Effect of Antioxidant on Peroxide Modification of LLDPE

TIM BREMNER and ALFRED RUDIN*

The Guelph–Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

SYNOPSIS

A commercial linear low density polyethylene (1-hexene comonomer) was reacted with dicumyl peroxide at appropriate levels to initiate chain extension without crosslinking. The peroxide modification was carried out both in the presence and absence of a common hindered phenolic antioxidant. Thermal treatment of the resin was also completed with and without antioxidant present to evaluate the contribution of classical thermooxidative degradation to the peroxide modification process. In terms of pure thermal degradation, the phenolic antioxidant was found to be effective in prevention of reduction of molecular weights at the high end of the molecular weight distribution, as reflected in changes in M_z. At the low end of the distribution, the opposite effect is seen, where the removal of the antioxidant actually allows an increase in the value of M_n, through chain coupling reactions. Processing of the resin with addition of the organic peroxide significantly increases the molecular weights of both antioxidant containing and antioxidant free resins. Increasing the reaction temperature increases the rate of degradative chain scission and nonenlarging disproportionation reactions. At low temperatures, the presence of the antioxidant acts negatively with respect to chain enlargement reactions, and an overall reduction is seen in the efficiency of the peroxide in its role of increasing molecular weights. As the reaction temperature is increased, chain scission reactions become more predominant, and the antioxidant free resin shows very substantial decreases in molecular weight. Retention of the antioxidant at higher reaction temperatures is beneficial to maintaining high molecular weights, both with and without peroxide present. As in the peroxide free case, branching is essentially unchanged by the absence of antioxidant in peroxide modification.

INTRODUCTION

Polymer modification by reaction with organic peroxides is becoming a more widely accepted and studied method of altering polymer properties. The low levels of peroxide needed to effect substantial changes in molecular weights, for example, present a cost effective route to varying desired product properties.

The peroxide initiated mechanism of degradation has been studied by many,[1-8] and closely parallels the thermally initiated mechanisms[9-11] because both are thermally sustained free chain radical processes. The generally accepted reaction mechanism of initiated thermooxidative degradation includes the principle steps shown in Table I. The addition of the peroxide does not considerably alter the steps outlined in the table, but the quantity of the peroxide relative to the oxygen present in the system is such that reactions 1, 2, and 8 become far more significant. These reactions are the essence of polyethylene (PE) crosslinking, long chain branch (LCB) formation, and chain extension in a peroxide initiated process.

Peroxide initiated chemical crosslinking or modification of PE in an industrial setting is normally carried out with little or no attention to the additives that may be present in the resin. Antioxidants, thermal stabilizers, or processing aids are present in small quantities, on the order of hundreds of ppm, and their effects are usually not considered. The processor simply changes the amount of peroxide

* To whom correspondence should be addressed.

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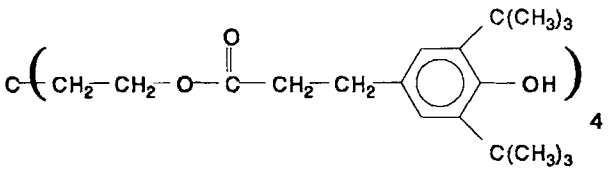
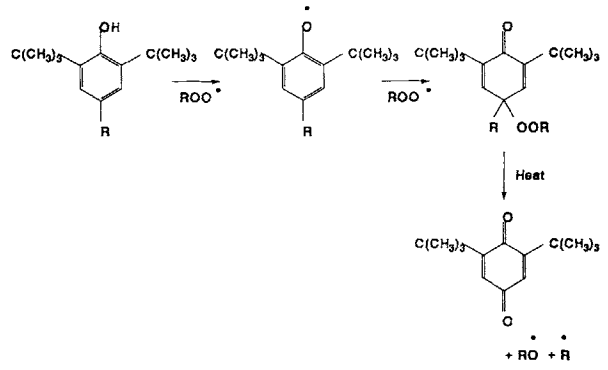
added to achieve the desired product. In a less forgiving process (smaller batch sizes, more stringent product specifications, etc.) it would be of benefit to be able to account for the effects of the various additives on the chemistry occurring during the processing stages, thereby allowing the processor better control of product properties and variability.

The role of the antioxidant specifically is of interest because of the mechanism by which it acts. Antioxidants of various forms are used, with each class or family having its own characteristic mechanism of arresting polymer degradation. This is normally accomplished by the antioxidant readily reacting with the propagating species to produce a stable nonpropagating free radical, or by undergoing a termination step with an existing radical to produce a stable molecule. In the current study, the antioxidant is of the family of chain breaking donor antioxidants, specifically a hindered phenolic antioxidant with the structure:



which is tetrakis[methylene(3,5-di-tertiary butyl-4-hydroxyhydrocinnamate)]-methane. The general mechanism of radical consumption for this family of hindered phenolic antioxidants is outlined below:



The initial abstraction of the phenolic hydrogen atom will proceed in the presence of a strongly abstracting radical, of which the alkoxy radical is a prime candidate. The resonance stabilized oxyradical thus formed may terminate with another radical, presenting the possibility of consuming two radicals per phenolic group. This second consumption is expected to be hindered somewhat by the bulkiness of the substituent at the para position to the phenol,

Table I Principle Reactions of Initiated Thermooxidative Degradation of Polyolefins

1.	$I \rightarrow 2\ r\cdot$
2.	$r\cdot + RH \rightarrow rH + R\cdot$
3.	$R\cdot + O_2 \rightarrow ROO\cdot$
4.	$ROO\cdot + RH \rightarrow ROOH + R\cdot$
5.	$ROOH \rightarrow RO\cdot + \cdot OH$
6.	$2\ ROOH \rightarrow ROO\cdot + H_2O + RO\cdot$
7.	$ROOH + RH \rightarrow RO\cdot + H_2O + R\cdot$
8.	$R\cdot + R\cdot \rightarrow RR$ *or* RH + olefin
9.	$ROO\cdot + R\cdot \rightarrow ROOR$
10.	$ROO\cdot + ROO\cdot \rightarrow ROH + O_2 + R{=}O$ *or* $ROOR + O_2$

and in the case of our antioxidant molecule, this is a factor to be considered.

In some cases,[12] antioxidant synergists are employed to limit the consumption of antioxidant during high temperature processing steps, making more of it available during the service life of the polymer. Potentially damaging, strongly abstracting free radicals generated during the article's lifetime, whether through radiation, thermal treatment, or other conditions of service may therefore react with the antioxidant remaining in the resin.

Although studies of peroxide crosslinking and modification of PE have been published[2,5,8,13-15] along with various characterization methods of such systems,[15-18] there is a dearth of literature dealing with the effect of thermal stabilizers and antioxidant additives on the actual chemical reactions that take place during reaction. The prime role of an antioxidant is the prevention of free radical initiation or propagation steps leading to polymer degradation during thermal processing. The role of the peroxide is to provide a strongly abstracting active free radical species that will initiate the desired reactions in the PE resin. There is clearly a conflict of goals when the two ingredients are considered separately. The radicals originating from the added peroxide may have enough energy to abstract the antioxidants' labile phenolic hydrogen atom, thus reducing the effectiveness of the antioxidant. From another perspective, the peroxide efficiency is reduced by having some of its reactive radicals consumed by the antioxidant.

