# Phenol-Modified Polypropylenes as Adhesion Promoters in Glass Fiber–Reinforced Polypropylene Composites

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**ABSTRACT:** This publication is based on research work done on functional phenol-modified polypropylenes (PPs) as adhesion promoters in glass fiber–reinforced PP composites. The glass fiber roving was first impregnated with different combinations of functional polymers and polypropylene in a melt impregnation die attached to an extruder to obtain prepreg. The prepreg was then tested in many ways both macro- and micromechanically. The tests included notched tensile tests, optical and electron microscopy, and DMTA (dynamic mechanical thermal analyzer) and DSC (differential scanning calorimetry) analyses as well as determination of the glass content. The tests were run on prepregs containing pure PP, PP with a commercial adhesion promoter, and PP with a number of functional, mostly phenol-based, polymers. Also, single-fiber tests were performed on individual glass fibers to test the level of adhesion with the above-mentioned material combinations. With these tests it could be seen that some of the phenol-based functional polymers provided the prepreg with better adhesion between the fibers and the matrix than did the commercial adhesion promoter. Optical and electron microscopy also were used in determining the level of adhesion as well as the deformation and fracture mechanisms of the prepreg. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 84: 1203–1213, 2002; DOI 10.1002/app.10441

**Key words:** functional polymer; adhesion; polymer composite

## INTRODUCTION

The problem with conventional adhesion promoters (coupling agents) and stabilizers, which are usually low–molecular weight compounds, has been their tendency to migrate to the internal interfaces of composites and in that way disturb each other and prevent each other from functioning properly. Silane compounds are one of the most used conventional adhesion promoters. First the reinforcing fibers are coated with a suitable silane, and then the reinforcements are mixed or impregnated with the matrix polymer. Bonding between silane and the matrix polymer is a complex phenomenon that can be best described by a formation of a large interphase where the polymer chains of the silane and the matrix are diffused and bound around each other but do not form any direct chemical bonds. If, for example, adhesion promoters are copolymerized directly to the polymer chain (to gain so-called functional polymers), they are not able to migrate and it is possible to achieve primary chemical bonds between the coating of the reinforcing fibers and the matrix polymer chains. In this case, the fiber/matrix interfacial properties are usually better

Exxelor
(maleic acid anhydride modified PP)
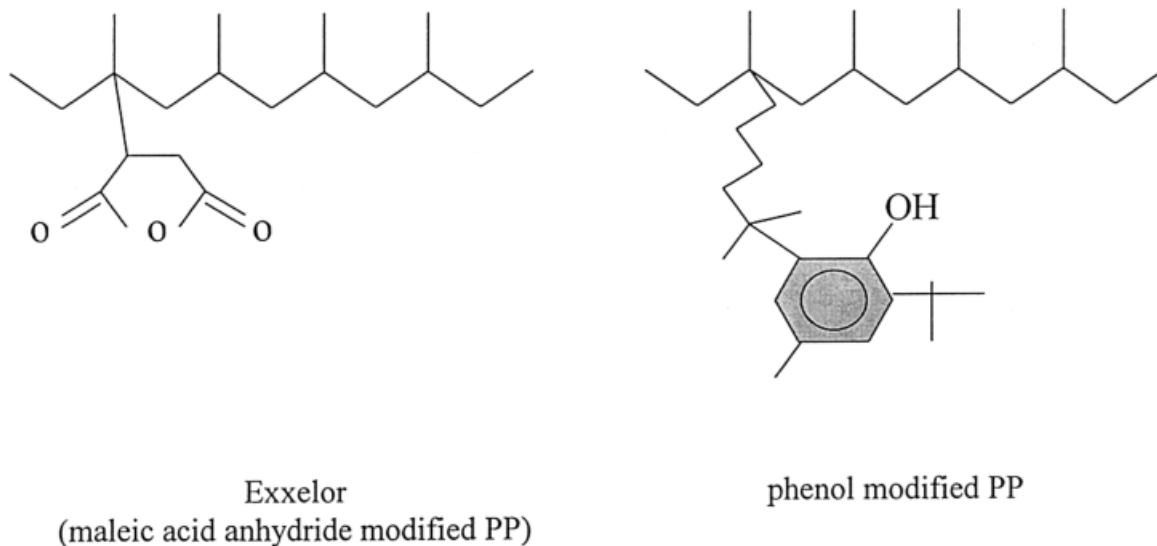
phenol modified PP

**Figure 1** Structures of Exxelor and phenol-modified adhesion promoters.

than with conventional adhesion promoters. Also, stabilizers, colorants, and so forth can be copolymerised to the polymer chain. Functional polymers are therefore ideal to be used with polypropylene, as the main problems with using thermoplastics as composite matrix materials have been their poor adhesion to the reinforcement and the poor stability of the matrix.

