Thermal Stability in Air of Acrylonitrile-Grafted Polyethylene by Electron Beam Prior Irradiation*

K. MORI,† K. KOSHIISHI, and K. MASUHARA

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

SYNOPSIS

Studies were made of the thermal softening and degradation behavior in air of low- and high-density polyethylene (PE) grafted with acrylonitrile (AN) by electron beam prior irradiation in nitrogen. It was found that both LDPE and HDPE were made to exhibit higher softening points by grafting and that this tendency increased with increasing percent graft. The starting temperatures of the thermal degradation and thermogravimetric curves were also found to shift to higher temperatures. On the other hand, in marked contrast to the thermal softening and degradation behavior of grafted PE in air, its behavior in nitrogen showed substantial dependance on oxidative degradation, suggesting that the oxidation of PE was inhibited by polyacrylonitrile (PAN), which forms graft chains. It was considered that the oxidation-inhibiting mechanism of PAN produced in the amorphous regions prevents oxygen from dissolving and diffusing into the amorphous phase, thus inhibiting the oxidative degradation of PE, and that, when heated, PAN undergoes nitrile oligomerization and the nitrile oligomer end radicals act to trap those radicals which participate in PE oxidative degradation.

INTRODUCTION

Radiation-induced crosslinking phenomenon has been studied extensively. As a result, it has been shown that, when irradiated, PE exhibits substantial improvement in its poor heat resistance, which is one of its principal disadvantages. The electron beam crosslinking technique is widely applied to PE-sheathed wires used in electronic equipment and automobiles.

In order to improve the heat resistance of PE, consideration has also been given to the use of radiation-induced grafting. Krul reported that among PE samples grafted with acrylonitrile (AN), acrylic acid (AA), vinylidene chloride (VC), methyl methacrylate (MMA), and styrene, those grafted with AN, AA, and VC were shown to exhibit an improvement in heat resistance in the presence of argon gas, which was explained by the increased intermolecular

interaction energy in the amorphous phase of PE caused by the formation of graft chains.[1]

The present paper is primarily concerned with the thermal stability in air of AN-grafted PE, prepared under controlled conditions as described in the previous paper, with regard to thermal deformation and decomposition behaviors, and also discusses the applicability of Krul's thermal stability mechanism to the behavior in air of grafted PE, in comparison with its thermal stability in nitrogen.

EXPERIMENTAL

Samples

LDPE and HDPE films irradiated at a dose of 30 Mrad were immersed in AN at 20–70°C to form AN-grafted PE samples. The grafting time was 60 and 120 min for LDPE and HDPE, respectively, until their grafting processes were apparently completed. Similarly, LDPE films irradiated at a dose of 30 Mrad were immersed in purified MMA and methacrylonitrile (MAN) at 70°C for 60 min for MMA and MAN grafting.

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* Fifth paper on grafting using low energy electron beam.
† To whom correspondence should be addressed.

Determination of Thermomechanical Deformation Curves

Thermomechanical deformation curves of the sample films were determined with a Shimadzu TMA-30 thermal stress measuring instrument, under the conditions of a temperature increase rate of 5 K min^{-1} and a sample loading of 40 g mm^{-2} over the range of room temperature to 350°C in air and nitrogen environments.

Infrared Spectroscopy

Infrared spectra of the films were determined with a JEOL JIR-40X Fourier transform infrared spectrometer, in the range of between 4000 and 600 cm^{-1}.

Thermogravimetric Analysis

Thermogravimetric analysis was performed using a Rigaku Corporation differential thermal analyzer, with a temperature increase rate of 5 K min^{-1} over the range of room temperature to 500°C in air and nitrogen atmospheres.

