Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Zhou, Hongmei , Han, Keqing and Yu, Muhuo(2006) 'Preparation of Long Glass Fiber Reinforced Poly(butylene terephthalate) Composites with Chemical Bonding Interphase', Journal of Macromolecular Science, Part A, 43: 11, 1835 — 1851

To link to this Article: DOI: 10.1080/10601320600941110

URL: http://dx.doi.org/10.1080/10601320600941110

Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry, 43:1835–1851, 2006

ISSN 1060-1325 print/1520-5738 online
DOI: 10.1080/10601320600941110

Preparation of Long Glass Fiber Reinforced Poly(butylene terephthalate) Composites with Chemical Bonding Interphase

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Long glass fiber reinforced poly(butylene terephthalate) composites (LGF/PBT) were prepared by a new process. PBT oligomers with low melt viscosity were impregnated into the reinforcing glass fiber and then grafted to the reinforcing glass fiber surface treated with a silane coupling agent during solid-state polymerization. The reinforcing glass fiber, after removing ungrafted PBT from LGF/PBT, was investigated with the result showing the presence of a grafted PBT layer on the surface of treated glass fiber. The mechanical properties of the composites were significantly improved owing to the grafting of the PBT macromolecules. The fiber length distribution and fiber arrangement in the injection molded composites were also studied and the results showed that a small amount long glass fiber could be connected at junction points in the composites, which were of benefit to the mechanical properties of the composites.

Keywords long glass fiber reinforced composites, PBT, solid-state polycondensation, mechanical properties, interface, grafting

Introduction

Fiber reinforced polymer composites offer a number of advantages, such as high modulus and specific strength and are widely used as structural materials. In engineering applications, metal parts have been partly replaced by thermoplastic composites reinforced with glass fiber because of reasonable cost and weight reduction. Mechanical properties of composite materials are closely linked both to the intrinsic characteristics of the matrix and of the fiber, and to the nature of the fiber/matrix interface. The latter is very important for reinforced composites because it is an essential controlling factor for the mechanical properties. The function of the interface is to allow an efficient transfer of stresses within the composites depending on physicochemical properties of both fibers and matrix. Impact and failure behavior of weft-knitted fiber reinforced thermoplastics were reported to be strongly dependent on the interface (1, 2). Zebarjad et al. (3) studied the role of interface on the deformation mechanism of glass fiber/polypropylene composites and found that, whether the interfacial adhesion at the fiber/matrix is strong or not, the craze thickening occurs after some neighboring craze extension. The effect of

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glass fiber/resin interface strength on the impact strength of fiber reinforced polyester was discussed by Yeung and Broutman (4). It was found the total impact energy for the laminates displays a minimum at a critical value of interlaminar shear strength (ILSS). Below this critical value, the total impact energy increases with decreasing shear strength and the dominant energy absorption mode appears to be delamination. Above the critical value, the impact energy increases with increasing values of ILSS and the fracture mode is predominantly one of fiber failure.

There are several aspects that influence polymer-matrix adhesion: adsorption interactions, electrostatic interactions, mechanical interlocking, as well as polymer inter-diffusion between the coupling agents layer and matrix. Many investigations were carried out in recent decades to improve the interface of the matrix and fiber. It can be enhanced by surface treatment of the fiber with different coupling agents, normally organosilane. Chemically, these are hybrid materials that possess the dual functionality of an organic reactive group at one end of the molecule and an inorganic methoxyl group on the other end. The inorganic group is capable of chemically bonding with the silicious surfaces and the organic group at the other end of the molecule may form chemical bonds with the resin. Bikiaris (5) found effective coupling was reflected in increased mechanical properties. Also the glass fiber is normally coated with sizing resins (6) via an aqueous emulsion to prevent them from damage and improve compatibility with selected polymers. Physical modifications aimed at improving mechanical interlocking have been proposed (7). Chemical (8, 9) and plasma (10) treatments have been used to enhance electrostatic and adsorption interactions.

Recently, more and more people have emphasized the grafting of polymer chains to improve adhesion between the matrix and reinforcements. Grafting of polyamides at the surface of plasma-treated Kevlar fibers has been reported (11). It was shown that grafted molecules could improve wetting and mechanical properties of Kevlar/PA composites. The use of a grafting reaction to place polycarbonate oligomers at the interface between glass fiber and polycarbonate matrix, which led to improved hydrolytic stability of the interface, was shown by the fragmentation test (12). The oligomers tightly bound to the glass fiber surface by the grafting reaction were not removed by extraction. X-ray photoelectron spectroscopy (XPS) and pyrolysis gas chromatography/mass spectrometry (Py-Gc/Ms) further confirmed the presence of grafted oligomers on the surface of the treated glass fiber. Noda et al. (13) studied the aggregation structure and molecular motion of glass fiber/matrix nylon 66 interface in short glass fiber reinforced nylon 66 composites by the means of photoacoustic infrared (PAS-IR), pyrolysis gas chromatography (Py-Gc) and XPS. Grafting of polyamide on the surface of glass fiber was investigated (14) and it was concluded that grafting caused the improvement of interfacial shear strength of the composites obtained by the fragmentation test. Interfacial polymerization to polyamide 6,6 followed by introduction of ionic groups was performed on the surface of short glass fibers (15), and tensile and bending properties of the composites were found to be improved.

Among the various methods to improve interfacial adhesion of composites, grafting of polymer chains is an available approach, which has various drawbacks in terms of industrial processibility and applications. Coupling agents have been extensively employed to the surface treatment of the reinforcing fiber to improve the comprehensive properties of composites. But, because reaction time between coupling agents and the matrix is much shorter in traditional processing, such as melt impregnation, normally only several minutes, coupling agents could not react sufficiently with the matrix.

In this study, we developed a new process to produce the grafting of macromolecular chains onto the surface of reinforcing fiber in long glass fibers reinforced thermoplastic composites. In this new process, the reinforcing continuous fiber was impregnated by poly(butylene terephthalate) (PBT) oligomers with low melt viscosity. Then the impregnated continuous fiber was cut to a desired length, named prepregs. Finally, the prepreg was processed *in situ* by SSP to form the high molecular weight matrix, and PBT oligomers were grafted onto the glass fiber surface. One of the advantages of this process over others was that sufficient wetting occurred owing to impregnating low viscosity oligomers into the reinforcing glass fiber, which was the basic requirement for grafting. The more important advantage of this process was the grafting of oligomer chains onto the surface of the reinforcing fiber in the composites. The interfacial polymerization of PBT also took place on the glass fiber surface during *in situ* solid-state polycondensation, while most oligomers underwent polycondensation to form the high molecular weight PBT matrix.

