Cross-Linking of Ethylene-Octene Copolymer (EOC) by Dicumyl Peroxide (DCP)

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ABSTRACT: Ethylene-octene copolymer (EOC) was crosslinked by dicumyl peroxide (DCP) at various temperatures (150–200°C). Six concentrations of DCP in range 0.2–0.7 wt % were investigated. cross-linking was studied by rubber process analyzer (RPA) and by differential scanning calorimetry (DSC). From RPA data analysis real part modulus s', tan δ, and reaction rate were investigated as a function of peroxide content and temperature. The highest s'_{max} and the lowest tan δ were found for 0.7% of DCP at 150°C. Chain scission was analyzed by slope analysis of conversion ratio, X in times after reaching the maximum. Less susceptible to chain scission are temperatures in range 150–170°C and peroxide levels 0.2–0.5%. Heat of reaction was analyzed by DSC at various heating rates (5–40°C min^{-1}). It was found to be exothermic. By projection to zero heating rate, the reaction was found to start at 128°C with the maximum at 168°C. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 521–530, 2011

Key words: ethylene-octene copolymer; dicumyl peroxide; cross-linking; chain scission; RPA; DSC

INTRODUCTION

EOC is soft rubbery material supplied in pellet form that can be very easily injection molded into a final part. While for low octene content copolymer with melting point (T_m) being around 90°C one could find an application, when the octene content is high (40 wt %) the T_m is very low (about 45°C) and application of such pure EOC could be much harder to find. However when such EOC with high octene content is chemically crosslinked the part made out of it will hold the shape even above T_m and there could be many practical applications. Therefore the study of chemical cross-linking of this high octene EOC has large practical significance in industry. While other olefin rubbers, such as EPDM (ethylene–propylene–diene monomer) have a double bond in the chain and can be crosslinked by traditional sulfur systems, EOC without a double bond cannot be crosslinked by sulfur and one has to use other methods. There are several possibilities how to crosslink EOC, such as electron beam exposure,[1–6] silane grafting followed by water cross-linking[7–13] and peroxide cross-linking.[14–19] All of these methods have practical importance.

In case of peroxide cross-linking it is necessary to blend it with the polymer below its activation temperature in an internal mixer or extruder. Extensive studies have been carried out on the cross-linking kinetics of EOC and related polymers.[20–27] Msakni et al. studied the cross-linking of different EOCs with one fixed peroxide level and one fixed temperature under static and dynamic conditions.[14] Liao and Wu studied the structural and mechanical properties of EOC crosslinked with various peroxide levels.[19] In this work we have focused on peroxide cross-linking using various peroxide levels and various temperatures measured by rubber process analyzer (RPA). While polyethylene is known to be crosslinkable with peroxide, polypropylene on the other hand undergoes a chain scission by peroxide. EOC has structure somewhere in between these two, so there is a question what will be happening in EOC-peroxide system. While in this article we are focusing only on the influence of peroxide content and temperature on cross-linking, the measurements of mechanical properties will be subject of our following article.

EXPERIMENTAL

Ethylene-octene copolymer was Engage 8842 supplied by Dow Chemicals. The octene content is 45 wt %. Density is 0.8595 g cm^{-3} and melt flow rate is 1.02 dg min^{-1} (at 190°C/2.16 kg).

Peroxide was Perkadox BC-40B-PD (DCP) having active peroxide content of 40%; temperature at which half-life time ($t_{1/2}$) is 1 h at 138°C and specific gravity of 1.53 g cm^{-3} at 23°C was supplied by Akzo Nobel. The influence of Perkadox was investigated for concentrations 0.50, 0.75, 1.00, 1.25, 1.50, and 1.75 wt %. The active peroxide content was then 0.2, 0.3, 0.4, 0.5, 0.6, and 0.7 wt % respectively.

Irganox 1010 was used as an antioxidant having density 1.15 g cm^{-3} with chemical name tetrakis-(methylene-(3,5-di(tert)-butyl-4-hydrocinnamate)) methane. It was supplied by Ciba, Switzerland. The antioxidant content was kept constant at 0.40 wt % for all experiments.

EOC, peroxide and Irganox 1010 were mixed in a Brabender Plasti-corder PL2000 mixing machine with mixing volume of 50 cm^3 at 100°C at mixing speed 50 rpm for 10 min. Compounded batches were stored in a freezer at -18°C to avoid unwanted cross-linking during storage.

A rubber process analyzer, RPA-2000 (Alpha Technologies) was used to measure the cure characteristics of EOC-DCP compounds, at various temperatures for various times. Testing conditions were maintained at an angle of 0.5° and a frequency of 100 CPM (1.667 Hz).

For the DSC analysis, the specimens were heated in nitrogen atmosphere (flow rate 20 mL min^{-1}) at various heating rates 5, 10, 20, 30, and 40°C min^{-1}. Cooling was performed with help of a cooling unit capable of -130°C. The temperature and heat flow of the apparatus was calibrated with an indium standard.

THEORETICAL BACKGROUND

Burhin[24] suggested a way of cross-linking kinetics analysis. For first order reaction, eq. (1) can be used

$$\ln (1 - X) = f(t) \tag{1}$$

where t is the time in min and X is the percentage of achieved cross-linking (0.9 for 90%) or the conversion variable. This mathematical function is linear for first order reaction and was derived from the reaction kinetics formula for any chemical process shown by eq. (2).

$$\frac{\partial X}{\partial t} = K^{(n)}(1 - X)^n \quad (t > t_i) \tag{2}$$

where, t is the time in min, dX/dt is the reaction rate, $K^{(n)}$ is the nth order conversion rate constant, n is the reaction order in respect of time, t_i is the incubation time in min or the predicted time for the start of vulcanization ($X = 0$).

