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THE EFFECT OF TEMPERATURE ON PEROXIDE INITIATED CROSSLINKING OF POLYPROPYLENE

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Abstract—Crosslinking of polypropylene at 10–220° was investigated. The process was initiated by radicals formed either by thermal or by u.v. decomposition of dicumyl peroxide. It was found that fragmentation of macroradicals is the most important reaction during thermal initiation and the crosslinking efficiency increases with decreasing temperature. For u.v. initiation, several chemical and physical factors are important; the efficiency is highest at 65–80°.

INTRODUCTION

Generation of free radicals in polypropylene leads to crosslinking as well as to significant polymer degradation because of the low stability of macroradicals on tertiary carbon. For this reason, it is necessary for gel formation to use either a large amount of initiator (when free radicals are formed by thermal decomposition of peroxide [1, 2]) or a high dose of radiation [3]. A high stationary level of macroradicals is necessary in the polymer, so that recombination prevails over fragmentation of macroradicals [4].

Generally, the activation energy for fragmentation is much higher than that for recombination of radicals so the efficiency of crosslinking is influenced by temperature. Some examples have been given recently [4]. In this work the influence of temperature on the crosslinking of polypropylene was investigated in detail and the process was studied over a wide range of temperature.

EXPERIMENTAL

Unstabilized isotactic polypropylene Tatren HPF (Slovnaft, Czechoslovakia) was used, having viscometric mol. wt 220,000 and degree of polydispersity approx. 10. Dicumyl peroxide (Perkadox SB) was recrystallized from ethanol.

Sample preparation

The required amount of initiator was added in the form of chloroform solution into a beaker with powdered polypropylene. After removing the solvent, the samples were pressed at 20 MPa cm^{-2}. The samples were heated in a press during 10 half-lives of dicumyl peroxide decay, when initiation by peroxide decomposition above the melting temperature of polypropylene was investigated. The samples for reaction below the melting temperature, as well as for initiation by u.v. decomposition of peroxide, were prepared as films of 1 mm thickness in a press at 170° for 5 sec. Less than 10% of initiator decomposed under these conditions. The films were heated in sealed ampoules under N_2 when thermal initiation was investigated. Crosslinking by u.v. irradiation was carried out in apparatus already described [5]. The same dose of irradiation was achieved for all samples. A Hg lamp was used as light source and temperature was maintained to ±0.5°. The reaction was carried out under N_2. The gel content was calculated according to weight loss after 14 hr extraction of samples in boiling xylene.

RESULTS

The amount of gel formed vs concentration of dicumyl peroxide at various temperatures is shown in Table 1. The gel content increases with increasing peroxide concentration at all temperatures. The significance of that effect can be evaluated if crosslinking efficiency is calculated from experimental results according to the equation [2]

$$e = \frac{[n]}{[i]} \tag{1}$$

where $[i]$ is the concentration of initiator and the concentration of crosslinks $[n]$ is given as

$$[n] = \frac{10^3 \gamma}{2\bar{M}_n} \tag{2}$$

$\bar{M}_n$ is number-average molecular weight and γ can be calculated from the soluble portion s according to the equation [6]

$$\gamma = \frac{1 - s^{0.5}}{s^{0.5} - s^{1.5}}. \tag{3}$$

Crosslinking efficiency data calculated from equations (1–3) are given in Table 2. The reason for the low efficiency has been discussed [2, 4]. It is caused mostly by fragmentation of a large proportion of the macroradicals. The observed decrease of crosslinking

Table 1. The amount of gel formed for various dicumyl peroxide concentrations (DCP) at various temperatures

T (°C)	Gel (%)				
150	35.6	59.6	61.8	80.0	81.9
160	11.6	67.6	64.8	74.9	75.9
170	5.5	38.0	60.0	66.9	76.1
180	1.0	16.7	49.9	60.0	65.4
190	2.5	3.8	45.1	50.2	60.5
200	0.6	—	20.8	—	56.0
220	1.2		1.5		3.8
DCP (M/kg)	0.274	0.367	0.455	0.538	0.617

Table 2. The efficiency of crosslinking (e) for various dicumyl peroxide concentrations (DCP) at various temperatures

T (°C)	e				
150	0.063	0.065	0.055	0.072	0.067
160	0.050	0.076	0.058	0.062	0.055
170	0.047	0.049	0.053	0.051	0.056
180	0.046	0.039	0.046	0.045	0.043
190	0.046	0.035	0.033	0.039	0.040
200			0.028		0.039
DCP (M/kg)	0.274	0.367	0.455	0.538	0.617

