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DEGRADATION OF POLYPROPYLENE UNDER THE EFFECT OF THE LOW-MOLECULAR-MASS ORGANIC PEROXIDES BELOW THE MELTING TEMPERATURE OF THE POLYMER

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ABSTRACT

The efficiency of five commercially available peroxides on the level of degradation of polypropylene (PP) at temperatures below its melting point has been studied. The efficiency extrapolated onto 100°C increases in the following order: tert. butylperoxy-2-ethylhexanoate ≈ tert. butylperoxy-isobutyrate < dilauroyl peroxide < 1,1-bis(tert. butylperoxy)-3,3,5-trimethyl cyclohexane ≈ tert. butylperbenzoate. The various effects of peroxides on the degradation of PP is explained by different reactivity of primary radicals of the peroxides and their solubility.

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INTRODUCTION

Modification reactions on polypropylene often take place under the initiation effect of peroxides. It is e.g. in controlled decrease of molecular mass [1-4], but also in crosslinking [5-8], maleination [9-11] or grafting of polypropylene with other monomers [12, 13].

The mentioned modification reactions are always accompanied with the fragmentation of the polypropylene chain. This fact is particularly evident in crosslinking, where high peroxide concentration is required to reach the gel point, i.e. to reach the predominance of crosslinking reaction over the simultaneously proceeding fragmentation of polypropylene macroradicals.

As it has been observed earlier, various types of peroxides have various efficiency in crosslinking [14, 15], maleination [11], or grafting of monomers onto polypropylene [16, 17]. On the other hand, a presumption has also been raised about a small influence of the efficiency of peroxides on the degradation of polypropylene. The dependence of melt flow index - MFI - on the amount of peroxide decomposed in polypropylene is described [4, 20] by linear equation. A remarkable discrepancy is observed in the slope of approximately linear dependence for the same peroxide. The reason for the discrepancy probably consists in a different polymer used (in molecular mass and its distribution), and in the presence of various antioxidants and their different concentration. From this aspect, clarification of the separated effect of initiation radicals on the degradation of polypropylene macromolecules below the melting temperature of polypropylene appears to be interesting.

In our experimental work, we studied peroxides with the half-time decay between 5 and 60 minutes at 90-140°C, i.e. in the range where polypropylene still remains in the powder form. The bottom temperature limits were determined by the rate of polypropylene swelling and the rate of radical polymerization of common monomers during grafting.

EXPERIMENTAL

All peroxides were of the commercial type and used as obtained:

TBPEH - tert. butylperoxy-2-ethylhexanoate, product of the firm AKZ0, 98%
TBPIB - tert. butylperoxyisobutyrate, product of AKZ0, 75%
DLP - dilauroyl peroxide, product of Merck, 97%

TBPB - tert. butylperbenzoate, product of Merck, 98%

BTBMC - 1,1-bis(tert. butylperoxy)-3,3,5-trimethylcyclohexane, product of AKZO, 75%.

Characterization of PP

Powdered polypropylene, type Daplen-B Pulver, product of ÖMV, Austria was used, MFI = 0.2 g/10 min.

Procedure in Peroxide-Initiated Degradation of PP

The peroxides were impregnated into 100 g powdered polypropylene samples. The effect of the peroxide concentration was examined at the same six molar concentrations. Peroxide impregnated samples [11] were annealed in an inert nitrogen atmosphere to the respective temperature under stirring to reach a more rapid heating of the polymer through the contact of the particles with the wall of the glass reactor placed in a liquid bath. The time of thermal degradation corresponded minimally to seven half-times of peroxide.

RESULTS AND DISCUSSION

Theoretical Approach

The measurement of the flow index (MFI) of the polymer melt at 230°C was used as a starting value for studying the changes in molecular mass of PP. We based our measurements on the fact that MFI, as a measure of the viscosity of the melt depends on the molecular mass M of the linear polymer in terms of Equation 1.

$$\mathrm{MFI} = \mathrm{const.}\, M^{-x} \tag{1}$$

where the exponent x is between 3.2 and 3.6 in the region of M where the entanglement of macromolecules is already applied [18]. The value $x = 3.4$ can be calculated for polypropylene from the experimental results of the variation of MFI with M_w [19].

