

NOTE

Development of Thermoplastic Prepreg by the Solution-Bond Method

Several approaches have been suggested so far for the purpose of preparing thermoplastic prepregs: (i) the high shear rate, high-temperature method, based on the fact that the resin viscosity usually drops with increasing temperature and shear rate (shear thinning effect); (ii) the fiber-mixing method,¹ where the impregnated strand is prepared by mixing the fiber-shaped resin and reinforcing fibers using a melt impregnation technique; (iii) the film method, according to which the fiber impregnation is made by heating two sheets of resin films containing the fiber bundles arranged between them; and (iv) the plasticizer addition method,² utilizing the phenomena that melting-point depression and viscosity reduction of the resin are caused by the addition of the diluents. However, all the methods mentioned above have respective disadvantages. For example, in the case of the plasticizer addition, the plasticizer must be removed in the after-treatment step of the prepreg manufacturing process, and for other methods, it is hard to achieve the complete wetting of fibers with molten resin because of the high viscosity of the resin.³ In particular, for the resin system whose melting point and thermal decomposition temperature do not differ so much, the lowering of melt viscosity by increasing temperature is hard to expect in view of thermal stability.

To overcome the deficiencies associated with resin viscosity, a new method has recently been proposed,⁴ where fiber bundles are covered with the dry powder of the impregnating resin and are passed through the heated nozzle to cause the melted resin to impregnate the fibers. But the application of this method is limited to the fiber-bundle system with relatively few filaments.

Because of the above mentioned problems, we have developed a convenient method for preparing thermoplastic prepregs by means of the "solution-bond method," similar to the solution-microbond method,⁵ for preparing the pullout test specimen. According to this method, the impregnated strand, and, hence, the prepreg, may be produced by dissolving the thermoplastic polymer in an appropriate solvent, immersing the strand in resin solution, then evaporating the solvent by vacuum-drying, followed by reheating above the melting temperature of the resin polymer for removal of any residual solvent and for complete, uniform wetting of the fibers.

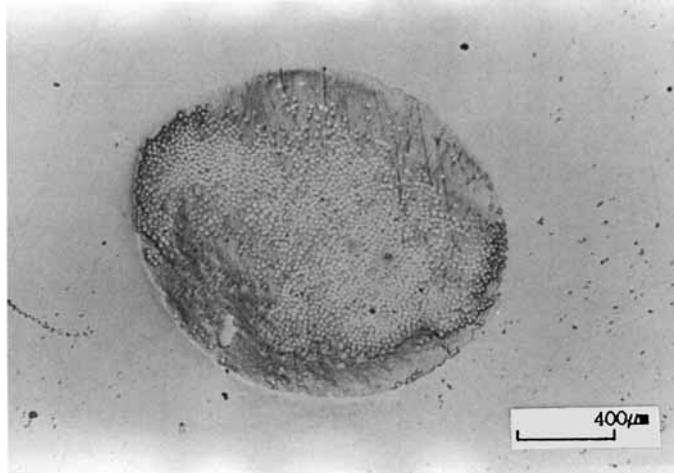
To test the validity of this method, the application to the glass fiber/high-density polyethylene (HDPE) system

was made using toluene as solvent. The specifications of glass fiber and HDPE used in this study were E-glass, supplied by Han Kuk Fiber Co.: density, 2.54 g/cm³; mean diameter, 19.5 μ m; tensile strength, 1.65 GPa; and supplied by Han Nam Chem.: density, 0.96 g/cm³; MW, 20,000, respectively. As stated before, the strand impregnated with resin is obtained by immersing a glass fiber bundle consisting of 600 filaments in 14.2 wt % toluene solution of HDPE at 100°C for a definite time interval, then subjecting the wet-out fibers to vacuum-drying at 120°C for 1 h, followed by reheating to 160°C (20°C above the melting point of the resin polymer) to ensure the complete removal of solvent and uniform wetting of the fibers.

