

Durability of radiation-sterilized polymers:

12. The effects of nucleating agent on the oxidative degradation of polypropylene

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The radiation stabilities of high- and low-molecular-weight polypropylene (PP) with and without nucleating agent (NA) are compared. It is found that PP with NA are less stable during irradiation than PP without NA, especially the lower-molecular-weight PP. In order to correlate these results with their morphology, haze measurements, differential scanning calorimetric analysis, dynamic mechanical relaxation studies, chemiluminescence analysis, pulsed nuclear magnetic resonance analysis and micrography of the PP have been carried out. In both cases (high- and low-molecular-weight PP), the addition of NA increased the transparency and peak crystallization temperature of the PP. These qualities are an advantage in the production of medical disposables. The high transparency and peak crystallization temperature in the PP with NA were found to be due to their small spherulite size. In the high-molecular-weight PP, the spherulite size of the PP without NA was 1.5 times larger than the PP with NA, while in the lower-molecular-weight PP, it was 5.0 times larger. From the dynamic mechanical relaxation studies and pulsed nuclear magnetic resonance analysis of the high-molecular-weight PP, the unstable PP with NA was found to be more crystalline than the PP without NA. Accordingly, a higher concentration of peroxy radicals, which cause the oxidative degradation of PP, was found in the PP with NA than in the PP without NA. In the low-molecular-weight PP, the PP with NA was also found to be more crystalline than the PP without NA from their dynamic mechanical relaxation studies. In contrast, the chemiluminescence measurements showed that a higher concentration of peroxy radicals was found in the PP without NA than in the PP with NA. Two reasons were given to account for this discrepancy. From pulsed nuclear magnetic resonance analysis, at the temperature at which the chemiluminescence measurement was carried out, the PP without NA was found to be more crystalline than the PP with NA. The other reason given was due to a difference in spherulite size between these PP.

(Keywords: polypropylene; nucleating agent; irradiation; sterilized polymers; oxidative degradation; spherulite)

INTRODUCTION

Sterilization of medical supplies has been widely carried out using both γ -ray and electron beam radiation. Polypropylene (PP) is one of the most popular polymers in the manufacture of medical disposables because of its high transparency and good mechanical properties. Since medical devices made from PP have good transparency, when used as a syringe, for example, its contents can easily be seen. It also has the advantages of cost and chemical inertness over other polymers. Its only setback is that it is adversely affected by γ -radiation, undergoing oxidative degradation if irradiated in air^{1,2}.

Polypropylene also undergoes post-irradiation degradation, which is also oxidative in nature, indicating that the residual radicals continue to react with oxygen in the atmosphere. It has been reported that the oxidative degradation of PP can be prevented by the addition of a radical scavenger² and by heat treatment of the

irradiated sample³. Degradation can be further minimized by introducing suitable additives to the PP⁴.

Our previous work on the oxidative degradation of PP has shown that a random copolymer of PP with 6% ethylene⁵, PP quenched at lower temperature during moulding⁶ and high-molecular-weight PP⁷ were stable on irradiation. These PP samples were more stable on irradiation because of their lower crystallinity compared with the unstable ones. It was also observed that the peroxy radical concentration, which caused the degradation of PP, was lower in PP of lower crystallinity. In our recent paper⁸, we found that the degradation of high-molecular-weight PP with lower crystallinity was less than that of low-molecular-weight PP, since the formation of peroxy radicals, which caused oxidative degradation, was also smaller. Therefore, control of crystallinity of the PP plays an important role in enhancing radiation stability.

In recent years, apart from antioxidant, nucleating agent has also been added to PP in order to obtain optimum physical properties and economic production

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of medical supplies. It has been shown that the presence of nucleating agent changes the polymer's crystallization temperature, spherulitic size, density, clarity, and impact and tensile properties considerably^{9,10}. However, no work has been carried out so far to study the effect of nucleating agent on the radiation stability of PP.

In this paper, we report on the radiation stability of PP in the presence of nucleating agent compared to PP without nucleating agent. Both high- and low-molecular-weight PP are studied. Their morphology is also studied in order to correlate the results with their radiation stability.

EXPERIMENTAL

Preparation of samples

PP of various molecular weights with and without nucleating agent (NA), obtained from Chisso Corporation, were irradiated (Table 1). The nucleating agent used was *p*-(*t*-butyl)benzoic aluminium (0.1 wt %).

PP sheets were prepared by moulding chips under a pressure of 150 kg cm⁻² for 5 min at 200°C using a spacer of 0.5 mm after preheating for 5 min at the same temperature. The sheets were then immediately cooled between the two plates of a cold press at 25°C. Dumbbell-shaped pieces for tensile tests were cut from these sheets.

Irradiation

The samples were irradiated with γ -rays at doses of 10, 25 and 50 kGy using a dose rate of 10 kGy h⁻¹.

Measurement of elongation at break

Elongation at break was determined from the stress-strain curves measured using a Toyoseiki Strogaph-R1. The tension speed used was 100 mm min⁻¹. Altogether eight samples were used for the tensile tests and an average of six data (the maximum and minimum data being discarded) was taken as the resultant value for the elongation at break.