A linear regression of the eq. (2) gives the slope K, the time value for a conversion variable (X) equal to zero or the time the vulcanization reaction starts, and the coefficient of regression. In the case of an order of reaction $\neq 1$, eq. (3) is to be used.

$$\frac{(1 - X)^{(1-n)}}{(1 - n)} = f(t) \tag{3}$$

Successive linear regressions give a value for "n" achieving the best fit for the eq. (3).

Considering the cross-linking reaction as a normal chemical reaction, we can apply the law of Arrhenius and Van't Hoff, which expresses the relationship of the conversion rate constant K^n (or the rate of reaction) with temperature under the following eq. (4).

$$K^n = K_0^{(n)} \cdot e^{-\frac{E_A}{RT}} \tag{4}$$

or

$$\ln K^n = \ln K_0^{(n)} - \frac{E_A}{RT} \tag{5}$$

where E_A is the activation energy in J mol^{-1}, R is the universal gas constant, 8.314 J mol^{-1} K^{-1}, T is the absolute temperature in K, $K_0^{(n)}$ is the product of the frequency factor $K_{c0}^{(n)}$ and $c^{\infty(n-1)}$.

This equation is applicable if the reaction order (n) and the concentration of the cross-linking (c^∞) are temperature independent. By carrying out a series of tests at various temperatures, the E_A value can be calculated from the slope of the eq. (6)

$$\ln K_{Ta} = f\left(\frac{1}{T}\right) \tag{6}$$

where K_{Ta} is the conversion variable at the temperature T (absolute temperature in K).

The linear regression of eq. (6) gives E_A and the regression coefficient tells how well the model fits on the Arrhenius and Van't Hoff law.

RESULTS AND DISCUSSION

Figure 1 shows the raw data out of the RPA, more specifically real part of the modulus, s'. From this graph one can notice that with increasing peroxide content the s' modulus increases to higher levels.
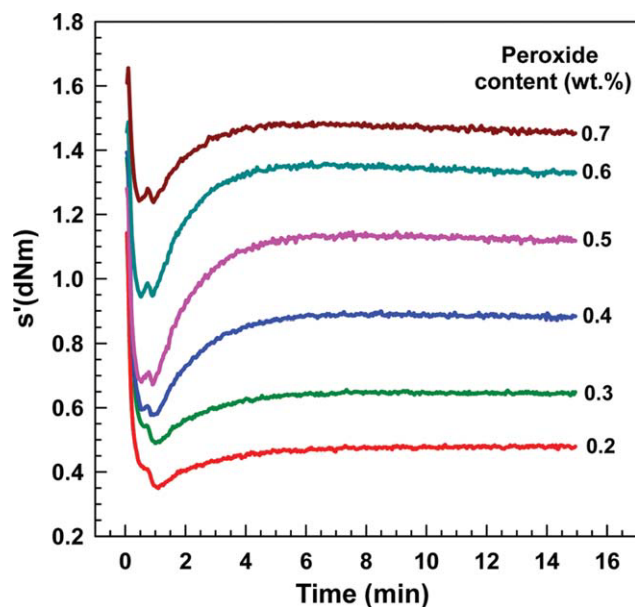
Figure 1 Plot of modulus (s') versus time at 180°C for various peroxide contents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
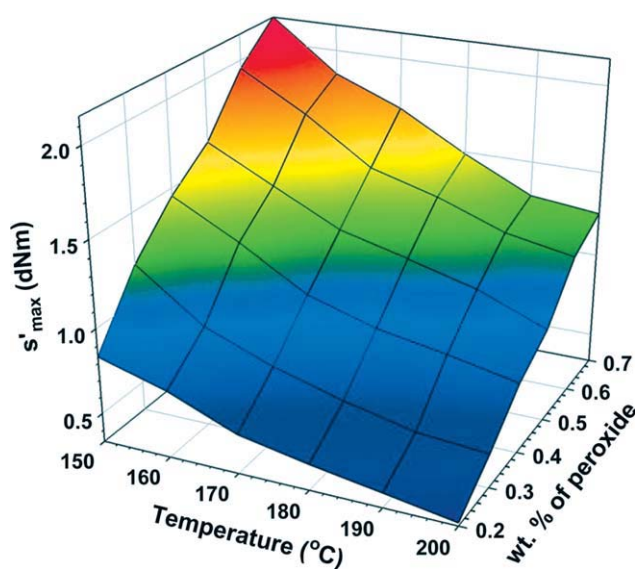

Figure 2 The 3D plot of s'_{max} as a function of temperature and peroxide content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

That would support the idea of cross-linking rather than chain scission. Both the minimum and maximum values of s' are growing with increasing peroxide content. The minimum of the s' value represents processability and the maximum of the s' contains information about mechanical properties after crosslinking. The peroxide was mixed into EOC carefully at low temperature (100°C) to avoid premature cross-linking. Apparently even at 100°C some crosslinking happened. The minimum of s' is quite peroxide level dependent. Figure 1 shows data just for one temperature: 180°C.

