Effect of Electron Beam Radiation on the Mechanical and Thermal Properties of Poly(4-Methylpentene-1)

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Synopsis

The changes in the mechanical and thermal properties of electron-beam-irradiated PMP of two different molecular weights ($\langle M_w \rangle = 9.2 \times 10^5$, $\langle M_w \rangle = 1.8 \times 10^6$) have been studied. Electron beam (EB) irradiation was performed either in a nitrogen or air atmosphere to a maximum dosage of 40 Mrad. Stress–strain behavior of the irradiated materials show that the lower molecular weight polymer is more affected within this dose range than the higher molecular weight material. The modulus of both PMP materials (at 23°C), however, was not affected by EB. Moreover, it was observed that by increasing radiation dose up to 10 Mrad the occurrence of yielding disappeared in the case of the lower molecular weight system but was still found in the high molecular weight material up to 20 Mrad. The elongation at break of both PMP materials was systematically decreased by increasing the dose level. The rate of stress–relaxation of irradiated samples increased as dosage increased. It is believed that oxidative degradation is promoted as a result of irradiation which induces chain scission. This result was confirmed by GPC analysis which showed that, by increasing radiation dose, the molecular weight systematically decreased. DSC measurements used to investigate the changes in thermal properties showed that the melting temperature and heat of fusion decreased as the dose increased. An interesting feature of the DSC studies was the presence of an endothermic doublet in the melting behavior that transformed into a single peak following irradiation.

INTRODUCTION

Changes in the chemical and physical properties of polymers caused by high energy radiation have received much attention. This is due to the fact that high energy radiation can induce both chain scission and/or crosslinking. For example, effects of ionizing radiation on the thermal and crosslinking behavior of fluoropolymers have been reported.[1-3] Furthermore, the degradation of mechanical and thermal properties of aromatic polymers by high energy radiation has been also investigated, showing that aromaticity generally promotes a higher stability.[4-9] Moreover, the effect of high energy radiation on the mechanical and crystallization behavior of two important polyolefins, polyethylene (PE) and isotactic polypropylene (PP), have been studied in some detail.[10-21] In this sense, a report showed that a marked reduction in ductility and an improvement in creep behavior could be achieved in ultrahigh

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modulus PE by controlling electron radiation crosslinking.[10] Moreover, the tensile strength and elongation of electron beam irradiated PE were shown to improve as a function of dose.[11] However, it was reported that when a low density PE sheet was uniformly irradiated by electrons, the tensile properties were remarkably sensitive to the dose distribution across the thickness direction.[12] Rapid degradation in tensile and elongation properties of electron beam irradiated PP were also reported.[11] Improvement in creep and crosslinking behavior of PP was observed after gamma irradiation in the presence of acetylene.[13,14] Moreover, a radiation stability investigation of various molecular weight PP materials showed that degradiation in elongation behavior was more important for lower molecular weight materials.[15]

Extensive studies have been carried out on the crystallization behavior of polyethylene that has undergone high energy irradiation.[16-20] Differential scanning calorimetry showed that the crystallinity and crystallization kinetics are affected by radiation induced crosslinking.[16] The crystallinity and melting enthalpy of low-density PE exposed to gamma radiation increased with increasing radiation dose.[17] Unusual changes in crystalline content were found upon exposure of ultrahigh molecular weight linear polyethylene (UHMWPE) and conventional high density polyethylene (HDPE) to electron beam radiation.[18-20] For example, it was observed that UHMWPE and HDPE show an increase in the degree of crystallinity upon irradiation. This increase continued even after aging at ambient conditions up to 31 months. Moreover, when UHMWPE and HDPE were physically blended, the thermal and tensile yield stress data indicated that radiation-induced chain scission was followed by recrystallization. This also suggested that chain scission did not continue with aging.

Another polyolefin, poly(4-methylpentene-1) (PMP), has also been studied to some extent. Most of the studies, however, have been concerned with gamma irradiated PMP. Electron spin resonance (ESR) of γ-irradiated PMP showed that photobleachable species are formed in the system.[21] Furthermore, the degradation of the optical clarity of PMP due to exposure to neutron and γ-radiation was studied at wavelengths in the range of 0.23–2.0 nm.[22] This study reported that PMP retained its optical clarity to doses up to 100 Mrad which is below the typical values for vessel windows in ignited fusion experiments.

To the authors' knowledge no studies have been involved with electron irradiation of PMP, or the effect of EB irradiation on its properties. Indeed this theme is the basis of the present paper.

Poly(4-methylpentene-1) is an interesting polymer due to the presence of its two tertiary carbon atoms per repeat unit: one present in the side chain, and the other in the main chain. Tertiary carbon atoms tend to promote a higher susceptibility to degradation by irradiation than secondary carbon atoms, e.g., polypropylene. Therefore, PMP should be highly prone to degradation by high energy irradiation. If the main chain tertiary carbon atom is preferentially attacked, as in the case of polypropylene, then a decrease of molecular weight is also expected.

PMP has some unique characteristics of commercial significance such as high optical transparency, high crystalline melting point, low density, good electrical properties, and heat resistance.[23] These properties allow the application of PMP as lens materials for infrared windows, membrane materials, and

food packaging. The study to be presented may be important with regard to the latter applications, since electron irradiation can be utilized for sterilization. It also provides information on the radiation sensitivity that might be utilized in EB resist applications if PMP chain structure was a part of such resist materials.

EXPERIMENTAL

Materials

Poly(4-methylpentene-1) materials used in this study were kindly supplied by the Phillips Petroleum Co. in the form of resin fluff. The weight average molecular weight (by GPC) of the lower molecular weight (LMPMP) and higher molecular weight (HMPMP) materials are 1.8×10^6 and 9.2×10^5, respectively. The dispersity factor was 15 for both PMP materials. Both materials were chemically stabilized to promote thermal oxidative resistance.

Film Preparation

Thin films were prepared by compression molding in a hot press at various temperatures and for various lengths of time to determine the suitable conditions that give a thin film with little thermal damage to the mechanical properties of PMP. These conditions will be discussed later.

