

Catalytic Grafting: A New Technique for Polymer/Fiber Composites. II. Plasma Treated UHMPE Fibers/Polyethylene Composites

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SYNOPSIS

In this paper, the catalytic grafting technique for preparation of polymer/fiber composites is extended to plasma treated ultra-high modulus polyethylene (UHMPE) fiber/high density polyethylene (HDPE) system. The OH groups introduced on the UHMPE fiber surface by oxygen plasma treatment were used to chemically anchor Ziegler-Natta catalyst which then was followed by ethylene polymerization on the fiber surface. The morphology and interfacial behavior, as well as the mechanical properties, of the HDPE composites reinforced by catalytic grafted or ungrafted UHMPE fibers were investigated by SEM, DSC, polarized light optical microscopy, and tensile testing. The experimental results show that the polyethylene grafted on the fibers acted as a transition layer between the reinforcing UHMPE fibers and a commercial HDPE matrix. The interfacial adhesion was also significantly improved. Compared with the composite reinforced by ungrafted UHMPE fibers, the composite reinforced by catalytic grafted UHMPE fibers exhibits much better mechanical properties.

INTRODUCTION

In a previous paper,¹ we presented a new asbestos/polyethylene composite prepared by the catalytic grafting technique. This technique is based on chemical anchoring of a catalyst on reinforcing agents containing OH groups on their surface and then conducting an olefin polymerization on the supported catalyst. The chemical bonds established between the matrix and the fibers improve the adhesion while the polymer grafted on the active sites of each fiber ensures a good dispersion and wetting of the fibers in the synthesized matrix. The asbestos/polyethylene composites obtained in this way exhibit much better performance than those of the composites made by in situ polymerization or conventional mixing. This demonstrates clearly that catalytic grafting improves the interface adhesion of composites in a way that cannot be achieved by blending or in situ polymerization. It is expected that this technique can be extended to other fiber/

polyolefins systems, even with those in which the reinforcing material is not OH-containing fibers, as long as OH groups or other active groups could be generated on the fiber surface by physical or chemical treatment.

We now focus on polyethylene fiber/polyethylene composites. The excellent mechanical properties of polyethylene fibers make them an important reinforcing material for thermoplastic polymer composites. Their main drawback remains their relatively low melting temperature which restricts their use with several engineering thermoplastics. The difference in the melting point of the PE fiber and commercial polyethylene, either HDPE or LDPE, offers the possibility of preparing a single polymer composite, a term used to designate a composite in which the matrix and the reinforcement are made from the same polymer with different morphologies.² Such a single polymer composite was intensively studied by Porter et al.,²⁻⁴ as well as Aji et al.^{5,6} They found that the structural similarity of the matrix and the fiber in the single polymer composite leads to the transcrystallization of polyethylene on the PE fiber surface and enhances the properties of the composite, mainly in the transverse direction of

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the fibers.⁶ The innovation of ultra-high modulus polyethylene fiber prompts the development of more advanced polymer composites which combine good mechanical properties with low specific weight. The chemical inertness of linear polyethylene and the complete absence of any polar groups, however, makes it a problem to achieve good adhesion between the UHMPE fiber and the polymer matrix. Many efforts have been therefore devoted to modifying the surface of UHMPE fibers. Modification by plasma treatment has drawn much attention, because it involves only a surface modification, and the bulk properties of the fibers, which are crucial for reinforcing materials, can be preserved.⁷

The oxygen plasma treatment is most effective in modifying the surface of Spectra™ fibers⁸ (the UHMPE fiber developed by Allied Fibre Inc.), resulting in effective oxidation of the surface. On average, one out of every three to four oxygen atoms on the surface of the treated fibers is a reactive site, consisting of either a hydroxyl, carbonyl, or carboxylic acid functional group. Ward et al.⁹⁻¹¹ reported that the adhesion between the UHMPE fiber and epoxy resin matrix was significantly improved when the fibers were plasma treated.

The hydroxyl or carboxylic acid groups generated on the UHMPE fibers by means of plasma treatment afford reactive sites for chemical anchoring of the catalyst, and therefore the possibility of preparing new UHMPE fiber/PE composites by the catalytic grafting technique. The polyethylene grafted on the UHMPE fiber is expected to act as a transition layer, and the chemical bonding established between the PE fiber and the PE matrix should improve the adhesion of the reinforcing material and the polymer matrix. This is expected to enhance the mechanical properties of the composite. In this paper, we studied the fixation of titanium tetrachloride on the plasma-treated UHMPE fiber, ethylene polymerization on the fiber surface, the morphological characterization, and interfacial behavior, as well as the mechanical properties of the plasma-treated UHMPE fiber/HDPE composite obtained by catalytic grafting by means of SEM, polarized light optical microscopy, DSC, X-ray energy-dispersive (ED) analysis, and tensile testing.

