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Influence of the Film Former on Fibre-Matrix Adhesion and Mechanical Properties of Glass-Fibre Reinforced Thermoplastics*

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The film former is in mass percentage the main component in most glass fibre sizes. Its influence on the fibre-matrix adhesion and the compound properties is studied in two thermoplastic matrices, i.e. polypropylene (PP) and rubber-modified styrene-co-maleic anhydride. The composition of the size is varied by changing the chemical nature and molecular mass of the film former and by leaving out the silane. The size's morphology on the glass fibres is studied with scanning electron microscopy and X-ray photoelectron spectroscopy. The effect on fibre-matrix adhesion is inferred from 0° bending and interlaminar shear strength measurements of unidirectional, continuous fibre reinforced composites. The possible effect of the film former on matrix crystallinity in PP is studied with differential scanning calorimetry and polarized-light microscopy. The same sizes are also tested in injection moulded, short fibre reinforced compounds by measuring their mechanical properties. In addition, the diffusion of the size into the matrix is studied by confocal scanning laser microscopy. The main conclusion of this study is that the film former plays a crucial role in the level of fibre-matrix adhesion because it does not diffuse away from the fibre-matrix interface into the matrix. Its effect may be larger than that of the silane. In addition, most mechanical properties of short fibre reinforced compounds improve with increasing fibre-matrix adhesion.

KEY WORDS unidirectional; continuous-fibre composites; polypropylene; PP; styrene-co-maleic anhydride; SMA; matrix-fibre stress transfer; fibre-matrix adhesion; sizing; size composition; film former chemistry; (in)compatibility; molecular mass; coupling additive; silane; coupling system; interdiffusion; morphology; crystallinity; short glass fibre reinforced compounds; tensile strength; flexural strength; Izod; Charpy; impact strength.

1 INTRODUCTION

Glass fibres are very suitable for reinforcing all kinds of polymers, both thermoplastics and thermosets.^{1–5} This is due to their relatively good price/performance ratio, easy processability and ample availability.

During production, glass fibres must be protected against fibre fracture and fuzz formation by a coating, which is called the "size".^{4,5} It is this size that also plays

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a crucial role in the level of fibre-matrix adhesion, in optimum matrix-fibre stress transfer and, as a result, in the mechanical properties of fibre reinforced polymers.

In the past, the role of one essential component of the size, *i.e.* the silane or keying agent,⁴ received a lot of attention due to the pioneering work of Plueddemann.⁶ However, the silane is not the only, not even the main, component of the size: the film former or binder, that keeps the individual fibres into coherent strands, is the principal component in mass percentage.^{4,5} The role of the film former on the fibre-matrix adhesion and the compound and composite properties has not received much attention, although results of various studies seem to indicate that its influence may be of importance.^{4,5,7-10}

In this paper the influence of the film former is studied in two types of thermoplastic matrices, *i.e.* semi-crystalline, shear-yielding polypropylene (PP) and two rubber-modified, glassy, amorphous, crazing (/yielding) copolymers based on styrene-co-maleic anhydride (SMA). The composition of the size is varied by changing the chemical nature and molecular mass of the film former and by leaving out the silane. The effect on fibre-matrix adhesion is inferred from 0° bending and interlaminar shear strength measurements of unidirectional, continuous fibre reinforced composites. The possible effect of the film former on matrix crystallinity in PP is studied with differential scanning calorimetry and polarized-light microscopy. The same sizes are also tested in injection moulded (IM), short fibre reinforced compounds by measuring the usual mechanical properties. In addition, the diffusion of the size into the matrix is studied with confocal scanning laser microscopy.

2 EXPERIMENTAL: MATERIALS AND METHODS

The thermoplastic matrices are two commercial products of DSM, PP 19MN10 and Stapron SM 300 (SN), and an experimental SN sample with a higher melt flow index than SM 300, DVS 28, also from DSM. The PP is a homopolymer with a high melt flow index; sometimes 1 mass % of a coupling agent additive, a PP resin grafted with maleic anhydride, PP-g-MA, was mixed in the PP matrix. The SN grades are rubber-modified SMA copolymers. DVS 28 is used to prepare the unidirectional (UD), continuous fibre composites and SM 300 for the short fibre reinforced compounds. Some of the experimental film former emulsions were prepared at DSM Italia, Como, some at DSM Research and some were emulsions commercially available; a glass fibre producer prepared the experimental sizes and provided the glass fibres coated with these sizes. The average fibre diameter was chosen dependent on the application: for the production of UD continuous glass fibre reinforced composites a diameter of 20 μm was chosen, for short fibre reinforced compounds it was 10 μm in SN and 13 μm in PP.

UD composites were produced by pultrusion of 480 tex glass fibre rovings through the thermoplastic in a device very similar to the one described in the literature.¹¹ The temperature in this device was *circa* 250 °C and the absence of degradation was verified by rheological measurements of the matrix material before and after processing. The pultruded filaments showed good fibre wet out, as checked microscopically. Subsequently, the pultrudate was wound with a small pitch around a rotating rectangular

metal frame and compression moulded for about 20 min, PP at 275 °C, DVS 28 at 220 °C. From these compression-moulded plates of about 2–2.5 mm thickness, UD composite samples were sawed for mechanical testing. The PP composites had a fibre volume fraction of 40–50% and the SN composites between 30 and 40%, which was established by ashing.

