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ANOMALOUS AGING PHENOMENA IN A CROSSLINKED POLYOLEFIN CABLE INSULATION

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Abstract—The radiation-thermal degradation of a commercial crosslinked polyolefin (XLPO) cable insulation material was investigated as a function of dose rate and temperature in the range of 22–120°C. Degradative changes in the material were monitored by ultimate elongation, density, gel content, O_2 consumption, infrared spectroscopy, and differential scanning calorimetry. Mechanical aging surprisingly occurred most rapidly at the *lowest* temperatures. This unusual phenomenon was corroborated by chemical measurements (gel content and density). When samples that had been irradiated at ambient temperature were subsequently annealed at elevated temperatures, recovery of mechanical properties and concurrent changes in gel content and density were observed. The involvement of residual radical species and hydroperoxide intermediates as well as the importance of molecular mobility in the semi-crystalline XLPO as contributors to these anomalous behaviors were evaluated and discussed. The observed inverse temperature effect, where polymer degradation occurs more rapidly at lower temperatures, represents an example in which material aging and life time prediction cannot be handled by conventional approaches, such as the commonly applied Arrhenius methodology. Publisheed by Elsevier Science Ltd

INTRODUCTION

One of the ultimate aims of polymer degradation studies is the ability to predict material lifetimes via a detailed understanding of the degradation mechanism and the controlling parameters involved. Despite the wealth of information currently available describing the various aspects of polymer degradation, both in chemical and physical terms, lifetime prediction remains very much an art plagued by the intrinsic dilemma of the need to extrapolate data from accelerated experiments (primarily at elevated environmental stress levels, e.g. higher temperatures, dose rates, etc.) to ambient conditions. One approach used to predict aging in thermal environments is the well known Arrhenius methodology, recently discussed for example in detail by Wise *et al.* (1995). The foundation of the Arrhenius approach is a consistent mechanism over the temperature range in question, which means that any temperature dependent changes affecting the fundamental degradation mechanism can lead to qualified or invalid predictions.

Due to the complex nature of the degradation process and the likely changes in the rate-determining parameters, it is questionable whether thermal aging can always be modeled by a simple Arrhenius relationship. For some amorphous elastomers, it was recently shown that the aging may be reasonably described by the Arrhenius approach, although a failure point independent of temperature is still implied in this study (Wise *et al.*, 1995). Considerable evidence has been obtained, however, showing that in some cases polymer lifetimes can easily be overestimated by extrapolations from high temperature aging (Tamblyn and Newland, 1965; Howard, 1973; Kramer and Koppelmann, 1986). The degradation has been shown to be influenced by changes in the solubility and volatility of stabilizers (Bair, 1973; Howard and Gilroy, 1975; Board and Ruddell, 1982), morphological aspects such as the semi-crystalline nature of some polymers, and their related transition temperatures (Billingham *et al.*, 1981). Further complications are the diffusion-limited oxidation at elevated temperature (Gillen *et al.*, 1987; Clough and Gillen, 1992; Wise *et al.*, 1995, 1996; Dole and Chauchard, 1995) and other heterogeneities observed in solid state polymer degradation (Celina and George, 1993; Celina and George, 1995b).

The evaluation of polymer degradation under combined radiation and thermal conditions has been of interest for many years and the complexity of this topic has been revealed in great detail (for reviews of this topic, see: Clough and Gillen, 1990; Gillen and Clough, 1991; Clough *et al.*, 1991). As with thermal aging, diffusion-limited oxidation effects are a significant complicating factor for combined radiation plus temperature environments (Gillen and Clough, 1985, 1989). Even so, for numerous polymers, a viable accelerated aging predictive approach, referred to as time–temperature–dose rate superposition, has been developed and successfully tested (Gillen and Clough, 1985, 1989, 1993). Significant complications can occur, however, for certain semi-crystalline materials such as the currently studied crosslinked polyolefin XLPO. For instance, many years ago, the complications observed

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for semi-crystalline polyethylene during irradiation were summarized by Chapiro (1962). Depending on the irradiation temperature, crystallinity and density changes were due to competing processes, i.e. the destruction of crystalline regions, or the formation of double bonds and crosslinking (Williams *et al.*, 1958). The autoxidation due to the presence of oxygen during irradiation was suggested to be confined primarily to the amorphous region, but also accompanied by an increase in crystallinity (Luongo, 1963). Similarly, chemi-crystallization due to considerable restructuring of polymer fragments after chain scission events was shown to lead to increased density (Carlsson and Wiles, 1971). Mechanical properties are, as reviewed by Popli and Mandelkern (1987), heavily influenced by structural and morphological features such as degree of crystallinity, structure of the amorphous region, crystallite thickness, or structure and relative amount of interfacial region (Mandelkern, 1985). The radiation-induced changes in polyolefins as suggested by O'Donnell and Whittaker (1992) may occur preferentially at crystalline surfaces and defects, which would explain why mechanical degradation may not always be directly related to the absolute extent of oxidation (Nishimoto *et al.*, 1991). The importance of the selective degradation of tie molecules was similarly shown by Torikai *et al.* (1990).

In the present study further evidence of considerable mechanistic changes with temperature in the combined radiation-temperature aging behavior of a common XLPO insulation are presented, which result in difficulties for the applicability of accelerated aging methods.

EXPERIMENTAL

XLPO cable insulation

The material used in this study is a commercial crosslinked polyolefin (XLPO) cable insulation material (0.9 mm wall thickness) which was removed from the conductor core of a power and control cable, commonly used in nuclear power plant applications and offered as a radiation-resistant and flame-retardant material. Samples were tested and aged in the tubular form which results after the stripping operation. Compositional elemental analysis with microprobe X-ray fluorescence combined with infrared spectroscopy resulted in the identification of the flame retardants as antimony oxide in combination with chlorinated and brominated organics (dodecachloro-dodecahydro-dimethano-dibenzo-cyclooctene and decabromo-diphenylether) and a small amount of TiO_2. The XLPO content of the insulation is estimated to be approximately 65%, with the polymer matrix being consistent with an ethylene–vinylacetate copolymer by infrared analysis as shown in Fig. 1. The compound density was measured to be 1.295 g/cm^3. The melting characteristic as studied by differential scanning calorimetry (DSC) (Fig. 2) clearly shows the typical response of an ethylene vinylacetate-mdpe to hdpe copolymer with a double melting peak at 93°C and 122°C; partial melting is apparent even at ambient temperature.