The focus of this article is the effect of antioxidant on the molecular weight modification of a commercial linear low density PE (LLDPE) resin by reaction with an organic peroxide, both in the presence and absence of a hindered phenolic antioxidant. Current literature on this topic is limited, but some does exist. A study of LDPE crosslinking in the

presence of additives using dicumyl peroxide and 1,3-bis(tertiary butyl peroxy)benzene was reported by Markert and Wiedermann.[19] The authors chose to measure the radical trapping efficiency of the antioxidant species by monitoring the evolution of methane gas, which is produced upon successful hydrogen atom abstraction by the active methyl radical. A higher rate of methane gas production was therefore associated with a less efficient antioxidant activity in the prevention of oxidative degradation. The predominant factor in decreasing the quantity of gaseous reaction products was found to be the steric barriers associated with the initial hydrogen atom abstraction from the antioxidant species.

The possibility of providing protection against thermal autoxidation while allowing the uninterrupted activity of organic peroxides in a crosslinking role was presented in a patent application by Bohen and colleagues.[20] They explored the utility of organic sulfide antioxidants as efficient inhibitors of PE autoxidation, and from understanding the mechanism rightfully assumed no interference of this antioxidant class with peroxide initiated crosslinking. The researchers realized that the organic sulfide acted only on peroxide linkages, being sacrificially oxidized to a dialkyl sulfur dioxide species with the successful consumption of two oxygen atoms from the peroxide linkage. The primary site of activity of the sulfide was speculated to be at the chain bound hydroperoxide groups, which are so potentially damaging in thermal processing stages. The inclusion of the organic sulfide had no effect on the LDPE curing reaction with 2,5-dimethyl-2,5-di-(tertiary butyl peroxy)hexane, yet maintained its antioxidant activity in inhibition of subsequent thermal degradation.

Thermal treatment of PE resins, whether in pelletization or manufacturing stages, has the effect of forming hydroperoxide units on the PE backbone. As previously mentioned, these hydroperoxides are effective initiators of degradation in any ensuing thermal treatment following homolysis to produce the strongly abstracting hydroxyl radical. In their series of articles on thermal degradation of PE,[9–11,21] Hölmstrom and Sörvik showed that pure thermal degradation follows a mechanism closely associated with peroxide initiated degradation. The influence of vinyl unsaturations on molecular enlargement reactions was found to actually produce insoluble material in high density PE (HDPE) samples with no added peroxide.[11] The authors contend that an important initiation source in the absence of oxygen at temperatures near 285°C is the allylic group, or more precisely the scission of the allylic carbon–carbon bond.[9] This is not unreasonable, because the dissociation energy of this bond has been measured[22] to be as low as 61.5 kcal mol^{-1}, with more recent values reported between 67 and 74 kcal mol^{-1}, and leads initially to the formation of a strongly initiating primary polymeric radical.

With this in mind, it is important to remember that the term "degradation mechanism" may have associated with it polymer chain extension reactions that actually increase molecular weights and may ultimately lead to crosslink formation. Early studies in this area normally assumed that random chain scission and beta scission of LCBs are the primary contributors to molecular weight decreases as measured by viscometry. The error in this assumption is in the use of intrinsic viscosity measurements without correction for LCB content,[23] the accepted view being that a branched polymer will have a higher molecular weight than a linear one at the same intrinsic viscosity.[24]

These early studies assumed an initiation by carbon–carbon bond scission[25] in the polymer backbone, giving two reactive primary radicals. The high bond dissociation energy and the likelihood of cage recombination reactions of the reactive primary radicals[26,27] make this an unlikely initiation source. More evidence for this improbability is in the study of model alkane systems,[28] where lower alkanes (C_{20}) show no obvious degradation until a temperature of 350°C, but PE readily degrades readily at temperatures of 200°C.

The present study was carried out to determine the effect of a common antioxidant on dicumyl peroxide modification of a commercial LLDPE resin. A commercial grade resin was treated to remove the antioxidant present, and both the virgin and the antioxidant free resin were reacted in parallel experiments to compare the additives' effect on our system. The peroxide level in this case was purposely kept low enough to maintain polymer solubility so that molecular weight determinations could be carried out on the modified polymers. This allows one to see very small differences in the efficiency of the peroxide acting as a polymer chain extender, in comparison with the inaccurate and somewhat uninformative measure of gel content of a crosslinked polymer.

EXPERIMENTAL

Sample Preparation

The PE used was a commercially available ethylene-1-hexene copolymer (M_w = 128,600, M_n = 34,100)

in powdered form containing 0.02% (w/w) of a hindered phenolic antioxidant, tetrakis[methylene-(3,5-di-tertiary butyl-4-hydroxyhydrocinnamate)]-methane (Irganox 1010, Ciba Geigy). Extraction of the antioxidant was completed by stirring 100 g of the powder resin at room temperature for 48 h with 750 mL of chloroform, in which the antioxidant powder is highly soluble (manufacturers claim >100 g/100 g of chloroform). After this time, the chloroform solution was filtered from the powder and a fresh 750 mL of chloroform was added for a further 48-h period. This second aliquot was found to not have any extracted material in it, as measured by UV and FTIR methods, and was therefore discarded. The first 750-mL aliquot, containing the desired extracted antioxidant, was reduced in volume and analyzed for antioxidant concentration using the UV absorbance maxima between 247 and 266 nm. The corrected concentration was found to correspond to 0.017% (w/w), which is close to the 0.02% value specified by the resin manufacturer, indicating a reasonably successful extraction. The chloroform-wet, additive free PE powder was placed in a vacuum oven at 90 kPa vacuum and 40°C for a period of 80 h to remove residual solvent.

Addition of 0.1% (w/w) dicumyl peroxide to the resin was carried out by dissolving the peroxide in cyclohexane solvent and adding this solution to the polymer powder. The solvent was then allowed to evaporate freely after an initial 24-h sealed mixing time. This procedure has been found to give uniform peroxide distribution throughout the resin.[8]

Reaction of the peroxide was completed by compression molding thin films (0.3-mm thickness) in rectangular frames in a hot press at a pressure of approximately 2800 kPa. Reaction temperatures were chosen over a range of 180–250°C, with a reaction time of 20 min for all samples. Thin film samples to be analyzed for thermal degradation effects in the absence of peroxide were pressed in an identical fashion. The absolute removal of all oxygen (dissolved and atmospheric) was not attempted in this study, mainly for practical reasons. The reaction conditions were chosen to mimic what might be encountered in a real processing situation, which is hardly free from oxygen exposure. Because sample preparation was identical for all sample sets, the amount of atmospheric oxygen trapped between the platens of the hot stage press would be essentially constant for all samples. Further, it is the authors' experience that the pressing of thin films at these high pressures excludes the possibility of significant quantities of atmospheric oxygen reaching the sample over the course of the 20-min reaction time, as indicated by carbonyl index measurements.

Sample Coding

Four sample sets in total were examined, and coded as follows. The first letter indicates whether virgin or antioxidant extracted resin was used (V or E), the second indicates whether the processing was purely thermal or in the presence of peroxide (T or P). The last three digits of the sample code indicate the reaction temperature in degrees Celsius. Hence, sample code EP200 indicates that antioxidant was extracted from the resin, peroxide was present in the processing step, and the temperature of reaction was 200°C. A summary of the experimental coding is shown below:

Resin	Peroxide?	Group Code
Virgin	No	VT
Virgin	Yes	VP
Extracted	No	ET
Extracted	Yes	EP

Sample Analysis

FTIR Analysis for Vinyl Unsaturation and Carbonyl Content

Thin films were analyzed using a Nicolet Model 520 FTIR, operating at a resolution of 1 wave number. Film thicknesses were measured with a digital micrometer to an accuracy of 0.01 mm. Quantification of the vinyl unsaturations present was completed by the method outlined by Haslam, Squirrel, and Willis.[29] Peaks from the absorbance spectra were assigned to out of plane C—H bends associated with terminal vinyls (908 cm^{-1}), and *trans* unsaturations (964 cm^{-1}). Cis vinyl unsaturations are unfortunately not quantifiable by this method, because their absorption peak at 735 cm^{-1} is obliterated by the large CH_2 absorption at 720 cm^{-1}. The absorption at 888 cm^{-1}, assigned to pendant vinylidene unsaturation, was also unfortunately unresolvable, owing to the interference of the 894 cm^{-1} band from short alkyl branch bending modes (the butyl branches in the 1-hexene copolymer). Vinyl group concentrations are reported as vinyl groups per 1000 carbons.