Table 4. Crosslinking efficiency calculated according to the data in Table 3

T (°C)	e					
10	0.0	0.0	0.034	0.0	0.0	0.020
18	0.071	0.046	0.035	0.028	0.024	0.022
35	0.076	0.053	0.047	0.047	0.048	0.034
60	0.083	0.065	0.051	0.042	0.041	0.036
85	0.098	0.067	0.051	0.046	0.039	0.030
115	0.086	0.057	0.046	0.035	0.033	0.031
DCP (M/kg)	0.176	0.274	0.367	0.455	0.538	0.617

efficiency with increasing temperature supports this view. Higher temperature increases the rate of fragmentation of the higher activation energy of that process compared with that for macroradical recombination.

Crosslinking of polypropylene was investigated also for initiation by u.v. irradiation instead of thermal decay of peroxides. The process can be followed at lower temperatures and the rate of initiation is supposed to be constant.

The amount of gel depends on initiator concentration as shown in Table 3. Reaction was carried out at various temperatures. The efficiency (Table 4) is in the range of the data for thermal crosslinking. In contrast to thermal initiation, the decrease of efficiency with increasing peroxide concentration is obvious. Also increase of temperature influences the process differently according to the mode of initiation. The efficiency decreases with higher temperature for thermal initiation but the plot of efficiency vs temperature exhibits a maximum when reaction is initiated by u.v. decomposition of the peroxide.

DISCUSSION

The efficiency of polypropylene crosslinking depends mainly on the competition between two reactions of the macroradicals. The rate of fragmentation is influenced mostly by temperature and the rate of recombination depends on initiator concentration and on the rate of its decay [4].

The effect of temperature on fragmentation is shown in Fig. 1. The concentration of crosslinks decreases with increasing temperature at any peroxide concentration. The concentration of crosslinks depends on the ratio of rates of macroradical recombination (W_R) and fragmentation (W_F) as well as on the initiator concentration [i]

$$[n] = \mathrm{K}\frac{W_R}{W_F}[i] \tag{4}$$

K is an empirical constant showing the contribution of macroradical side-reactions.

The average value of the temperature coefficient of the process is $E_n = -24.2\ \mathrm{kJ\ mol^{-1}}$ according to Fig. 1. If the activation energy for macroradical recombination is taken as close to zero, $E_n = E_i - E_F$. The activation energy of dicumyl peroxide decomposition in polymers is [7] $E_i = 139.4\ \mathrm{kJ\ mol^{-1}}$ and the energy of fragmentation E_F is calculated as $163.6\ \mathrm{kJ\ mol^{-1}}$.

Figure 2 demonstrates the influence of initiator concentration on crosslinking efficiency. The efficiency of thermal crosslinking increases slightly with peroxide concentration at any temperature. The quantitative explanation of this tendency is not simple. The crosslinking efficiency according to equation (1) is

$$e = \mathrm{K}\frac{W_R}{W_F} \tag{5}$$

The simplest scheme for polypropylene crosslinking

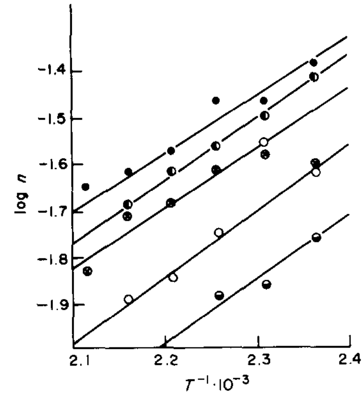

Fig. 1. Concentration of crosslinks (n) at various temperatures for various peroxide concentrations: 0.274 (◒); 0.367 (○); 0.455 (⊗); 0.538 (◐); 0.617 (●) M kg^{-1}.

Table 3. The amount of gel formed by u.v. initiation for various dicumyl peroxide concentrations at various temperatures

T (°C)	Gel (%)						
10	0.0	0.0	0.0	0.5	0.0	0.1	0.5
18	0.0	0.7	2.3	2.8	1.2	6.3	9.3
35	0.0	8.1	18.7	35.3	52.7	63.0	50.6
60	1.1	19.4	37.7	41.6	44.4	54.3	54.8
85	0.0	35.5	40.5	42.9	51.3	50.8	42.6
115	0.1	33.9	25.5	34.3	27.4	39.0	43.5
145	0.0	0.0	0.0	0.2	0.0	0.0	0.9
DCP (M/kg)	0.073	0.176	0.274	0.367	0.455	0.538	0.617