RESULTS AND DISCUSSION

Nitrile Group Oligomerization of Polyacrylonitrile

Figures 1 and 2 show the thermomechanical deformation curves of LDPE and HDPE grafted with AN, respectively. Both the LDPE and HDPE samples showed intermolecular crosslinking when irradiated by electron beams (at a dose of 30 Mrad), and their softening points (i.e., temperatures at which the film fully stretched) rose beyond the melting points (at
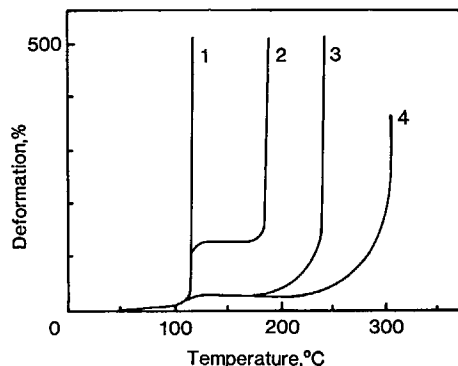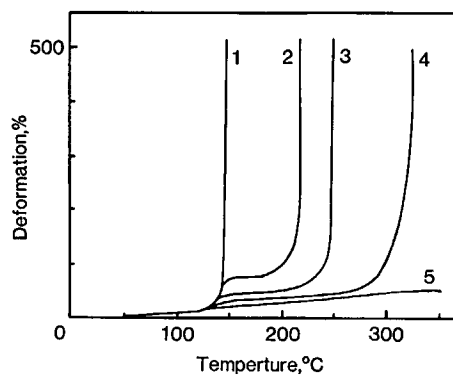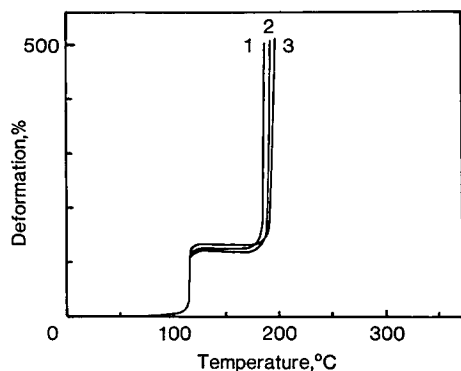
Figure 2   Thermomechanical deformation curves of AN-grafted HDPE in air: (1) control; (2) irradiated; (3) grafted (percent graft 10.0%); (4) grafted (31.5%); (5) grafted (48.2%).

115°C for LDPE and 145°C for HDPE) without dissolution or frictional flow. AN-grafted PE, on the other hand, exhibited an even higher softening point, which increased with increasing percent graft. With regard to thermal softening behavior, grafted PE showed virtually no stretching at the melting point of PE, as compared to that for irradiated PE. HDPE with 48.2% graft exhibited a softening temperature of more than 350°C.

Krul reported that, when grafted with AN, PE was shown to exhibit more stable thermomechanical deformation and degradation behavior under an inert gas (argon gas), and that this observation may be explained by the increase in intermolecular interaction energy caused by the formation of graft chains in the amorphous phase of PE.[1] As is clear from the results shown in Figures 1 and 2, when grafted with AN, PE exhibited increased thermal stability, suggesting that its intermolecular interaction energy increased as noted by Krul. It should be noted, however, that Figures 1 and 2 represent the results in air, which differ from those obtained in the test atmosphere reported by Krul.

Figure 3 shows the thermomechanical deformation curves of LDPE grafted with MMA and MAN. Both the MMA- and MAN-grafted PE samples showed similar thermal softening behavior to that of irradiated PE. More specifically, unlike the case of the AN-grafted PE sample mentioned above, no significant increase in softening points was observed in MMA- and MAN-grafted PE samples. This phenomenon was also noted by Krul, indicating that MMA-grafted PE does not show the improvement in thermal stability found in AN-grafted PE.
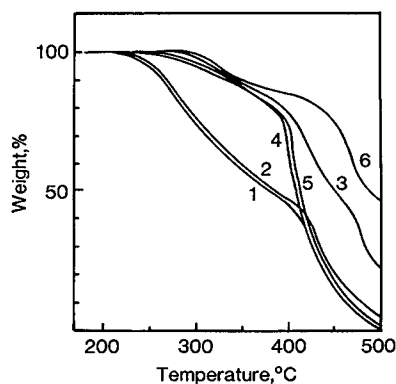
Figure 4 shows the thermogravimetric curves of unirradiated PE, irradiated PE, and AN-grafted PE. For both LDPE and HDPE, electron beam induced