Electron Beam Irradiation Processes

Electron beam irradiation was carried out at room temperature with an electrocurtain type accelerator manufactured by Energy Science, Model CB/150/180. Samples for irradiation were machined in dog-bone shape and exposed to EB irradiation in the presence of air as well as in the presence of nitrogen. Dose rate effects were investigated by changing the conveyor speed line and the electron beam current intensity according to the following equation:

$$D = KI/S$$

where D is the total dose, $K = 66.1$ Mrad ft/mA/min, I is the current intensity (mA), and S is the conveyor speed. The samples were placed on steel plates in aluminum trays and run through the conveyor system of the EB instrument. The inserts were used to minimize the EB sample-to-window distance. The stainless steel plate substrates were utilized to minimize the rise in temperature of the samples during irradiation. This effect will be discussed later. The maximum available dose per pass was 20 Mrad; hence, for the highest dosages used in this study (40 MRad) two passes were required.

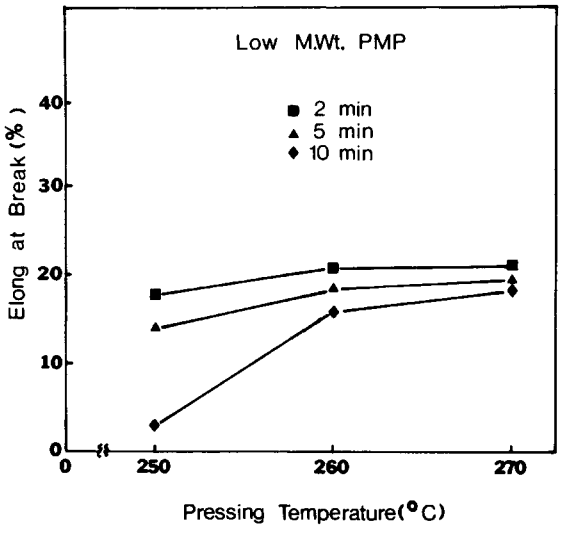
Mechanical Properties

The dog-bone irradiated samples were tested for tensile strength, elongation at break, and Young's modulus at room temperature using ASTM D638 specifications. An Instron tensile tester (Model 1122) was used throughout this work utilizing an extension rate of 20% per minute based on the initial sample length. Young's modulus was calculated from the initial slope of the

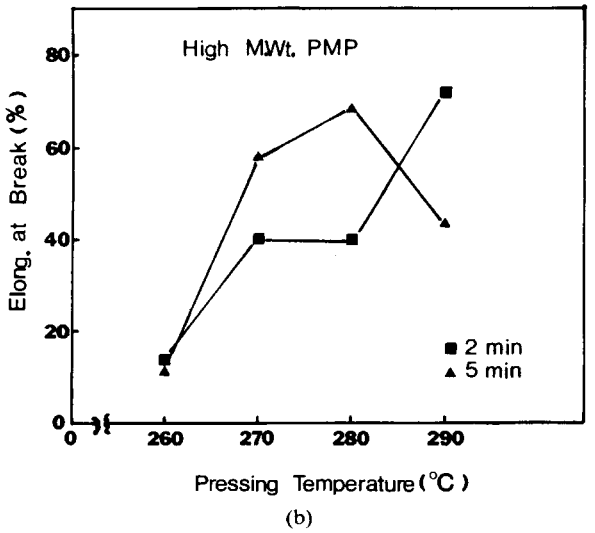
stress–elongation curves. The yield stress and tensile strength were obtained at the yield and break points respectively. Stress–relaxation behavior of the unirradiated and EB irradiated samples was assessed using the same form of samples. These samples were loaded in tension to a fixed strain of 3% on a 10 mm gauge length at a crosshead speed of 2 mm/min. The stress–relaxation was determined over a period of 45 min. All measurements were performed at ambient conditions.

Thermal Properties

Differential scanning calorimetry (DSC) measurements were performed using a Perkin-Elmer DSC-4 calorimeter equipped with a TADS data station. An indium standard was utilized to calibrate the temperature scale. The



(a)



(b)

Fig. 1. Dependence of elongation at break on pressing conditions: (a) HMPMP; (b) LMPMP.

melting point of semicrystalline PMP was determined as a function of radiation dose. A heating rate of 10°C/min was utilized, and the determinations were performed under a nitrogen atmosphere. The melting points determined for each sample after irradiation were labeled "first run." After melting the samples at 260°C for 5 min, they were cooled to room temperature at 10°C/min, and the melting point was determined again. These data were labeled "second run." These experiments allowed the determination of the effect of electron beam irradiation on the melting point of PMP (first run) and recrystallization of PMP (second run). The enthalpy of fusion was determined from the area under the fusion peak of the DSC scans. The results of melting points and enthalpy of fusion determinations are the average of at least two measurements per data point.

RESULTS

A first set of experiments was made with the objective of obtaining thin films by thermal compression molding of PMP with good mechanical properties. While compression molding is a routine preparation method, for the high

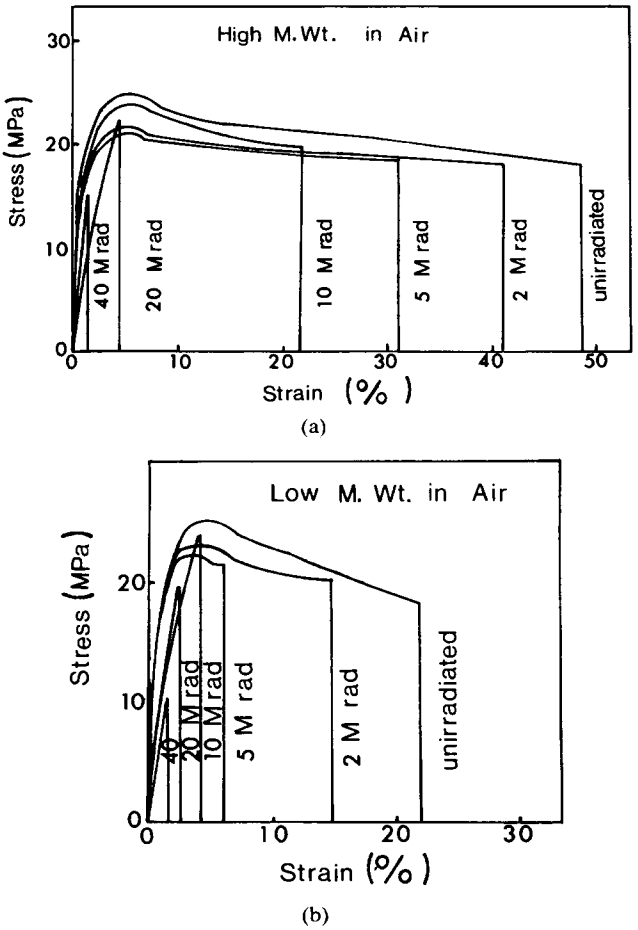


Fig. 2. Stress–strain curves of electron beam irradiated PMP in air: (a) HMPMP; (b) LMPMP.