Haze measurements

Haze measurements were carried out using an integrating sphere-type hazemeter made by Nippon Precision Optical Instrument Co. Ltd (model SEP-H-S-D). The integrating sphere has a diameter of 150 mm and conforms to the ASTM D1003 specification. By measuring the total transmittance (T_t) and the diffused component (T_d) using a reflecting plate, the haze (H) of the specimen is expressed by:

$$H = (T_d/T_t) \times 100\%$$

Differential scanning calorimetry

For the thermal analysis, a Shimadzu DT-30 Thermal Analyzer was used. The measurements were carried out at a heating rate of 15°C min⁻¹ under nitrogen. A 10 mg sample was placed in an aluminium pan before being put in the sample cell. For the first run, the cell was heated from room temperature to 185°C and then cooled to 50°C. A second run was made immediately after the first run was completed using the same conditions as before.

Dynamic mechanical relaxation measurements

A torsion pendulum-type apparatus (Rhesca RD1100)

Table 1 Molecular weights of the PP

Sample no.	NA ^a	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$
1a	No	4.63	35.5
2a	No	2.71	20.5
3a	No	2.11	16.3
1b	Yes	4.63	35.5
2b	Yes	2.71	20.5
3b	Yes	2.11	16.3

^a NA: nucleating agent

was used for these measurements. The measurements were carried out at a frequency of 0.2–1.0 Hz over a temperature range of –150 to +140°C.

Chemiluminescence measurements

The PP samples were cut into 4 cm diameter discs before being irradiated with γ -rays at 50 kGy dose. These irradiated samples were stored at –78°C during CL analysis to avoid decay of the radicals. CL measurement was carried out using the CL Analyzer OX-7 made by Tohoku Electronic Industrial Co. Ltd. The gate time used for the CL measurement was 1 s.

Pulsed nuclear magnetic resonance

A Jeol pulsed n.m.r. spectrometer (model JNM-FSE-60) operating at a frequency of 2 kHz was used to measure the relaxation times at temperatures of 60, 80 and 100°C. The spin-spin relaxation decays were obtained using the 90°– τ –90° pulse sequence, the spin-echo amplitude (occurring at 2 τ) being measured as a function of pulse separation τ .

Observation of spherulites

For the observation of the spherulites, a polarized optical microscope model MK-801 was used. A thin film of PP was prepared as follows: 100 mg of PP pellets was dissolved in 10 ml tetralin (15 ml in the case of PP samples with NA) on a hot plate; a drop of this solution was then placed on a glass microscope slide and the tetralin allowed to evaporate completely.

The PP film between microscope coverglasses was placed in a melting-point block held at 220°C for 3 min. The film was then quickly transferred to the microscope hot stage, set at the crystallization temperature of 125°C. After some time, small spots appeared and gradually grew in size. Photomicrographs were then taken at intervals to record the changes observed.

RESULTS AND DISCUSSION

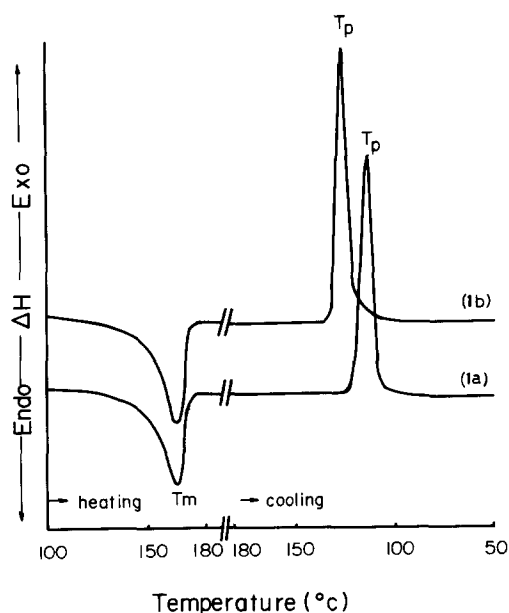
Haze values of unirradiated PP

The haze values of various PP with and without NA are tabulated in Table 2. On comparing the PP of different molecular weights, it can be observed that the haze values increase with decreasing molecular weight, indicating that the transparency of the PP decreases with decreasing molecular weight.

From Table 2, it can also be seen that for all of these PP the haze values decrease on addition of NA, indicating an increase in transparency. The difference in haze values between PP with and without NA is greater in the low-molecular-weight PP than in the high-molecular-weight PP. Our data are in agreement with those of Beck

Table 2 Haze values of various PP

Sample no.	NA	Haze, H (%)
1a	No	52.2
1b	Yes	49.2
2a	No	77.6
2b	Yes	62.2
3a	No	78.4
3b	Yes	62.0

**Figure 1** Typical d.s.c. curves of PP in the first run: (1a) without NA; (1b) with NA**Table 3** Values of T_m and T_p for various PP

Sample no.	NA	First run		Second run	
		T_m (°C)	T_p (°C)	T_m (°C)	T_p (°C)
1a	No	166	112	167	112
1b	Yes	166	125	169	126
2a	No	169	117	170	118
2b	Yes	167	124	170	124
3a	No	170	118	167	118
3b	Yes	167	125	169	126

*et al.*⁹, who also found that the addition of NA to PP improves the transparency of the PP. Thus, addition of NA to PP is an asset for producing medical supplies.