## EXPERIMENTAL

### Materials

The matrix polymer used was Propathene D714, which is a powdery polypropylene made by ICI (Gothenburg, Sweden). A 1200 tex glass fiber roving Cosmostrand R16EX23, manufactured by Owens Corning Fiberglass (Visé, Belgium), was used as continuous reinforcement for the prepreg. Irganox B 215 FF (Ciba Specialty Chemicals, Inc., Basel, Switzerland) was used to stabilize the matrix. Adhesion promoters used included maleic acid anhydride modified polypropylene Exxelor PO 1015 (Exxon Mobil Chemical, Gothenburg, Sweden), which was used as a commercial reference. Other functional adhesion promoters were mostly phenol based. Figure 1 illustrates the differences in the generic structure between Exxelor and phenol-modified adhesion promoters. The structure of the phenol used in the copolymerization of functional polymers is shown in Figure 2.

The functional phenol-modified polypropylenes used differ from each other only in the content of this phenol and molecular weight. This information can be found in Table I. For Propathene $M_w$ = 470,000 g/mol, $M_n$ = 47,000 g/mol, and $M_w/M_n$ =10, where $M_w$ is weight-average molecular weight and $M_n$ is number-average molecular weight.

### Prepreg Processing Equipment

The prepregs were manufactured on a melt impregnation line. The line itself, as well as the impregnation die, had to be modified to minimize loss of material during processing. This was because the phenol-modified polypropylenes were polymerized in a laboratory scale (i.e., about 100 g).

The impregnation line consisted of the following parts: a device to unroll the glass fiber roving from the spool, a device to control the flow of the roving, a plasticizing unit (extruder), a control-
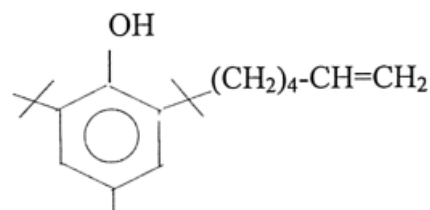


**Figure 2** Structure of the phenol used in the copolymerization of functional polypropylenes.

**Table I.   Phenol Contents and Molecular Weights of Phenol-Modified Polypropylenes**

| Sample | Phenol Content (g) | $M_w$ (g/mol) | $M_n$ (g/mol) | $M_w/M_n$ |
|--------|------|--------|--------|------|
| D140 | 1 | 227726 | 115167 | 1.98 |
| D142 | 1.5 | 148143 | 80829 | 1.83 |
| D144 | 1.5 | 77793 | 30119 | 2.6 |
| D145 | 1.5 | 169736 | 92639 | 1.8 |
| E017 | 1 | 201000 | 59700 | 3.36 |
| E018 | 1 | 188800 | 53700 | 3.51 |
| E019 | 1 | 156000 | 56400 | 2.77 |
| E020 | 2 | 52700 | 25700 | 2.05 |
| E021 | 1.5 | 135000 | 53000 | 2.68 |
| E022 | 1.5 | 146900 | 47900 | 3.07 |
| E023 | 1.5 | 148900 | 53000 | 2.81 |

ling unit of the extruder, a melt impregnation tool, a cooling bath, and a pulling device and its controlling unit.

The parameters used during the processing were as follows: the temperatures in the cylinder were 210°, 225°, 240°, 250°C; the rolling speed of the screw was 8 Hz; and the pulling speed was 12%.

The melt impregnation line is schematically illustrated in Figure 3.

The glass fiber roving was pulled into the impregnation die in a vertical direction. The plasticized polymer was fed to the impregnation die through four different flow channels. The wetting and impregnation of the fiber roving was achieved by using four rods from which the melted polymer was directed to the roving through small grooves. To optimize the wetting properties of the melt, the grooves were situated so that they come in contact with the roving at the position where the roving first touches the surface of the rod. After passing the rods, the impregnated roving was directed through a shaping nozzle to produce prepreg in tape form (it's also possible to use a shaping nozzle with a round circumference to gain a prepreg with a round cross-section). Figure 4 clarifies the structure of the melt impregnation tool.

The recipies for the prepregs were as follows: pure polypropylene (PP)-prepreg as zero reference: 0.2 wt % stabilator, Propathene; commercial reference: 8.0 wt % Exxelor, 0.2 wt % stabilator, Propathene; prepregs containing functional polymers: 7.0 wt % functional polymer, 0.2 wt % stabilator, Propathene.

The optimum content for the phenol-modified polymers was determined by manufacturing prepregs containing different amounts of functional polymers, performing a notched tensile test for them, and in this way determining the mixture at which the adhesion is at its best. It can be seen from Figure 5 that a mixture containing 7% functional polymers gave the best results, which is why this percentage is used in the recipe.

