

# Improvement of Mechanical Properties of Structural Thermoplastic Composites Using a Reactive (Low Molecular Weight) Matrix Component

M. Aurilia,<sup>1</sup> L. Sorrentino,<sup>2</sup> S. Iannace<sup>2</sup>

<sup>1</sup>IMAST, Technological District on Polymeric and Composite Materials Engineering and Structures, P. E. Fermi 1 - loc. Granatello, Portici 80055, (NA), Italy

<sup>2</sup>Institute for Composite and Biomedical Materials, National Research Council of Italy, P. E. Fermi 1 - loc. Granatello, Portici 80055, (NA), Italy

**An innovative manufacturing process for continuous fiber composites with the polymeric matrix made up of polypropylene and epoxy resin, as a model reactive low molecular weight component, was developed; variable process parameters give rise to different morphologies of matrix components surrounding the woven fabric reinforcement. Furthermore, the combination of both thermoplastic and thermosetting polymers permitted intimate fibers impregnation, typical of thermosetting matrix composites, with short process cycle time, which usually occurs in manufacturing process of thermoplastic matrix composites. Polypropylene (PP) films, glass fibers fabric, and epoxy resin film were used to produce flat composite through film-stacking technique. The preparation process focused on control of both epoxy resin cure process and polypropylene melting. The process was able to induce the two matrix components to form either a planar (sandwich-like) structure or a three-dimensional (3D) network by means of controlling the process parameters such as pressure and heating rate. The strong enhancement of the mechanical properties (Young's modulus and tensile strength of the composites with the 3D structure were almost twice as high of those of the composites with sandwich-like matrix structure) was due to the different microstructures produced by the interplanar flow of the thermoplastic polymer. POLYM. COMPOS., 31:1762–1769, 2010. © 2010 Society of Plastics Engineers**

## INTRODUCTION

Organic matrix composites are widely used in many applications, from functional use such as acoustic absorption in cars interiors to structural components in aircraft assembly. Most of these applications were historically

dominated by thermosetting matrix composites; in the 1980s, many studies demonstrated that thermoplastic matrix composites could be a valid alternative to thermosetting matrix composites even in advanced applications such as aerospace and other high-performance industries. Thermosetting matrices are used for their high modulus, good environmental resistance, good reinforcement impregnation, and strong interaction with fibers; however, the thermosetting matrix composites consolidation is governed by the matrix curing reaction; hence, their manufacturing cycle is very slow [1].

On the contrary, thermoplastic matrices composites show high toughness, no chemical reactions during fabrication, short manufacturing cycle, possibility of both scraps recovery, and in-use repairing; nevertheless, the high thermoplastic matrix viscosity prevents the reinforcement impregnation and hence the process must be performed at elevated temperatures [1]. Thermoplastic matrix composites are generally preferred to thermosetting composites when high toughness and high productivity are required.

In the recent years, many efforts have been done to improve the processability and the properties of both thermosetting and thermoplastic composites. The manufacturing process of the thermosetting matrix has been continuously developed starting from conventional process in autoclave [2, 3], characterized by good quality products but also by long cycles and elevated costs, arriving to out of autoclave process such as resin transfer molding (RTM) [4, 5], and resin film infusion (RFI) [6, 7]. These processes utilize closed mold and/or vacuum bag (smaller tools than autoclave) that furnish good fibers impregnation in shorter time and with lower costs compared to manufacturing carried out in autoclave. Furthermore, many studies have been performed to improve the processability and mechanical properties of thermosetting matrixes modifying their composition

Correspondence to: M. Aurilia; e-mail: marco.aurilia@ismast.it

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chemically or with the addition of thermoplastic polymer particles [8].

In the same way, the manufacturing process of thermoplastic composites have been extensively studied and many fibers impregnation techniques have been proposed [9], such as solvent impregnation, fluidized bed impregnation, commingling and coweaving [10], melt impregnation by film stacking, continuous melt impregnation (double belt press), and slurry deposition. Almost recently, Bernet et al. [11, 12] have developed predictive models relating the properties (e.g. void content) of thermoplastic composite (commingled yarn preforms) to both processing condition and production costs; these models show that the manufacturing of thermoplastic composites is cost effective when compared with traditional thermosetting production processes. Hence, the research in the field of polymeric matrix composites has been driven by material properties improvement and by reduction of both production time and manufacturing costs.