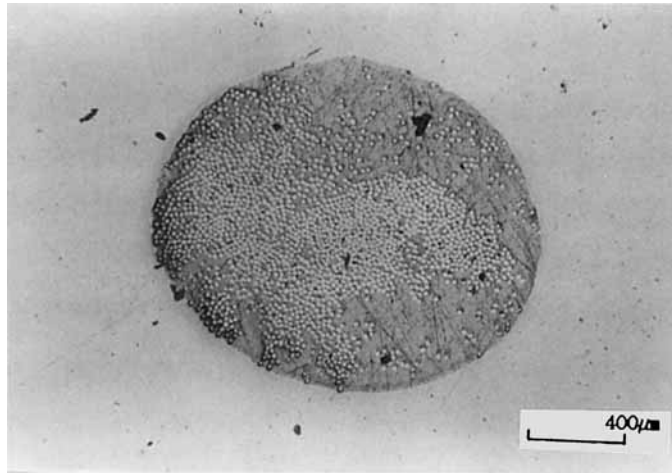
To investigate the effect of the impregnation time on the impregnation state (such as efficiency and uniformity) of a resin within the strand, resin-impregnated strands were prepared using different impregnation times ranging from 3 to 120 s by the solution-bond method and further treated to give the specimen for optical observation through a microscope by covering the impregnated strand with epoxy resin, curing it at 80°C for 24 h, and polishing it with a mirror surface. The optical microphotographs of cross sections of the resin-impregnated strands obtained at different impregnation times are given in Figure 1. Referring to the cross-sectional view of the impregnated strand shown in Figure 1, it appears that the cross section of the strand consists of the fiber-rich region and the resin-rich region and that sufficient impregnation of fibers by the resin has already been attained for the impregnation times above 3 s; therefore, this value is taken as the standard impregnation time for preparing prepregs hereinafter. In addition, as the impregnation time increases, the spacing between fibers broadens, and, hence, better dispersion of fibers in the matrix may be obtained due to the increased infiltration effect of the resin between the fibers.

The mean fiber content within the strand for the impregnation time of 3 s as determined by measuring the weight of the impregnated strand before and after thermal decomposition in an electric furnace at 450°C for 12 h was 34.5 vol %, this value being adjusted to 40 vol % later because of the flowing out phenomenon of the resin caused by the pressure applied during the manufacturing process of the prepreg.

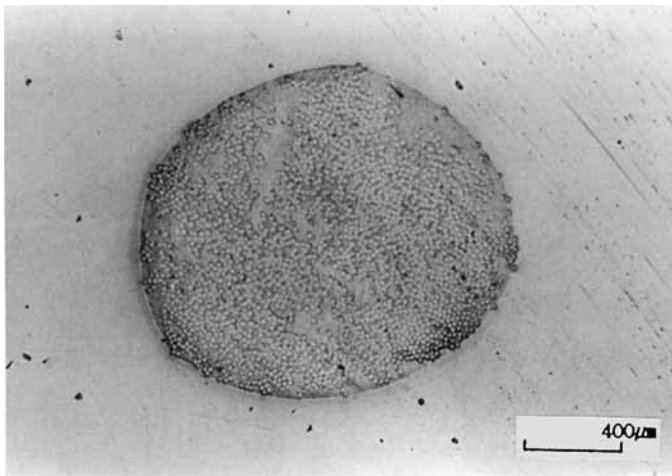
As evident from Figure 1, as the impregnation time increases, the mean fiber content tends to somewhat decrease initially, but to change little beyond 20 s (around 30.2 vol %). Similarly, with increasing impregnation time, the interfiber distance becomes a little wider initially, but



(a) 10 sec



(b) 20 sec



(c) 120 sec

Figure 1 Optical microphotographs of the cross section of impregnated strands obtained at different impregnation times, showing the distribution state of the resin in strand: (a) 3 s; (b) 20 s; (c) 120 s.