## Test Methods and Results

The prepregs were tested as follows: To determine adhesion and mechanical properties, notched tensile tests (for functional compounds named Exxx
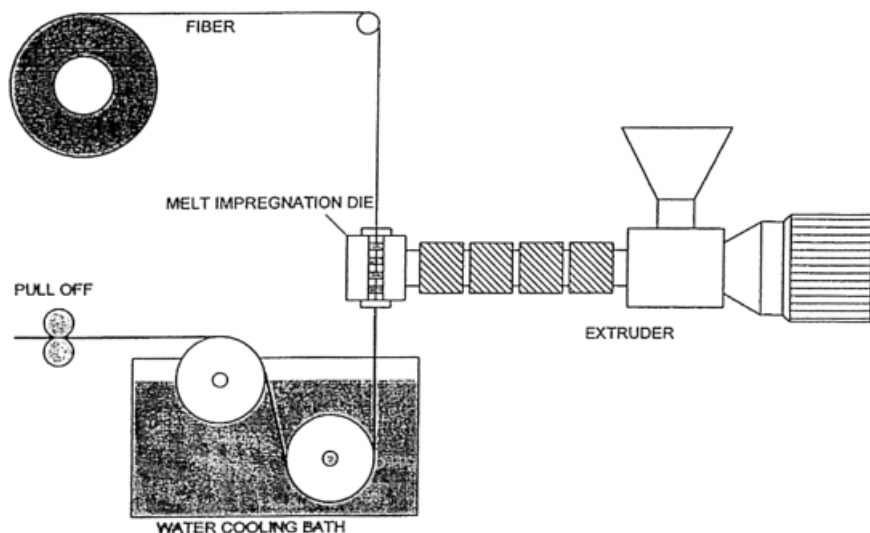


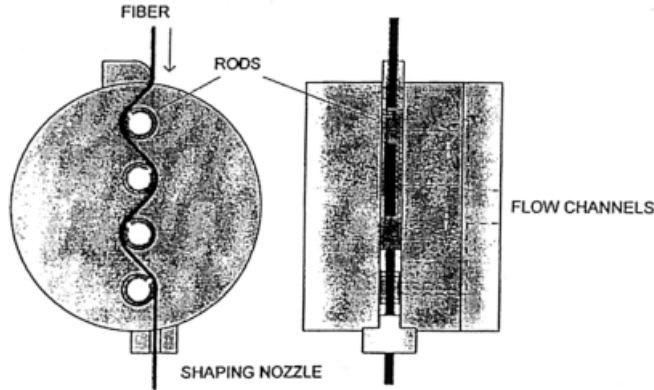**Figure 3**   Melt impregnation line.

**Figure 4**    The structure of the melt impregnation tool.

only these tests) and single-fiber tests were performed; for optical microscopy, the degree of impregnation was determined; electron microscopy was performed to test both adhesion and deformation and fracture mechanisms; the dynamic and thermal tests performed were DMTA (dynamic mechanical thermal analyzer), DSC (differential scanning calorimetry); finally, we determined the glass content.

### Notched Tensile Tests

Information about adhesion between the fiber and the matrix can be gained with a notched tensile

test. When notches are made in the prepreg, as illustrated in Figure 6, shear stress during tension and the fracture surface are directed to the interface between the fibers and the matrix. It's essential that the tips of the notches go beyond the central axis of the prepreg. Numerous other methods can also be used for measuring adhesion.[1–17]

In the first test series, a prepreg tape manufactured earlier at TUT (PP1), prepreg impregnated with polypropylene containing commercial adhesion promoter Exxelor (PP2) and prepreg impregnated without adhesion promoter (PP3) were
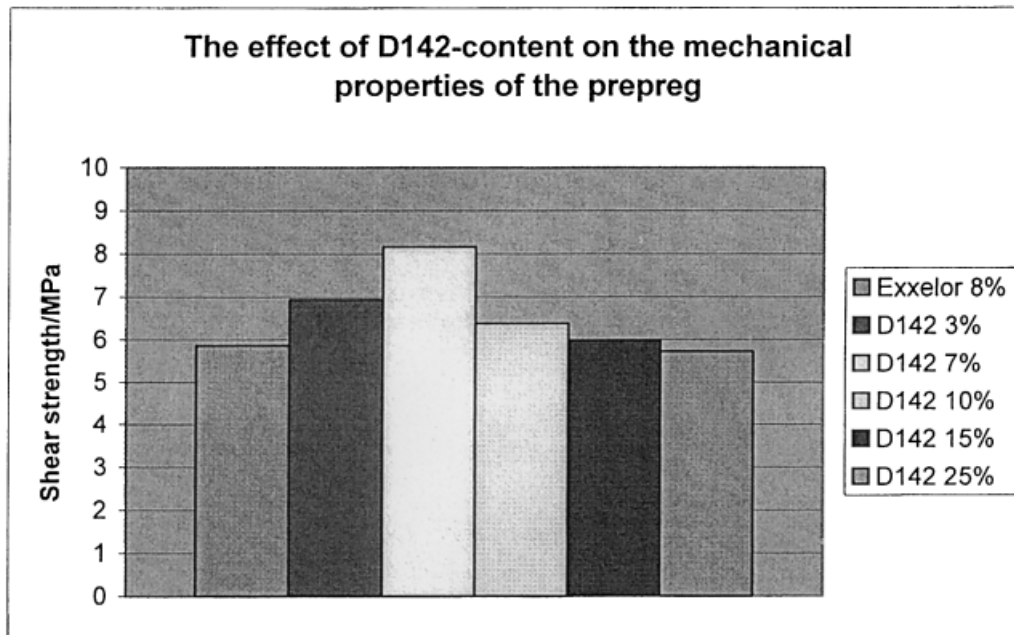