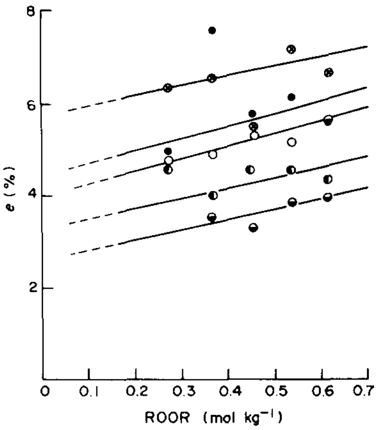

Fig. 2. Crosslinking efficiency (e) vs peroxide concentration at: 150 (⊗); 160 (●); 170 (○); 180 (◐); 190 (⊖) °.

involves four reactions

$$I \xrightarrow{k_1} 2\,RO\cdot \qquad \textbf{(I)}$$

$$RO\cdot + PH \xrightarrow{k_2} ROH + P\cdot \qquad \textbf{(II)}$$

$$P\cdot \xrightarrow{k_3} P'_{\cdot} + P''_{=} \qquad \textbf{(III)}$$

$$2\,P\cdot \xrightarrow{k_4} P\text{-}P \qquad \textbf{(IV)}$$

where PH is a polymer molecule and P· is a macroradical formed from polymer by proton abstraction.

The rates of recombination and fragmentation respectively are given as

$$W_R = k_4[P\cdot]^2 \qquad (6a)$$

$$W_F = k_3[P\cdot]. \qquad (6b)$$

The concentration [P·] in the steady state is given by the quadratic equation

$$k_4[P\cdot]^2 + k_3[P\cdot] = k_2[RO\cdot][PH].$$

The solution leads to two roots, one being meaningless; the other is written in the form

$$[P\cdot] = \frac{\sqrt{k_3^2 + 4k_1k_4[i]} - k_3}{2k_4}. \qquad (7)$$

Substituting (7) in (6) and (5) leads to the equation

$$e = \frac{K}{2}\left(\sqrt{1 + \frac{4k_1k_4}{k_3^2}[i]} - 1\right) \qquad (8)$$

which can be transformed to

$$K_A[i] = \frac{e}{K}\left(\frac{e}{K} + 1\right) \qquad (9)$$

where

$$K_A = \frac{k_1k_4}{k_3^2}.$$

In an ideal case, equation (9) should describe quantitatively the data in Fig. 2. If K is close to unity, i.e. most macroradicals react according to reactions **(III)** or **(IV)** and e is small, the crosslinking efficiency is proportional to the initiator concentration. In a real case, K may be influenced by inhomogeneous dispersion of initiator, formation of aggregates etc. This leads to increase of various side reactions owing to increased local concentration of macroradicals and consequently to decrease of K.

Crosslinking is different in certain respects when initiated by u.v. irradiation. The much lower temperature causes decrease of the fragmentation rate on the one hand but also decrease of the mobility of the segments bearing radical centres. The latter is the reason for almost no gel being formed at 10°; at 18° the amount of gel is still very low. For given reaction conditions, the optimal temperature is in the range 65–80°. The fragmentation is not very fast and macroradical mobility is high enough for effective crosslinking. However, the "macroradical mobility" must not be considered as diffusion of a whole macromolecule bearing a radical centre. Actually it is either an oscillation of segments allowing close approach of two neighbouring macroradicals if two radicals are formed in close proximity after decomposition of a peroxide molecule, or the motion of a free valency from one macrochain to another one by a transport radical mechanism [8]. Further increase of temperature leads to faster fragmentation and the crosslinking efficiency decreases.

The gel point is reached at lower amounts of initiator for u.v. irradiation compared with thermal initiation. Slow fragmentation leading to longer mean lifetime of macroradicals is the most important effect. Thus, there is a higher probability that a macroradical will meet a partner for recombination before its decay by fragmentation. On the other hand, at high peroxide content, aggregates are formed leading to various side reactions ineffective for crosslinking, e.g. disproportionation. The overall amount of gel is lower than for thermal initiation. Moreover, the decrease of light intensity in the polymer must be taken into account due to absorption of u.v. irradiation near the polymer surface because of high concentration of the absorbing initiator. Also absorbance by products of peroxide decomposition may be important; this effect may explain the decrease of gel content at high dicumyl peroxide concentrations.

At high temperatures, photothermal degradation must be considered as important. It manifests itself significantly over 100° and leads to molecular weight decrease [9]. As a consequence no gel is formed at 145° although, by extrapolation of temperature dependence for thermal initiation (Fig. 1), quite a high amount of gel would be expected.

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