In this work, a hybrid production process of continuous fiber composites based on a two-component matrix (thermoplastic and thermosetting) has been proposed; the composites were prepared in short production time, typical of thermoplastic composite manufacturing, and presented good fibers impregnation (typical of thermosetting matrix composites). Film-stacking technique was utilized as the manufacturing process. The composite matrixes were composed by polypropylene and epoxy resin. The latter furnished good fibers impregnation, while the polypropylene provided toughness properties to the structures. The preparation process was governed essentially by the thermosetting resin cure reaction and by the melting/solidification process of the polypropylene. The high temperature speeded up the curing reaction allowing the overall epoxy resin consolidation process within the time frame employed for the preparation of thermoplastic composite. The film stacking manufacturing parameters (such as the applied pressure, the temperature, and cycle time), the reinforcement permeability, and matrix composition controlled the final conformation of the two components in the matrix, in particular, influencing the PP/epoxy resin distribution respect to the reinforcement. The coupling of the thermoplastic and the thermosetting components in the composite matrix allowed to combine the main characteristics of these two classes of polymers: good fibers impregnation and short manufacturing time. The compatibility and the interface properties between PP and epoxy resins were not specifically taken into consideration since the hybrid matrix was intended as a model whose components could be replaced by more suitable polymers couples. In the last years, many reactive thermoplastic polymers have been studied and developed [13]. A wide polymer selection is available, from engineering plastics (thermoplastic polyurethane, polymethylmethacrylate, polyimides, polyesters, polycarbonate) to high performance ones (polyetheretherketone, polyetherketone, polyethersulphone, polyphenylenesulfide). This wide variety of reac-

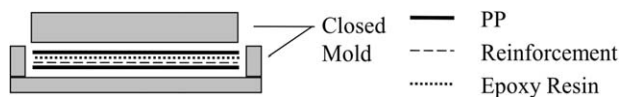


FIG. 1. Lay up of glass fiber composite in the closed mold before compression molding.

tive thermoplastic polymers can be taken into account to produce either (a) continuous fiber composites with a two-component matrix (e.g., reactive-polyethyleneterephthalate/polyethyleneterephthalate) or (b) composites with matrices based on a polymer blend (e.g., reactive polycarbonate/polyamide 6).

The aim of this work is to illustrate a viable route to produce hybrid matrix fiber composites to exploit the main advantages of both reactive matrix and thermoplastic matrix composites.

## EXPERIMENTAL

The glass-fiber-woven fabric used as reinforcement was of the VR32 type produced by Teximpianti (330 g/m<sup>2</sup>, warp/weft 6.5/5.5). The homopolymer polypropylene films were produced by compression molding from PP pellets purchased from Sigma Aldrich. The epoxy resins film used as reactive component was the AF-163-2 type (recommended cure temperature = 121°C) from 3M Chemical Company.

The film-stacking process was used to prepare the composite samples. A layer of glass fiber fabric was stacked between two layers of PP (dimensions: 250 × 250 mm<sup>2</sup>) in a closed mold (see Fig. 1) and then inserted in a hydraulic hot press (Collin GmbH, model P 300P) that was able to control the temperature and pressure profile applied to the mold. The composites with epoxy resin were prepared laying up an epoxy film between PP layers and the reinforcement.

Two distinct sets of process conditions were used: (1) low-pressure process (LPP), in which the mold was inserted between press plates at room temperature and then heated up to 200°C, holding the applied pressure at a constant value of 6 bar (Fig. 2a); (2) high-pressure process (HPP), in which the manufacturing process started by inserting the mold between the press plates at 200°C; instantaneously a pressure of 100 bar was applied for 5 min, subsequently decreased to 6 bar (Fig. 2b). In both the processes, the cooling conditions were the same, as showed by the temperature profile. To highlight the effects on the composite structures of both process parameters and amount of epoxy resin film, four classes of samples were prepared and tested. In the following, we indicate with S1 and S2 the composites produced with LPP and with S3 and S4 the samples produced through the HPP. Only S2 and S4 were prepared with the epoxy resin layer (14.26% and 8.26% volume fraction, respectively). The composites compositions are reported in Table 1.