**Figure 5**    The effect of D142 content on the mechanical properties of the prepreg (Exxelor as commercial reference).
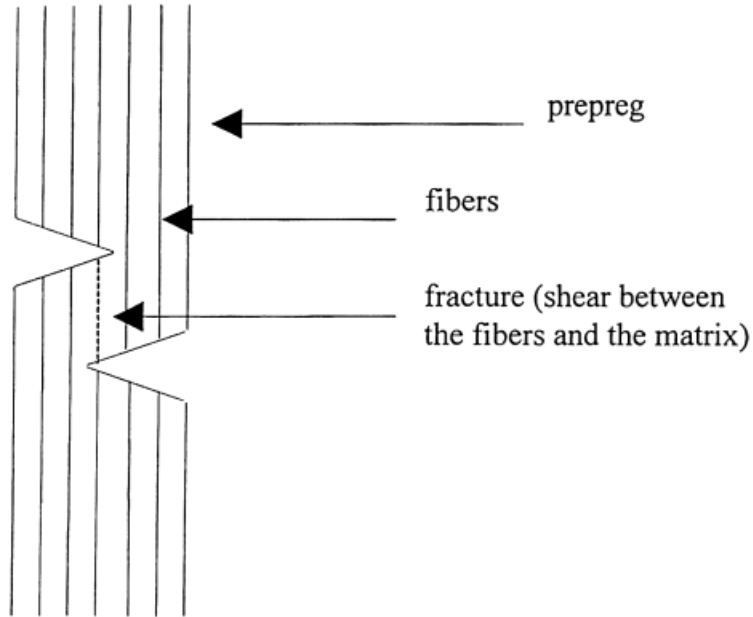
**Figure 6**   Notched tensile test.

compared. In Figure 7 it can be seen that the best results were obtained with PP2 and the worst with PP3.

Figure 8 (a–c) illustrates the results obtained with phenol-modified adhesion promoters compared to zero and commercial references. It can be clearly seen that very often at least similar or even better adhesion (i.e., higher shear strength in the notched tensile test) can be achieved with functional polymers.
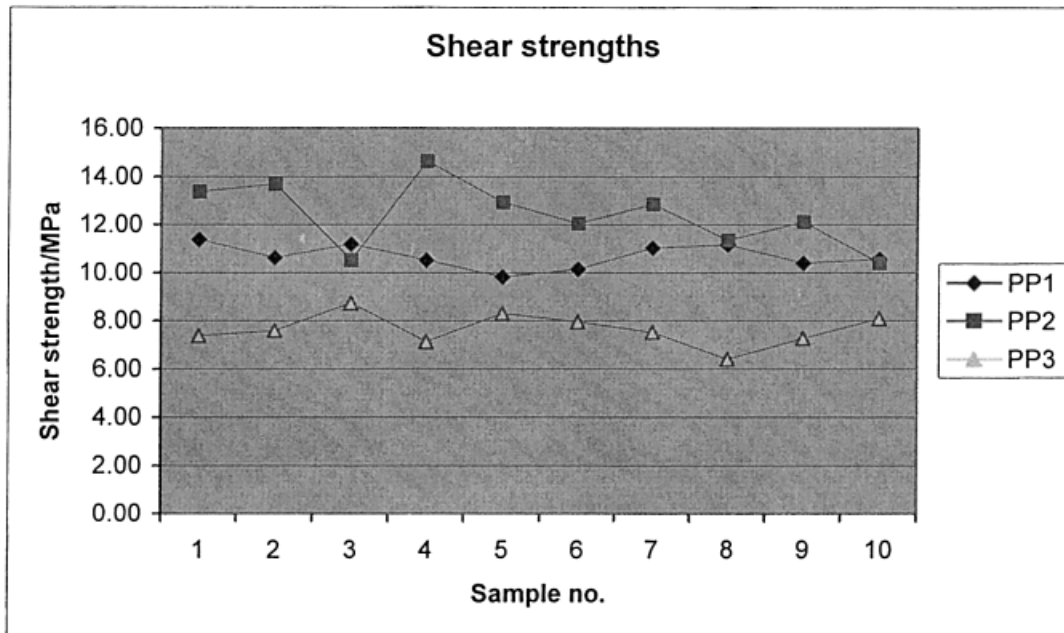


