

Irradiation of Highly Oriented Polyethylene Fibers in the Atmosphere of Some Vinyl Monomers: Effect on Compressive Strength

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ABSTRACT: Highly oriented polyethylene fibers have been modified by γ -irradiation in the presence of some vinyl monomer vapors, followed with further annealing in the atmosphere of the same monomer. Two types of vinyl monomers that are known to produce polymers with different glass transition temperatures, namely methyl methacrylate and vinyl acetate, were studied for their effect on the compressive strength of the fiber. It was found that a significant improvement in compressive strength, measured by tensile recoil test, was obtained. The level of improvement was affected by heat treatment and the presence of monomer during irradiation. Modification with vinyl acetate was found to be more effective than methyl methacrylate. These facts suggest that the improvement in compressive strength was attributable to several factors, including structural relaxation, the presence of graft copolymer, and energy dissipation ability of the graft copolymer. It is speculated that lateral integrity of the fiber is one of the key factors that prevents sliding of microfibril and possibly lateral or circumferential expansion of the fiber to accommodate kink band. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 2494–2502, 2001

Key words: high modulus polyethylene fiber; irradiation; compressive strength

INTRODUCTION

Polyethylene (PE) fibers with high stiffness and high strength can be produced via various routes.^{1–4} Many advances have been achieved in recent years including fibers with very high strength and modulus,^{5,6} with improved creep properties.^{7–9} Similar to other high-performance fibers, highly oriented PE fiber has relatively low compressive strength.^{10,11} However, the low com-

pressive strength of this fiber has received little attention compared with others such as Kevlar, poly(*p*-phenylene benzobisthiazole), and poly(*p*-phenylene benzobisoxazole). Many attempts have been made to improve the compressive strengths of these latter highly oriented fibers. The methods can be classified into two routes, i.e., using a new precursor to get better properties^{12–15} and modification of the commercial fibers. The latter, which is less involved, includes polymer infiltration¹⁶ and coating with ceramic material.¹⁷

Recently Amornsakchai and Kubota¹⁸ observed that grafting reaction of methyl methacrylate (MMA) on PE in vapor phase could occur below the surface of highly oriented PE. Their results also suggest that the depth of the grafting layer decreases with increasing draw ratio. At

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this point, it is conceivable that there are some similarities between the structure of these modified highly oriented PE and the infiltrated or coated fibers mentioned above. It is, therefore, natural to assume that the technique could offer a new way to improve the compressive property of highly oriented PE fiber. In the present work, modification of highly oriented PE by grafting in vapor phase was studied for its effect on the compressive strength of the fiber.

EXPERIMENTAL

Material

The material used was commercially available high density PE grade, Thai-Zex 1600J (Bangkok Polyethylene Co. Ltd., Bangkok, Thailand), with a melt flow index of 18 g/10 min. Isotropic PE fiber of about 0.5 mm in diameter was prepared with a rod spinner at a temperature of 180°C. The isotropic fiber was subsequently drawn with an in-house built apparatus, through a hot glycerol bath set at 65°C, to draw ratios of 15 and 25. Vinyl monomers used in this study were reagent grade MMA and vinyl acetate (VAc) purchased from Fluka (Thailand) and used as received.

Irradiation

About 0.5 g of isotropic fiber or 0.2 g of drawn fiber (~15 m) was wound on a glass frame and placed in a glass cell made from test tubes. Monomer was added into the cell, frozen, and the cell was evacuated. This was repeated a few times and the cell was sealed under reduced pressure. No attempt was made to measure the cell pressure. It was expected that the pressure in the cell would be that of vapor pressure of the monomer at ambient temperature. The fiber was left in the atmosphere of saturated monomer vapor for approximately 40 h. γ -Irradiation was performed at ambient temperature in a Gammacell 220, Nordion International Inc. (Kanata, Ontario, Canada), capable of giving a dose rate of approximately 1 Mrad/h. The irradiation was performed for 2 h (total dose of approximately 2 Mrad). After irradiation, the fiber was further annealed at 80 °C for 5 h in the presence of monomer vapor to eliminate trapped radicals and also promote further reactions. The sample was then refluxed in acetone for 24 h to remove homopolymer, and left to dry under reduced pressure (ca. 1 h).

