

Crosslinking Reactions in Pigmented Olefinic Polymers

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SYNOPSIS

Thermally initiated crosslinking reactions have been studied in a linear low-density polyethylene, and an ethylene-propylene rubber. The polymers contained conventional thermal stabilizers or one of three surface-coated rutile pigments. Enthalpies of crosslinking and reaction kinetics depended on the degree of terminal vinyl unsaturation in the polymers, that characteristic being greater in the rubber than in the polyethylene. The presence of thermal stabilizers did not exert any measurable influence on measured parameters of the crosslinking processes. The effects of rutile varied, depending on their surface acidity or basicity, as determined from chromatographic measurements. Basic rutile was found to reduce heats and to slow rates of reaction, while acidic rutilites did not affect the reactions. These observations may be attributed to interaction between the basic pigment surface and acidic moieties involved in the crosslinking reaction. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

Commodity polymers, notably the olefinic thermoplastics, have long been attractive subjects for crosslinking procedures. Early research by Charlesby and co-workers¹ developed the mechanisms and consequences of crosslinking reactions triggered by radiation. The use of peroxides for thermally initiated crosslinking reactions also has been developed in much detail.^{2,3} Various reasons can be advanced for crosslinking the host polymer. These include modifications of polymer physical and mechanical properties, of its processing behavior, and of its morphology in the solidified state. In recent years reactive processing of thermoplastics has become in vogue,⁴ and has added a widely applicable, large-scale approach to polymer property modifications, frequently through the use of crosslinking agents.

While the mechanisms and kinetics of thermally initiated crosslinking reactions have been studied in detail for pure polymers, polymers in practice are highly unlikely to be used without a variety of minor additives, including thermal and UV stabilizers, reinforcing fibers, fillers, etc. It seems possible that

these minor additives may influence crosslinking processes. A definition of that influence therefore represents a worthwhile objective. The present brief communication contributes to the objective by reporting on peroxide-initiated crosslinking events in two polyolefinic hosts also containing thermal stabilizers and rutile pigments.

EXPERIMENTAL

Materials

Two polyolefins were used as hosts. One was a butene copolymer linear low-density polyethylene (LLDPE), with $M_n = 36,300$ and a polydispersity index (M_w/M_n) of 3.6, as determined by size exclusion chromatography. The second host was an ethylene-propylene rubber (EPR), with an ethylene content of 42 mol % and a Mooney viscosity (120°C) of 31. Given the evidence^{5,6} that terminal vinyl unsaturation is a leading variable in crosslinking olefinic thermoplastics, infrared spectroscopy (Bomem DA-3 FTIR Spectrometer), notably the absorption peak at 909 cm^{-1} , was used to determine that variable. The LLDPE used here was found to have 0.112 vinyl unsaturations/1000C, while in EPR the corresponding datum was 0.370/1000C.

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The crosslinkers employed were dicumyl peroxide, (dicup), with a 10-h half-life at 122°C, and 2,5-dimethyl-2,5-di(*t*-butylperoxy)hexyne (L-130), with a 10-h half-life at 135°C. In the specimens used for study, peroxides were present at concentrations of 0.5, 1.0, 1.5, and 2.0 parts per hundred of polymer. The thermal stabilizers were commercially marketed chemicals, Santowhite, Santonox, and Irganox 1010, always added at concentrations of 0.1 wt % of host polymer. The pigment selected was rutile TiO₂, from Tioxide Canada, Inc. Three versions of the solid were employed. Sample R-1 was pure rutile, with no surface coating, while R-2 and R-3 bore coatings as applied by the manufacturer. BET analysis showed that the surface areas of these pigments fell in a narrow range of 8.8–9.5 m²/g. Compounds studied contained pigments at 1.0, 2.0, 4.0, 5.0, and 10 parts per hundred of host polymer.