Radiation-thermal aging

Combined radiation-thermal aging was carried out under flowing air conditions in an underwater

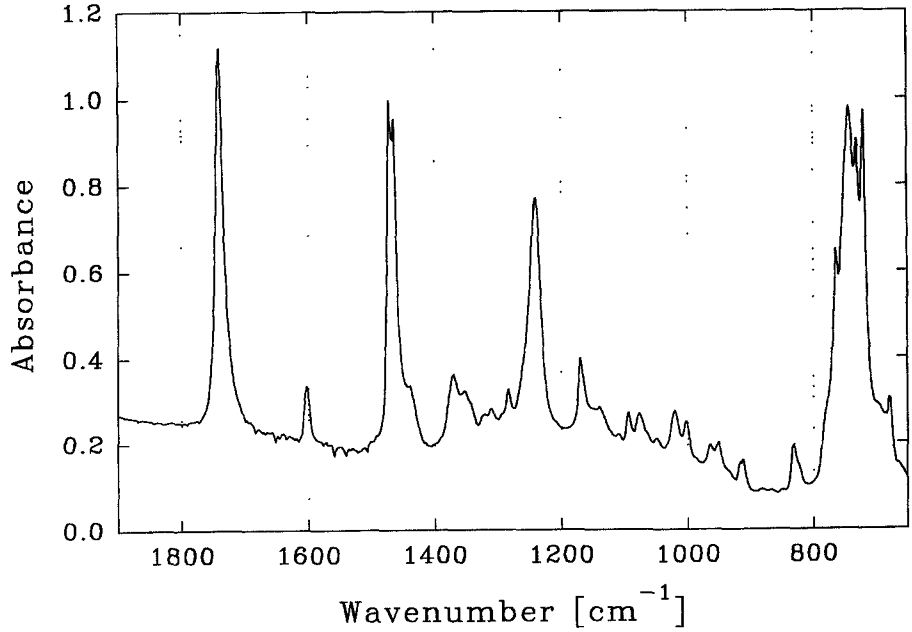

Fig. 1. Microtome (10 μm) transmission infrared spectrum of the new XLPO material.

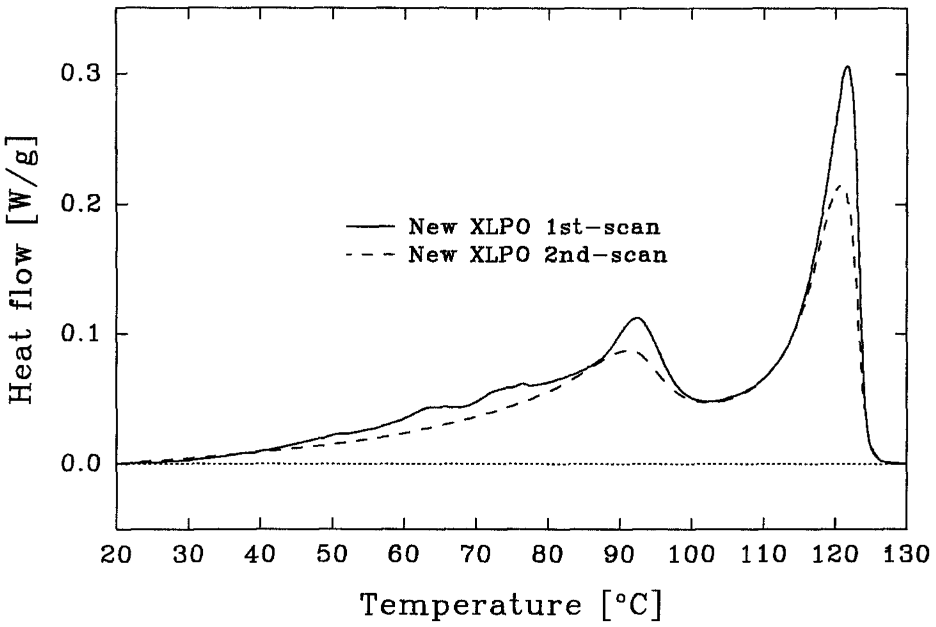

Fig. 2. DSC-scans of new XLPO insulation.

cobalt-60 aging facility using water-tight aging cans (Gillen and Clough, 1989, 1993) and dose rates ranging from 17 to 5200 Gy/h (1.7–520 krad/h) at temperatures from ambient (22°C) to 120°C. Aging under nitrogen was accomplished by placing the samples in ampoules followed by vacuum removal of residual oxygen and backfilling with nitrogen. The sealed ampoules were then placed in the water-tight cans.

Annealing of samples

Annealing refers to a thermal treatment at elevated temperatures. Our standard annealing process was to hold the sample at 140°C for 24 h in a circulated air oven and then allow it to cool by natural convection at ambient temperature. The temperature of 140°C was chosen because it is above the main crystalline melting peak of the XLPO. Annealing under nitrogen was carried out by placing samples in sealed ampoules filled with nitrogen, after prior vacuum removal of residual air for a minimum of 24 h.

Mechanical testing

Tensile tests were performed with an Instron Table Model Testing Machine (Model 1000) equipped with pneumatic grips and an extensometer. The strain rate was 12.7 cm/min for an initial crosshead separation of 5.1 cm.

Differential scanning calorimetry (DSC)

The melting characteristics were investigated using a Perkin–Elmer Model DSC-7 after calibration with an indium standard. Sample weights of approx. 5 mg were analyzed with a scanning rate of 5°C/min.

Oxygen consumption

Oxygen consumption measurements were performed by sealing known amounts of the XLPO with 160 mm Hg of O_2 in glass containers of known volume. The containers were then aged for times which resulted in consumption of approximately 40% of the O_2. (This resulted in an average partial pressure of O_2 that was roughly equal to ambient air conditions in Albuquerque.) The O_2 content remaining after aging was determined by gas chromatography (Wise *et al.*, 1995).

Infrared spectroscopy

Microtomed specimens (10 μm) were analyzed by FTIR-microscopy using a Biorad FTS-40 Model spectrometer with microscopy attachment, and by emission spectroscopy using a similar hot stage as described previously (Vasallo *et al.*, 1992; George *et al.*, 1995). Both techniques utilized a liquid-nitrogen-cooled MCT detector; 64 scans were averaged at a resolution of 4 cm^{-1}.

Gel content analysis

A gel content analysis was carried out by solvent swelling and extraction of the sample with refluxing *p*-xylene (b.p. 133°C in Albuquerque) (Voigt, 1976; Hendra *et al.*, 1987; Lazar *et al.*, 1990; Celina and George, 1995a). Samples of 10–20 mg (w_0) of the XLPO were accurately weighed to ± 0.01 mg and placed in approx. 50 ml of *p*-xylene using a 100 ml round bottom flask with water cooled condenser and heating mantle. After extraction for a minimum of 8 h, the sample was quickly recovered from the hot solvent with the help of a funnel and filter paper and transferred into a sealable pre-weighed sample vial to determine the weight of the swollen gel (w_{sw}) in solvent equilibrium. Final drying was carried out in a vacuum oven at 80°C for a minimum of 2.5 h and the weight of the insoluble fraction (w_{gel}) was obtained. The gel content was calculated as the ratio of $(w_{gel}/w_0)100\%$.

Density measurements

The density (ρ_{sample}) was determined using the Archimedes principle by accurately (0.01 mg) determining the weight of a sample specimen in the range of 10–20 mg in air (w_{air}) and comparing it with its weight (w_{liquid}) when immersed in a liquid of density ρ_{liquid}. This approach has been described before (ASTM Standard D792-91). The virtual weight loss is related to the density of the material by:

$$\rho_{sample} = \frac{W_{air}}{(W_{air} - W_{liquid})}\rho_{liquid} \qquad (1)$$

The exact density of the liquid, in this case isopropanol (0.78 g/cm^3), which exhibits excellent wetting properties without penetrating into the XLPO, was determined by reference to small glass beads of known density (normally used to calibrate density gradient columns) by:

$$\rho_{liquid} = \frac{(W_{air} - W_{liquid})}{W_{air}}\rho_{glass\ bead} \qquad (2)$$

where the weights now refer to the glass beads.