The value of the number of scissions A in PP macromolecules under the effect of the initiator radicals can be expressed by the difference between the reciprocal of the number-average molecular mass (M_d) of the degraded macromolecules and the original molecular mass M_o,

$$\frac{1}{M_d} - \frac{1}{M_o} = A \qquad (2)$$

Since the value A depends on the concentration of peroxide decomposed in the polymer and the mechanism of the effect of radicals formed in PP, then, with respect to the preceding equations, we can write (Equation 3).

$$MFI_d^{0.294} - MFI_o^{0.294} = k\,[RO - OR]^n \qquad (3)$$

where the exponent 0.294 are reciprocent value of x.

According to this equation, we calculated the exponent **n** for various peroxides. The value of **n** was determined by the method of least squares as a slope of the logarithmic dependence of Equation 3. In the first phase of PP degradation, the distribution of molecular masses decreases, which appears as an additional influence on MFI. The complicating contribution of the varying distribution of molecular masses to the number of scissions was not included into the evaluation because of its negligible significance for a relative comparison of the effect of various peroxides within approximately the same range of PP degradation.

The Effect of Concentration and the Type of Peroxide

Five peroxides were selected for studying the effect of the structure of initiating radicals on polypropylene degradation (Figure 1).

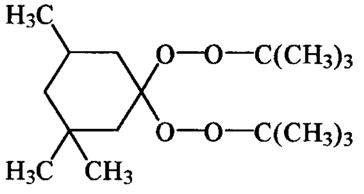
The melt flow indexes (MFI) of polypropylene measured after the decomposition of TBPEH and TBPIB in a polymer at various concentrations indicate a general increase in MFI with an increasing decomposed amount of peroxide (Table 1). The decrease in average molecular mass of PP or, the other way round, the increase in the flow index of the melt will depend on the amount of formed PP macroradicals which are able to fragment into smaller polymer chains. Within the lower concentration range of peroxides applied, fragmentation of PP macroradical formed by transfer reaction of radicals $R^{\bullet}$ from the peroxide being decomposed, prevails (Equation 4).

$$\dot{R} + PP \longrightarrow RH + \dot{PP} \qquad (4)$$

The $\dot{PP}$ radicals formed have an unpaired electron on the macromolecular backbone. In fragmentation of $\dot{PP}$ (Equation 5)

$$\dot{PP} \longrightarrow PP_f + PP_f^{\bullet} \qquad (5)$$

$(CH_3)_3 - O - O - (CO)CH(C_2H_5)(C_4H_9)$	**TBPEH**
$(CH_3)_3C - O - O - (CO)CH(CH_3)_2$	**TBPIB**
$C_{11}H_{23}(CO) - O - O - (CO)C_{11}H_{23}$	**DLP**
$(CH_3)_3C - O - O - (CO)C_6H_5$	**TBPB**



BTBMC

Figure 1. A Scheme of the Structure, Names, and Symbols for Peroxides Used.

TBPEH - tert. butylperoxy-2-ethylhexanoate
TBPIB - tert. butylperoxyisobutyrate
DLP - dilauroyl peroxide
TBPB - tert. butylperbenzoate
BTBMC - 1,1-bis(tert. butylperoxy)-3,3,5-trimethylcyclohexane

the polymer chain is split into a smaller fragment PP and he end radical $PP_f^{\bullet}$ with the polymerization degree lower than was that of the original macroradical $\dot{P}P$.

If we assume that primary radicals $\dot{R}$ obtained by the decomposition of peroxide initiator R-R react only by transfer reaction with polypropylene macromolecules (Equation 4) and in termination only macroradicals $\dot{P}$ ($\dot{P}P$ or $PP_f^{\bullet}$) decay (Equation 6),

$$\dot{P}_x + \dot{P}_y \xrightarrow{k_t} P\,(P_x + P_y) \qquad (6)$$

then their concentration in the reaction system will be proportional to the square root of the concentration of the peroxide decomposed since k_i [R-R] = $k_c[P]^2$. The number of scissions in polymer chains is proportional to the number of $PP_f^{\bullet}$

TABLE 1. Melt Flow Indexes (MFI) as a Function of Polypropylene Degradation Under the Effect of Tert. Butylperoxy-2-Ethylhexanoate (TBPEH) And Tert. Butylperoxy Isobutyrate (TBPIB). The Given Exponent **n** from Equation 3 is Calculated from MFI Data for Various Temperatures