Procedures

All compounds were prepared by first dry blending the ingredients in a Brabender mixing apparatus at room temperature and then using the same apparatus to fuse the materials. The latter step took place at 120–125°C, and mixing at these temperatures was restricted to <3 min to ensure stability of the peroxides. Specimens cut from the fused mass were placed in a Perkin-Elmer DSC-2 scanning calorimeter, previously calibrated by fusing pure indium. Crosslinking reactions were followed under isothermal conditions in the range 140–170°C. The effectiveness of crosslinking reactions was evaluated by comparing IR analyses of residual terminal vinyl unsaturation following crosslinking.

The capability of rutile surfaces to interact with constituents of the crosslinking process through

specific, nondispersion forces, was measured by the method of inverse gas chromatography⁷ (IGC). In IGC the pigments are the stationary phase, and vapor probes included the series of *n*-alkanes from hexane through nonane, in addition to chloroform and diethylether. This convention follows current applications to IGC of Gutmann's theory of Lewis acids and bases.⁸ By this procedure, chloroform and diethylether are designated, respectively, as reference acid and base vapors. Their retention volumes are compared with those for the dispersion force *n*-alkanes, leading to the designation of acidity and basicity numbers, AN and DN, for the solid surfaces.^{9,10}

RESULTS AND DISCUSSION

Isotherm Analysis

The exothermic signals generated during isothermal exposures were used to identify two parameters for closer analysis. The parameters are shown in Figure 1, which illustrates the DSC trace (150°C) for LLDPE containing 0.5 wt % dicup. The exothermic heat of reaction, ΔH_r , is given by integrating the shaded area in the figure. Throughout this work, we have selected the maximum deviation from the baseline as a terminal point for integration. While this does not evaluate the total exothermic heat, it designates a fractional heat value with a sample-to-sample reproducibility of better than 8%. Integration of the total area increased the error to nearly 15%, largely because of baseline drift. The second parameter defined in the figure, t_c , is a characteristic reaction time. It measures the time elapsed from the onset of the reaction signal to the maximum excursion from the baseline.

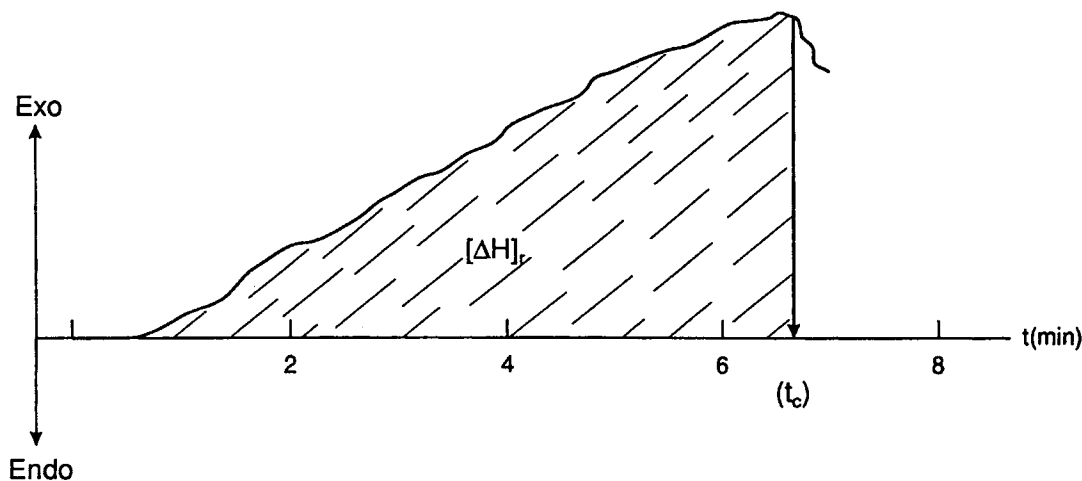


Figure 1 Illustration of exothermic heat signal for LLDPE with 0.5% dicup. $T = 150^\circ\text{C}$.