Figure 2 is mapping the maximum s' value as a function of peroxide level and temperature altogether in 3D plot. For all cross-linking temperatures the s'_{max} value increases with increasing peroxide content. On the other hand, with increasing temperature the s'_{max} values decrease for all peroxide levels. To obtain the maximum s'_{max} real modulus, one has to use the highest peroxide level (0.7%) together with the lowest cross-linking temperature (150°C). The lowest s'_{max} value was found for the lowest peroxide level (0.2%) and the highest cross-linking temperature (200°C). The numerical values of s'_{max} are summarized in Table I.

Another useful and important value is tan δ (tan δ = s''/s'). The lower tan δ value the better elasticity one can expect. For example, in tire industry the lower tan δ value is connected with lower rolling resistance and lower consumption of gasoline by the car. So the companies are trying to develop new formulations to get lower tan δ or even new polymers such as solution type of butadiene-styrene rubber (SBR).

The raw graphs with tan δ curves from RPA are shown in Figure 3. The highest values of tan δ were found for 0.2% of peroxide and the lowest ones for 0.7% of peroxide. Initially, tan δ increases as the sample is melting and getting viscous. Then tan δ starts to decrease with progressing cross-linking. Finally it reaches certain equilibrium value (shown by line) that will be compared in Figure 4. It is important to also note the time to reach the maximum. It is getting shorter with increasing peroxide content. While t_{max} is about 1 min for 0.2% of peroxide, it is only few seconds for 0.7% of peroxide. One could call that induction period of cross-linking and plot it as a function of peroxide content as shown in the inserted picture of Figure 3.

Figure 4 shows the equilibrium tan δ values as a function of peroxide content and temperature in the form of 3D plot. There is a tremendous decrease in tan δ values in peroxide range 0.2–0.5%. Then, in range 0.5–0.7% there is also a decrease but much more moderate. The difference in tan δ is quite small at higher peroxide levels (0.6–0.7%). The largest

TABLE I
s'_{max} (dNm) Values for Various Peroxide Content at Different Temperatures

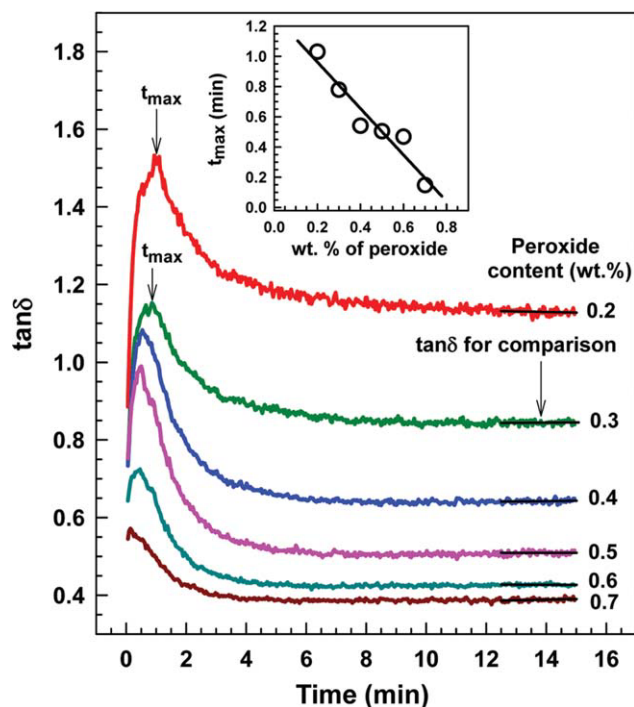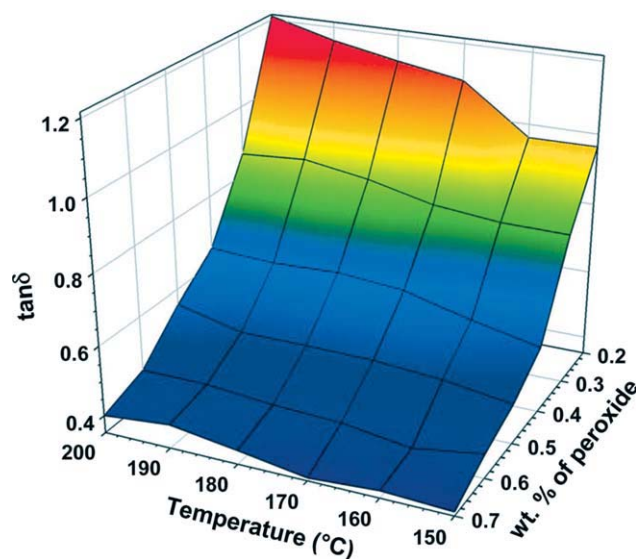|	Temperature (°C)					
wt % of peroxide	150	160	170	180	190	200
0.2	0.84	0.76	0.56	0.48	0.42	0.35
0.3	1.21	0.92	0.77	0.65	0.56	0.53
0.4	1.45	1.25	1.02	0.90	0.83	0.74
0.5	1.63	1.44	1.25	1.15	1.04	0.88
0.6	1.95	1.78	1.47	1.36	1.22	1.14
0.7	2.15	1.79	1.71	1.49	1.30	1.25

Figure 3 tan δ versus time at 180°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

difference in tan δ values was found to be for the lowest peroxide level (0.2%). Concerning cross-linking temperature for the 0.2% of peroxide the tan δ values are the largest (the worst elasticity) and the dependence on temperature is also the largest. With increasing temperatures the tan δ value increases as well with exception to 150 and 160°C when the tan δ

