{R^\cdot})[R^\cdot] + K_d^{RO^\cdot}[RO^\cdot] \tag{7}$$

Since n_t is the change of macromolecules in a unit weight of polymer it is related to molecular weight by:

$$n_t = 1 \cdot 10^3 \left[\frac{1}{(M_n)_t} - \frac{1}{(M_n)_0}\right] \tag{8}$$

And for the extrusion

$$\frac{dn_l}{dl} = -1 \cdot 10^3 \frac{d(Mn)_l V}{(M_n)^2\, dl} \tag{9}$$

$$-\frac{d(Mn)_l}{dl} = \frac{(Mn)^2}{1 \cdot 10^3 V}(K_d^{R^\cdot} - K_i^{R^\cdot})[R^\cdot] + K_d^{RO^\cdot}[RO^\cdot] \tag{10}$$

This model can be used to predict possible changes of molecular weight and the amount of absorbed oxygen. These two parameters have a significant effect on physical and mechanical properties of the polymer. No less important is the information about the quantities of accumulated hydroperoxide and of inhibitor consumed during processing. This data will permit one to assess the lifetime of the polymer under operating conditions.

For such a complex model it is very important to properly determine the values of kinetic parameters. Some of these parameters were determined many times at low temperatures, namely $K_2 \cdot K_6^{-1/2}$, $K_7 \cdot K_6^{-1/2}$.

The scatter of activation energies on preexponents of these parameters is relatively small and should not be arbitrarily altered.

Values of other parameters used in calculations, for example reaction rate constant related to bonding of O_2 to alkyl radical K_1, the rates of quadrupole recombination of alkyl (K_4) and peroxide (K_6) radicals, as well as reactions of inhibitor $J_n^\cdot$ and peroxide $RO_2^\cdot$ – (K_8) are measured rather seldom. Their magnitudes are high but they vary within a narrow range. Papers[3,5] contain experimental values of the constants of kinetic chain transfer to inhibitor's radicals both without the involvement (K'_{10}) and with the involvement (K''_{10}) of oxygen.

Little data is available about the rate constants of alkoxy radical: for decomposition ($K_d^{RO^\cdot}$) and for chain growth ($K_2^{RO^\cdot}$). In our case, however, the main contribution to the calculations is done not by the absolute value of these constants but by the ratio of the decomposition rate constant to the constant of $RO^\cdot$ radical consumption. The value of this ratio is close to the number of oxygen molecules needed to break one bond. For high temperatures it is within the range of 3–15. Extensive data is, however, available for the decomposition constant of PE hydroperoxide (K_3). Since its decomposition mechanism is not quite clear, a simple monomolecular decomposition at high processing temperature was used in the calculations.

This decomposition process is characterised by a high activation energy which may amount to 35 kcal/mol and a preexponent exceeding $1 \cdot 10^{13}$ sec^{-1}.

There is no information about W_0 (the rate of thermal oxidational and mechanochemical initiation of radicals). The upper limit of this value, $W_0 = 1 \cdot 10^{-3}$ mol/kg·sec was chosen for the following reasons: at certain process conditions the inhibitor can be fully absorbed at its initial concentration of $[J_nH]_0 \approx 1 \cdot 10^{-2}$ mol·OH/kg. At the extrusion times of approximately $1 \cdot 10^2$ sec the above mentioned W_0 value can be achieved.

Figure 2 shows oxygen concentration (1′, 1″) peroxide concentrations (2′, 2″) and inhibitor concentrations (3′, 3″) for the following conditions: $[O_2] = 8 \cdot 10^{-3}$ and $5 \cdot 10^{-3}$, $[K_2]_0 = 1 \cdot 10^9$ kg/mol·sec, $[K_3]_0 = 5, 4 \cdot 10^{16}$ sec^{-1}, $W_0 = 1 \cdot 10^{-4}$ mol/kg·sec.

Temperatures of the extruder zones vary within the range between 150–220°C. It was discovered that the consumption of oxygen at the entry side of the extruder is negligible (this holds for 1/5-th of extruders length). Beyond this section, oxygen consumption gradually increases and at the point of 0,7 of the extruder length all oxygen is consumed. Concentration of hydroperoxide attains maximum and then drops to zero. After a similar period of time the consumption of inhibitor also stops.