Infrared Spectroscopy

The presence of grafted polymethylmethacrylate (PMMA) on the surface of the modified PE fiber was measured using attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy. The experiment was performed on a Perkin-Elmer (Beaconsfield, England) model PE2000 with KRS-5 set at an incident angle of 45°. To determine an average amount of carbonyl group, the fiber was melted and pressed into thin film for measurement of the infrared spectrum in transmission mode.

Mechanical Testings

Tensile Test

Tensile testing was performed at room temperature with an Instron testing machine (High Wycombe, England). The gauge length was 50 mm and initial strain rate was 50% min⁻¹.

Tensile Recoil Test (TRT)

The TRT was performed following the method developed by Allen.¹¹ The sample was clamped with a gauge length of 50 mm in an Instron testing machine. The sample was then stretched at an initial strain rate of 50% min⁻¹ and subsequently cut with a sharp scissors at different loads to allow the sample to snap back. Each piece of the cut sample was examined for the presence of kink band. The compressive strength was calculated from the lowest load where a kink band was observed.

Dynamic Mechanical Analysis

The dynamic mechanical analysis was performed in tensile mode using a Polymer Laboratories Mk II machine (PL Thermal Science, Loughborough, England). Sample length was 25 mm and the measurement was performed at a frequency of 10 Hz over a temperature range of -150 to 100°C at a scan rate of 10°C/min.

Scanning Electron Microscopy

The surface of samples with kink bands was examined with scanning electron microscopy. These kink bands were created either by peeling off the fiber skin¹⁷ or TRT. The samples were coated with palladium and observed with a Hitachi S-2500 set at accelerating voltage of 15 kV.

RESULTS

Infrared Spectroscopy

Modified fibers were characterized with ATR-FTIR to determine the success of the grafting