A summary of ΔH , and of t_c values for the compositions of this work are found in Tables I and II, the former listing information for the LLDPE host, the latter for EPR. The following are noteworthy features of the results:

1. The temperature dependence of ΔH , is considerably greater for L-130 than for the dicumyl peroxide. This is due, evidently, to the greater tolerance of L-130 to elevated temperatures. Thus, only at $T > 160^\circ\text{C}$ does this peroxide lead to exothermic heats which are comparable to those produced by dicup.

2. A similar situation exists relative to t_c ; in both tabulations there is a sharp decrease in t_c with increasing temperature. L-130 initiated crosslinking, however, proceeds much more slowly at $T < 160^\circ\text{C}$.

3. The variation of ΔH , and of t_c with peroxide concentration is slight for both host polymers. Evidently the major proportion of crosslinking effects is attained even at 0.5% peroxide content.

4. A comparison of Tables I and II reveals that the ΔH parameter for EPR is always higher than that for the LLDPE. Further, longer reaction times are needed for crosslinking the rubber. These effects are consistent with the initially higher terminal unsaturation levels in the EPR. Differences between the two polymers are accentuated in the lower isotherms. IR analyses shown in Table III are consistent with the above suggestion. They compare the residual vinyl unsaturation levels for the partially

Table I Crosslinking Parameters: LLDPE

T ($^\circ\text{C}$)	140	150	160	170
ΔH (J/g)				
0.5% Dicup	21.5	23.6	24.4	25.0
1.0%	22.7	24.1	25.6	25.3
1.5%	24.0	25.5	27.0	26.6
2.0%	24.2	25.8	26.6	26.8
0.5% L-130	17.0	19.0	23.5	25.5
1.0%	17.5	20.5	24.5	26.1
1.5%	18.8	21.7	26.0	26.4
2.0%	19.1	22.0	26.4	27.0
t_c (s)				
0.5% Dicup	365	350	295	270
1.0%	410	375	310	275
1.5%	485	420	355	290
2.0%	480	420	360	285
0.5% L-130	620	575	355	325
1.0%	625	570	375	340
1.5%	660	590	390	355
2.0%	670	610	400	345

Table II Crosslink Parameters: EPR

T ($^\circ\text{C}$)	140	150	160	170
ΔH (J/g)				
0.5% Dicup	36.4	38.5	39.5	39.5
1.0%	37.0	39.5	41.5	41.5
1.5%	38.8	41.0	42.0	42.0
2.0%	39.0	40.7	41.5	42.5
0.5% L-130	25.0	27.7	36.0	38.0
1.0%	25.0	28.5	37.5	40.5
1.5%	26.5	30.0	38.5	39.5
2.0%	27.0	29.5	39.0	41.0
t_c (s)				
0.5% Dicup	490	440	325	295
1.0%	520	460	325	300
1.5%	530	475	340	310
2.0%	570	480	358	310
0.5% L-130	665	585	430	380
1.0%	700	570	440	375
1.5%	710	570	445	390
2.0%	715	585	445	385

crosslinked polymers at 160°C . The data are limited to this temperature, since the information at other temperatures was incomplete. The vinyl unsaturation remains perceptibly greater in EPR than in LLDPE. A systematic decrease with rising peroxide level is noted, but the most significant drop in the level of unsaturation is incurred at the lowest peroxide concentrations. A small difference is detected in the ultimate effect on unsaturation due to the two peroxides ($-\Delta\%$ datum in Table III). This suggests that at 160°C L-130 is a marginally more effective initiator of thermally triggered reactions than is the dicumyl peroxide.

