Dynamic Mechanical Properties of the Chemical Oxidation on UHMWPE Fibers for Improved Adhesion to Epoxy Resin Matrix

HSIEN-TANG CHIU, JYH-HORNG WANG

Graduate School of Textile and Polymer Engineering, National Taiwan University of Science and Technology, 43, Keelung Road, Section 4, Taipei, Taiwan 10672

ABSTRACT: The improved adhesion of an ultrahigh molecular weight polyethylene (UHMWPE) fiber to an epoxy from applying polypyrrole (PPy) was investigated using chemical oxidation polymerization. The interfacial shear strength of the PPy-treated fiber/epoxy was enhanced by 280%. Such an improvement was verified in the previous research using a pull-out test. Dynamic mechanical analysis (DMA) and a morphological examination were performed to evaluate the characteristics of the molecular motions of the UHMWPE fiber/PPy/epoxy composites. Two composite materials, a UHMWPE fiber/PPy and a UHMWPE fiber/PPy/epoxy, were tested by DMA. The results show that both the α_c transitions of the PPy-treated fibers and its composites shift toward higher temperature. In the SEM photos of the UHMWPE fiber/PPy, a very clear roughening effect on the surface of PPy-treated UHMWPE fiber was also observed, which contributes much to the modification of the interface to the epoxy. The results show that an adhesion improvement mechanism for the PPy-treaded UHMWPE fiber is due to the surface roughening effect and the intermolecular interaction. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 1387–1395, 1998

Key words: UHMWPE fiber; dynamic mechanical properties; polypyrrole (PPy); improved adhesion; pull-out test

INTRODUCTION

The UHMWPE fiber is a high-performance fiber with high strength and modulus. It has been widely used and researched recently. Due to lack of the polarity and a functional group on the surface of this kind of fiber, the surface energy is, therefore, very small. With this, the delamination can easily occur on the interface of this kind of the composite.[1] Therefore, it cannot easily be made into composites due to the characteristics of poor interfacial bonding with the matrix. As a result, improving the adhesion of the UHMWPE fiber has been a widely researched subject. In the past, many researchers used technologies of plasma treatment[2,3] and chromic acid etching[4,5] to improve the adhesive effect of the UHMWPE fiber. Recent researchers (Chiu and Lin[6]) used polypyrrole (PPy) to enhance the interface of carbon fiber and achieved great accomplishments in improving the adhesion of carbon fiber to epoxy. Heisey et al.[7] also employed a PPy coat to enhance the adhesive effect for nylon fiber to epoxy. It therefore was intended in this article to investigate the improvement on the adhesion of UHMWPE fiber to epoxy by utilizing PPy. In the previous research,[8,9] PPy/UHMWPE fiber was prepared using the chemical oxidation polymerization method. A 280% en-

hancement on the pull-out shear strength was obtained for PPy-treated UHMWPE fiber to the epoxy. Such an improvement was verified by investigating the morphology of the surface and by performing the zeta potential and pull-out test.

However, research for the mechanism of the above-mentioned improvement was seldom done. The object of this article was to investigate the interfacial interaction of the molecular motions among the UHMWPE fiber/PPy/epoxy in an attempt to understand the improvement mechanism. The investigation for the characteristics of molecular motions was achieved by dynamic mechanical relaxation analysis.

The relaxation behavior[10] of the crystalline polymer has been discussed extensively. It was often employed to investigate the aggregate structure or the intermolecular motions mode. In addition, it could also be used to investigate the miscibility of the polymer blend and the copolymerization for different kinds of polymers. Generally, the relaxation of the polymer could be categorized into three types,[11] including the α_c transition at the maximum temperature. It is believed to be caused by the motion of the defective molecular chains in the crystalline phase of the semicrystalline polymer; however, it is observed only in the highly crystalline polymer, as in high-density polyethylene and isotactic polypropylene,[12] whereas the α_a transition, also known as the glass–rubber transition, is considered as the molecular motions of the amorphous phase of the semicrystalline polymer. Also, the temperature of the α_a transition is defined as the "glass transition temperature (T_g)." The relaxation behavior at a lower temperature is referred to as the β transition, which is generally caused by the local motions in the amorphous fraction of the polymer.

The viscoelastic behavior of polyethylene was first reported by Kline et al.[13] in 1956. The α_a transition of the polyethylene was reported to be within -30 to 20°C. Such a type of relaxation behavior is the result of the energy absorption due to the diffusional motions of the molecular segments of the amorphous portion. Later, Takayanagi et al.[14] reported an α_c transition at approximately 77°C, which is the energy absorption due to the crystalline melting process or due to the perfection of the crystallite itself. The dispersion of the α_c transition reflects the effect from the external shear strength or the frictional loss resulting from crystalline deformation acting on the plane (200) under the vibrational strain when the crystalline phase was forming. According to Ta-

kayanagi et al.'s research,[14] the intensity at the α_a transition increases dramatically and the α_c transition vanishes when the polyethylene was quenched. Due to this finding, the existence of the α_c transition was therefore proven and that the α_c transition shifted to high temperature with increasing crystallization. It was further inferred that the intensity at the α_c transition of the UHMWPE fiber could increase with increasing orientation and crystallinity.