Figure 1   Thermomechanical deformation curves of AN-grafted LDPE in air: (1) control; (2) irradiated; (3) grafted (percent graft 9.3%); (4) grafted (30.0%).
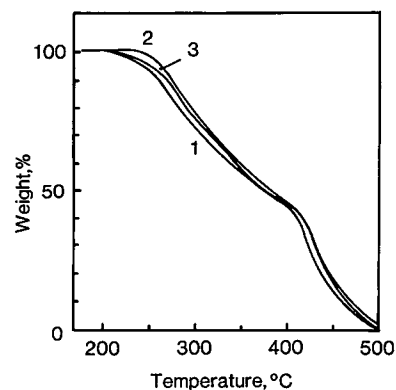
Figure 3 Thermomechanical deformation curves of MMA- and MAN-grafted LDPE in air: (1) irradiated; (2) MMA-grafted (percent graft 22.0%); (3) MAN-grafted (19.2%).

Figure 5 TG curves in air for: (1) control LDPE; (2) MMA-grafted LDPE (percent graft 22.0%); (3) MAN-grafted LDPE (19.2%).

crosslinking was found to exert almost no influence on their thermal degradation behavior. Increases in the starting temperatures of thermal decomposition were observed in AN-grafted PE and its weight losses were inhibited, as compared to the unirradiated and irradiated PE samples. This indicates that degradation residues still existed at 500°C in the AN-grafted PE. On the other hand, the LDPE grafted with MMA and MAN shown in Figure 5 exhibited similar thermal degradation behavior to that of the irradiated PE shown in Figure 2. In short, improvement in thermal stability was observed only in AN-grafted PE, also in terms of thermal degradation behavior.

Polyacrylonitrile (PAN) is formed as graft chains on AN-grafted PE. In the PAN thermal degradation process, HCN elimination occurs only to a minor extent, and the predominant reaction taking place at 250–300°C is cyclization in which adjacent nitrile

groups are conjugated, i.e., nitrile group oligomerization.[2-6] Because its polypyridine structure imparts superior heat resistance, the existence of degradation residues is suggested. It has been proposed that oligomerization, which is a radical reaction, is initiated by the thermal scission at some weak bonds.[2-4] The results of the present study also indicate that oligomerization of graft chains is initiated by thermal scission of PE molecules. It is also supposed that nitrile group oligomer end radicals combine with radicals that participate in the thermal scission of PE molecules, thus inhibiting the thermal decomposition of PE.

Figure 6 shows changes in the infrared spectra before and after measurements of the thermome-
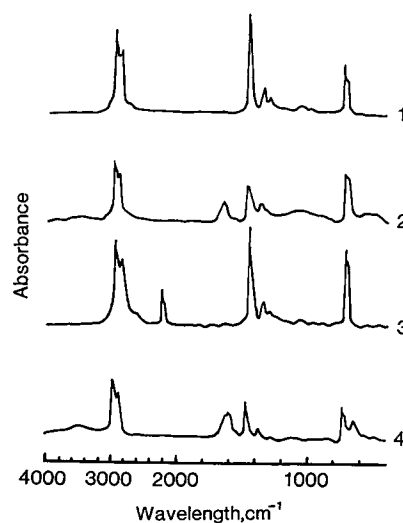

Figure 4 TG curves in air for: (1) control LDPE; (2) irradiated LDPE; (3) AN-grafted LDPE (percent graft 30.0%); (4) control HDPE; (5) irradiated HDPE; (6) AN-grafted HDPE (48.2%).