Peroxide	**TBPEH**			**TBPIB**		
mmol/kg	**90 °C** **440 min**	**97 °C** **230 min**	**115 °C** **40 min**	**96 °C** **420 min**	**102 °C** **230 min**	**120 °C** **55 min**
0	0.30	0.30	0.33	0.30	0.30	0.33
4.62	0.56	0.40	0.36	0.93	0.45	0.42
9.24	0.66	0.46	0.43	-	0.60	0.86
18.5	1.00	0.49	0.47	1.42	0.60	0.88
37	1.58	0.50	0.62	1.25	0.70	1.14
74	1.10	0.70	0.74	2.32	1.20	1.30
139	1.20	0.90	0.97	-	1.65	1.90
n	**0.28** [a]	**0.40**	**0.73**	**0.23**	**0.45**	**0.53**
b	**0.836**	**0.970**	**0.968**	**0.897**	**0.971**	**0.871**

a) - exponent **n** calculated from the ascending part of the MFI dependence is 0.56 at the correlation coefficient 0.994

b) - correlation coefficients

macroradicals formed. Hence, assuming the given degradation mechanism, the value of the exponent **n** (Equation 3), should be 0.5. $\overset{\bullet}{PP}$ radicals leading to the lowering of the molecular mass of PP can also be formed by reaction (7)

$$PP_f^{\bullet} + PP \longrightarrow \overset{\bullet}{PP} + PP_f \qquad (7)$$

which will change the efficiency of degradation (or the value k in Equation 3), but not the exponent **n.** The experimentally obtained values of **n** deviate from the ex-pected value in both peroxides (Table 1). The deviation can have several reasons. The value of **n** higher than 0.5 will be given by termination of the $PP_f^{\bullet}$ end radicals with initiator radicals. In the case, if one initiator radical will abstract hydrogen atom from PP chain and the second primary radical will react with fragmented macroradical $PP_f^{\bullet}$, then the exponent **n** = 1. The value of **n** lower than 0.5 will correspond to the participation of initiator radicals in the reaction with non-fragmented macroradicals $\overset{\bullet}{PP}$, which leads to polymer modification (formation of double bonds or linking of initiator radicals to PP chain) but without substantial changes in average molecular mass of AP. In the boundary case, when one radical initiator abstracts hydrogen from polypropylene and the second initiator radical reacts with a not-yet-fragmented macroradical $\overset{\bullet}{PP}$, then **n** = 0. The independence of MFI on the amount of decomposed peroxide (**n** = 0) will also be the case if initiator radicals are not able to abstract hydrogen from PP but will mutually combine. Both processes are probable at the low reactivity of initiator radicals and their high local concentration. The mutual interaction of primary radicals can be raised by a potential formation of initiator clusters by raising its concentration in the polymer.

Further complications are introduced into the relation between the number of scissions in PP chains and the peroxide concentration by possible recombinations of non-fragmented $\overset{\bullet}{PP}$ macroradicals or additions of the macroradicals of both types to the double bonds in PP macromolecules, since through these reactions the average molecular mass of PP increases. The presence of building reactions which increase the molecular mass of PP competing significantly with macromolecular fragmentation of $\overset{\bullet}{PP}$ macroradicals is clearly confirmed by the observed maxima of melt flow indexes in concentration relations of some other peroxides (Tables 2 and 3). Competition reactions increasing the molecular mass of a polymer can also be expected with previous peroxides (Table 1) but in those cases, they are less significant and can be influenced by an error of measurement. The smaller manifestation of reactions which cause the maximum as a functionof the melt flow index is associated with the lower reactivity of primary radicals in

TABLE 2. Melt Flow Indexes as a Function of the Degree of Polypropylene Degradation Under the Effect of Dilauroyl Peroxide (DLP) and Tert. Butyl Perbenzoate (TBPB). The Given Exponent **n** (Equation 3) is Calculated from MFI Data for Various Temperatures

