

Studies on the Mechanical Properties of a Glass-Fiber Reinforced Polypropylene/4-(hept-6-enyl)-2,6-di-*tert*-butylphenol Copolymer

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SYNOPSIS

The mechanical properties of a short glass-fiber reinforced composite based on a commercial polypropylene grade was compared to a composite system where the bulk material had been replaced by a propylene/4-(hept-6-enyl)-2,6-di-*tert*-butylphenol copolymer. The mechanical properties of the composites were determined by standard tensile tests. The results indicated that the composite based on the copolymer exhibited a noticeable improvement in tensile properties compared to the composite based on commercial polypropylene. The improved mechanical properties can be attributed to higher wetting of the fibers and to enhanced interfacial adhesion between the fiber and the matrix relative to the composite based on the commercial polypropylene. These assumptions are supported by scanning electron microscopy analysis. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The mechanical properties of glass-fiber reinforced composites are significantly affected by several factors: the interfacial adhesion between the glass fiber and the polymer matrix; by the concentration, orientation, and spacial distribution of the fibers in the composite sample; and by the wetting abilities of the polymer.¹⁻⁶ In addition, the morphology of both the fiber and polymer matrix play an important role in controlling the composite performance.⁷ The main objective of the work presented here was to investigate how the mechanical properties of the fibrous composite are effected by changing the matrix from polypropylene to propylene/4-(hept-6-enyl)-2,6-di-*tert*-butylphenol copolymer. In theory, it is known that phenolic groups are strongly adsorbed to glass fiber surfaces.⁸⁻⁹ Therefore, the composite prepared from the present copolymer with chemically attached phenolic groups was likely to show improved interfacial adhesion in comparison to the composite based on the commercial polypropylene matrix.

EXPERIMENTAL

Materials

The following two starting materials were used as polymer matrices:

1. A Mitsubishi polypropylene grade having an average pellet size of 0.3–0.5 mm. The molecular weights were $M_n = 21,000$ and $M_w = 165,000$ with a polydispersity of 7.9. The melt index was ≈ 60 at 230°C and 2.16 kg. The Mitsubishi polypropylene grade was mixed with 1 wt % of Irganox B220 prior to composite preparation.
2. A propylene/4-(hept-6-enyl)-2,6-di-*tert*-butylphenol copolymer prepared under conditions described by Wilén et al.^{10,11} The copolymer contained 0.89% by weight of 4-(hept-6-enyl)-2,6-di-*tert*-butylphenol of which 16% was chemically bound to the polypropylene backbone. The phenyl units were uniformly distributed in the copolymer matrix.¹¹ The average pellet size was 0.3–0.5 mm. The molecular weights were $M_n = 20,000$ and $M_w = 94,000$ with a polydispersity index

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of 4.7. The melt index was ≈ 70 at 230°C and 2.16 kg.

The glass fibers used to obtain composites with 30 wt % of reinforcement were 12-mm long E-glass fibers. The fibers were supplied by A. Ahlström OY, Kuitulasi, Karhula, Finland, under the trade name of TM 3565 12H. A coupling agent, supplied by Finndispersion, under the trade name of K-200 was used to promote the fiber-matrix adhesion. Nonylbenzeneoxyethylene was used as the dispersion agent and Irganox B220 (supplied by Ciba Geigy) was used as the stabilizer for the commercial polypropylene grade.

Sample Preparation

The composite plates were prepared as follows: A 9-L water mixture was charged with 50 mL of nonylbenzeneoxyethylene under vigorous stirring. Then, the propylene/4-(hept-6-enyl)-2,6-di-*tert*-butylphenol copolymer was introduced to the suspension together with the appropriate short glass-fiber percentage (30 wt %) under continuous stirring within 40 s. Then, the polymer-glass-fiber suspension was immediately poured in two portions into an open-type mould consisting of two parallel plates separated by 3-mm thick spacers (mould was developed by A. Ahlström Laboratory). The mould was provided with suitable guiding so the glass fibers were uniaxially oriented in the flow direction. Then the excess water was removed by suction. The formed composite plate was then glued with a 5% solution of K-200 by means of manual roll-out in order to avoid breaking of the plate during drying. The excess glue was removed by suction, after which the composite plate was dried at 150°C in a vented oven for 165–180 s. The dried plate was then placed under a 3-kg weight after which the composite plate was pressed at $\approx 220^\circ\text{C}$ for a period of 5 min in order to consolidate the fibers. After removing the spacers, the composite plate was additionally pressed for 30 s. Then the composite plate (area = 623 cm², surface weight = 3000 g/m²) was cooled at room temperature under a weight for approximately 15 min. Dog-bone tensile specimens (type 1 specimens described in the International Standard 3268) were obtained by longitudinal and vertical slicing of the composite plate. In this manner, two kinds of specimens were obtained: specimens where the fibers were uniaxially aligned and specimens where the fibers were uniaxially and perpendicularly oriented with respect to the length of the dog bone. For comparison, the commercial polypropylene that had