Figure 4 The 3D plot of tan δ as a function of temperature and peroxide content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II
tan δ Values for Various Peroxide Content at Different Temperatures

wt % of peroxide	Temperature (°C)					
	150	160	170	180	190	200
0.2	0.96	0.96	1.10	1.13	1.16	1.21
0.3	0.78	0.78	0.80	0.85	0.87	0.86
0.4	0.54	0.58	0.63	0.64	0.64	0.65
0.5	0.46	0.49	0.51	0.51	0.51	0.55
0.6	0.42	0.39	0.42	0.43	0.44	0.44
0.7	0.36	0.37	0.36	0.39	0.42	0.40

values are almost the same. There is strong dependence on peroxide content and much smaller dependence on cross-linking temperature. The lowest tan δ values were found for 0.7% of peroxide crosslinked in 150–170°C range, tan δ being in 0.3–0.4 range. The largest tan δ values were found for 0.2% of peroxide in 180–200°C range, tan δ being in 1.1–1.2 range. The numerical values of tan δ are summarized in Table II.

The manufacturer of RPA 2000 instrument[24] recommends the aforementioned analysis of cross-linking kinetics. X is defined as the percentage of achieved cross-linking. The s' curve is recalculated so that it is in range 0.0–1.0 (or 0–100%). The examples of such curves are shown in Figure 5(a,b). Figure 5(a) covers very long time period (150 min) that was required for very slow cross-linking at 150°C. Figure 5(b) focuses on high temperature cross-linking (180–200°C) that is finished in less than 15 min. The times necessary for the conversions 20, 25, 30,…..80% were calculated by the RPA software. When these points were plotted according to eq. (1) straight lines were obtained for all temperatures indicating first order reaction. We have calculated also activation energies E_A according to Arrhenius equation in logarithmic form (eq. 6) and found them in range 144–159 kJ mol^{-1}.

In rubber industry the t_{90} value is frequently evaluated to set the proper vulcanization time. The t_{90} value represents time in min required for the 90% of cross-linking reaction to be completed. All the t_{90} numerical values are listed in Table III and examples of the t_{90} values for three peroxide levels as a function of temperature are shown in Figure 6. The curves have exponential decay shape. In inserted picture of Figure 6 the natural logarithmic values of t_{90} are plotted as a function of temperature. There is a linear relationship in 150–190°C temperature range confirming the exponential nature of this temperature-dependent phenomenon.

As it was shown previously in Figure 5, the conversion curves exhibit a maximum and then the X values decrease differently for different temperatures. The decrease in X value represents a degradation. The network created by cross-linking is being
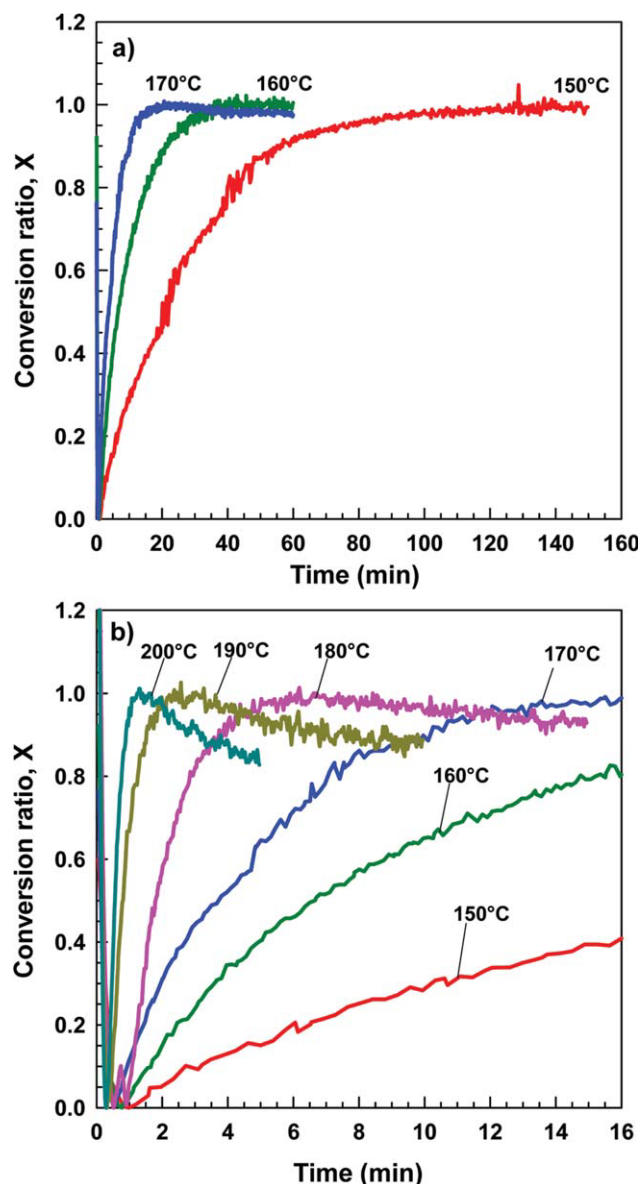
Figure 5 Plot of conversion ratio, X versus time for 0.6 wt % of peroxide at various temperatures. (a) 150–170°C and (b) 150–200°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

damaged most likely by chain scission. Possible chemical reactions occurring in the system are shown in Figures 7 and 8. In the peroxide the O—O bond breaks first rendering two free radicals. Then this free radical RO reacts with the hydrogen of EOC chain. Then two macro-radicals react together forming a longer molecule. This reaction repeats many times until a crosslinked network is formed. Macro-radicals can sometimes break by chain scission mechanism as shown in Figure 8. There are two possibilities of chain scission. The bond energy of C—H bond in case of tertiary carbon is slightly lower than that of secondary carbon (96.5 versus 98.6 kcal mol^{-1}, respectively).[28] There is one octene unit per about five ethylene units