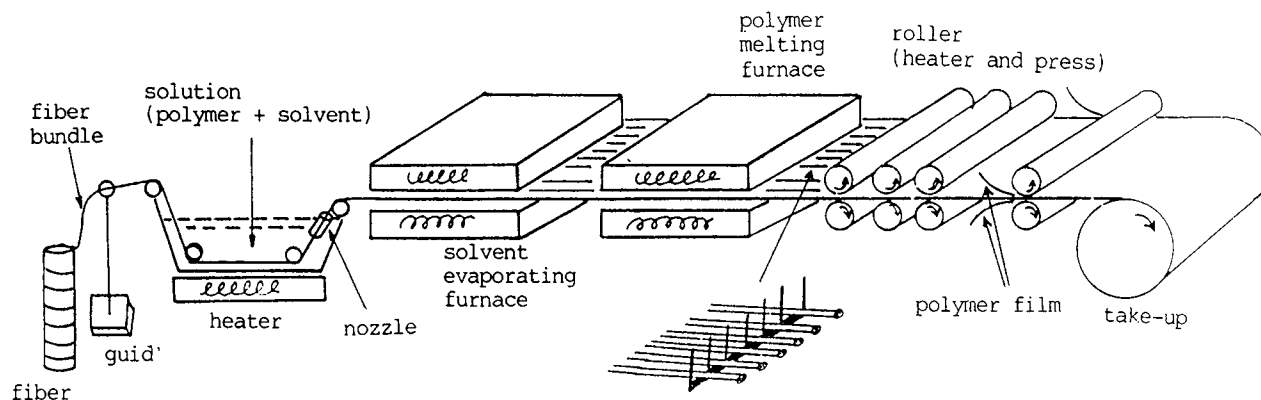


Figure 2 Schematic illustration of the equipment for continuously producing thermo-plastic preregs based on the solution-bond method.

has a nearly constant value beyond 20 s. Both these tendencies are considered to be due to the result that the fiber impregnation with the resin has attained a saturation state beyond 20 s.

Meanwhile, it will be helpful to the understanding of the results obtained in this study to discuss criteria on the selection of a suitable solvent and the optimum concentration of a resin solution for preparing the impregnated strand, and, hence, prepreg, by the solution-bond method. First of all, requirements for a suitable solvent include the following: (i) a lower boiling than melting point of the resin (in view of thermal stability); (ii) a low viscosity (in view of impregnation efficiency); and (iii) a lower density than that of the resin (for easy removal during the molding). Next, the optimum concentration of a resin solution should be determined by making a com-

promise between the content of the resin to be impregnated and the impregnating ability (or wettability). As pointed out previously, a low viscosity of the resin solution is principally required for effective wetting of the fibers. Hence, the resin solution viscosity can be reduced by using a lower viscosity solvent and/or by lowering the content of the resin. However, if the impregnating system is too fluid (or the resin content is too low), problems in process control and in uniformity of the resin content to be impregnated will be encountered. For the present HDPE/toluene system, the optimum concentration of the resin solution has been found to be 14.2 wt %; furthermore, the fiber content within the strand (or prepreg) could be properly controlled by a suitable combination of concentration of resin solution and impregnation time.