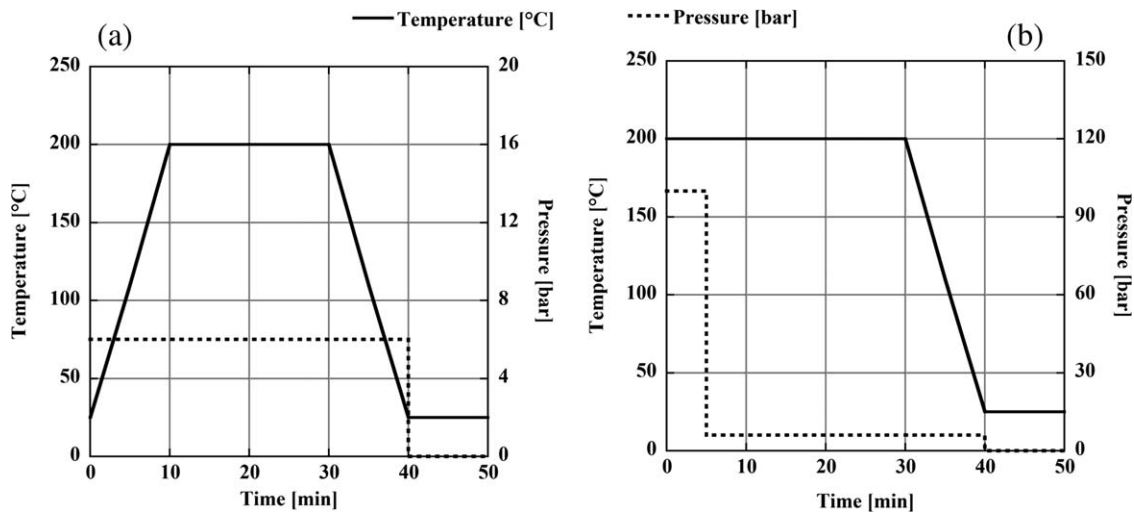


FIG. 2. Temperature and pressure profiles in the compression molding process: (a) The LPP used to prepare S1 and S2 composites and (b) the HPP used to prepare S3 and S4 composites.

A Differential Scanning Calorimetry system (DSC-TA Instruments, model 2920) was used to study the epoxy resin cure reaction; isothermal scans at 200°C were carried out on 9-mg resin samples.

Tensile mechanical tests were performed by using an Instron 3310 universal testing machine on samples cut from the composites panels, according to ASTM 3039, at room temperature. The Young's modulus was measured, by applying an extensometer to samples, at crosshead speed of 2 mm/min. For each kind of composite panel, five samples have been tested and the average values and standard deviation were calculated from the measured data.

The distribution of epoxy resin and PP in the composite matrices was analyzed with both optical microscope (Olympus BX51) and Leica S440 scanning electron microscope (SEM).

## RESULTS AND DISCUSSION

In this section, the results of our tests will be presented, and the influence of manufacturing on the morphology of the epoxy resin/PP matrix will be analyzed; furthermore, the effects of both the morphology and the process parameters on the composites' mechanical properties will be discussed.

### Matrix Morphology

The curing kinetic of the epoxy resin was analyzed with isothermal DSC runs, and the degree of cure  $\alpha$  was evaluated according to the Eq. 1:

$$\alpha(t) = \frac{\int_0^t \left(\frac{Q(t)}{dt}\right) dt}{\int_0^{t_f} \left(\frac{Q(t)}{dt}\right) dt} \quad (1)$$

where  $Q(t)$  is the heat of cure reaction and  $t_f$  the time required to complete the reaction (measured from isothermal DSC experiment) [14]. In Figure 3, the time dependence of  $\alpha$  is shown. According to the epoxy resin data-sheet, the indicated cure temperature is 121°C, at which the reaction completes in 90 min, but at 200°C, which is the temperature used for the film stacking processes, the cure reaction became very fast and was completed after  $\sim 18$  min. At this temperature, the resin gelification ( $\alpha = 0.2-0.5$  [15]) started after few seconds (square symbol in Fig. 3) indeed the very high resin viscosity reached after few seconds did not allow further flow into reinforcement phase.

TABLE 1. Tensile mechanical properties and compositions of composite samples.

Samples	% Volume content			Young's modulus (GPa)	Tensile strength (MPa)	Ultimate strain (%)	Modulus efficiency factor	Strength efficiency factor
	Glass fiber	Epoxy resin	PP					
S1 (LPP)	12.81	—	87.18	5.62 ± 0.53	116 ± 6	6.29 ± 0.58	0.48	0.20
S2 (LPP)	11.40	14.26	74.33	6.63 ± 0.42	119 ± 12	5.92 ± 0.87	0.66	0.22
S3 (HPP)	16.84	—	83.16	8.15 ± 0.86	155 ± 9	6.61 ± 0.13	0.58	0.22
S4 (HPP)	16.99	8.26	74.74	12.27 ± 1.18	195 ± 24	5.52 ± 0.43	0.89	0.28