Experimental

Materials

Terephthalic acid (PTA) and 1,4-butanediol (BDO) were provided by SINOPEC Shanghai Petrochemical Co., Ltd (China). Middle alkali non-twist glass fiber, treated with a coupling agent, (3-glycidoxypropyl) trimethoxy silane (KH560), was a commercial product made by JuShi Co. (China). Phenol, tetrachloroethane and acetone were chemical reagents made by Shanghai Jinghua Science and Technological School (China).

Synthesis of Low Melt Viscosity PBT Oligomers and the Preparation of Long Glass Fiber Reinforced PBT Pellets

PBT oligomers ($T_m = 225°C$) were prepared in a commercial, continuous melt polycondensation reactor. When the PBT oligomers melt reached the desired viscosity, the melt was extruded from the reactor by N_2 into the impregnation equipment where the continuous glass fiber was preheated up to an appropriate temperature. Finally, the wetted glass fiber was chopped to 6 mm pellets after cooling, named prepregs. The prepregs were put into a biconical vacuum dryer drum for solid-state polycondensation which was protected with heated flowing nitrogen gas at the constant temperature of 215°C for different time, such as 5 h, 10 h, 15 h, 20 h, 25 h and 30 h, and then the long glass fiber reinforced PBT pellets were obtained.

The Preparation Grafted Glass Fiber

The glass fiber specimens with grafted PBT were prepared as follows: the pellets after SSP was dissolved in tetrachloroethane/phenol, the glass fiber was filtered from the solution, and then washed by the same solvent for more than 5 times to remove PBT polymer that was not chemically grafted to the glass fiber surface. Finally, the glass fibers were washed with acetone and dried at 120°C.

Intrinsic Viscosity Measurement

The pellets were dissolved in tetrachloethane/phenol, the glass fiber were filtered, dried and weighed. The content of filtrate could be calculated from the weight of the pellet and the filtered fiber. Intrinsic viscosity of the filtrate was determined using an

Ubblohde viscometer at 25 ± 0.1°C, yielding the intrinsic viscosity of PBT in the composites.

Injection Molding

The LGF/PBT pellets with 6 mm length were injection molded into testing bars using a MateuSole 90/140 with a clamping force of 882 kN. Temperature profile of the injection unit was 220-250-270-270-270°C. Injection pressure was 60 Mpa and backpressure was 0.3 Mpa.

Mechanical Properties Tests

The mechanical properties testing was performed at room temperature (23°C) and at a relative humidity of 50%. Tensile properties were measured in accordance with the procedures in ASTM D-638. Flexural properties were measured in accordance with the procedures in ASTM D-790, at a crosshead rate of 0.1 inches/min and a span width of 2 inches. Izod impact properties testing were performed using the Ceast Resil impactor according to ASTM D-256-02. Heat distortion temperature (HDT) under load (1.82 MPa) of specimens was measured according to ASTM D-648.

Fiber Length in Injection Molded Composites

Fiber obtained after incinerating the matrix were dispersed in a 1 wt% solution of glycerol in water. Some drops of this suspension were placed on a glass slide. After drying, the slides were observed using an Olympus optical microscope. The number average fiber length, *Ln*, and the weight average fiber length, *Lw*, were calculated (16).

Fiber Arrangement in Injection Molded Composites

The arrangement of the fibers was directly observed using a digital camera after incinerating the matrix and without changing the original structure of the glass fibers in the composites.

Morphology Observation by Scanning Electronic Microscope (SEM)

The fracture surfaces broken in the mechanical properties tests and the reinforcing glass fiber surface after removing ungrafted PBT were observed by SEM, model JSM-5600LV, made by JEOL Electronic Co. (Japan).

Fourier Transform Infrared-Raman Spectrometer (FTIR) Spectra of the Reinforcing Fiber Surface

A Fourier Transform Infrared-Raman Spectrometer (NEXUS-670, Nicolet Co., USA), was used to measure the FTIR spectra of the reinforcing glass fiber surface after removal of weakly adhered PBT.

Pyrolysis/Gas Chromatography/Mass Spectrometry (Py-Gc/Ms)

A QP-2010 Py-Gc/Ms instrument (Shimadzu, Japan) was employed to pyrolyze the reinforcing glass fiber after removing ungrafted PBT to prove the presence of the PBT macromolecular chain on the reinforcing fiber surface. The samples were inserted into the filament coils of the pyrolysis head, and then heated to 570°C. The pyrolysates were injected in split mode with the injector at 300°C. The pyrolysis products were identified by mass spectrometry with the ion source temperature of 200°C, and interface temperature of 300°C.

Differential Scanning Calorimetric (DSC) Measurements

The DSC experiments were performed on a Mettler Toledo® System DSC 822e. The reinforcing glass fibers, after removing ungrafted PBT, were heated at a heating rate of 10°C/min, and each thermogram was recorded from 150 to 300°C.

Results and Discussion

Mechanical Properties of LGF/PBT Composites

LGF/PBT composite specimens were prepared by injection molding of LGF/PBT pellets polycondensed for 30 h in the solid-state. Tensile strength, flexural strength, Izod impact strength, and HDT of the composites are listed in Table 1. With increasing fiber content, the tensile strength, flexural strength and impact strength all increased. For comparison with LGF/PBT in this study, the mechanical properties of a short glass fiber reinforced PBT (SGF/PBT) and a LGF/PBT prepared by a melt impregnation process are also listed in Table 1. The results showed that the mechanical properties of LGF/PBT composite prepared by *in situ* solid-state polycondensation were better than those of the short glass fiber reinforced PBT composites. This improvement was attributed to two

Table 1
Mechanical properties of long glass fiber reinforced PBT composites

	LGF/PBT[a]			SGF/PBT[b]	LGF/PB[c]	
	20%	30%	36%	30%	30%	ASTM
Tensile strength (MPa)	141	156	176	132	138	D638
Elongation at break (%)	2	2	2	2.5	3	D638
Flexural strength (MPa)	202	235	258	186	207	D790
Impact strength (J/m)	114	156	175	98	160	D256
Heat distortion tempature (°C)	220	220	220	205	213	D1525

[a] LGF/PBT composites were prepared by the new process in this study.
[b] SGF/PBT and [c] LGF/PBT composites were commercial products prepared by melt impregnation.

aspects: Firstly, fiber length was longer and they were connected at junction points, which could shift failure modes to pull out and breakage modes. Secondly, the good wetting was due to the *in situ* grafting of PBT oligomer onto the glass fiber surface during the *in situ* solid-state polycondensation by reaction of the end carboxyl groups of PBT with the active groups of the coupling agent on the glass fiber surface. This surface grafting results in the improvement of the interfacial adhesion between reinforcing glass fiber and the matrix PBT polymers.