melting olefins, it is desirable to minimize the exposure to excessive heating times yet still obtain good fusion of the fluff resin particles. Figures 1(A) and (B) presents the dependence of the elongation at break on the pressing temperature and time in the melt for low and high molecular weight PMP (LMPMP and HMPMP), respectively. In both cases, for any fixed melt time, the elongation at break tends to increase by increasing the molding temperature. For both polymers, an increase of time in the melt causes a decrease of the elongation at break undoubtedly caused by thermal oxidative degradation. Therefore, the conditions chosen to obtain uniform thin films of LMPMP and HMPMP of suitable mechanical properties were a pressing temperature of 270°C for 2 min for LMPMP and 285°C for 3 min for HMPMP, respectively. The more extreme conditions needed for the HMPMP material are due to the longer fusion time required of this higher molecular weight system.

Mechanical Properties

Properties at Yield

Figures 2(A) and (B) show the typical stress–strain curves for electron beam irradiated HMPMP and LMPMP in air. Following yield, elongation occurred by necking for both PMP materials. Irradiation of LMPMP to 10 Mrad causes the samples to break prior to yield. On the other hand, increasing the

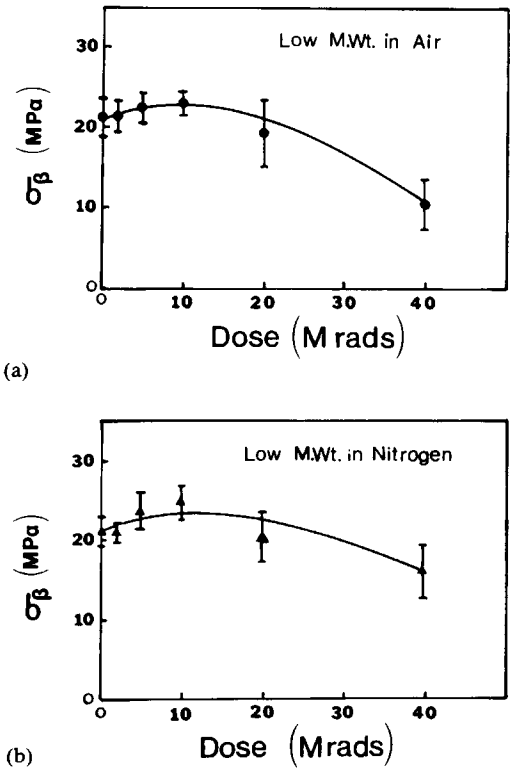


Fig. 3. Effect of electron beam irradiation on the tensile strength at break of low molecular weight PMP: (a) irradiation in air; (b) irradiation in nitrogen.

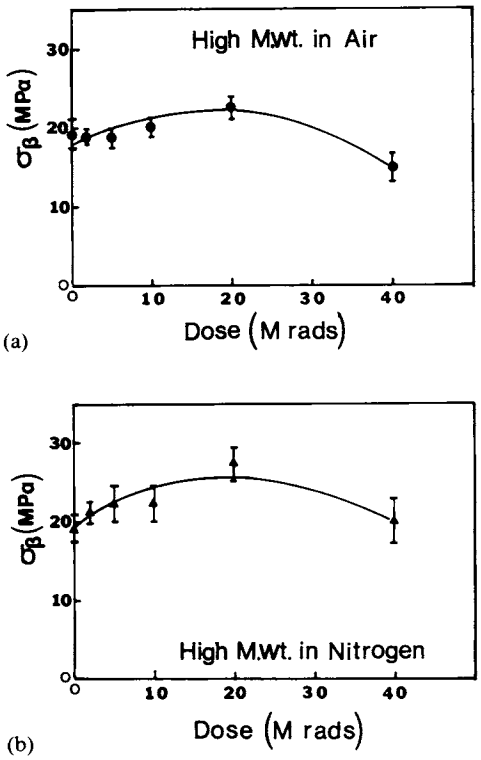


Fig. 4. Effect of electron beam irradiation on the tensile strength at break of high molecular weight PMP: (a) irradiation in air; (b) irradiation in nitrogen.

radiation dose up to 20 Mrad, the occurrence of yielding of HMPMP also disappeared. This loss of yield behavior occurs whether irradiation is performed either in an air or nitrogen atmosphere. At low dosage in air, there is a slight decrease in the yield strength of both PMP materials with increasing dose. However, irradiation in the presence of nitrogen for the same dosage was found to have no effect on yield strength. The yield elongation of both PMP materials was not affected by irradiation up to 5 Mrad in air or a nitrogen atmosphere.

Properties at Break

The tensile strength at break, σ_B, for both molecular weight samples is plotted as a function of dose in Figures 3 and 4 for the irradiation environment of air and nitrogen. Comparing Figure 3 with Figure 4 shows that the tensile strength at break of LMPMP is more affected than that of HMPMP under the dose levels studied, regardless of the irradiation atmosphere. This may be expected since HMPMP has an initially larger elongation at break than LMPMP. Moreover, this is in accordance with a previous report, which showed that the decrease of elongation during irradiation is much smaller for high molecular weight polypropylene than in the same material of low molecular weight.[15] As shown in Figure 3, the tensile strength at break of LMPMP is slightly increased by increasing the dose from 2 to 10 Mrad.