EXPERIMENTAL

Materials

The polyethylene used in this study was a high-density polyethylene (HDPE) XS84672.07 from Dow

Chemical (melt flow index of 6.0 g/10 min). The oxygen plasma treated ultra-high modulus polyethylene (UHMPE) fiber Spectra™-1000 was supplied by Plasma Science Inc. According to the manufacturer,⁸ after oxygen plasma treatment, hydroxyl and carbonyl groups each account for 6.9% of the total oxygen in the Spectra™-1000 samples, and the carboxylic acid groups account for 16.7% of the total oxygen. On average it appears that one out of every three to four oxygen atoms is a reactive site containing either a hydroxyl, carbonyl, or carboxylic acid group. Since the oxidation of the fibers occurs only on the surface, 25% to 30% of the fiber surface oxygens consist of reactive sites. These reactive sites could be used to chemically anchor the catalysts. TiCl_4 and $\text{Al}(\text{C}_2\text{H}_5)_3$ were used as catalysts for ethylene polymerization. The ethylene (Canadian Liquid Air Ltd.) used as monomer was dried and deoxygenated by bubbling through hexane containing a small amount of $\text{Al}(\text{C}_2\text{H}_5)_3$ before polymerization. Hexane was also used as solvent during polymerization and was dried over sodium for one day and distilled under nitrogen prior to use.

Preparation of Composites

The procedure of catalyst anchoring and the subsequent Ziegler-Natta polymerization of ethylene on fiber surface were described elsewhere.¹ The difference with the present system is that since the UHMPE fiber is a long fiber, a monofilament of a certain length was wound on a plastic frame. Several such frames were fitted together at a distance of 2 mm from each other, and were then put in the reactor. A magnetic stirring bar was used during the catalyst grafting reaction, as well as the ethylene polymerization.

Two different plasma-treated UHMPE fiber/HDPE composites were prepared, namely, the composite reinforced by catalytically grafted UHMPE fiber (PEG) and the composite reinforced by ungrafted UHMPE fiber (PEF). The fibers were wound parallel to each other on HDPE frames and then sandwiched between previously pressed HDPE films, pressed for 25 min at 132°C, 20 min for contacting and 5 min for pressing, using a 6-ton Carver laboratory press. The sample was cooled to 110°C, held at that temperature for 10 min, and then cooled to room temperature under press. The dumbbell specimens for tensile testing were cut along the fiber direction from these compressed sheets.

Composite films each containing a single filament, of either catalytically grafted or ungrafted

UHMPE fiber, were prepared in a similar way for examination under the optical microscope.

Characterization

The surface morphologies of the plasma-treated UHMPE fibers, either the original or the ones reacted with catalysts or covered with the catalytic grafted polyethylene, were examined through a Jeol JSM-III SEM microscope. The surface elements of the fibers were analyzed by X-ray ED spectra. The melting endotherms were determined using a computerized Perkin-Elmer DSC-4 at a heating rate of $10^{\circ}\text{C}/\text{min}$. The composite films containing single filaments were observed through a Zeiss optical microscope fitted with a Mettler FP-80 temperature regulated hot-stage between 120 and 160°C at a heating rate of $1^{\circ}\text{C}/\text{min}$. Photographs were taken at various temperatures. The mechanical properties of the two different composites were examined using an Instron tensile instrument at a cross head speed of $0.5\text{ cm}/\text{min}$.

RESULTS AND DISCUSSION

The SEM micrographs (Fig. 1) compare the surface morphologies of the plasma-treated UHMPE fibers before and after they have reacted with TiCl_4 or $\text{Al}(\text{C}_2\text{H}_5)_3$. It seems that the anchoring of catalysts on the fiber surface acts like a chemical etching on the fiber surface, resulting in an obvious change in the surface morphology. Furthermore, the X-ray ED spectra (Fig. 2) confirm qualitatively that the Ti and Al were introduced on the fiber surface after the fibers reacted with the catalysts.

The UHMPE fibers with chemically anchored TiCl_4 served as a supported catalyst for ethylene polymerization. As soon as $\text{Al}(\text{C}_2\text{H}_5)_3$, the co-catalyst, was injected into the reactor under positive pressure of ethylene, the fibers became brownish, and ethylene was polymerized on the fiber surface. The SEM micrographs (Fig. 3) demonstrated clearly that the catalytically grafted polyethylene covers the fiber, forming a polymer coating on its surface.