Effect of Additives

Results of experiments relating to the main objectives of this research are reported in Figures 2-4. The effects of thermal stabilizers on the heat and time parameters of crosslinking reactions are shown in Figure 2, an intermediate concentration of peroxides having been chosen for illustration. Comparisons span the entire range of temperatures used in this work. The discussion can be very brief, in that none of the three stabilizers appears to interfere significantly with the progress of crosslinking reactions. Either these are unable to interact chemically with constituents of the crosslinking process or at the levels normally used in practice their effects are too slight to be detected by the ΔH , and t_c pa-

Table III Unsaturation Analysis: Response to Crosslinking ($T = 160^\circ\text{C}$)

A. Dicap Conc (%)	0	0.5	1.0	2.0	($-\Delta\%$)
Vinyl Unsaturation					
LLDPE	0.112	0.062	0.091	0.031	(72)
EPR	0.370	0.118	0.095	0.066	(82)
B. L-130 Conc. (%)	0	0.5	1.0	2.0	
Vinyl Unsaturation					
LLDPE	0.112	0.047	0.030	0.027	(76)
EPR	0.370	0.128	0.077	0.054	(85)

rameters. Thus, at the indicated levels of addition, thermal stabilizers of the kind represented here may be used with impunity in reactive processes involving peroxide initiators.

The addition of rutile pigments complicates the issue. Their effects on the performance parameters for LLDPE are given in Figure 3. Those for the EPR host are summarized in Figure 4. Both representations are for 160°C , both at 1% levels of crosslinking agent. It is evident that no simple generalization of effects is possible. The presence of rutile not only

complicates the reaction mechanisms and kinetics, but the influence exercised by the rutile varies broadly among the three pigment versions. Since the solids have equivalent specific surface areas, the variations displayed in these figures are attributable to the distinct surface chemistries of the pigments. Whereas the uncoated version, R-1, and the surface-coated R-2, produce significant reductions in ΔH_c and attenuations of t_c , the presence of the surface-modified R-3 has only a minimal effect on the crosslink performance parameters. Clearly, a careful selection of pigment is essential if crosslinking reactions are not to be affected by its presence. The results recall a similar conclusion reached for the effects of rutile pigments on the effectiveness of fluoroelastomer flow aids, used for improved processing of LLDPE.¹¹

The data available to us do not justify an explicit account of chemical changes in the crosslinking processes brought on by the presence of the rutile pigments. The IGC analyses referred to above, however, point to an important involvement of physico-chemical factors. Using the acid/base analysis described elsewhere,^{9,10} we find that the three rutile surfaces have markedly different specific interaction potentials:

R-1: AN = 11.2; DN = 9.7;

this solid is classified amphoteric.

R-2: AN = 4.4; DN = 13.0;

this solid is a strong base.

R-3: AN = 10.3; DN = 5.9;

this solid is a moderate acid.

Of the three, only the acidic R-3 leaves the crosslinking parameters essentially unaffected. A reasonable conclusion therefore is that thermally triggered crosslinking in the present systems generates

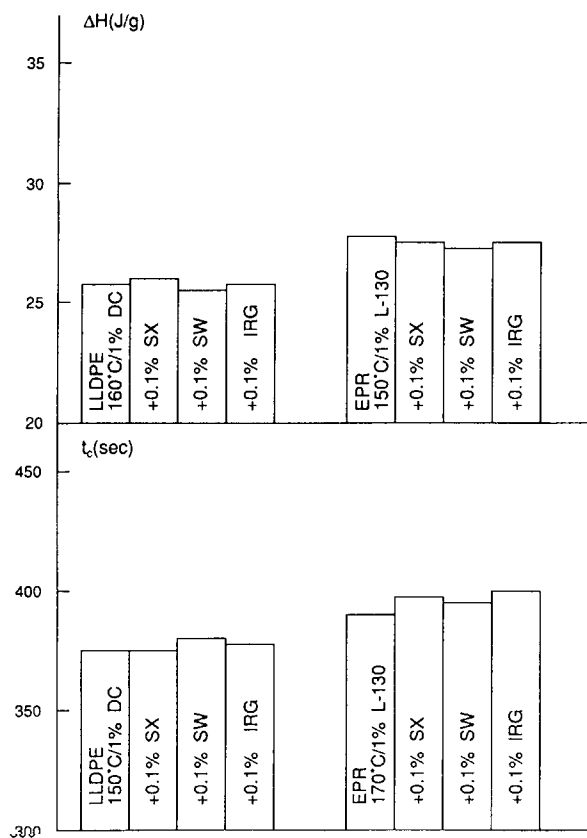


Figure 2 Effect of thermal stabilizers on crosslink heat and time parameters: SX = Santonox; SW = Santowhite; IRG = Irganox 1010.