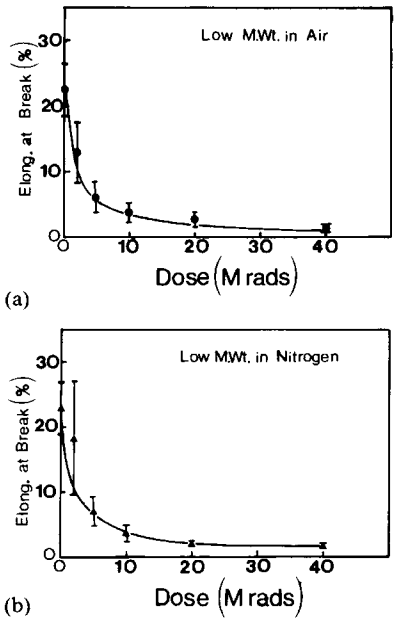


Fig. 5. Elongation at break of low molecular weight PMP as a function of radiation dosage: (a) irradiation in air; (b) irradiation in nitrogen.

Increasing the dose to 40 Mrad is accompanied by a marked decrease in tensile strength at break by close to 50% of its initial value. The same trends are observed when irradiation is performed in nitrogen; however, the magnitude of the change is slightly smaller [Fig. 3(B)]. Similar trends are found to persist in the HMPMP materials [Figs. 4(A) and (B)] except that an initially slight increase is found to continue up to about 20 Mrad. This point appears in agreement with the data given in Figures 2(A) and (B), which indicate that above 10 and 20 Mrad the occurrence of yield disappeared in LMPMP and HMPMP, respectively.

The presence of oxygen seems to have an important role in the degradation of the properties of PMP upon irradiation. As reported by Goodhead,[24] oxygen can diffuse readily into PMP to form peroxy species that contribute to the degradation process. Consequently, the degradation of the tensile strength at break may be expected to be more important when PMP is irradiated in air.

Figure 5 and 6 present the elongation at break for LMPMP and HMPMP as a function of radiation dose, respectively. These plots indicate that irradiation has a pronounced effect on this parameter in the presence of either atmosphere. The elongation at break of both materials decreases dramatically as dose increases. The largest change occurs at low dose levels, indicating the very strong sensitivity of PMP to radiation. This severe effect can be represented numerically, e.g., at a dose level of 10 Mrad in air, the loss in elongation at break is about 80% for LMPMP and 60% for HMPMP. Increasing the dose up to 40 Mrad, produces an even lower elongation at break and both PMP materials become brittle.

As expressed before, it is understood that the presence of air during irradiation favors the formation of peroxy radicals which decompose and

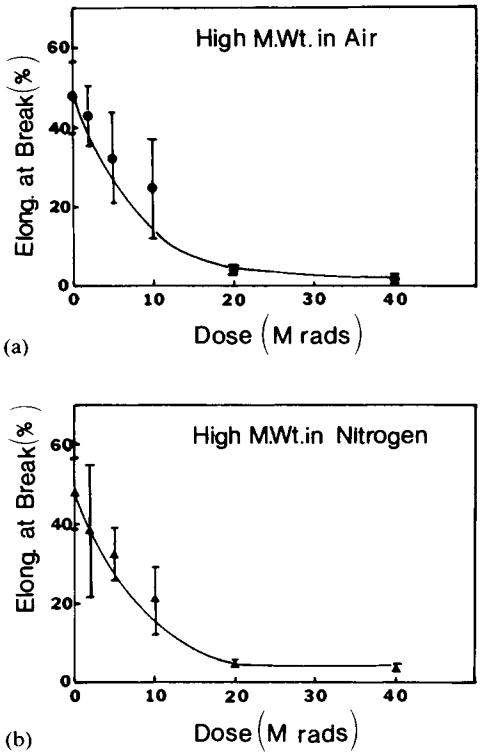


Fig. 6. Elongation at break of high molecular weight PMP as a function of radiation dosage: (a) irradiation in air; (b) irradiation in nitrogen.

cause degradation of PMP. However, the results of the elongation at break are the same regardless of the atmosphere utilized during irradiation. It is believed that active free radicals are formed in the presence of nitrogen. These radicals can interact with oxygen from the atmosphere during the period between irradiation and testing, therefore, causing degradation to be nearly comparable to PMP irradiated in air. In this context, the study of aging behavior after irradiation might be expected to be important as will now be discussed.

Aging Effects on the Elongation at Break

It was postulated that samples irradiated in nitrogen may interact with atmospheric oxygen during the period between irradiation and testing. The study of the effect of storage time after irradiation on elongation at break could shed some insight into this postulate. If the postulate is correct, the elongation at break of samples irradiated in nitrogen should display a more pronounced decay with aging time than that of samples irradiated in air. Figure 7 shows the effect of aging time on the elongation at break of irradiated HMPMP in the presence of air and nitrogen. Indeed, the presence of oxygen on irradiation seems to have an effect. The elongation at break of PMP irradiated in nitrogen decreases slightly more with aging time than that of PMP irradiated in air. However, this difference is *only observed* in samples irradiated to low doses (2 Mrad). The decrease in elongation due to storage,

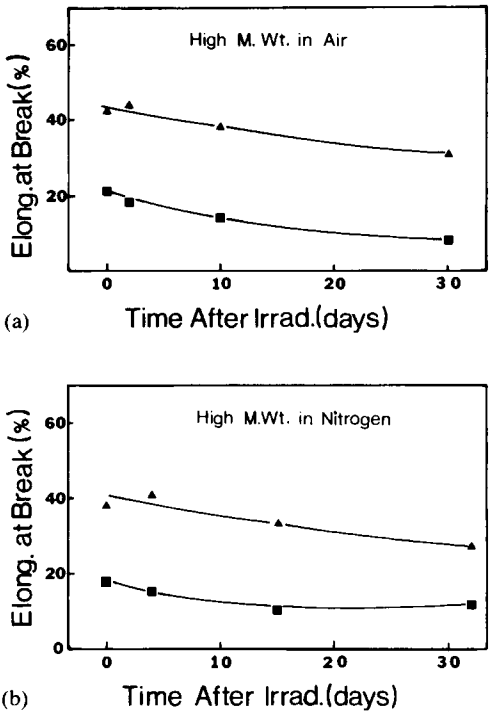


Fig. 7. Aging effect on the longation at break of preirradiated HMPMP: (a) irradiation in air; (b) irradiation in nitrogen.

then, may be interpreted in terms of the presence of trapped free radicals in the glassy (amorphous) or crystalline structure of PMP. Subsequently, these radicals can form peroxy radicals that cause degradation. Furthermore, the larger loss in elongation in the case of samples irradiated at low doses can be a result of consuming most of the proxy radicals in degradation in the early stages after irradiation. Likely, this behavior implies that the aging behavior may be thickness dependent if oxygen is diffusion limited. We have not, however, investigated this variable.