The short fibre reinforced specimens were fabricated by compounding and injection moulding (IM). The glass fibre percentage in the compounds was aimed at 30 mass % in PP 19MN10 (*i.e.* about 15 vol%) and 20 mass% in SM 300 (*i.e.* about 8 vol%) and verified by ashing.

Mechanical testing of the UD composites in 0°, 4-point flexural strength (FS, at an l/d of 32) and interlaminar shear strength (ILSS, at an l/d of 5) was performed according to the standards ASTM-D 790M and DIN 65145, respectively. Because the fibre length and orientation are well defined in these UD composites, these data can be interpreted in terms of fibre-matrix adhesion, as will be shown below (3.1). Typically, four FS- and six ILSS-values were determined and averaged. All these samples could be sawed from a single plate of about 15 × 20 cm².

Mechanical testing of the IM test bars in tensile and flexural strength (TS and FS, respectively), Izod and Charpy was performed according to the ISO standards 527, 178, 180 and 179, respectively.

Fibre impregnation and fibre dispersion were checked with differential interference contrast light microscopy of the UD composites with an Axiophot of Zeiss. Small samples were sawed perpendicularly to the fibre direction and embedded in an epoxy resin that was subsequently cured, abraded and polished. The PP composites showed very good fibre impregnation and good fibre dispersion; the SN composites showed reasonably good fibre impregnation but rather poor fibre dispersion. The same microscope was also used to study the PP-matrix morphology with polarized light. Differential scanning calorimetry (DSC) was performed with a Perkin Elmer DSC-7.

Migration of the size/film former from the fibre surface into the matrix was studied in IM compounds of PP and SMA with a confocal scanning laser microscope (CSLM) in the fluorescent mode.^{12,13} Preliminary observations were performed in the Department of Molecular Cell Biology, University of Amsterdam, with their home-built equipment.¹² Later results were obtained with a Biorad MRC 600 at DSM.

Surface analysis was performed with X-ray Photoelectron Spectroscopy (XPS), an analytical technique to measure quantitatively atomic compositions in surface layers of about 2–5 nm thick, with a Leybold MAX 200 instrument. The film former morphology on the glass fibres was studied with a Philips 515 scanning electron microscope (SEM).

3 RESULTS AND DISCUSSION

3.1 UD Composites

Four glass fibre rovings, coated with experimental size formulations, were tested in PP. Unless stated otherwise, all wet sizes contained the same concentration of the common-

ly-used aminopropyl silane.^{4,6} The size content of the rovings after drying varied between 0.5 and 1.0 mass %. In this study it was found that the size chemistry is a much more important variable than the average size content: an increase in the size content of 100% increases the level of fibre-matrix adhesion by only about 15%. The silane was chosen in such a way that it can interact/react *via* (covalent) acid-base interactions/reactions with maleic anhydride groups in the film former and the coupling additive which is sometimes added to the PP matrix. These interactions/reactions are clearly demonstrated by prolonged extraction of sized glass fibres with chloroform (at room temperature) and trichlorobenzene (at 130 °C) and subsequent surface analysis with XPS. Even after this severe treatment, part of the film former remains at the fibre surface, presumably because it is chemically anchored with the aminosilane (which is grafted onto the glass surface⁶).

Size no. 1 contains the silane and an optimized emulsion of a PP resin grafted with maleic anhydride (PP-g-MA) as film former that reacts/interacts with the silane *via* acid-base interactions. The composition and way of production of these PP-g-MA emulsions are well described in the patent literature.¹⁴⁻¹⁶ Size no. 2 contains the same silane and film former, but the emulsifier is not optimum. Size no. 3 is identical to size no. 1, but without the silane, and size no. 4 contains the same silane as nos. 1 and 2 but a PP-incompatible high molecular mass acrylate latex as film former.

Figure 1 shows the flexural strengths (FS) of UD composites prepared with these rovings *versus* their glass fibre content (in vol%). To rank the fibres and their sizes/film formers with respect to fibre-matrix adhesion, it is assumed that the simple rule of mixtures is applicable to these data.¹ Ranking can be performed in several ways, *e.g.*

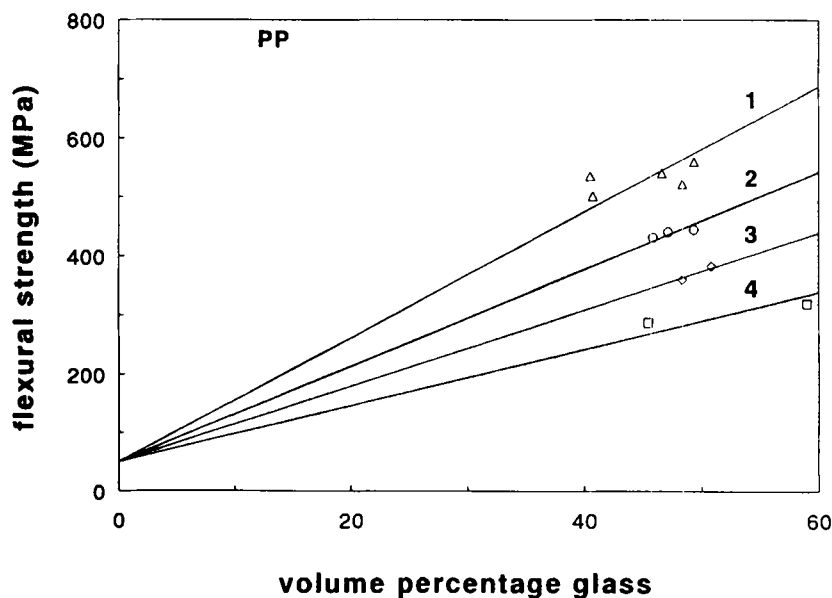


FIGURE 1 Influence of film former and size chemistry of the glass fibres on flexural strength *versus* volume percentage glass in continuous-fibre, unidirectional PP composites.