ANOMALOUS AGING BEHAVIOR

The change in the mechanical properties of the XLPO material for each combined radiation-thermal environment was studied by measuring ultimate tensile elongation. The total dose required for the elongation to decrease to 100% (arbitrary choice to represent mechanical failure) from its initial value of approx. 310% was determined from these data. Those values, referred to as dose to equivalent damage (DED), when plotted against dose rate and temperature, are particularly useful to represent and analyze complex combined-environment data (Gillen and Clough, 1989, 1993). For this study, moderate dose rate effects are immediately apparent from the DED plot (Fig. 3), which shows that the DED value for any given temperature depends on the dose rate (i.e. a slightly enhanced degradation rate per unit dose when the dose rate is lowered). For constant dose rate conditions at temperatures of 60°C and higher, the degradation rate increases (lower DED value) with temperature, in agreement with normal expectations. The results at the lower temperatures of 41 and 22°C are, however, surprising, since the apparent degradation rate *increases* considerably when the temperature is lowered from 60 to 41°C and then to ambient conditions. Since our current understanding of polymer aging is unable to easily explain enhanced degradation rates when the environmental stress level is reduced, we decided to monitor a quantity which is more closely related to the polymer degradation chemistry, in particular the oxygen uptake.

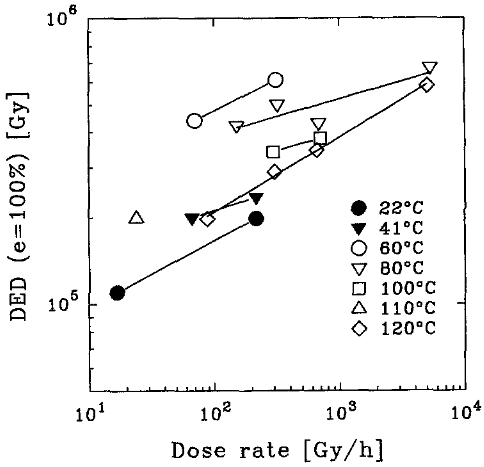

Fig. 3. Plot of dose to equivalent damage (DED) at different temperatures and dose rates.

Oxygen uptake

Since mechanical degradation in air-containing environments normally correlates with chemical oxidation, the consumption of oxygen as well as formation of volatiles (CO and CO$_2$) was measured as a function of temperature at a dose rate of 38 Gy/h. The oxygen uptake data (Fig. 4) are representative of the early stages of the degradation (total dose of less than 10 kGy). These results suggest that the radiation-induced oxidation rate is insensitive to temperature from ambient conditions to 60°C. Above this point, the rate begins to increase slowly with temperature, thus displaying the expected qualitative temperature dependence. That the relative chemical and mechanical changes in the material vary in

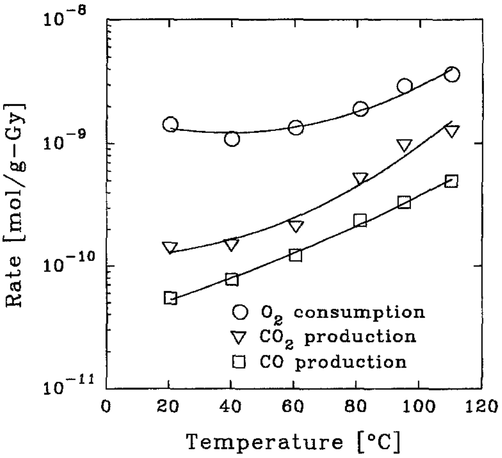

Fig. 4. Oxygen consumption and CO, CO$_2$ formation rates vs temperature at a constant dose rate of 38 Gy/h.

different directions as the temperature is decreased suggests a fundamental change in the degradation mechanism at the lower temperatures. Thus, the material is either extremely sensitive to tiny amounts of oxidation at the lower temperatures or is able to compensate for chemical oxidation with some repair mechanism to retain mechanical properties at elevated temperature conditions.

Annealing of degraded XLPO, mechanical recovery

If the material, when aged at elevated temperatures, is indeed capable of retaining mechanical properties via a temperature-dependent repair process, it should be possible to induce a recovery of mechanical properties for the low temperature aged samples by thermal annealing. Partial melting of the semi-crystalline XLPO might, for example, enable an exchange of tie molecules connecting the crystalline and amorphous regions, which would result in improved properties if the previous damage had occurred primarily in the interfacial regions. Indeed, it has been shown that oxidative degradation can lead to damage concentrated in the tie molecules connecting the crystalline and amorphous regions (Winslow and Matreyek, 1964; Nishimoto *et al.*, 1986; O'Donnell and Whittaker, 1992), which is due to the fact that radicals produced in the crystalline region are protected from further reactions with oxygen until they slowly diffuse to the surface of the crystallite where enhanced oxidative damage can then occur. It is also well known that the number of tie molecules (Torikai *et al.*, 1990) and their condition play an important role in the tensile properties of polymers (Dunn and Williams, 1983), and that annealing and melting of heavily degraded polyolefins can in fact reestablish useful mechanical properties (Winslow and Matreyek, 1964).

Samples of material which had been aged at room temperature at 200 Gy/h, and which exhibited a substantial loss of tensile elongation after a dose of 328 kGy (as shown in Fig. 5), were annealed at 140°C for 24 h. The tensile elongation of these samples, which was initially about 25%, recovered to approx. 230%. This dramatic change corresponds to a recovery of about three-quarters of the relative tensile elongation of the new material (which was 310%, absolute). Upon continuation of the aging process at ambient conditions for the annealed samples, mechanical failure occurred rapidly again (594 kGy total dose). A second annealing step at this stage (see Fig. 5) resulted in another recovery of mechanical properties. This process could be repeated a third time (849 kGy). It is important to note that the three data points obtained after the three annealing steps (which represent the recoverable mechanical properties) correlate reasonably well with the degradation curve occurring for a sample aged at 60°C (dashed curve in Fig. 5). Annealing of these latter samples (aged at 60°C), and of samples aged at higher temperatures, did not lead to any recovery of mechanical properties, which suggests a limitation of the recovery effect to aging temperatures below 60°C.

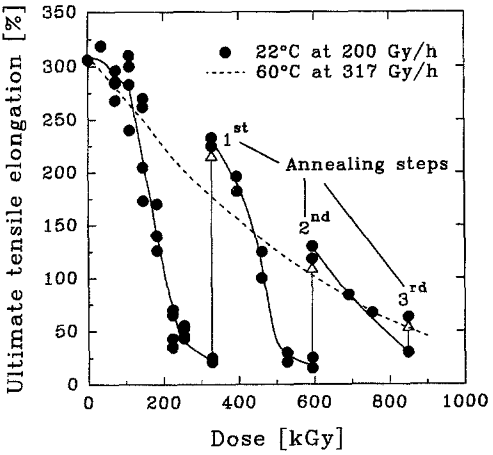

Fig. 5. Decrease in ultimate elongation during degradation at 22°C and 200 Gy/h and the recovery of mechanical properties upon annealing at 140°C for 24 h after 328, 594 and 849 kGy.

When the degradation is carried out at 22°C under nitrogen, mechanical damage is greatly reduced and little recovery effect is observed upon annealing: a sample aged for 400 kGy at 22°C under N_2 showed a residual elongation of approx. 240%, and yielded a value of 260% upon annealing (which represents no significant change within experimental error). This shows that oxidative chemistry must be involved in the unusual low temperature effects that lead to enhanced degradation. We therefore conclude: (1) that oxidative chemistry underlies the degradation of this XLPO material in combined radiation-temperature environments; (2) that oxidative intermediates are the precursors of the annealing phenomenon observed; and (3) that the extended lifetime at 60°C and above is due at least partially to a "healing" process, which is the same mechanism operating in the annealing of the samples aged at room temperature. To further elucidate these phenomena, the following investigations were undertaken to identify whether this process is primarily related to partial melting, to mobility aspects, to repair of tie molecules or to any other unexpected reaction.

