

Photoinitiated Grafting of Methyl Methacrylate on Highly Oriented Polyethylene: Effect of Draw Ratio on Grafting

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ABSTRACT: Modification of highly oriented polyethylene was performed using a photoinitiated grafting technique. The samples were first coated with photoinitiator and then exposed to methyl methacrylate vapor under UV light ($\lambda > 290$ nm) at 60°C. The extent of grafting was studied as a function of draw ratio. It was found that the extent of grafting decreased significantly as the draw ratio was increased. Control samples of undrawn samples with different thermal histories suggested that there was another factor in addition to crystallinity that influences the extent of grafting. It is proposed that amorphous orientation or taut-tie molecules reduce the photoinitiation process. Gravimetric and attenuated total reflectance-IR measurements indicated that the grafting reaction can occur below the sample surface (or internal grafting) and that the proportion of surface grafting increases with increasing draw ratio. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 465–470, 1998

Key words: high modulus polyethylene fiber; surface modification; photografting

INTRODUCTION

The production of high stiffness and high strength fibers from polyethylene (PE) has been developed over the last 20 years by various routes.^{1–5} In recent years many advances have been achieved. These include a method to produce a very high strength and high modulus fiber^{5,6} and a method to improve the creep properties.^{7–9}

Owing to its high specific modulus and strength, much attention has been paid to studying high modulus PE composites.^{10–14} However, there is a problem of poor adhesion between highly oriented PE fiber and the matrix.^{15,16} Many techniques have been developed to modify the surface properties of this type of fiber, such as wet chemical oxidation,¹¹ plasma treatment,^{11,17–20} and grafting by various means.^{20–25} Reviews of surface modification tech-

niques can also be found.^{15,16} The technique that has great potential for industrial applications is photoinitiated grafting due to its simplicity and continuous nature.²⁰ This technique also allows a flexible choice of monomers to suit the structure of the matrix.

Although many studies have been reported and a successful technique to surface graft some monomers onto PE has been developed, the initiation mechanism of the reaction is not clear. Rånby and Rabek²⁶ showed that photodegradation of semicrystalline polyolefins mainly occurs in the amorphous regions. Rånby et al.²⁰ also briefly compared surface-grafted low density PE (LDPE) sheet and highly oriented PE fiber and found that crystallinity could significantly reduce the amount of grafting. However, the comparison was made between two different types of PE, isotropic LDPE sheet and highly oriented PE tape. It is known that the structure of drawn PE is completely different from the spherulitic structure found in isotropic PE. This drawn PE has a mi-

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crofibrillar structure with taut-tie molecules and crystalline bridges.^{27,28} The susceptibility of these components to the photoinitiation process is likely to be very different. Therefore, the study of the effect of drawing on the photoinitiated grafting performance of PE is very interesting.

This work studied the effect of crystallinity and drawing on the photoinitiated grafting of methyl methacrylate (MMA) onto PE. Two sets of high density PE (HDPE) sheets with controlled thermal treatment and a series of drawn samples were prepared to study their susceptibility to surface grafting.

EXPERIMENTAL

Sample Preparation

The material used was commercially available HDPE grade H5690S (Thai Polyethylene Co. Ltd., Bangkok, Thailand) with a melt flow index (MFI) of 0.9 g/10 min.

Isotropic PE sheets of 1-mm thickness were prepared by compression molding at 160°C. Two sets of sheets with different thermal histories were prepared. One set was fast cooled by transferring the mold to a cold press that was cooled with circulating water (30°C). The other set was slowly cooled by turning off the platten heaters and leaving the mold in the hot press to cool. The cooling rate was measured at approximately -1°C/min. When the mold reached 110°C, it was transferred to a cold press.

The drawing technique by Capaccio and Ward⁴ was followed and is briefly described here. Dumb-bell-shaped samples with gauge dimensions of 30 × 4.1 mm were cut from isotropic sheets and drawn with an Instron tensile testing machine at a temperature of 75 ± 1°C. A crosshead speed of 100 mm/min was used. To achieve high draw ratios, the samples were first drawn to draw ratios between 8 and 10. A second drawing stage was then carried out to obtain samples with higher draw ratios. The draw ratio was calculated from the increase in the separation between two ink marks on the samples.

Differential Scanning Calorimetry (DSC)

The melting behaviors of both isotropic and drawn samples were examined using a Perkin-Elmer DSC-7. The DSC thermograms were obtained at a heating rate of 10°C/min.