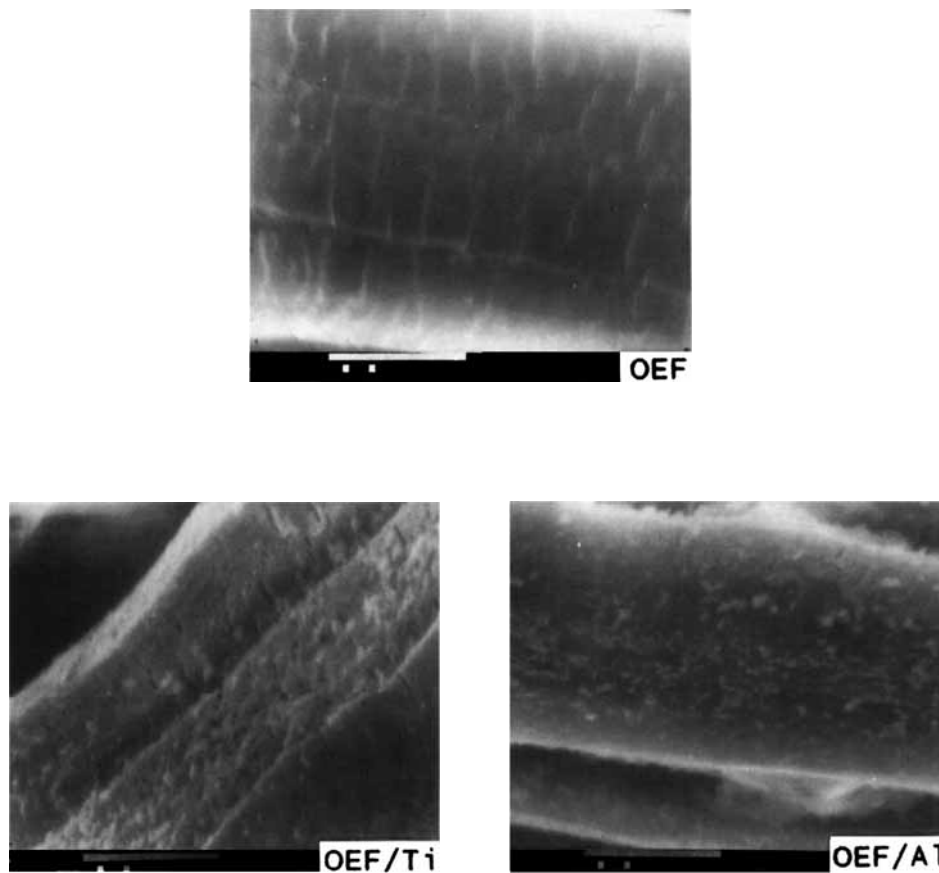


Figure 1 SEM micrographs of the plasma-treated UHMPE fibers before (OEF) and after they are reacted with TiCl_4 (OEF/Ti) or $\text{Al}(\text{C}_2\text{H}_5)_3$ (OEF/Al) (original magnification $\times 3000$).

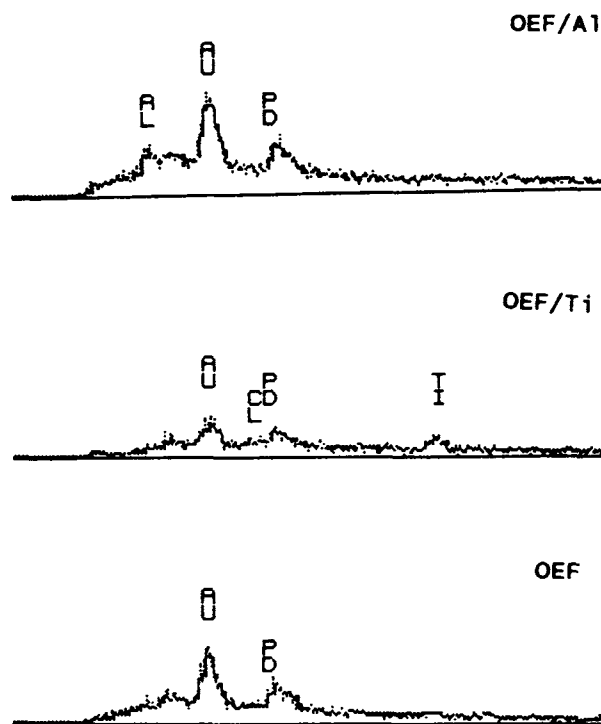


Figure 2 Energy-dispersive spectra of the plasma-treated UHMPE fibers before (OEF) and after reacted with TiCl_4 (OEF/Ti) or $\text{Al}(\text{C}_2\text{H}_5)_3$ (OEF/Al).

Figure 4 shows the thermal behavior of commercial HDPE and the ungrafted UHMPE fibers (OEF), as well as the catalytically grafted UHMPE fibers (CEG). Figure 4(a) shows the first scanning curves of the samples at a heating rate of $10^\circ\text{C}/\text{min}$. For commercial HDPE the endothermal peak appears at 128°C , and for the ungrafted fibers, the small peak at 135°C corresponds to the melting point of isotropic PE.¹² The peak at 147°C is common for

highly chain-extended PE,¹² and the peak at 153°C is due to the hexagonal phase of PE.¹² It is clear that the difference in morphologies leads to a difference in melting points. The melting point of the UHMPE fiber is much higher than that of commercial HDPE, offering the opportunity of obtaining a single polymer composite. It is interesting to note that for the catalytically grafted UHMPE fiber, the peak at 147°C becomes smaller and the peak at

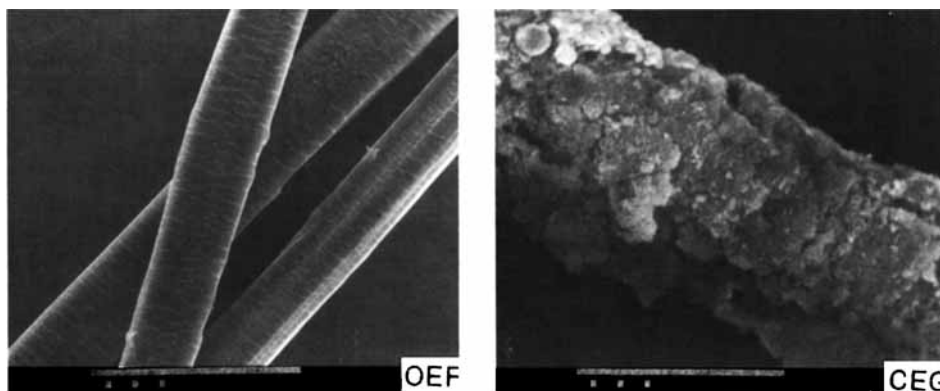


Figure 3 SEM micrographs of the plasma-treated UHMPE fibers before (OEF) and after catalytic grafting polymerization of ethylene on the fiber surface (CEG) (original magnification $\times 450$).