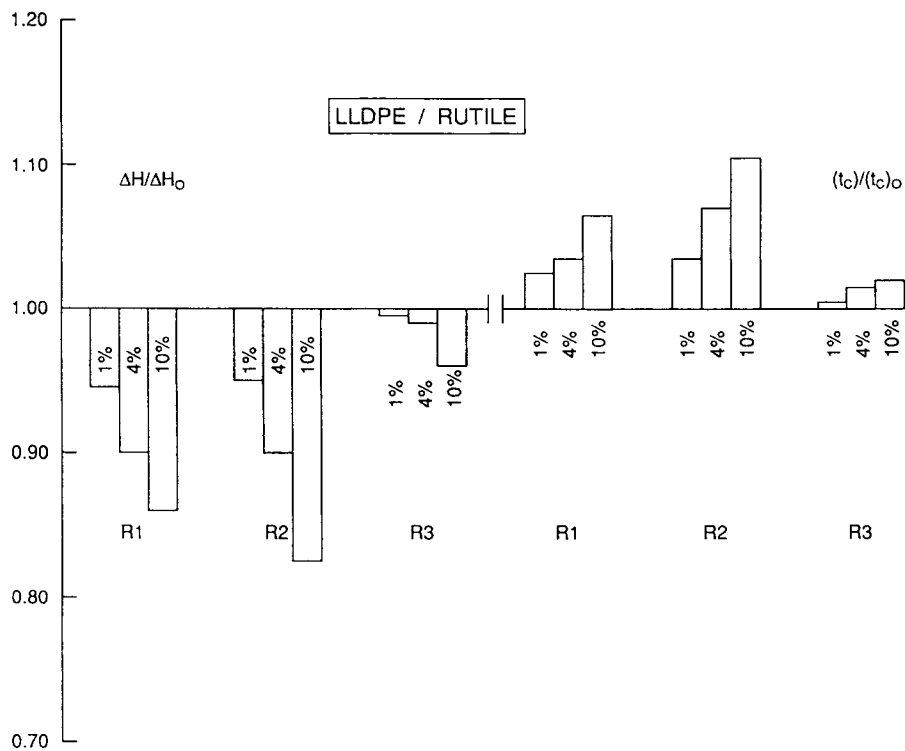


Figure 3 Effect of rutile on crosslink heat and time parameters for LLDPE, 160°C, 1% dicup.