Photoinitiated Grafting

All chemicals used in this experiment were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). The photoinitiator was reagent grade xantone, which was used without further purification. MMA was purified by distillation under reduced pressure.

The photografting technique used in this experiment followed an established method.²⁹ A 60 mm length sample of either isotropic or drawn PE was first dipped in an acetone solution containing 0.3 wt % xantone and 0.5 wt % poly(vinyl acetate) [PVAc; weight average molecular weight (\bar{M}_w) = 100,000] and left to dry under reduced pressure (ca. 1 h). A Pyrex tube for photopolymerization was prepared as follows: 1.5 mL of MMA monomer and the initiator-coated sample fixed on a piece of cardboard were placed inside the tube. The tube was then evacuated to remove the air and filled with nitrogen. The process was repeated 3 times. Finally, the tube was evacuated again and kept under reduced pressure. The monomer vapor was in equilibrium with the pure liquid monomer at the bottom of the tube. No attempt was made to measure the pressure inside the tube. The reaction was carried out in a Riko rotary photochemical reactor (RH400-10W) fitted with a high pressure mercury lamp (400 W) at 60°C for 1 h.

Extraction of Homopolymer

After removing the sample from the reaction tube, it was refluxed in boiling acetone for 24 h and left to dry under reduced pressure (ca. 1 h). The extent of grafting was expressed as the weight increase per surface area of the sample.

Attenuated Total Reflectance-IR Spectroscopy (ATR-IR)

ATR-IR was used to measure the amount of grafted polymer on the surface of the sample. The experiment was carried out on Nicolet model MAGNA-IR750 using a standard procedure. The amount of grafted chains on the surface was expressed in terms of the relative intensity of the C=O stretching to CH₂ bending peaks at 1750 and 1450 cm⁻¹, respectively.

RESULTS

DSC

A DSC technique was used to evaluate the crystallinity of the samples. The heats of fusion for

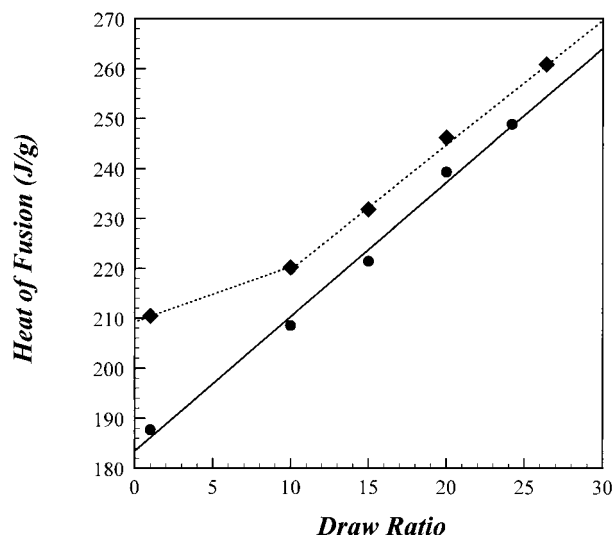


Figure 1 Heat of fusion of (◆) slowly cooled and (●) fast cooled polyethylene drawn to various draw ratios.

drawn samples are shown against the draw ratio in Figure 1. Fast cooled PE shows a linear increase in heat of fusion as the samples were drawn to higher draw ratios. A slightly different behavior was found for the slowly cooled PE. As a result of thermal treatment, slowly cooled isotropic PE had a higher heat of fusion than its fast cooled counterparts. Drawing the sample to a draw ratio of approximately 10 did not impart more crystallinity. Beyond a draw ratio of 10, the heat of fusion increased linearly with increasing draw ratio. The gradient of the curves was the same for both fast and slowly cooled samples. The heat of fusion of the slowly cooled sample and its drawn products was higher than the fast cooled counterparts for all draw ratios.

Photoinitiating Grafting

A long reaction time of 1 h was chosen so that the extent of grafting could be easily followed gravimetrically. Figure 2 displays the extent of grafting as a function of draw ratio. It is clear that the extent of grafting decreases significantly with increasing draw ratio for both fast and slowly cooled samples. A clear difference between the fast and slowly cooled samples is seen for isotropic (or undrawn) samples. The difference diminishes as the samples are drawn to higher draw ratios. The fast cooled samples show higher amounts of grafting for all draw ratios.