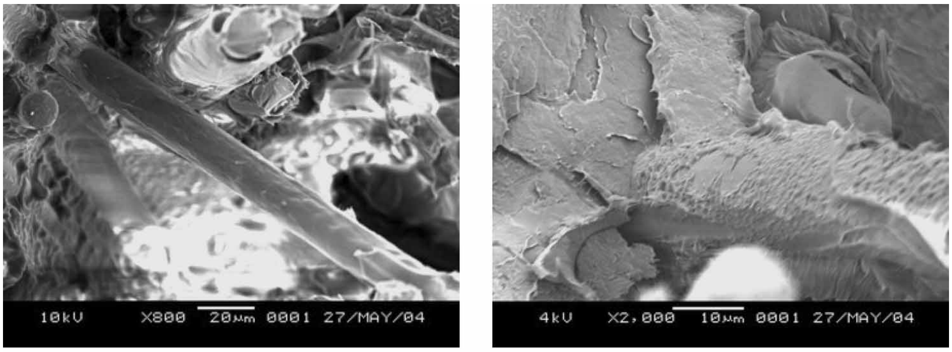
Figures 1–3 show SEM photos of the fracture surface of LGF/PBT composites broken by the impact test, flexural test, and tensile test respectively. The glass fibers were pulled out from the matrix and most of them were covered with matrix PBT. This means that matrix crack propagation was the main fracture mechanism and rather perfect interfacial adhesion was set up in LGF/PBT composites prepared by the new process.

Fiber Arrangement, Fiber Length and its Distribution of Injection Molded LGF/PBT Composites

The arrangement of the glass fibers in the composites are shown in Figure 4. The glass fibers are connected at junction points, which was the advantage of long glass fiber reinforced composites over short glass fiber reinforced composites. It could shift failure modes to pullout and breakage modes, which would absorb more energy.

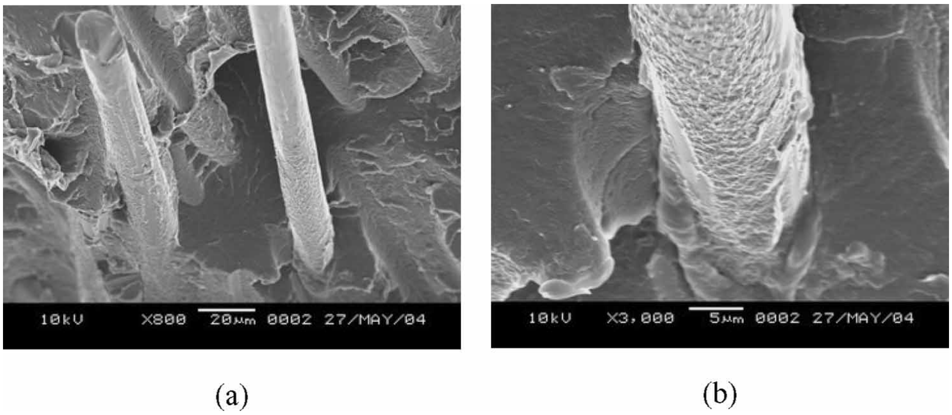
The fiber length in the injection molded LGF/PBT composites is an important factor. Fiber reinforced materials, during a mechanical destruction event, absorb energy via three major mechanisms: fiber breakage, fiber pullout, and matrix crack propagation. By increasing fiber length, the benefits of the crack arresting network are retained. The result is a much higher level of fiber pullout and breakage, with substantially higher energy absorption. The increase of glass fiber length corresponds to the increased surface area, which can provide higher pullout forces. In addition, the reduced number of crack initiation sites in long glass fiber reinforced composites provides a much higher level of damage resistance.

The fiber length and its distribution in the injection molded specimens are plotted in Figure 5. The average fiber length decreased with increasing fiber content. It is believed



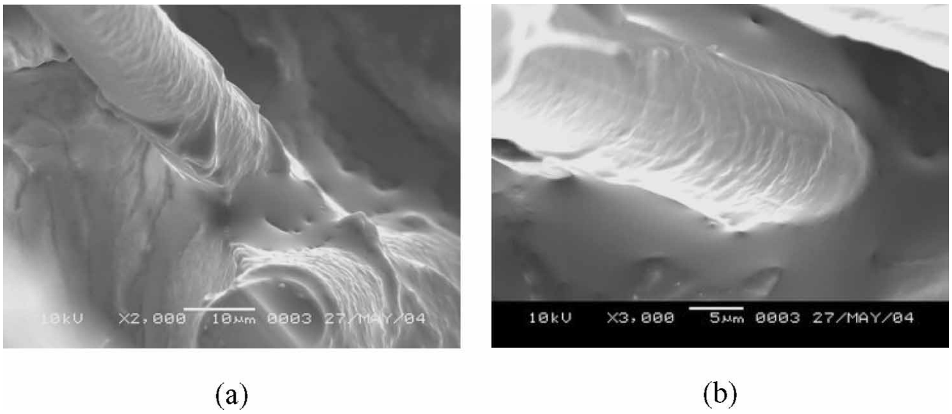
(a) (b)

Figure 1. SEM images of fracture surface of LGF/PBT composites broken by the impact tests.



(a) (b)

Figure 2. SEM images of fracture surface of LGF/PBT composites broken by the flexural tests.



(a) (b)

Figure 3. SEM images of fracture surface of LGF/PBT composites broken by the tensile tests.