An important result of the calculations is the existence of an extruder zone in which there is no oxygen and hence no oxidation. Such processing conditions might be needed to obtain products with increased stability to thermal oxidation because in such a case the peroxide content is zero. During processing of secondary polymers

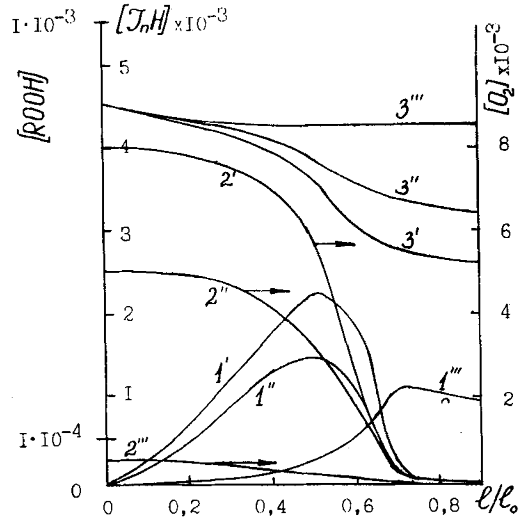


FIGURE 2 Profiles of peroxide [ROOH] (1′, 1″, 1‴), oxygen $[O_2]$ (2′, 2″, 2‴) and the inhibitor $[J_nH]$ (3′, 3″, 3‴) along extruder length. Calculating conditions are the following: (′)—$[O_2] = 8 \cdot 10^{-3}$; (″)—$[O_2] = 5 \cdot 10^{-3}$; (‴)—$[O_2] = 0.5 \cdot 10^{-3}$; for all cases $W_0 = 1 \cdot 10^{-4}$; $(K_2)_0 = 1 \cdot 10^9$; $(K_3)_0 = 5.4 \cdot 10^{16}$.

(or used polymers) which accumulated peroxide during their previous use it is needed to decrease peroxide concentration. Despite a theoretical and practical feasibility of creating an "improvement" zone within the extruder barrel, there have been no investigations to demonstrate this effect.

Figure 3 shows peroxide profiles at different W_0 values and various shear rates. Thermal oxidation is somewhat accelerated in comparison with the conditions presented in Figure 2. Note that the decomposition constant of the peroxide is higher by an order of magnitude. This resulted in the shift of peroxides primarily at the entry side of the extruder.

Figure 4 shows oxygen profiles at different kinetic oxidation rate constants. The increase in these constants represents the change from less to more oxidizable polymers, for example, from PEVP to PP.

As it is seen from Figure 4, the increase of $(K_2)_0$—permanent oxidation rate brings about the shift of the starting point of the acceleration towards the loading zone of the extruder. This in turn, increases the size of the "improvement" zone. Similar results were obtained with the increase of W_0 value, i.e. the capability of the reactor to operate at a higher shear rate, $\dot{\gamma}$, and therefore at a higher rate of mechanically-initiated breakage of macromolecules.

Figure 5 shows oxygen profiles at W_0 values varying from $1 \cdot 10^{-6}$ up to $1 \cdot 10^{-3}$ mol/kg·f. At $W_0 < 4 \cdot 10^{-5}$ mol/kg·f the influence of W_0 is small. When W_0 becomes $\geq 4 \cdot 10^{-5}$ mol/kg·f it starts producing a more significant impact on the whole process than the autooxidation process itself. It should be noted that the gap between Curve 2 and Curve 4 (minimal and maximal influence of W_0, respectively) is rather narrow. The actual gap for $\dot{\gamma}$ values can be still narrower because it is possible that W_0 will increase exponentially with increasing $\dot{\gamma}$.

The behaviour of the inhibitor can be regarded as a critical factor for the rate

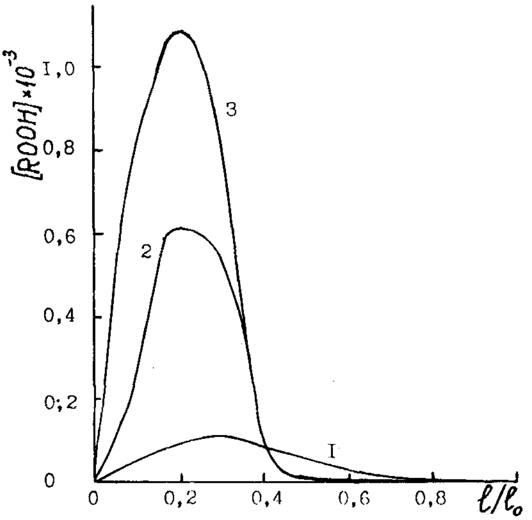


FIGURE 3 Peroxide concentration profiles along extruder length at various rates of primary initiation: 1. $W_0 = 1 \cdot 10^{-5}$; 2. $W_0 = 1 \cdot 10^{-4}$; 3. $W_0 = 1 \cdot 10^{-3}$. Calculating conditions are the following: $[O_2] = 1 \cdot 10^{-2}$; $(K_3)_0 = 5.4 \cdot 10^{-17}$.