A measure of the reproducibility of the vinyl unsaturation content was completed by analysis of five different samples of the same material. It was found that an accuracy of ±0.03 per 1000 carbons in a set of five samples could be obtained with ease.

Table II Some Bond Dissocation Energies for Hydrogen Atoms with Potential Abstracting Radicals

Radical Species	Parent Compound	Bond Dissocation Energy (kcal/mol)
$-CH_2-CH=CH\cdot$	$-CH_2-CH=CH_2$	87
$C_6H_5O\cdot$	C_6H_5O-H	88
$(CH_3)_3C\cdot$	$(CH_3)_3C-H$	91
$(R)_2CH\cdot$	$(R)_2CH-H$	95
$RCH_2\cdot$	RCH_2-H	98
$CH_3\cdot$	CH_3-H	104
$(CH_3)_3CO\cdot$	$(CH_3)_3CO-H$	105
$C_6H_5\cdot$	C_6H_5-H	112

The carbonyl index is commonly used as a measure of the generation of oxidation products in a thermal degradation process. The intensity of the carbonyl absorbance at 1726 cm^{-1} was measured and divided by the film thickness, giving a carbonyl index with units of reciprocal millimeters.

Molecular Weight Measurement

Molecular weight analyses were carried out with a high temperature gel permeation chromatograph (GPC), equipped with differential refractive index (DRI), differential viscometer (DV), and low angle laser light scattering (LALLS) detectors. The samples were analyzed at a temperature of 145°C in 1,2,4-trichlorobenzene (TCB) solvent. Sample concentrations were typically 2×10^{-3} g mL^{-1}, and complete dissolution of the PE was insured by tumble mixing the solution at 160°C for a period of 24 h. Thermal degradation was minimized by including 0.1% (w/w) antioxidant in the TCB solvent. Full operating parameters have been described elsewhere.[30,31] Molecular weight distribution plots presented here are taken from the DV detector, as it is most uniformly sensitive across the entire range of the distribution. The LALLS suffers from insensitivity in the low molecular weight regime, and the DRI detector has the opposite deficiency.

Branching Analysis

Measurements of average LCB and butyl branching were made on a Bruker AC-300 NMR spectrometer operating at a frequency of 75.47 MHz, for carbon nuclei observation. Quadrature detection was used, utilizing an inverse-gated pulse sequence to minimize nuclear Overhauser effect. Samples were prepared in 5-mm NMR tubes at a concentration of 20% (w/w) in TCB solvent, and spectra were obtained with sample temperature at 125°C. An 8.2 μs 90°-pulse width was used, with a 12-s relaxation delay between pulses, acquiring 32,768 data points over a sweep width of 140 ppm, giving a digital resolution of 0.649 Hz/pt. Samples were normally allowed to run for 2000–3000 scans. The main $-CH_2-$ backbone resonance was used as spectral reference, and was assigned the commonly accepted value of 29.99 ppm.

Butyl branches are measured by considering the resonance at 23.37 ppm, which corresponds to the carbon adjacent to the methyl group on a butyl branch ($2B_4$). Long branches (i.e. $\geq C_6$) were measured using the resonance at 32.2 ppm. Butyl and LCB contents are reported as branches per 1000 backbone carbons.

RESULTS AND DISCUSSION

The basic mechanism of radical consumption by the antioxidant under study was presented in the introductory section. Tertiary butyl phenoxy radicals do not dimerize,[32] and therefore the possibility exists for two radicals to be consumed per phenolic ring by a combination reaction of a second radical with the phenoxy radical. The antioxidant we are studying in this case is a quaternary centered hindered phenolic, with four phenolic groups per molecule giving this species the stoichiometric possibility of consuming eight radicals per molecule, although the peroxydienone formed in the consumption of a second alkylperoxy unit is known to be unstable and will reinitiate.[32]

At this point, it becomes necessary to attempt to quantify the distinction between "strong" and "weak" radicals. The strength of a radical as a hydrogen atom abstractor is usually closely related to the bond dissociation energy of the molecule thus formed upon abstraction. Table II shows examples

of commonly encountered free radical species, ranked in order of bond dissociation energies. Using examples from the table, it is likely that the methyl radical will be a strong abstractor of the phenolic hydrogen atom, with the driving force of the reaction being the production of a more stable radical species. It is also obvious why the hindered phenolic group is a good choice as a hydrogen atom donor, with a relatively low bond energy, and the phenoxy radicals' correspondingly low propensity for hydrogen atom abstraction. This ranking of relative activities has been shown to be an acceptable method of predicting the activity of various radical species in the degradation process.[33]

It is also appropriate at this time to introduce an additional set of reactions more specific to the initiated degradation of PE, which will be used in the discussion that follows. These reactions, shown in Figure 1, have been generally agreed upon in the literature as the predominant reactions in modifications of PE by free radical degradative mechanisms.[1,2,8-11]

Antioxidant Role in Suppressing Thermal Degradation

In an investigation such as this, it is first necessary to determine the effectiveness of the antioxidant in the prevention of pure thermal degradation effects, without the addition of any peroxide. To do this, a comparison must be made between the virgin resin (VT) and the extracted resin (ET) before and after subjecting samples to thermally degradative conditions. As described in Experimental, samples were heated in a hot press at temperatures from 180 to 250°C and under considerable pressure, in hopes of limiting excessive exposure to oxygen.

The simplest, commonly used indicator of thermooxidative degradation is the carbonyl index, where new carbonyl groups are assumed to form as a result of reactions with molecular oxygen and specific termination reactions such as beta scission reactions (e.g. reaction 10, Table I). The result for sample sets VT and ET are shown in Figure 2, and in this case little or no difference is seen in the carbonyl index for the two sample sets. This may suggest low rates of degradation at the lower reaction times and temperatures, as the index increases considerably at 250°C. Because carbonyl groups are produced, this indicates that oxygen on (hydro) peroxides are involved to the same extent in the thermal degradation processes in the study.

The molecular weight distributions for sample sets VT and ET are shown in Figures 3 and 4, respectively. Figure 5 shows the changes in terminal and *trans* unsaturation contents for samples thermally treated without peroxide over a temperature range of 180 to 250°C. The changes in unsaturation content, for both types, are not significant when a reproducibility of ± 0.03 is used, except in the behavior of *trans* unsaturation content of the virgin resin. The increase seen here is significant, although small, and is noticeably different from the behavior of the extracted resin. An application of the reaction model of Figure 1 associates increases in *trans* unsaturations with either terminal allylic radical coupling with other polymeric radicals (reaction 16), or a disproportionation reaction between a primary radical and a secondary polymeric radical (reaction 11). The allylic radical coupling reaction has associated with it increased molecular weights, which are shown in Table III, and reflected in Figure 3 for the virgin resin. At all reaction temperatures, the virgin resin (VT) has higher M_z and M_w values than the extracted resin (ET) except for one instance at the maximum temperature studied (see ET250), which correlates well with the differences seen in *trans* unsaturation content. The M_n values are higher for the extracted resin than the virgin resin, which is consistent with more active thermooxidative processes in the extracted polymer.[11]

The molecular weight differences between the extracted and virgin resins prior to any reaction (as shown in Fig. 6, and in the first two rows of Table III) are within experimental error. We can therefore consider molecular weights and distributions of the untreated resins as equal in the following discussion.

