

Study on the Grafting of PET onto the Glass Fiber Surface during *In Situ* Solid-State Polycondensation

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ABSTRACT: An *in situ* solid-state polymerization process was developed to produce long glass fiber reinforced poly(ethylene terephthalate) (PET) composites. As reported in our last article, one advantage of this new process is that the good wetting of reinforcing fiber can be obtained for using low-viscosity oligomer as raw materials. In this article, the grafting of PET macromolecular chain onto the surface of reinforcing glass fiber during *in situ* solid-state polycondensation (SSP) will be investigated, which was believed to be another advantage for this new process and should be very important for thermoplastic composite. The reinforcing glass fiber after removing ungrafted PET from a long glass

fiber reinforced PET composite by solvent extraction was investigated by SEM, pyrolysis-gas chromatography mass spectrometry (Py-GC/MS), DSC, and FTIR. The information from morphology of SEM photos of glass fiber surface, the spectrum of Py-GC/MS, the melt peak at differential scanning calorimetric (DSC) curve, and the spectrum of Fourier transform infrared Raman spectroscopy (FTIR) gave a series evidence to prove the presence of grafted PET layer on the surface of silane-coupling-treated glass fiber. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 775–781, 2006

Key words: GF/PET; composites; interface; grafting; SSP

INTRODUCTION

The use of fiber reinforced thermoplastic composites is becoming increasingly more extensive, due to their excellent mechanical properties, low density, and relative ease of fabrication. The interfacial adhesion is very important for reinforced composites, especially for the thermoplastic matrix composites. Many studies have been performed in recent years on the role of the interface region in determining the mechanical properties of these materials. Fatigue behavior of short glass fiber reinforced nylon 66 under stress-controlled fatigue tests was studied on the basis of the nonlinear dynamic viscoelasticity measurements by Noda et al.¹ The role of the interface on the deformation mechanism of glass fiber/polypropylene composites was discussed by Zebarjad et al.² Experimental investigations were conducted to study the effect of thermal processing of microstructures of glass fiber/polyamide 6 (GF/PA6) composites by Cartledhe and Bailie.³ Silane-coupling agents are widely used for various surface treatments of glass fiber.⁴ The surface treatment of glass fiber by coupling agent induces higher strength and fracture toughness. Several models of interface strengthening have been proposed and many factors influence interfacial adhesion. Adsorp-

tion interactions, electrostatic interactions, mechanical interlocking, as well as polymer interdiffusion have been involved to explain polymer–matrix adhesion.⁵ A number of attempts have been made to overcome adhesion problems encountered with glass fiber reinforced thermoplastic composites. Physical modifications aimed at improving mechanical interlocking have been proposed.⁶ Chemical^{7–11} and plasma^{12,13} treatments have been used to enhance electrostatic and adsorption interactions. However, in many cases, the adhesion improvement was not sufficient to justify costly treatments.

More recently, grafting of polymer chains were proposed as a means to improve adhesion. This approach combines benefits from polymer interdiffusion of the grafted chains into the reinforcing glass fiber and electrostatic and adsorption interactions between the components. For instance, it has been shown that *in situ* polymerization of monomers onto functionalized fibers offers a unique way to modify the interphase chemistry and morphology in composite systems.^{14,15} Polymerization of styrene onto Kevlar fibers¹⁴ led to an increase of up to 38.2% in the tensile strength of Kevlar–polystyrene composites. Koschinski and Reichert¹⁵ used this approach to modify poly(phenylene sulfide)–carbon fiber composites properties. This resulted in a significant improvement of fiber–matrix adhesion, an increase in resistance to corrosive media, and a marginal improvement in strength when compared to composites prepared by physical blend-

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TABLE I
Mechanical Properties of Long Glass Fiber Reinforced PET Composites

	Our samples	BASF product Petra 130FR	ASTM test method
Tensile strength (Mpa)	171	155	D-638
Flexural strength (Mpa)	235	210	D-790
Notched izon impact (J/m)	171	90	D-256
Glass fiber content		30%	

ing *in situ* polymerization of nylon-1010 onto carbon fibers but the resulting poor composite properties were attributed by the authors to the low molecular weight of the matrix materials. Bhama and Stupp¹⁶ performed an *in situ* synthesis of chain-grafted fibers by polycondensation of *p*-acetoxybenzoic acid, diacetoxyhydroquinone, and pimelic acid. They obtained improved wetting and interfacial bonding of the liquid crystalline matrix on the carbon fiber surface. Wang et al.¹⁷ used functionalized Kevlar fibers obtained by cold oxygen plasma treatments. By fixing a Ziegler–Natta catalyst on these active sites, ethylene polymerization was performed on the fiber surface. Better fiber–matrix adhesion and wetting resulted in improved mechanical properties of the composites. There have been some reports on chemical structure at the (GF/matrix) interface. Noda et al. sufficiently discussed the aggregation structure and molecular motion of (glass fiber/nylon 66) interface in short glass fiber reinforced nylon 66 composites by means of X-ray photoelectron spectroscopy (XPS) and SVM.¹⁸