Gel content analysis

The determination of the gel content of a crosslinked polyolefin as a function of aging is an excellent method to investigate the mechanistic aspects of the degradation process (Charlesby, 1960; Celina and George, 1995a). Scission and crosslinking reactions both occur during aging; an increase in the gel content indicates degradation dominated by crosslinking, while a decrease indicates a process controlled mainly by scission. Figure 6 shows the changes in the gel content of the XLPO material at the various aging temperatures. It is apparent that the aging at the higher temperatures (60, 80 and 100°C) is accompanied by an increase in the gel content, indicating considerable crosslinking. The aging at the lower temperatures (22 and 41°C) correlates with a reduction in the gel and thus suggests a process dominated by scission. It is, however, also apparent that the annealing steps (i.e. at 328, 594 and 849 kGy for the material aged at 22°C) coincide with a considerable increase in the gel content. Interestingly, the absolute gel contents for the annealed specimens are similar to those for samples aged to the same total dose at the higher temperatures. In contrast, the gel content of samples aged at 60°C and subsequently annealed does not show an increase (Fig. 6). Additionally, the gel content of samples aged at 22°C under nitrogen is similar to samples aged at 60°C under air, both before and after annealing: a sample aged for 400 kGy at 22°C under N_2 had a gel content of 70.2% before and 71.5% after annealing. Thus, aging under nitrogen at 22°C does not result in crosslinking during annealing, which is consistent with the non-recovery of mechanical properties as described before.

The results suggest that material aged in air at the lower temperatures of 22 or 41°C has the inherent ability to crosslink, but does not do so until the temperature is raised. The net effect for ambient temperature irradiation is dominance by the scission component of the degradation. Although this component is likely present at the higher temperatures, the release of the repressed crosslinking mechanism leads to domination by crosslinking. Thus, the gel content analysis clearly indicates a fundamental change in the degradation mechanism between 40 and 60°C. Within the time periods utilized in the current experiments, the crosslinking reaction can occur only above a threshold temperature. This threshold may be due to the restricted mobility of radicals within the polymer matrix or the reactivity of other intermediates which are stable at the lower temperatures.

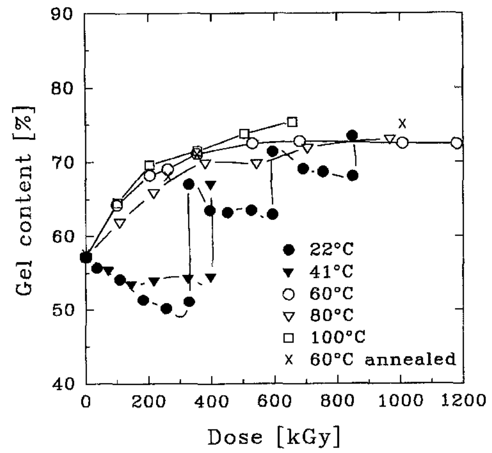

Fig. 6. Changes in the gel content during combined radiation-temperature exposures as a function of temperature showing predominantly scission at lower temperatures and crosslinking at higher temperatures as well as a marked increase in the gel content during annealing of the samples aged at 22 and 41°C.

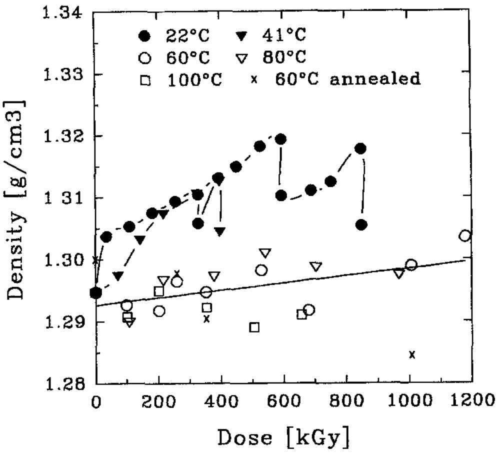

Fig. 7. Density changes under combined radiation-temperature exposures as a function of aging temperature showing pronounced increases at 22 and 41°C and decreases during annealing.

Density and crystallinity changes

To further elucidate the mechanistic differences in the two temperature regimes, we monitored density as a parameter representative of morphological and physical properties. The density data obtained are presented in Fig. 7; it is apparent that aging at the lower temperatures correlates with a considerable increase in the density, whereas a nearly unchanged density is measured for all samples aged at the elevated temperatures. The data also reveal a decrease in the density during the annealing steps. For polymeric materials, several mechanisms can lead to density increases. The first mechanism involves crosslinking, which leads to shrinkage and therefore to modest density increases (Gillen *et al.*, 1986; Gillen, 1988). Since the gel results indicate that more crosslinking occurs under the elevated temperature conditions, crosslinking effects cannot be responsible for the low temperature results shown in Fig. 7. Aging in air leads to large density increases (Gillen *et al.*, 1986), as oxidative products are incorporated into the material. Again, since the oxygen consumption results, shown in Fig. 4, imply similar oxidation levels at 22, 41 and 60°C, oxidation effects are also not responsible for the density differences seen at low temperatures in Fig. 7. For semicrystalline materials such as the current XLPO, a third mechanism leading to density increases involves an increase in sample crystallinity. One likely contributing mechanism for the current material involves chemicrystallization (Winslow *et al.*, 1966). When oxidation of semicrystalline materials leads to chain scission, the scission products have less restricted mobility. Disentanglement of such fragments allows them to crystallize into imperfect, low melting crystals, increasing the overall crystalline content, and therefore increasing the density for the lower temperature experiments. At higher temperatures, crosslinking induces irregular structures within the chain and also reduces chain mobility, both of which reduce crystallinity.

Unfortunately, a precise determination of the crystallinity for these commercial polyolefin compounds is difficult, and techniques such as X-ray diffraction, differential scanning calorimetry (DSC) or small angle X-ray scattering may provide only approximate information. Nevertheless, because even approximate information may provide useful mechanistic insights, we chose DSC to investigate crystallinity changes. In Fig. 8 the melting enthalpies determined by DSC from the first scan of the samples aged at 22 and 60°C are presented. Peak integration was carried out between 15 and 127°C, but it is difficult to calculate crystallinity since the material is a complex copolymer formulation. As a crude estimation, a melting energy of 75 J/g would correlate with an approximate crystallinity of 40% when using the melting energy of 280–290 J/g of an ideal polyethylene crystal (Chiang and Flory, 1961; Quirk and Alsamarraie, 1989) and assuming 65% polyolefin content of the compound. It is, in any event, apparent that annealing correlates with a reduction in crystallinity, since a considerable drop in the melting energy is observed. While crystallinity for the samples aged at 60°C appears to be fairly constant, as expected, the measured increase in the density for the samples aged at 22°C does not easily relate to an overall increased melting energy in the DSC measurements, except at the lower doses as shown in Fig. 8. This may be due to the considerable shift in the melting peaks for the 22°C samples (see discussion in Section 4.3, since the relative energy contribution of crystalline material with a lower melting temperature may be somewhat lower and thus compensate for an actual increase in crystallinity. Therefore, while the pronounced density increase for the samples aged at temperatures below 60°C may be related to crystallinity changes, chemicrystallization during the radiation degradation, or some internal stress build-up, it is not fully understood why this behavior occurs abruptly and is so pronounced at the lower temperatures.