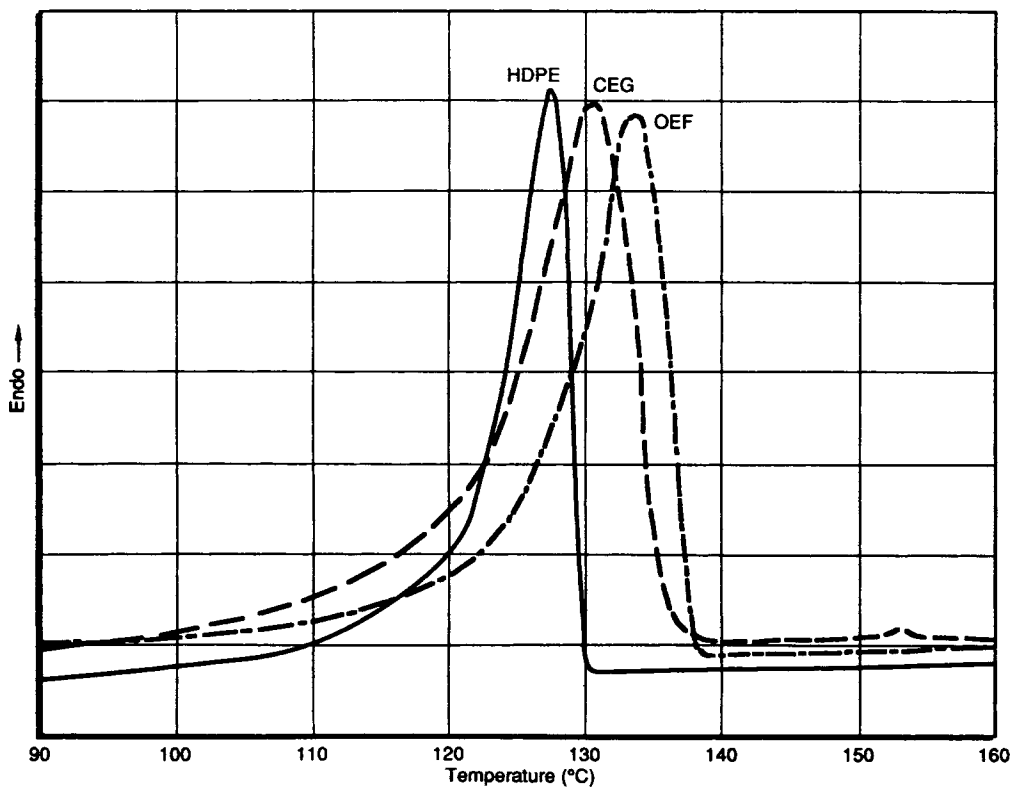
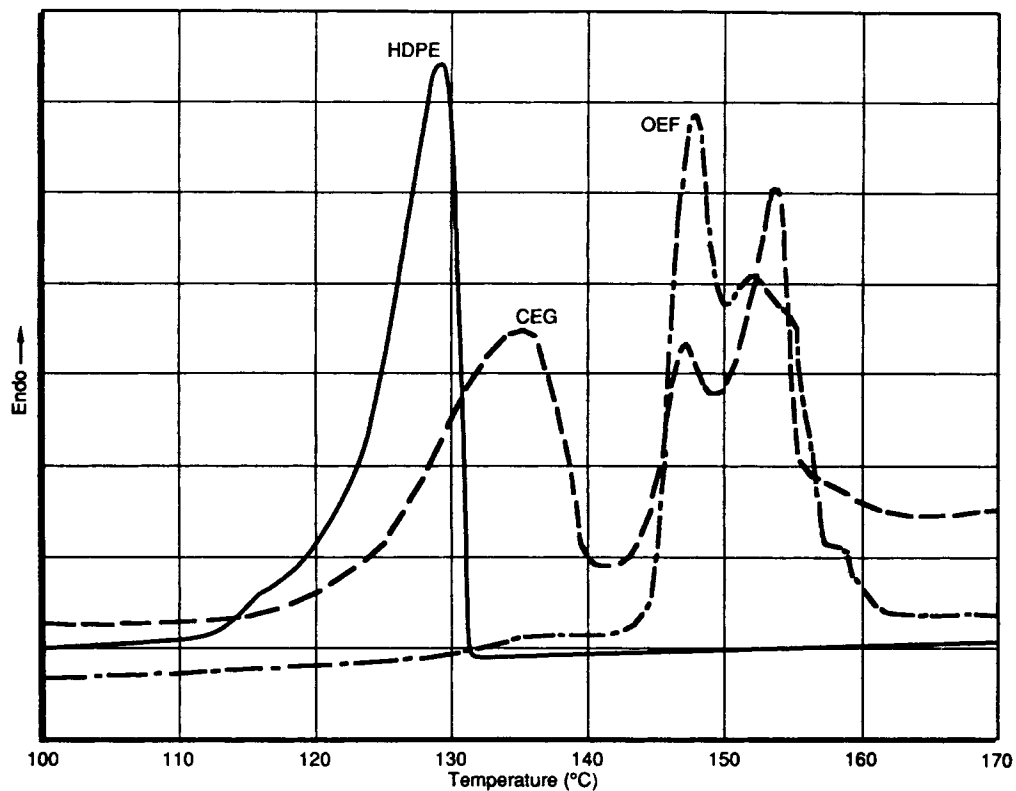
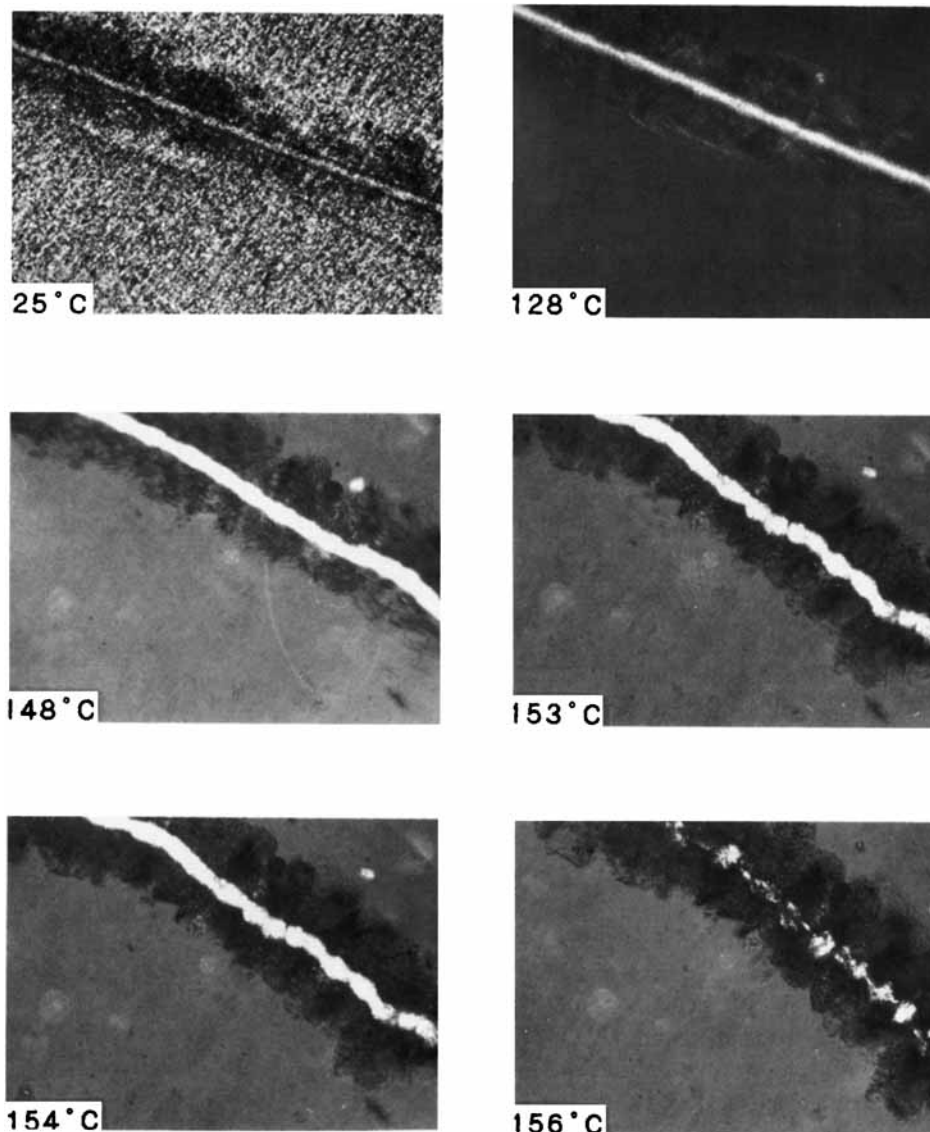