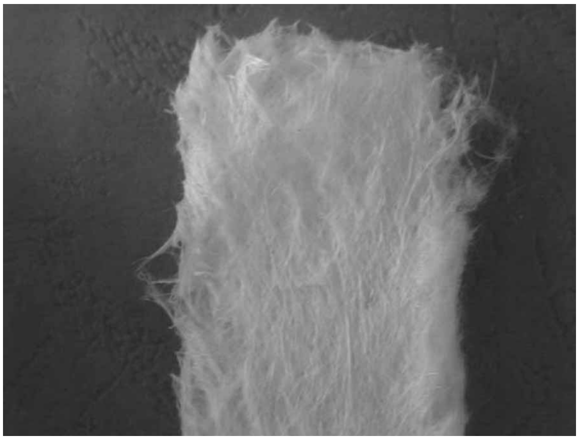
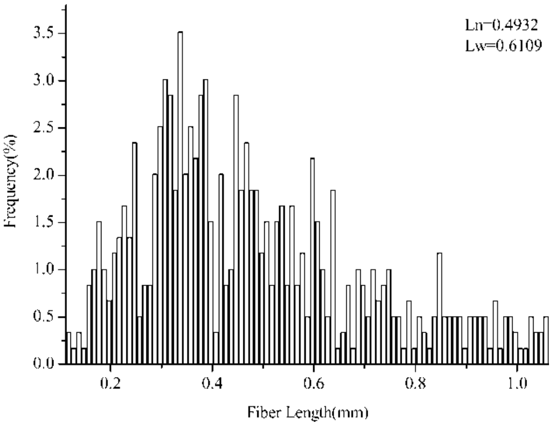
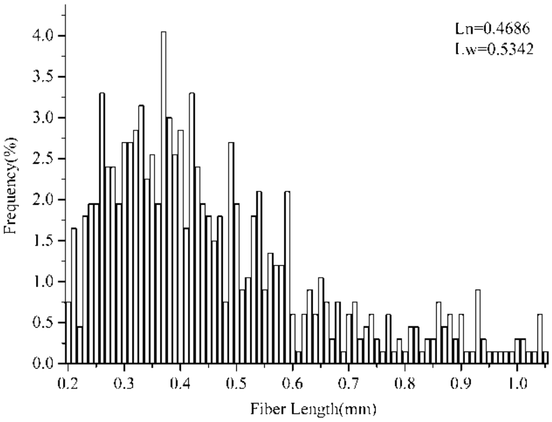


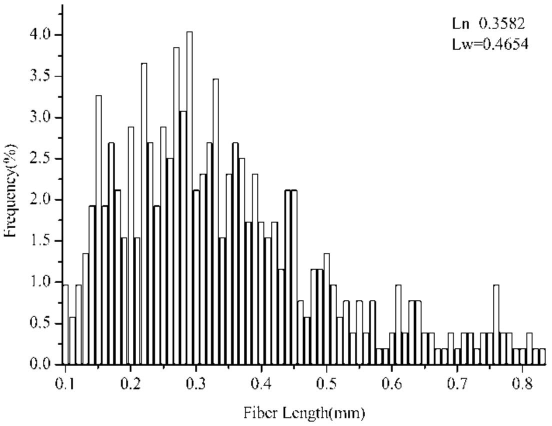
Figure 4. Optical microscopy photo of fiber arrangement after incinerating PBT matrix.



(a) 20% fiber content



(b) 30% fiber content



(c) 36% fiber content

Figure 5. Histograms of the fiber length distribution in LGF/PBT composites with different fiber content.

that the reinforcing fibers are damaged owing to fiber friction, which is severe with the increase of fiber content. The number average length and weight average length with different glass fiber content are plotted in Figure 5.

The number average fiber length was 0.47–0.6 mm for our LGF/PBT with fiber content from 20% to 36%, while the number average fiber length for the long fiber reinforced thermoplastic composites in the literature was greater than 0.98 mm (17). That is to say, the fiber length of the LGF/PBT composites in this study was shorter than that reported. There are two possible reasons to explain it. First, the original fiber length in the pellets was only 6 mm, not the 9–15 mm in the literature. Second, the injection molding conditions were set for short glass fiber reinforced PBT composites. Despite the short length, however, the mechanical properties as listed in Table 1 were a little better than that of commercial products prepared by melt impregnation. This improvement of reinforcing effect could be attributed to the strong interfacial adhesion resulting from grafting of PBT molecular chains onto the surface of the reinforcing glass fiber during *in situ* solid-state polycondensation.

Interfacial Properties of Long Glass Fiber Reinforced PBT Composites

In this *in situ* grafting process, the reinforcing glass fiber was firstly impregnated by low viscosity oligomers to obtain a sufficient wetting. The prepregs were then put into a biconical dryer drum for solid-state polycondensation, in which most of the oligomers were polycondensed to form the high molecular weight PBT matrix. As shown in Figure 6, the molecular weight of the matrix PBT oligomers could be significantly increased by SSP. At the beginning of SSP, the intrinsic viscosity of PBT in composite increased rapidly. But, with prolonged reaction time, the rate decreased, which means that the molecular weight of the matrix PBT could be easily adjusted by controlling the SSP time.

During SSP, the grafting reaction and interfacial polymerization of PBT took place on the glass fiber surface simultaneously. Two kinds of reactive groups, epoxy and hydroxyl groups, were present at the surface of the glass fiber treated with coupling agents. The

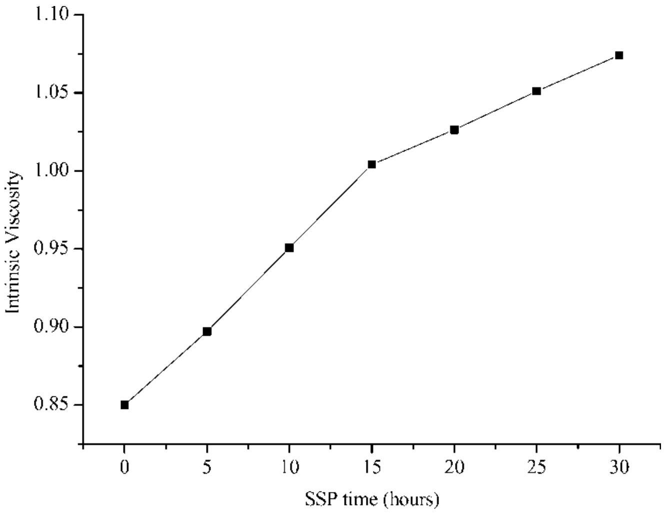
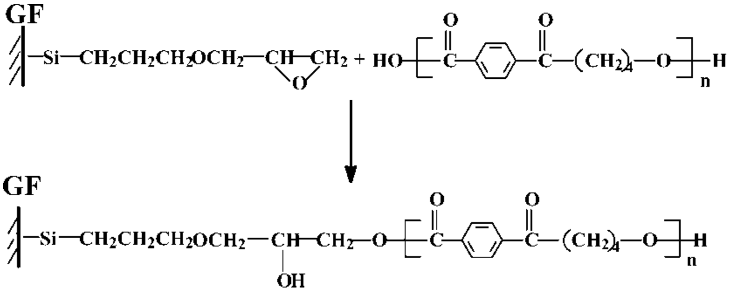


Figure 6. Relationship between intrinsic viscosity of PBT and SSP time.