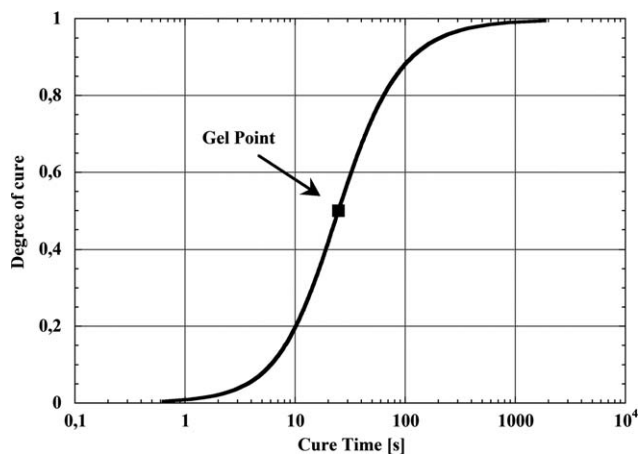


FIG. 3. Degree of cure of epoxy resin AF-163-2 at 200°C measured with an isothermal DSC run. The square symbol represents the gelification point.

In the LPP conditions, the mold reached the temperature of 200°C after 10 min. During the increase of the temperature, epoxy resin was able to flow and impregnate the glass fibers. In the mean time, the nonisothermal cure reaction started and when the temperature approached 200°C, the cure process was already activated and completed. The resin was already partially cured and the viscosity was high when the PP began to melt. This hindered the PP to flow between the fiber tows and the matrix morphology was frozen in a sandwich-like structure, as shown both in Fig. 4b, where the SEM of the tensile test fracture surface is illustrated (schematically in Fig. 5a). As a result, the matrix morphology was determined in the early stage of the film-stacking process.

Diversely, with the HPP conditions, the press plates temperature was set at 200°C at the beginning of the process and, even if the temperature slightly decreased for few seconds (as monitored by the press control panel) after the mold insertion, it could be considered constant. In these conditions, the PP melting was rapid and the high pressure used at the beginning of the manufacturing process allowed the PP to flow throughout the glass fiber reinforcement, already rapidly impregnated by epoxy resin as soon as the pressure was applied. When the resin reached the gel point, the PP just formed a surrounding network around the fiber bundles intimately impregnated by epoxy resin as shown in Figs. 7 and 8 and sketched schematically in Fig. 5b.

The tensile test fracture surface of the S3 composite prepared by using the HPP conditions without the epoxy resin is shown in Fig. 6. A low affinity between fibers and matrix is evident. The morphology of the S4 composite, produced by adding the epoxy resin film, are illustrated in Fig. 7. Several zones of the fracture surface are reported in this figure: glass fibers impregnated exclusively by the epoxy resin (Fig. 7a); glass fibers impregnated by PP (Fig. 7b); and in Fig. 7c, PP crossed the fabric net, the latter impregnated by the epoxy resin.

A particular of the S4 composite polished surface was analyzed by using also an optical microscope (see Fig. 8). In Fig. 8a, the picture was taken parallel to laminate plane and it is possible to see the glass fibers thoroughly wetted by the epoxy resin (characterized by dark/red color) and the square space between the fiber bundles filled by the PP (light/grey color). In Fig. 8b, the through thickness picture illustrates the PP domains (light color) within the fiber bundles impregnated by epoxy resin. The PP–epoxy interface is very clear, indicating, as expected, a poor interaction between the two matrix components. Nevertheless, the three-dimensional (3D) distribution of the blended matrix resulted in higher mechanical properties (S4 sample) with respect to sandwich structured matrix (S2 samples).

### Composites Mechanical Properties

The composite tensile properties are reported in Table 1. The modulus and tensile strength were higher in composites prepared with HPP conditions (coupon S3 and S4)