**Figure 7**   Effect of adhesion promoter to the shear strength of PP prepreg. PP1 = prepreg previously manufactured at TUT; PP2 = prepreg with Exxelor as adhesion promoter; PP3 = prepreg without adhesion promoter.
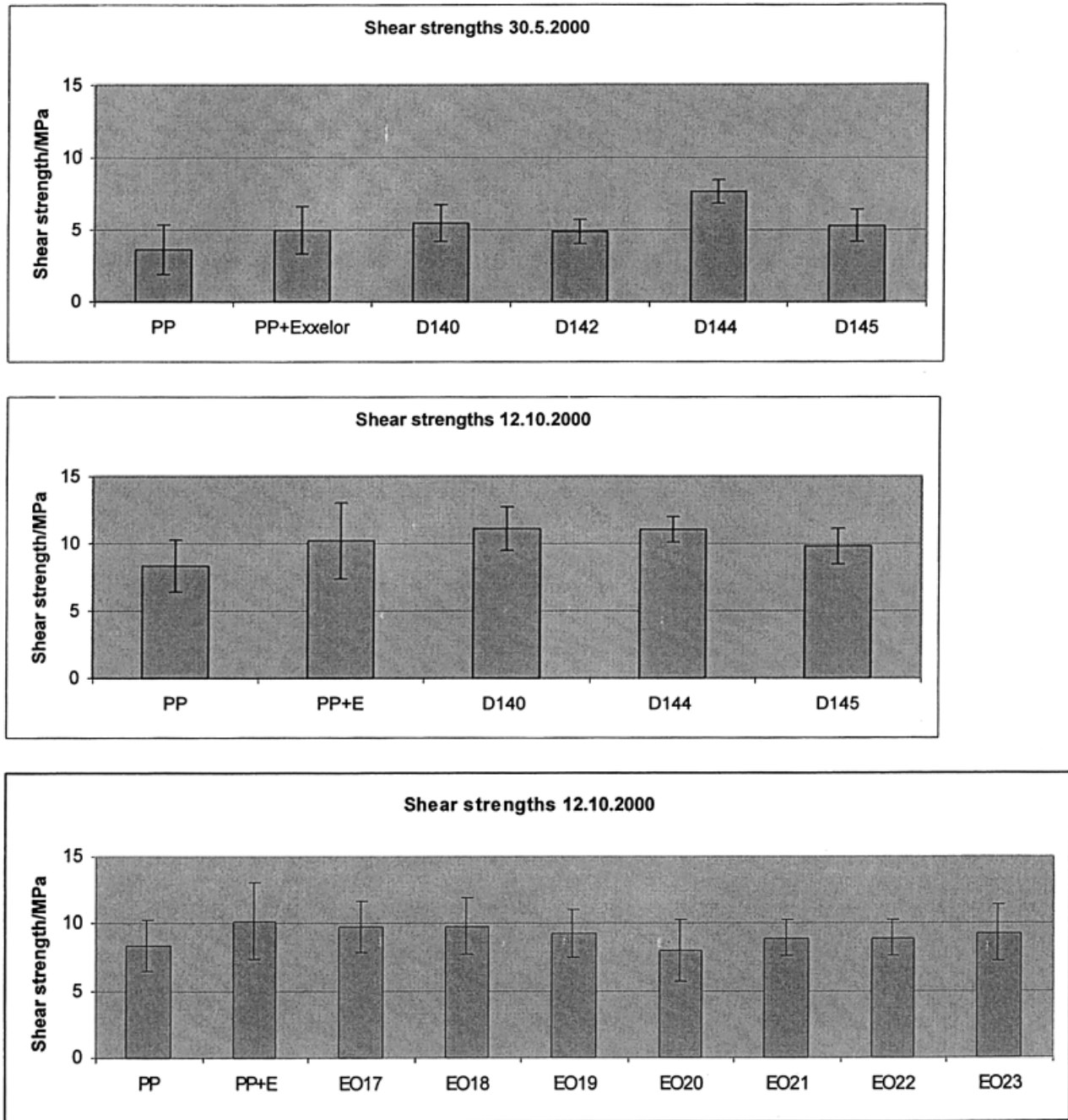
**Figure 8**  Shear strengths obtained from notched tensile tests. PP = pure polypropylene; PP + E = PP + Exxelor; Dxxx and Exxx = PP + functional polymer.

## Single-Fiber Tests

The adhesion between the fiber and the matrix can also be examined, for example, with single-fiber tests. The idea of single-fiber testing is to melt some of the matrix material around the fiber and then measure the force needed to pull the fiber out of the matrix. These tests have been performed by a method illustrated in Figure 9. The arrow points out the direction of tension.