When comparing different approaches proposed in the literature, various drawbacks can be noted in terms of industrial processibility and applications. We have reported a new process of the long fiber-reinforced thermoplastic composite prepared by *in situ* solid-state polymerization process carried out in our laboratory to explore a new impregnation process which will have effective impregnation and be suitable for most thermoplastic matrix resins such as poly-

(ethylene terephthalate) (PET), polybutylene terephthalate (PBT), polycarbonate (PC), PA6, polyamide 66 (PA66), and polyamide 1010 (PA1010). In this new process, named the *in situ* solid-state polymerization process, the reinforcing continuous fibers are impregnated in the oligomers of polycondensation polymers, and then the impregnated continuous fibers are cut to a desired length, named prepreg, and finally, the oligomer of the prepreg is *in situ* polymerized in solid state to form the high molecular weight matrix; meanwhile, PET oligomer is grafted onto the glass fiber surface. The advantage of this new process is that the good wetting of reinforcing fiber can be obtained for using low-viscosity oligomer as raw materials. As the recent researching results, another advantage of this process is that the end groups of PET oligomer can react with the functional groups on the coupling agent and the glass fiber surface to form the grafting during the *in situ* solid-state polycondensation, which could be very significant for the thermoplastic composite. The purpose of this study was to investigate this *in situ* grafting and related morphology and mechanical properties.

EXPERIMENTAL

Materials

Long fiber-reinforced PET composite samples were prepared by *in situ* solid-state polycondensation process as described in a previous article¹⁹ and then molded by press molding and injection molding. Middle alkali nontwist glass fiber was a commercial product made by Jushi Co. (Tongxiang, China). The fiber surface was treated by a coupling agent, KH560. Phenol and tetrachloroethane was a commercial chemical reagent made by Shanghai Jinghua Science and Technological School (Shanghai, China).

Mechanical properties test

The mechanical properties of composite specimen were tested by ASTM methods.

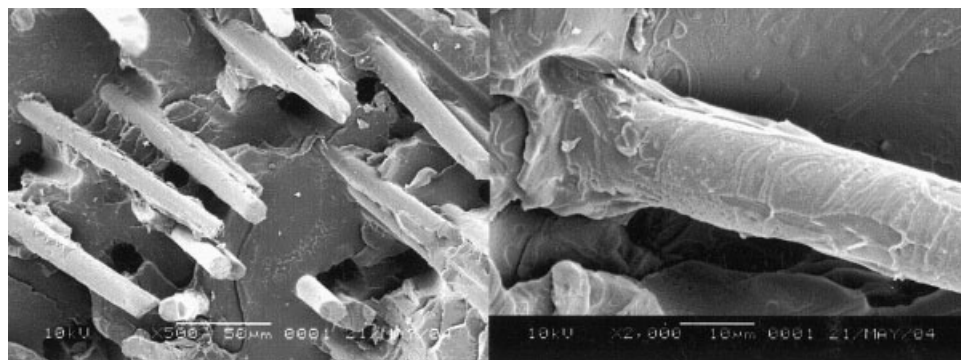
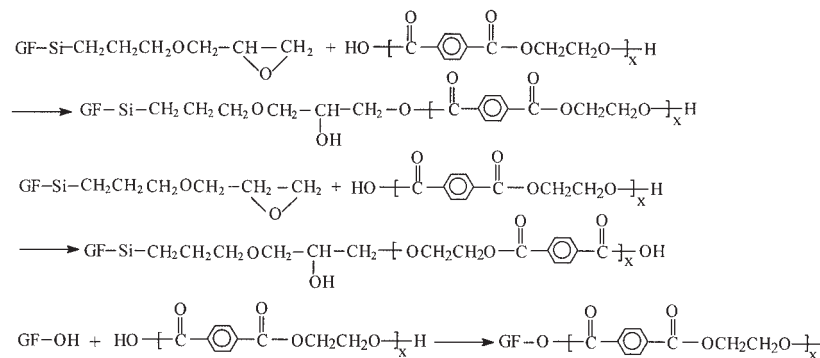


Figure 1 SEM photos of composite specimen broken by impact test.