TABLE III
t_{90} **(min) Values for Various Peroxide Content at Different Temperatures**

wt % of peroxide	Temperature (°C)					
	150	160	170	180	190	200
0.2	86.0	25.6	9.47	5.43	2.98	2.95
0.3	66.4	25.4	9.34	5.28	2.28	1.17
0.4	77.3	25.4	8.50	4.45	2.01	0.97
0.5	69.9	24.0	8.69	4.10	1.84	0.94
0.6	68.0	22.0	7.73	3.88	1.61	0.90
0.7	48.6	19.1	7.54	3.54	1.63	0.95

in the EOC chain. Thus there are many CH$_2$ groups compared to tertiary CH ones.

One can practically evaluate the chain scission by slope analysis as shown in Figure 9(a). Initially the X curve increases in time rapidly that indicates the progress of cross-linking reaction. After reaching the maximum the X value decreases. This decrease slope (chain scission) can be analyzed for various temperatures as indicated in Figure 9(b) where the cross-linking slope is also shown. One can plot the scission/cross-linking ratio as a function of temperature [see Fig. 9(c)]. This ratio has very small value in 150–170°C temperature range; one could assign this temperature range as "safe for cross-linking." However in 180–200°C this scission/cross-linking ratio has much higher value and scission starts seriously compete with cross-linking. The inserted picture in Figure 9(b) shows an Arrhenius plot for evaluation of activation energy of degradation. In our case the
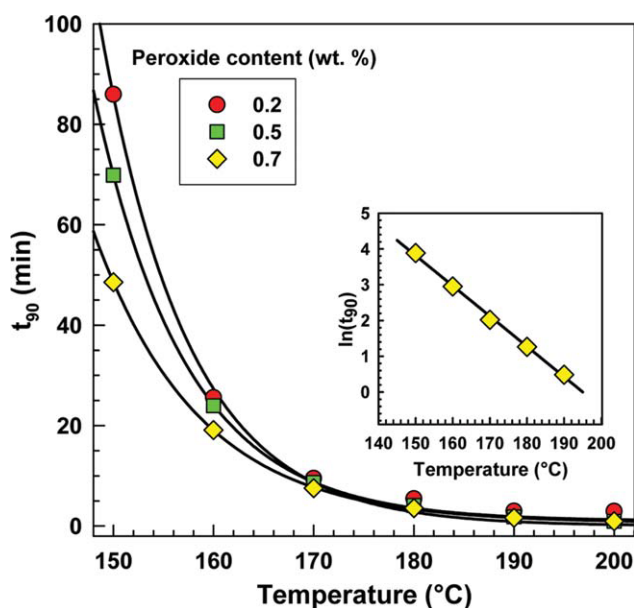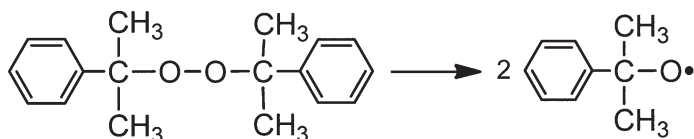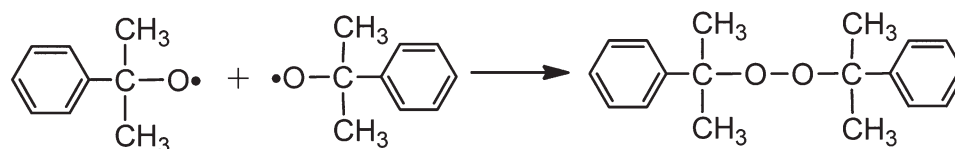

Figure 6 t_{90} as a function of crosslinking temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Initiation

Possible peroxide recombination
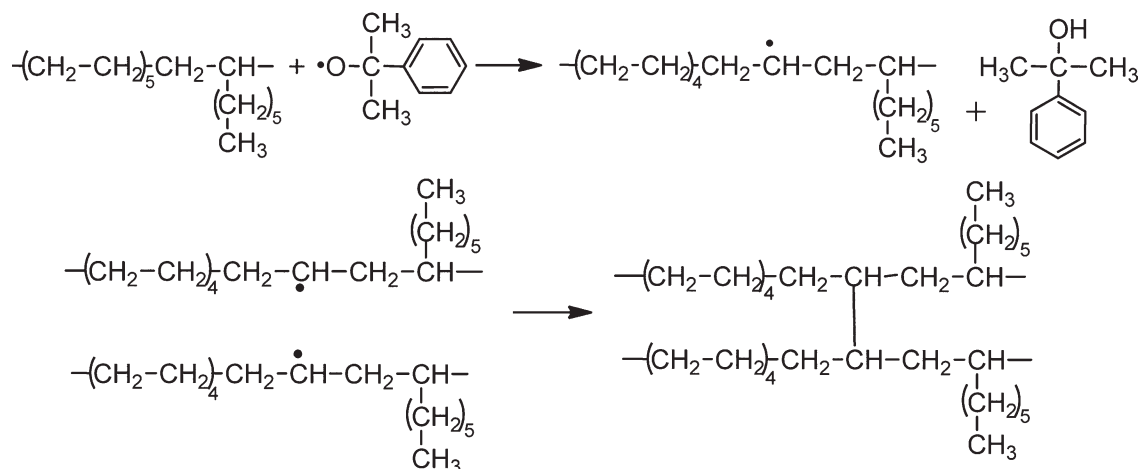

Cross-linking reaction

Figure 7   Peroxide initiation and possible recombination, crosslinking of EOC by DCP.