based on the flexural strengths at 50 vol%, obtained by inter-/extrapolation, or based on the values of the slopes of the straight lines, $d FS_c/d \text{ vol}\%$, the “incremental FS” of the composites. In practice, the latter is preferred because it does not contain a contribution of the matrix strength. In addition, the value of $d FS_c/d \text{ vol}\%$ can be directly related with an efficiency factor of matrix-fibre stress transfer or adhesion, ϵ_{m-f} , with the following relations:

$$FS_c = \phi_m FS_m + \epsilon_{m-f} \phi_f FS_f \tag{1}$$

$$d FS_c/d \text{ vol}\% = [\epsilon_{m-f} FS_f - FS_m]/100 \approx \epsilon_{m-f} FS_f/100 \tag{2}$$

where the subscripts *c*, *m* and *f* stand for composite, matrix and fibre, respectively, and ϕ is the volume fraction (= vol%/100); FS_m equals 50 MPa for PP and 80 MPa for SN. FS_f is estimated to be 2.5 GPa,¹⁷⁻¹⁸ so that the maximum value of $d FS_c/d \text{ vol}\%$ with optimum matrix-fibre stress transfer ($\epsilon_{m-f} = 1$) equals 25 MPa/vol%, much larger than the values found experimentally.

It is interesting to note that a good correlation is observed between the level of fibre-matrix adhesion and the failure mode in 4-point bending, as described by Shih and Ebert.¹⁹ Thus, the lowest values of $d FS_c/d \text{ vol}\%$ correspond with shear failure, whereas the highest values correspond with compressive failure at the two inner points of loading, which show quite symmetric damage zones of buckled, broken fibres.

Figure 2 gives the ILSS of the same UD composites as functions of their glass contents; all samples fail in shear in the mid-plane. In contrast to the FS, the ILSS

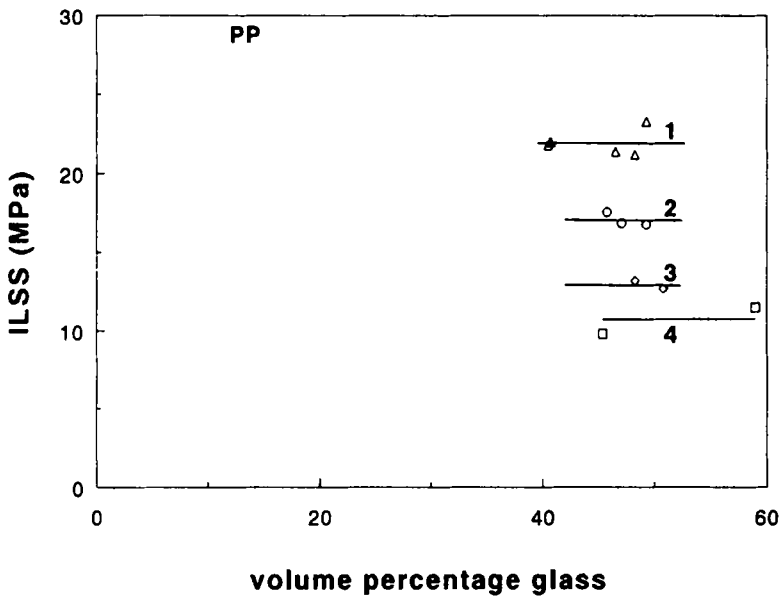


FIGURE 2 Influence of film former and size chemistry of the glass fibres on interlaminar shear strength (ILSS) in continuous-fibre, unidirectional PP composites.

TABLE I
 dFS_c/d vol%, ϵ_{m-f} and ILSS values for sizes 1–4 in PP

size no.	dFS_c/d vol% (MPa/vol%)	ϵ_{m-f}	ILSS (MPa)
1: optimum size ¹⁴⁻¹⁶	10.8	0.43	22.1
2: as 1, but non-optimum emulsifier	8.1	0.32	17.2
3: as 1, but no silane	6.5	0.26	13.0
4: as 1, but PP-incompatible film former	4.9	0.20	10.8

values can be taken to be independent of fibre content in this narrow range.¹ The ILSS is a well-known characteristic for the fibre-matrix adhesion.^{20,21} Table I lists the averaged data of dFS_c/d vol%, ϵ_{m-f} , calculated with equation (2), and ILSS for these four sizes.

As can be learned from Table I, there is a very close correlation between these three characteristics for fibre-matrix adhesion.

From the above results it can be concluded that the size chemistry plays a crucial role in fibre-matrix adhesion. Comparison of sizes 1, 3 and 4 shows that the right type of film former has an even larger influence than the presence of silane, which is known to be a very important size component.^{4,6} Comparison of sizes 1 and 2 shows that the emulsifier plays an important role as well.