Figure 4 DSC scanning curves of commercial HDPE, ungrafted UHMPE fibers (OEF), and the catalytically grafted UHMPE fibers (CEG) (a) First scanning at heating rate of 10°C/min. (b) Second scanning at heating rate of 10°C/min after the samples were heated to 180°C and quickly cooled to 70°C.

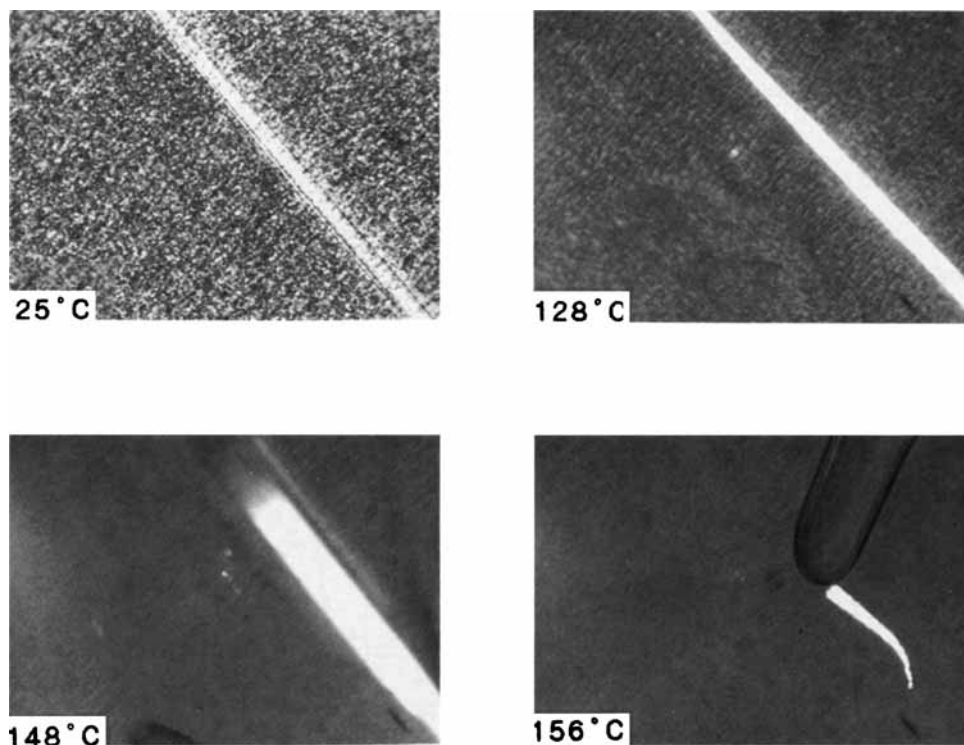


PEG

Figure 5 Polarized light optical photographs of the composite films containing a single filament of the catalytically grafted UHMPE fiber (PEG) and the ungrafted UHMPE fiber (PEF) taken at different temperatures (original magnification $\times 35$).