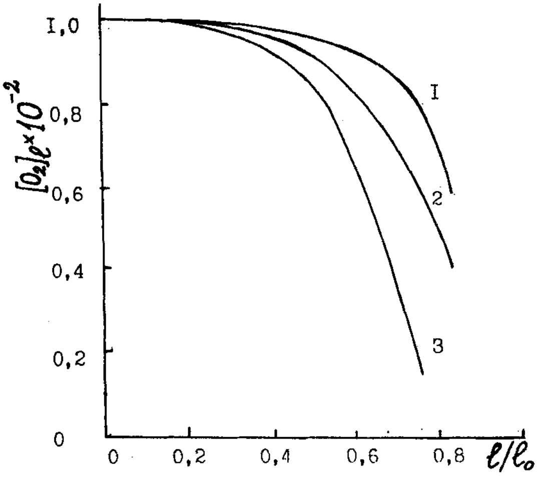


FIGURE 4 Oxygen absorption kinetics versus $(K_2)_0$: 1. $(K_2)_0 = 0.27 \cdot 10^8$; 2. $(K_2)_0 = 0.8 \cdot 10^8$; 3. $(K_2)_0 = 2.7 \cdot 10^8$.

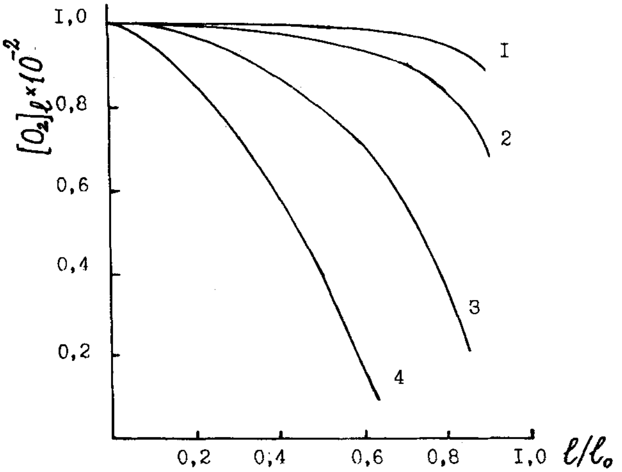


FIGURE 5 Oxidation rate versus initiation rate $/W_0/$: 1. $1 \cdot 10^{-6}$; 2. $1 \cdot 10^{-5}$; 3. $1 \cdot 10^{-4}$; 4. $1 \cdot 10^{-3}$.

of oxygen absorption. It is known that the increases in inhibitor content improve the stability of polymer during extrusion. This is the reason why PE insulations contain up to 5% of antioxidant when they are used for critical applications.

Studies of the mechanism of inhibited autooxidation conducted recently have shown that at high temperatures the inhibitor acts as an initiator of the oxidation process. The model described in this paper takes this phenomenon into account by describing the transfer of kinetic chain with and without the involvement of oxygen. Figure 6 shows the amounts of absorbed oxygen versus inhibitor concentration. Note that at low inhibitor concentrations the amount of absorbed oxygen first sharply decreases to its minimum, and then increases when inhibitor concentration gets higher. The action of the inhibitor becomes self-destructive at $[J_nH] \simeq 4.5 \cdot 10^{-2}$ mol OH/kg, i.e. at 1% for "hindered" phenols. During this phase the