Thermal analysis of unirradiated PP

Figure 1 shows typical d.s.c. thermograms for PP with and without NA, while Table 3 shows the crystal melting point (T_m) and peak crystallization temperature (T_p) of these PP in the first and second runs. No direct correlation can be found between the T_m values of the PP with and without NA. However, the T_p of all the PP with NA are found to be higher than those of the PP without NA. According to Beck *et al.*⁹, the high T_p in PP with NA is associated with small spherulite size. Thus, it is expected that the samples with NA have a smaller spherulite size compared to the samples without NA.

This is indeed so, as will be shown later in the photomicrographs of these samples.

The high T_p values in PP samples with NA also show that crystallization occurs faster in these samples than in PP samples without NA. In the mass production of medical supplies, this means that the moulding cycle will be shorter and hence more economic. This is another advantage of adding NA to PP.

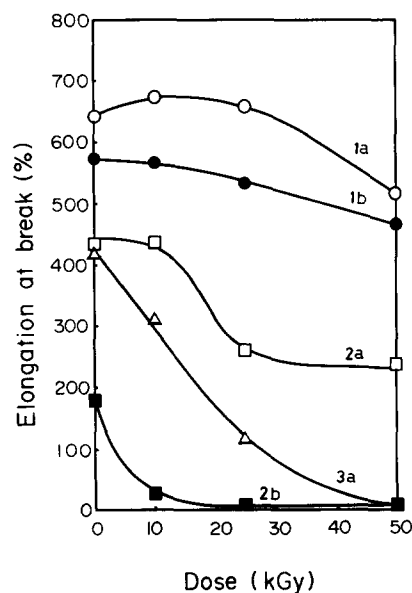
Oxidative degradation of PP during irradiation and storage

The PP with NA have the advantages of transparency and high peak crystallization temperature for producing medical supplies. It is thus important to study the oxidative degradation of these samples after irradiation with γ -rays and during storage, since medical product sterilization using γ -radiation has become very popular recently.

It has been reported that PP degrades in two stages: during irradiation and after storage. This process is due to chain scission because of the decrease in the molecular weight of the PP^{2,11}. Figure 2 shows the per cent elongation at break at different doses for the various PP samples with and without NA (Table 1). The decrease in the elongation at break reflects the degradation of PP.

From Figure 2, on comparing samples 1a, 2a and 3a it can be clearly seen that sample 1a is the most stable since the elongation at break begins to decrease at 50 kGy. For sample 2a, the elongation lowers remarkably at 25 kGy; while for sample 3a, a decrease in elongation is observed even at lower dose, 10 kGy. This shows that the high-molecular-weight PP (sample 1a) is more stable than the lower-molecular-weight PP, and this finding is in accord with our previous findings^{7,8}.

After the addition of nucleating agent, the stability of the PP is reduced. For sample 1b, a decrease in elongation occurs at 25 kGy and continues gradually till 50 kGy. Furthermore, in the lower-molecular-weight PP with NA (sample 2b), the elongation decreases markedly at 10 kGy and becomes almost zero at 25 kGy. In this case, as described later in Figures 12 and 13, since the spherulite sizes of PP are so much more different than the molecular

**Figure 2** Per cent elongation at break at different doses for PP

weights, it is suggested that the radiation stability of PP is affected by spherulite size before irradiation rather than by molecular scission during irradiation. The addition of NA to low-molecular-weight PP reduced the radiation stability of the PP greatly. For sample 3b, the elongation at break was very low even before irradiation. Hence, the elongation at break during irradiation was not determined. Since, for the low-molecular-weight PP, the stability is reduced markedly after irradiation, the degradation effect during storage cannot be studied.

The degradation during storage of high-molecular-weight PP with and without NA (samples 1a and 1b) after 25 and 50 kGy irradiation is shown in Figures 3 and 4, respectively. From Figure 3, it is observed that PP with and without NA show the same tendency of degradation. Degradation occurs rapidly in the early stage, that is, after 3 weeks storage, and then stabilizes.

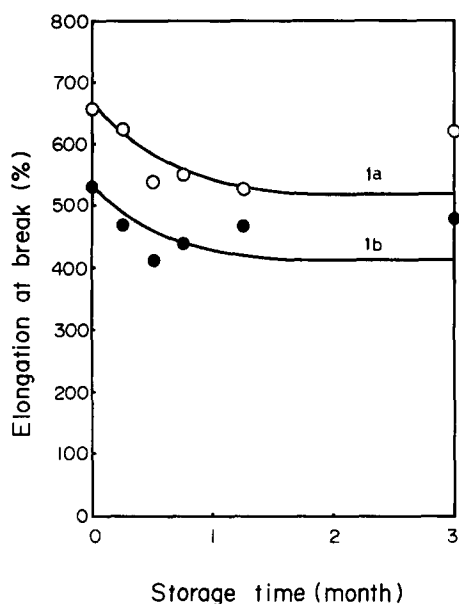


Figure 3 Degradation during storage of 25 kGy irradiated high-molecular-weight PP