In the virgin polymer (containing antioxidant) thermal treatment alone causes a narrowing of the molecular weight distribution (VT series, Fig. 3) at temperatures up to 225°C. This is to say, heat treatments at 180–225°C cause an increase in M_n, a decrease in M_z and no significant change in the central part of the distribution, as shown by M_w values (see Table III). The 250°C-treated material has shifted to lower molecular weights.

The extracted resin (no antioxidant) shows even more narrowing of the molecular weight distribution with heat treatment. In this case, both the low and high molecular weight tails are truncated on heating in the press. This is seen in the numerical averages listed in Table III, where M_n and M_z of the ET series polymers are significantly higher and lower, respectively, than the corresponding averages of the untreated resin. At the same time, M_w is not changed significantly.

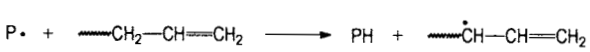
The molecular weight changes seen are not consistent with kinetic chain processes initiated by

Initiation

1. Abstraction to form secondary polymeric radical

2. Abstraction at branch site to form a tertiary radical

3. Abstraction of allylic hydrogen - terminal site

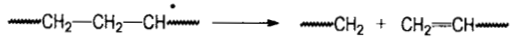


4. Abstraction of allylic hydrogen - vinylidene site

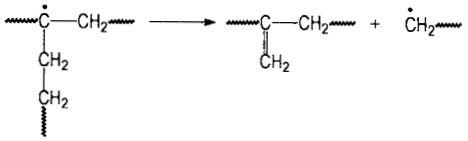
5. Abstraction of allylic hydrogen - *cis* or *trans* site

Propagation

6. Beta scission - chain

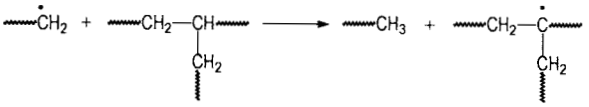


7. Beta scission - branch point



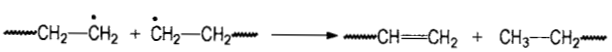
8. Intramolecular abstraction - "backbiting" reaction

9. Intermolecular abstraction



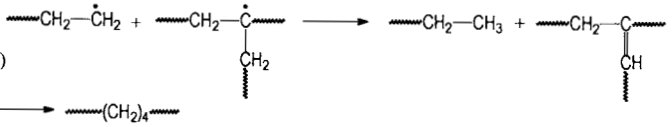
Termination

10. Disproportionation (primary + primary)

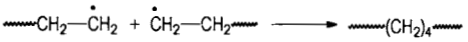


11. Disproportionation (primary + secondary)

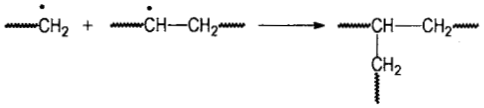
12. Disproportionation (primary + tertiary)



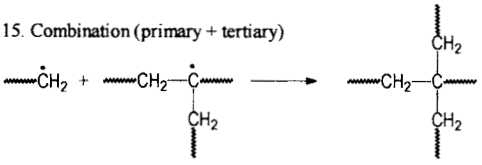
13. Combination (primary + primary)



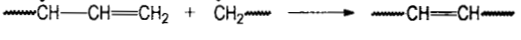
14. Combination (primary + secondary)



15. Combination (primary + tertiary)



16. Allylic radical termination - terminal site



17. Allylic radical termination - *trans* site

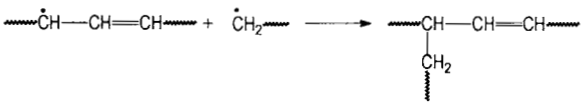


Figure 1 Contributing reactions to overall polyethylene degradation.

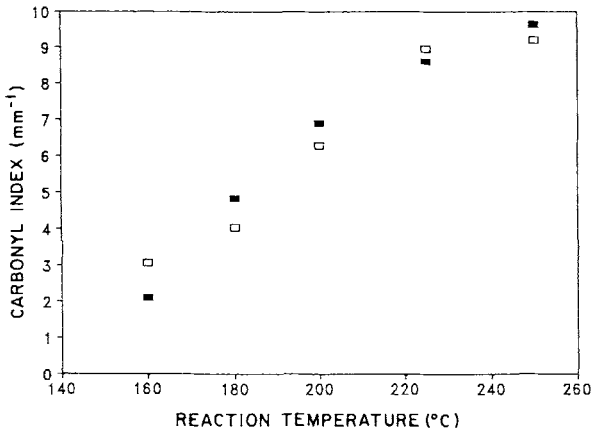


Figure 2 Carbonyl index vs. reaction temperature for virgin resin and extracted resin, examining pure thermal degradation. No peroxide has been added to these samples. (□) virgin resin; (■) extracted resin. The samples shown at 160°C have had no peroxide added and have not been subjected to any thermal treatment. They are included to act as a reference only.

random bond breakages, because such a mechanism results eventually in a random molecular weight distribution ($M_w/M_n \rightarrow 2$). Although the molecular weight distributions do narrow on heat treatment, M_w/M_n does not approach 2 with increasing heating temperatures. Hölmstrom and Sörvik[9] concluded that initiation of the free radical processes involved here was by scission of allylic C—C bonds. This is plausible, from considerations of bond dissociation energies, but we believe also that polymer-bound hydroperoxides are likely to also trigger the radical kinetic chains. The results of Hölmstrom and Sörvik[9–11] are similar in some, but not all, respects to our data on heated LLDPE.

Hölmstrom and Sörvik studied an LDPE resin, that we believe may have contained residual peroxide initiator from the high pressure, free radical process used to make the material. In addition, their experiments were performed at significantly higher temperatures than ours. It is, of course, well known that free radical chain processes in polymers involve simultaneous chain scission and molecular enlargement effects. Hölmstrom and Sörvik note that the high molecular weight tail of the molecular weight distribution of their LDPE is largely retained, even at treatment temperatures as high as 335°C. This observation, which we did not see in our experiments, is consistent with the presence of small concentrations of the radical precursors such as peroxides or hydroperoxides. It is plausible, also, that adventitious low concentrations of oxygen in our experiments produced hydroperoxides.

Comparison of the ET and VT series at temperatures between 180 and 225°C indicates that both the chain scission and chain enlargement processes are more important in the extracted resins that contain no antioxidant. This is consistent with the report[34] that phenolic antioxidants react more ef-

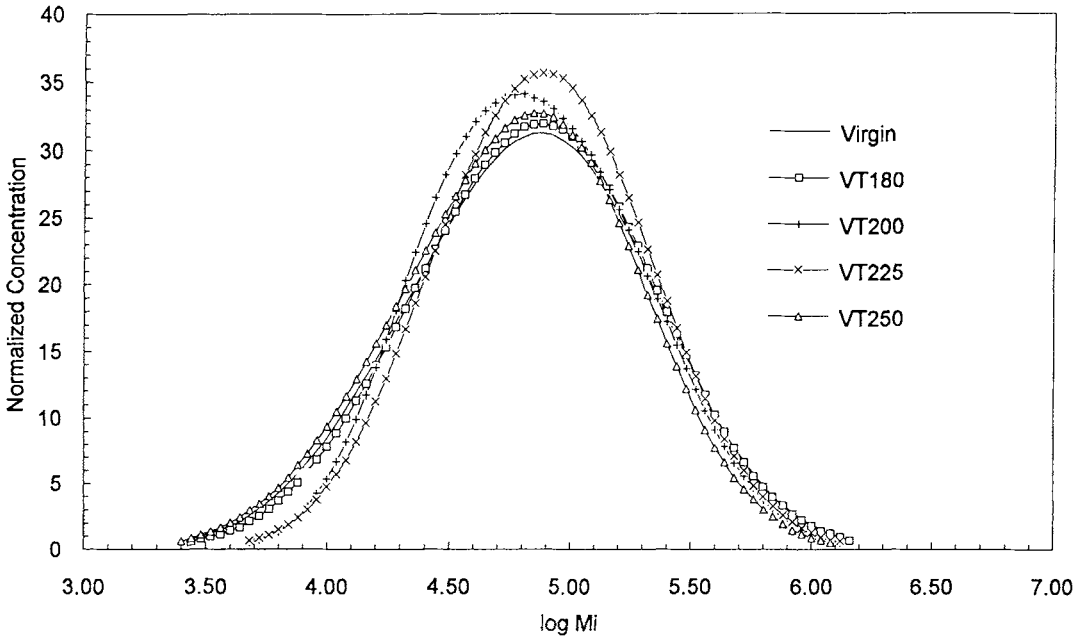


Figure 3 Molecular weight distributions of sample set VT, virgin polymer, thermal treatment only.