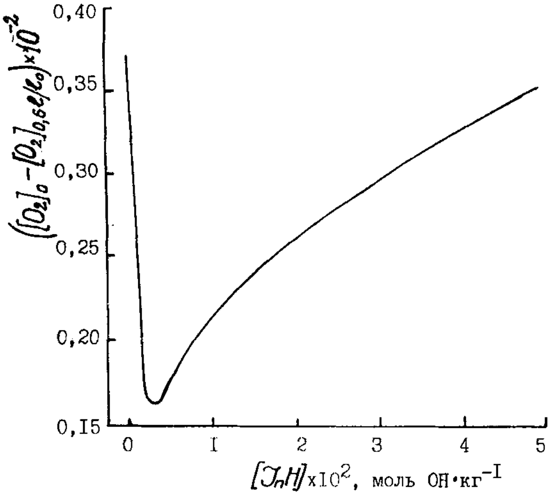


FIGURE 6 Mean oxygen absorption rate versus initial inhibitor's concentration.

oxidation rates of inhibitor-doped and inhibitor-free polymers become the same. This simplified approach of describing inhibitor's action indicates that there is a certain optimal inhibitor's concentration which ensures maximal retardation of polymer oxidation. For IONOL or NONOX WSP this concentration can constitute less than 0.1% by weight.

Future investigations aimed at determining optimal stabilization conditions for thermoplastic materials will have to include the results of present studies conducted in the field of kinetics of inhibited oxidation.

It is also important to take into account such phenomena (that have been recently recognized) as the ramp of inhibited oxidation at increasing inhibitor concentrations. High effective activation energy of oxidation and low solubility of oxygen in the crystallic fraction of semicrystallic polymers are the indicators of high oxidation rates taking place during polymer processing. These rates are higher than those occurring normally under operating conditions. Therefore, it is more important to stabilize PE during its processing than to try to reduce PE oxidation when it is under operating conditions. When polymer is used in finished products other types of destruction would cause a reduction in PE's lifetime, namely photooxidation and mechanical destruction.

Changes in molecular weight during processing are particularly important. Equation 10 shows that the decomposition reflected in W_0 rate can be caused by a mechano-chemical initiation process which will eventually result in RO$^\bullet$ radical decomposition, isomerization and breaking of R$^\bullet$ radical at a rate constant being $K_d^{RO^\bullet}$. The growth of macromolecules is explained by the fact that R$^\bullet$ radicals get attached to the double bond.

The growth of macromolecules does not take into account the recombination of R$^\bullet$ radicals because at oxygen concentrations of $[O_2] \geq (5\cdot10^{-5} - 1\cdot10^{-4})$ mol/kg the kinetic importance of this reaction is small. This group of reactions is noted by considerable differences in their activation energies. W_0 value, being the kinetic characteristic of the mechano-chemical process, does not exhibit a tangible temperature coefficient and should be defined arbitrarily. The activation energies of joining R$^{\bullet}$ radical to the double bond, and isomerization energy of R$^{\bullet}$ radical are 4–6 and 15–20 kcal/mol, respectively. The RO$^{\bullet}$ radical decomposition (this radical is derived from peroxide) is characterized by a still higher activation energy amounting to 30–35 kcal/mol.

The changes in molecular weight are, therefore, expected to be in a very complex relation with the temperature of polymer processing. The molecular weight changes during processing cannot be predicted because the temperature keeps varying along the length of extruder barrel. To present relevant relationships, the calculations connected with the molecular weight changes are carried out at a constant temperature for every processing regime.

Figure 7 shows profiles of cross-link breakages along the extruder at different temperatures at very small and practically negligible $W_0 = 2 \cdot 10^{-6}$ mol/kg·s. The curves given in Figure 7 are of autoaccelerative nature. This shows that the oxidation reaction is overriding over other chemical reactions resulting in molecular weight changes. At lower temperatures the chain length tends to grow. This effect increases up to temperatures of 190°C and then decreases. At temperatures of 210–220°C a transition from molecular growth to reduction in length takes place.

The presented data show that the thermal oxidation reactions lead to two types of changes in polymer chain length, low temperature growth and high temperature shortening.

