

Study on Long Fiber-Reinforced Thermoplastic Composites Prepared by *In Situ* Solid-State Polycondensation

Weixia Yan, KeQing Han, LiuLiang Qin, MuHuo Yu

State Key Laboratory of Modification for Chemical Fibers and Polymer Materials, Donghua University, Shanghai 200051, China

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ABSTRACT: Long glass fiber-reinforced thermoplastic composites were prepared by a new process, *in situ* solid-state polycondensation (INSITU SSP). In this process reinforcing continuous fibers were impregnated by the oligomer of PET melt, and then the impregnated continuous fibers were cut to a desired length (designated prepreg); finally, the prepreg was *in situ* polymerized in the solid state to form the high molecular weight matrix. SEM, FTIR spectra, short-beam shear stress test, flexural strength test, impact strength test, and the intrinsic viscosity measurement were used to investigate the wetting and interfacial adhesion, the mechanical properties of the composite, and the molecular weight of matrix resin in the composite. The results showed that the molecular weight of PET in the matrix resin and

mechanical properties could be adjusted by controlling the SSP time and that the high level of interfacial adhesion between reinforcing fibers and matrix resin could be achieved by this novel INSITU SSP process, which are attributed to the good wetting of reinforcing fibers with low molecular weight oligomer melt as the impregnation fluid, the *in situ* formation of chemical grafting of oligomer chains onto the reinforcing fiber surface, and the *in situ* formation of the high molecular weight PET chains in the interphase regions. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3959–3965, 2004

Key words: *in situ* solid-state polycondensation (INSITU SSP); fibers; matrix; resins; adhesion

INTRODUCTION

Thermoplastic polymers are used as matrix materials for a wide range of fiber-reinforced composites, ranging from injection-molded, short-fiber composite to high-performance, continuous-fiber structural composites. Long fiber-reinforced thermoplastic composites have a number of advantages over short fiber-reinforced thermoplastic composites, for example, greater impact resistance, higher stiffness, better fracture toughness, and thermoresistance. Because of these beneficial properties, they have been used for structural materials in aircraft and space vehicles. It is estimated that they will experience increasing demand in the next decades.

Several routes to manufacture of long fiber-reinforced thermoplastic composite intermediate are known and a key issue is the achievement of good impregnation of the continuous fibers with the thermoplastic polymer. Such impregnated continuous fibers are usually cut to a desired length. Example processes for impregnation of continuous fiber reinforcement include hot-melt impregnation, solvent-based

impregnation, fluid bed/powder impregnation, powder suspension impregnation, and the commingling of thermoplastic fibers with reinforcing fibers.¹ All of these processes adapt the high molecular weight resin to impregnate reinforcing fibers, for which the most serious problem exists as to how the wetting between the matrix resin and the reinforcing fiber may be improved. Several investigations have been carried out to address this issue.^{2–4} Blends of poly(ethylene terephthalate) (PET) and epoxy have been used as matrix materials for continuous-fiber-reinforced composites.⁵ The characterization of wetting and adhesion in glass fiber/PA12 composite are of practical relevance for tailoring the fiber-matrix interface, to minimize the fiber impregnation time during processing and optimize the mechanical performance of the composite during service.⁶ The interfacial effects on differently treated carbon fibers and a new *in situ* PA12 polymerized matrix system were investigated.⁷ Researchers at General Electric have patented an effective impregnation process, designated *in situ* polymerization process, in which the continuous reinforcing fibers are first impregnated into a cyclic oligomer of poly(butylene terephthalate) (PBT), and then the cyclic oligomers are *in situ* polymerized to form the thermoplastic matrix by an anionic mechanism.⁸ The great advantage of this *in situ* polymerization process is that higher production speeds can be used to achieve good

Correspondence to: W. Yan (yanwx@sohu.com).