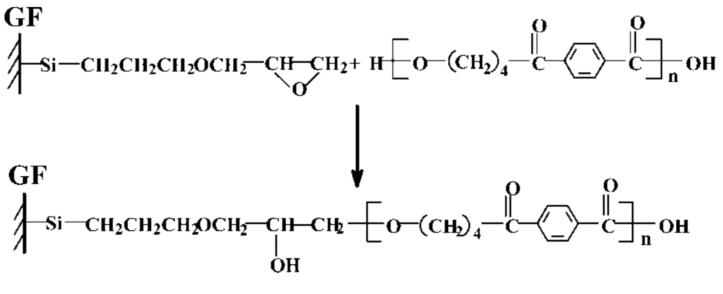
Scheme 1. Reaction of epoxy groups with end carboxyl groups at PBT oligomers.

chemical grafting of PBT oligomers onto the glass fiber surface took place by reaction of epoxy groups with end carboxyl groups in PBT oligomers (Scheme 1), or end hydroxyl groups in PBT oligomers (Scheme 2), or by reaction of hydroxyl groups on the glass fiber surface with end carboxyl and hydroxyl groups of PBT oligomers (Scheme 3). Moreover, SSP could take place between the grafted PBT oligomer chains and the ungrafted PBT oligomer chains to form high molecular weight polymer chains in the interphase regions, as described in Scheme 4, which would be of additional benefit for the improvement of interfacial adhesion (18).

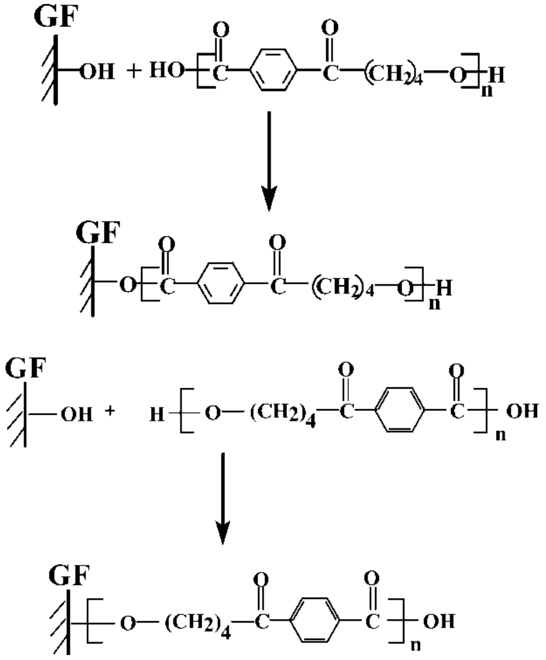
In order to prove this *in situ* grafting, the matrix PBT was removed from LGF/PBT composites to obtain the glass fiber chemically coated with PBT, and then a series of testing methods were used to gain the evidence of the presence and growth of the PBT macromolecules on the glass fiber surface.

The Interface Morphology Between the Glass Fiber and Matrix

Figure 7 shows the SEM images of different glass fiber samples, such as the pure glass fiber surface, and the glass fiber surface after a removal of adhered polymer with different SSP time. In Figure 7(a), a smooth glass fiber surface was observed although it was sized with silane coupling agent. Only a few polymer aggregations appeared on the glass fiber surface for SSP 5 h (Figure 7b) because the SSP time was so short that PBT oligomers could not sufficiently react with coupling agents. In Figures 7(c) and (d), adhered polymer aggregations were observed on the glass fiber surface. With the increase of the SSP time, more polymer aggregations were observed on the fiber surface. These polymer aggregations



Scheme 2. Reaction of epoxy groups with end hydroxy groups at PBT oligomers.

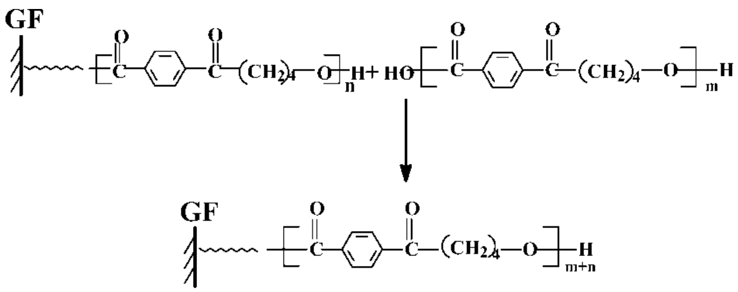


Scheme 3. Reaction of hydroxyl groups at glass fiber surface with end carboxyl groups and hydroxyl groups at PBT oligomers.

