

Electron-Beam Irradiation-Induced Grafting of Acrylonitrile onto Polyethylene

K. MORI,* K. KOSHIISHI, and K. MASUHARA

New Materials Research Laboratories, Nisshin Steel Co., Ltd., Ichikawa, Chiba, Japan

SYNOPSIS

Low- and high-density polyethylene (PE) films were grafted with acrylonitrile (AN) by electron beam prior to irradiation. The distribution of graft chains over the cross section of the sample film was analyzed in terms of the distribution of nitrogen atoms contained in the AN by means of an electron probe microanalyzer (EPMA), and graft sites were studied in relation to the effect of grafting temperature on the percent graft and the oxygen permeability of the sample films. It was found that diffusion of AN into the film was the rate-limiting step in the grafting process, thus restricting the grafting to the surface of the film in the initial grafting stages. However, the grafting shifted to the center of film as the graft process proceeded, until a uniform distribution of graft chains was observed across the entire film thickness. High-density polyethylene (HDPE) was found to display a higher percent graft than did low-density polyethylene (LDPE), and percent graft tended to increase with increasing grafting temperature. On the other hand, film oxygen permeability decreased with increasing percent graft, but this decreasing trend decreased with increasing percent graft. These findings suggest that the grafting is initiated by radicals trapped in the amorphous phase near the crystalline regions and at the surface of crystallites and that graft chains grow toward the amorphous regions. As for the radicals contributing to graft polymerization, it appears that AN permeates deeper near the crystalline surface and that graft chains grow from these sites.

INTRODUCTION

One of the most powerful tools for modifying polymeric materials is radiation-induced grafting. A search of the literature reveals a number of papers dealing with irradiation-induced graft polymerization techniques, including simultaneous and prior irradiation methods for various monomer-polymer combinations.¹ However, ⁶⁰Co or high-energy-type electron accelerators were used in almost all of these studies, and virtually no investigations with low-energy-type electron accelerators have been conducted. Low-energy electron accelerators have various advantages, such as relatively low cost, compactness, and high capacity for extremely high-dose rates

(more than 10 Mrads⁻¹). Therefore, such accelerators have drawn attention as highly effective industrial processing devices. In view of these advantages of the low-energy-type electron accelerator, the authors were motivated to conduct studies of low-energy-beam irradiation-induced grafting.

With a view to modifying the surfaces of polymeric materials, studies have been conducted using simultaneous irradiation techniques, whereby a material together with a superimposed monomer liquid phase is irradiated by electron beams.^{2,3} However, because simultaneous irradiation involves only about 1 s of reaction time, the diffusion of the monomer is restricted to areas near the material surface. Therefore, it appears that monomer diffusion is not fully reflected in the bulk characteristics in such a short reaction time. To cope with this problem, bulk characteristics are modified by prior irradiation techniques, whereby prior irradiation is performed and graft polymerization is achieved using radicals trapped in the materials.

* To whom correspondence should be addressed.

This is the fourth paper on grafting using a low-energy electron beam.

The distribution of grafts in a material is considered to be substantially dependent on the bulk characteristics. Kaji⁴ reported that the hydrogen atoms of carboxyl groups on graft chains were substituted by potassium in the grafting of methacrylic acid onto high-density polyethylene (HDPE) fiber. Momose et al.⁵ analyzed the graft chain distribution in terms of the distribution of metal salts in various materials by sulfonation of styrene and subsequent substitution with potassium in the grafting of α,β,β -trifluorostyrene onto poly(ethylene tetrafluoroethylene).

In the present study, the distribution of nitrogen atoms in nitrile groups was directly measured using a high-sensitivity electron probe microanalyzer (EPMA) to study electron-beam irradiation-induced grafting of acrylonitrile onto polyethylene films. Correlations between the graft chain distribution across the film cross section and the reaction time as well as the temperature were studied for industrial purposes. In addition, the effects of grafting temperature on percent graft and the film oxygen permeability were investigated in order to study the graft sites in polyethylene (PE) that have substantial effects on the physical properties of grafted films.