Figure 10 shows the results obtained from the single-fiber tests. The fiber used was E-glass fiber made by Ahlström Oy, and it was thicker than the fiber used in the prepregs, to make its handling easier when preparing the samples. The devia-
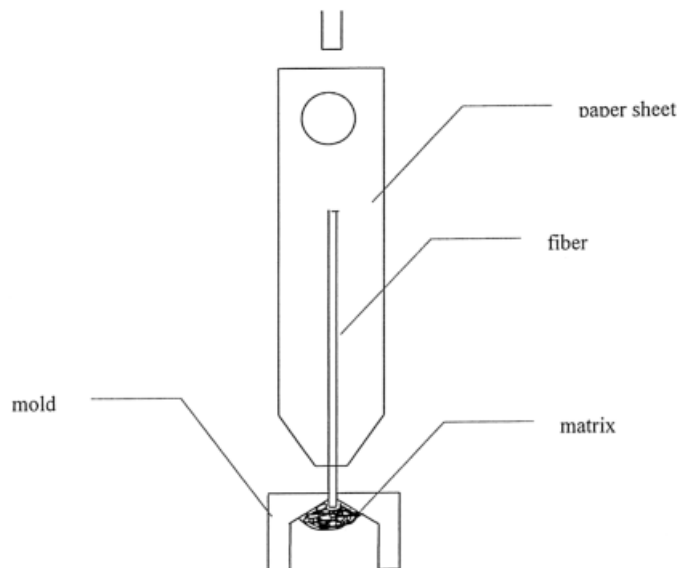
**Figure 9**   Single-fiber test sample.

tions were partly very large, and many other factors that lower the reliability of the results are also present in this method as well as in other single-fiber test methods.[15,16] However, the results in a way confirm those obtained from notched tensile tests because at least one of the phenol-based functional polymers gives better results than Exxelor despite the large deviations.

### Optical Microscopy

Optical microscopy was used to determine the impregnation degrees of the prepregs. The prepreg is first cast into a button of plastic. Then the surface of the sample is polished to reveal the cross section of the prepreg. Some ink is then spread on the cross section, where it is able to penetrate the prepreg at locations where the matrix does not properly surround the fibers. The

number of nonwetted fibers can be calculated when examining the sample under the microscope, and the impregnation degree can be determined as follows:

Impregnation degree-%

$$= \text{(number of wetted fibers}$$

$$/\text{total amount of fibers in the roving)} \times 100\%$$

Figure 11 shows the impregnation degree for zero and commercial references as well as for four prepregs where phenol-modified functional polymers were used as adhesion promoters. It can be seen that an impregnation degree of almost 80% can be achieved by using adhesion promoters. Without adhesion promoters, impregnation degree falls down to 60%.
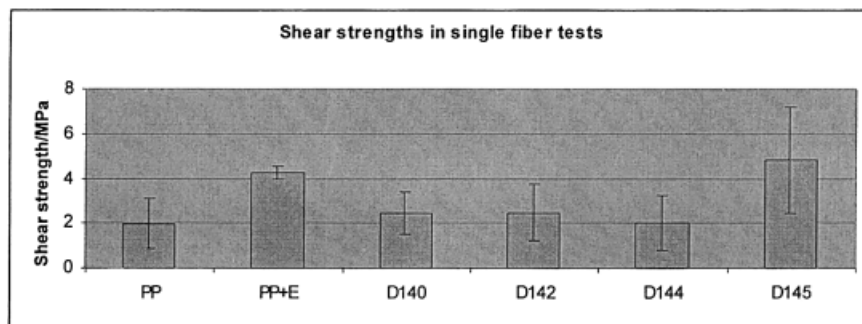


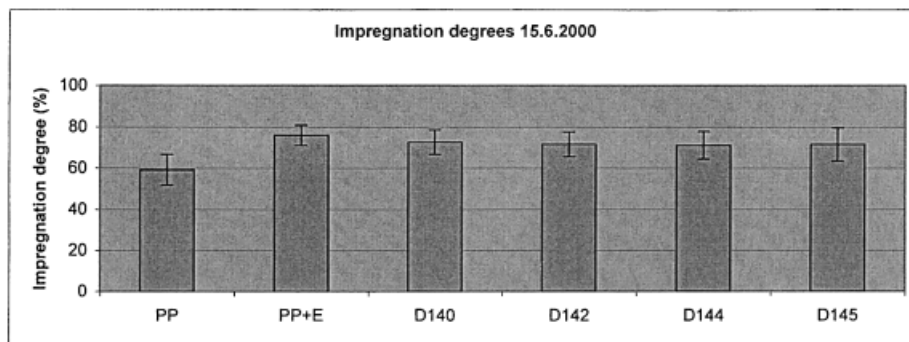**Figure 10**   Shear strengths obtained from single-fiber tests.

**Figure 11**   Impregnation degrees.

## Electron Microscopy

Scanning electron microscopy (SEM) micrographs can be used to examine both the adhesion between the fibers and the matrix more deeply as well as the deformation and fracture mechanisms of the prepreg. The micrographs can also be used to confirm the results obtained from tensile tests (the higher the shear strength the better the adhesion). This can be used, for example, to determine the best mixing ratio with PP and the functional polymer. The level of adhesion can be approximated from the pictures by the amount of matrix that has been stuck onto the surface of the fiber. If the fiber surface is smooth, the adhesion is poor. Another sign of poor adhesion are holes in the cross section of the prepreg or long fiber ends sticking out from it (pull-out phenomenon). If the fibers have fractured near the cross section and there are no holes in it, the adhesion is better. There are a couple of SEM-micrographs in Figures 12 and 13.