According to the report of the mechanical properties of uniaxially and biaxially drawn films by Sakai et al.,[15] the E' and E'' of the UHMWPE drawn films increase with increasing draw ratio and decrease with increasing temperature. It was also found in this research that the α_c transition is within $50-80$°C, in which the molecular motions of polyethylene are observed in the crystal grain boundary. Due to the highly crystallinity and orientation of this drawn film, the molecular motions of the α_a and β transitions could not therefore be observed.

In this study, the extended chain structure of the UHMWPE fiber dipped in pyrrole was prepared with $FeCl_3$ into the PPy/UHMWPE fiber for forming chemically oxidative polymerization. The PPy/UHMWPE fiber obtained was then combined with the epoxy and made into UHMWPE fiber/PPy/epoxy composites. The relaxation behavior of the PPy/UHMWPE fiber and the UHMWPE fiber/PPy/epoxy composites were then determined by DMA in an attempt to investigate the characteristics of the molecular motions among the UHMWPE fiber, PPy, and epoxy and, consequently, the interfacial adhesion mechanism.

EXPERIMENTAL

The UHMWPE fiber used in this research is SPECTRA 1000 (Allied Signal Co., VA); its specification is 650 denier/120 number filaments. The surface of the fiber was treated by dipping the fiber in the pyrrole monomer (Tokyo Chem. Co., Tokyo, Japan) directly at 70, 80, and 90°C, holding each temperature constant for 30 min. The dipped fiber was then removed from the pyrrole to the saturated ferric chloride solution ($FeCl_3$; Hayashi Pure Chem., Osaka, Japan) for the chemical oxidization polymerization process for 30 min. The residual PPy on the fibers was then washed
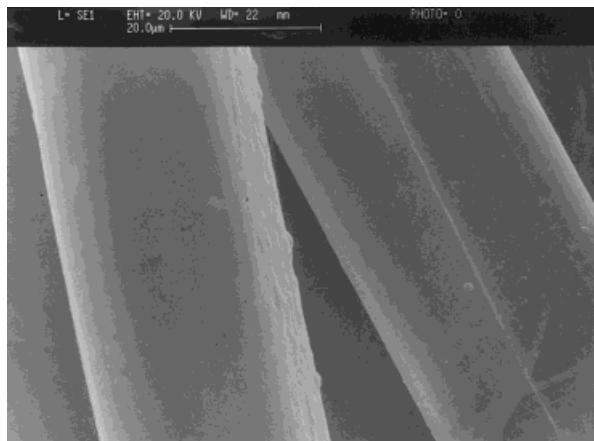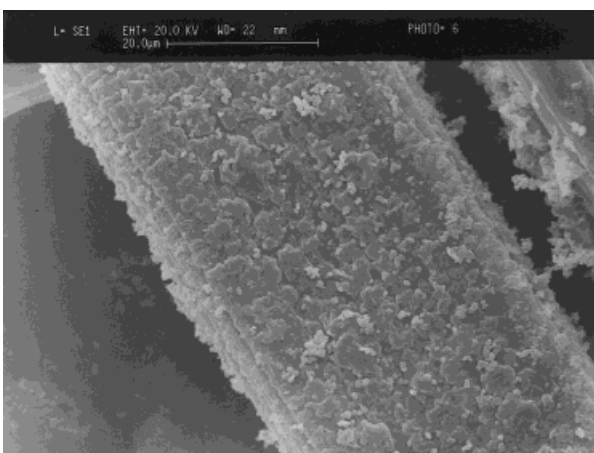
Figure 1 SEM surface photograph of UHMWPE fiber.

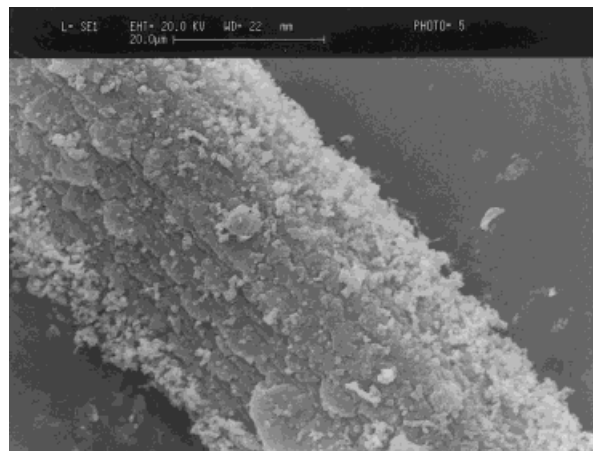**Figure 3** SEM surface photograph of UHMWPE fiber modified by PPy at 80°C.

off by water. After all these processes were completed, the PPy-treated UHMWPE fiber was black in color. Finally, the PPy-treated fiber was then placed in an oven for baking at 65°C for 24 h for dehydration purposes.

The original UHMWPE fiber and the PPy/UHMWPE fiber were then arranged in order. Both ends of the fiber were secured at the PET film and impregnated with the epoxy resin. The thickness of the composite sheet was controlled at 2.0 mm. The resin system was at ambient temperature for curing the epoxy (Ciba-Geigy; GY6010, Basel, Switzerland) with the curing agent (HY943) mixed in a proportion of 100 : 20 and cured at 20°C for 120 min. The UHMWPE fiber/PPy/epoxy composites were then cut to a size of 8.0 × 1.0 × 2.0 mm for the measurements.