Scheme 1 The chemical grafting reaction.

The preparation of grafted glass fiber

The glass fiber specimens with grafted PET were prepared as follows: a composite specimen was dissolved by a phenol and tetrachloroethane mixture; then the glass fibers were filtrated from dilute solution, washed by the same solvent more than five times to remove the PET polymer without chemicals grafted to the glass fiber surface, washed with acetone, and dried at 150°C.

The FTIR spectrum of the reinforcing fiber surface

Fourier transform infrared Raman spectrometer, model NEXU S-670, made by Nicolet Co. (Waltham, MA), was used to measure the FTIR spectrum of the reinforcing glass fiber surface with the removal of weakly adhered PET.

Morphology observation by SEM

The fracture of impact test and the reinforcing glass fiber surface by removing weakly adhered PET was observed by SEM, using a JSM-5600LV (JEOL Electronic Co., Japan).

Pyrolysis gas chromatography/mass spectrometry

A pyrolysis gas chromatography/mass spectrometry (Py-GC/MS) instrument (model QP-2010 Shimadzu Co., Japan) was used to perform the pyrolysis of the reinforcing glass fiber after removal of ungrafted PET to prove the presence the PET macromolecular chain on the reinforcing glass fiber surface.

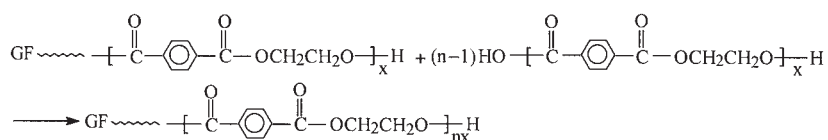
Differential scanning calorimetric (DSC) measurements

DSC experiments were performed on a Mettler Toledo® System DSC 822^e. The reinforcing glass fiber samples after removal of ungrafted PET were heated at a rate of 50°C/min; each thermogram was recorded from 150 to 350°C.

RESULTS AND DISCUSSION

The pellets after solid-state polycondensation (SSP) were injection molded into standard specimens for mechanical properties according to ASTM D256 and the test results are listed in Table I. Comparing a similar commercial product, the mechanical properties of composites prepared by this *in situ* solid-state polycondensation process are equal to or better than that of long glass fiber reinforced composites produced by BASF Corp. Figure 1 shows the SEM photos of composite specimens broken by impact test, which implicates that very good adhesion between reinforced glass fiber and matrix PET was present in this composite. This improvement could be attributed to more PET chain grafting on the glass fiber surface for enough reaction time (more than 15 h) during solid-state polycondensation process, whereas only several minutes were needed for grafting reaction during other prepared methods.

In the present process, the reinforcing glass fiber was first impregnated by a low-viscosity oligomer to give sufficient wetting, and then the glass fiber impregnated by oligomer was going to perform the solid-state polycondensation. In this *in situ* solid-state



Scheme 2 The propagation of grafted PET chain.

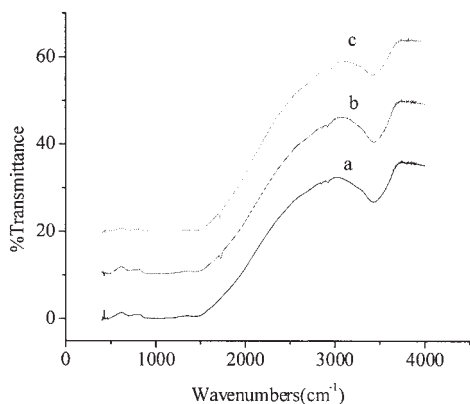


Figure 2 The FTIR spectrum of reinforcing fiber surface. (a) Pure glass fiber; (b) after 5 h SSP; (c) after 30 h SSP.

polycondensation, while most oligomers performed the polycondensation to form the high molecular weight PET matrix, the interfacial polymerization of PET also took place on the glass fiber surface. Two reactive groups were believed to be present at the glass fiber surface treated by coupling agent, epoxy, and hydroxyl groups. The chemical grafting of PET oligomer onto the glass fiber surface may take place as described in Scheme I. Moreover, the solid-state polymerization can take place between the grafted PET oligomer chain and the ungrafted PET oligomer chain

to form high molecular weight polymer chains in the interphase regions, as described in Scheme II.