EXPERIMENTAL

Samples

The low-density polyethylene (LDPE) samples used were NUC-8506 (density 0.923 g/cm³, MI 0.8) supplied by Nippon Unicar Co., and the HDPE samples were Y6111 (density 0.953 g/cm³, MI 1.2) furnished by Tonen Sekiyukagaku K.K. These samples were formed to a film thickness of about 50 μ m by a uni-

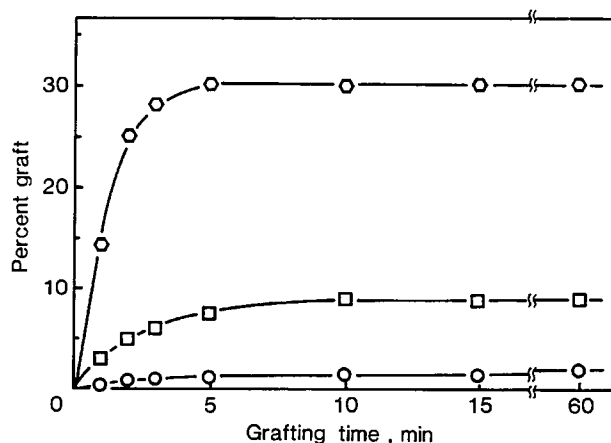


Figure 1 Relationship between percent graft and grafting time for LDPE; dose 30 Mrad: (○) grafting temperature 20°C; (□) 50°C; (◇) 70°C.

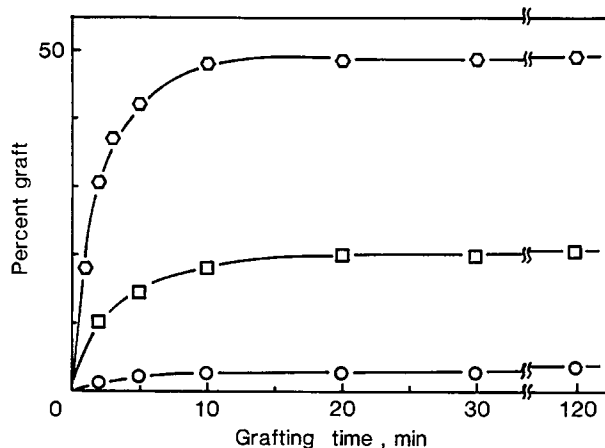


Figure 2 Relationship between percent graft and grafting time for HDPE; dose 30 Mrad: (○) grafting temperature 20°C; (□) 50°C; (◇) 70°C.

axial extruder. Acrylonitrile samples supplied by Tokyo Kasei Kogyo Co. were purified as follows prior to use in the experiments: At first, acrylonitrile was washed with 5% aqueous NaOH, 5% aqueous H₃PO₄, and distilled water in sequence, then dried with potassium carbonate. Subsequently, the monomer was distilled under dry N₂.

Electron-Beam Radiation-Induced Grafting

LDPE and HDPE samples placed on a stainless steel plate were irradiated under nitrogen gas (with an oxygen concentration of less than 500 ppm) by electron beams with an accelerating voltage of 200 kV at a dose rate of 12 Mrads⁻¹ and total doses ranging from 5 to 30 Mrad. Immediately after irradiation, the film was immersed in acrylonitrile at predetermined temperatures (20–70°C) for grafting. Subsequently, the film was immersed in *N,N*-dimethylformamide for 72 h to extract unreacted monomers and homopolymers. The resulting product was dried under vacuum for 24 h to yield the grafted film. The percent graft was calculated by dividing the increment in film weight after grafting by the weight before grafting.