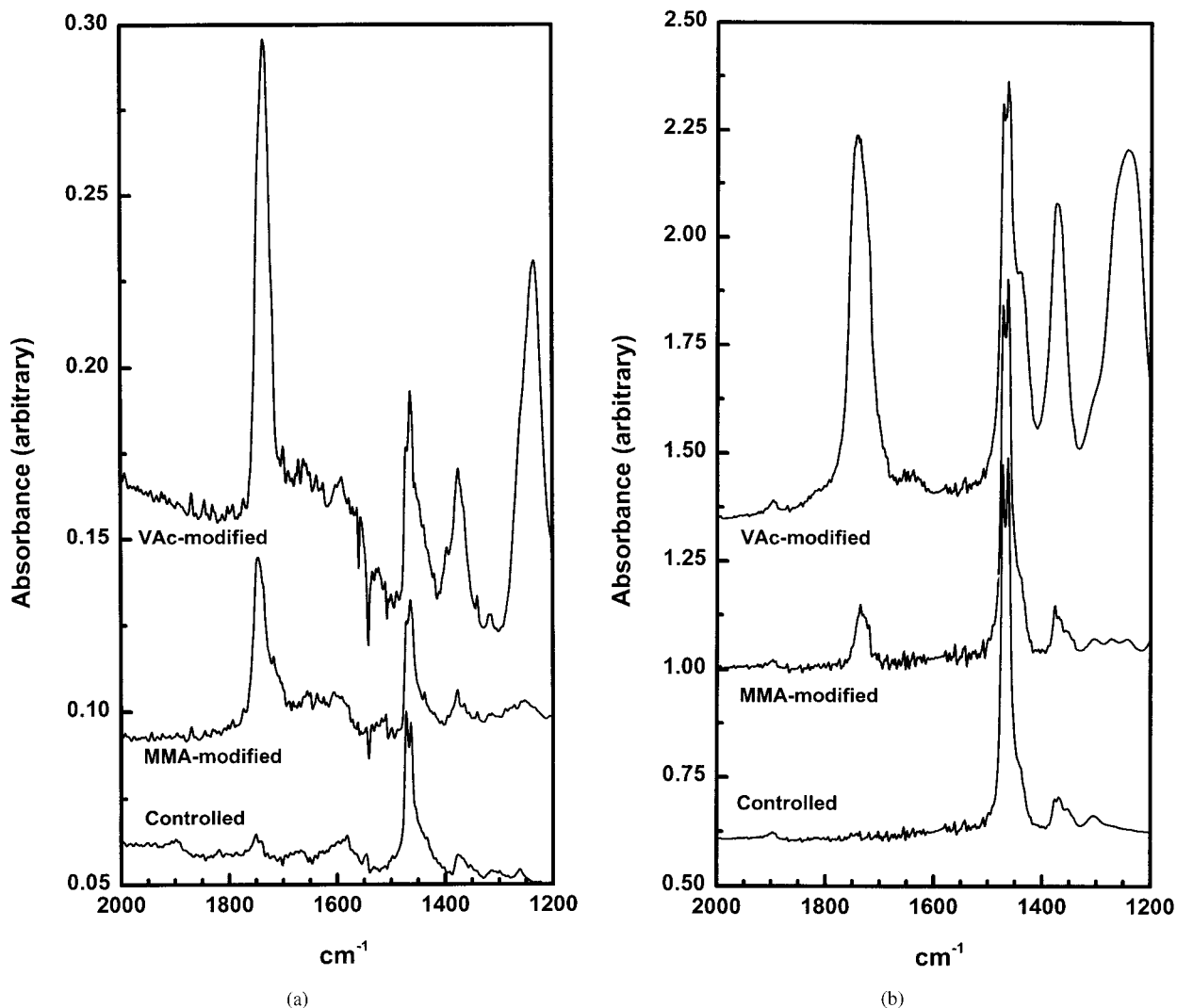


Figure 1 (a) (ATR-FTIR) spectra of controlled (bottom), MMA-modified (middle), and VAc-modified (top) fibers; (b) transmittance spectrum of melt-pressed films of controlled (bottom), MMA-modified (middle), and VAc-modified (top) fibers.

procedure. The signal of carbonyl group absorption was used as a sign of successful grafting and it was found that all modified fibers showed such signal. Results for fibers with DR15 are shown herein. Figure 1(a) displays the ATR-FTIR spectra of the controlled, MMA-modified and VAc-modified fibers. It can be seen that there is a strong absorption because of the carbonyl group (C=O) at around 1750 cm⁻¹. The melt pressed film of the same sample displays, however, only a weak band (as compared with the CH₂ bending at 1450 cm⁻¹), as shown in Figure 1(b). The results strongly suggest that the grafting reaction is confined to the surface of the fiber. This is in agreement with the previous observation.¹⁸ The more

intense signal of carbonyl absorption in the case of VAc-modified was attributed to higher extent of grafting. The extent of grafting (measured gravimetrically after extraction of homopolymer) for MMA-modified DR15 and DR25 were 1.7% and 0.9%, respectively; VAc-modified DR15 and DR25 were 11.9% and 6.4%, respectively.

Tensile Test

Tensile properties of controlled and modified fibers are shown in Table I. For fibers with DR15, no change in tensile properties was observed. The tensile modulus remains approximately unchanged with modification. However, for fibers

Table I Tensile Properties of Controlled and Modified Fibers

Properties	Controlled		MMA-Modified		VAc-Modified	
	DR15	DR25	DR15	DR25	DR15	DR25
1% secant modulus (GPa)	12	20	12	18	12	8
Tensile strength (GPa)	0.50	0.68	0.55	0.65	0.57	0.41
Elongation at break (%)	11	5	10	6	9	11

with DR25, the modification process can be seen to cause a slight drop in the tensile modulus from 20 to 18 GPa in the case of MMA-modified fiber. A very large drop from 20 to 8 GPa was found in VAc-modified fiber.

TRT

The compressive strength of controlled fiber of DR15 and its modified counterparts are shown in Table II. Kink band formation is observed at dif-

ferent levels of stress for different fibers. For controlled fiber with DR15, the compressive strength can be easily determined to be about 220 MPa. Above this stress, kink band is formed in all specimens. For both MMA- and VAc-modified fibers (with DR15), the stress level where kink band is formed could not be easily determined. There were cases where the fibers could survive very high compressive stresses. It can be seen that the stress level where some modified fibers still sur-