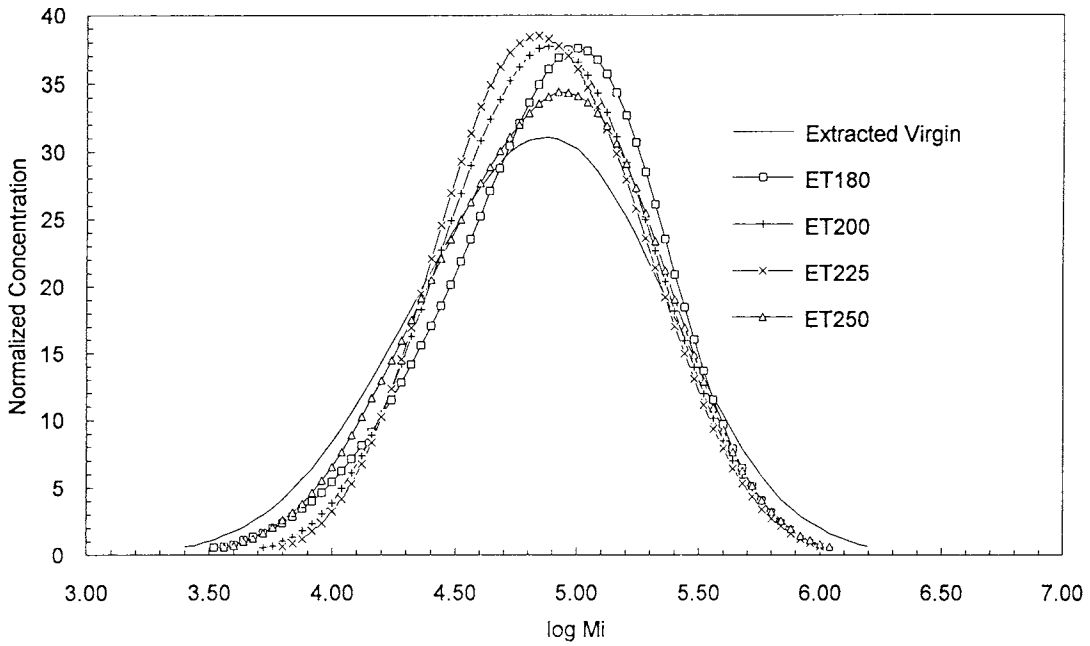


Figure 4 Molecular weight distributions of sample set ET, extracted resin, thermal treatment only.

ficiently with oxygen-centered radials than with carbon-centered radicals. The latter are the intermediates in scission and/or chain enlargement reactions in polyolefins. The differences noted between the VT and ET samples are thus more likely due to the chain-breaking activity of the phenolic antiox-

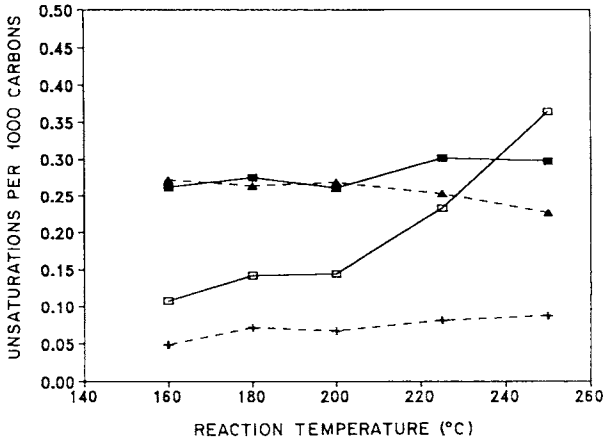


Figure 5 Vinyl unsaturation content vs. reaction temperature examining pure thermal degradation. No peroxide has been added to these samples. Solid lines connect data points for the virgin resin. (□) virgin, *trans* unsaturation; (■) virgin, terminal unsaturation. The dashed lines connect data points for the extracted resin. (+) extracted, *trans* unsaturation; (▲) extracted, terminal unsaturation. The samples shown at 160°C have had no peroxide added, and have not been subjected to any thermal treatment. They are included to act as a reference only. The inclusion of connecting lines is intended as a visual aid only, and does not imply any specific trend.

Table III Summary of Molecular Weight Measurements

Sample	M_n	M_w	M_z	M_w/M_n
Virgin resin	34,100	128,600	417,200	3.77
Extracted resin	34,400	131,000	434,100	3.81
VT180	36,600	128,800	400,400	3.52
VT200	43,600	118,100	322,600	2.70
VT225	46,900	125,600	323,400	2.68
VT250	31,700	107,300	295,900	3.35
ET180	49,500	112,700	257,500	2.28
ET200	48,800	116,700	264,900	2.39
ET225	44,800	123,900	268,700	2.76
ET250	41,400	118,100	277,800	2.85
VP180	48,800	210,000	650,800	4.30
VP200	72,100	193,400	536,000	2.68
VP225	64,400	174,600	472,900	2.71
VP250	45,900	153,600	400,500	3.35
EP180	89,700	252,200	828,400	2.81
EP200	61,500	192,800	613,700	3.13
EP225	47,100	160,600	474,100	3.41
EP250	45,800	126,200	341,300	2.76

Values for M_n are taken from a differential refractive index detector; M_w and M_z are taken from a differential viscometer detector. V, virgin resin; E, extracted resin; T, thermal treatment; P peroxide treatment.

idant, as executed on the hydroperoxide units in the polymer molecules. If the antioxidant is acting in a chain-breaking mode[32] and inhibiting the degradative processes by halting the activity of initiating radicals, its effectiveness decreases as the concentration of hydroperoxide increases. This is what is observed, in effect, in the VT series.

The antioxidant seems to be effective in limiting the amount of LCB scission (see Table IV). Although the differences are small, samples reacted at 200 and 225°C have a lower LCB content when the antioxidant is absent.

Effect of Antioxidant on Peroxide Modification of LLDPE

The question now turns to whether or not such low levels of antioxidant ($\sim$ 0.02% w/w) will have any inhibitory effect on the effects of the peroxide modification (at 0.1% w/w concentration) of the commercial LLDPE resin. In this case, the sample codes VP (virgin resin, peroxide modified) will be compared to those with codes EP (extracted resin, peroxide modified).