135°C increases dramatically. This indicates that some changes in crystal structure took place during the catalytic grafting and that the grafted polyethylene is different from both the highly chain-extended PE fiber and commercial HDPE. The second scanning curves [Fig. 4(b)], which are obtained after heating the samples up to 180°C followed by rapid cooling to 70°C, and then heating again at a rate of 10°C/min, show that all the three samples possess one endothermal peak. This occurs at 127°C

for commercial HDPE, 134°C for the ungrafted fibers, and 131°C for grafted fibers. The higher melting points at 147°C and 153°C disappear due to the collapse of the highly extended structure upon heating. It can also be seen that the thermal behavior of the catalytically grafted polyethylene is between that of commercial HDPE and of the original UHMPE fibers. It is therefore concluded that the grafted polyethylene acts as a transition layer between the reinforcing fibers and the commercial HDPE matrix



PEF

Figure 5 (continued from the previous page)

in the single polymer composite, and that it thus improves interface adhesion.

The observation of the composite films, each containing a single filament of the catalytically grafted UHMPE fiber (PEG) or ungrafted UHMPE fiber (PEF), through a polarized light optical microscope equipped with a Mettler hot-stage is especially interesting (Fig. 5). At room temperature, the filament in the PEG and PEF being embedded in crystalline matrix of HDPE, the structure formed by grafted polyethylene can be observed. At 128°C, as the commercial HDPE began melting, the grafted polyethylene layer became clearer. At 148°C, a temperature higher than the melting point of the highly extended polyethylene, the single filament of ungrafted UHMPE fiber in PEF melted and shrank very quickly—so quickly that it was difficult to take a static image at a given exposure time. This may suggest a weak adhesion between the commercial HDPE and the reinforcing fiber. In contrast, the single filament of the catalytically grafted UHMPE fiber in PEG still preserved its oriented structure, even though it more or less shrank. At 156°C, a temperature higher than the maximum melting point of

the UHMPE fiber, the ungrafted UHMPE fiber reduced to a small piece. The catalytically grafted UHMPE fiber also melted, but constrained by the grafted polyethylene, showing a quasi-fiber shape. This procedure demonstrated clearly that grafted polyethylene acted as a transition layer between the commercial HDPE matrix and the reinforcing UHMPE fibers, and suggests that the adhesion between the fibers and the matrix is strong enough to constrain the fiber to maintain its orientation. If we examine the photographs of PEG in detail, we find that upon heating, when the temperature was over 148°C, the grafted UHMPE fiber more or less shrank, but did so together with the adjacent layer of the grafted polyethylene. This might be due to possible chemical bonding established by catalytic grafting between the UHMPE fiber and the grafted polyethylene. This would be responsible for the improvement in interface behavior of the composite film containing the single filament of grafted UHMPE fiber.

DSC scanning curves of the different composites also demonstrated the transition effect of grafted polyethylene (Fig. 6). The peak at 127–128°C due