With DSC and polarization microscopy it is verified that the chemistry of the fibre size does not affect the crystallinity or morphology of the PP matrix. No significant differences in melting temperature or enthalpy are observed for composites prepared with fibres containing the best and worst sizes, and only minor differences are observed with the pure matrix material (probably due to nucleation by the glass fibres, see below). Microscopically, no transcrystallinity is visible, but nucleation of large spherulites (radius about 30–40 μm) along the glass fibre surfaces is present in all PP composites, with no significant differences between the best and worst size. Thus, nucleation seems to be caused by the presence of the glass fibres and not by the chemistry of the sizes. On the basis of these results it is concluded that the differences in fibre-matrix adhesion and mechanical properties are not the result of differences in amount or type of crystallinity in the PP matrix.

Figure 3 show the flexural strength of UD composites prepared with fibres sized with sizes nos. 1–3 and the same PP, but mixed with 1 mass % of a coupling agent additive, a PP resin grafted with maleic anhydride, PP-g-MA. The values of dFS_c/d vol% and ϵ_{m-f} increase up to 11.6 and 0.46, respectively, for no. 1 and to 9.8 and 0.39, respectively for nos. 2 and 3. A similar increase is also observed in the ILSS of these “coupled” PP composites.

Figures 4 and 5 shows the relative improvement of the FS and ILSS for ten different sizes by adding this coupling additive to the PP matrix. The y-axis in Figure 4 shows the ratio of FS at 50 vol% in PP with 1 mass % coupling additive over that in plain PP, and the x-axis represents the FS in plain PP, also normalized to 50 vol% glass fibres.

In a similar way, Figure 5 shows the ratio of ILSS measured in coupled PP over that in plain PP on the y-axis, versus ILSS in plain PP on the x-axis. Notice that the same letters in Figures 4 and 5 refer to the same fibre-matrix combination. It is clear from

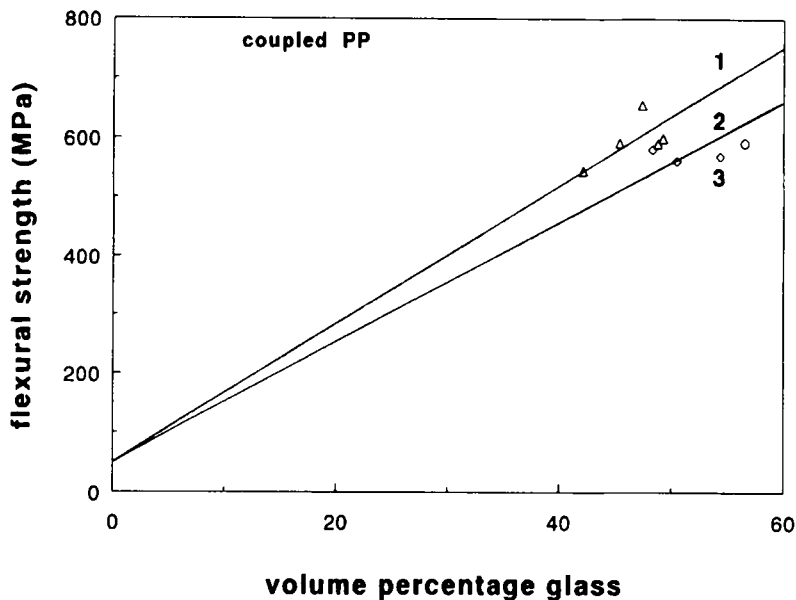


FIGURE 3 Influence of film former and size chemistry of the glass fibres on flexural strength *versus* volume percentage glass in continuous-fibre, unidirectional composites of PP with 1 mass % of a coupling additive.

these figures that the effect of the coupling additive on FS and ILSS decreases with increasing quality of the size. These two graphs seem to indicate that sizes for PP can still be further improved, so that a coupling additive becomes superfluous.

The above results demonstrate that the coupling additive has a positive effect on fibre-matrix adhesion, but they do not indicate why. Model experiments with glass plates silanized with aminopropyl silane and subsequently compression moulded against plain PP and PP with the coupling additive provide a plausible explanation. After careful pull off, both flat surfaces are analysed with XPS. The addition of the PP-g-MA coupling additive to the PP gives a large enrichment of the oxygen content at the PP side of the PP-glass interface and of the carbon content at the glass side. Apparently, this is due to excessive migration of the additive to the PP-glass interface, as a result of its low molecular mass and high acidity, and to subsequent acid-base interactions/reactions of the maleic anhydride groups with the amino groups of the grafted silane.

Combination of these model experiments with the results in UD composites provides the following explanation for the UD results. The coupling additive preferentially migrates to those parts of the glass fibres not covered by film former, but coated with a silane layer (see 3.2. below). By the resultant acid-base interactions/reactions with the silane this additive becomes (covalently) grafted onto the glass fibre; by its chemical structure it is compatible with the matrix. Thus, a "coupling system" is formed by this additive and the silane, and this coupling system compatibilizes the glass fibre surface with respect to the matrix and increases the adhesion between fibres and matrix. Presumably, the film former plays a role very similar to that of the coupling agent