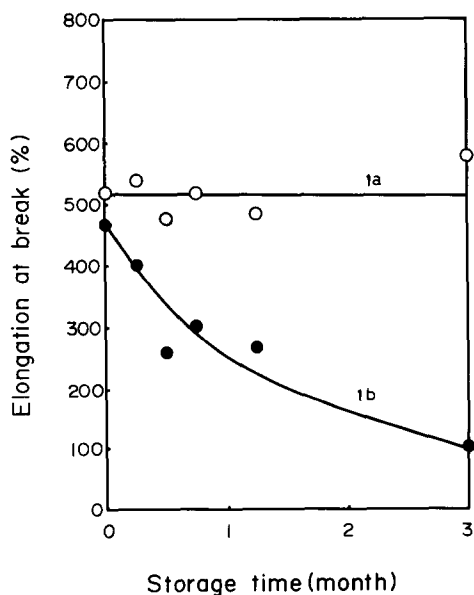


Figure 4 Degradation during storage of 50 kGy irradiated high-molecular-weight PP

For the storage of the PP samples after 50 kGy irradiation (Figure 4), the PP without NA is found to be more stable than the PP with NA (sample 1b). Sample 1b degrades markedly during the early stage of storage and continues to degrade further after 3 months storage. It can be concluded from the above data that the addition of NA to PP reduced the stability of the PP during irradiation, especially in the lower-molecular-weight PP.

Dynamic mechanical relaxation analysis of unirradiated PP

To correlate the effect of polymer morphology with their radiation stability, the dynamic viscoelastic properties of the high- and low-molecular-weight PP with and without NA before irradiation were determined. Figure 5 shows the mechanical loss (logarithmic decrement) and shear modulus (G') as a function of temperature for unirradiated samples 1a and 1b, while Figure 6 shows the same graphs but for samples 3a and 3b.

The mechanical loss of the PP shows three processes, α , β and γ ¹². The high-temperature α -relaxation is used to determine the crystallinity of the sample: the higher the α -relaxation, the more crystalline is the sample. The β -relaxation is related to the amorphous fraction and is associated with the glass transition (T_g) state of the polymer. An increase in the β -relaxation indicates a decrease in the crystallinity. The low-temperature γ -relaxation is due to local motion of various chemical groups in the polymer chain. Shear modulus G' , on the other hand, was found to decrease with decrease in crystallinity.

From Figures 5 and 6, it can be clearly seen that for both the high- and low-molecular-weight PP the samples with NA are more crystalline than the samples without NA. As we have previously reported⁵⁻⁸, the lower the crystallinity of the PP, the more stable is the PP against γ -radiation. In our present work, we also confirmed that, since the crystallinity of the PP with NA is higher than the PP without NA, the radiation stability of the PP with NA is also lower than the PP without NA.

Chemiluminescence analysis of irradiated PP

We have found that CL analysis is a useful method of estimating the oxidative degradation of the PP after irradiation^{13,14}. The CL is emitted from an excited ketone formed by recombination of the peroxy radical in the termination step. Since the degradation of PP is caused by residual radicals^{2,11}, estimation of the CL decay curves will indicate the stability of the PP on irradiation. Thus, CL measurement could estimate the degree of oxidative degradation of the irradiated PP since the CL intensity is proportional to the concentration of peroxy radicals⁸.

Figures 7 and 8 show the CL decay curves of high-molecular-weight PP with and without NA at 40 and 50°C, respectively. The CL intensity is higher in sample 1a (Figure 7) in the initial stage and decreases very fast with time. In sample 1b, however, the CL intensity decreases gradually. This same tendency is seen in Figure 8 for both samples, but with higher CL intensity since the temperature is higher. According to these CL data, a higher concentration of peroxy radicals is found in the PP with NA. Hence, as expected, the radiation stability of sample 1b is lower than that of sample 1a.