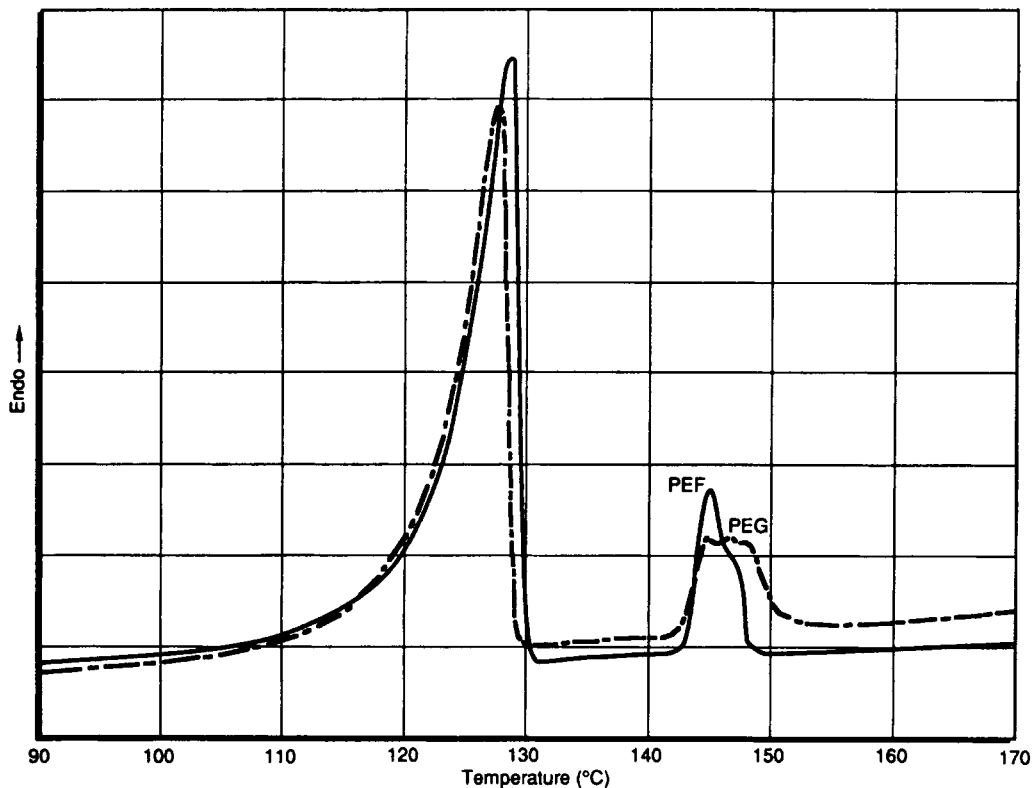


Figure 6 DSC scanning curves of the composite reinforced by catalytically grafted UHMPE fibers (PEG) and the composite reinforced by ungrafted UHMPE fibers (PEF). Fiber content: 8%.

to commercial HDPE are almost the same for both composites, but the peak due to the UHMPE fiber in the composite reinforced by the catalytically

grafted UHMPE fiber (PEG) is broader than that of the composite reinforced by the original one (PEF), and extends to higher temperature. Van

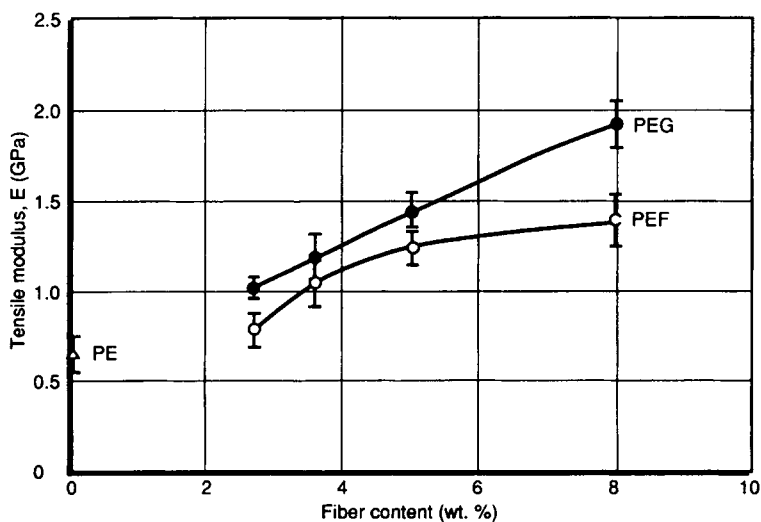


Figure 7 Modulus of PEG and PEF types of plasma-treated UHMPE fiber/HDPE composites.

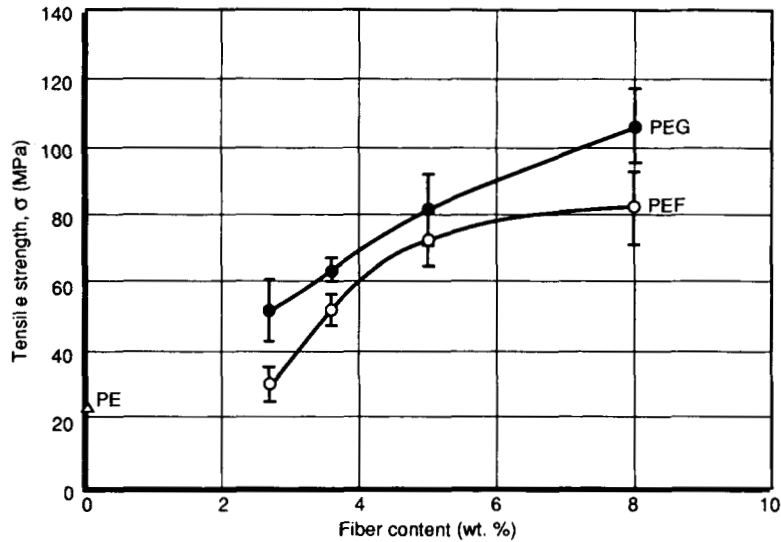


Figure 8 Tensile strength of PEG and PEF types of plasma-treated UHMPE fiber/HDPE composites.

Aerle et al.¹² reported a similar phenomenon, i.e., the chain-extended ultra-high molecular weight polyethylene can be constrained effectively by embedding in an epoxy resin to prevent complete melting of the polyethylene even above its melting point.

Figures 7-9 compare the tensile properties of plasma-treated UHMPE fiber/polyethylene composites reinforced by catalytically grafted UHMPE fiber (PEG) or by ungrafted fiber (PEF). The tensile properties of pure polyethylene are also listed for comparison. It is evident that the PEG composite

is clearly superior to the PEF composite in tensile properties. The modulus and the tensile strength of PEG are higher than those of PEF over the whole experimental range. For example, when the fiber content is 8%, the modulus and tensile strength of the PEG composite reach around 1.9 GPa (Fig. 7) and 106.7 MPa (Fig. 8) respectively, significantly higher than the values of 1.4 GPa and 82.1 MPa for the PEF composite. And the elongation at break for the PEG composite improved even more significantly, reaching 19.2% for a fiber content of 5%, and 14.7% for a fiber content of 8%, compared to