Figure 6 Changes of infrared spectra for LDPE and an AN-grafted one with heating: (1) control (LDPE); (2) heated 1; (3) grafted LDPE (percent graft 16.4%); (4) heated 3: heating, room temperature to 350°C (5 K min^{-1} in air).

chanical deformation of unirradiated LDPE and AN-grafted LDPE (temperature increase rate of 5 K min⁻¹, heat treatment in air up to 350°C). Spectral pattern 2, which represents an unirradiated PE sample subjected to heat treatment, indicates absorption spectra, which are assigned to various carbonyl compounds, in the 1700 cm⁻¹ region. This suggests that heat treatment in air contributes to the oxidative degradation of PE. In the case of AN-grafted PE, the absorption of nitrile group completely disappears at 2270 cm⁻¹ due to heat treatment. Instead, the absorption of polypyridine occurs in the 1600 cm⁻¹ region, which suggests that the above-mentioned nitrile group oligomerization has taken place. The fact that there is little absorption of carbonyl group in the 1700 cm⁻¹ region, as shown by spectral pattern 2 in Figure 2, may be attributable to PAN contributing to the inhibition of PE oxidation. One of the inhibiting factors may be the combination of nitrile group oligomer end radicals with radicals contributing to the thermal scission of PE molecules as discussed above. More concretely, radicals contributing to the thermal scission of PE molecules react with oxygen and the resulting peroxides are decomposed to form carbonyl compounds, which are trapped by the nitrile group oligomer end radicals.

On the other hand, in MMA- and MAN-grafted PE samples, both poly(methyl methacrylate) (PMMA) and polymethacrylonitrile (PMAN), which form graft chains, are thermally degraded, predominently by depolymerization.[7] In other words, depolymerization of these graft chains upon heating accounts for the similar thermomechanical deformation and decomposition behavior of MMA- and MAN-grafted PE samples to that of irradiated PE.

Oxidative Degradation of PE and Inhibition by PAN of Its Oxidation

Figure 7 shows the thermomechanical deformation curves of AN-grafted LDPE in nitrogen. In a nitrogen atmosphere, neither the irradiated nor grafted PE samples showed significant thermomechanical deformation beyond the melting point of LDPE and up to 350°C, and their softening points exceeded 350°C in the presence of nitrogen. This finding implies that thermal softening behavior in air over the temperature range exceeding the melting point as shown in Figure 1 is dependent on oxidative degradation; i.e., the oxidation of PE is inhibited by PAN. Figure 8 shows the thermogravimetric curves of unirradiated and AN-grafted PE samples in a nitrogen atmosphere. Both the starting temperature
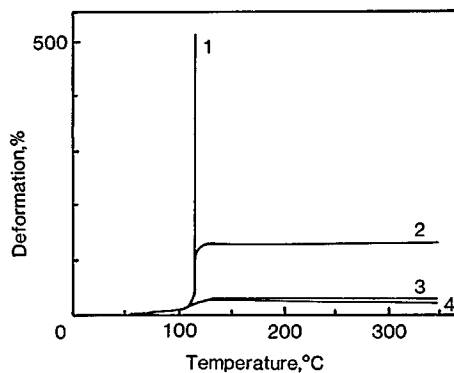

Figure 7 Thermomechanical deformation curves of AN-grafted LDPE in nitrogen atmosphere: (1) control; (2) irradiated; (3) grafted (percent graft 9.3%); (4) grafted (30.0%).