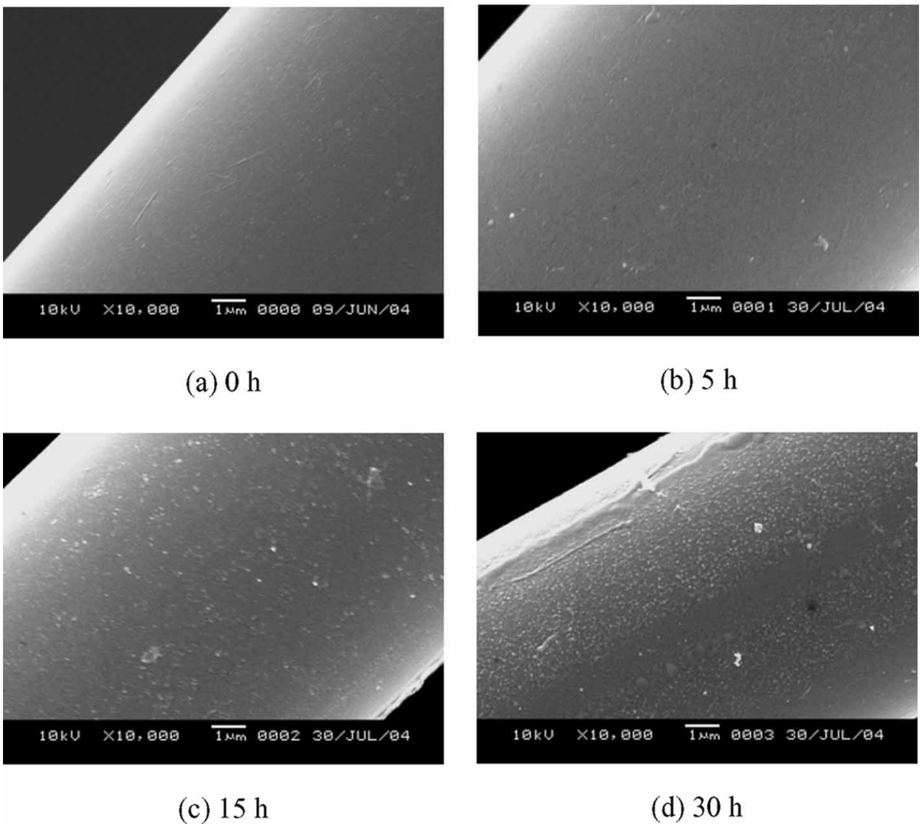
were attributed to the *in situ* grafting of the PBT oligomers onto the reinforcing glass fiber and the growth of grafted macromolecular chains.

Melting Behavior of Grafted PBT by DSC Measurement

DSC was used to determine the melting behavior of the grafted PBT on the glass fiber surface in LGF/PBT composites. PBT melts at a temperature around 225°C on a DSC curve. From DSC heating curves (Figure 8), as expected there was no any endothermic peak around 225°C for pure glass fiber. There was also no obvious melting peak on curve (b), which might be due to the small quantity and low molecular weight of the PBT grafted on the glass fiber surface with no crystalline structures being formed during the initial period of SSP. In the cases of



Scheme 4. The propagation of grafted PBT chains on the surface of glass fiber.



(a) 0 h (b) 5 h

(c) 15 h (d) 30 h

Figure 7. SEM photos of glass fiber surface removed ungrafted PBT with different SSP time.

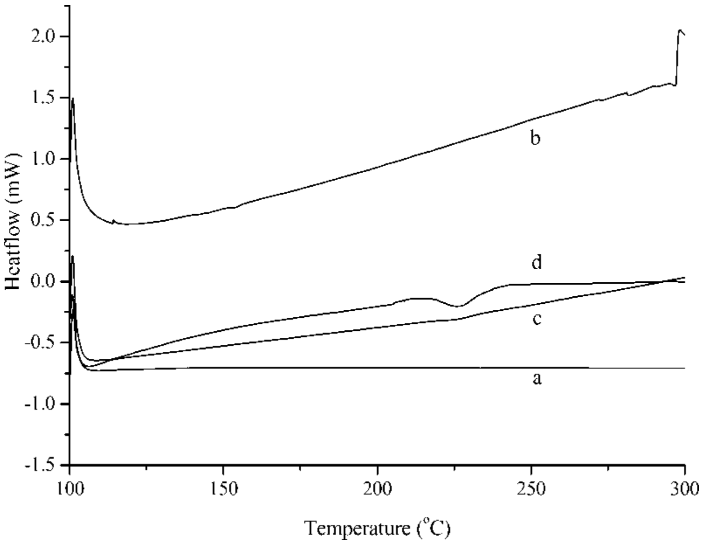
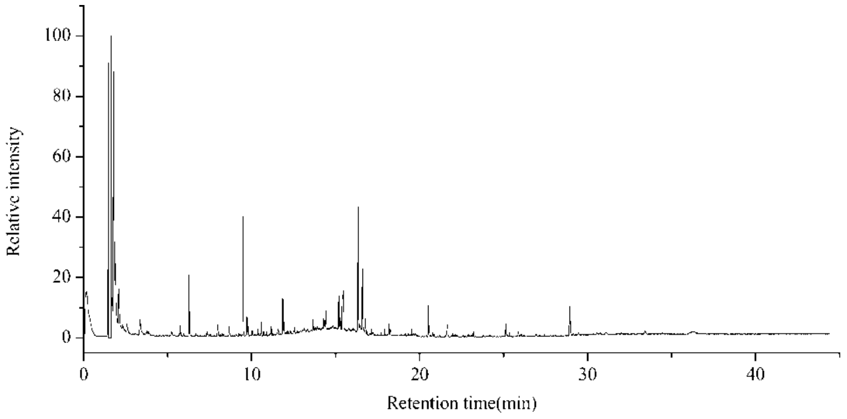


Figure 8. DSC curves of different reinforcing fiber specimens, a) pure glass fiber; b) glass fiber with 5 h SSP; c) glass fiber with 15 h SSP; d) glass fiber with 30 h SSP.

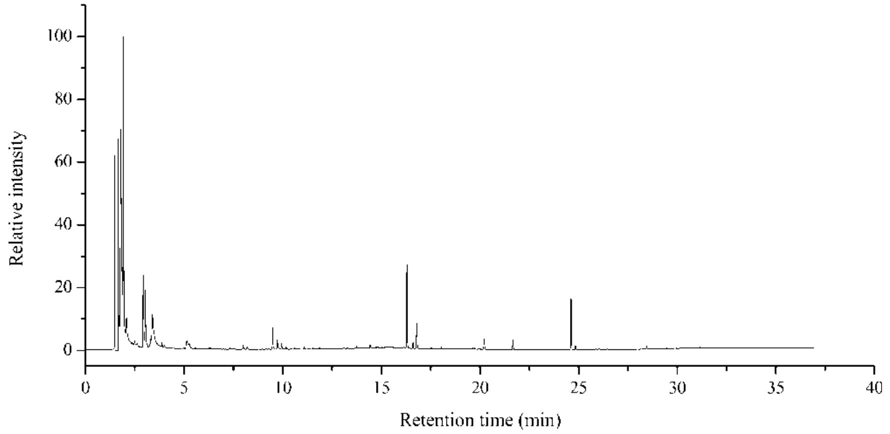
curve (c) and (d), there were observable peaks near 225°C, which indicated that there were crystalline PBT macromolecular chains strongly adhered on the glass fiber surface. With increase of the SSP time, the reactive groups on the reinforcing fiber surface had fully reacted with end groups of PBT, and the growth of the grafted PBT chain took place as described in Scheme 4. Therefore, it is believed that the endothermic peaks observed at 225°C could be attributed to PBT melting. From the SEM photos of the grafted glass fiber surface after extraction, it could be clearly observed that for the earlier SSP, as in case of (b), the grafted polymer was rather small and distributed uniformly, while when the SSP time reached 15 h, as in the case (c), the thickness of grafted polymer increased and some crystalline packing structure formed. It was these crystals that were detected by DSC.