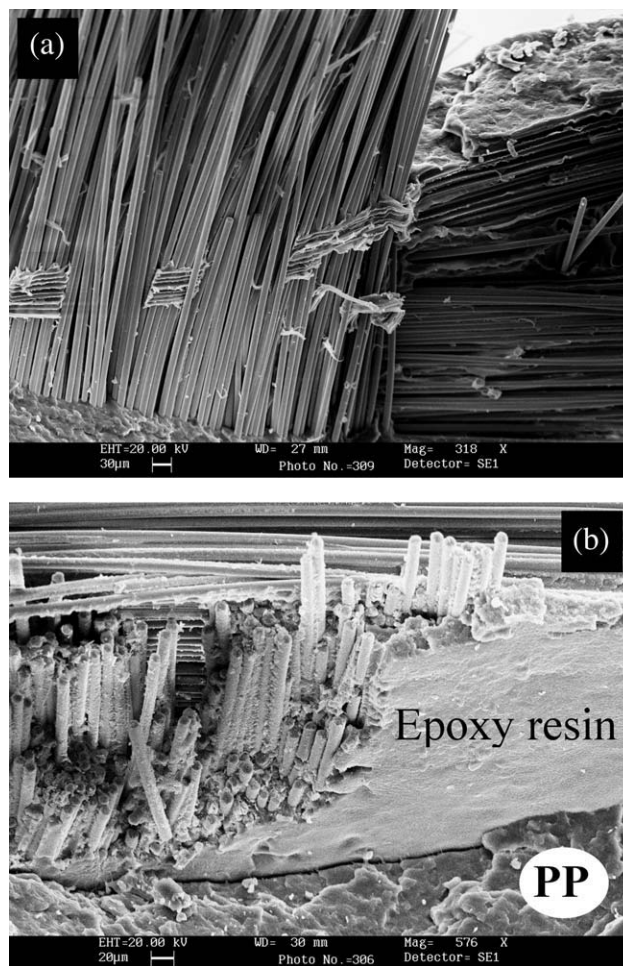


FIG. 4. SEM analysis of the tensile test fracture surfaces of the composites prepared with LPP: (a) S1 composite with PP as matrix and (b) S2 composite with epoxy resin that impregnates the fibers; the outer skin is made up of PP.

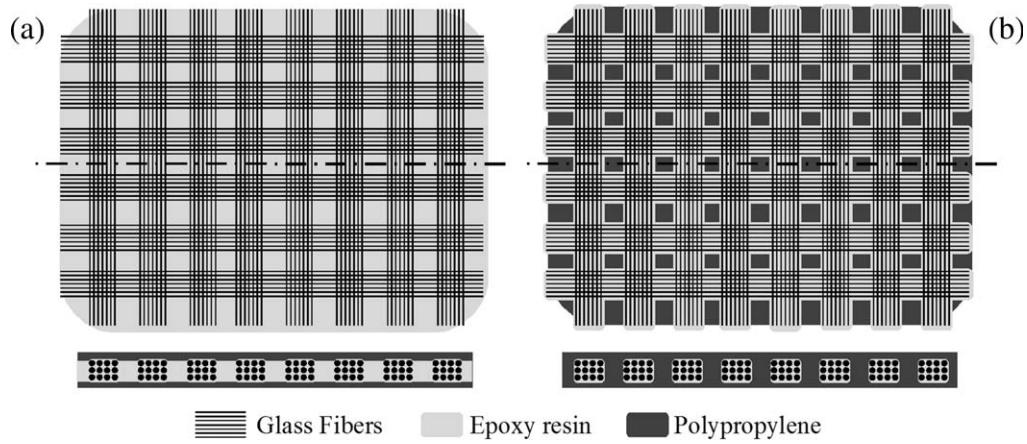


FIG. 5. Epoxy resin and PP distribution in the matrix of the glass fiber composite: (a) morphology induced by LPP conditions and (b) morphology induced by process HPP.

compared to composites processed with LPP conditions (coupons S1 and S2). Samples containing epoxy resin (S2, S4) show a slight reduction of the ultimate strain respect to resin-free samples (S1, S3) and an increase of both Young's modulus and tensile strength.

However, the fiber content of LPP composites (11.40 and 12.81 vol%) is lower than that of HPP composites (16.84 and 16.99 vol%). To evaluate and discuss the effect of both two film-stacking processes and epoxy resin content on the composites' performances, it was useful to define the Young's modulus and tensile strength efficiency factors, respectively, as  $\varepsilon_E$  and  $\varepsilon_\sigma$  in *Eqs. 2* and *3*. These factors are generally used to predict the modulus and the tensile strength of short fibers composites and are suitable to give estimation of the aspect ratio and of the orientation retained by the reinforcing fibers [9, 16–19]. Here, slightly modified formulas are proposed to take into account the matrix formed by two components (mechanical properties of composite components are reported in Table 2):

$$E_c = E_{PP}\phi_{PP} + E_{Epox}\phi_{Epox} + E_{GF}(1 - \phi_{PP} - \phi_{Epox})\varepsilon_E \quad (2)$$

$$\sigma_c = \sigma_{PP}\phi_{PP} + \sigma_{Epox}\phi_{Epox} + \sigma_{GF}(1 - \phi_{PP} - \phi_{Epox})\varepsilon_\sigma \quad (3)$$

As we used a woven fabric as reinforcement the Young's modulus efficiency factor ( $\varepsilon_E$ ) does not provide the average orientation of the short fibers in the load direction, but it furnished an estimation of the composite efficiency with respect to a unidirectional laminate tested in fibers direction ( $\varepsilon_E = 1$ ). The tensile strength efficiency factor, on the other hand, was used to obtain an estimation of the fiber/matrix interaction: a higher matrix/fiber interfacial strength results in increased efficiency factor.