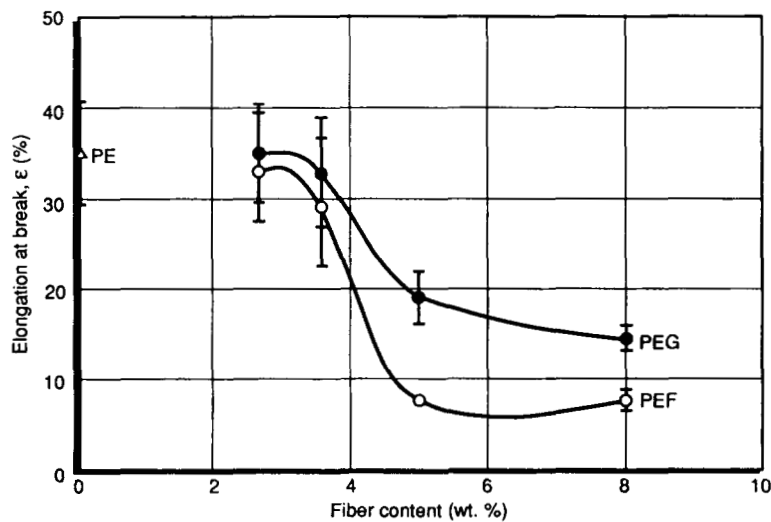


Figure 9 Elongation at break of PEG and PEF types of plasma-treated UHMPE fiber/HDPE composites.

values of 7.3% and 6.6% for the PEF composite with the same fiber content. On the basis of fiber concentration, an efficiency coefficient of the fibers K , can be defined as⁵:

$$K = [P_c - (1 - V_f)P_m] / P_f V_f$$

where the subscripts c , m , f stand for the composite, the matrix and the fiber, and P is the physical property (e.g. modulus or strength). V_f represents the volume fraction of fibers within the composites. This coefficient (K) depends on the nature of the fibers, the fiber concentration, the nature of the interface, and the orientation and length of the fibers. It can give some information about the efficiency of the fiber as a reinforcing agent. Figures 10 and 11 compare the K_E (efficiency coefficient for the tensile modulus) as well as K_S (efficiency coefficient for the tensile strength) of PEG and PEF types of composites as a function of fiber content, calculated according to the above formula. It can be seen that the values of both K_E and K_S of PEG composites are significantly higher than those of PEF composites. This suggests a better adhesion between the reinforcing fibers and the polymer matrix in the PEG type of composites, because the only difference in the two kinds of composites is the nature of the interface. It is evident that the improvement in interfacial behavior achieved by means of catalytic graft-

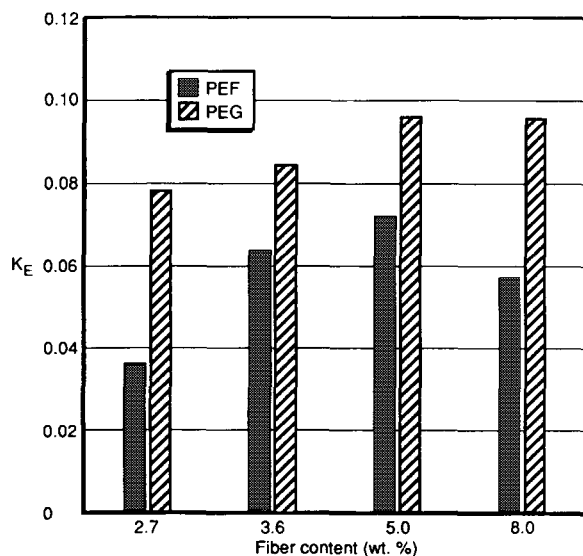


Figure 10 Efficiency coefficient of tensile modulus for PEG and PEF types of plasma-treated UHMPE fiber/HDPE composites as a function of fiber content.

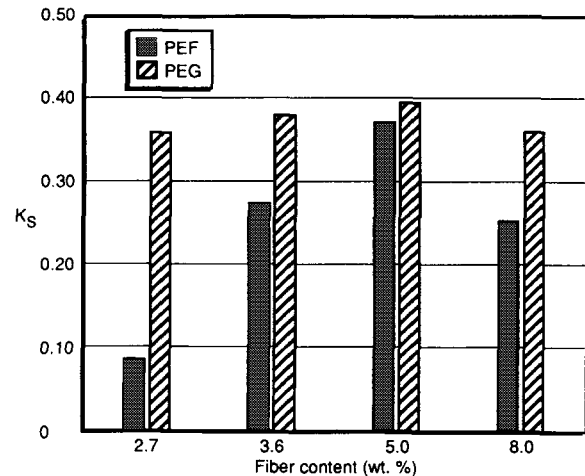


Figure 11 Efficiency coefficient of tensile strength for PEG and PEF types of plasma-treated UHMPE fiber/HDPE composites as a function of fiber content.

ing significantly enhances the mechanical properties of the PEG type of composites.

CONCLUSIONS

The catalytic grafting technique has been successfully applied to the plasma-treated UHMPE fiber/polyethylene composite. The OH groups generated on the PE fiber surface by oxygen plasma treatment are the reactive sites where catalysts may be chemically anchored. By Ziegler-Natta polymerization of ethylene on the UHMPE fiber, the grafted polyethylene covers the fiber, and the grafted polyethylene acts as a transition layer, improving the interface adhesion significantly, and resulting in improvement of the mechanical properties of the new plasma-treated UHMPE fiber/polyethylene composite.

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