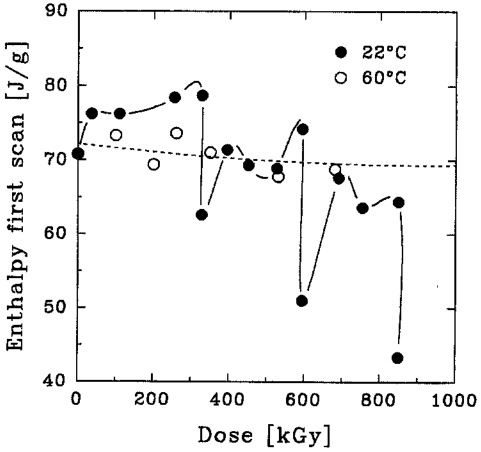

Fig. 8. Changes in the DSC melting enthalpies showing a decrease during annealing.

INVESTIGATION OF MECHANISTIC DIFFERENCES

The study of the radiation-thermal degradation of the XLPO insulation at the various temperatures clearly shows a fundamental difference between two temperature regimes. This is evident by the analysis of data obtained as dose to equivalent damage (DED), tensile elongation, gel content, and density changes during the degradation. Mechanical properties of the material degrade much more rapidly at 22 and 41°C than at 60°C and above. We sought to explain this anomalous aging behavior and to determine whether the aging is dominated by, for instance, chemical differences such as in reactive intermediates or morphological aspects. Of particular interest is to elucidate why the material aged at the higher temperatures is accompanied by an increase in the gel content while the samples aged at 22 or 41°C display a reduction in gel content which, however, can be reversed upon annealing.

Residual free radicals studied by ESR

One possible mechanism is that the crosslinking during annealing may be attributed to residual radicals immobilized during the irradiation. The radiation treatment of polyolefins leads to generation of stable residual radicals, primarily localized in the crystalline phase where, because mobility is restricted, they can have lifetimes of many years. In contrast, recombination in the amorphous phase occurs rapidly (Charlesby, 1960; O'Donnell and Whittaker, 1992). Electron spin resonance (ESR) analysis of the XLPO samples aged at 22°C, but not annealed, revealed low spin concentrations (on the order of 10^{15} spins/gram); only a minor reduction in spin concentration was observed following annealing. The G-values also indicated a more ionic species rather than true $RO_2^{\cdot}$ or $R^{\cdot}$ radicals. The contribution of these free radicals to a crosslinking reaction can only be of minor nature, since the observed crosslinking would require a high concentration of radicals, as for example during the peroxide crosslinking of polyethylene, which is carried out with initiator concentrations on the order of 10^{-4} mol/g (Kircher, 1987; Lazar *et al.*, 1990)

Hydroperoxides as intermediates

Unlike the samples aged at higher temperatures, which crosslink immediately, the samples aged at lower temperatures develop the potential for sub-

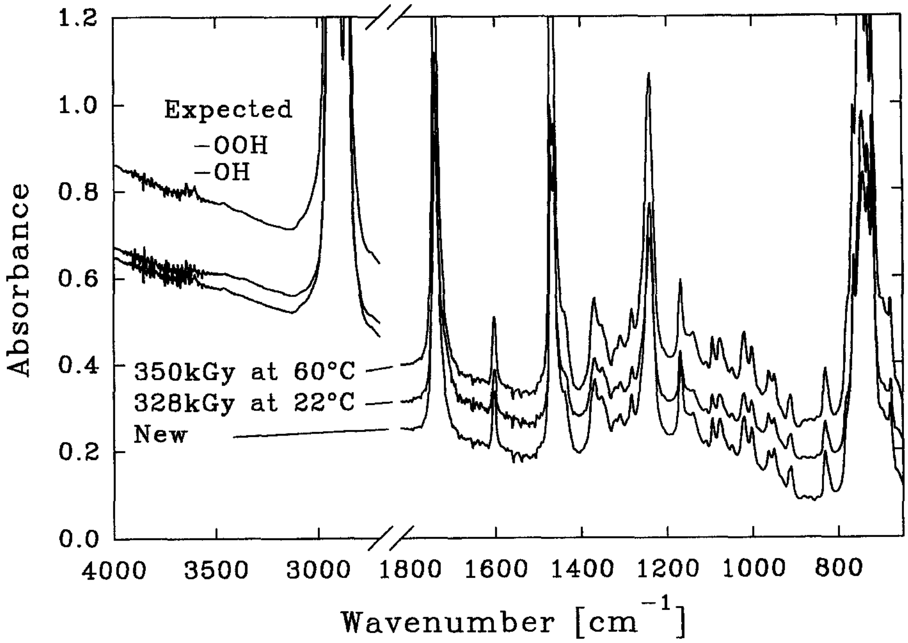

Fig. 9. Transmission FTIR spectra of the new, aged 328 kGy at 22°C (shifted by 0.1 absorbance) and aged 350 kGy at 60°C samples (shifted by 0.2 absorbance).

sequent crosslinking, which becomes evident during the annealing step. Since crosslinking is a chemical reaction often initiated or achieved by radicals, it is reasonable to postulate that low temperature aging leads to stable intermediates, such as peroxides, which could react at higher temperatures.

We first attempted to identify hydroperoxides or their derivatives by using infrared spectroscopy. This choice was motivated by the fact that isolated and adjacent hydroperoxides (for example produced during the UV-degradation of polyethylene) have characteristic strong OH-vibrations around 3500 cm^{-1} (Carlsson *et al.*, 1987). Transmission FTIR spectra (Fig. 9) of the unaged XLPO material and samples aged at 22 and 60°C for a dose of approx. 350 kGy (equivalent to severe degradation before the first annealing step) were obtained by FTIR microscopy on microtomes (10 μm). No significant hydroperoxide bands or differences between the samples were identified, but it is possible that relatively low concentrations of hydroperoxides or the complex composition of the XLPO may lead to difficult detection by normal FTIR methods.

An excellent alternative technique for detecting hydroperoxides in polyolefins exists by using derivatization with reactive gases such as nitric oxide (Carlsson *et al.*, 1987; Carlsson and Lacoste, 1991), sulfur dioxide (Henman, 1985; Carlsson *et al.*, 1986), or sulfur tetrafluoride (Carlsson *et al.*, 1991). Upon derivatization, the hydroxyl band is transformed into specific nitrate or sulfate bands, respectively (Carlsson *et al.*, 1987; Carlsson and Lacoste, 1991; Henman, 1985). We verified the potential of the technique by analyses of a HDPE film sample irradiated at 22°C for 93 kGy and subsequently exposed to nitric oxide for 1 h as demonstrated in Fig. 10, which shows the changes in the IR spectrum. Secondary hydroperoxides were transformed into secondary nitrates with new characteristic bands at 1630, 1273 and 860 cm^{-1}; secondary nitrites from alcohols are expected to produce a specific band at 1645 and 778 cm^{-1} (Carlsson *et al.*, 1987). Microtome cuttings of the XLPO samples aged at 22 and 60°C (350 kGy) were exposed to nitric oxide and were conveniently analyzed by FTIR emission spectroscopy (George *et al.*, 1995), as shown in Fig. 11, as well as FTIR transmission spectroscopy (same spectral features, but higher water noise). A weak reaction of double bonds with nitric oxide led to the formation of nitroolefins, evident from a characteristic band at 1560 cm^{-1}. No significant bands related to nitrates could be detected with the exception of a small band at 1630 cm^{-1} for the sample aged at 22°C, which is however in a region of intrinsic high water noise. Although no clear evidence of hydroperoxides was obtained, it is possible that they exist but at a concentration below the detection limit.