previously been mixed with 1 wt % Irganox B220 was used as a reference material, and therefore subjected to the same sequence of processing cycles.

Testing Procedure

Tensile tests were carried out with an Instron tensile testing machine after sample conditioning in accordance to International Standard ISO 291. The cross head speed was 2 mm/min, the grip separation was 115 mm, and the gauge length was 50 mm in accordance with the International Standard ISO 3268. At least five specimens of each material were tested. The features of the fracture surface of the test specimens obtained after tensile failure at room temperature, were studied on a Leica Cambridge Stereoscan 360 scanning electron microscope.

RESULTS AND DISCUSSION

For the purpose of this discussion, the tensile strengths of the tested samples are taken as the maximum stress in the stress-strain curve. The results of the tensile tests for the composite based on the copolymer, designated as CoPPGF, and the commercial polypropylene, designated as PPGF, are presented in Table I.

It is apparent from Table I that the PPGF composite specimen shows mechanical anisotropy. Generally, short-fiber composites exhibit a high strength parallel to the fiber axis and comparatively weak under transverse load,³ which is the case for PPGF, whereas for COPPGF there is no statistically significant difference in mechanical properties with respect to the fiber orientation. Apart from the differences in the stress at break values for the composite specimens, the CoPPGF exhibited significantly higher values of the modulus of elasticity than the PPGF, regardless of the fiber orientation.

Table I Tensile Strength Measurements for Fibrous Composites

Sample	E-Modulus (N/mm ²)	Stress at Break (N/mm ²)	Strain (%)
COPPGF ^a	4423 ± 520	75 ± 18	2.2 ± 0.3
COPPGF ^b	4727 ± 490	88 ± 10	2.5 ± 0.1
PPFG ^a	3739 ± 400	77 ± 5	2.6 ± 0.4
PPFG ^b	3139 ± 400	63 ± 7	2.7 ± 0.2

COPPGF, copolymer; PPGF, commercial polypropylene.

^a Stress applied parallel to the fiber axis.

^b Stress applied transverse to the fiber axis.

The strength advantage of CoPPGF in comparison to PPGF is probably due to a better interfacial bond between the fiber and the matrix. The improved interfacial bond ensures efficient stress transfer to the fibers during the tensile test. Another factor that may contribute to the higher strength of the CoPPGF samples is that a higher percentage of the total surface area of the fiber mass has been wetted with the matrix. The propylene/4-(hept-6-enyl)-2,6-di-*tert*-butylphenol copolymer matrix is more compatible with the glass fiber than the commercial polypropylene due to its higher polarity. It is known that sterically hindered phenolic stabilizers such as pentaerythrityl-tetrakis (3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate), commercially known as Irganox 1010 and 4-(hept-6-enyl)-2,6-di-*tert*-butylphenol are strongly adsorbed to the high-energy surfaces of different fillers, that is, to glass-fiber surfaces.^{8,9} Consequently, the present copolymer matrix with uniformly and covalently bonded phenol units results in a more homogeneous composite with enhanced interfacial adhesion and wetout via polar interaction. The wetting of the fibers when incorporated in the polyolefin depends naturally also on the polymer rheology. Both the starting materials have somewhat similar rheological properties because the melt indexes are quite close and the M_n values are almost equivalent, although the commercial polypropylene has a significantly higher polydispersity index that in fact should enhance wetout. One may conclude that the rheological properties of the two polymers should not cause a major difference in their wetting properties.

Scanning electron microscopy was used to ocularly study the extent of interfacial adhesion between



Figure 1 SEM view of the fiber/matrix interface of the COPPGF sample ($\times 3600$).



Figure 2 SEM view of the fiber/matrix interface of the PPGF sample ($\times 2400$).

the fibers and the polymer matrix. Scanning electron micrographs of the fracture surfaces of the dog-bone specimens tested until failure are presented in Figures 1–4.