Table II Tensile Recoil Test Results for Controlled and Modified PE-15 Fibers

Controlled PE-15			MMA-g-PE			VAc-g-PE		
Stress (MPa)	Observation		Stress (MPa)	Observation		Stress (MPa)	Observation	
93	N	N	160	N	N	171	N	N
154	K	N	168	K	N	189	K	N
154	N	N	193	N	N	192	N	N
157	N	N	204	N	N	200	N	N
180	N	N	215	N	N	211	N	N
191	N	K	229	K	K	224	N	N
196	N	N	243	K	N	232	N	N
216	N	N	250	K	K	236	K	N
220	K	K	267	N	N	253	K	N
225	K	K	270	N	N	265	N	K
236	K	K	284	N	K	267	N	K
333	K	K	286	N	N	269	K	K
			297	K	K	279	K	K
			302	N	K	284	N	N
			322	N	K	287	K	K
			323	K	K	306	K	N
			366	K	K	321	N	N
			441	K	K	349	K	K
						358	N	N
						381	K	K
						390	N	N
						407	N	N
						427	K	K
						444	K	K
						498	K	K

Observation indicates the presence of a kink band in each end of the cut specimen. N, no kink band formed; K, kink band formed.

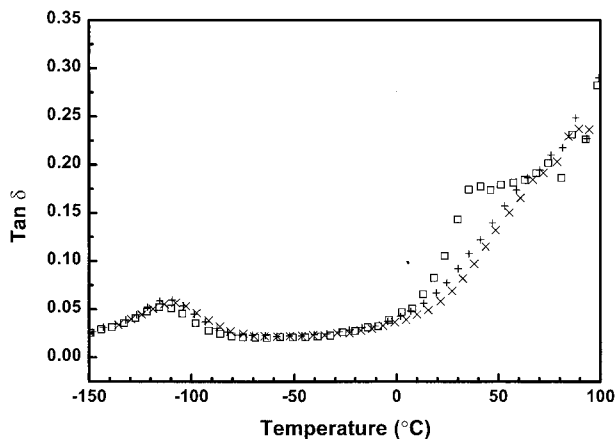
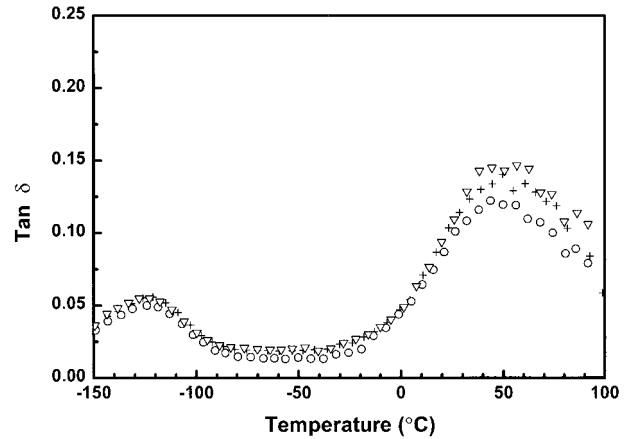
Table III Maximum Compressive Strength of Controlled and Modified Fibers

Materials	Compressive Strength (MPa)
PE fiber DR15	
Controlled	220
MMA-modified	320
VAc-modified	407
PE fiber DR25	
Controlled	246
MMA-modified	324
VAc-modified	480

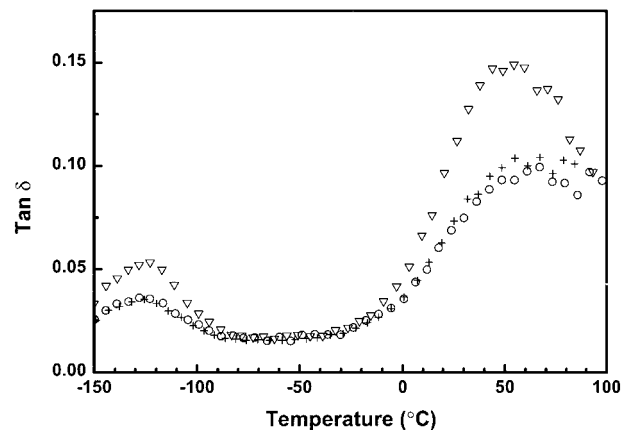
vive the failure is higher than that for controlled fiber. VAc-modified fiber shows higher compressive strength according to the measurements. To avoid the complication in determining of the compressive strength, maximum compressive stress where the fibers could not survive failure will be used as a criterion. Table III shows the maximum compressive strength obtained from TRT measurements for different fibers. It can be seen that modification of highly oriented fibers with the present technique could increase the compressive strength of the fibers significantly.