To prove this *in situ* grafting, the matrix PET was removed from the glass fiber reinforced PET composites to obtain the glass fiber surface chemically adhered with PET, and then a series of methods were used to give the evidence of the presence and the growth of the PET macromolecules on the glass fiber surface. Phenol and tetrachloroethane solvent was selected so as to dissolve the matrix PET, selectively without corroding the interfacial layer of silicane coupling-PET on the glass fiber surface. It was confirmed with FTIR and Py-GC/MS that the silicane-coupling agent was detected on the glass fiber even after solvent extraction, as shown in Figures 2 and 3.

The morphology of the glass fiber surface

Figure 4 shows the SEM images on the received glass fiber surface (a) and the glass fiber surface after removing PET from the composite for different SSP times of (b) 5 h and (c) 30 h. In the case of Figure 4(a), the smooth glass fiber surface was observed, although it was sized with silane-coupling agent, while in the case of Figure 4(b) and (c), the strongly adhered polymer aggregation was observed on the glass fiber surface. With the increase of the SSP time, more density of polymer aggregation was observed on the fiber sur-

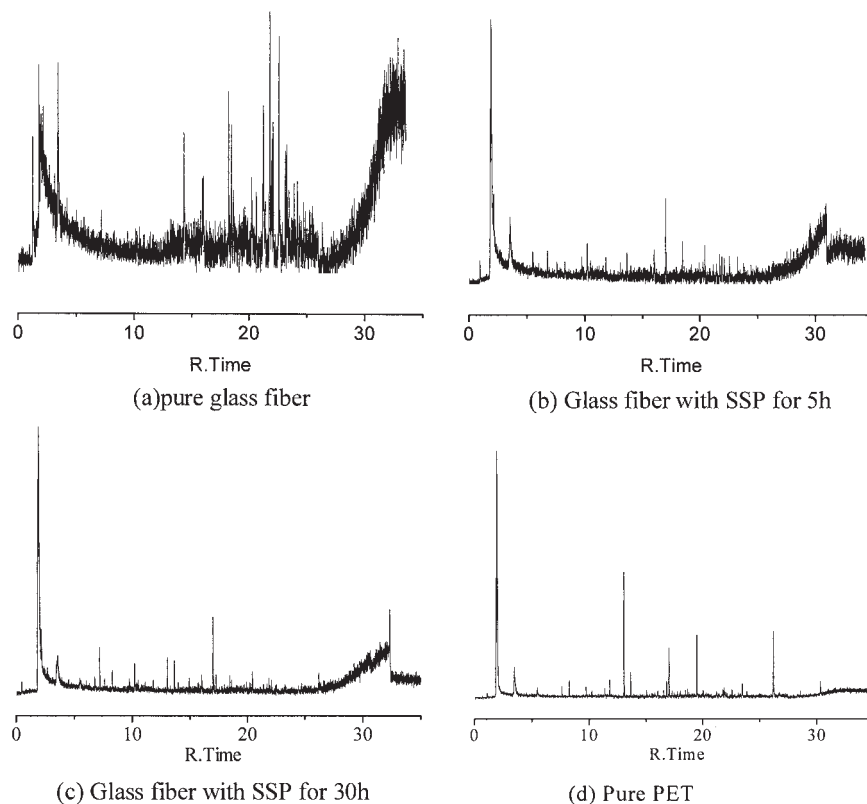


Figure 3 PY-GC/MS spectrum curves of reinforced fiber and pure PET.