The DMA analysis was performed using a GABO

Qualimeter 3031 Ahlder/Aller in a tension mode for both the PPy/UHMWPE single-fiber and UHMWPE fiber/PPy/epoxy composites. The PPy/UHMWPE single fiber was tested with the dynamic strain controlled at 0.15%, the frequency at 3 Hz, and a heating rate of 3°C/min within the range of −120 to 160°C, whereas the UHMWPE fiber/PPy/epoxy composites were tested in a constant force mode with the dynamic force maintained at 0.8N, the frequency at 5 Hz, and a heating rate of 3°C/min within the range of −120 to 160°C. The SEM for the PPy-treated fibers was performed using a Cambridge S-360 to observe the surface morphology.

RESULTS AND DISCUSSION

The surface morphology of the controlled UHMWPE fiber and the PPy-treated UHMWPE fiber

Figure 2 SEM surface photograph of UHMWPE fiber modified by PPy at 70°C.
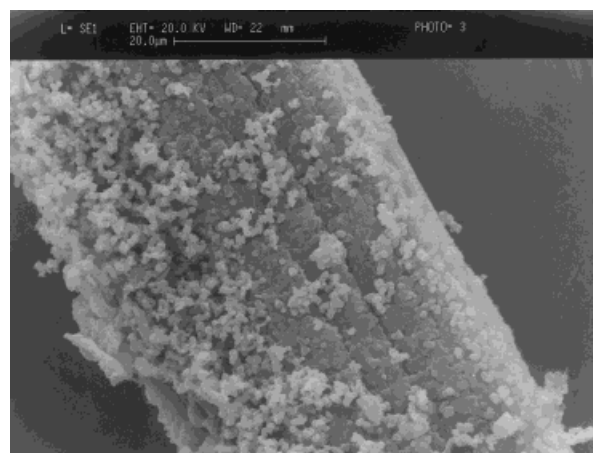
Figure 4 SEM surface photograph of UHMWPE fiber modified by PPy at 90°C.

Table I Comparison of Pull-Out Shear Strength of Various PPy-Treated UHMWPE Fibers

| Sample	Pull-out Shear Strength
UHMWPE fiber/epoxy	87.2 N
70°C + PPy–UHMWPE fiber/epoxy	171.5 N
80°C + PPy–HUMWPE fiber/epoxy	224.4 N
90°C + PPy–UHMWPE fiber/epoxy	180.3 N

at 70, 80, and 90°C is shown in Figures 1–4, respectively. The surface of the fiber shown in Figure 1 is found to be very smooth, while the PPy-treated fiber surfaces in Figures 2–4 are observed with some particles attached, which produces a roughening effect on the surface and contributes to the surface modification considerably.

Table I shows the influence of PPy-treated UH-MWPE fibers on the pull-out shear strength obtained from the previous report.[8] From the observation of the surface morphology, we find the obvious roughness on the UHMWPE fibers by various PPy treatments. There are some relationships between the surface roughness and the pull-out shear strength. This phenomenon is due to that the epoxy acts on both sides of the UHMWPE fibers as a tensile force tends to pull the fibers out of the epoxy, while the PPy-treated fibers forming the surface roughness caused the anchorage reinforcement to supply the mechanical locking and enhanced the pull-out shear strength. As with the other types of mechanisms of interfacial modification, this category of fiber anchorage is used often.

On the other hand, the contributions of PPy to the UHMWPE fiber adhesion to the epoxy resin is not only the anchorage mechanism but also the intermolecular interaction to be considered. Through DMA measurements, we tried to elucidate the mechanism of adhesion except the anchorage effect.