E_A value was calculated to be 210 kJ mol^{-1} which is greater than that of cross-linking.

The chain scission depends not only on temperature but also on peroxide level as it is shown in Figures 10 and 11. Figure 10 shows the conversion curves at 180°C and various peroxide levels. The degradation slopes were analyzed and plotted in Figure 11.

In Figure 11, we have not seen any degradation for the 0.2% of peroxide in the 15 min time frame. However, for all other peroxide levels there was degradation. The degradation kinetics increases with the increasing peroxide level. These data show the danger of losing mechanical properties when the time of cross-linking is not kept precise. This risk of mechanical property loss is greater for higher peroxide levels. For thick rubber articles, one has to count with very low thermal conductivity of EOC and thus very slow cooling rate. During this slow cooling, chemical reaction still proceeds and there is always risk of degradation and mechanical property loss.

In Figure 2 the modulus s' has the highest value at lower temperatures. However the situation is not completely clear. The temperature of s' measurement was also the cross-linking temperature in case of Figure 2. It is interesting to compare the s' values of samples crosslinked at different temperatures but measured at the same temperatures. This is shown in Figure 12. First experiment indicates very long cross-linking at low temperature (150 min at 150°C). Then the s' values were immediately measured at 170 and 200°C. In contrast the second experiment shows very fast cross-linking at high temperature (3 min at 200°C). Then the s' values were immediately measured at 190, 180, 170, 160, and 150°C. Clearly the s' values are higher in case of low temperature cross-linking. The difference is about 0.22 dNm^{-1}. In industry the productivity of work pushes to lower times but one has to be careful about the mechanical property loss in case of high temperature cross-linking.

The samples were stored in a freezer at -18°C to prevent unwanted cross-linking and preserve good
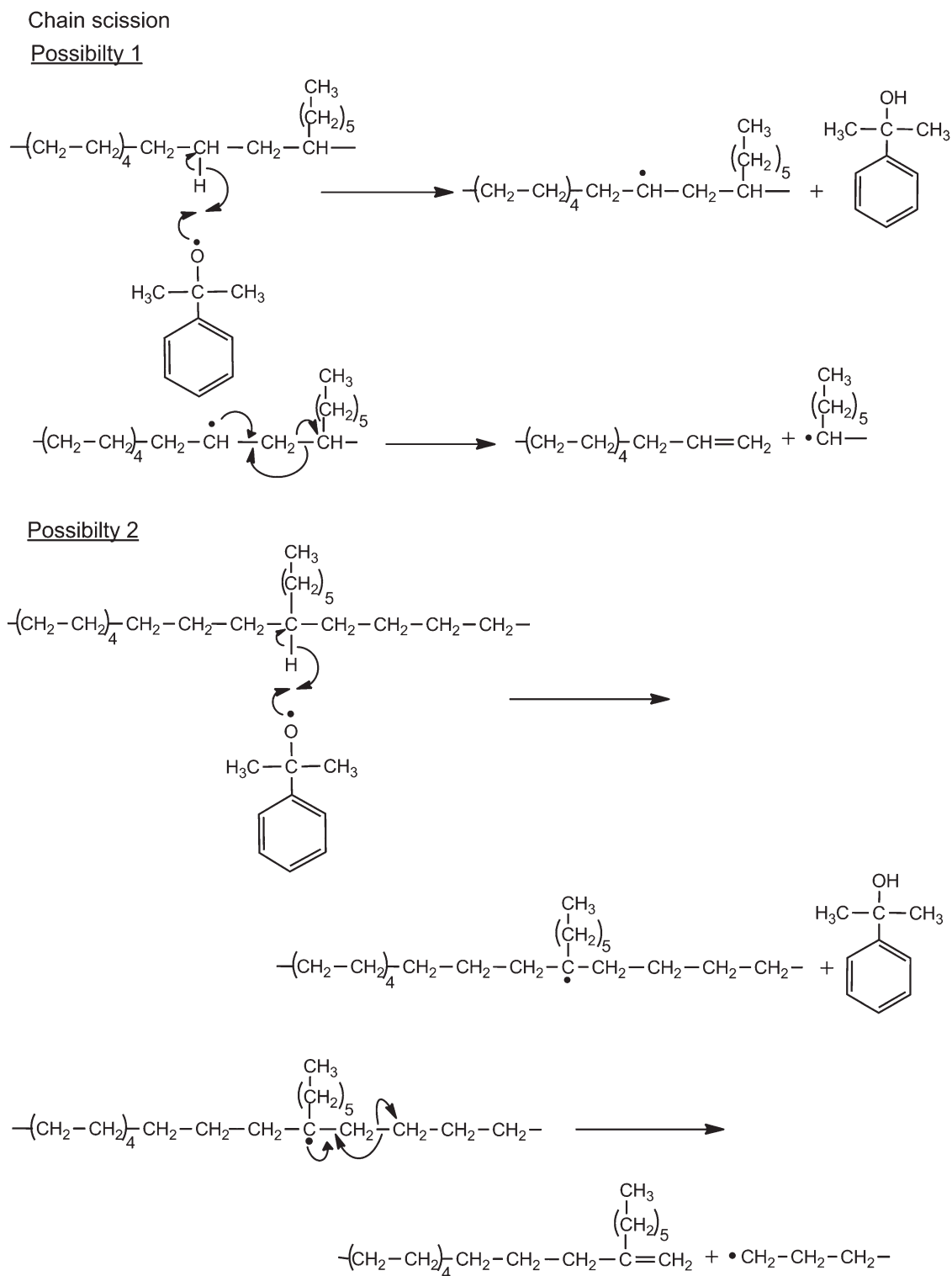
Chain scission