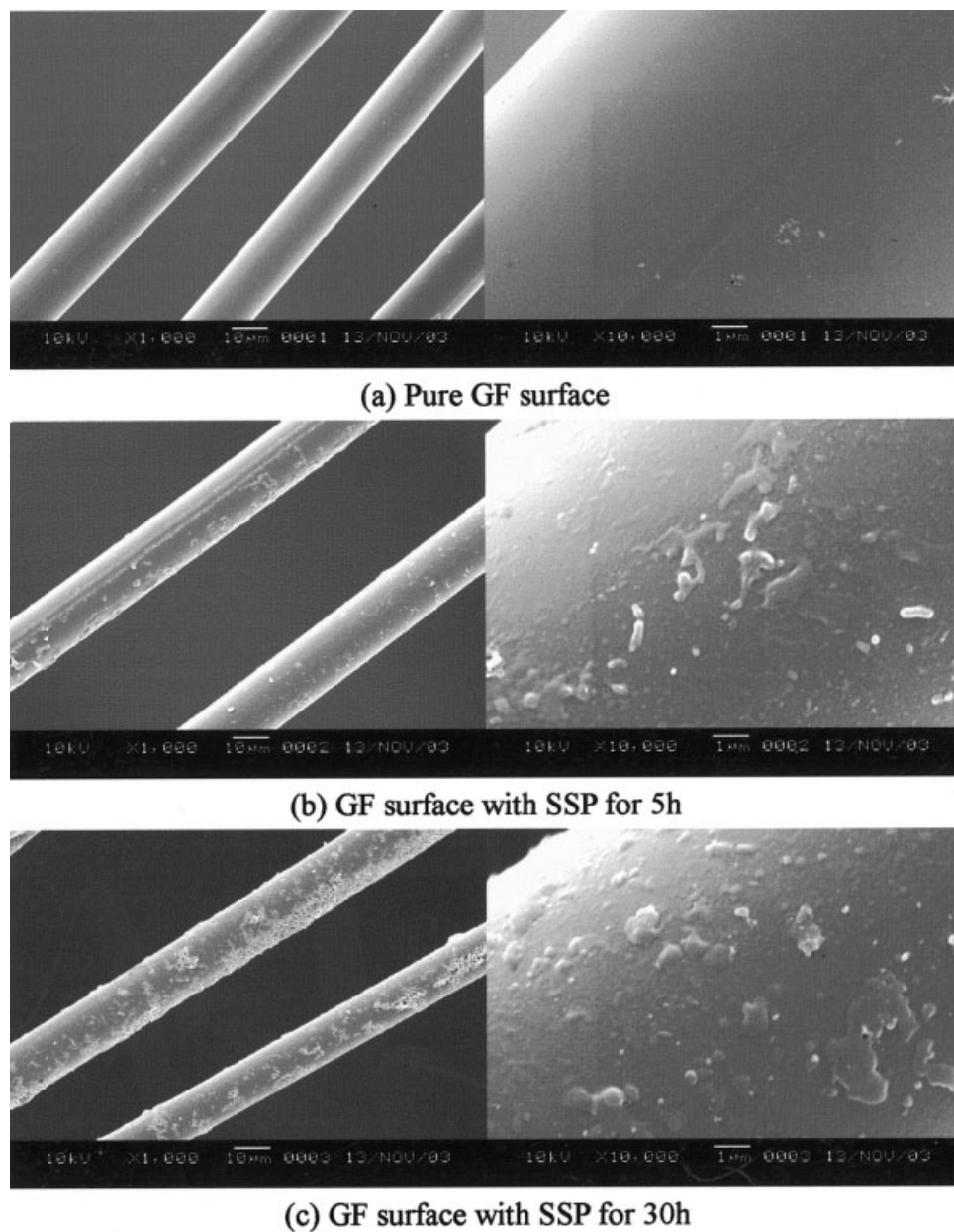


Figure 4 SEM for GF surfaces (a), (b), (c) were glass fiber with a removal of PET.

face. This polymer aggregation can be attributed to the *in situ* grafting of the PET oligomer onto the reinforcing glass fiber and the growth of grafted macromolecular chain to form the crystal packing.

The melting behavior of grafted PET by DSC measurement

DSC was used to determine the melting endotherms of glass fiber samples after removal of ungrafted PET. Figure 5 shows the result of melting curves (a) as received glass fiber, (b) as SSP for 5 h, and (c) as SSP for 30 h. As shown, there is no endotherm peak around 250°C in (a); just as we knew, glass fiber does not show any endotherm in the 30–300°C region. PET,

on the other hand, melts at a temperature around 250°C on DSC curve. However, there is also no obvious peak of PET melting on the curve (b), which may be due to the finding that, during initial period of solid-state polycondensation, the PET oligomer was grafted onto the glass fiber surface as described in Scheme 1; however, the small quantity and short molecular chain of grafted PET oligomer was not enough to form the crystal structure on the glass fiber surface. Although, in the case of curve (c), there is an observable peak at around 250°C, which indicated that PET macromolecular chain strongly does strongly adhere in the glass fiber surface. With the prolonging of the SSP time, as the reactive groups have fully reacted