## Dynamic Mechanical Thermal Analysis

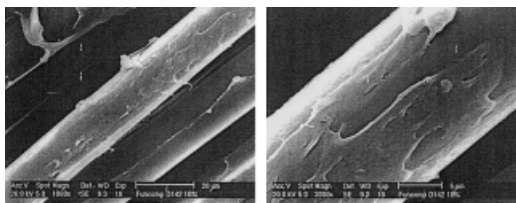DMTA analysis was used to measure dynamic-mechanical properties of the prepregs as a function of temperature. In the main, the changes in the stiffness of the prepreg can be seen from the DMTA curves. Figure 14 illustrates the fact that adhesion promoters do not affect the stiffness very much, as the curves are nearly in the same range for all different prepregs.

## Differential Scanning Calorimetry

DSC was first used to find suitable processing temperatures for Propathene. Propathene melted at 182°C and started to decompose at 268°C. According to these values, the suitable processing temperature range was evaluated at 210°–250°C.

DSC was also used to determine the melting points of the functional polymers as well as to analyze their behavior in the processing temperatures of the prepreg. The aim of the DSC tests was mainly to assure that the functional poly-
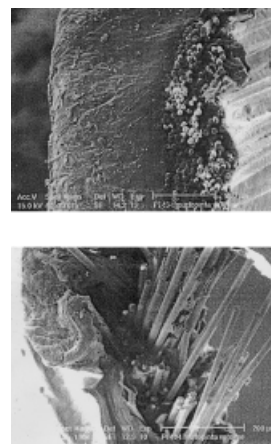




**Figure 12**   The level of adhesion between the fiber and the matrix can be examined from scanning electron microscopy micrographs. These pictures show the adhesion for D142 at 10%.

**Figure 13**   Signs of good (upper) and poor adhesion. Upper picture is taken from a sample containing 8% of Exxelor as the adhesion promoter. In turn, the lower sample contains no adhesion promoter (zero reference). The difference in pull-out tendency can be seen clearly.
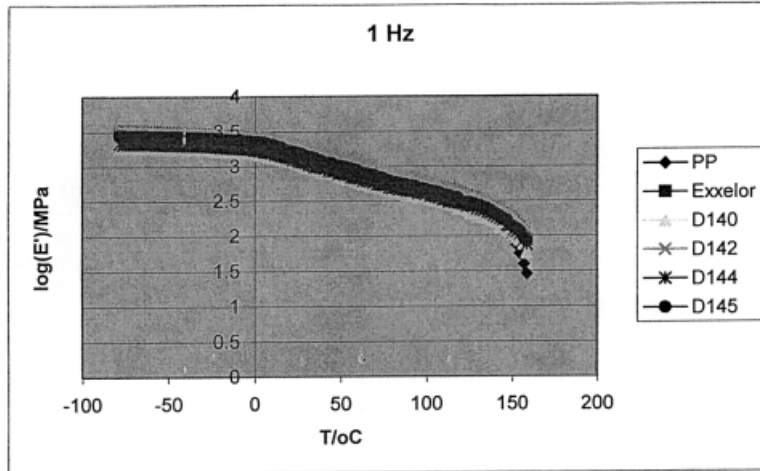
**Figure 14** Dynamic mechanical thermal analyzer test curve.

mers last through processing without deteriorating.

### Glass Content

The glass content was determined by weighing a piece of prepreg and placing it in an oven to burn the matrix off the prepreg. After the oven treatment, the prepreg was weighted again to gain the mass of the glass; the mass of the glass was then compared to the mass of the whole prepreg to get the glass content. The glass content describes how uniformly the roving has been impregnated by the matrix: If there is a lot of variation, it means that the process has not been stable.

The glass contents were about 50 wt % and 30 vol %. Test results are shown in Figure 15. It can
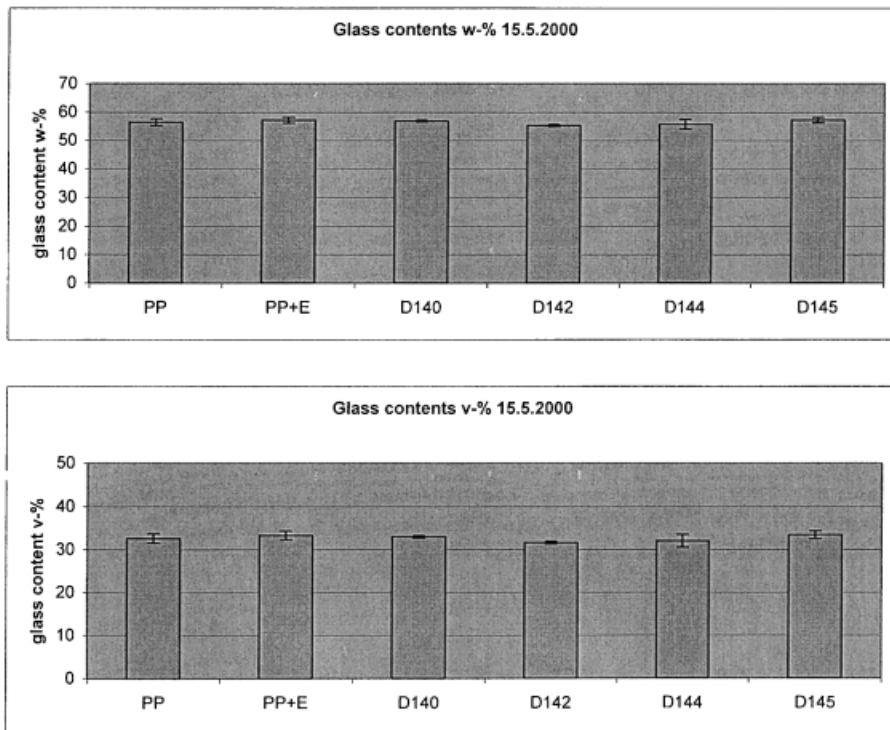