The test temperature range is -120 to $160°C$. According to the test results obtained at the low temperature, no other transition is displayed for the UHMWPE fiber and for the composites at the temperature below $0°C$. Therefore, we will concentrate on the temperature range of $0-160°C$. The storage modulus (E') and dissipation factor $(\tan \delta)$ of the PPy/UHMWPE fiber vs. temperature are plotted in Figures 5 and 6, respectively. From these figures, it is found that the E' of each PPy/UHMWPE fiber and the original UHMWPE fiber
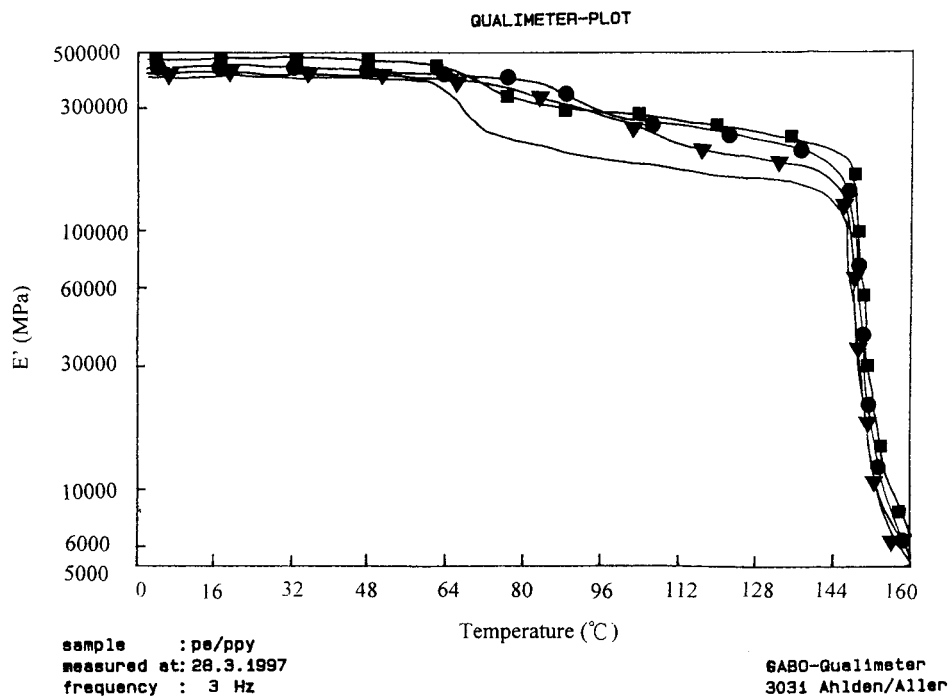
Figure 5 Influence of temperature on storage modulus (E') of UHMWPE fiber under various PPy treatment temperatures: (——) original UHMWPE fiber; (— ■ —) 70°C PPy treatment; (— ● —) 80°C PPy treatment; (— ▼ —) 90°C PPy treatment.
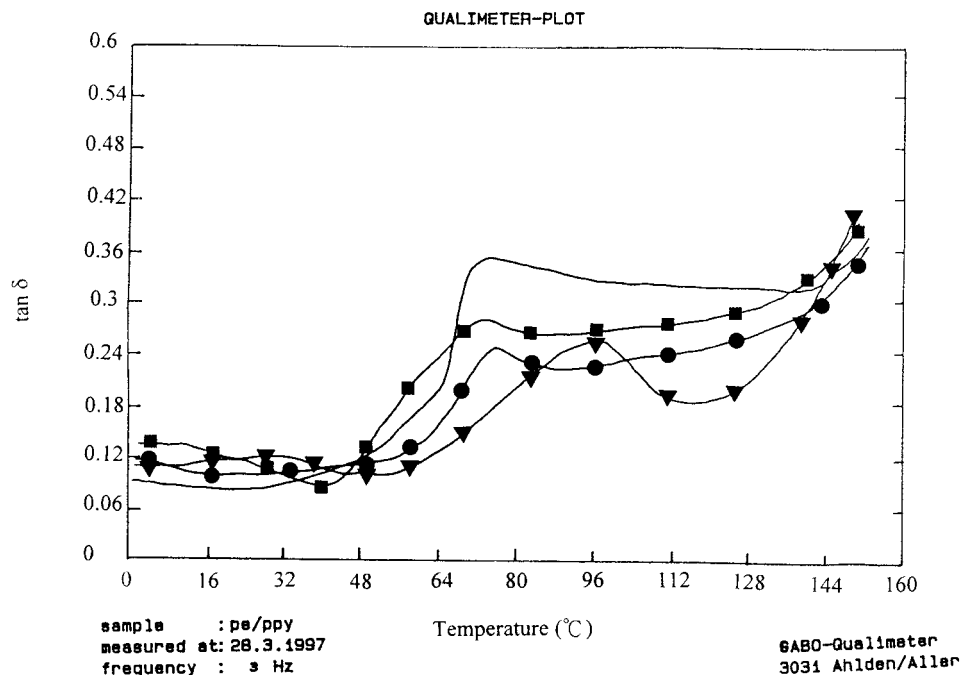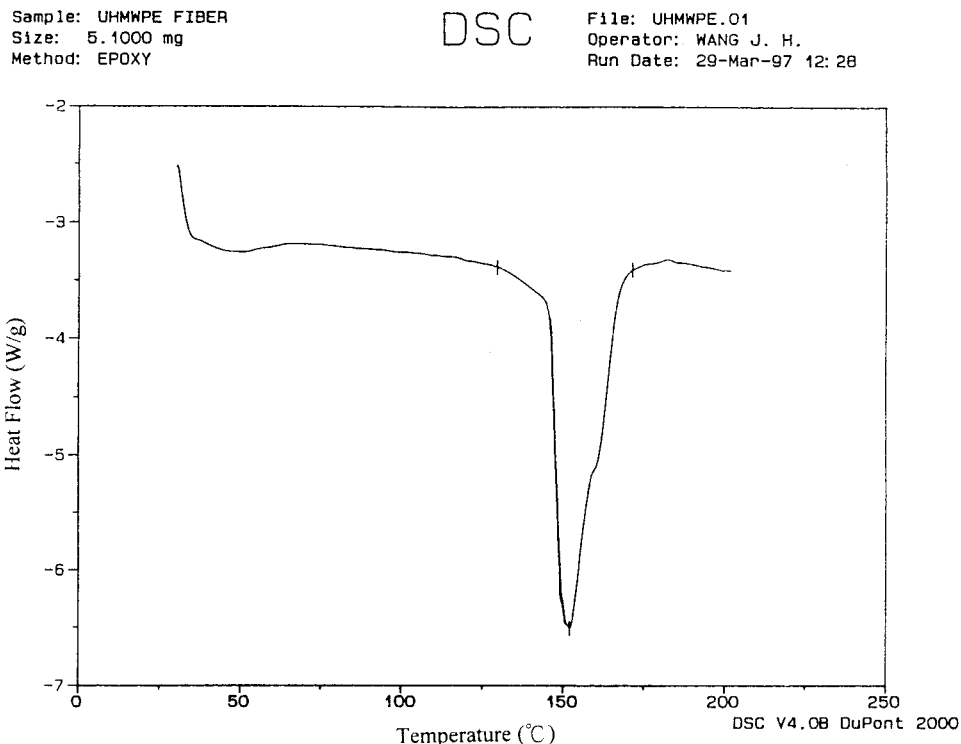
Figure 6 Influence of temperature on the dissipation factor (tan δ) of UHMWPE fiber under various PPy treatment temperatures: (——) original UHMWPE fiber; (— ■ —) 70°C PPy treatment; (— ● —) 80°C PPy treatment; (— ▼ —) 90°C PPy treatment.