ATR-IR Results

In addition to gravimetric measurement of the extent of grafting, ATR-IR analysis of the grafted

samples was also performed. Figure 3 displays the ATR-IR spectra of original drawn PE and grafted PEs. It can be seen that a strong peak appears at about 1750 cm^{-1} in the grafted samples. This peak corresponds to C=O stretching. The relative intensity (RI) of C=O stretching to CH_2 bending in the two grafted samples are different, and the drawn PE shows a higher RI than the undrawn. The RI for the whole range of samples as a function of draw ratio is shown in Figure 4. It can be seen that the isotropic fast cooled sample shows a very low RI. The isotropic slowly cooled sample, on the other hand, shows a very high RI. For both fast and slowly cooled samples, the RIs increase with increasing draw ratio.

DISCUSSION

The results presented above clearly indicate that when PE is drawn it becomes more difficult to graft. Structural factors controlling the susceptibility to photoinitiated grafting of drawn PE will be discussed below.

First it is necessary to clarify the effect of PVAc in the initiator solution on the measured extent of grafting. Kubota and Hata²⁹ showed that PVAc played virtually no role in the grafting reaction. The main function of PVAc is to hold the initiator on the sample surface with good distribution. The increase in weight of the grafted sample can therefore be regarded as grafting on the PE chain.

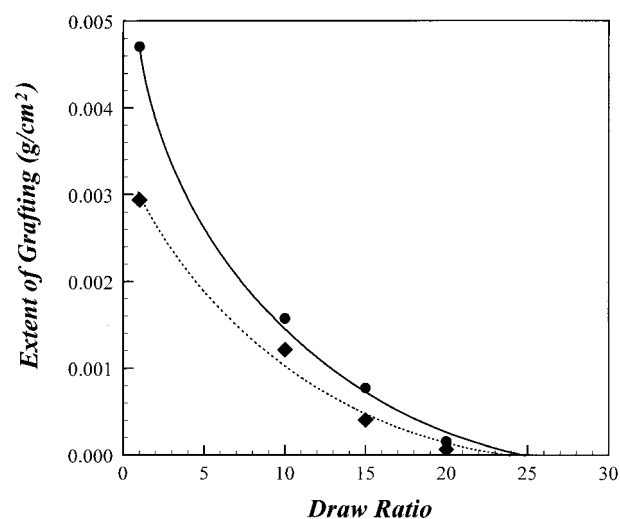


Figure 2 Extent of grafted PMMA on (◆) slowly cooled and (●) fast cooled polyethylene drawn to various draw ratios.