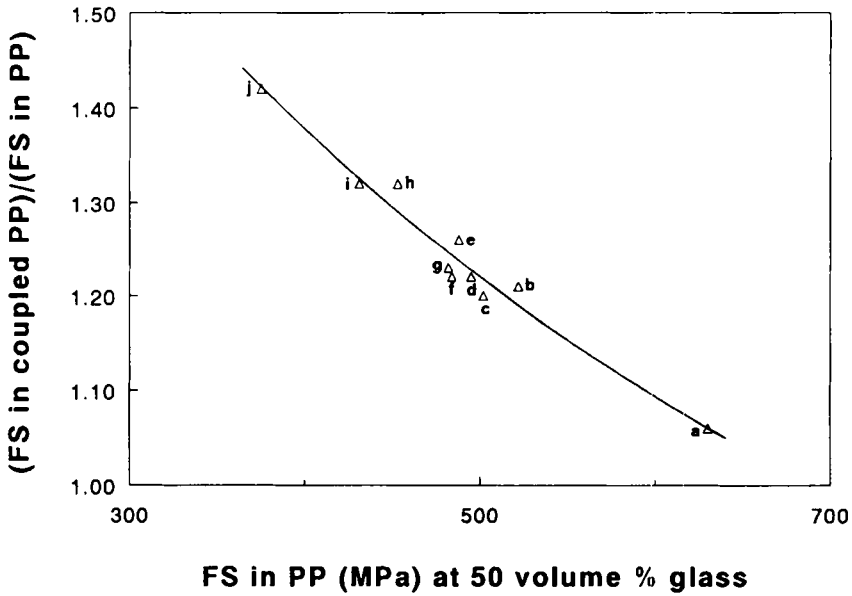


FIGURE 4 Improvement of the flexural strength (FS) of continuous-fibre, unidirectional PP composites by 1 mass % of a coupling additive as a function of the size quality determined in plain PP.

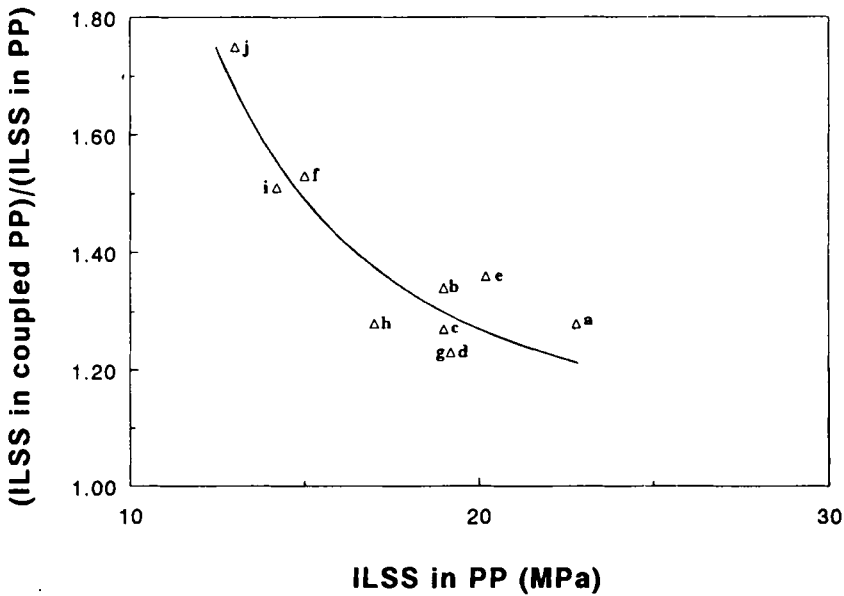


FIGURE 5 Improvement of the interlaminar shear strength (ILSS) of continuous-fibre, unidirectional PP composites by 1 mass % of a coupling additive as a function of the size quality determined in plain PP.

additive, resulting in a coupling system between film former and silane as well, as evidenced by the surface analysis after extraction, reported above.

Figure 6 shows a collection of data obtained with plain and coupled PP; it clearly demonstrates the good correlation between the two characteristics for ranking sizes and film formers with respect to fibre-matrix adhesion in PP and the positive effect of the coupling additive on it.

Figure 7 shows the flexural strength of UD composites of several glass fibre rovings in Stapron DVS 28 (SN). The upper line 5 (with a slope of 13.8 MPa/vol% and $\epsilon_{m-f} = 0.55$) refers to various sizes all containing matrix-compatible film formers with a high molecular mass (typically above 100 kg/mol). Apparently, the maximum level of fibre-matrix adhesion in SN is higher than that in PP. This is attributed to the more polar (acidic²²) character of SN, which provides ample opportunity for acid-base interactions with the aminosilane, and to the higher modulus^{23,24} of this glassy matrix. The lower line 6 (with a slope of 7.7 MPa/vol% and $\epsilon_{m-f} = 0.31$) refers to two variations in the film former emulsion: one is a PP emulsion and thus incompatible with the matrix, the other is very compatible with the matrix, but has a low molecular mass of only about 2 kg/mol. This graph again shows the dramatic differences in fibre-matrix adhesion due to variations in only the film former chemistry and structure: the silane type and concentration is kept constant in all these experiments.