Peroxide mmol/kg	**DLP**			**TBPB**		
	85 °C 210 min	**95 °C 130 min**	**105 °C 45 min**	**110 °C 360 min**	**129 °C 230 min**	**145 °C 55 min**
0	0.24	0.30	0.31	0.30	0.33	0.65
4.62	0.24	1.12	1.64	-	2.2	3.1
9.24	0.28	2.34	1.75	28.4	4.7	9.8
18.5	0.35	3.24	2.81	35.0	15.1	23.3
37	0.38	5.44	3.55	87.4	18.6	71.0
74	0.48	9.79 [a]	2.61	38.4	5.8	72.0
139	0.77	4.12 [b]	3.41	43.1	0.2	6.0
n	**0.73**	**0.46** [c]	**0.14**	**0.31** [c]	**0.56** [c]	**0.60** [c]
d	**0.980**	**0.986**	**0.836**	**0.943**	**0.968**	**0.958**

a, b - repeated other independent measurements of MFI from new samples:
a (10.8 and 11.5), b (4.56 and 7.85)

c - exponent **n** calculated from the ascending part of the dependence of MFI on peroxide concentration

d - correlation coefficients

TABLE 3. Melt Flow Indexes (Equation 3) for Polypropylene Degradation Under the Effect of 1,1-Bis(tert. butylperoxy)-3,3,5-trimethylcyclohexane

mmol/kg	**110 °C** **360 min**	**120 °C** **210 min**
0	0.30	0.33
4.62	11.3	1.9
9.24	30.9	3.8
18.5	27.5	7.2
37	61.1	31.8
74	53.6	53.8
139	53.4	75.0
n	0.55 [a]	0.55
b	0.924	0.982

a - **n** calculated from the ascending part of the dependence

b - correlation coefficients

transfer reaction with a polymer and greater participation of initiator radicals in reactions with polymer macroradicals. The last reaction limits the fragmentation of $\mathrm{P\dot{P}}$ macro-radicals.

The Effect of Temperature

The different temperature effect on the values of exponent **n** for different peroxides is interesting (Tables 1-3). Only the exponent **n** for DLP evidently decreases with increasing temperature, in comparison with other peroxides. The decrease in the exponent **n** with increasing temperature ssociated with the increasing rate of the fragmentation of primary lauroyloxyl radicals into alkyl radicals which are less active in transfer reactions with PP. This results in the rise of the level of alkyl radicals in the polymer; therefore, the proportion of the reactions between alkyl radicals and PP macroradicals increases. The proportion of the mutual reaction between initiator radicals increase at higher temperature. These reactions are the processes lowering the exponent **n**. The indicated explanation agrees with our prev-ious findings [1] that the DLP-initiated efficiency of maleination of PP increases with the decreasing temperature of peroxide decomposition. The importance of radical decarboxylation in the case of DLP is highlighted by the fact that only in this particular peroxide both radicals being formed can be decarboxylated by the decomposition of the initiator molecules.

The growth of the exponent **n** with increasing temperature is in the case of the majorityof peroxides used associated with the increasing rate of the fragmentation of PP macroradicals and the increasing proportion of the reaction of initiator radicals with fragmented macroradicals.

Another type of contribution to the growth in the exponent **n** can also partially be associated with the increase of the amorphous portion in semicrystalline polypropylene at higher temperature. A similar effect has been observed during oxidation e.g. initiated by gamma radiation [21] or thermal decomposition of dibenzoyl peroxide [22].

Efficiency of Peroxides on PP Degradation

It is impossible to present the number of scissions of macromolecules per the number of peroxide molecules decomposed because the molecular mass of degraded polypropylene samples was not determined. On the other hand, the measured melt flow indexes of PP at known peroxide concentrations enable us to compare the relative efficiency of particular peroxides in the PP degradation. Looking at the results of the melt flow indexes of degraded polypropylene, we clearly see that the efficiency of degradation depends on the structure of peroxide.

The melt flow index of degraded PP at the given concentration of the particular peroxide is the experimental parameter of the reactivity of peroxides in the degradation of macromolecules. Using the values of the melt flow indexes listed in Tables 1, 2 and 3 as a basis, then under optimum conditions of degradation the relative order of peroxides is as given in Table 4.

TABLE 4. The Reactive Efficiency of Peroxides on PP Degradation

Type of peroxide	**TBPEH**	**TBPIB**	**DLP**	**BTBMC**	**TBPB**
MFI - A	0.90	1.03	3.12	46.5	59.0
MFI - B	0.66	1.01	2.66	27.9	57.3
MFI - C	0.64	1.03	2.64	48.9	64.7
MFI - D	0.86	0.64	4.70	14.5	7.16
MFI - E	0.63	0.63	4.01	8.68	6.96

A - average value of all MFI measurements of PP after decomposition of 37 mmol/kg PP peroxide at various temperatures (see Tabs. 1-3)

B - average calculated values of MFI after decomposition of 37 mmol/kg PP peroxide. The calculation of MFI has been carried out from the group of values at which the concentration of peroxide caused their increase at each temperature, on the assumption: $MFI = MFI_o + k\,[peroxide]$.