EPMA Analysis of Graft Chain Distribution

The distribution of graft chains in the graft film was analyzed using a Shimadzu model EPM-810 EPMA, on the basis of the distribution of nitrogen atoms contained in the nitrile groups of polyacrylonitrile (PAN). To prepare test samples, a grafted film was first embedded in a two-part epoxy resin adhesion (Konishi Bondic 5), and after the resin had set, a

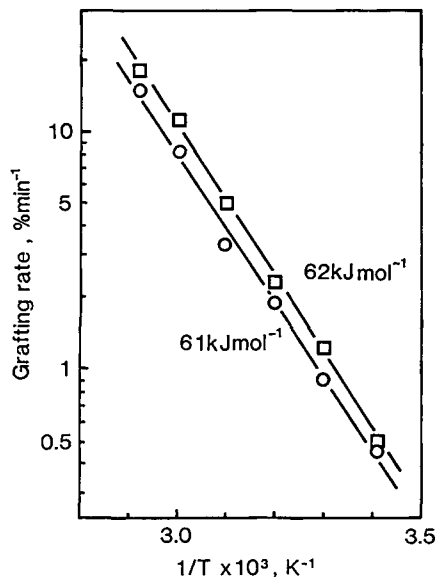


Figure 3 Arrhenius plot of grafting rates; dose 30 Mrad: (○) LDPE, (□) HDPE.

cross section vertical to the film surface was cut away using a thin-blade knife. Then, after fixing the specimen with an aluminum block with the cross section in a horizontal attitude, carbon was vapor-deposited onto the specimen to a thickness of about 10 nm. Using the resulting specimen, the graft chain distribution was measured with an accelerating voltage of 8 kV and a current of 0.2 μ A.

Measurement of Oxygen Permeability

The oxygen permeability of the film was measured at 23°C with a Toyo Seiki automatic computer-based gas permeability analyzer in accordance with ASTM D-1434-75M.

RESULTS AND DISCUSSION

Changes in Graft Chain Distribution across Film Cross Section

Figure 1 shows the relationship between the percent graft and reaction time for LDPE, and Figure 2 shows the corresponding data for HDPE. For both LDPE and HDPE, the reaction rate and percent graft increased with increasing grafting temperature. Graft polymerization was apparently completed in about 5 min at 70°C for LDPE and in about 10 min for HDPE. The time required to complete apparent grafting increased with decreasing grafting temperature for both LDPE and HDPE and was greater

for HDPE than for LDPE. Also, HDPE exhibited a higher percent graft value than did LDPE.

The short apparent graft completion time and low percent graft is attributed to a process in which the monomer concentration in PE increases substantially after the PE film is immersed in the liquid monomer, so that the monomer reacts rapidly with radicals to produce a large number of graft initiation sites. More specifically, because of the very high concentration of growing chain radicals in the graft polymerization, a recombination reaction or a heterogeneous reaction presumably occurs, resulting in a higher rate of termination reaction, thus reducing the graft completion time and percent graft accordingly.

Figure 3 shows the Arrhenius plot of the initial grafting rates. Both LDPE and HDPE display apparent activation energies of about 60 kJ mol^{-1} . Since the grafting of AN onto HDPE oxidized with ozone has been found to involve an activation energy of 90 kJ mol^{-1} ,⁶ it is clear that grafting induced by prior irradiation in nitrogen involves a smaller activation energy than does grafting via peroxides.

Figure 4 shows the distribution of graft chains in the grafted film obtained with EPMA. For both LDPE and HDPE, the grafting is limited to the vicinity of the surface of the film in the initial stages of grafting. However, the graft chains diffuse deeper into the film with increasing reaction time, until a uniform concentration of graft chains is obtained across the entire film thickness. Morgan and Corelli⁷ showed that for grafting of AN onto LDPE powder the low equilibrium concentration of AN in PE and

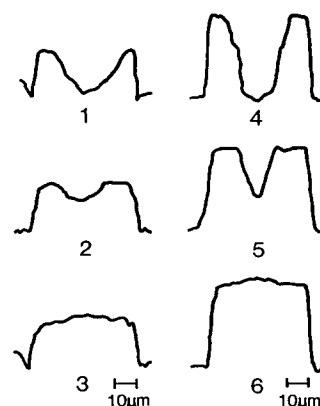


Figure 4 Distribution of nitrogen in polyethylene films grafted with acrylonitrile by EPMA: (1-3) LDPE; (4-6) HDPE; dose 30 Mrad; grafting temperature 70°C; (1) grafting time 1 min (percent graft 14.3%); (2) 2 min (24.8%); (3) 5 min (30.0%); (4) 2 min (30.3%); (5) 5 min (42.1%); and (6) 10 min (48.2%).