Effect of Dose Rate on Elongation at Break

Investigation of the effect of *dose rate* was performed by changing the line conveyor speed and the electron current intensity proportionally to give the same total dosage at a faster rate. For example, to obtain a varied dose rate for a total dosage of 2 Mrad, the conveyor speed runs are 20, 40, 80, and 120 ft/min and the corresponding electron current intensities are 0.6, 1.2, 2.4, and 3.6 mA, respectively.

The relation between dose rate and elongation at break of HMPMP is shown in Figure 8. At a low total dose of 2 Mrad no effect is noticed by changing the dose rate. On the other hand, at a total dose of 10 Mrad, the elongation at break somewhat decreases as the dose rate increases. Therefore, the elongation at break is somewhat dependent on the rate of energy deposition. As the conveyor speed increases, the rate of energy deposition also

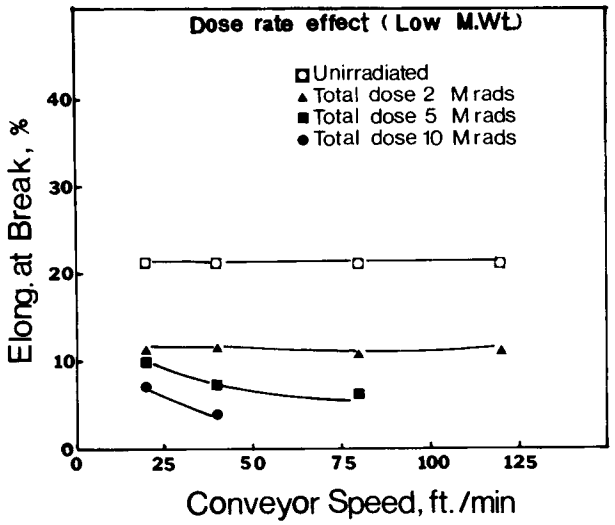


Fig. 8. Effect of dose rate on the elongation at break of high molecular weight PMP at several radiation doses.

increases. Consequently, at constant energy (total dose) as the rate of energy deposition increases, a considerable rise in the sample temperature occurs during irradiation. Using the energy equivalent of 2.4 cal/g/Mrad and a general heat capacity value of 0.4 cal/g/°C, a rise in temperature of ca. 6°C/Mrad can be estimated. Accordingly, by increasing dose rate, the material is distinctly brought to temperature above T_g (30°C) for sufficient time to permit a higher mobility of the free radicals in the amorphous phase. If this is so, a larger number of radicals may be effective at higher dose rates in promoting more peroxy species that can contribute to the degradation process.

Modulus of Elasticity

There is no significant effect of irradiation on the modulus of elasticity of LMPMP and HMPMP as determined at ambient temperatures in either atmosphere. Moreover, no noticeable change in modulus was observed by increasing the radiation dose in both PMP materials. Indeed, little change was expected in this variable at ambient temperature since the system is in the lower edge of its glass transition region at the time of measurement.

Effect of Irradiation on Stress–Relaxation

The study of the effect of irradiation on stress–relaxation is very important since the rate of stress decay indicates whether crosslinking or chain scission occurs. If chain scission dominates, the rate of stress decay would increase as radiation dose increased. However, if crosslinking occurred, then the rate of stress decay would decrease with increasing radiation dose. Figure 9 presents the stress relaxation results for HMPMP at various levels of irradiation. The stress decay of irradiated samples is distinctly faster than that of unirradiated PMP. Furthermore, the rate of stress decay increases as the dose increases. After a relaxation time of 45 min, the stress is considerably lower for PMP

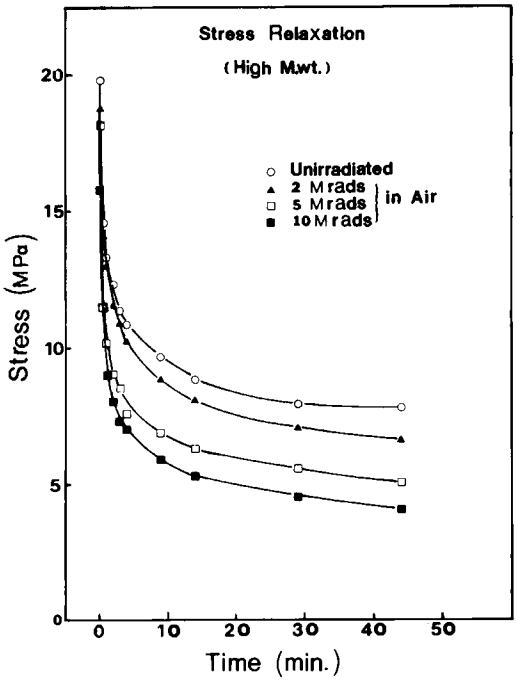


Fig. 9. Stress–relaxation curves for HMPMP irradiated in air to various doses.

irradiated to higher doses. Since stress decay occurs due to disentanglement of polymer chains and molecular reordering as influenced by relaxation times, an increase of the rate of decay upon irradiation clearly implies the occurrence of polymer degradation by chain scission—likely the dominant amount occurring in the amorphous phase.

Thermal Properties

Figure 10 presents "first run" thermograms for the HMPMP material irradiated to various doses. Unirradiated PMP presents two melting endotherms: the major peak occurs at 239°C, while a small one peaks at 231°C. The presence of a doublet melting peak has been previously observed in PMP.[25,26] However, in these two earlier studies, the doublet melting peak was attributed to a change in morphology caused by uniaxial drawing. Wide angle X-ray scattering of the PMP samples used in the present study shows no sign of orientation following molding. Therefore, there may be other reasons for the presence of the second peak, and they will be discussed later.