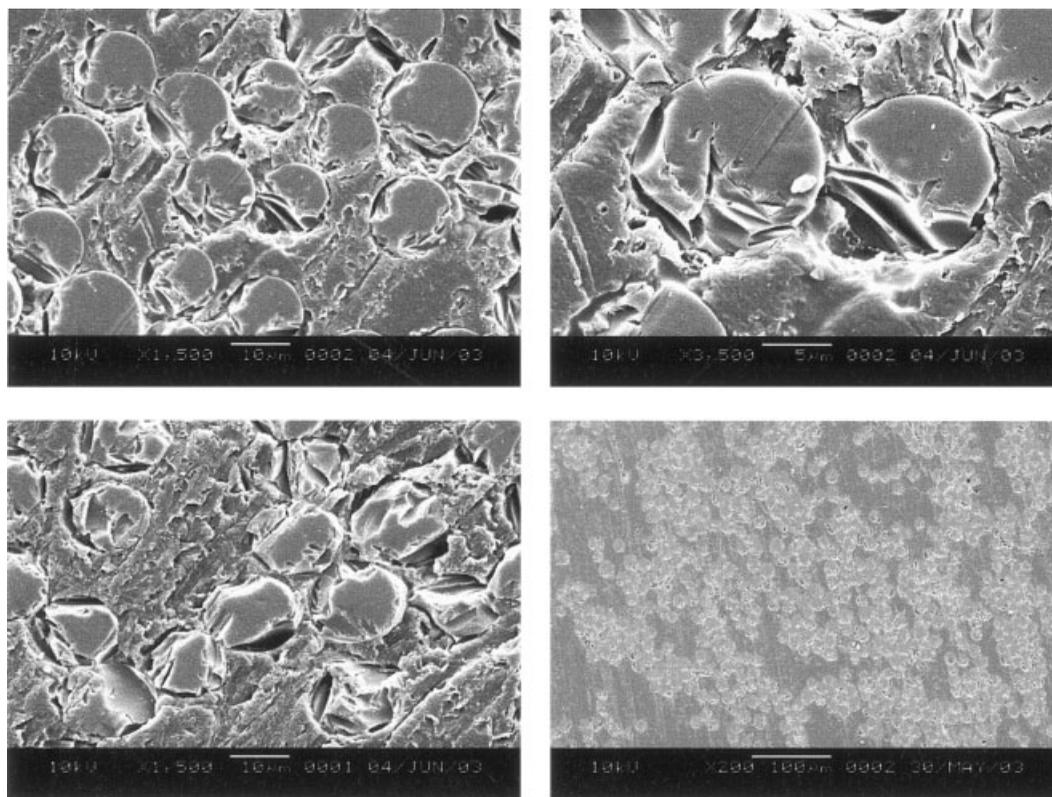


Figure 1 SEM microphotographs of prepreg specimen after *in situ* SSP with polishing.

wetting of the fibers or filaments because the oligomer has rather low viscosity compared to that of high molecular weight melts. However, limitations do exist in this new *in situ* polymerization process; for example, a special raw material, cyclic oligomer, is used, which explains the high cost of product; and an anionic polymerization mechanism is used, which is highly sensitive to moisture.

Recently, the *in situ* solid-state polymerization process to manufacture long fiber-reinforced thermoplastic composites was carried out in our laboratory to explore a new impregnation process that would have effective impregnation and be suitable for most thermoplastic matrix resin, related patent applications for which are presently being registered. In this new process, designated the *in situ* solid-state polymerization (INSITU SSP) process, the reinforcing continuous fibers are impregnated in the oligomers of polycondensation polymers, such as oligomers of PET, PBT, PC, PA6, PA66, and PA1010. The impregnated continuous fibers are then cut to a desired length (designated prepreg) and finally the oligomer of the prepreg is *in situ* polymerized in the solid state to form the high molecular weight matrix. The great advantage of *in situ* solid-state polymerization is that good wetting of the fibers or filaments will be easily achieved for using the rather low viscosity melt of oligomer than using

high viscosity melt of high molecular weight polymer melt; the second advantage of this new process is that the process will be widely suitable for most thermoplastic polymers that are synthesized by polycondensation; yet another advantage of this new process is that the process will be cost-effective for using the intermediate of polycondensation polymer as raw materials, which are easy to produce and of low cost in the industry.

In this study, long glass fiber-reinforced PET composites were manufactured by this novel INSITU SSP processing method. The morphology and mechanical properties of PET/glass fiber-reinforced composites were investigated for the first time.

EXPERIMENTAL

Materials

An oligomer of low molecular weight PET (intrinsic viscosity = 0.25) was kindly supplied by Shanghai LianJi Synthetic Fiber Co. (China). Middle alkali non-twisted glass fiber was a commercial product made by JuShi Co. (China). The fiber surface was treated by a coupling agent, KH560. Phenol and tetrachloroethane were chemical reagents supplied by Shanghai Jingshua Science and Technological School (China).