decreases with increasing temperature. The E' of the original UHMWPE fiber without PPy treatment is approximately 140 GPa. Also, it increased slightly after the fiber was PPy-treated at various temperatures. Among them, the best effect was obtained from the 70°C treatment, whereas for the PPy treatment at 80 and 90°C, the E' from these two temperatures decrease slightly because the orientation of the fiber is destroyed as a result of the treatment temperatures being higher than the α_c transition (70.8°C). However, these two storage moduli are still higher than that of the untreated UHMWPE fiber.

While the temperature increases, there exist two significant transitions of the storage modulus: One is at 148°C, which is close to the endothermic peak in Figure 7, obtained from the DSC. This transition temperature is therefore proven to be the melting point of the UHMWPE fiber. The other is at 70.8°C. It is inferred that this transition is caused by the molecular defects existing in the crystalline phase of the fiber or by the energy absorption for the molecular motions of defective molecular chains that form the crystalline phase.[13,14] This temperature is also known as the α_c transition. Further observation shows that the α_c transition of the UHMWPE fiber with PPy

treated at 70, 80, and 90°C increases from 70.8°C (without treatment) to 79.0, 88.1, and 94.3°C, respectively. There are two explanations for such a phenomenon: 1) The PPy itself is a charge-transfer complex (PPy^+X^-), which possesses some ionic force to restrain the motion of the molecular chains of the polyethylene, causing the α_c transition of the PPy/UHMWPE fiber to shift toward the higher temperature; and 2) the PPy itself is a rigid polymer. When these rigid molecules are filled in the polyethylene, the polymer molecular chains may be absorbed on the surface of the filler, forming a layer. The polyethylene molecular chains are therefore restrained and the α_c transition, consequently, shifts toward the higher temperature. This finding is identical to the one discovered by Gandhi and Salovey,[16] in which the motion of the molecular chains is affected by the addition of carbon black to polystyrenes and poly(butyl methacrylate). Furthermore, as the treatment temperature increases, the molecular chains have more free volume due to the more vigorous molecular motions. Also, more PPy molecular chains are added as a result. Consequently, the α_c transition shifts to higher temperature with the increasing PPy treatment temperature.

Sample: UHMWPE FIBER
Size: 5.1000 mg
Method: EPOXY

DSC

File: UHMWPE.01
Operator: WANG J. H.
Run Date: 29-Mar-97 12:28

DSC V4.0B DuPont 2000

Figure 7 DSC thermograph of UHMWPE fiber.

The storage modulus (E') and the dissipation factor (tan δ) of the ambient temperature cured epoxy used in this experiment are plotted versus temperature in Figure 8. From this figure, a significant transition at 62°C is found, which is the α_a of the epoxy.

The E' and tan δ of the UHMWPE fiber/PPy/ epoxy composites are plotted versus temperature in Figures 9 and 10, respectively. It is observed in the figures that the UHMWPE fiber/epoxy prepared from the original UHMWPE fiber and represented by the solid line also has two transitions: The first one is at 62.8°C, which is the α_a of the ambient temperature-cured epoxy. The other one is at 94°C, which is the α_c transition of the UHMWPE fiber. The α_c transition obtained from this type of composites is higher than that (70.8°C) determined from the single fiber. This phenomenon is explained as follows: The surface of the UHMWPE fiber is covered by the epoxy. The resin covering the fiber thus forms an insulation layer. Due to this, it takes more energy to activate the motion of the molecular chains and the α_c transition of the fiber, consequently, becomes higher. In another words, the α_c transition of the original fiber is at 70.8°C. Also, there are two transition peaks of the composites: One is at 62.8°C, the α_a

of the epoxy, and the other one is at 94°C, the α_c transition of the fiber, which is higher than that of the original fiber because extra energy needs be provided through heat conduction to activate the motion of the fiber.