Upon an increase of radiation dose, two effects are noticed. The temperature at the maximum of the high melting peak (melting point) decreases, and the lower melting peak decreases, and, in fact, vanishes at the higher dose levels. The decrease of the melting point is illustrated in Figure 11 as a function of dose. The melting temperature decreases from 239°C at 0 Mrad to 222°C at 40 Mrad. Following recrystallization, the melting temperature (second run) was again determined. It was found that the melting temperature before and after recrystallization *is the same*. This indicates that, although

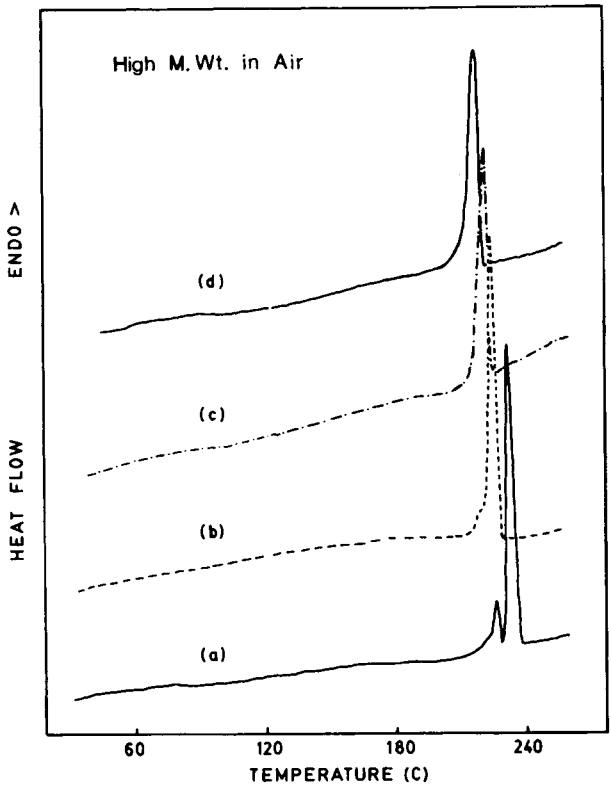


Fig. 10. Effect of irradiation dose on the melting behavior of HMPMP: (a) unirradiated; (b) irradiated 10 Mrad; (c) irradiated 20 Mrad; (d) irradiated 40 Mrad.

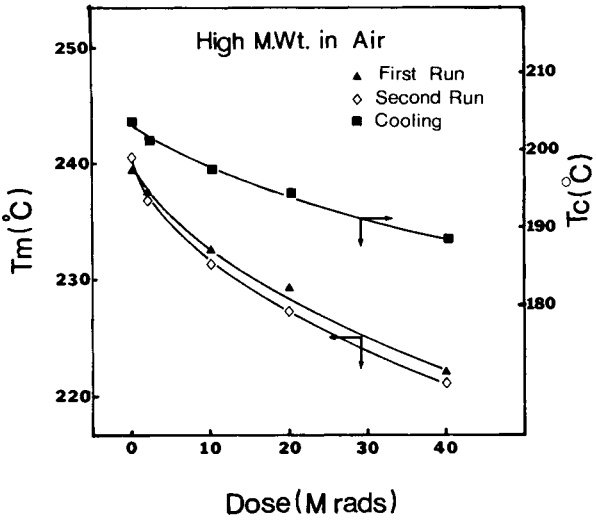


Fig. 11. Effect of irradiation dose on the melting and recrystallization temperatures of HMPMP.

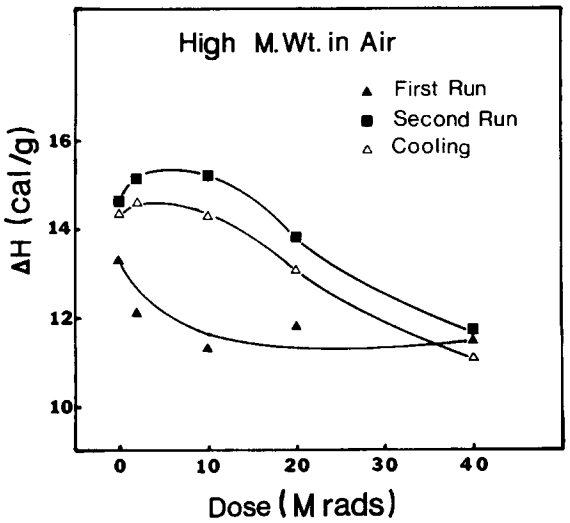


Fig. 12. Effect of irradiation dose on the enthalpy of fusion and recrystallization of HMPMP.

irradiation decreases the melting point, it does not seem to change the perfection of the crystals formed upon recrystallization. Figure 11 also shows that the crystallization temperature from the melt decreases as radiation dose increases. These data in conjunction with the decrease of melting temperature indirectly suggest a decrease of molecular weight with EB radiation.

The observed enthalpy of fusion (ΔH_f) is presented in Figure 12 as a function of dose. The enthalpies of fusion reported represent the area under the whole melting endotherm including *both melting peaks*. The value of ΔH_f decreases by 25% with increasing dosage. The "first run" determinations show the largest decrease at low EB doses (below 10 Mrad). Above 10 Mrad, ΔH_f seems to level off at ca. 11 cal/g. In *recrystallized PMP* (*second run*) ΔH_f goes through a slight maximum at 10 Mrad and then decreases monotonically to a value of 11 cal/g at 40 Mrad. Restated, irradiation of PMP to 10 Mrad provokes a small increase of the crystalline content after recrystallization. But, at higher doses, the crystalline content decreases monotonically. These changes follow the variation of crystallization enthalpy with radiation dose. Therefore, the crystallinity attained during cooling varies as the irradiation dose increases.

At this point, the second effect of radiation dose on the melting endotherms should be addressed. As was shown in Figure 11, the lower melting peak at 231°C vanishes *after* an irradiation dose of 20 Mrad. However, a different situation is found in the "second run." After melting at 260°C for 5 min and cooling at 10°C/min two endotherms are *again observed* for any dose level. Recrystallization by cooling at 10°C/min causes the *second endotherm* (*lower melting*) *to reappear*. Recrystallization at higher cooling rates (20, 40, 60°C/min) also promotes the same effect.