Possibilty 1

Possibilty 2

Figure 8 Two possible chain scission reactions.

processability so that final article can be molded before cross-linking. Is something happening in the freezer? How long is the shelf life of the EOC/DCP mixture? We have compared the s' values of samples having different storage history, shorter, 10 or 20 days and longer, 90 days. The measurements were carried out at 150 and 200°C as shown in Figure 13. In both cases the s' values at maximum were higher for longer storage time while the minimum s' values were not almost changed. Thus after
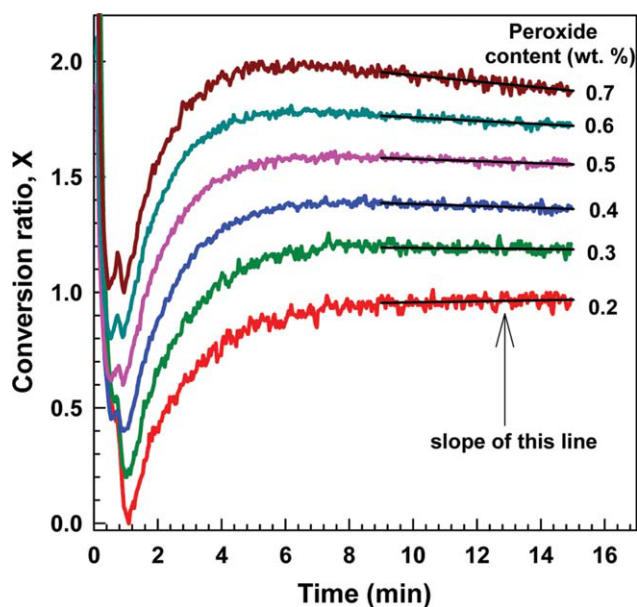
Figure 10 Plot of conversion ratio X versus time for different peroxide content at 180°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

We have tried to measure the reaction heat by DSC. Figure 14 shows the exotherm peaks in heat flow for various heating rates. The peak area (reaction heat in J g^{-1}) is smaller for lower heating rate as it is shown in the insert of Figure 14. The start, middle, and the end points of these reactions are shifted to higher temperatures with increasing heating rate. This is clearly visible in Figure 15. One
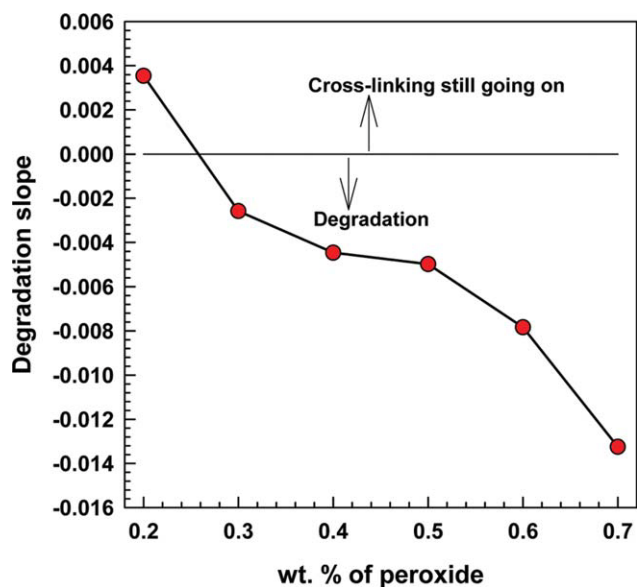
Figure 9 (a) Crosslinking and scission slope analysis in EOC with 0.6% of DCP, (b) Crosslinking and scission slopes as a function of temperature and, (c) Scission/cross-linking ratio as a function of temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

longer storage time we can expect better mechanical properties without losing good processability. This is good news.