of thermal decomposition and thermogravimetric curves show a drastic shift to higher temperatures, as compared to the thermogravimetric curves in air shown in Figure 1. This indicates that, similarly to the foregoing thermal softening behavior, the thermal decomposition behavior in air is also substantially dependent on oxidative degradation. This also accounts for the inhibition by PAN of the oxidative degradation of PE. The starting temperature of thermal decomposition of AN-grafted PE in nitrogen shown in Figure 8 is higher by 50–60°C than that of unirradiated PE. This indicates that PAN contributes to the increased intermolecular interaction energy of PE, as reported by Krul.[1]
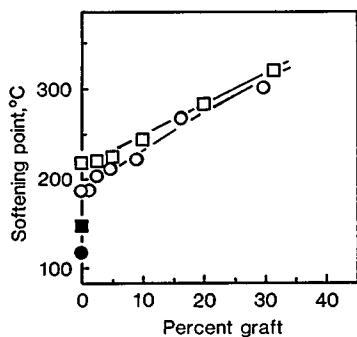
Figure 9 shows the influence of the percent graft on the softening point in air of AN-grafted PE. For both the LDPE and HDPE samples, the softening points increased monotonically with increasing percent graft, the degree of increase corresponding to a higher percent graft being greater for LDPE than for HDPE. This finding indicates that if the percent graft is equal, LDPE exhibits a higher rate of increase in softening temperature than HDPE.

Figure 10 shows the relationship between the increase in softening point and the decrease in oxygen permeability of AN-grafted PE in comparison with irradiated PE. The softening point increases with decreasing oxygen permeability, and this trend follows the almost identical characteristic curves for LDPE and HDPE. In other words, it is assumed that the volume of graft chains in the amorphous phase, which contributes to gas permeability, dictates the rise in the softening point. The fact that the LDPE sample exhibited a higher rate of increase in softening temperature associated with increasing percent graft may be explained by the higher graft chain packing efficiency of LDPE in the amorphous
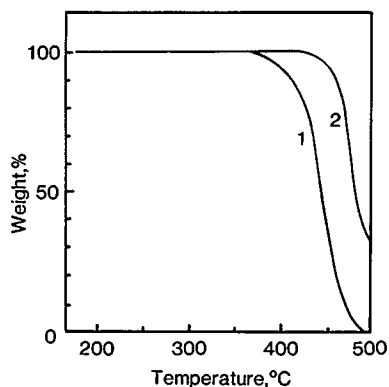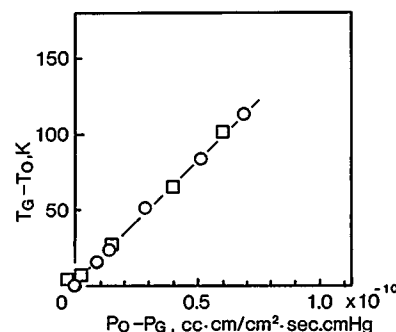
Figure 8 TG curves in nitrogen atmosphere for: (1) control LDPE; (2) AN-grafted LDPE (percent graft 30.0%).

regions as described in the previous paper. This observation shows fairly close agreement with the results shown in Figure 10. Because oxygen dissolves and diffuses into PE in the amorphous phase, it is presumed that oxidation also occurs in the same amorphous regions, which results in the oxidation dependence of thermal softening behavior in air in the amorphous phase. PAN, which forms as graft chains in the amorphous regions, is considered to inhibit the oxidation in those regions. This suggests that the inhibition mechanism of PAN, which imparts a superior barrier against oxygen permeation, acts to inhibit oxidative degradation by retarding the dissolution and diffusion of oxygen in the overall amorphous region and that, under the influence of

Figure 10 Relationship between increase in softening point and decrease in O_2 permeability: ($\bigcirc$) LDPE; ($\square$) HDPE.

nitrile group oligomerization of PAN, nitrile group oligomer end radicals trap the radicals that contribute to the oxidative degradation of PE, thus inhibiting its oxidative degradation.

In summary, it appears that the phenomenon of the increased thermal stability in air of AN-grafted PE is based on an increase in the intermolecular interaction energy in the amorphous regions of PE caused by PAN, as reported by Krul. However, the results of the present study suggest that the inhibition by PAN of the oxidative degradation of PE in the amorphous phase also does much to improve the thermal stability in air of AN-grafted PE.

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Figure 9 Influence of grafting on softening point in air of AN-grafted LDPE and HDPE: ($\bigcirc$) LDPE; ($\square$) HDPE.