The sample S2 containing 14.26 vol% of epoxy resin and manufactured with LPP presented higher Young's modulus and tensile strength when compared with S1 composite (only PP matrix).

However, the Young's modulus and the tensile strength efficiency factors of S2 composite improved, respectively,

of 38% and of 10% when compared with those of S1 composite (Table 1); in this case, the increased mechanical properties are essentially related to the better epoxy/glass fiber interfacial adhesion and to the higher Young's modulus of the epoxy resin; in fact, the SEM image of tensile test fracture surface of S1 samples (Fig. 4a)

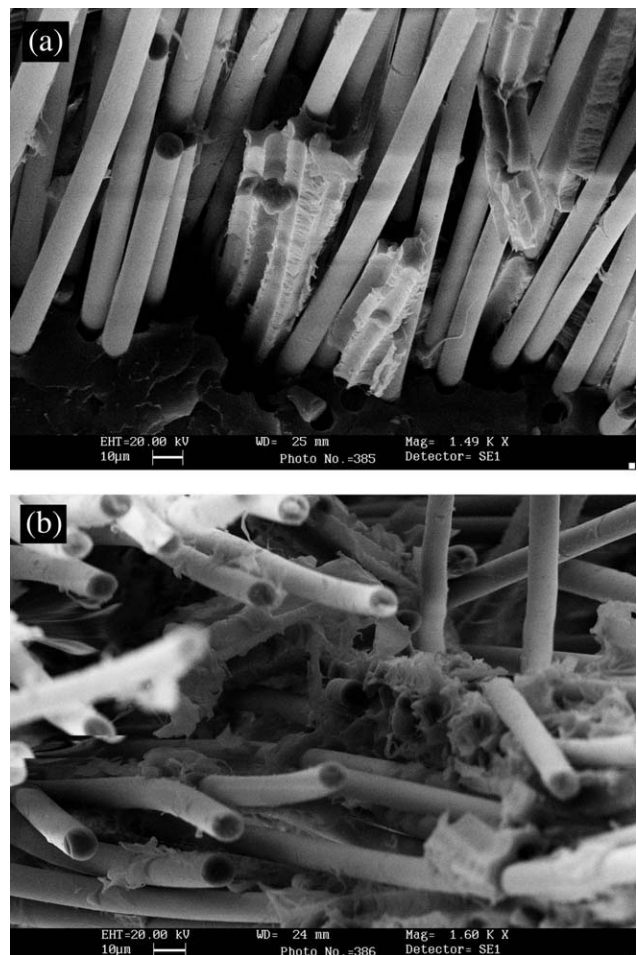


FIG. 6. SEM analysis of the tensile test fracture surfaces of S3 composite.