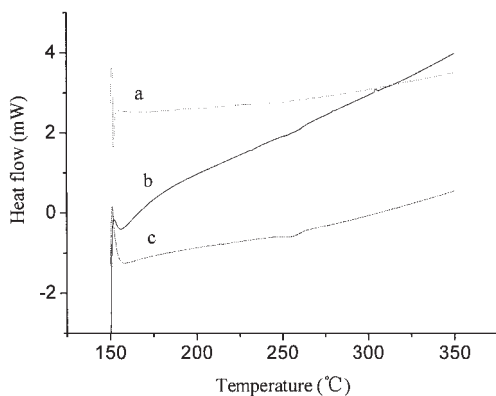


Figure 5 DSC curves of different reinforced fiber specimens. (a) Pure glass fiber; (b) glass fiber of SSP for 5 h; (c) glass fiber of SSP for 30 h.

with PET, the growth of the grafted PET chain does take place as described in Scheme 2, and the pervasive and crystallization process became the main method of the adhesion. The endotherm peak observed at 256 °C can therefore be attributed to PET melting. From the area of the melt endotherm, the ΔH value of crystalline phase of PET at fiber surface is obtained, and the content of crystallized PET on glass fiber surface is 1.76 mg/g glass fiber, calculated using a value of 250 J/g for ΔH of PET. Is the value measured by DSC representative of the actual quantity presented? If the grafting polymer was distributed equally on the fiber surface, it could be in the order of magnitude of one to several monolayers, and therefore, would have little probability of crystallizing. It is believed that the crystallization can only occur by chain folding in a manner very similar to that occurring in the bulk. Indeed, from the SEM photo of the grafted glass fiber surface after extraction, it can be clearly observed that at the first period, as in case of (b), the grafted polymer is rather less and rather uniform in distribution, whereas with long-time SSP, as in the case (c), the polymer grafting thickness was not uniform along the fiber, and forming some packing structure. Only this packing structure can form the crystalline and can be detected by the DSC method. Therefore, DSC can only be taken as a measure of the minimum amount of polymer present on the fiber surface.

The pyrolysis spectrum of the reinforcing glass fiber with PET surface grafting

Pyrolysis at 570 °C for various reinforcing glass fiber samples after removal of ungrafted PET was carried out to determine the grafted PET macromolecular chain on the glass fiber surface; the pyrolysis products were identified by mass spectrometry detection in negative chemical ionization (NCI). The resulted PY-

GC spectrum curves are shown in Figure 3 as (a) received glass fiber, (b) SSP for 5 h, (c) SSP for 30 h, and (d) pure PET. The important pyrolysis product peaks of pure PET and their retention times are clearly seen from these curves; through mass spectrum analysis, these peaks are mainly CO, CO₂, ethylene, benzene, toluene, ethylbenzene, and biphenyl, respectively. These are consistent with the results reported by Martin-Gullon et al.²⁰ Most of such pyrolysis product peaks can also be found on the Py-GC spectrum curve of the reinforcing glass fiber samples by removing ungrafted PET [see curve (a)–(c)], while such pyrolysis product peaks are absent in the Py-GC spectrum curve of received glass fiber seen in (a). It is reasonable to believe that the surface of the glass fiber is grafted with PET matrix. Comparing the curve (b) and (c), some differences can be found in the Py-GC spectrum for the 5 and 30 h SSP time, which may be attributed to the different lengths of the grafted PET molecular chain, that is, as prolonging the SSP time, causing not only more grafted points to form but also the growing of grafted PET molecular chain can take place.

The FTIR spectrum of the reinforcing glass fiber surface after removing ungrafted PET

FTIR was carried out to analyze the matrix grafted on the glass fiber surface. Figure 2 is the FTIR curves of (a) received glass fiber, (b) SSP for 5 h, and (c) SSP for 30 h. As is shown in the region of about 1722.5 cm⁻¹, there are peaks in both (b) and (c) because of the carboxyl group, which cannot be seen in (a), which clearly indicated that the strongly adhered PET was grafted onto the glass fiber surface after even 5 h SSP. It is reasonable to consider the reaction of the silicane-coupling agent with PET at the glass fiber surface.

CONCLUSIONS

Glass fiber reinforced PET composite prepared by *in situ* solid-state polycondensation has a relatively high mechanical property, which could be partly attributed to the grafting of PET on the glass fiber surface. The glass fiber surface with a removal of PET from the composite was studied on the basis of FTIR, Py-GC/MS, SEM, and DSC. The information from FTIR, Py-GC/MS showed that the PET macromolecules chain existed on glass fiber surface, and the surface morphology and its thermal behavior indicate that the PET macromolecular chain aggregated, even crystallized, on the glass fiber surface. These results suggest that the strongly adhered PET grafted onto the glass fiber surface and the weight of the grafted PET was increased with prolonged SSP time through both chemical grafting reaction and molecular chain grafting reaction.

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