Pyrolysis Spectra of the Reinforcing Glass Fiber Grafted PBT

The pyrolysis of the reinforcing glass fiber with different SSP time was performed in N_2 atmosphere at 570°C to further determine the amount of grafted PBT macromolecular

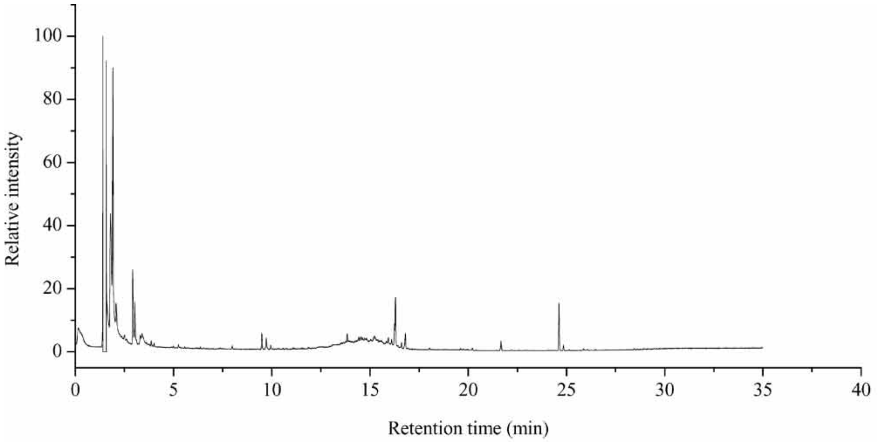


(a) pure glass fiber

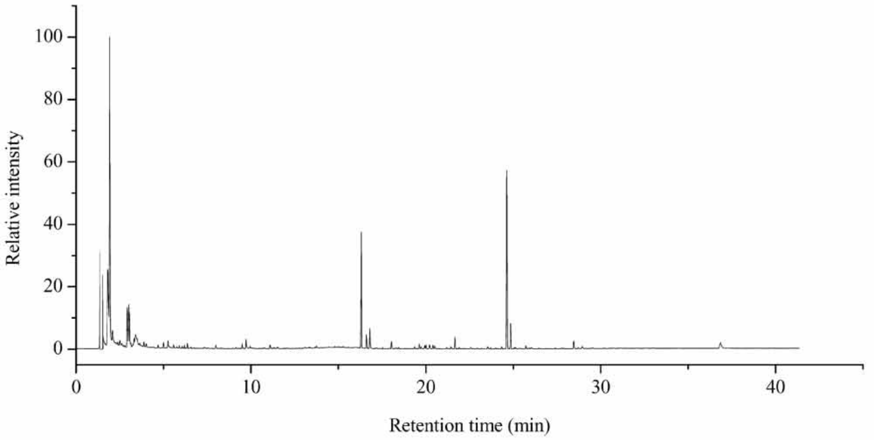


(b) glass fiber with 5 h SSP

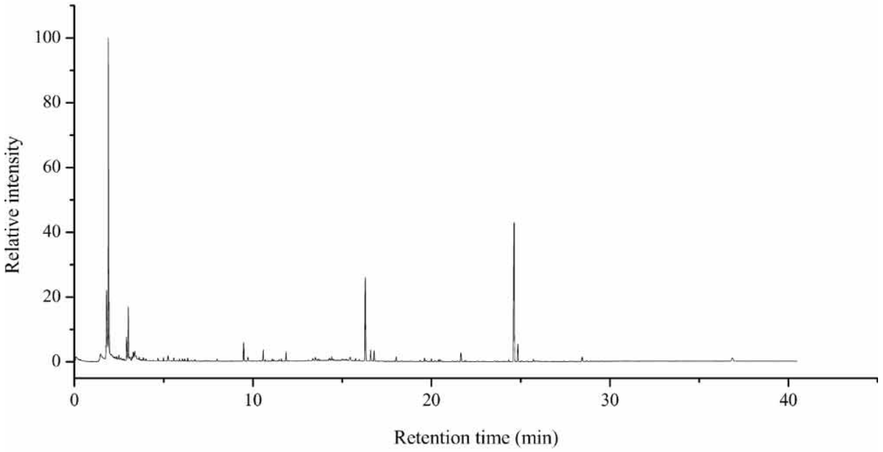
Figure 9. Py-Gc/Ms Spectra of reinforcing glass fiber and pure PBT.



(c) glass fiber with 15 hours SSP



(d) glass fiber with 30 hours SSP



(e) Pure PBT

Figure 9. Continued.

Table 2
Primary pyrolysis products of PBT in the experimental conditions

		Relative strength				
Retention time (min)	Compound name	Pure GF	GF with 5 h SSP	GF with 15 h SSP	GF with 30 h SSP	Pure PBT
1.915	Bicyclo[1,1,0]butane	ND	+	+	+	+
2.920–2.925	Tetrahydrofuran	ND	+	+	+	+
3.020	3-Butenyl alcohol	ND	+	+	+	+
9.485–9.500	Benzaldehyde	ND	+	+	+	+
16.295–16.300	7-Benzoyloxynorbornadiene	ND	+	+	+	+
16.595–16.600	n-Butyl benaoate	ND	+	+	+	+
16.8	2-ethenyl-naphthalene	ND	+	+	+	+
24.84	1,4-Benzenedicarboxylic acid, bis(2-methylpropyl)ester	ND	+	+	+	+

"ND", denotes not detected, " + ", be detected.