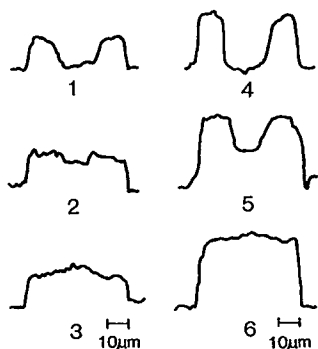


Figure 5 Distribution of nitrogen in polyethylene films grafted with acrylonitrile by EPMA: (1–3) LDPE; (4–6) HDPE; dose 30 Mrad; grafting temperature 50°C; (1) grafting time 2 min (percent graft 4.9%); (2) 5 min (7.3%); (3) 10 min (9.3%); (4) 2 min (10.1%); (5) 5 min (14.5%); and (6) 20 min (20.0%).

slow diffusion of AN in both PE and PAN should limit the grafting to a very thin layer near the surface of the material. The results obtained in the present study, however, indicate a virtually uniform AN grafting across the entire film. It is clear from Figure 4, where the ordinate represents the graft chain concentration, that HDPE has a higher graft chain concentration than does LDPE. It has also been found that diffusion of graft chains into the film requires a longer time in HDPE than in LDPE. These observations are in good agreement with the results shown in Figures 1 and 2, which indicate that HDPE has a higher percent graft and a longer graft completion time than does LDPE. The graft chain concentration near the film surface remains virtually unchanged with increasing reaction time. This suggests that the radicals trapped in PE quickly react with coexistent AN so that grafting is nearly completed at the sites of these radicals. Therefore, the results of the present study support the view that the diffusion of AN in the film is a limiting factor in the grafting process. Graft diffusion into the film is slower in HDPE than in LDPE, presumably because HDPE has a more limited amorphous region contributing to the dissolution and diffusion of AN.^{8–10}

Figure 5 shows the distribution of graft chains obtained at a grafting temperature of 50°C. The change in the graft chain distribution with increasing reaction time at this temperature displayed a similar trend to that observed at 70°C (Fig. 4). The time required for graft chains to disperse uniformly across the film thickness at a grafting temperature of 50°C was greater than at 70°C. This is presumably attributable to the slower diffusion of AN in the film

and is consistent with the data shown in Figures 1 and 2, which suggest that the apparent graft completion time should be prolonged. The fact that LDPE and HDPE displayed almost identical initial grafting rates, as shown in Figure 3, may be explained by the assumption that opposing factors of these polyethylenes counteract each other, i.e., faster AN diffusion and lower graft concentration of LDPE and slower AN diffusion and higher graft concentration of HDPE.

Graft Sites in PE

Figure 6 shows the relationship between percent graft and reaction time obtained at a dose of 10 Mrad. Both LDPE and HDPE exhibit a lower percent graft at a dose of 10 Mrad than at 30 Mrad, but virtually the same apparent graft completion time. Figure 7 shows the relationship between percent graft and dose. The percent graft increases with increasing dose, but the rate of increase in percent graft decreases with increasing dose. This is presumably attributable to the recombination of radicals formed in PE. The ratio of percent graft for LDPE to that for HDPE is about 1.7, independent of dose. Tamura et al.¹¹ reported that the ratios of the experimental values for LDPE to the corresponding values for HDPE were 1.86 for percent graft of styrene, 1.83 for degree of crystallinity, and 1.98 for radical concentration, suggesting that the acrylic radicals trapped in the crystalline regions contribute to the grafting. The results of the present study also support this argument, although the types of PE used were different.