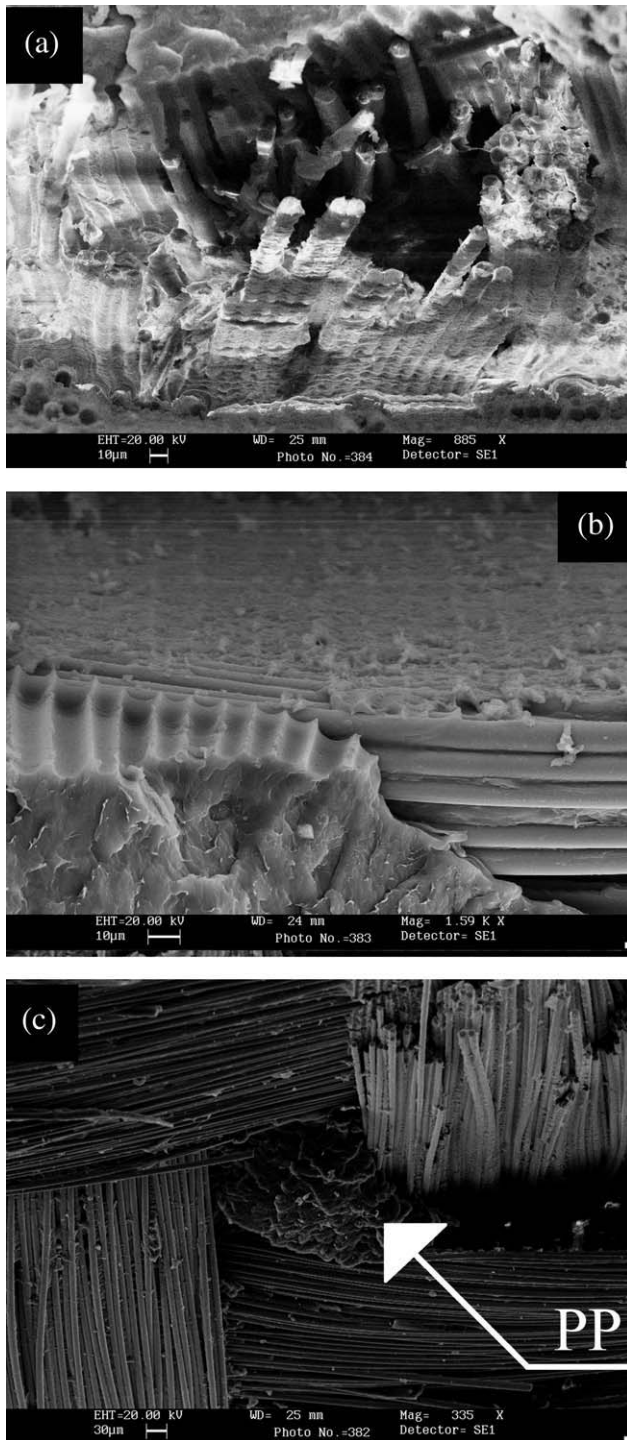


FIG. 7. SEM images of the tensile test fracture surface of S4 composite in different zones: (a) Epoxy resin impregnated the glass fibers; (b) PP matrix completely impregnated the glass fibers; and (c) Epoxy resin impregnated the glass fibers bundles and PP occupied the room among the glass bundles.

evidenced that PP matrix impregnated glass fibers but the adhesion fiber/matrix was poor since many fibers are “pulled out” after the damage propagation. In the S2 samples, the epoxy resin completely impregnated the fibers and the fiber/matrix adhesion was very strong as

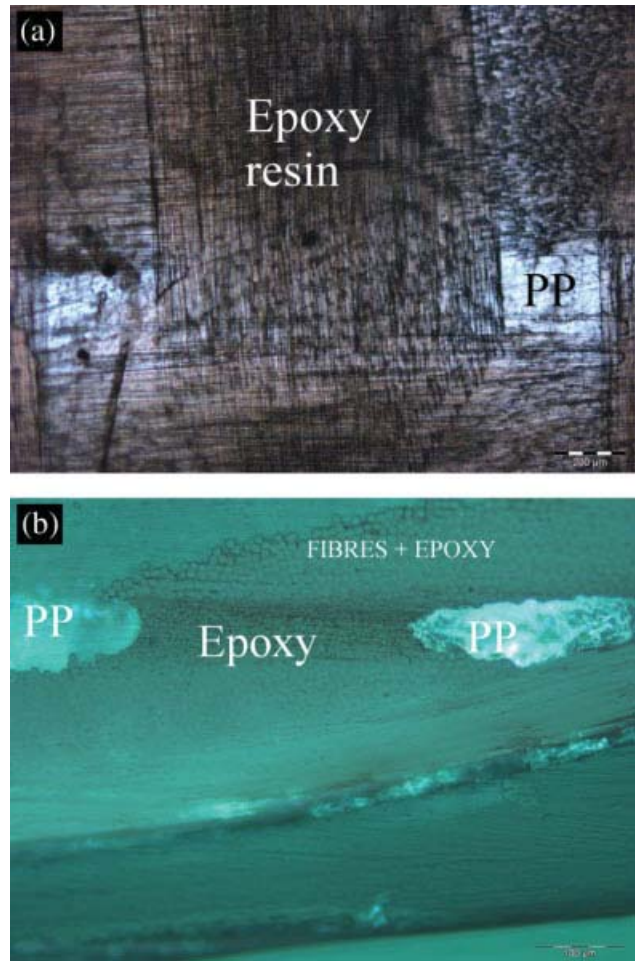


FIG. 8. Optical microscope images of the S4 composite polished surface: in composite plane (a) where the fibers are impregnated by the epoxy resins (red-dark zones) and the PP occupies the room between the bundles (clear-grey zones); through the thickness (b) where PP domains (clear color) are surrounded by glass fibers impregnated by epoxy resin and by epoxy resin alone. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

shown in Fig. 4b, where most of the fibers were surrounded by the matrix and very few were pulled out. Furthermore the SEM image in Fig. 4b clearly revealed the poor epoxy resin/PP bonding by the wide fracture front propagated between the two polymer layers. In this sample the PP matrix did not impregnate the fibers and the thermoplastic appeared like a coating of epoxy resin/fiber system as schematically illustrated in Fig. 5a.