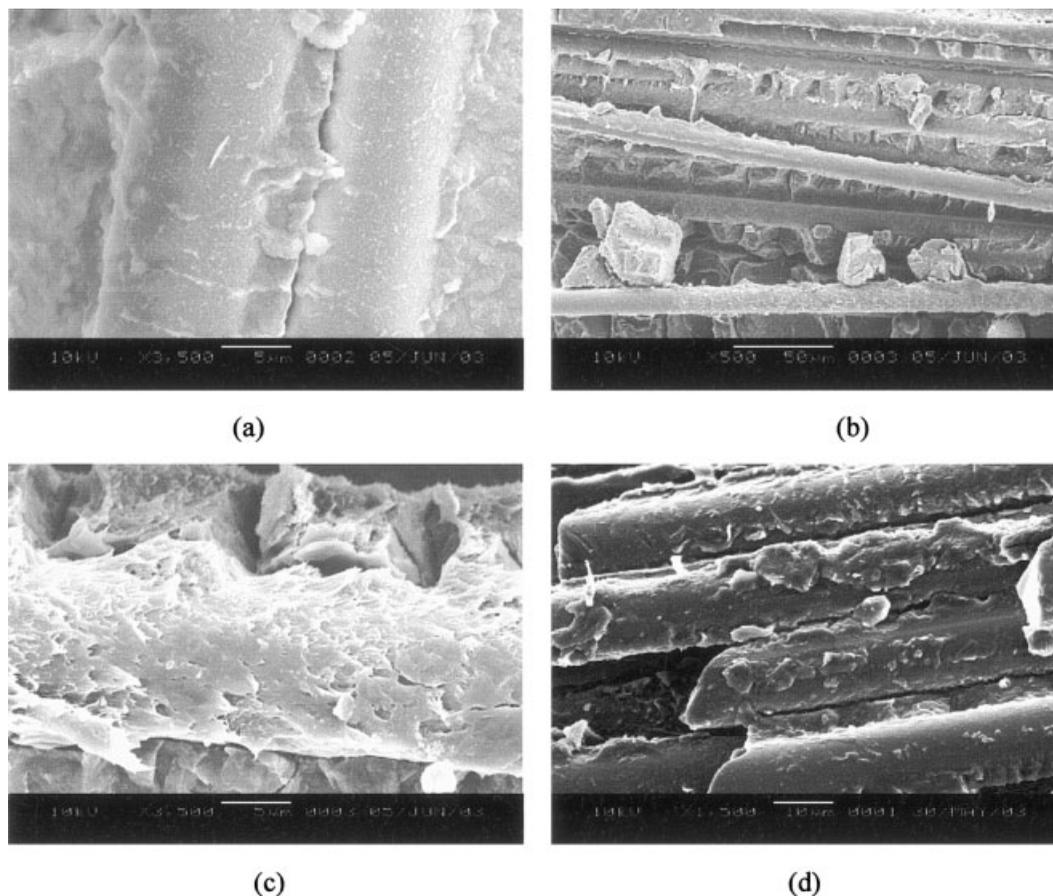


Figure 2 SEM microphotographs of composite specimen broken by the short beam shear test.

Preparation of long glass fiber-reinforced PET prepreg

The low molecular weight PET oligomer was charged to a reactor with stirring and protected by the flow nitrogen gas. When the melt reached the desired viscosity, it was pumped out from the valve in the bottom of the reactor and into an apparatus where the long glass fiber was passed through customized equipment designed to achieve the desired degree of wetting and to reduce breakage of the reinforcing fiber; after cooling the impregnated fibers were cut to the desired length. The flux of the PET oligomer melt, the towing speed of the glass fiber, and the temperature of melt were controlled to achieve good wetting and the desired fiber volume fraction. The fiber volume fraction was set to be 35%.

Preparation of PET/long glass fiber composites by solid-state polycondensation

The PET/long glass fiber composite prepregs were cut to specified length and were then placed in a biconical vacuum dryer drum for solid-state polycondensation, protected with heated flowing nitrogen gas at a constant temperature of 240°C for various times.