The peroxide under study is dicumyl peroxide, one of the more commonly used peroxides in PE modification. The initial homolysis to produce an oxygen-centered radical is followed by a beta cleavage reaction giving the reactive methyl radical. The rate of this secondary reaction, and hence the reactive lifetime of the alkoxy radical, is dependent upon the stability of the alkyl radical and carbonyl compound produced.[35] An effective way of ranking the relative rates of this beta scission process in

Table IV Branching Results as Measured by ^{13}C-NMR Analysis

Sample	Long Chain Branches	Butyl Branches
Virgin resin	1.4	14.1
Extracted resin	1.4	14.2
VT180	1.3	13.4
VT200	1.4	13.8
VT225	1.4	12.9
VT250	1.0	13.6
ET180	1.2	14.2
ET200	0.8	14.4
ET225	0.8	14.3
ET250	1.0	14.3
VP180	1.2	14.3
VP200	1.0	13.1
VP225	1.2	14.6
VP250	1.2	14.3
EP180	1.4	13.9
EP200	1.3	13.6
EP225	1.4	14.7
EP250	1.0	14.6

Branching is reported as "branches per 100 backbone carbons."

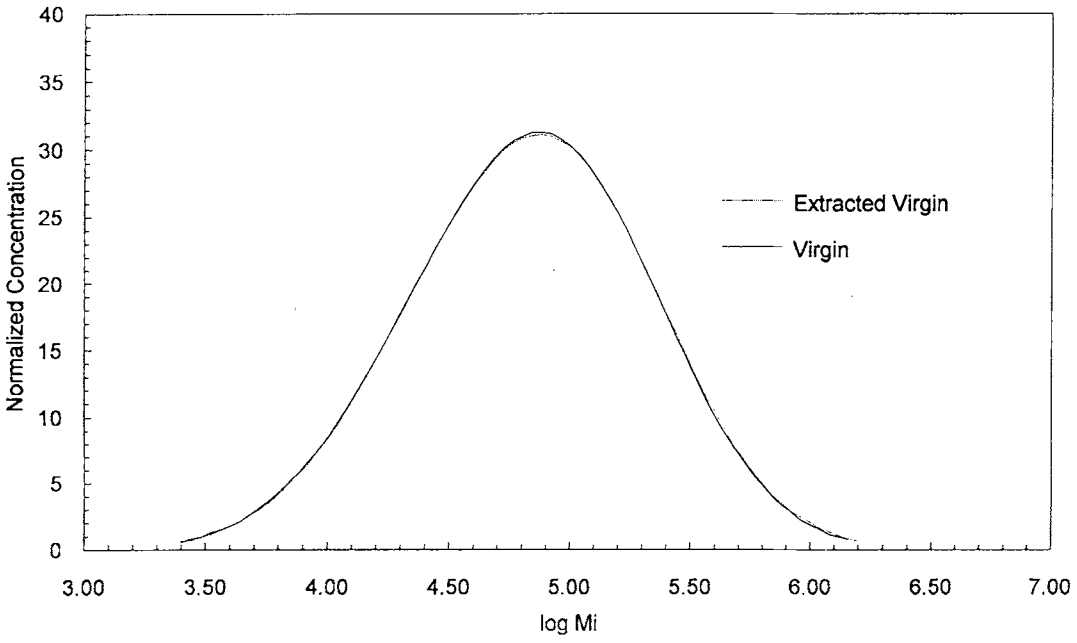
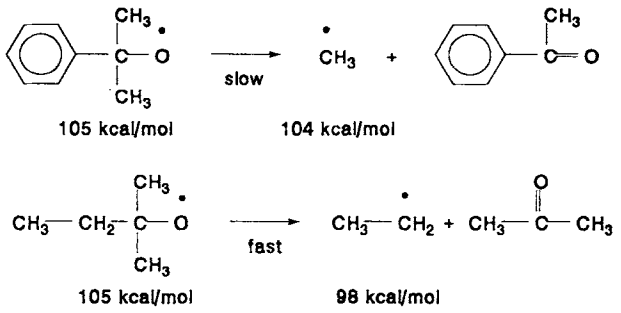


Figure 6 Molecular weight distributions of virgin and extracted resins, showing essentially identical distributions.

peroxides has been illustrated by Callais and Kazmierczak[36] which uses the relative bond dissociation energies of reactant and product to predict the relative rate of the beta scission process. This is not unlike the use of relative bond energies to predict the rate of reaction of radicals in thermal degradation,[33] as discussed previously. To show an example of how this comparison is made, consider the following two beta scission reactions, the first of the cumyloxy radical with which we are concerned, the second a tertiary amyloxy radical:



The energies shown below each radical are the bond dissociation energies of that moiety bonded to a hydrogen atom (Table II). Because the driving force behind this beta scission is dependent upon the stability of the radical produced, the second reaction occurs faster due to the production of a lower energy radical, assuming similar ketone stabilities. The possibility does then exist for oxygen centered radicals to be present in the PE modification mechanism; but clearly, both the methyl and alkoxy radicals have sufficient energy to abstract the phenolic hydrogen atom from the antioxidant molecule, thus reducing the amount available for reaction specifically with chain bound peroxy units. The implications of this fact will become clear in the following discussion.

In a similar comparison as discussed above, Figure 7 shows the carbonyl index of sample sets VP and EP. Within experimental error, these two sets of data are the same, indicating that the addition of peroxide does not interfere with the mechanism of formation of chain bound carbonyl groups. Also, a comparison of Figure 7 with Figure 2 shows almost identical carbonyl index values up to 225°C, yet the sample sets are considerably different with respect to molecular weights and distributions.

Figures 8 and 9 show the molecular weight distributions of sample sets VP and EP, respectively. A summary of the vinyl unsaturation contents are shown in Figure 10. The first comparison to be made is of the peroxide free resins (shown at 160°C) with

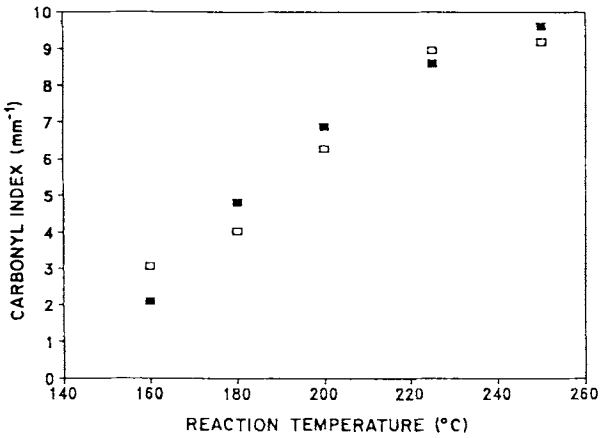


Figure 7 Carbonyl index vs. reaction temperature for virgin resin and extracted resin, with peroxide added at a level of 0.1% (w/w) to both resins. (□) virgin; (■) extracted. The samples shown at 160°C have had no peroxide added, and have not been subjected to any thermal treatment. They are included to act as a reference only.

those reacted at 180°C. In both the extracted resin and the virgin resin, the terminal unsaturations show a marked decrease, accompanied by a considerable molecular weight increase (Table III) that is consistent with a mechanism of terminal unsaturation coupling reactions to extend polymer chains and increase molecular weights. The *trans* unsaturation of the virgin resin also shows an increase, but the *trans* vinyl group of the extracted resin remains essentially invariant, as was the case in the study of peroxide-free thermal degradation.

As the temperature is increased, both the virgin and extracted resins show increases in terminal unsaturation, with a decidedly sharper rise in the proportion seen in the extracted resin. If our suggested mechanism is correct, this increasing terminal unsaturation concentration should correspond with a decreasing molecular weight, as β-chain scission reactions become more predominant with increasing temperature (such as reaction 6 in Fig. 1). An examination of Table III and Figures 8 and 9 show this to be true.