Figure 11 Degradation slope as a function of peroxide content at 180°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
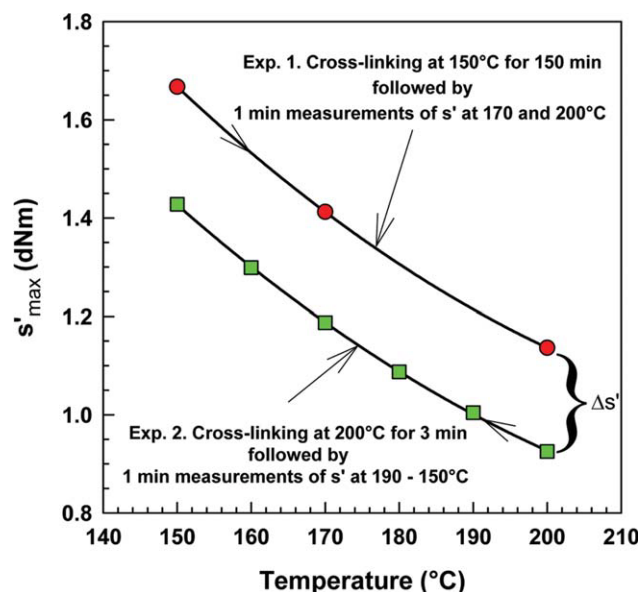
Figure 12 Comparison of s' modulus for two crosslinking temperatures: 150 and 200°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 14 Heat flow versus temperature for EOC with 0.7% of peroxide. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

could extrapolate the temperature range for zero heating rate to be about 128–205°C.

CONCLUSIONS

EOC can be effectively crosslinked by dicumyl peroxide. The maximum modulus values were found for 0.7% peroxide content crosslinked at
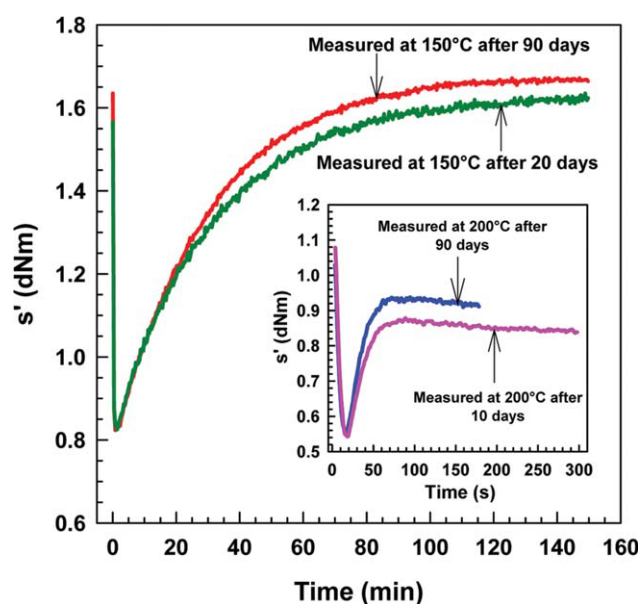
150°C for 150 min. Higher temperatures speed up the process at the cost of lower modulus. The lowest tan δ values were found also for this 0.7% peroxide content crosslinked in 150–170°C temperature range. The scission/cross-linking ratio study suggested performing cross-linking in the 150–170°C temperature range and 0.3–0.5% of peroxide level to avoid possible fast chain scission immediately following cross-linking.

Figure 13 Effect of storage time on s' evolution during crosslinking at two temperatures: 150 and 200°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
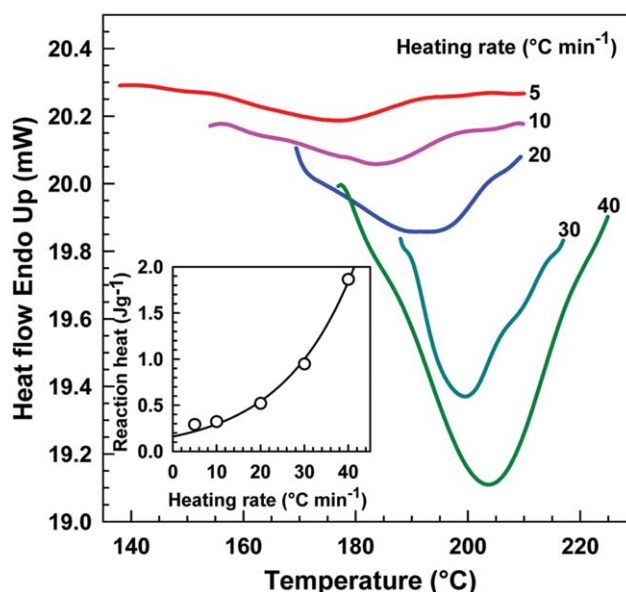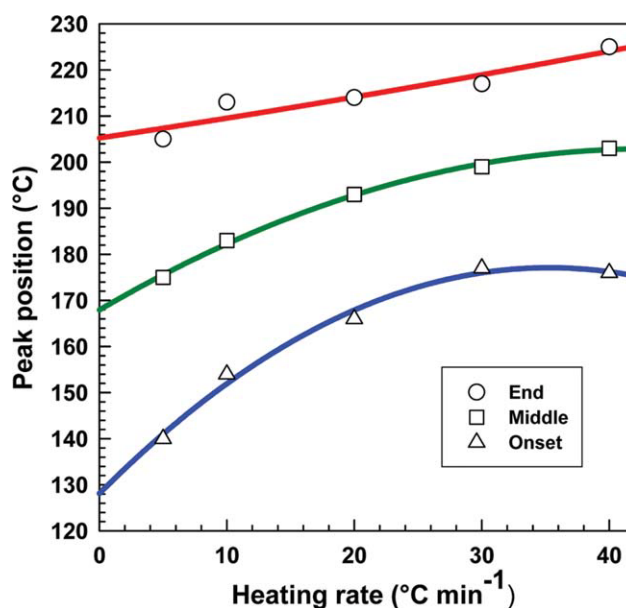

Figure 15 Peak position versus heating rate for EOC with 0.7% of DCP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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