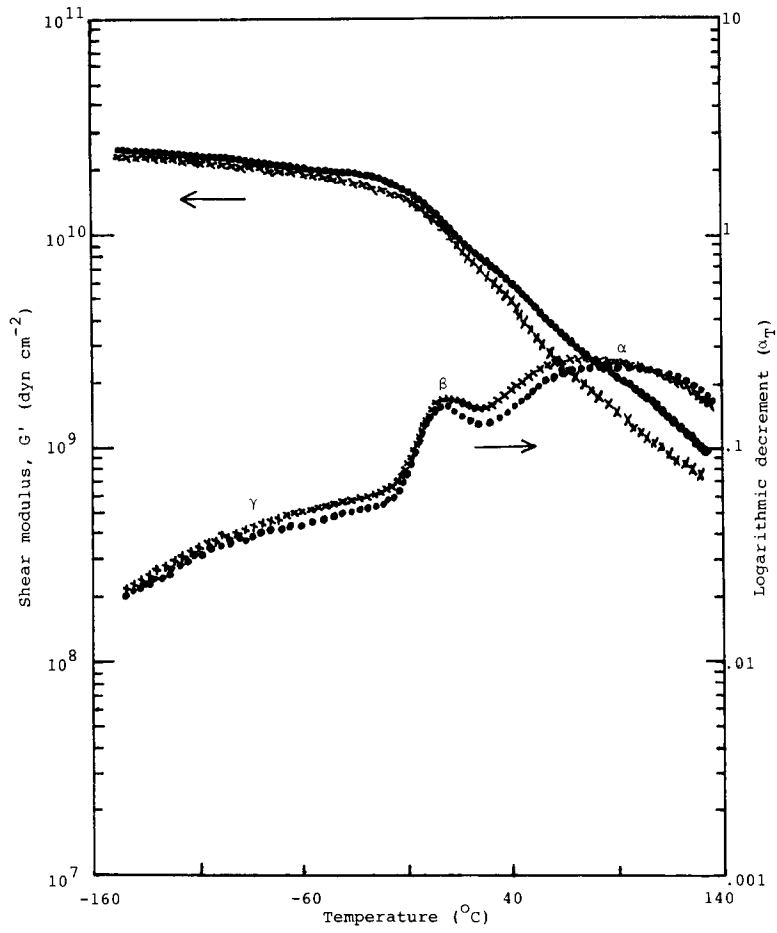


Figure 5 The mechanical loss and shear modulus at different temperatures for high-molecular-weight PP: (x) 1a; (●) 1b

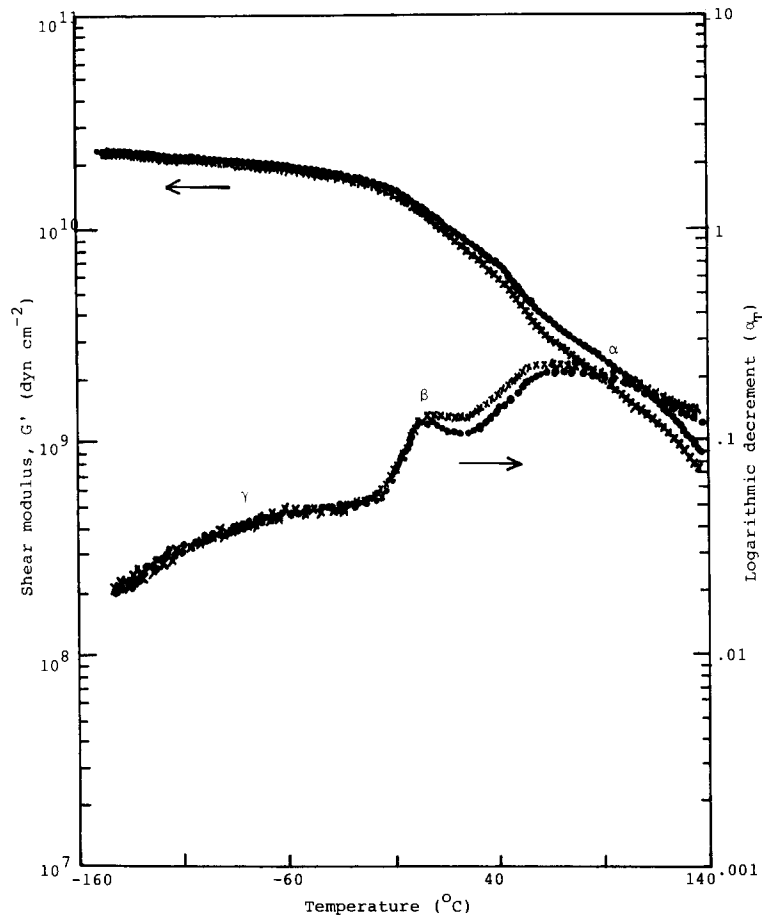


Figure 6 The mechanical loss and shear modulus at different temperatures for low-molecular-weight PP: (x) 3a; (●) 3b

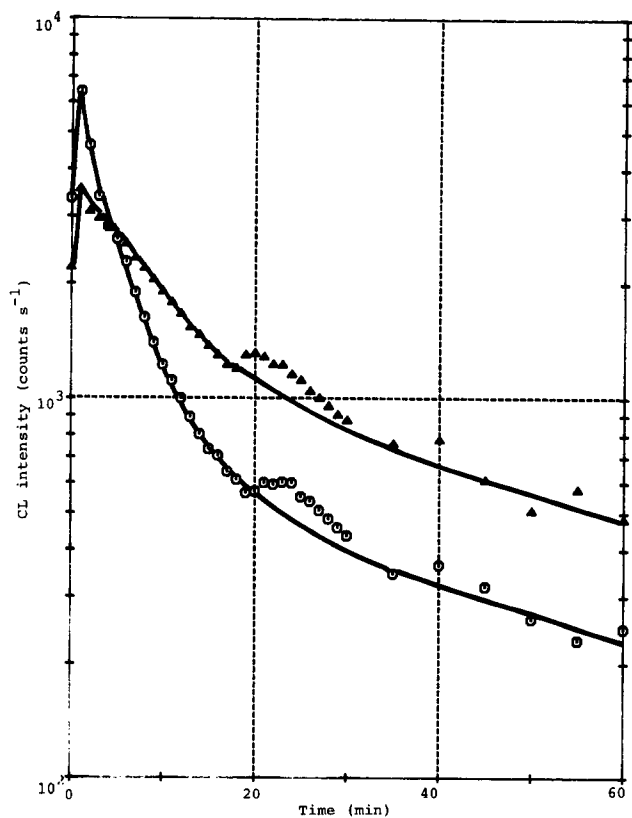


Figure 7 Chemiluminescence decay curves of irradiated high-molecular-weight PP at 40°C: (O) 1a; (Δ) 1b