There is no significant variation noted among the α_a of the epoxy of the UHMWPE fiber/PPy/ epoxy composites being treated at 70, 80, and 90°C. Figure 11 shows the variation of the α_c transition with respect to the PPy treatment temperature. It is noted that the α_c transition increases from 94°C (without treatment) to 108.6, 115.1, and 120.1°C for the PPy treatment at 70, 80, and 90°C, respectively. The increase is due to the surface roughening effect from the PPy treatment and to the interphase layer formed within the UHMWPE fiber/PPy/epoxy as a result of the interfacial force existing in the C–T complex/epoxy interface. Such an interphase layer is an interfacial force formed between the two phases of the PPy/ epoxy and PPy/UHMWPE fiber. It is the superposition of the mechanical anchor effect from the surface roughening effect and the ionic force of the C–T complex. Because the motion of the molecular chains of the fiber is restrained due to the above effect, the transition peak α_c transition therefore shifts toward higher temperature.

QUALIMETER-PLOT
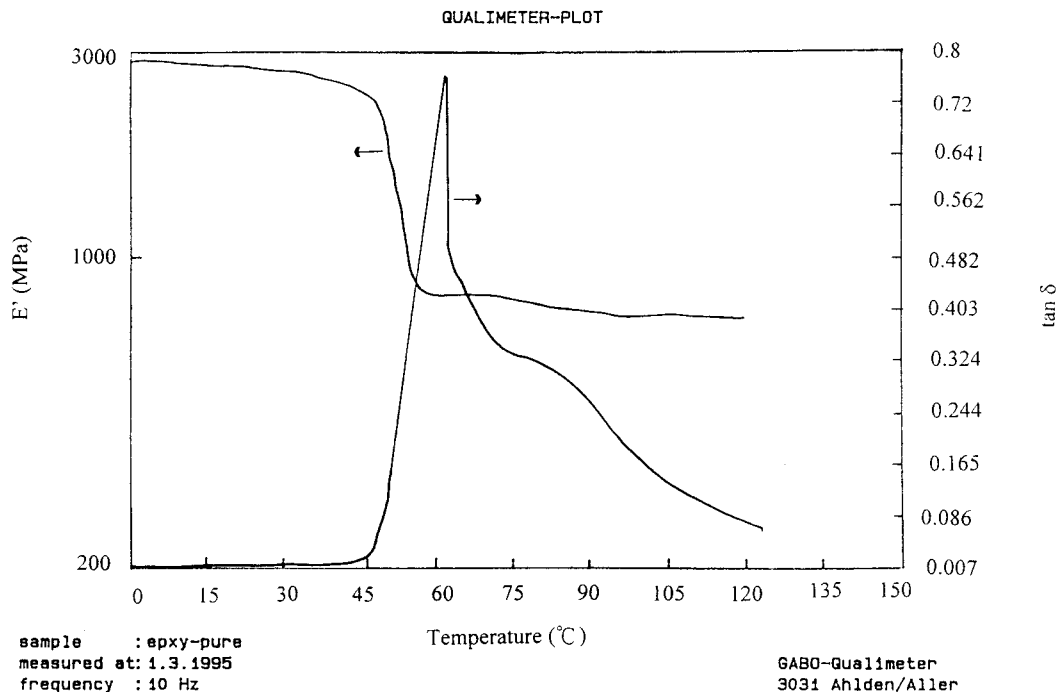
Figure 8 Influence of temperature on the storage modulus (E') and dissipation factor ($\tan \delta$) of the epoxy resin.

Moreover, it is also found that as the PPy treatment temperature increases more PPy molecular chains will be added due to the more vigorous motion of the molecular chains. Also, the $\tan \delta$ also tends to shift toward higher temperature.
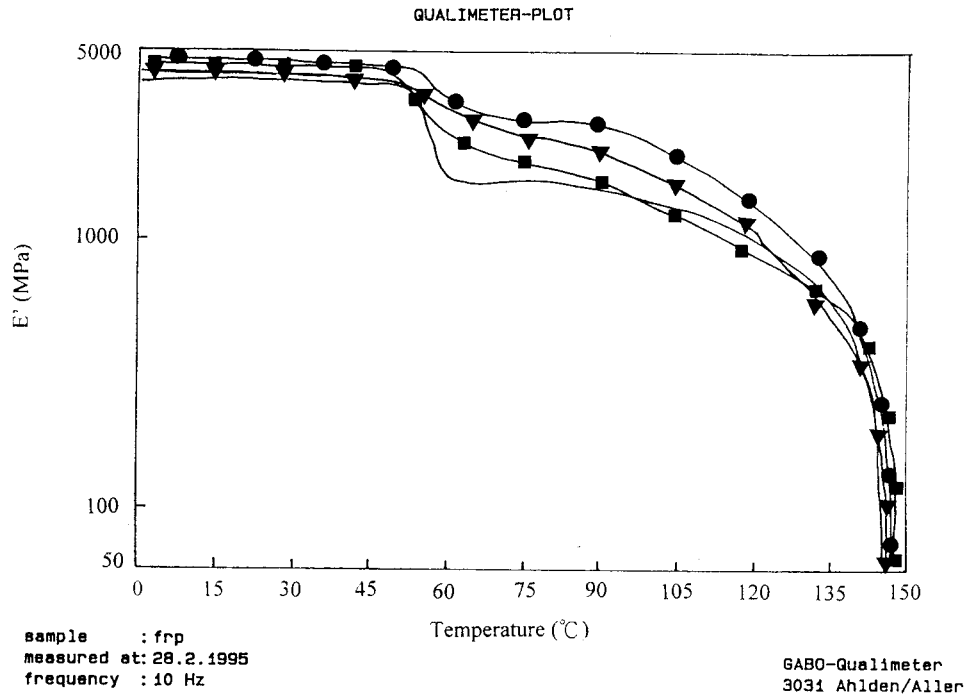
The same results also were found in many PPy/polymer systems. Among the research on the viscoelastic behavior of PPy/polymer films, Kunugi and Ookuzaki[17] found that the α_a transition of the TsO/PPy films shifted to high temperature with increasing PPy polymerization temperature. Moreover, the α_a transition of the TsO/PPy films shifted to higher temperature with the zone drawing. The explanation for the above findings is that the micro-Browning motion of the molecular segments is suppressed because the molecular friction between the adjacent chains is increased. Pawde and Bhat[18] found that the α_c and α_a transitions of PPy/PVDF shifted to higher temperature due to the addition of PPy. Such an effect is commensurate with the antiplasticizing action. According to this research, the addition of PPy would affect the crystalline phase and the amorphous phase. The shifting of the α_a transition of the PPy/polymer to high temperature is because the PPy molecular chains are a rigid filler. Such a shifting effect is equal to the effect from the filling of carbon black,[16] in which polymer molecular chains