The Young’s modulus and the tensile strength efficiency factors as well as the ultimate strain of the S3

TABLE 2. Tensile mechanical properties of composite bulk materials.

	Tensile modulus (GPa)	Tensile strength (MPa)	References
Glass fibers	72.4	3450.0	[4]
PP	1.3	34.0	Measured
Epoxy resin	3.8	140.7	[4]

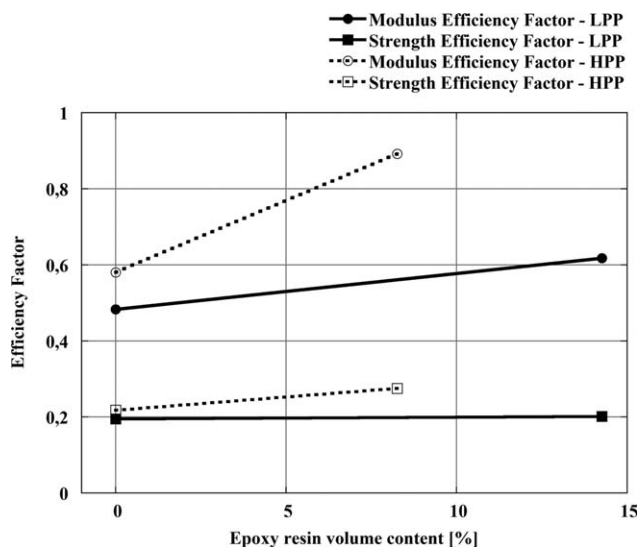


FIG. 9. Young's Modulus and tensile strength efficiency factors of the composites—effect of the preparation processes (LPP and HPP).

samples increased when compared with those of the S1 samples; the higher pressure and the higher initial temperature of the HPP resulted in a better glass fiber woven fabric impregnation as evidenced by the fracture surface in Fig. 6, even if the PP/glass fiber interaction was poor.

The S4 composite was characterized by an increase of 50% of the Young's modulus and of 26% in the tensile strength, and a reduction of 16% of the ultimate strain with respect to the S3 composite (without the epoxy resin); the performances were even more outstanding with respect to S2 composite.

The enhancement of mechanical properties in the HPP composite with epoxy resin (see Fig. 9) can be attributed to the formation of the 3D network. In fact, comparing the efficiency factors of the S2 and S4 samples, a strong dependence on the matrix morphology can be observed, although the epoxy resin content was lower in the S4 sample.

The structure formed by the woven fabric, the epoxy resin, and the PP can be defined as a three-phase interpenetrated polymer network (IPN), because three cocontinuous phases are present. As also showed in literature [20–22], the polymeric IPNs present improvement of the mechanical properties and, in some cases, their properties are even higher than those of the components. The mechanical properties increase of S4 can be accounted for by the 3D composite morphology that, we suppose, resulted in better stress distribution within the three components of composite with respect to the more simple sandwich-like structured composite.

## CONCLUSIONS

In this work, woven-glass-fiber fabric composites with two components matrix, formed by an epoxy resin (as a model reactive component) and PP, were prepared by using a film stacking technique. The epoxy resin in matrix

allowed a good fibers impregnation such as in conventional thermosetting composites and increased the mechanical properties, but with the advantage of a manufacturing process time typical of the thermoplastic composites.

By varying the film-stacking process parameters, it was possible to determine different matrix morphologies; the LPP produced a sandwich-like matrix morphology where the epoxy resin impregnated the glass woven fabric and PP appeared as an external layer of the composite structure. When the HPP was used, the PP flowed through the woven fabric impregnated by epoxy resin forming, upon consolidation, a three-dimensional network in the composite matrix, as evidenced in SEM and optical analyses.

This morphology resulted in higher Young's modulus and tensile strength with respect to sandwich-like morphology.

The epoxy/PP matrix was used as a model system, even though the adhesion strength between PP and epoxy resin is poor, to demonstrate that the mechanical performance of structural thermoplastic composites can be enhanced by using both low reactive low molecular weight oligomers and high molecular weight thermoplastics. The reactive component (thermosetting or thermoplastic [1, 13]) increases the fibers' impregnation quality while the nonreactive component (thermoplastic polymer) yields typical thermoplastic properties in the composite. Furthermore, the proposed approach opens the way to design new matrices for continuous fiber composite through a suitable selection of reactive and nonreactive components.

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