Intrinsic viscosity measurement

The molecular weight of PET in the composites was determined by viscosimeter. The samples were dissolved in phenol-tetrachloroethane at 25°C; the glass fibers were filtrated and intrinsic viscosity of the solution was measured. The glass fiber volume can be calculated from the weights of the sample strip and the filtrated fibers. The molecular weight of the matrix resin was calculated by the following equation:

$$[\eta] = 2.1 \times 10^{-4} M^{0.82} \quad (1)$$

FTIR spectra of the reinforcing fiber surface

An FTIR-Raman spectrometer (model NEXU S-670; Nicolet Analytical Instruments, Madison, WI) measured the FTIR spectra of the reinforcing fiber surfaces. Fiber specimens were prepared as follows: the prepreg after SSP was dissolved by phenol and tetrachloroethane mixture, the glass fibers were filtrated from dilute solution, washed by the same solvent more than 5 times to remove the PET polymer without chemical grafting to the glass fiber surface, washed with acetone, and dried at 150°C.

TABLE I
Mechanical Properties of PET/Long Glass Fiber Composite for Different SSP Times at 240°C

SSP time (h)	10	15	20	30
Flexural strength (MPa)	480.4	481.5	510.52	610.6
Impact strength (kJ/m ²)	102.4	143	181.6	221.7
Short beam shear stress (MPa)	21.25	26.21	28.68	33.16

Preparation of PET/long glass fiber composite sheets

After the SSP, the prepregs were placed unidirectionally in the mold and pressed with a 25-mN molding pressure and cooling without removing the pressure until it reached room temperature. The produced composite sheet was about 3 mm in thickness.

Mechanical properties tests

The short-beam shear and flexural strength properties of all the samples were measured using a universal testing machine (JMT5204; SANS, China), interfaced with a computer, which provided direct control of test sequences and data acquisition. The specimens for all the tests were cut to required dimensions using a wheel cutter.

The specimens for the short-beam shear tests were cut to dimensions according to ASTM D2344. The ratio of span to thickness was set to be 4; the nose radii of the loading cylinder and the supporting fixture were 4 and 1 mm, respectively; and the crosshead speed was set to be 1 mm/min.

Specimens for the flexural stress tests were cut to dimensions according to ASTM D790-02, and the speed was set to be 0.1 mm/min.

The impact resistance tests were performed using the Ceast Resil impactor; the specimens for the impact tests were recommended by ASTM D256-02.

Morphology observation by SEM

The wetting of fibers in the prepreg samples after *in situ* solid-state polymerization with polishing was directly observed by SEM, and the fracture of composite samples broken by the short-beam shear test was also directly observed by SEM, using a JSM-5600LV apparatus (JEOL Electronic Co., Tokyo, Japan).

RESULTS AND DISCUSSION

Wetting of reinforcing fibers in prepreg and the interfacial adhesion in the composites

The interface between reinforcing fibers and matrix resin is the key factor in the thermoplastic composite, concerning which many researchers have carried out comprehensive investigations. It has been established that the low level of adhesion between thermoplastic matrices and reinforcing fibers is attributed to lack of formation of strong covalent bonds, insufficient wetting, and interlocking with the fiber surface.

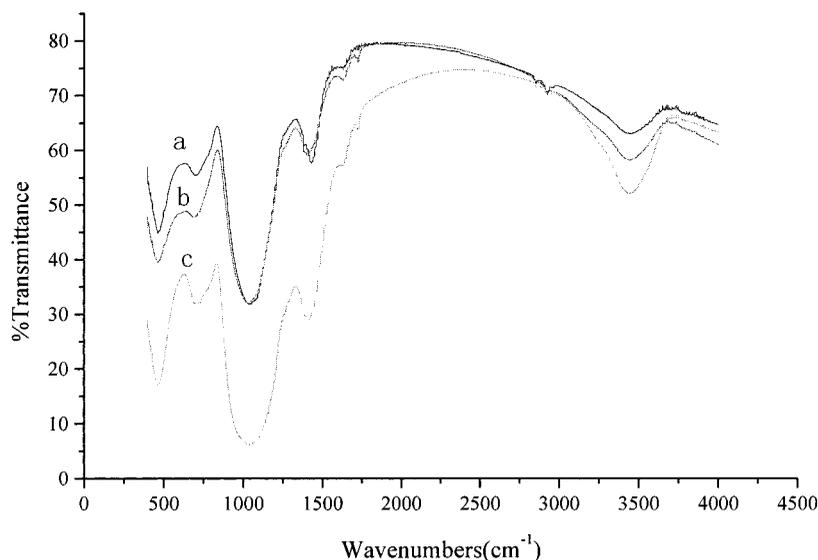


Figure 3 FTIR spectra of reinforcing fiber surface: (a) as-received fiber; (b) after 15 h SSP; (c) after 30 h SSP.