Figure 13 represents the results of an experiment designed to determine if irradiation is causing the decrease of the lower melting peak. Curve (a) corresponds to the "first run" of a sample irradiated at 20 Mrad. As expected, only one endotherm is observed. Curve (b) shows the "second run" of the same

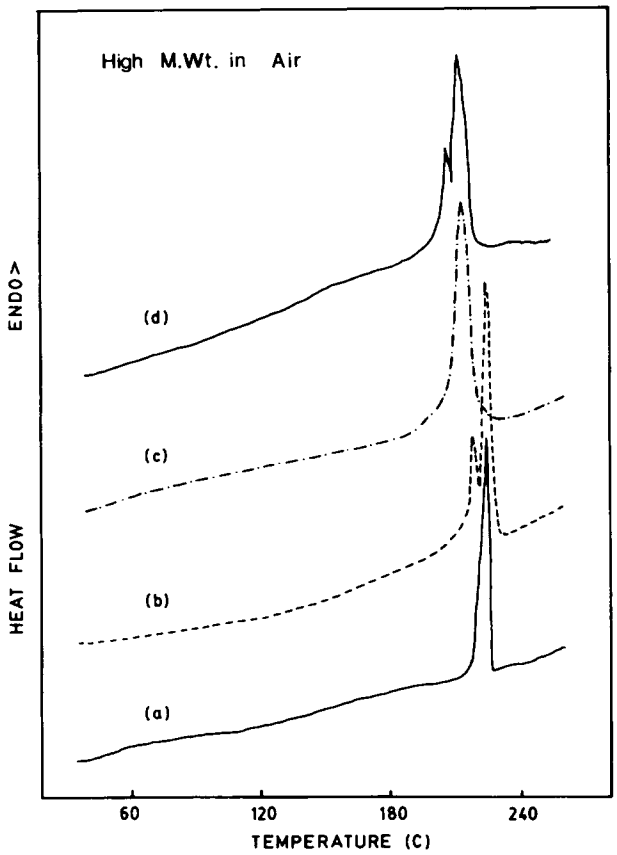


Fig. 13. Effect of stepwise irradiation on the melting behavior of HMPMP: (a) irradiated 20 Mrad, first run; (b) same as (a), second run; (c) sample (b) following solidification was again irradiated 20 Mrad (cumulative dose = 40 Mrad), first run; (d) same as (c), second run.

sample. Two endotherms are now present. The higher melting endotherm is located at the same temperature as in (a) (229°C), and the lower melting endotherm is located at 222°C. Curve (c) represents the identical sample from (b) that was irradiated another 20 Mrad. The total *cumulative* dose is 40 Mrad before any melting. This is a "first run" scan and only one endotherm seems apparent. The melting temperature (221°C) and the heat of fusion (11 cal/g) are in excellent agreement with samples irradiated to 40 Mrad in one step. Curve (d) is a "second run" scan of sample (c). Again, the two melting endotherms are observed at 215 and 221°C. Some conclusions can be drawn from this series of experiments. First, electron beam irradiation is suppressing the lower melting peak. Second, the presence or absence of this peak seems to be reversible in the sense that, by irradiating or recrystallizing the sample, the lower melting peak can be suppressed or can be made to appear respectively. Another interesting feature is that the temperature difference between the two peaks remains almost constant after further irradiation.

The presence of two melting endotherms might be due to the existence of two different crystal structures that melt at different temperature, and/or to the crystallite size distribution or its perfection. The first speculation might be

invoked that PMP is a polymorph; i.e., it can crystallize in different unit cells depending on the crystallization conditions. Five polymorphic forms, in fact, have been reported. However, four of these are obtained from solutions using different solvents and thermal history.[27] Modification I (tetragonal) appears to only be obtained from the melt, thereby suggesting that a polymorph is not the explanation. Furthermore, wide angle X-ray scattering patterns of unirradiated PMP and PMP irradiated to 40 Mrad do not show any evidence of different unit cell parameters. Also it would be difficult to understand why a given polymorph would be particularly dependent upon irradiation. A second argument comes about because the melting endotherm represents a distribution of the crystallite sizes present in the samples. Higher melting species represent larger crystallite sizes (or greater perfection). Therefore, the two endotherms may represent a bimodal distribution of crystallite sizes but it is still difficult to account for why irradiation would cause the less perfect (or smaller) crystallite to change the DSC melting response as observed. Indeed, a suitable explanation for the DSC response with radiation is still not available.

DISCUSSION

Overall the experimental data indicate that PMP experiences chain scission by electron beam irradiation. For example, the stress at break decreased as the dose increased. Similarly, the elongation at break decreased dramatically as dose increased, making PMP very brittle at dose levels approaching 20 Mrad. Furthermore, the stress–relaxation experiments also point to similar conclusions for the stress decay of irradiated samples was considerably faster than that of unirradiated PMP. Also, the rate of decay increased as the dose increased. The stress decay that occurs can be interpreted to result from the disentanglement and relaxation of stressed chains. Other factors being equal, the higher the molecular weight of the polymer, the more entanglements per chain occur; consequently, the slower the rate of stress decay. Therefore, the increase of the rate of stress–relaxation observed upon irradiation implies the occurrence of polymer degradation by chain scission.

The thermal analysis behavior of irradiated PMP also indicated that PMP may undergo chain scission upon irradiation. The melting temperature of HMPMP decreased as the dose increased. It is a fact that the thermodynamic melting point of semicrystalline polymers decreases as molecular weight decreases and/or as the number of defects increases.[28,29] The melting temperature reported in this manuscript are clearly not equilibrium determinations. However, the observed melting points are expected to follow the same trend of thermodynamic melting points. Therefore, the DSC results indicate that PMP is undergoing chain-scission induced by irradiation. It was also observed that the crystallization temperature from the melt decreased as radiation dose increased. This may seem contradictory since lower molecular weight polymer may crystallize faster at a higher temperature. However, the important factor to be considered is the undercooling; i.e., the temperature difference between equilibrium melting point and crystallization temperature. In Figure 13, it was observed that the melting temperature decreased by 17°C after radiation to 40 Mrad, whereas the crystallization temperature only decreased by 11°C with the same dose level. Consequently, the undercooling decreased as radiation dose increased, suggesting that there is chain scission.