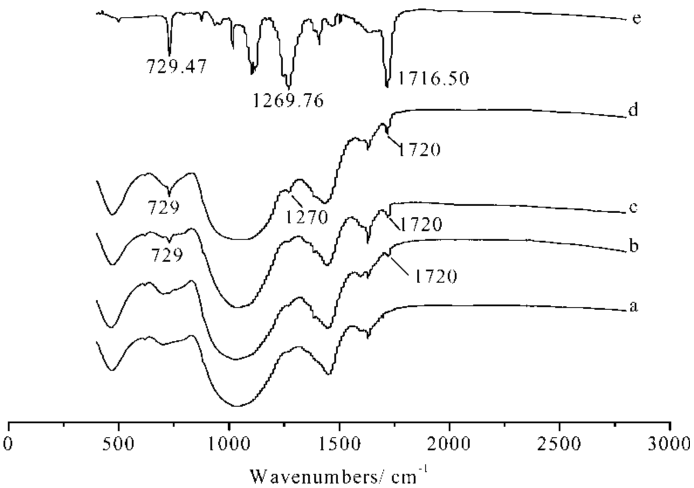


Figure 10. FTIR spectra of reinforcing glass fiber. a) glass fiber with coupling agent; b) glass fiber with 5 h SSP; c) glass fiber with 15 h SSP; d) glass fiber with 30 h SSP.

chains on the glass fiber surface. The pyrolysis products were identified by mass spectrometry detection. The resulting Py-Gc spectra are shown in Figure 9. The peaks of the important pyrolysis product of pure PBT and their retention time are shown on curve (e). Under different pyrolysis conditions, the pyrolysis products were different. In this study, the pyrolysis products of pure PBT included CO_2, bicyclo[1,1,0]butane, tetrahydrofuran, benzaldehyde, 7-benzoyloxynorbornadiene, etc. Most of these pyrolysis products peaks could also be found in the Py-Gc spectra of the reinforcing glass fiber samples, while they were absent in the Py-Gc spectrum of pure glass fiber. The retention time and the compound names of these peaks are listed in Table 2. Some differences in the Py-Gc spectra for the reinforcing fiber with different SSP time were found; for example, the peak at retention time 24.84 min for glass fiber with 30 h SSP was stronger than that for the glass fiber with 5 h SSP, which might be owing to the different length of the grafted PBT molecular chains. That is to say, with prolonged SSP time, not only more grafted sites formed but also the growth of the grafted PBT molecular chains took place.

FT-IR Spectra of the Reinforcing Glass Fiber Surface After Removing Ungrafted PBT

FT-IR was carried out to analyze the matrix grafted on the glass fiber surface. Figure 10 shows FT-IR spectra of pure glass fiber, grafted glass fiber and pure PBT. The characteristic carbonyl stretching frequency region shows weak peaks in the spectra, as shown in Figure 10 (b), (c), and (d), while it could not be found in pure glass fiber as shown in Figure 10 (a). The C-H in phenyl stretching frequency at about 729 cm^{-1} appeared, which also could not be seen in Figure 10 (a) and (b).

Conclusions

PBT oligomers with low melt viscosity were impregnated into reinforcing long glass fiber in this study. During this new process, PBT macromolecules were grafted onto the reinforcing glass fiber surface treated with a silane coupling agent. Some testing techniques, such as Py-Gc/Ms, DSC and FT-IR, were used to demonstrate the presence of PBT on the glass fiber surface. The results showed that the PBT oligomers were grafted onto the glass fiber surface during the SSP, which resulted in stronger interfacial adhesion. The good interfacial adhesion could be observed from the SEM images of fracture surfaces, which would be of benefit for the improvement of mechanical properties of LGF/PBT composites. In other words, because of the grafting, the mechanical properties of LGF/PBT composites were improved, being better than those of a counterpart composite prepared by conventional melt impregnation. Owing to the ease of this process, it will be an effective means of manufacturing long fiber reinforced thermoplastic composites.

References

1. Karger-Kocsis, J., Yuan, Q., Mayer, J., and Wintermantel, E. (1997) *J. Thermoplast. Compos. Mater.*, 10: 163–172.
2. Mayer, J. and Wintermantel, E. (1995) *Proc SAMPE, Tokyo, Japan*, 667–672.
3. Zebarjad, S.M., Lazzeri, A., Bagheri, R., Seyed Reihani, S.M., and Forunchi, M. (2002) *J. Mater. Sci. Lett.*, 21: 1007–1011.
4. Yeung, P. and Broutman, L.J. (1978) *Polym. Eng. and Sci.*, 18: 62–72.
5. Bikiaris, D., Matzinos, P., Prinos, J., Flaris, V., Larena, A., and Panayiotou, C. (2001) *J. Appl. Polym. Sci.*, 80: 2877–2888.
6. Berg, J. and Jones, F.R. (1998) *Composites Part A*, 29A: 1261–1272.
7. Eagles, D.B., Brumentritt, B.F., and Cooper, SL. (1976) *J. Appl. Polym. Sci.*, 20: 435–448.
8. Andreopoulos, A.G. (1989) *J. Appl. Polym. Sci.*, 38: 1053–1064.
9. Yu, Z., Ait-Kadi, A., and Brissson, J. (1991) *Polym. Eng. and Sci.*, 31: 1222–1227.
10. Wade, G.A. and Cantwell, W.J. (2000) *J. Mater. Sci. Lett.*, 19: 1829–1832.
11. Salehi-Mobarakeh, H., AIT-Kadi, A., and Brisson, J. (1996) *Polym. Eng. and Sci.*, 36: 778–785.
12. Ranade, S.V., DiBenedetto, A.T., and Goldberg, A.J. (1996) *Polym. Prepr. Am. Chem. Soc., Div. Polym. Chem.*, 37: 851–85.
13. Noda, D., Tsuji, M., Takahara, A., and Dajiyama, T. (2002) *Polymer*, 43: 4055–4062.
14. Salehi-Mobarakeh, H., Brisson, J., and Ait-Kadi, A. (1997) *J. Mater. Sci.*, 32: 1297–1304.
15. Salehi-Mobaradeh, H., Brisson, H., and Ait-Kadi, A. (1998) *Polym. Compos.*, 19: 264–274.
16. Yilmazer, U. and Cansever, M. (2002) *Polym. Compos.*, 23: 61–71.
17. Feng, W., Ait-Kadi, A., Brisson, J., and Riedl, B. (2003) *Polym. Compos.*, 24: 512–524.
18. Raghaverdran, V.K., Waterbury, M.C., Rao, V., and Drzal, L.T. (1997) *J. Adhes. Sci. and Technol.*, 11: 1501.