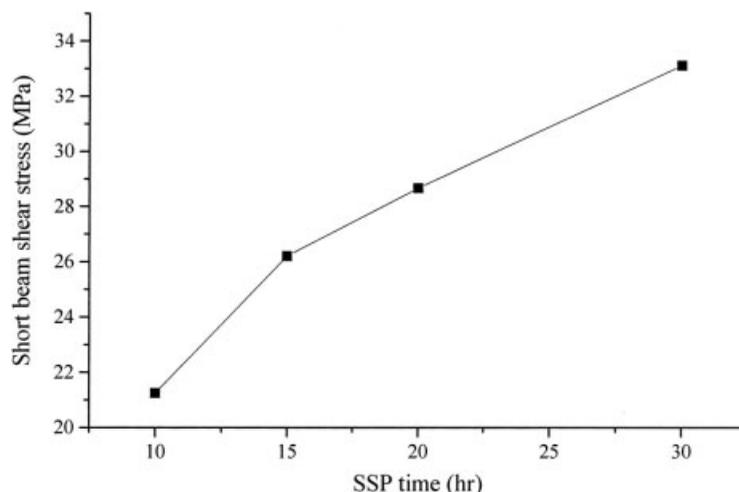
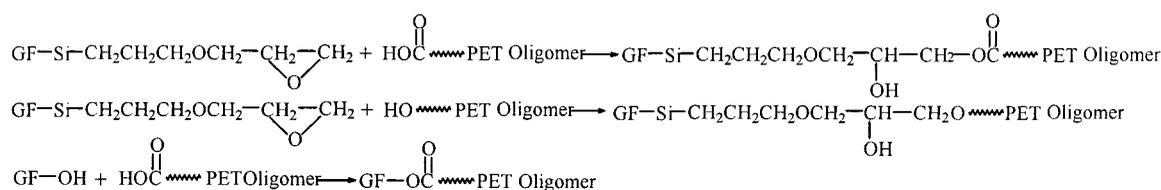


Figure 4 Short beam shear stress of PET/glass fiber composite versus SSP time.

Figure 1 shows typical SEM microphotographs of prepreg with polishing after INSITU SSP. The good wetting of the reinforcing fibers in the prepreg samples may be clearly seen from the SEM micrographs. This good wetting was attributed to the fact that the low molecular weight oligomer melt of low viscosity was used as the impregnation fluid. The sufficient wetting of the reinforcing fiber was further confirmed from the composites after INSITU SSP and pressure-molding formation. Figure 2 shows typical SEM microphotographs of a composite specimen broken after the short-beam shear stress test, from which it may be clearly seen that the fracture occurred mostly in the matrix phase rather than in the interface between reinforcing fibers and the matrix, implying that the high level of adhesion between the matrix and the reinforcing fibers was achieved.

The interlaminar shear stress of the composite specimen could be calculated from the short-beam shear test and the results are listed in Table I. From the test results, it was found that the high level of interfacial adhesion could be achieved by this *in situ* solid-state polycondensation process. The high level of interfacial adhesion could be attributed to the sufficient wetting with low molecular weight oligomer melt as impregnation liquid. Another important reason for the high level of interfacial adhesion may be attributed to the maintenance of the high molecular weight polymer chains in the interphase region. This maintenance could be achieved in two ways. First, the chemical grafting of oligomer onto the glass fiber surface may occur as described in the following reaction scheme:



This grafting reaction was confirmed by FTIR spectra. Figure 3 shows the IR spectra of the surface of the reinforcing fibers in composite specimens, where spectrum (a) is of the as-received glass fiber, treated with KH560 coupling agent; spectrum (b) is of the glass fiber in the composite prepreg after 15 h SSP; and spectrum (c) is of the glass fiber in the composite prepreg after 30 h SSP. The peaks of 1772.5 cm^{-1} in spectra (b) and (c) revealed the existence of the PET polymer chains on the reinforcing fiber surface, and which could be chemically bonded only to the reinforcing fiber surface. The difference strengths at 1772

cm^{-1} between spectra (b) and (c) may be the result of the different molecular weight of grafted PET chains and different amount of grafted chains.