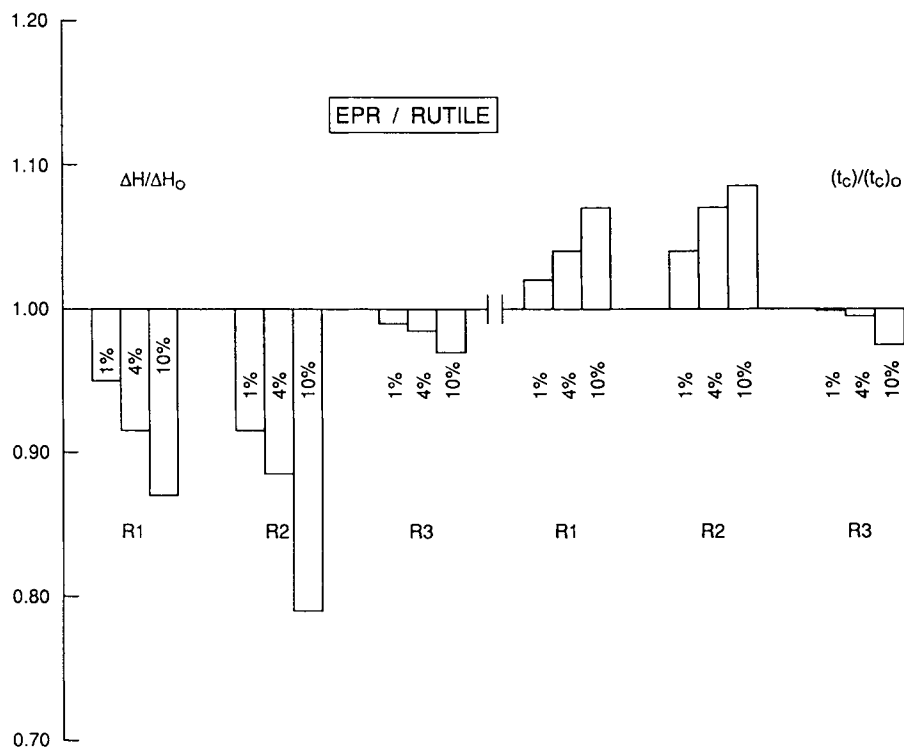


Figure 4 Effect of rutile on crosslink heat and time parameters for EPR, 160°C, 1% dicup.

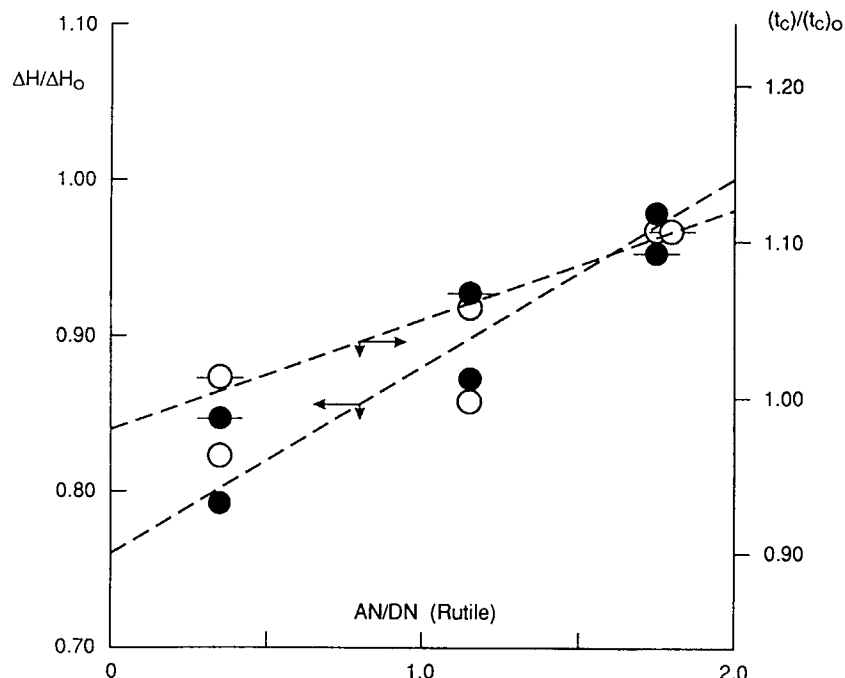


Figure 5 Apparent relation between acid/base properties of pigments and crosslink parameters, 160°C. Full circles = LLDPE; open circles = EPR.

reactive fragments with distinct acidic (electron acceptor) properties. These fragments may be assumed to interact with high surface area solids through acid/base forces, leading to the reduced heats of crosslinking reactions, and to the longer reaction times reported above for the compounds with R-1 and R-2. The acidic rutile is unable to exert acid/base interactions on the reaction products, and crosslinking proceeds unimpeded.

The trends shown in Figure 5 support the implied link between crosslinking mechanisms and acid/base effects. The rutile solids are here characterized by the ratio AN/DN, and that ratio is plotted against fractional heat and time parameters, the reference being the datum for unpigmented host polymer. The figure is restricted to results at 160°C; both of the peroxides are included in the comparison. The data points are clearly inadequate to establish quantitative relationships. The pattern in Figure 5 nevertheless is persuasive in supporting an hypothesis of acid/base effects as stated above.

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