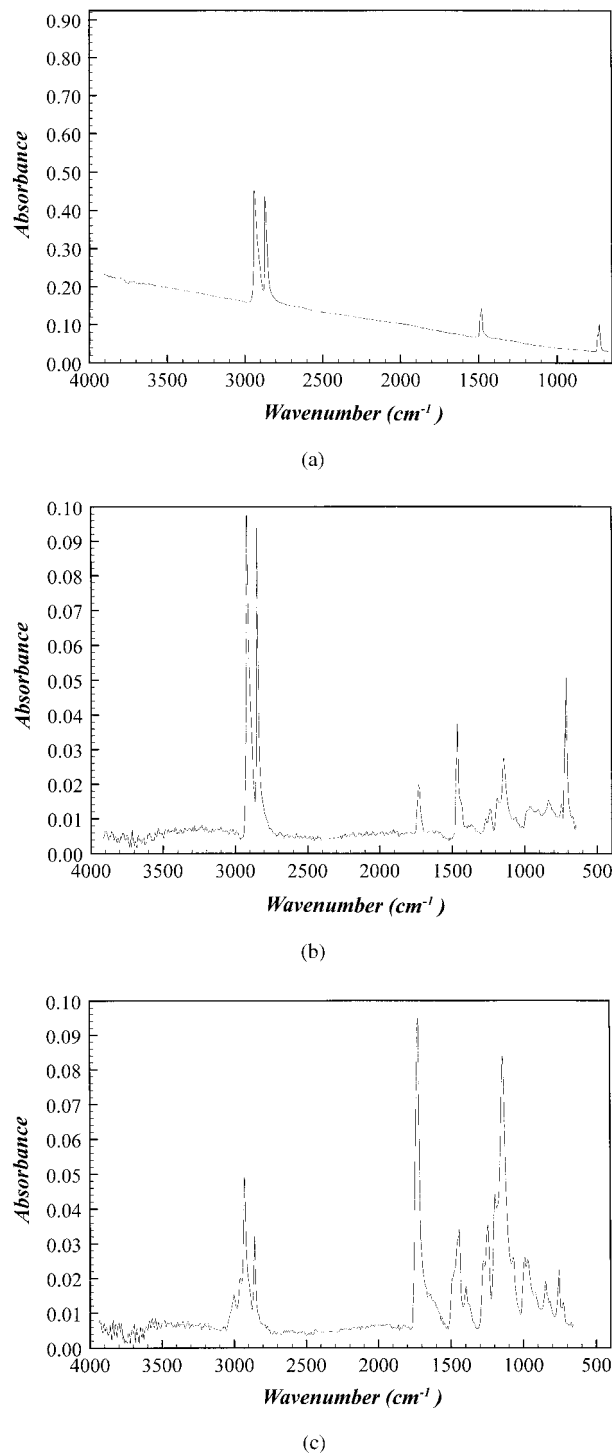


Figure 3 ATR-IR spectrum of (a) original drawn polyethylene of draw ratio 9, (b) grafted fast cooled isotropic polyethylene, and (c) grafted drawn polyethylene of draw ratio 15.

Figure 2 shows that isotropic PE can be easily grafted. The extent of grafting decreased, however, if the sample had been slowly cooled from

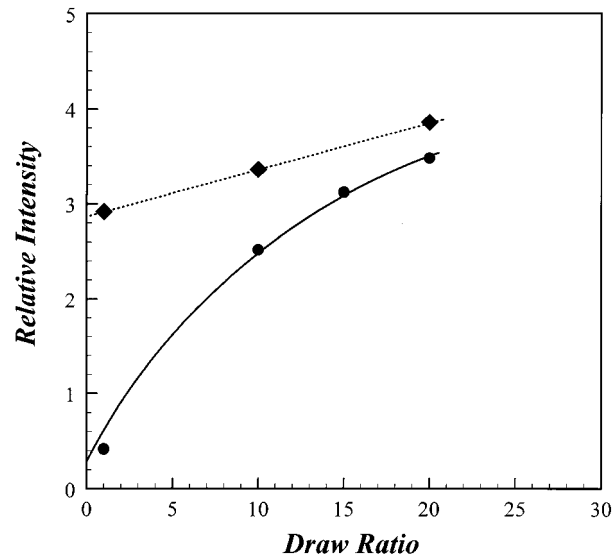


Figure 4 Relative intensity (C=O stretching to CH₂ bending) of grafted samples of various draw ratios: (♦) slowly cooled and (●) fast cooled.

the melt. This can therefore be attributed to an increase in crystallinity in such samples. When PE was drawn to higher draw ratios, the extent of grafting dropped sharply for both fast and slowly cooled samples.

Comparison of Figures 1 and 2 suggests that the extent of grafting is not governed solely by the amorphous fraction. Figure 5 displays a clearer picture of the extent of grafting as a function of heat of fusion. It is appropriate to first consider the isotropic samples. It can be seen that the low

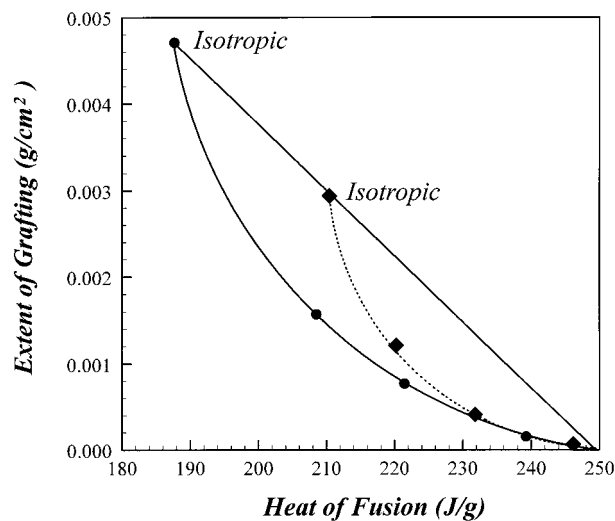


Figure 5 Extent of grafting of isotropic and drawn polyethylene as a function of draw ratio: (♦) slowly cooled and (●) fast cooled.

crystallinity sample (fast cooled) gave a higher extent of grafting. A straight line can be drawn connecting the two points. Although there are only two data points, this line is believed to give a good approximation of the effect of crystallinity (or equivalently amorphous fraction) on grafting efficiency. The results from drawn samples fall far below this line and curve toward the line again at higher draw ratios. This would suggest that drawn PEs are more resistant to the photo-initiation process than isotropic PEs.