During the *in situ* solid-state polymerization, the major reaction may occur between the OH end group

TABLE II
Intrinsic Viscosity (IV) of PET in PET/Long Glass Fiber Composite During SSP at 240°C

SSP time (h)	0	3	6	9	12	15	20
IV	0.25	0.476	0.605	0.6587	0.6776	0.76	0.807

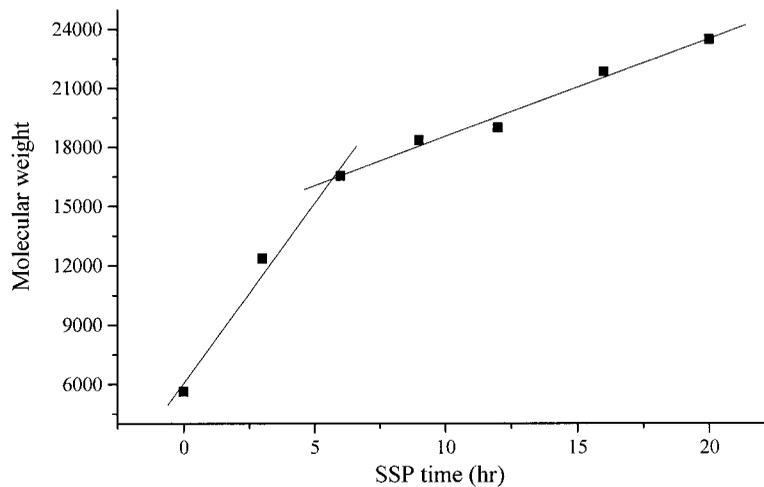


Figure 5 Molecular weight of PET in the composite versus SSP time.

and the COOH end group of oligomer to form the high molecular weight polymer chains. This solid-state polymerization can also occur in the interphase region to form high molecular weight polymer chains in the interphase regions. When plotting the interlaminar shear stress versus the SSP time (Fig. 4), it was found that the interfacial shear stress increased with increasing SSP time. It revealed that the high molecular weight polymer chains were introduced into the interfacial region during the *in situ* solid-state polymerization, resulting in the high level of interfacial adhesion.

Drzal and coworkers⁴ reported a similar experimental result in which an improvement in the interfacial adhesion was achieved with increasing molecular weight of the BPA-PC. They explained it as that the improvement in the level of adhesion with higher molecular weight was attributed to the formation of a beneficial interphase in which the PC experienced

stronger adsorption. They also found that the use of polydisperse matrices improved the processability results in entropically driven segregation of low molecular weight chains to the interface, resulting in a decrease of the level of adhesion. They concluded that the ability to maintain the concentration of high molecular weight polymer at the interphase and prevent it from being displaced by lower molecular weight polymer are important goals to be achieved for improvement of adhesion of thermoplastics to the reinforcing fibers.

As discussed earlier, the new *in situ* solid-state polymerization process is a successful route to maintain the concentration of high molecular weight polymer chains at the interphase and to prevent it from being displaced with chemical grafting and *in situ* formation of high molecular weight polymer chains in the interphase. This special chemical grafting and *in situ* formation of high molecular weight polymer chains in

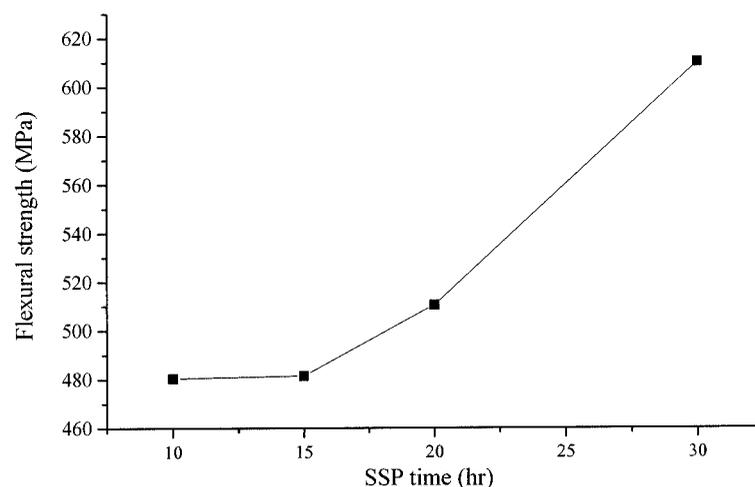


Figure 6 Flexural strength of PET/glass fiber composite versus SSP time.