It was of interest to evaluate whether an air or nitrogen atmosphere *during* the annealing had any influence on the crosslinking process. As shown in Fig. 12 and indicated before, crosslinking during annealing does not occur for samples aged under inert atmosphere, which implies that oxidation products participate in the crosslinking reaction. Further oxidation during the annealing, however, is not required, since an air-aged sample annealed

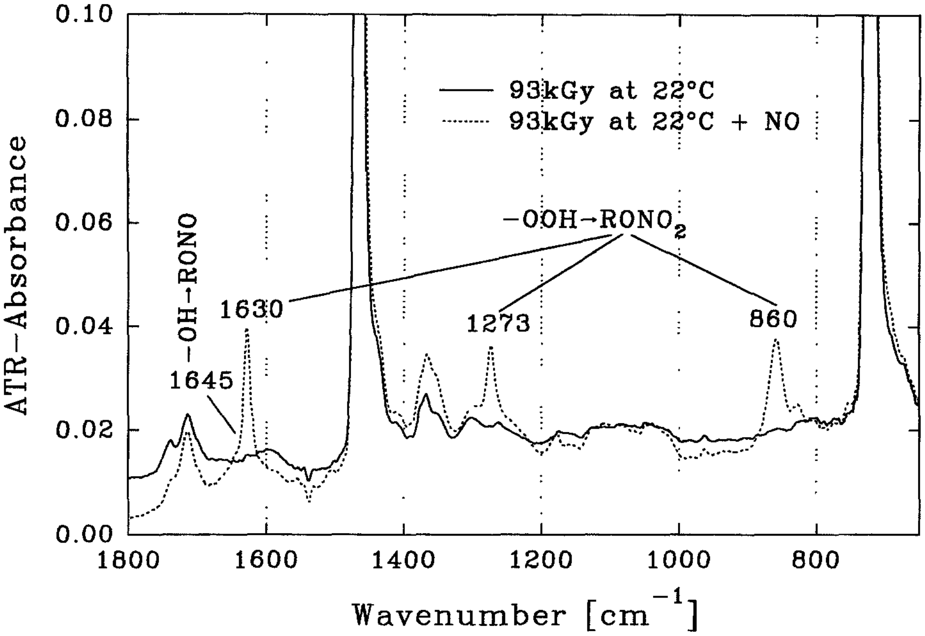

Fig. 10. ATR-absorbance FTIR spectra of an aged (93 kGy at 22°C) HDPE film sample and the same material treated for 1 h with nitric oxide showing additional bands.

under inert atmosphere still shows considerable crosslinking, which suggests that the crosslinking is inherently linked to oxidation products already present in the material.

We next attempted destruction of possible hydroperoxides with reactive gases before the annealing step (Clough and Gillen, 1981) which would reduce crosslinking efficiency. Despite extensive exposure (sufficient time to allow for gas diffusion to occur) of air-aged samples to nitric oxide (NO), sulfur dioxide (SO_2), or phosphine (PH_3), all of which react with and deactivate hydroperoxides, it was not possible to prevent the crosslinking reaction during subsequent annealing. The results of these experiments are

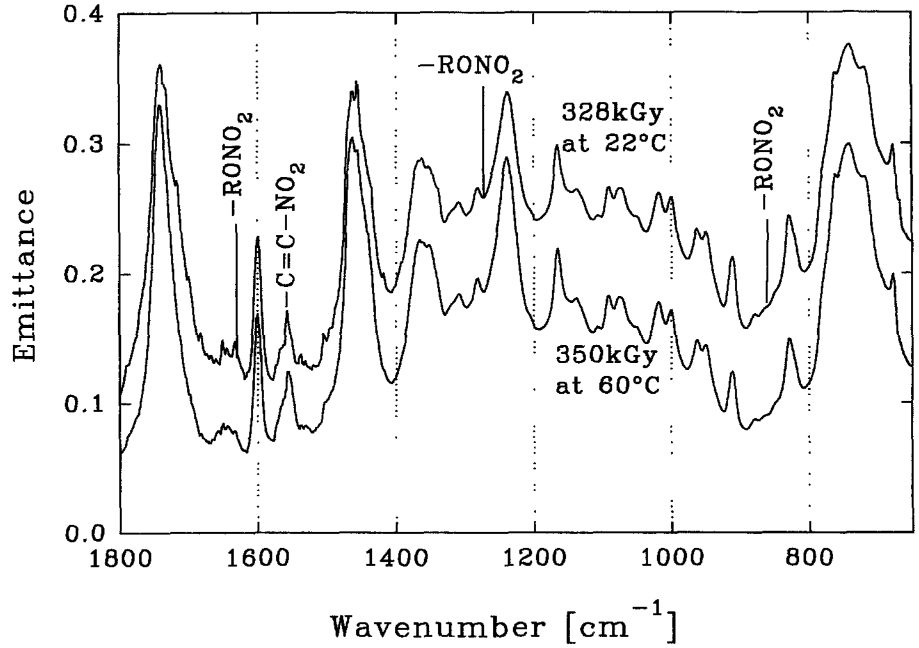

Fig. 11. FTIR-emission spectra (measured at 150°C) from microtomes of the aged XLPO samples (328 kGy at 22°C and 350 kGy at 60°C) after 1 h exposure to nitric oxide.

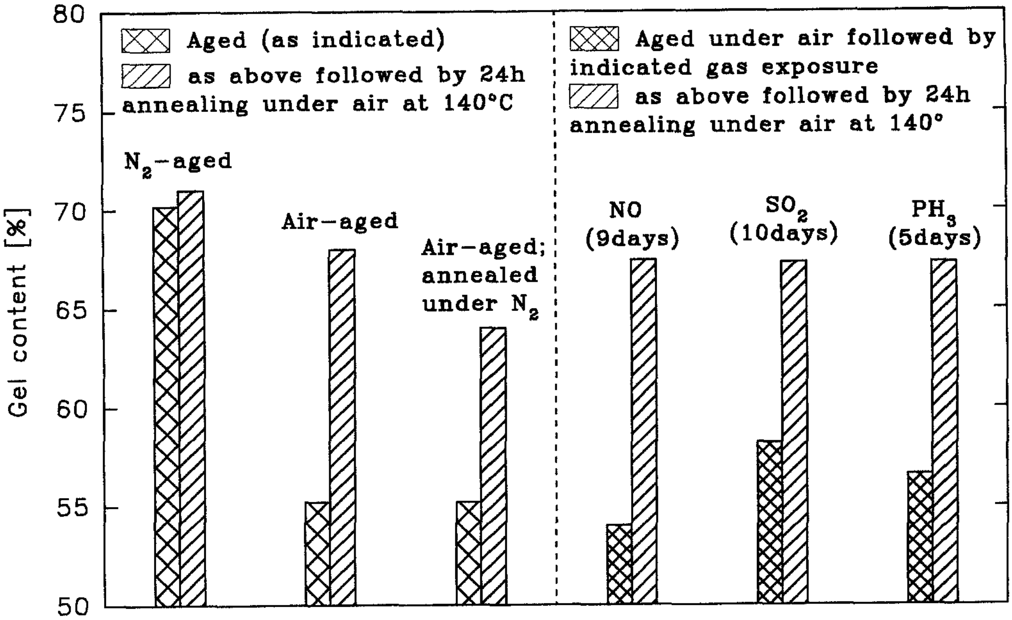

Fig. 12. Investigation of crosslinking behavior during the annealing step. The XLPO was aged to complete mechanical failure at 22°C and 485 Gy/h for a total dose of 400 kGy. Crosslinking during annealing does not occur for samples aged under N_2 and is slightly lower when annealing under N_2. Hydroperoxide deactivating gases such as nitric oxide (NO), sulfur dioxide (SO_2) or phosphine (PH_3) do not significantly reduce crosslinking.

summarized in Fig. 12. This would imply either: (1) that hydroperoxides are not the primary species responsible for the crosslinking during annealing; (2) that some peroxidic species of higher chemical stability is responsible; or (3) that a large portion of the peroxidic species may be resident in pseudo-crystalline regions at the morphological boundaries, providing protection against deactivation with reactive gases.