On the other hand, sketches of the equipment for pro-

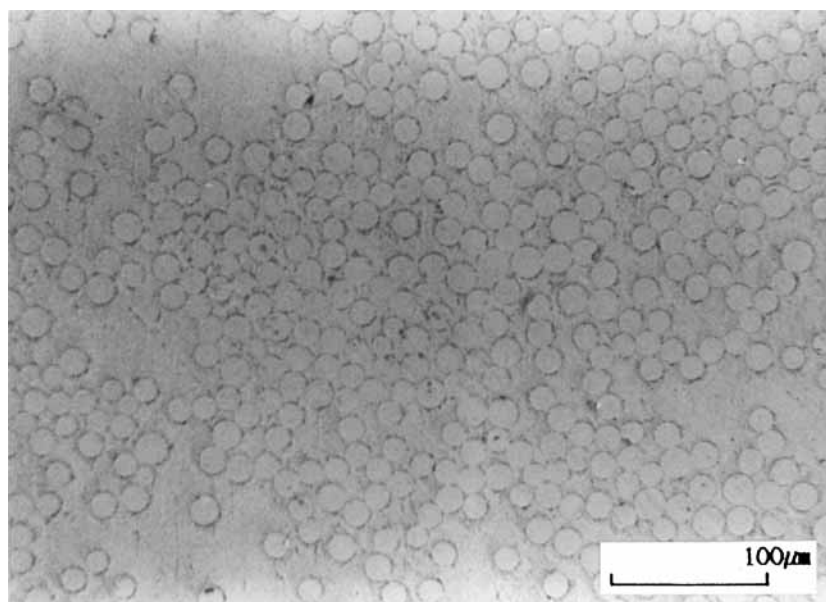


Figure 3 Optical microphotograph showing the distribution state of the fibers in the prepreg prepared from strands impregnated for 3 s.

ducing continuously impregnated strands, and, hence, thermoplastic prepregs, by the solution-bond method devised at our laboratory are given in Figure 2. For reference, a brief explanation of the procedures for producing uniformly impregnated strands as well as the functions of the main parts of the equipment will be given in the following. As mentioned above, continuous fibers are impregnated by passing them through a resin solution tank mounted on an electric heater. Impregnated strands are then passed through a solvent-evaporating furnace maintained above the boiling point of the solvent and a polymer melting furnace maintained above the melting point of the resin for complete removal of any residual solvent and for uniform wetting of fibers through the evaporating and diffusing processes. Next, impregnated strands thus obtained are passed through a calender consisting of a series of rotating heated rollers maintained at a temperature a little below the melting point of the resin, between which impregnated strands with nearly circular cross sections are spread out and squeezed into sheet (or tape) form, the thickness of the sheet being adjusted by the clearance between the calender rollers. Finally, fiber-impregnated polymer sheets are wound on a takeup tool to give thermoplastic prepregs. In this equipment, the nozzle located near the exit of a resin container plays a role in controlling the extent of impregnation (or impregnation efficiency) and, therefore, the fiber content in the final prepreg.

To test the validity of this equipment based on the solution-bond method, the HDPE prepregs have been prepared with the glass fiber strands impregnated in a toluene solution of HDPE by means of this equipment. The optical microphotograph of a cross section of the prepreg thus obtained is shown in Figure 3, according to which polymer-dense regions are partly observed on upper and lower parts of the photograph. This is probably because the resin polymer present abundantly around the circumferential part of the impregnated strand has been migrated inward by the pressure applied during the manufacturing process of the prepreg, reflecting that the distribution of fibers within the impregnated strand might also be improved by the manufacturing process. On the other hand, from the IR analysis on the prepreg, it was confirmed that there was no solvent remaining in the completely molded prepreg.

In addition, to investigate the fiber-dispersion state and interfacial structure between the fiber and matrix within the impregnated strand, tensile tests were performed on the strands impregnated for 3 s using an extensometer at

a crosshead speed of 1.5 mm/min, yielding the mean tensile strength of 1.60 Gpa, elongation at break of 2.4%, and tensile modulus of 76.5 Gpa. These tensile data are found to be very close to those for the single fiber, implying that the complete, uniform wetting of the fibers with the resin, and thereby the reinforcing effect of the fibers, may have been achieved by this method.

Though not reported here in detail, the laminated composite for the present system has been successfully prepared by laying up the prepregs at high pressure and temperature using a specially made mold, with silicone oil diluted in acetone as the mold-release agent.

In view of the results obtained so far, the solution-bond method is judged to be very effective for preparing thermoplastic prepregs, provided that a suitable solvent meeting the requirements discussed above is available.

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Received August 12, 1991

Accepted February 27, 1992