Dynamic Mechanical Test

Dynamic mechanical behavior of controlled and modified fibers was investigated in order to study the effect of the modification process. Figure 2 displays results obtained from isotropic PE fibers. Controlled, MMA-modified and VAc-modified fi-

**Figure 2** $\tan \delta$ for controlled or irradiated (+), MMA-modified (\times), and VAc-modified (\square) isotropic PE fibers.**Figure 3** $\tan \delta$ for controlled or irradiated (+), MMA-modified (\circ), and VAc-modified (∇) fibers of draw ratio 15.

bers all display very similar behavior in $\tan \delta$ over the temperature range studied, except that there is an additional $\tan \delta$ peak at about 35°C in VAc-modified fiber. Figure 3 shows results for fibers with DR15, no change in dynamic behavior, as far as the $\tan \delta$ is concerned, can be observed. There is, however, a slight increase in the height of $\tan \delta$ peak at 50°C for VAc-modified fiber. Results for fibers with DR25 are shown in Figure 4. Again, controlled and MMA-modified fibers display very similar $\tan \delta$ traces. VAc-modified fiber, however, shows very large $\tan \delta$ peaks at both -125 and 50°C as compared with the other two fibers. Virtually no change in positions of the $\tan \delta$ peaks are observed.

**Figure 4** $\tan \delta$ for controlled or irradiated (+), MMA-modified (\circ), and VAc-modified (∇) fibers of draw ratio 25.

DISCUSSION

As in our previous communication,¹⁹ the modified fibers showed strong carbonyl absorption ($\sim 1750\text{ cm}^{-1}$) in ATR-FTIR spectra. The absorption decreased significantly (when reference was made to the 1450 cm^{-1} CH_2 bending) when the samples were melt-pressed into film and measurement was performed in transmission. This strongly indicates that modification of drawn fibers by the present technique results in surface grafting. For isotropic fiber, internal grafting results. These findings are in accord with that found by Kubota and Hata^{20,21} and Amornsakchai and Kubota¹⁸ for similar systems. The fact that VAc-modified fiber shows an additional $\tan \delta$ peak at about 35°C , which is very close to the glass transition temperature of PVAc (32°C),²² naturally leads to the conclusion that the newly formed polymer is phase-separated at microscopic level with the PE amorphous region. This phase-separated structure has been previously observed in γ -irradiated methacrylic acid grafted low-density PE.²³ No additional $\tan \delta$ peak was observed when MMA was used as monomer. It is likely that the glass transition temperature of PMMA is very close to, and superimposed on, the α -relaxation of PE.

For highly drawn PE, the modified fibers display no other relaxation except those of original PE. This could be attributed to a very small amount of grafted polymer. Only change in the height of $\tan \delta$ peaks was observed. It has been shown that the height of $\tan \delta$ peaks both at about -125 and 50°C decreases with increasing draw ratio or equivalently tensile modulus.²⁴ Therefore, the increase in the height of $\tan \delta$ peaks, for both DR15 and DR25 VAc-modified fibers, could be interpreted as structural relaxation of the fiber during long heat treatment of the modification process. The large structural relaxation found for DR25 VAc-modified fiber may be attributed to plasticizing effect of dissolved VAc. This structural relaxation manifests itself clearly in the low tensile modulus of DR25 VAc-modified fiber. For fibers with both DR15 and DR25, treatment in the presence of MMA results in negligible structural relaxation.

The improvement in compressive strength of the modified fibers will now be considered. The compressive strength was found to increase after modification with both MMA and VAc. The level of improvement was, however, different with VAc, giving larger improvement. It was very difficult to quantify the level of improvement as the compressive

strength of the modified fibers are not well-defined. This fact may indicate difficulty in controlling the chemical reaction during irradiation.