It should be noted that at acceptable constant values of peroxide decomposition, K_3, and constant oxidative kinetic chain growth rate, K_2, the entire RO$^{\bullet}$ input into the destruction process will be negligible. In fact, only two competing reactions of R$^{\bullet}$ radical should be studied: the reaction of attaching the R$^{\bullet}$ radical to the double bond and the isomerization reaction which ends up in a break. The maximal stability

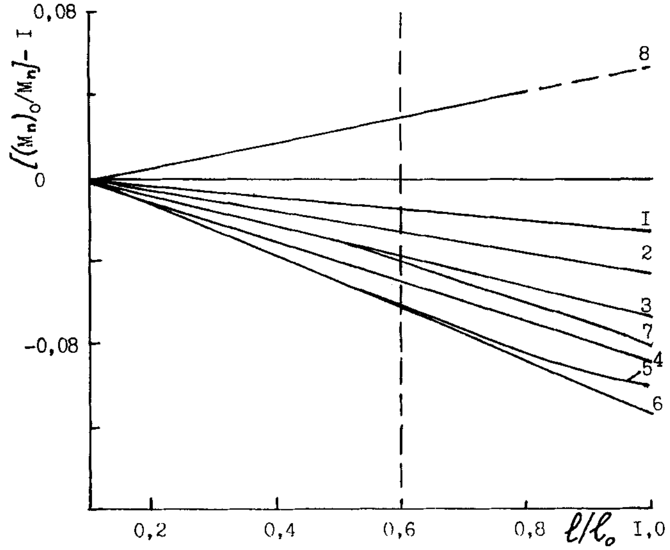


FIGURE 7 Profiles of cross-link scissions along extruders at the temperatures: 1—140°C, 2—150°C, 3—160°C, 4—170°C, 5—180°C, 6—190°, 200°C, 7—210°C, 8—220°C (calculation conditions: $W_0 = 2 \times 10^{-6}$, $(k_2)_0 = 2.7 \times 10^{7}$, $(k_3)_0 = 5.4 \times 10^{13}$, $(k_d)_0 = 1 \times 10^{10}$, $(k_i)_0 = 1 \times 10^{6}$).

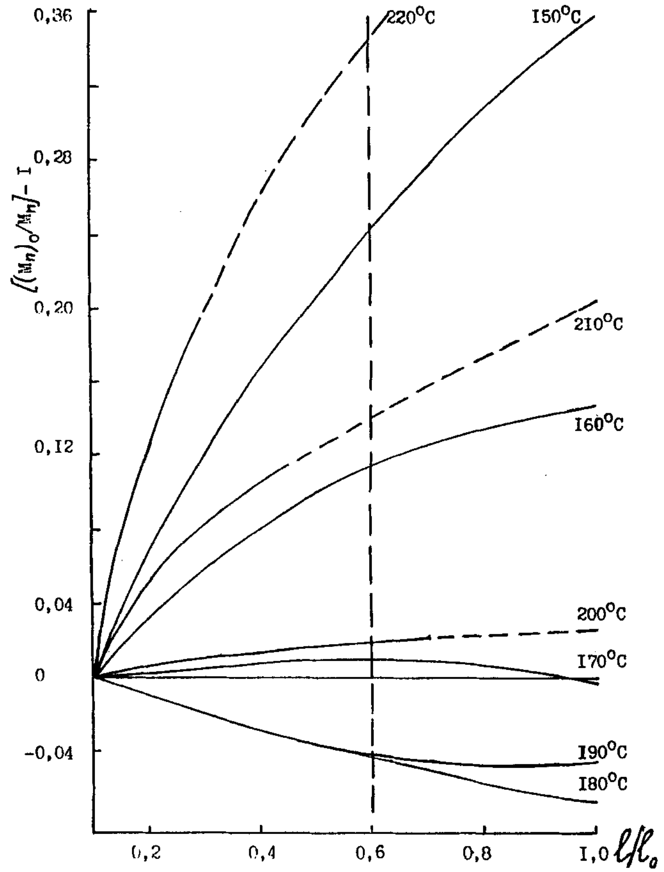


FIGURE 8 Profile of macromolecular breaks at various temperatures along the extruder's length. Calculating conditions: $W_0 = 2\cdot10^{-4}$; $(K_2)_0 = 2.7\cdot10^7$; $(K_3)_0 = 5.4\cdot10^{13}$; $(K_d)_0 = 1\cdot10^{10}$; $(K_i)_0 = 1\cdot10^5$.

of the material during processing can be obtained at temperatures close to 220°C. Figure 8 shows the number of cross-link breaks per molecule, $S = [(M_n)_0/M_n] - 1$ at various processing temperatures and W_0 values. When temperature rises from 150 to 180°C the macromolecules tend to grow at a decreasing rate. At 190°C the temperature growth is of the same magnitude as at 180°C. Further increases of temperature slow down the growth rate which eventually becomes zero at 210–220°C. At still higher temperatures, the polymer starts to decompose. Such phenomenon was observed on testing of low density PE in rotary-type viscometer in inert atmosphere and in experiments simulating extrusion conditions.[48]

The relative number of cross-link breaks versus temperature at midpoint of extruder's barrel is shown in Figure 9. Low temperature decomposition starts at $W_0 = 2\cdot10^{-5}$ mol/kg·s (curve 2). It is noteworthy that the right side of the curve is steeper than the left side.