In these SN composites a clear trend between fibre-matrix adhesion and failure behaviour in 4-point bending¹⁹ is observed as well. In the SN composites the highest values correspond with tensile failure. The failure mechanism of the SN composites in ILSS is always shear in the mid-plane, with values ranging from 20 MPa for the worst sizes up to 40–45 MPa for the best sizes. As in the PP composites, a strong correlation is

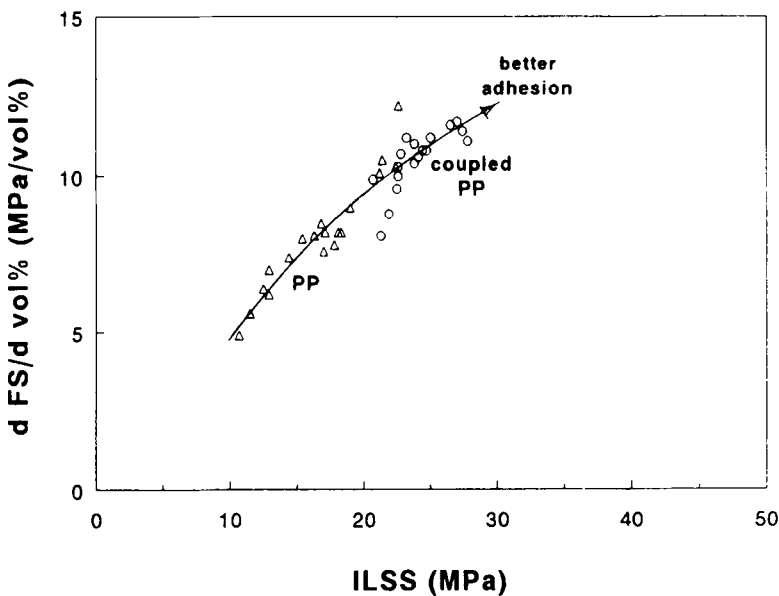


FIGURE 6 Correlation between the incremental flexural strength ($d FS/d vol\%$) and the interlaminar shear strength (ILSS) of various unidirectional composites in plain (Δ) and coupled (\circ) PP.

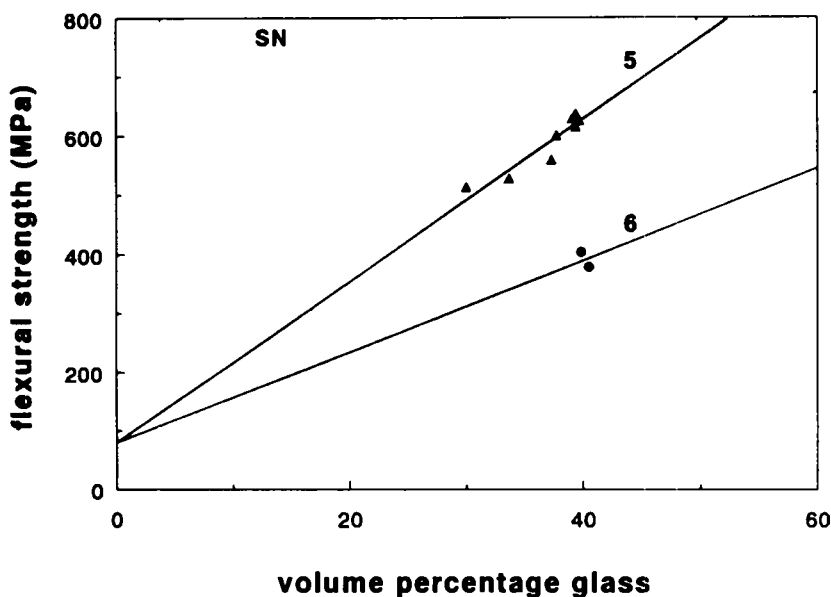


FIGURE 7 Influence of film former and size chemistry of the glass fibres on flexural strength versus volume percentage glass in continuous-fibre, unidirectional SN composites.

observed between the two characteristics, demonstrated in Figure 8. This graph contains data on many different fibre/SN and fibre/PP combinations. Unexpectedly, all these results follow the same empirical relationship between the incremental FS and the ILSS. Obviously, the optimum film former and size is situated in the upper right corner of this graph.

It is interesting to see that the maximum values of the ILSS in the two matrices come close to the tensile yield stress or strength of the matrix (25–30 MPa for PP, 45–50 MPa for SN). Thus, for the best sizes the matrix apparently starts to become the limiting factor in these tests. Besides, the values for the matrix-fibre efficiency factor ϵ_{m-f} all remain far below 1, with a maximum of about 0.45 for PP and 0.55 for SN. This might also be indicative of a matrix-limited property.

3.2 Film Former Topography in Injection Moulded Compounds Studied with CSLM

Figure 9 shows a scanning electron micrograph (SEM) of glass fibres that perform well in SN. This picture shows small “pancakes” of film-formed emulsion droplets that cover the glass surface only partly. Additional XPS measurements show that the surface in between these droplets is completely covered with a silane layer, usually several monolayers thick and only partly covered with the film former. Thus, no bare glass surface can be detected with XPS as a result of a silane multilayer, but the coverage by film former is only very incomplete, in agreement with the qualitative interpretation of the SEM photograph. This incomplete film formation is attributed to the high molecular mass of the film former ($M_m > 100 \text{ kg/mol}$), as assessed by size exclusion chromatography after extraction of the fibres.