Figure 8 shows the distribution of graft chains obtained at a dose of 10 Mrad (with a grafting tem-

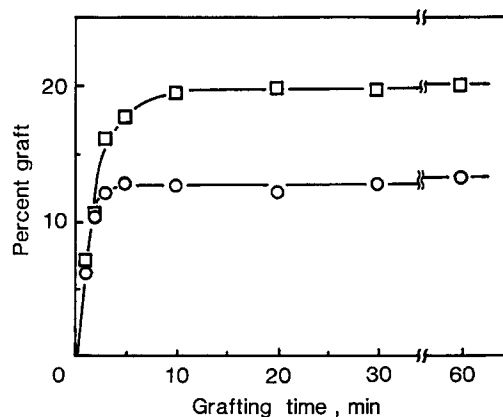


Figure 6 Relationship between percent graft and grafting time: dose 10 Mrad; grafting temperature 70°C; (○) LDPE; (□) HDPE.

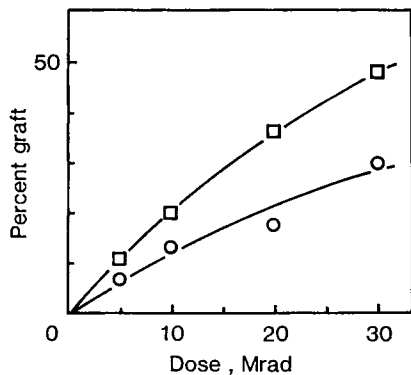


Figure 7 Relationship between percent graft and dose grafting temperature 70°C; grafting time 60 min; (○) LDPE; (□) HDPE.

perature of 70°C). The changes in graft chain distribution associated with increased reaction time displayed a trend similar to that obtained at a dose of 30 Mrad, indicating that changes in distribution are dependent on grafting temperature rather than on the dose. The fact that the changes in the graft chain distribution associated with the increased reaction time were not dependent on dose, i.e., radical concentration, suggests that the diffusion of AN into PE, rather than the reaction of radicals with AN, is a limiting factor in this graft polymerization process. This conclusion is consistent with the preceding argument.

Figure 9 shows the Arrhenius plot of percent graft. For the rates of grafting used in this plot, the values obtained with a grafting time of 60 min for LDPE and 120 min for HDPE were used for evaluation as the ultimate attainable percent grafts. The resulting

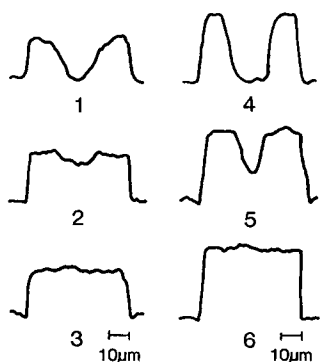


Figure 8 Distribution of nitrogen in polyethylene films grafted with acrylonitrile by EPMA: (1-3) LDPE; (4-6) HDPE; dose 10 Mrad; grafting temperature 70°C; (1) grafting time 1 min (percent graft 6.3%); (2) 2 min (10.3%); (3) 5 min (12.6%); (4) 2 min (6.8%); (5) 5 min (17.6%); and (6) 10 min (19.5%).

plots for both LDPE and HDPE exhibit a linear relationship. Although the percent graft increases with increasing temperature, the quantities of radicals trapped in the PE are almost identical for LDPE and HDPE. This implies that at lower grafting temperatures AN would fail to sufficiently attack the trapped radicals during the foregoing reaction times. Tamura et al.^{11,12} stated that the sites of trapped radicals are located in the crystalline regions and at the crystalline surface and that the radicals produced in the amorphous regions recombine rapidly even below room temperature and, hence, are deactivated. In the present study, based on prior irradiation in nitrogen, the radicals produced in the amorphous region were also found to be recombined and deactivated, so that the sites of trapped radicals are presumed to be in the crystalline regions, at the crystalline surface, and in the amorphous phase near the crystalline regions. The radicals that participate in the grafting are thus considered to be located in the crystalline surface and amorphous phase near the crystalline region, into which AN diffuses and attacks these radicals.

Therefore, the results shown in Figure 9 indicate that the polymer segment movement of PE becomes more active with increasing grafting temperature, resulting in the increased dissolution and diffusion of AN into the crystalline regions, which, in turn, suggests that AN may well attack the radicals trapped in the amorphous phase near the crystalline regions and still deeper at the crystalline surface. This explanation supports the view that the Arrhenius plot shown in Figure 9 is related to the viscosity of PE and diffusion of AN.