may be absorbed on the surface of the filler. Therefore, a layer is formed near where the molecular mobility is substantially reduced, and the α_a transition of the polymer increases.
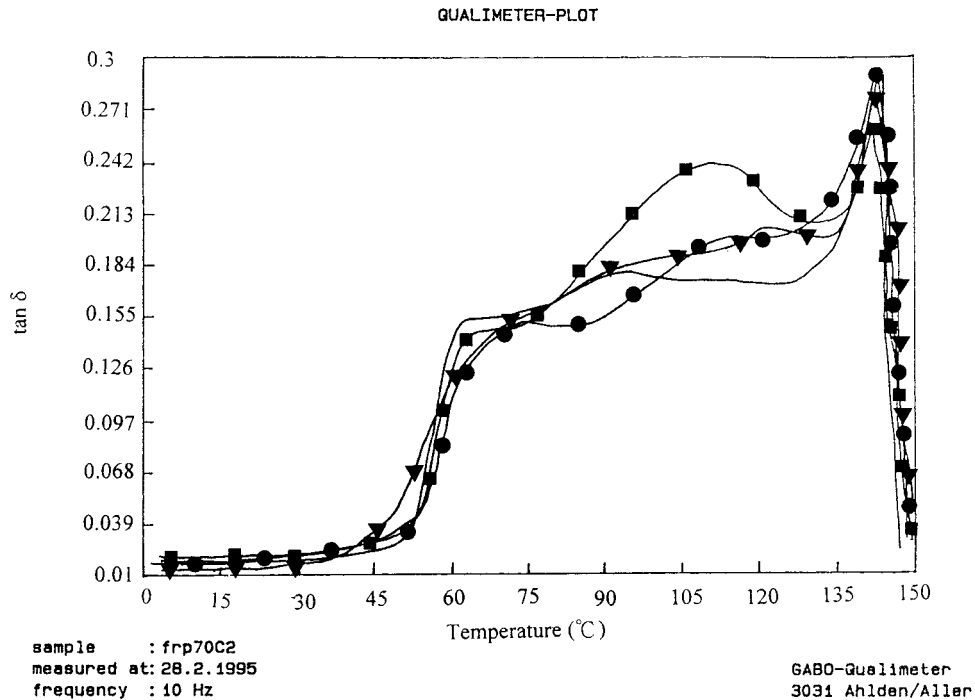
CONCLUSIONS

The improved adhesion of the UHMWPE fiber to the epoxy was achieved through PPy chemical oxidation polymerization. Also, the interfacial force between the molecular chains in different interfaces of the UHMWPE fiber/PPy/epoxy was investigated using dynamic mechanical relaxation analysis. Three conclusions for PPy modification were reached as follows:

1. The PPy molecular chains are introduced and inserted into the amorphous phase of the fiber due to the PPy treatment. As a result, a strong adhesive force is generated within the fiber and a surface roughening effect is formed. Both of them enhance the mechanical anchor effect to the epoxy.
2. The improved adhesion between the PPy/UHMWPE fiber and the epoxy is achieved due to the interfacial force of the C–T com-

QUALIMETER-PLOT

sample   : frp
measured at: 28.2.1995
frequency : 10 Hz

GABO-Qualimeter
3031 Ahlden/Aller

Figure 9   Influence of temperature on the storage modulus (E') of UHMWPE fiber/ PPy/epoxy composites under various PPy treatment temperatures: (——) original UHMWPE fiber; (— ■ —) 70°C PPy treatment; (— ● —) 80°C PPy treatment; (— ▼ —) 90°C PPy treatment.