Additional information about the initiating species responsible for crosslinking may be obtained by

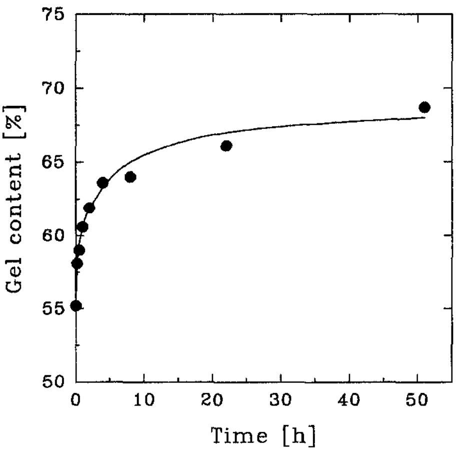

Fig. 13. Changes in the gel content of an aged sample (400 kGy at 22°C under air) with annealing time at 140°C.

studying the time dependence of the crosslinking reaction. Figure 13 shows that the increase in the gel content and thus the crosslinking during annealing at 140°C is highly time dependent. The radical crosslinking of polyethylene has been described as being controlled by the rate determining decomposition of the hydroperoxide, which follows simple first order kinetics, with the rate constant being dependent on temperature (Kircher, 1987; Beyer, 1987). Although it is difficult in our case to obtain a precise determination of the consumption of the initiating species from the measured gel formation, we attempted to compare the observed crosslinking with existing data on polyethylene hydroperoxide decomposition characteristics. Chien (1968) studied the decomposition of these hydroperoxides and found a fast decomposition reaction to approximately 85% completion followed by a slower secondary decomposition. The rate constants at 140°C were calculated to be 3.34 and 0.24 h^{-1}, respectively; the activation energy was approx. 109 kJ/mol (Chien, 1968). Similarly, for tertiary polypropylene hydroperoxide decomposition, rate constants were determined to be approx. 10.5 and 0.26 h^{-1}, respectively (Chien and Jabloner, 1968). After 1 h, a rate constant of 3.3 h^{-1} would correspond to at least 96% consumption of the hydroperoxide, which is basically equivalent to a complete reaction; a rate constant of 0.25 h^{-1} would correspond to 22% consumption. Within the same 1 h timescale, the observed gel formation in the XLPO at 140°C (Fig. 13) has only occurred to

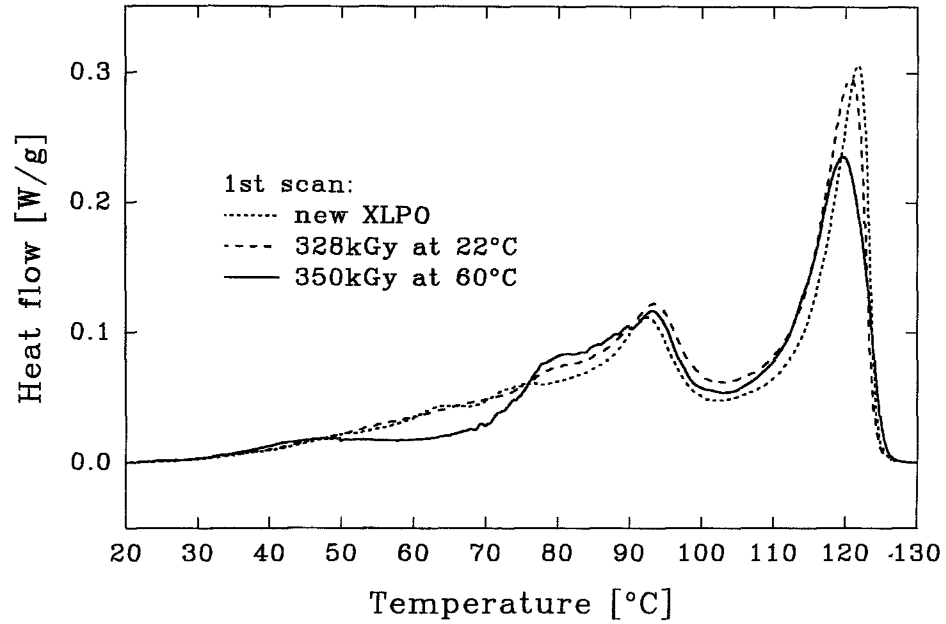

Fig. 14. DSC-scans of new XLPO and samples aged at 22°C for 328 kGy (mechanical failure) and 60°C for 350 kGy. At 22°C only small changes occur whereas at 60°C new peaks are formed at approx. 45 and 80°C.

approx. 30%. This indicates a considerably slower reaction than expected for rapid decomposition and crosslinking by hydroperoxides, but may also suggest that the initiating species is a peroxide of higher stability than typical hydroperoxides. This could, however, also be explained if in the present case the mobility of radicals which recombine and crosslink within the molten polymer is the rate determining step.

Mobility aspects studied by DSC

Partial melting of the semicrystalline polyolefin is observed over the temperature range studied. The mobility of reactive species near crystalline interfaces might play an important role in the annealing phenomenon, as discussed above. Furthermore, it is known that the exchange of tie molecules acting as the binding force between the crystalline and amorphous fraction may contribute to recovery of mechanical properties during annealing (Dunn and Williams, 1983; Nishimoto *et al.*, 1986; O'Donnell and Whittaker, 1992). Hence, the changes in the melting properties of the material during aging were investigated using DSC. The first scans are indicative of stress formed and morphological changes occurring during degradation. In Fig. 14, the scans of samples aged for approx. 350 kGy at 22 and 60°C are compared with the scan of a new material. While the sample aged at 22°C retained features identical to the unaged XLPO, it is apparent that aging at 60°C led to the formation of two new small peaks at approx. 45 and 80°C. It also appears that in the latter sample, the fraction melting at around 60°C separated into material with higher and lower melting ranges, consistent with an annealing process at this temperature. The analyses of additional samples aged at 60°C for different doses (Fig. 15), indicates that this annealing effect has occurred in all samples to a similar extent and does not correlate with an increase in dose. A minor change in the melting temperature of the main peak is also apparent, but extensive degradative changes have not appeared. The general changes for samples aged at 22°C followed by annealing at 140°C, are more pronounced (Fig. 16). The main melting peak temperature drops considerably and nearly disappears, although the material is unchanged in the lower melting regime. Despite considerable morphological changes and degradative damage, the material can retain mechanical properties.