There is an obvious effect on the overall mechanism, as revealed by FTIR and GPC analysis, caused by the absence of the antioxidant. The virgin resin shows an increasing *trans* and terminal unsaturation content with reaction temperature, and a corresponding decreasing molecular weight. This observation is consistent with the results shown in previous work,[8,15] where terminal unsaturations were found to be a prime reaction site, and coupling of terminal allylic radicals with other polymeric radicals accounted for the formation of new *trans* un-

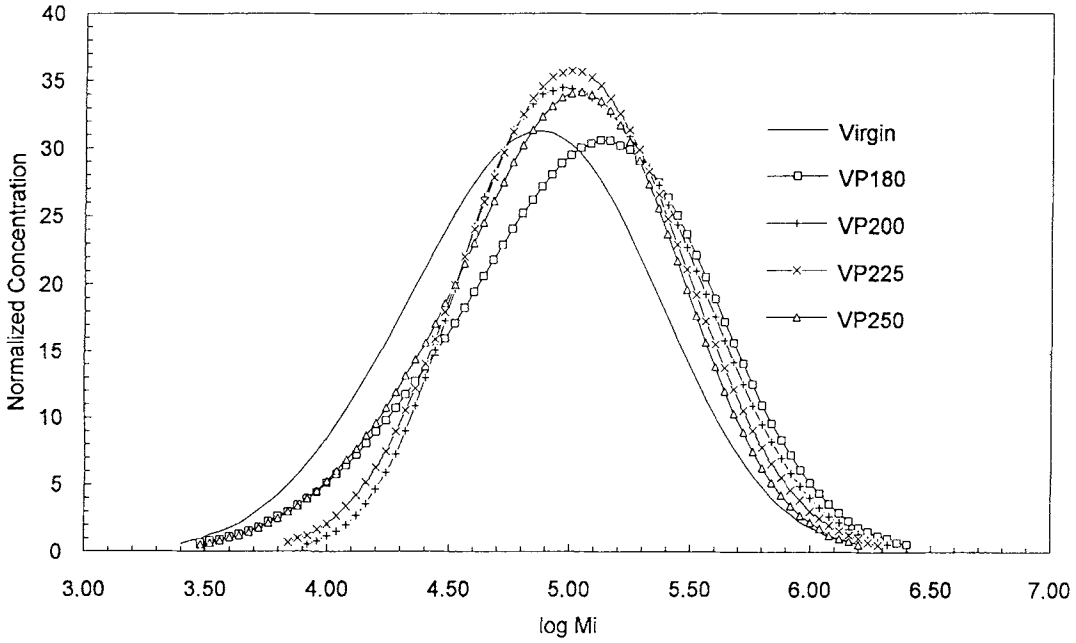


Figure 8 Molecular weight distributions of sample set VP, virgin resin, peroxide added.

saturations, and increased molecular weights. As temperatures increase, β-chain scission becomes more significant in relation to allylic radical coupling and molecular weights fall.

This view does not hold for the extracted resin. There is an initial large decrease in terminal unsaturation, associated with a very significant increase in molecular weight (see Table I, sample EP180 and Fig. 9), but no increase in the *trans* unsaturation content is seen, as would be expected if terminal allylic radical coupling were the prime source of molecular weight increase. One explanation for this observation is that the absence of the antioxidant in some way allows a chain enlargement reaction to

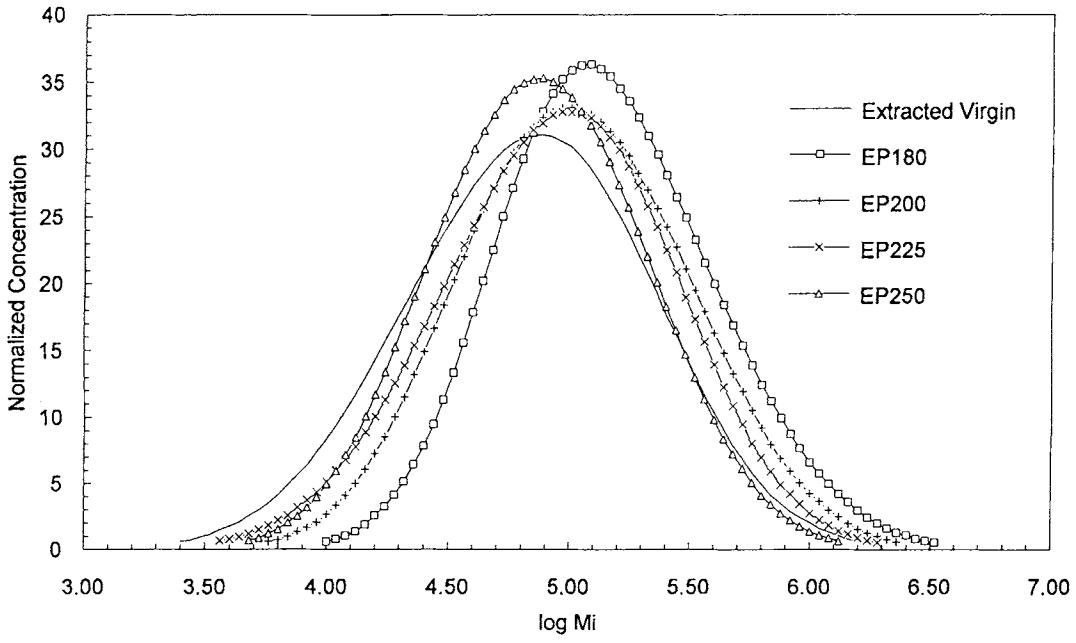


Figure 9 Molecular weight distributions of sample set EP, extracted resin, peroxide added.

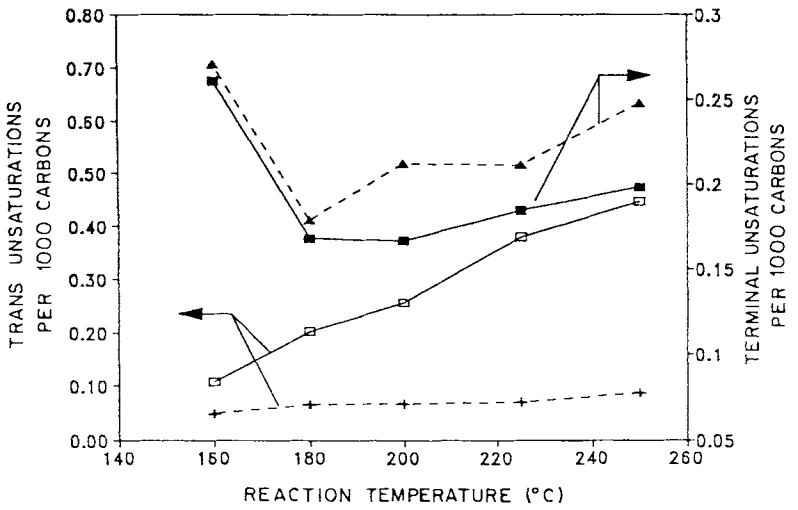


Figure 10 Vinyl unsaturation content vs. reaction temperature with peroxide added at a level of 0.1% (w/w) to both resins. Solid lines connect data points for the virgin resin; (□) virgin, *trans* unsaturation; (■) virgin, terminal unsaturation. The dashed lines connect data points for the extracted resin; (+) extracted, *trans* unsaturations; (▲) extracted, terminal unsaturations. The samples at 160°C have had no peroxide added, and have not been subject to any thermal treatment. They are included to act as a reference only. The inclusion of connecting lines is intended as a visual aid only, and does not imply any specific trend.

occur to a significant extent through reactive species other than the terminal unsaturation. In Figure 1, a combination of polymeric alkyl radicals occurs (reactions 13, 14, and 15) to increase molecular weights without changing the concentration of any of the detected vinyl species. These reactions are certainly feasible, and are expected to contribute to some degree to molecular weight enlargement reactions, considering the relatively high concentration of potential alkyl radicals compared to vinyl species (by approximation, neglecting the branch carbon atoms, in the virgin resin approximately 0.7 vinyl groups per 1000 carbons were detected by FTIR, and 15.5 tertiary carbons were detected by NMR resulting in $\{1000 - 15.5 = 984.5\}$ secondary carbons). And lower reaction temperatures have been found to reduce the amount of disproportionation reactions in this type of modification.[8,15] It can be envisaged that the alkyl radicals previously consumed by antioxidant are now free to couple reactively in the extracted resin.