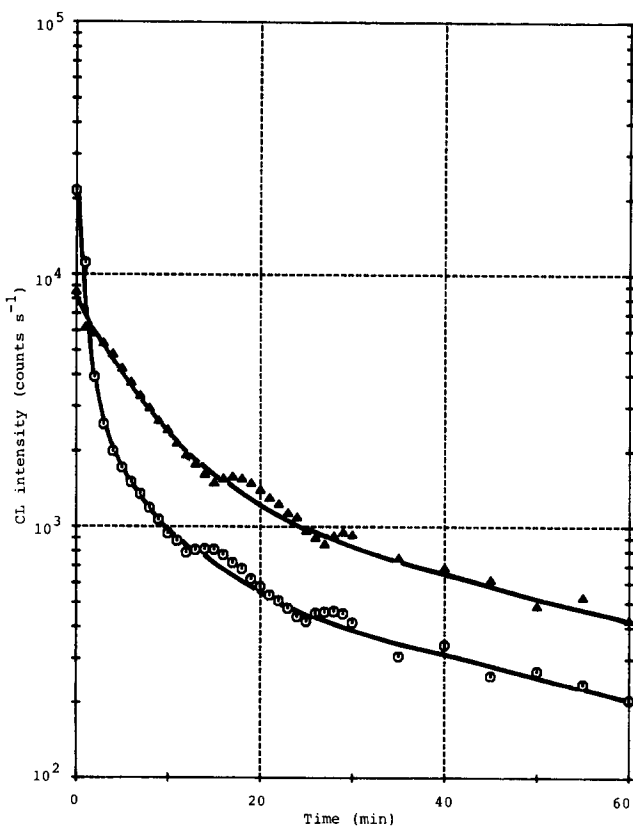


Figure 8 Same as Figure 7 but at 50°C

The CL decay curves of the low-molecular-weight PP with and without NA at 40 and 50°C are shown in Figures 9 and 10, respectively. Unlike the high-molecular-weight PP, the low-molecular-weight PP with NA has a lower concentration of peroxy radicals than the sample without

NA. This indicates that the radiation stability of the PP with NA should be higher than that of the PP without NA. However, from our study on the elongation at break, it was found that the radiation stability of the PP with NA was very much lower than that of the PP without

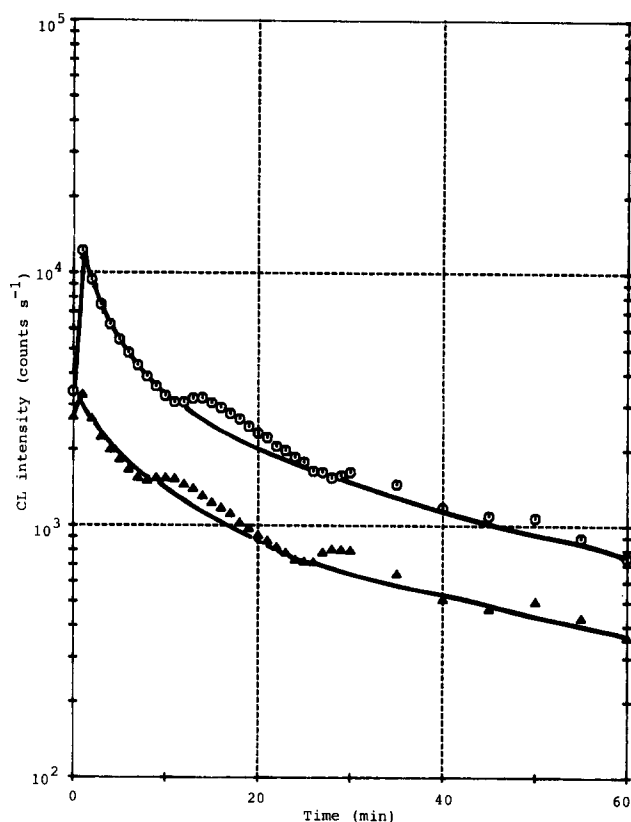


Figure 9 Chemiluminescence decay curves of irradiated low-molecular-weight PP at 40°C: (O) 3a; (Δ) 3b