QUALIMETER-PLOT

sample   : frp70C2
measured at: 28.2.1995
frequency : 10 Hz

GABO-Qualimeter
3031 Ahlden/Aller

Figure 10   Influence of temperature on the dissipation factor (tan δ) of UHMWPE fiber/PPy/epoxy composites under various PPy treatment temperatures: (——) original UHMWPE fiber; (— ■ —) 70°C PPy treatment; (— ● —) 80°C PPy treatment; (— ▼ —) 90°C PPy treatment.
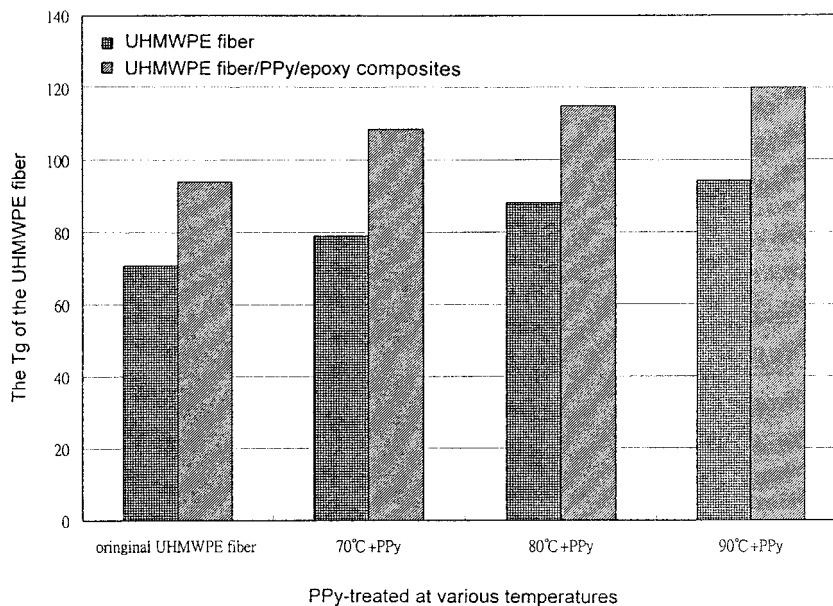
Figure 11 Influence of the interphase on T_g in comparison with both the PPy/UHM-WPE fiber and UHMWPE fiber/PPy/epoxy composites.

plex formed between the interphase of the PPy and the epoxy.

3. PPy is a kind of rigid polymer. The motion of the molecular chains of the UHMWPE fiber and epoxy will be restrained and the α_c transition of the fiber will shift toward high temperature when PPy is filled in the UHMWPE fiber/PPy/epoxy composites.

From the above investigation for the characteristics of molecular motions, the adhesion improvement mechanism for the PPy-treated UHMWPE fiber is the superposed result of the surface roughening effect and ionic force. In addition, the heat resistance of the fiber is also improved because the motion of the molecular chains is restrained.

REFERENCES

1. N. H. Ladizeky and I. M. Ward, *Compos. Sci. Tech.,* **26,** 199 (1986).
2. S. Gao and Y. Zeng, *J. Appl. Polym. Sci.,* **47,** 2063 (1993).
3. S. Gao and Y. Zeng, *J. Appl. Polym. Sci.,* **47,** 2093 (1993).
4. M. S. Silverstein, O. Breuer, and H. Dodiuk, *J. Appl. Polym. Sci.,* **52,** 1785 (1993).
5. M. S. Silverstein and O. Breuer, *J. Mater. Sci.,* **28,** 4718 (1993).
6. H. T. Chiu and J. S. Lin, *J. Mater. Sci.,* **27,** 319 (1993).
7. C. L. Heisey, J. P. Wightman, E. H. Pittman, and H. H. Kuhn, *Text. Res. J.,* **63**(5), 247 (1993).
8. H. T. Chiu and J. H. Wang, *J. Chin. Inst. Text. Eng.,* **13**(2), 53 (1995).
9. H. T. Chiu and J. H. Wang, *Chin. J. Mater. Sci.,* **27**(4), 249 (1995).
10. R. H. Boyd, *Polymer,* **26,** 323 (1985).
11. J. D. Ferry, *Viscoelastic Properties of Polymers,* 3rd ed., Wiley, New York, 1980, Chap. 16, pp. 457–485.
12. S. K. Roy, T. Kyu, and R. S. J. Manley, *Macromolecules,* **21,** 499 (1988).
13. D. E. Kline, J. A. Sauer, and A. E. Woodward, *J. Polym. Sci.,* **22,** 455 (1956).
14. M. Takayanagi, T. Aramaki, M. Yoshino, and K. Hoashi, *J. Polym. Sci.,* **46,** 531 (1960).
15. Y. Sakai, K. Umetsu, and K. Miyasaka, *Polymer,* **34,** 318 (1993).
16. K. Gandhi and R. Salovey, *J. Polym. Sci.,* **41,** 2103 (1990).
17. T. Kunugi and H. Ookuzaki, *J. Polym. Sci. Part B Polym. Phys.,* **34,** 1269 (1996).
18. S. Pawde and N. Bhat, *J. Polym. Sci.,* **54,** 201 (1994).