In answering the obvious question of why the antioxidant did not also halt the coupling action of the allylic radicals, one is asked to recall the mechanism of the antioxidant. A hindered phenolic antioxidant acts by sacrificing its phenolic hydrogen atom to some strongly abstracting radical, and terminating the propagation sequence. If we again consider the relationship between bond energies and radical reactions, the answer becomes clear. The bond dissociation energy for this hydrogen–oxygen bond[34] is on the order of 88 kcal mol^{-1}. The bond dissociation energy for an allylic hydrogen is slightly less at 87 kcal mol^{-1}; dissociation energies for secondary and tertiary alkyls are 95 and 91 kcal mol^{-1}, respectively. What this means is that from consideration of relative energies, the abstraction of the phenol hydrogen atom by an allylic radical is not a favorable process, but it is favorable for either of the secondary or tertiary alkyl radicals. Therefore, the antioxidant will terminate alkyl radicals preferentially to terminating allylic radicals.

This is certainly not the only explanation for the phenomena observed, but it is obvious that initial molecular weight increases for the extracted resin (from peroxide free to sample EP180) are substantially larger than in the virgin resin (from peroxide free to sample VP180) for all molecular weight averages, and we can therefore state that the chain extension reactions at low temperatures are more efficient in the antioxidant free resin.

As discussed above, the initial increase in molecular weights is greater in the extracted resin than in the virgin resin. As the temperature is increased, and reaches the highest experimental value of 250°C, the situation is reversed, and the extracted resin shows lower average molecular weights than the virgin resin. This is clearly shown by the data in Table III and the distributions shown in Figures 8 and 9. The trend is attributable to the onset of considerable

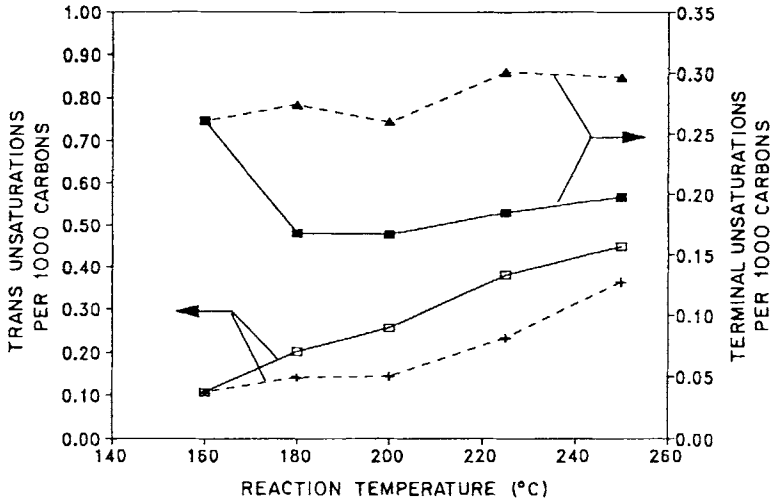


Figure 11 Vinyl unsaturation content vs. reaction temperature for virgin resin, comparing degradation with and without peroxide added. Solid lines connect data points for the peroxide modified (0.1% w/w) resin; (□) *trans* unsaturation; (■) terminal unsaturation. The dashed lines connect data points for the resin with no peroxide added; (+) *trans* unsaturations; (▲) terminal unsaturations. The samples at 160°C have had no peroxide added, and have not been subject to any thermal treatment.

chain breaking degradation in the antioxidant free resin at higher temperatures, and reflects the efficiency of the antioxidant in preventing damaging chain scission reactions in the virgin resin.

At low temperatures then, the antioxidant acts to hinder the success of the peroxide in fulfilling its role as promoter of polymer chain extension, presumably by termination of some initiating free radicals and stoppage of the kinetic chain. As temperatures increase, thermal degradation effects play a more significant role in molecular weight changes, and scission or nonenlarging disproportionation reactions increase. In this case, the antioxidant acts effectively to retard the destructive mechanism and slow the rate of chain scission.

The effects of the presence or absence of antioxidant on changes in both long and short chain branching are very small, bordering on the edge of the limits of reproducibility. These are summarized in Table IV. The level of LCB is initially low, and does not show any considerable change or discernible trend for any of the samples measured, with the possible exception of sample set ET, which is the peroxide and antioxidant free resin. At temperatures of 200 and 225°C, a lower branch content is seen for this set, which may be related to the discussion above in which it was postulated that the absence of antioxidant allowed more reactions at alkyl radical sites to occur. If the chain scission reaction proceeds primarily by a beta scission mechanism at a tertiary radical site (reaction 7, Fig. 1), then perhaps this lower branch content is a result of this difference. A similar trend is not seen in the peroxide modified extracted resin, possibly because of the availability of free radicals for coupling reactions with the tertiary alkyl radical. In the presence of high concentrations of free radicals, this tertiary radical is more likely to terminate by coupling with another radical than undergo a further beta scission reaction, because this reaction involves production of a high energy primary radical, which is unfavorable on a thermodynamic basis.

Comparison of Peroxide Degradation with Thermal Degradation

Lastly, and briefly, it is worthwhile to compare the effects of pure thermal degradation and peroxide degradation in the virgin resin. The changes in terminal and vinyl unsaturation for sample sets VP (virgin, peroxide modified) and VT (virgin, thermal degradation only) are shown in Figure 11.

As above, the initial terminal unsaturation decrease is associated with a large molecular weight increase due to the action of the peroxide (compare virgin resin to VP180 and VT180, Table III). The peroxide free resin does not show the same decrease in terminal unsaturation, and little or no increase in molecular weights. Increasing *trans* unsaturation with increasing reaction temperature is greater for the peroxide modified resin than the peroxide free, and a comparison of molecular weight averages at

all reaction temperatures shows higher values for the peroxide modified resin. This is supportive of the expected participation of terminal unsaturations in polymer chain extension mechanisms, and conversion to *trans* unsaturations via reaction 16 in Figure 1.

The molecular weight data in Table III show that thermal degradation decreases molecular weight in the high molecular weight species of the distribution (as evidenced in M_z) from the onset in peroxide free resin, whereas peroxide addition slows the diminution of molecular weight with increasing temperature, again by initiating a proportion of successful chain extension mechanisms.

CONCLUSION

An organic peroxide has the effect of significantly increasing the molecular weights of both virgin and antioxidant containing resins. Increasing reaction temperature increases the rate of degradative chain scission and nonenlarging disproportionation reactions. At low temperatures, the antioxidant acts to consume free radical species that participate in chain building reactions, reducing the efficiency of the peroxide in its role of increasing molecular weight. Thus, antioxidant free LLDPE which has been reacted with peroxide at temperatures of 180°C shows greater weight gain than resin with antioxidant present. As the reaction temperature is increased, chain scission reactions become more important, and a greater proportion of antioxidant molecules are consumed in stopping thermal degradation. Retention of the antioxidant at higher reaction temperatures is beneficial to maintaining high molecular weights. As in the peroxide free case, branching is essentially unchanged by the absence or presence of antioxidant in peroxide modification.

It is unlikely that purely thermal degradation occurred in this study. "Weak links" and hydroperoxides derived from adventitious oxygen probably served as initiating sites for free radical chain processes.

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