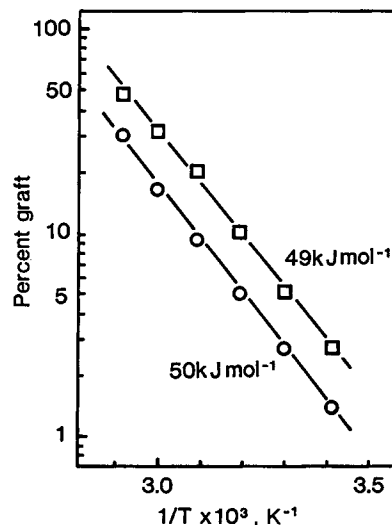


Figure 9 Arrhenius plot of percent graft, dose 30 Mrad; (○) LDPE; (□) HDPE.

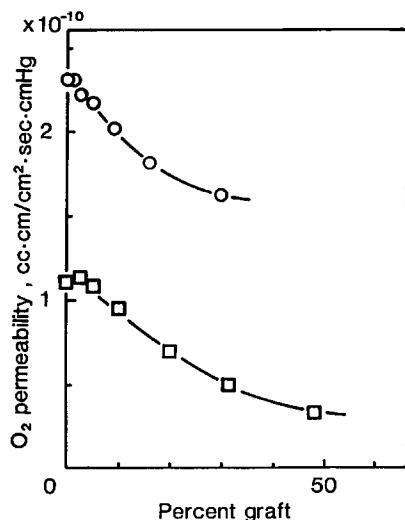


Figure 10 Influence of percent graft on O₂ permeability of AN-grafted PE films, dose 30 Mrad: (○) LDPE; (□) HDPE.

Figure 10 shows the relationship between percent graft and oxygen permeability. Klute and Franklin^{8,9} and Michaels and Parker¹⁰ proposed that the permeability P of material in PE is given by the relation

$$P = PaXa\Psi \quad (1)$$

where Pa is the permeability of the amorphous phase; Xa , the volume ratio in the amorphous phase; and Ψ , the permeability function. LDPE exhibits a higher oxygen permeability than does HDPE because of its greater Xa value. Although gas permeation occurs in the amorphous regions, crystallines act to hinder the polymer segment movement in the amorphous phase near the crystallite regions and thus retard gas permeation.

Oxygen permeability decreased with increasing percent graft for both LDPE and HDPE. This may be explained by the packing of graft chains produced in the amorphous regions.¹³ This explanation implies that the permeability is lower in these regions than in other regions, which leads to a reduction in the apparent amorphous regions, resulting in a decrease in the apparent value of Xa . The decrease in oxygen permeability associated with increased percent graft is more pronounced for LDPE than for HDPE. This suggests that LDPE has a greater packing efficiency. Considering the location of graft sites, graft chains are presumably initiated and grow when AN attacks the radicals trapped in the amorphous phase near the crystalline regions and at the crystalline surface, as discussed above. HDPE, which has a higher degree of crystallinity, has a greater volume of amor-

phous phase near the crystalline regions and a larger crystalline surface area. Therefore, for a given value of percent graft, HDPE presumably has more graft chains occupying the amorphous phase near the crystalline regions and at the crystalline surface. On the other hand, LDPE apparently has a larger volume of graft chains in the amorphous regions, that is, a greater packing efficiency for percent graft in the amorphous phase that participates in gas permeability. For both LDPE and HDPE, the decreasing trend in oxygen permeability diminishes with increased percent graft. The results of the present study indicate that PE with a high percent graft involves a higher grafting temperature and that in such PE samples AN attacks radicals trapped in the amorphous phase near the crystalline regions and even deeper at the crystalline surface. Moreover, it appears that graft chains initiated at those sites also include branches that have not grown to the amorphous phase that participates in gas permeation. This process is believed to retard the decreasing trend in oxygen permeability associated with increased percent graft.

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