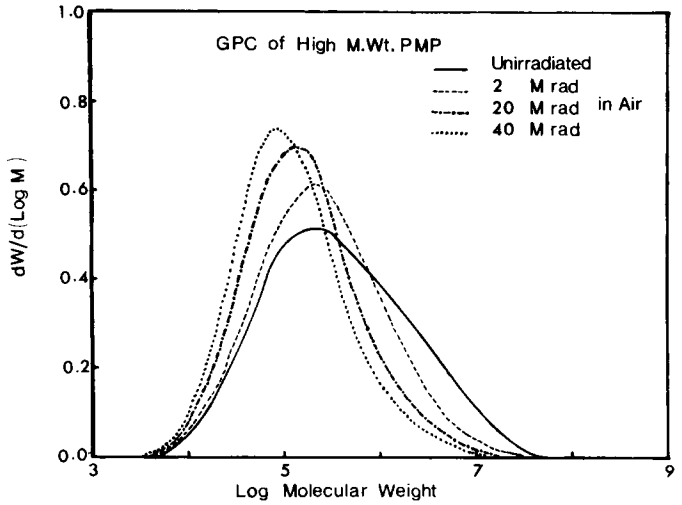


Fig. 14. Molecular weight distribution curves of HMPMP as a function of electron beam irradiation dose.

Some of the data obtained, however, did not clearly suggest the presence of chain scission. For example, the enthalpy of fusion was found to decrease upon irradiation, indicating a lower crystalline content. Lower molecular weight polymer might well present a higher crystalline content. Therefore, to determine whether chain scission had indeed occurred, the technique of gel permeation chromatography was utilized. Figure 14 shows plots of the molecular weight distribution of the HMPMP material for various radiation doses. The figure clearly indicates a shift of the distribution towards lower molecular weights as the dose increases. The weight average molecular weight decreases from 1.8×10^6 at 0 Mrad to 0.42×10^6 daltons at 40 Mrad. Furthermore, the molecular weight distribution also narrows as radiation dose increases. The polydispersity ratio decreases from a value of 15.7 at 0 Mrad to 7.0 at 40 Mrad. Thus, the GPC experiments confirm the fact that PMP undergoes significant chain scission upon EB irradiation, likely an oxidative mechanism of degradation in this case. In this respect, Goodhead[24] has proposed that oxygen can readily diffuse into PMP to form peroxy species that contribute to the degradation process of irradiated PMP.

In the present report, we observed that the presence of air during irradiation had an important effect on some of the properties tested after irradiation. For example, the tensile strength at break decreased to lower values upon irradiation in air than upon irradiation in nitrogen. However, the elongation at break was the same regardless of the atmosphere used during irradiation. Nevertheless, it was observed that aging time after irradiation decreased the elongation at break (Fig. 7). In addition, the decay was more important in samples irradiated in nitrogen. That is, the elongation at break of HMPMP irradiated in nitrogen decreased more than that of PMP irradiated in air. Hence, not only does oxygen seem to play an important role on the degradation mechanism, but also radiation in nitrogen seems to induce the formation of free radicals that at a later time can undergo attack by oxygen from the environment and lead to degradation. It can be postulated, then, that electron

beam irradiation induces chain scission of PMP through an oxidative mechanism involving the production of free radicals that can abstract oxygen from the environment to form peroxy species and further contribute to degradation likely through the beta scission process. However, it is important to recall that the PMP utilized for these studies contained antioxidants. Since it has been reported that antioxidants can effect the nature of degradation by irradiation, one must recognize that the stabilization of a given polymer may have an influence on the results.[30]

It was mentioned in the introductory section that PMP may be highly prone to degradation by high energy radiation due to the presence of two tertiary carbon atoms per repeat unit. Recall that isotactic polypropylene possesses a tertiary carbon in its repeat unit and is known to be quite prone to damage by radiation effects. It is therefore of some interest to attempt to compare these two polymers. Wang et al.[11] reported that upon electron beam irradiation of highly isotactic polypropylene to 40 Mrad; the tensile strength and elongation at break could not be determined because the samples became too brittle and broke spontaneously, i.e. there was high degradation. In the present study, however, the tensile strength of PMP only decreases by 50% after 40 Mrad irradiation dose. Similarly, the elongation at break decreases by 60% after irradiation but the properties can still be easily determined. Consequently, this may surprisingly suggest that PMP may have a higher resistance to electron beam radiation. This statement is possibly presumptuous, however, since, to make an equal comparison, similarity in initial molecular weight (and distribution) as well as stabilizer may be demanded. These variables certainly have not been considered within our study. In addition, irradiation at ambient will be above T_g for isotactic polypropylene but will be below or near T_g for PMP unless the dose rate is high enough to produce local heating by irradiation. This factor may also influence the behavior of the two polyolefins since mobility of the amorphous phase will be quite different, which, in turn, is important in assessing irradiation effects. Hence, it seems that a more "matched" comparison of PMP with polypropylene would be required taking into account the variables mentioned above and possibly others as well before passing judgment on the relative stability difference of these two polyolefins.

CONCLUSIONS

Based on the experimental results obtained from mechanical and thermal properties tests several points can be stated:

1. The effect of atmosphere (nitrogen vs. air) displayed little difference in final properties—at least up to a 5 Mrad dose. However, above this dosage level the effect of nitrogen is to reduce the loss in mechanical behavior relative to that observed for an air environment. This can be accounted for on the basis of differences in oxidative scission.
2. Upon increasing the radiation dose up to 10 Mrad, the occurrence of yielding disappeared in LMPMP but was still observed for HMPMP up to a higher dose level of about 20 Mrad.
3. The tensile strength at break of LMPMP is more affected by dose than that of HMPMP. Moreover, no effect was observed by changing the irradiation atmosphere from air to nitrogen.

4. Electron beam irradiation has a remarkable effect on the elongation at break, it decreases dramatically as dose increases. However, the change in ambient temperature modulus is very small for both PMP materials—likely due to being below the T_g of the amorphous phase.
5. The stress–relaxation behavior of irradiated samples is faster than that of unirradiated PMP and systematically increases in relaxation rate as dosage increases.
6. The elongation at break further decreases with time (aging) after irradiation regardless of LMPMP or HMPMP and atmosphere. This is believed to be by further oxidative beta scission due to the remaining radicals and peroxide groups.
7. The melting temperature and heat of fusion both decrease as the dose increases. This occurs for both initial as well as later (2nd) DSC scans. In addition, the DSC analysis presented doublet melting peaks that were transformed into singlet peaks by EB irradiation. A suitable explanation for this transformation is not yet available.
8. GPC results indicate that by increasing radiation dose, the molecular weight systematically decreases and clearly displays that the molecular weight of PMP is very sensitive to dose level. *This observation clearly accounts for the mechanical property dependence on dosage level.*

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