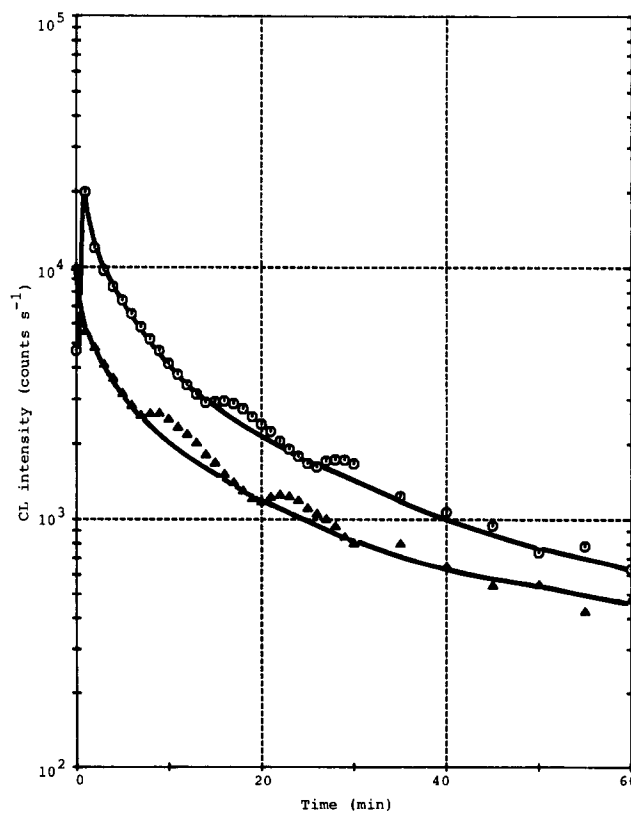


Figure 10 Same as Figure 9 but at 50°C

NA. This strongly suggests that the CL decay curves alone do not directly indicate radiation stability, in this case, but some other more important factor such as spherulite size.

In order to resolve this discrepancy, pulsed n.m.r. analysis has been carried out at 60, 80 and 100°C to find the crystallinity of these samples at different specific temperatures. The spherulite sizes of these samples were also compared.

Pulsed n.m.r. analysis of unirradiated PP

The pulsed n.m.r. relaxation decays in the PP melt comprised two components^{15,16}: a shorter non-exponential decay with time constant T_{2S} and a longer exponentially decaying component with time constant T_{2L} . The T_{2L} component is attributed to the mobility of the amorphous part while T_{2S} is attributed to the mobility of the crystalline part.

From the decay curves, the rigid and mobile parts were calculated using Gaussian and Lorentzian time dependences, respectively. The experimental and calculated values were compared to get the best-fit curves. Also from the above calculations, the percentages of crystalline and amorphous parts, Y_S and Y_L respectively, can be obtained.

Figure 11 shows a plot of the crystallinity and the amorphous parts of the high- and low-molecular-weight PP melts with and without NA at different temperatures. Comparing samples 1a and 1b, it can be seen that, at all the temperatures studied, the crystallinity of the PP with NA is higher than that of the PP without NA. This result confirmed our previous dynamic viscoelastic studies and also our CL studies, namely that more peroxy radicals were found in the more crystalline sample and hence the radiation stability is also lower. The oxidative degradation of irradiated PP relates closely with peroxy radical concentration¹³. A peroxy radical formed in the amorphous region reacts and disappears easily at early times owing to its high mobility. On the contrary, a radical formed in the crystalline region is relatively stable for long times. Accordingly, after the radical migrates to

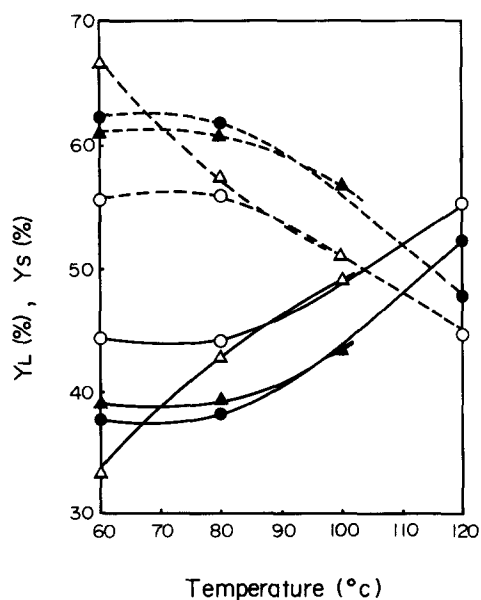


Figure 11 The crystalline (---) and amorphous (—) parts of the high- and low-molecular-weight PP melts at different temperatures: (O) 1a; (●) 1b; (▲) 3a; (△) 3b

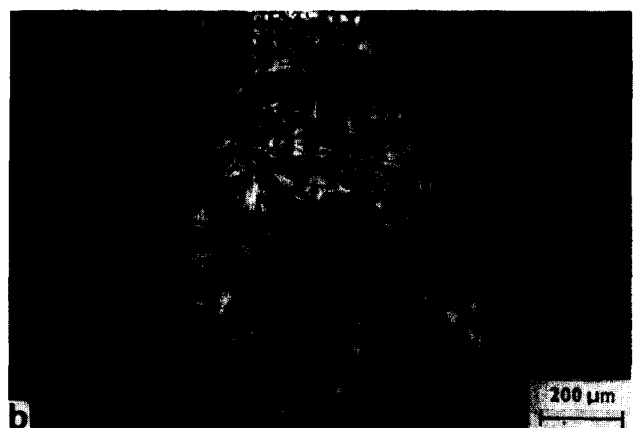


Figure 12 Photomicrographs of maximum spherulite size observed at 125°C for high-molecular-weight PP: (a) 1a; (b) 1b

the crystal surface, a peroxy radical connected with oxygen is formed and causes degradation¹⁷.