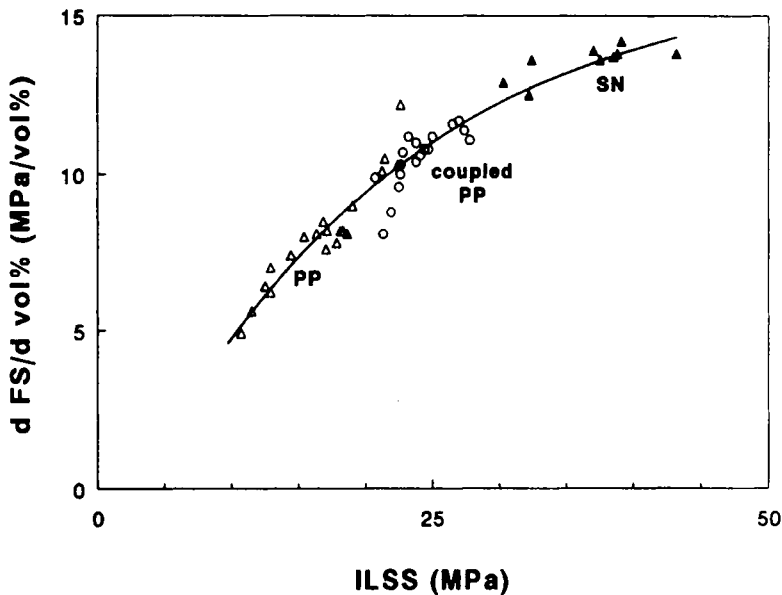


FIGURE 8 Correlation between the incremental flexural strength ($d FS_c/d vol\%$) and the interlaminar shear strength (ILSS) of various unidirectional PP (Δ , \circ) and SN (\blacktriangle) composites.

Fortunately, the size on these fibres appears to be fluorescent. By confocal scanning laser microscopy (CSLM) on IM compounds of these fibres in SMA, a picture can be obtained of the size in the SMA matrix after compounding and injection moulding. Figure 10 shows a picture reconstructed from several optical slices¹² (each with a thickness of about $1 \mu m$) through a glass fibre in the compound. The SMA matrix is not fluorescent, the size indeed is. Surprisingly, the size morphology, that can be observed because of its fluorescence, is not much changed by the processing, which is estimated to be rather severe. The fluorescent layer (the "interphase") is never thicker than the lower limit of this technique, *i.e.* $0.5 \mu m$. Similar results are obtained with other sizes in SMA, SN and PP. Thus, it is concluded that in these thermoplastics the majority of the size and film former does not diffuse away from the fibre-matrix interface into the matrix. This is probably due to the poor miscibility of thermoplastics, as a result of their high molecular mass. It explains why the film former is so important for fibre-matrix adhesion (3.1.) and for mechanical compound (3.3.) or composite (3.1.) properties.

3.3 Mechanical Properties of Injection Moulded Compounds

In Figure 11 the tensile strength of short glass fibre reinforced IM compounds of PP 19MN10 (30 mass% glass fibres) and SM 300 (20 mass % glass fibres) is plotted *versus* their flexural strengths. This graph must be compared with Figure 8, which pertains to corresponding UD composites. The correspondence is good, with the same ranking of the sizes in UD composites and in IM compounds. The relatively low position of the SN compounds in Figure 11 (and 12) is attributed to their lower glass fibre content. In

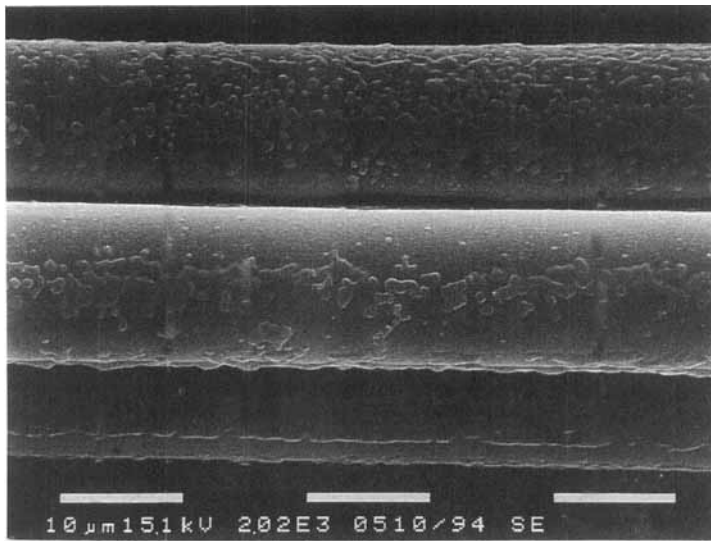


FIGURE 9 SEM photograph of a sized glass fibre (diameter = $13\mu\text{m}$).

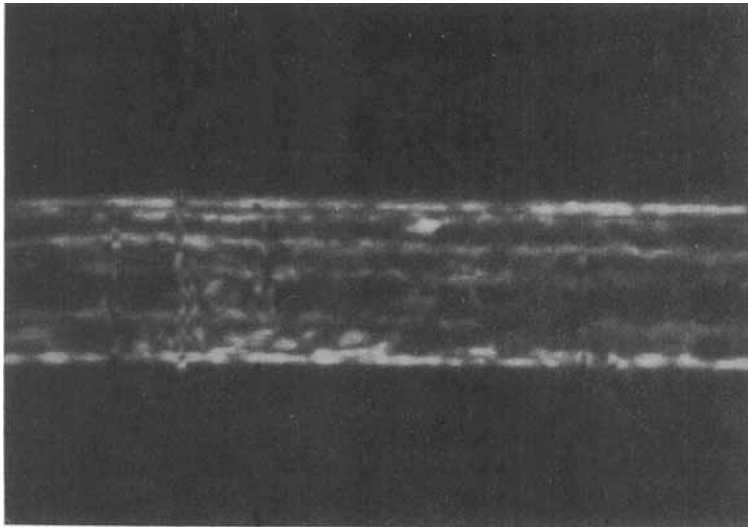


FIGURE 10 Reconstructed CSLM picture of a glass fibre of Figure 9 in a SMA matrix after compounding and injection moulding (diameter = $13\mu\text{m}$).