Before considering the mechanism of compressive strength enhancement, it is worth addressing the magnitude of the compressive strength obtained in the present study. The compressive strengths of the controlled fibers were measured in the range of 220–246, MPa depending on the draw ratio. These values are significantly higher than that reported for commercial gel-spun PE fiber.¹¹ The difference in compressive strengths of these fibers could be attributed to the difference in their structure and lateral integrity of the fiber. The lateral integrity of melt-spun PE fiber reported by Amornsakchai et al.²⁵ is significantly higher than that of commercial gel-spun fiber found by McGarry and Moalli.²⁶ For the reason that will be discussed later, the high lateral integrity would suppress interfibrillar slip, which is one of the mechanisms for compressive failure in highly oriented PE,^{10,27} and render high compressive strength.

It is now appropriate to consider the mechanism of compressive strength enhancement. It appears that there are several factors that play a part in determining the compressive strength of highly oriented PE fiber. The interplay between these factors and compressive strength seem to be very complex and each factor will be considered in turn. The fact that structural relaxation was observed in a particular sample necessitates an evaluation of the effect of heat treatment on compressive strength of the fiber. To clarify the benefit of the modification technique presented in this work, a set of controlled experiments was performed. Fibers were irradiated in vacuum and then further annealed in the presence of N_2 , MMA, and VAc vapors at atmospheric pressure. It was found that there was a significant improvement of the compressive strength for all samples, as shown in Table IV. Treatment in inert atmosphere (N_2) could improve the compressive strength of the fiber to the same extent as that conducted in MMA and VAc vapors. This observation suggests that the improvement achieved in this case was attributable to the heat treatment. It is likely that during such a long heat (annealing) treatment, structural relaxation might occur. The relaxation is likely to occur in the oriented amorphous interfibrillar region and result in a lower degree of anisotropy. Consequently, lateral integrity of the fiber would be improved and sliding of microfibrils passing each other to accommo-

Table IV Percentage Improvement in Compressive Strength of PE Fibers after Different Treatments

Draw Ratio	% Improvement in Compressive Strength				
	N ₂ ^a	MMA ^a	Vac ^a	MMA- <i>g</i> -PE ^b	VAc- <i>g</i> -PE ^b
15	36	36	21	10	40
25	21	15	18	20	43

^a Irradiated in vacuum and then annealed in the respective atmosphere, compared with original fibers.

^b Irradiated and annealed in the presence of monomers, compared with fibers obtained from (a).

date strain during kink band formation would become more difficult. Fibers with higher draw ratio (DR25) show lower improvement because of high thermal stability.

When the fibers were first irradiated in the presence of monomers and also further annealed in the presence of the same monomer, it was found that further significant improvements can still be obtained. This is a strong indicator that the presence of monomer vapor during irradiation is important. The level of improvement was low for MMA and high for VAc. For fiber with DR25 and modified with VAc, a significant drop in tensile modulus and large $\tan \delta$ peaks suggest that the improvement in compressive strength is due primarily to structural relaxation.

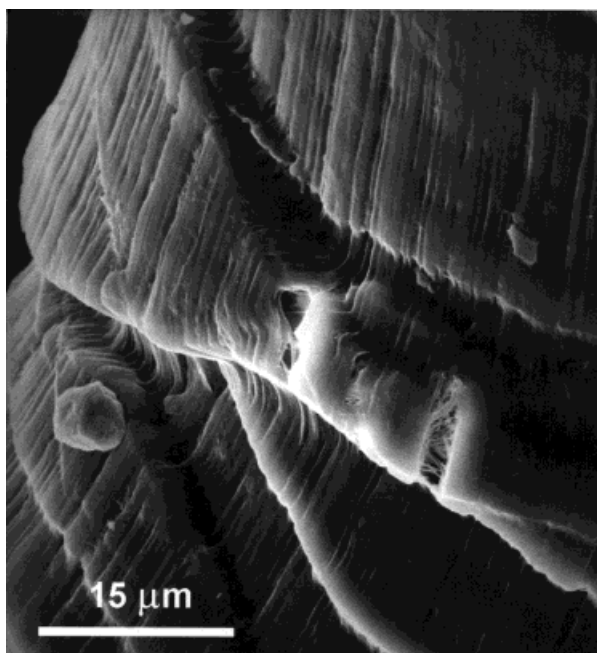
The effect of monomer type on compressive strength of the fiber may be deduced from fiber with DR15 where structural relaxation is limited. It appears that VAc-modified fiber has higher compressive strength than MMA-modified fiber. It is plausible that the rubbery nature of PVAc may help dissipate the kinetic energy imposed on the fiber during snapping back in TRT. The fact that MMA-modified fiber also displays higher compressive strength than the controlled fiber suggests that grafted polymer contributes significantly to preventing compressive failure. It is not certain how this is achieved. The following mechanism is speculated. Compressive failure of highly oriented PE is known to be associated with kink band formation^{10,27} and its formation mechanism has been proposed to be a combination of c-shear deformation and intermicrofibril (or intercrystallite) slip. Kink band has been found to form first on the fiber outer surface and the associated strain was said to dissipate in the interior by interfibrillar slippage. In the present study, oriented PE fibers were exposed to monomer vapors both before and during irradiation. It has been reported that small organic molecules like toluene can still diffuse into the amorphous region of