In the initiator coating process, the initiator should be distributed homogeneously on the sample surface. Due to the limited solubility of the initiator in the PE, the majority of initiator is likely to stay on the sample surface. The amount of initiator per surface area for all samples should be the same. When the samples were irradiated with UV, the number of excited-initiator species for all samples should again be very similar. The molecular mechanism for active site formation is via hydrogen abstraction from the PE chain.²⁰ The fact that the extent of grafting decreased with increasing draw ratio suggests that there is a certain fraction of amorphous material, in addition to the crystalline regions, that is not susceptible to hydrogen abstraction. It is plausible that this fraction is an oriented amorphous phase or in other words it comprises taut-tie molecules.³⁰

The composition [or ratio of poly(MMA) (PMMA) to PE] of the sample surface up to a few microns deep was obtained by ATR-IR. Figure 4 displays the RI as a function of draw ratio. It is clearly seen that the fast cooled samples, despite having a very high extent of grafting (see Fig. 2), have relatively low RIs. This phenomenon can be explained by the grafting reaction occurring below the sample surface (or in the bulk) as reported by Kubota and Hata for LDPE.^{29,31} When the PE was drawn to higher draw ratios, the RI increased. This suggests that the grafting reaction occurs more on the sample surface for drawn samples. It must be emphasized that each data point in Figure 4 only represents the relative amount of PMMA (on the sample surface) to PE for a particular sample. It does not convey any information regarding the relative amount of grafting between samples.

It is worth pointing out that the above discussion is based on a constant penetration depth of the incident IR. However, it is still true when the different penetration depths between samples are considered. The penetration depth of incident IR depends on the refractive index of the sample.³² In this study a change in refractive index resulted

from drawing and also grafted PMMA. The effect of drawing will be considered first. As the samples were drawn to higher draw ratios, their refractive indices increased slightly. This would result in slightly larger penetration depth for high draw ratio samples. Therefore, a larger PE contribution in the spectrum is expected in high draw ratios samples. The observed RIs are thus lower than they would be at an equivalent depth to the undrawn sample. The gradient of the line in Figure 4 would be expected to be slightly higher if a comparison was made at equivalent penetration depth. The effect of grafted PMMA on the resulting RI and ATR depth of penetration will now be considered. Refractive indices of PMMA and PE are 1.489 and 1.545, respectively.³³ It is considered that the resulting refractive index of the grafted samples, either when a surface-grafted PMMA layer or internally grafted PMMA is formed, is lower than that of PE. It would be expected that the depth of penetration would decrease with increasing grafting extent. This effect would again result in a slightly steeper gradient of the line in Figure 4. Another point to be made concerns a change in shape and intensity of the CH₂ bending peaks. The peaks are known to become sharper and more intense as the crystallinity increases.³⁴ Taking this effect into account would result in a higher RI for high crystallinity and drawn samples. Again, the gradient of the line in Figure 4 would be expected to be even steeper. To summarize, when the different depth of penetration between samples due to a change in RI of the samples and a change in the reference peak intensity (CH₂ bending) are considered, the general conclusion regarding surface grafting in drawn samples still holds.

Studies of the transport properties or diffusion of gases through highly drawn polymers have been published.³⁵⁻³⁹ It was found that when PE was drawn to higher draw ratios, structural changes (i.e., formation of oriented structures, microfibrillar structures, taut-tie molecules, and amorphous orientation) significantly reduced the diffusion coefficient of gas. The solubility of gas was found to decrease with increasing draw ratio. Therefore, the above finding can be explained as follows. A relative large amount of MMA can dissolve in the isotropic fast cooled PE, hence, the high grafting. The grafting reaction of dissolved MMA also results in internal grafting that displays a low RI in ATR-IR. When the crystallinity is increased by either slow cooling or drawing, the amount of dissolved MMA decreases. The grafting reaction in these high crystallinity samples could

then occur as MMA monomer slowly diffuses in and results in more grafting on the surface.

CONCLUSIONS

1. For isotropic PE, the extent of grafting is governed by the amount of amorphous fraction present in the sample.
2. The extent of grafting of highly oriented PE is less than that of isotropic PE with equivalent crystallinity.
3. The photoinitiation process can only occur in the unoriented amorphous phase. The oriented amorphous region exhibits high resistance to the photoinitiation process similar to the crystalline region.
4. For vapor phase photoinitiated grafting, highly amorphous PE gives rise to grafting below the sample surface (or internal grafting). The proportion of surface grafting increases with increasing draw ratio.

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