C - calculated values of MFI according to the procedure described at B), which have been extrapolated to the temperature of 100 °C of the belonging peroxide, using Arrhenius equation.

D - values of MFI - A extrapolated onto 100 °C for each peroxide using average temperature coefficient (activation energy = 93.2 kJ/mol).

E - values of MFI - B extrapolated onto 100 °C according to the procedure D)

By quantitative comparison of the activity of peroxides in polypropylene degradation, the order of peroxides is divided into three groups. In the first group of the less active peroxides (TBPEH, TBPIB), one of the radicals formed by thermal decomposition decarboxylates very rapidly in the cage of the polymer medium leading to a decrease in the reactivity of transfer reaction with polypropylene. On the other hand, the alkyl radical, which has low reactivity for transfer reaction with PP, is effective in a termination reaction with polymeric radical, which decreases the probability of polymeric radicals fragmentation. A little higher reactivity of DLP, which gives, on decomposition, two less reactive alkyl radicals, requires additional expla-nation. When two alkyl radicals are formed from DLP, the decay of the radical pair is partly retarded by two CO_2 molecules in the cage. The lower reactivity of alkyl radicals in the transfer reaction with PP will be reflected in the possibility of greaterdiffusion of alkyl radicals from the original cage, which finally leads to a greater distance between $\overset{\bullet}{\mathrm{PP}}$ macroradical and the second alkyl radical. This fact suppresses termination of the new radical pair and supports thus fragmentation of the $\overset{\bullet}{\mathrm{PP}}$ macroradical.

The high reactivity of BTBMC in polypropylene degradation can be understood on the basis of the double content of peroxide bonds in the molecule (Figure 1). In addition, the activity of alkoxy and tert-butyloxy radicals applied in the case of this peroxide is higher than that of acyloxy or even alkyl radicals for hydrogen atom abstraction from polypropylene chain.

An increase in the reactivity of TBPB is due to the known fact that decarboxylation of benzoyloxy radical is by about 3 to 5 orders slower than that of aliphatic acyloxy radicals [23]. Another contribution of the higher reactivity of TBPB follows from the fact that decarboxylation of benzoyloxy radicals gives phenyl sigma-radicals which abstract hydrogen from polypropylene more quickly than alkyl pi-radicals.

The lower activity of alkyl radicals, as compared to alkoxy or acyloxy radicals, is also supported by the direct experimental fact that during peroxide decomposition in the presence of methyl methacrylate, much lower degradation of PP takes place over the whole concentration region of peroxides. Although, at the highest peroxide concentrations (74 and 139 mmol/kg), the trapping of primary radicals by methyl methacrylate is no longer complete.

The degradation efficiency is markedly influenced by reaction temperature, which controls the macroradical fragmentation and intermolecular radical transfer reactions. Using all calculated values MFI for individual temperature and at peroxide concentration = 37 mmol/kg PP (independent of the type of peroxide) the value of activation energy $E_a = 93.2$ kJ/mol, which corresponds with E_a of fragmentation of terciary alkyl radicals [24].

CONCLUSION

The effect of five peroxides on the growth of the melt flow index of PP melt was studied. The values obtained were used for determination of the relative efficiency of peroxides in polypropylene degradation and the exponents over peroxide concentration were calculated from the dependence of the scission of polypropylene macromolecules. The value of the experimentally found exponents varies around 0.5 for the majority of peroxides. This is explained by the mechanism within which hydrogen abstraction from polypropylene takes place by primary initiator radicals giving rise to fragmentation of polypropylene macroradicals. Fragmented macroradicals take part in termination of the degradation process. The efficiency of peroxides at the PP degradation extrapolated onto 100°C increases in the following order: tert. butylperoxy-2-ethylhexanoate ≈ tert. butylperoxy-isobutyrate < dilauroyl peroxide < 1,1-bis(tert. butylperoxy)-3,3,5-trimethyl cyclohexane ≈ tert. butylperbenzoate.

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