As shown in Figure 11, in the lower-molecular-weight PP, sample 3a is more crystalline than sample 3b at 60°C, but at 80 and 100°C sample 3b is more crystalline than sample 3a. These data clearly explain why in the CL decay curves more peroxy radicals were found in sample 3a than 3b even though the radiation stability is higher in sample 3a than 3b. The CL analysis was carried out at 40 and 50°C, and at these temperatures the pulsed n.m.r. data show that the crystallinity is higher in sample 3a than 3b. Hence, the concentration of peroxy radicals was found to be higher in sample 3a than 3b.

Observation of the spherulites of unirradiated PP

Spherulite size has been correlated with the transparency of the PP by Beck *et al.*⁹. The opacity is associated with large spherulites in non-nucleated PP and the clarity is associated with the small spherulite size in nucleated PP. The high peak crystallization temperatures can also be correlated with small spherulite size.

Figures 12 and 13 show the maximum size of spherulite in the high-molecular-weight PP (samples 1a and 1b) and low-molecular-weight PP (samples 3a and 3b), respectively. From these figures, it can be seen that the spherulite sizes in samples without NA (Figures 12a and 13a) are larger than in samples with Na (Figures 12b and 13b). A summary of spherulite sizes when growth of spherulites stopped is given in Table 4. The shapes of the spherulites in all these samples are similar, that is, a

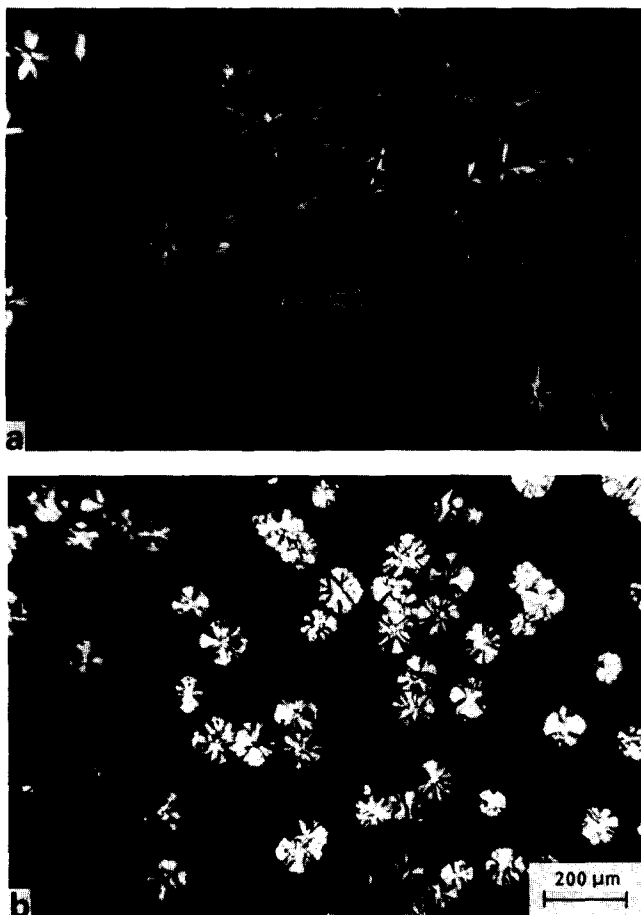


Figure 13 Photomicrographs of maximum spherulite size observed at 125°C for low-molecular-weight PP: (a) 3a; (b) 3b

Table 4 Spherulite size at final stage for various PP

Sample no.	NA	Spherulite size (µm)
1a	No	266
1b	Yes	173
3a	No	467
3b	Yes	93

Table 5 Summary of the effect of NA on morphology and radiation stability of PP

Variables	High molecular weight		Low molecular weight	
	Added NA	No added NA	Added NA	No added NA
Transparency	>		>	
Crystallization temperature	>		>	
Radiation stability	<		<	
Crystallinity	>		>	
CL intensity	>		<	
Spherulite size	<		<	

mixed spherulite type often referred to as α -spherulites^{18,19}. It should be noted that the spherulite size in high-molecular-weight PP without NA is 1.5 times larger than in the sample with NA, while for the lower-molecular-weight PP it is 5.0 times larger.

With these data, a correlation can be made with the difference in concentration of peroxy radicals in the high- and low-molecular-weight PP with and without

NA. In the high-molecular-weight PP, a higher concentration of peroxy radicals was found in sample 1b than in 1a, while in the low-molecular-weight PP, a higher concentration of peroxy radicals was found in sample 3a than in 3b. This indicates that only for samples with almost the same spherulite size can the CL data be compared; samples with a large difference in spherulite size cannot be compared using the CL data alone.

CONCLUSIONS

A summary of the data obtained is shown in Table 5. The addition of nucleating agent to PP has its advantages and disadvantages. The advantages are that it improves the transparency of the PP and the peak crystallization temperature is higher. The high transparency and peak crystallization temperature are due to the small spherulites found in the PP with NA. However, the radiation stability is lower than in the PP without NA. For the low-molecular-weight PP with NA, the radiation stability is reduced markedly compared to the PP without NA, rendering this PP useless for producing medical disposables if radiation sterilization is to be used. The radiation stability of the PP with NA is less than that of the PP without NA owing to its high crystallinity and small spherulite size.

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