DSC-analysis thus shows that for aging at 60°C, partial melting occurs and some of the XLPO polymer chains have sufficient mobility to allow for a weak annealing effect to contribute to morphological changes. If the aging is carried out at 22°C, this partial melting does not take place which suggests that molecular mobility is highly restricted. During subsequent annealing steps, considerable reorientation and crystallization of the material occurs.

Of the many cable insulation materials whose radiation-thermal degradation behavior we have studied to date, several semicrystalline materials such as the presently studied XLPO are the only materials found to exhibit the inverse temperature dependence

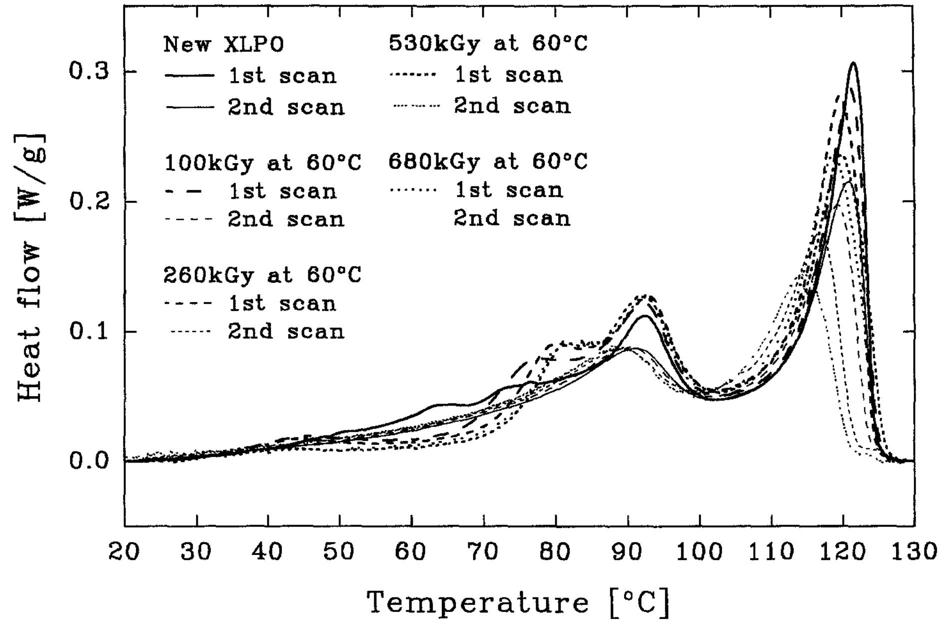

Fig. 15. DSC-scans of new samples and samples radiation aged at 60°C. The first scans show indications of new peaks at 45 and 80°C, whereas all second scans primarily display changes in the main melting peak from 122 to 115°C.

and annealing/recovery phenomenon. This supports the conclusion that crystalline morphology plays a role in the temperature dependent crosslinking responsible for these phenomena. We are presently investigating other types of partially crystalline materials.

CONCLUSIONS

The radiation-thermal degradation of an XLPO cable insulation compound was studied over a wide temperature range. Surprisingly, the material ages considerably *faster* at ambient conditions than at

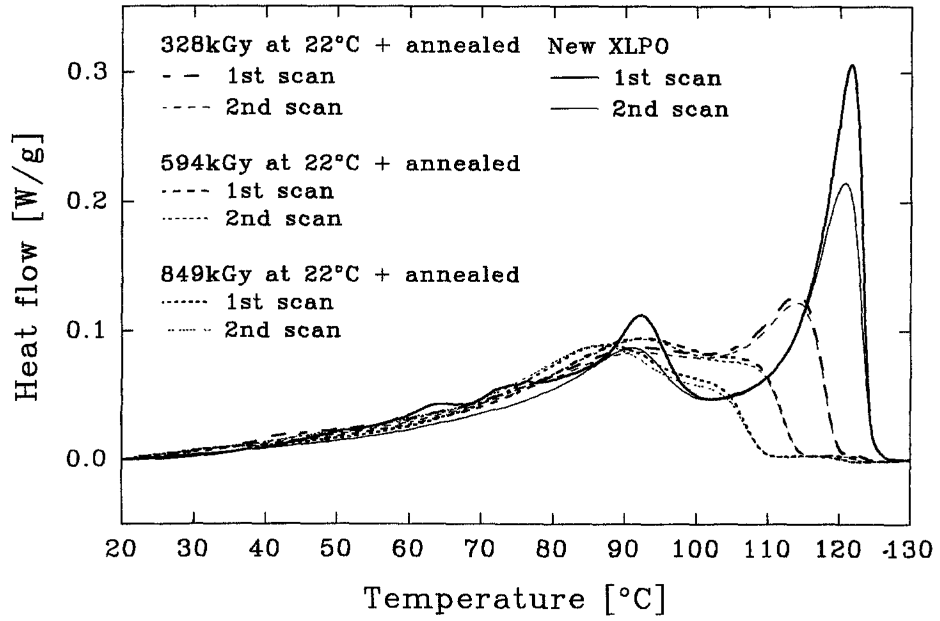

Fig. 16. DSC-scans of new samples and samples radiation aged at 22°C after the three annealing steps (328, 594 and 849 kGy). The melting behavior below 80°C is virtually unchanged whereas extensive changes are found in the main melting peak from 122 to 100°C.

elevated temperatures. This inverse temperature dependence is contrary to all established procedures for carrying out accelerated aging (eg. the Arrhenius approach), since the fundamental tenet of such approaches requires an increase in the environmental stress level to accelerate the degradation.

The aging carried out at elevated temperatures clearly differs from that at ambient conditions with regard to changes in mechanical properties, dose to equivalent damage, gel content, density, crystallinity and morphology. Following their rapid loss at ambient temperature, however, useful mechanical properties can be recovered during a subsequent annealing step above the main melting temperature of the XLPO. This recovery is accompanied by a dramatic increase in the gel content of the polymer network. Recovery does not occur for samples aged at 60°C and higher. Since oxygen must be present during the radiation aging for these anomalous effects to occur, oxidized species *must* be involved in both the rapid loss of mechanical properties at low temperatures and in the subsequent crosslinking during annealing.

The thermally-induced changes in the XLPO clearly involve chemical crosslinking reactions (and not just physical crosslinking due to changes in tie molecules), as evidenced by the dramatic increase in gel content associated with exposure to elevated temperature. From the analysis by ESR, it was concluded that the minor concentrations of radicals trapped in crystalline regions were not an important factor in the crosslinking. Also, when the degradation is carried out under nitrogen it would be expected that similarly-formed free residual radicals should result in additional crosslinking, which is not the case. The obvious conclusion that hydroperoxide species might be responsible for the chemical crosslinking could not be confirmed. Detailed FTIR analysis and attempts to deactivate any hydroperoxides by chemical treatment gave only negative evidence on the participation of hydroperoxides. The considerable time required for the crosslinking to occur, even at 140°C, provides a further indication that typical hydroperoxides (which should decompose and initiate very rapidly at 140°C) may not be responsible. The evidence indicates that some relatively stable peroxidic species is responsible for the unusual aging behaviors seen in the XLPO material. Of particular significance is the observation that for aging carried out at the elevated temperatures, or when samples aged at ambient temperature are subsequently annealed, partial melting of the XLPO compound imparts enough mobility for the latent chemical crosslinking reaction to occur. The necessity of mobility for the crosslinking to occur may indicate that any peroxides (whether hydroperoxides or other peroxidic species) may be resident in pseudo-crystalline regions at the morphological boundaries, which could also lead to enhanced stability with respect to their thermal decomposition, and to protection against deactivation with reactive gases.

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