drawn PE^{28,29} although at a much lower rate (or permeability) as compared with isotropic PE. Drawing was found to affect the equilibrium sorption of toluene to a much lesser extent, as the value only drops by a factor of 4. It is, therefore, very likely that irradiation of the drawn PE fiber, which has been left in the atmosphere of either MMA or VAc vapor, results in graft copolymer of either PMMA or PVAc in the amorphous interfibrillar region. The structure of these modified fibers may be assumed to be phase-separated as that found in VAc-modified isotropic fiber already discussed. The presence of such graft copolymer would prevent or inhibit sliding of the microfibrils already mentioned and render higher compressive strength.

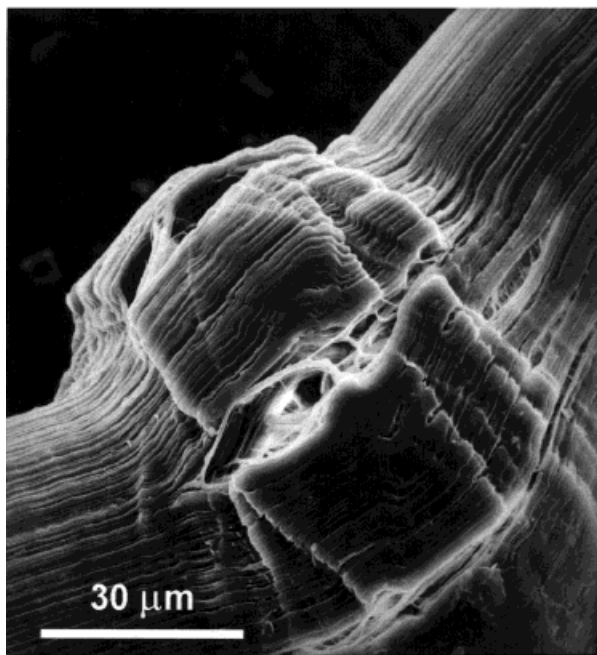
Examination of kink bands formed in the bent sample [Fig. 5(a)] and in the sample after TRT [Fig. 5(b)] revealed that lateral splitting may also occur in places. This may provide further evidence that, in addition to sliding of microfibrils, lateral or circumferential expansion of the fiber also plays a part in accommodating the kink formation. The presence of grafted polymer in the interfibrillar region of the fiber is likely to increase the interfibrillar bonding. The effect of stronger interfibrillar bonding would be to prevent or reduce lateral or circumferential expansion of the fiber and, as a result, higher compressive force is required to cause kink band formation.

CONCLUSION

A novel technique to improve the compressive strength of highly oriented PE fiber has been presented. The technique consists of soaking the fiber in the vapor saturated atmosphere of some vinyl monomers. This is then followed with γ -irradiation and further annealed in the presence of the same monomer. It was found that significant



(a)



(b)

Figure 5 SEM of kink bands formed in MMA-modified PE-15 fibers. (a) Kink bands created by peeling fiber surface and bent back, and (b) kink bands formed after TRT.

improvement of compressive strength was obtained. Several factors are believed to play a part in that improvement. These factors include struc-

tural relaxation of the fiber and the presence of graft copolymer. It is speculated that the effects of these factors are to increase lateral integrity, hence preventing microfibrillar sliding and/or circumferential expansion of the fiber and if the graft copolymer is of rubbery nature, energy dissipation by the grafted polymer may be one of an important additional mechanism.

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