**Figure 15** Glass contents.

be seen that the glass content did not vary much with different matrixes and the deviations were quite small. This means that the impregnation process was quite stable.

## DISCUSSION

Some of the results in notched tensile tests may be affected by the fact that the concentration of 7 wt % is not necessarily optimum for all functional compounds (the optimization was done only for one material because of the small amounts of the phenol-based functional polymers available). Although the phenolic functional polymers used were structurally the same, they had differences in their phenol content, molecular weight, and $M_w/M_n$ ratio (i.e., molecular weight distribution). From Figure 8 it can be seen that a phenol content of 1 g seems to be the best; when comparing these test results with the information in Table I, it can be seen that functional polymers containing 1 g of phenol usually give slighter better results than those containing 1.5 and 2 g, respectively, of phenol. For some light materials, the vol % content in the mixture was quite high because Propathene weighed a lot more, which certainly may affect the results because that strong a content may change the physical properties of the mixture and mechanical properties of the prepreg.

Also, the difficulties in making similarly notched test samples may affect the results, as it was sometimes difficult to obtain identical notches in all the prepreg samples. If in some cases, for example, one of the notches does not cross the central line of the prepreg, the strength of the sample can be higher than that of a sample where both of the notches cross the central line. Also, the difference in how far away from the central line the notch goes certainly affects the strength (the further away it goes, the lower strength).

Typical problems that decrease the reliability of the results in single-fiber tests include the following: differences in surface quality of the glass fiber (notable effect)—the typical effect of this is to have a few low and high values and a lot of values in between → large deviations; accuracy of the metering device used to measure the diameter of the fiber; reliability of the force value given by the testing machine; effect of friction and stress concentrations; and the size of the contact area and the ways to measure it—if the contact area is

too large, it is possible that the fiber breaks in or outside the matrix before it is pulled out.

In the method we used, one of the main problems was getting a contact area small enough, as the sample breaks very easily when gluing the paper sheets or when attached to the testing machine. Also, the effects (stresses, distortion) of gluing the paper sheets to the sample are unknown.

Impregnation degree measurements did not give very large differences with various matrix/adhesion promoter combinations. Some human error may occur when calculating the nonimpregnated fibers from the samples, but as the deviations are small, this error has not had any notable effect on the results. When comparing Figures 8 (a) and 11, it can be seen that those adhesion promoters that give stronger adhesion (i.e., better shear strength) have somewhat lower impregnation degree. This is quite surprising because it would be easy to conclude that a better degree of impregnation would also give better mechanical properties to the prepreg. These results certainly prove that a lower degree of impregnation does not usually lower the mechanical properties of the prepreg, in fact, it is preferably the reverse. Two things that speak for producing better-impregnated prepreg are that its appearance is more even and smooth and that it looks better to the eye. However, differences in as small a scale as those of these impregnation degree measurements do not yet contribute to major differences in appearance.

The reliability of the SEM micrographs is lowered by the fact that the person who is taking the graphs may (even without recognizing it) choose a "representative" location of the sample to be photographed that does not represent the general nature of the sample. This problem can be avoided by, for example, taking the graphs blindly; that is, from the very first location on the surface without any further examination of the sample.

## CONCLUSION

It can be concluded from the test results that, with suitable functional polymers, it is possible to achieve better adhesion between the matrix and the reinforcing fibers, in this case between polypropylene and glass fiber, than with conventional coupling agents. Some of the new structures for functional polymers give better results than the ones that are now commercially avail-

able. More research work will still be needed to examine other functional structures in addition to phenol-based polymers to have sufficient comparison with different functional groups and with their contribution to promoting adhesion to help choose the best elements for further research activities. Also, some of the testing methods should be made more reliable by developing them further. It might then be possible to commercialize some adhesion promoters that provide the matrix and the fibers with better adhesion at lower concentrations and lower cost than the ones available today.

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