Macromolecules grow at temperatures between 150–215°C. When W_0 reaches $2\cdot10^{-4}$ mol/kg·s (curve 3) the macromolecules become shorter. This is because

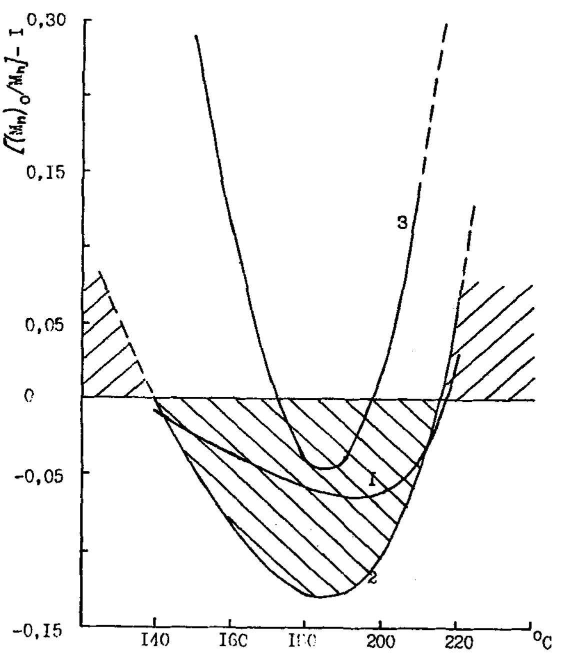


FIGURE 9 Relative changes occurring in macromolecules at the midpoint of extruder barrel: 1. $W_0 = 2\cdot10^{-6}$; 2. $W_0 = 2\cdot10^{-5}$; 3. $W_0 = 2\cdot10^{-4}$.

the concentration of radicals increases the rate of the process, and the balance of reactions tend to move toward decomposition. The domain of polymer chain growth is reduced to the temperature range between 170–195°C and the number of cross links per molecule is 0.05 instead of 0.15.

The experiments confirmed these findings. At low values of W_0 no low temperature degradation was observed. At high W_0 (when testing material in a disc extruder) no cross linking was observed,[13] and the temperature boundary between decomposition and growth was similar to the data obtained by calculations.

Particular attention should be paid to the role of oxidation rate in the entire process of molecular length change. At high W_0 values the oxidation process proceeds independently of mechanical degradation. Curve 2 shows that similar changes in molecular weight can occur at temperatures differing by 40–50°C (for example, when the number of breaks $S = -0.05$). Oxidation rates in such cases are quite different. It shows that mechanical degradation prevails over thermal oxidation. We stated before that the concept of what prevails, oxidation or mechanical destruction, may not have a "chemical meaning." However, this question should not be regarded as an academic issue because it has a practical value. Depending on the concentration of oxygen and relation between chain growth and chain shortening processes, they should be retarded either by means of antioxidants or by using acceptors of $R^{\cdot}$ radicals. It is obvious that in situations when mechanical degradations prevail (high W_0 values), the use of antioxidants will be less efficient. In fact, during extrusion one should use compounds comprising antioxidants, peroxide decomposers and acceptors of alkyl radicals.

CONCLUSIONS

1. There is an extruder zone in which there is no oxygen in the polymer material, hence, no oxidation, no inhibitor consumption and no peroxide. Such a zone can be called an "improvement" zone.

2. To obtain the required stabilizing effect the inhibitor concentration should be at optimum. During normal extrusion it should be $[J_nH]_{opt} = 3 \cdot 10^{-3}$ mol OH/kg. This is substantially lower than the concentrations currently used by polymer industry.

3. There are three temperature regimes of processes that result in shortening or growth of polymer chains:

low temperature decomposition caused by mechanically initiated scission;

medium temperature polymer growth resulting from attaching of alkine $R^{\cdot}$ radicals to polymer double bonds;

high temperature decomposition caused by isomerization which leads to breakage of polymer chains. The effect of the above processes depends on the properties of polymer being processed and on processing conditions.

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