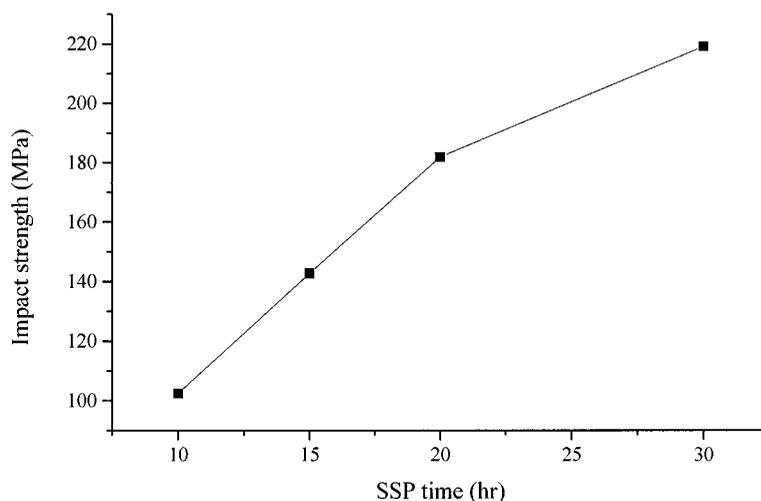


Figure 7 Impact strength of PET/glass fiber composite versus SSP time.

the interphase region can also lead to the improvement of other mechanical properties as discussed next.

Effect of SSP time on molecular weight of the matrix resin

The molecular weight (MW) of matrix resin in the prepreg was changed with different SSP times. Table II lists the intrinsic viscosity (IV) of PET in the PET/long glass fiber composite for different SSP times at the temperature of 240°C.

The IV of PET in the PET/glass fiber composites was shown to increase with increasing time. The increasing trend may be seen more clearly in Figure 5. The change in MW with time was found to be in two linear segments of different ratios. At the beginning of SSP, the MW increased rapidly; the linear relationship between MW and SSP time indicated that SSP was controlled by the chemical reaction. With longer times, the rate of increase of the MW was much lower, and this process was controlled by diffusion propagation.⁹ When the SSP was for 20 h, the IV was 0.807, attaining to the plastic grade. The effect of long glass fiber on the SSP will be presented in more detail in a future study.

The flexural and impact properties of the glass fiber-reinforced PET composite specimens are given in Table I for various SSP times (h). When plotting the impact strength and flexural strength versus the SSP time (Figs. 6 and 7), it was found that the impact strength and the flexural strength were improved as the SSP time was prolonged. This was attributed to an increasing of the molecular weight in the matrix, the formation of special chemical grafting, and the high molecular weight polymer chains in the interphase region by the *in situ* solid-state polymerization as discussed earlier. It was obvious that adjustment of the

SSP time, which is the most convenient controlling factor in the industrial SSP practice, could easily control the mechanical properties.

CONCLUSIONS

With the new INSITU SSP process, the high level of interfacial adhesion between reinforcing fibers and matrix resin in long glass fiber-reinforced poly(ethylene terephthalate) (PET) composites was achieved, attributed to the good wetting of reinforcing fibers with low molecular weight oligomer melt as the impregnation fluid, the *in situ* formation of chemical grafting of oligomer chains onto the reinforcing fiber surface, and the *in situ* formation of the high molecular weight PET chains in the interphase regions. The molecular weight of matrix resin and the mechanical properties (interlaminar shear strengths, flexural strength, and impact strength) of the long fiber-reinforced PET composites could be conveniently adjusted by controlling the SSP time.

References

1. Thornton, P. H. *J Compos Mater* 1979, 13, 147.
2. Yokochi, M.; Murakami, H. *Jpn. Pat.* JP 04039334, A2, 1992.
3. Li, G.; et al. *U.S. Pat.* 4,393,020, 1983.
4. Raghavendran, V.; Waterbury, M. C.; Rao, V.; Drzal, L. T. *J Adhes Sci Technol* 1997, 11, 1501.
5. Saalbrink, A.; Mureau, M.; Peijs, T. *Plast Rubber Compos Process Appl* 2001, 30, 213.
6. Bernet, N.; Bourban, P. E.; Manson, J. A. E. *J Thermoplast Compos Mater* 2000, 13, 434.
7. Rosso, P.; Friedrich, K.; Wollny, A. *J Macromol Sci Phys* 2002, 41, 745.
8. Ciovacco, J. P.; Winckler, S. J. *Proc Int SAMPE Symp Exhib* 2000, 45, 1074.
9. Schiavone, R. J. *J Appl Polym Sci* 2002, 86, 230.