The most obvious feature of the micrographs shown in Figures 1 and 2 is that the CoPPGF sample clearly shows adhesion between the fiber and matrix whereas such adhesion cannot be observed in the micrograph of the PPGF sample. Instead, gaps exist around the fibers in the PPGF sample. Also, fiber pullout seems to have occurred to a greater extent in the PPGF sample than in the CoPPGF sample as shown in Figures 3 and 4. The lack of short protruding fibers in the PPGF sample is indicative of poor interfacial adhesion and impregnation of the fibers with the matrix. In contrast, the micrographs

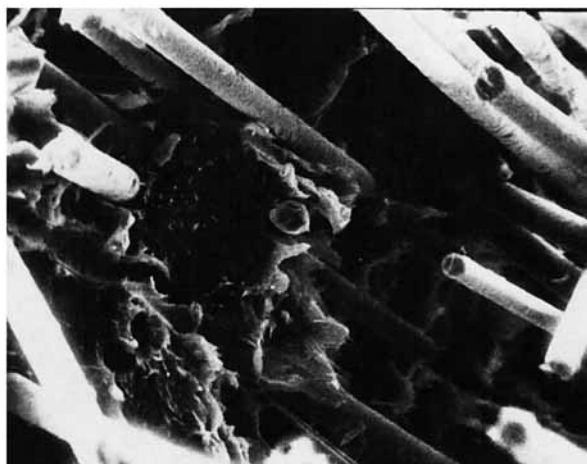


Figure 3 Partial view of the fracture surface of the COPPGF sample ($\times 850$).

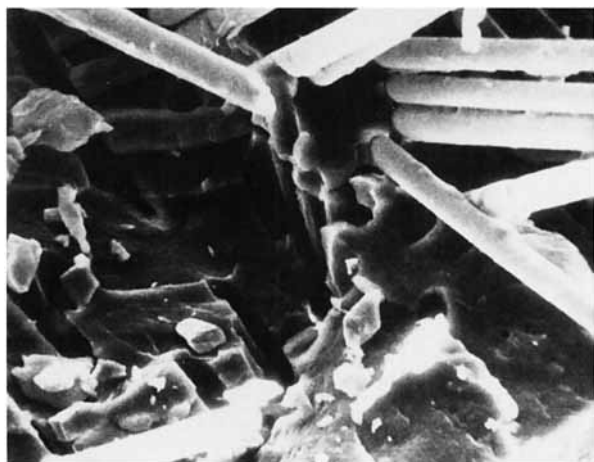


Figure 4 Partial view of the fracture surface of the PPGF sample ($\times 820$).

of the CoPPGF sample show a relatively high amount of short protruding fibers that have been chopped near the fracture surface. Furthermore, it appears that as a consequence of the poor interfacial adhesion and the existing gaps in the PPGF sample the remaining fibers have become misoriented during the tensile test, whereas the fiber orientation remains well defined after the tensile test for the CoPPGF sample. These remarks are based on several micrographs that have been taken from different locations of the composite samples.

CONCLUSION

From the present investigation on the effects of changing the polymer matrix from polypropylene to propylene/4-(hept-6-enyl)-2,6-di-*tert*-butylphenol copolymer on the mechanical properties one may draw the following conclusions.

The replacement of the commercial polypropylene matrix with the present copolymer matrix results in a marked increase of the composite tensile strength, whereas the composite percent of elongation at break is slightly decreased. The difference in the tensile properties between the PPGF and CoPPGF composites is particularly noticeable when the tensile strengths are measured across the direction of the fiber orientation. For the PPGF composite, mechanical anisotropy is clearly observed, whereas the sample indicated as CoPPGF shows no

statistically significant difference in mechanical properties with respect to the fiber orientation. The slightly higher elongation values for the PPGF samples compared to the CoPPGF samples suggest that from the former composite matrix the fibers are more easily separated. These findings are paralleled by a relative increase in the number of matrix-fiber bonds in the CoPPGF composite compared to the PPGF composite. The strong copolymer-fiber interaction indicates that the phenol units of the copolymer are strongly adsorbed to the high-energy surfaces of the glass fibers. Consequently, the fibers in the copolymer matrix are able to carry a relatively higher load than the fibers in the commercial polypropylene matrix. Further work should be conducted in order to establish the relationship between the tensile strength of the composite and the amount of bound phenolic stabilizer in the copolymer.

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