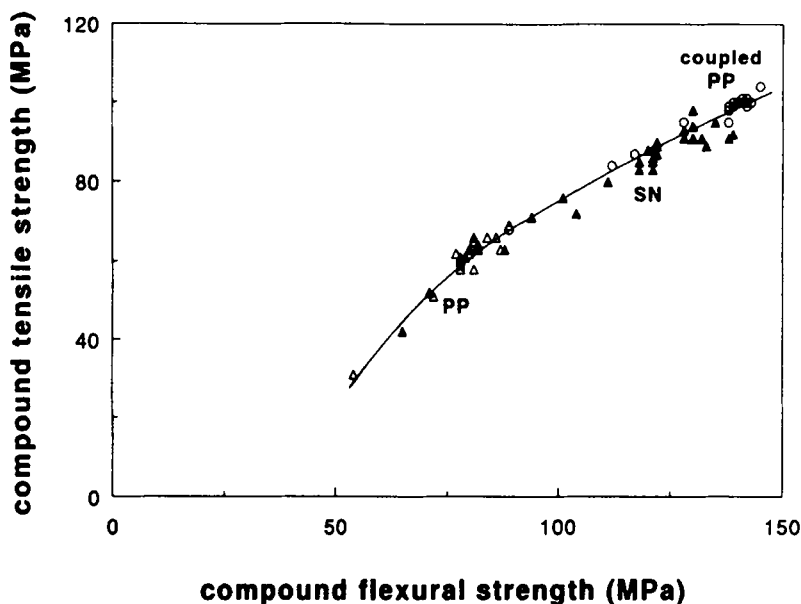


FIGURE 11 Tensile strength *versus* flexural strength for various glass fibre/PP (30 mass % glass) and glass fibre/SN (20 mass% glass) short fibre reinforced compounds.

both thermoplastic compounds a clear improvement of tensile and flexural strength is observed with increasing fibre-matrix adhesion.

Finally, Figure 12 shows the unnotched Izod and Charpy values of the same IM compounds *versus* their tensile strength. For a broad range of fibre-matrix adhesion values, corresponding with a range in compound tensile strength between about 40–80 MPa, the level of impact strength is rather constant, but above this range a distinct improvement of impact is observed with higher fibre-matrix adhesion.

The modulus of all of these compounds and composites is found to be very much dependent on fibre content, length and orientation, but essentially independent of fibre-matrix adhesion.

4 CONCLUSIONS

The main conclusion of this study is that the film former plays a crucial role in the level of fibre-matrix adhesion in polypropylene and rubber-modified styrene-co-maleic anhydride composites and compounds. A too-low molecular mass of the film former or incompatibility with the matrix are detrimental for a high fibre-matrix adhesion. The effect of the film former may be larger than that of the silane.

In PP the optimum film former and the coupling additive form a “coupling system” with the silane *via* reactions or strong (acid-base) interactions. Thus, increased fibre-matrix adhesion is obtained with these coupling systems by chemical reaction of the silane with the glass surface and by interdiffusion of the film former and/or coupling

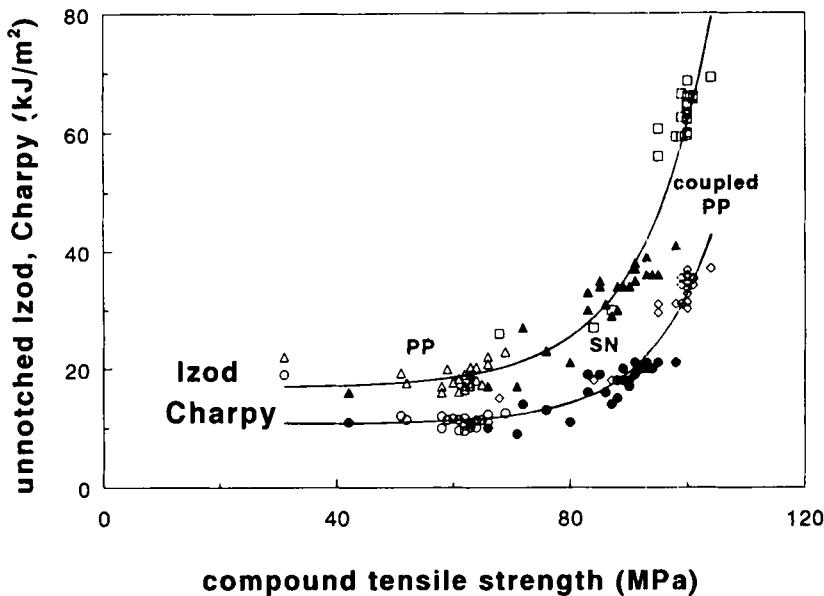


FIGURE 12 Unnotched Izod and Charpy values *versus* tensile strength for various glass fibre/PP (30 mass % glass) and glass fibre/SN (20 mass % glass) short fibre reinforced compounds.

additive into the matrix. In the PP composites no effect of the size chemistry is detected on the matrix morphology or crystallinity; trans-crystallinity is absent.

In SN the fibre-matrix adhesion level reaches higher values than in PP, presumably due to a higher matrix polarity (acidity, with the possibility to form strong acid-base interactions with the silane) and a higher matrix modulus. Experimental evidence shows that after compounding and injection moulding the size (and thus also the film former) can remain at the fibre-matrix interface and does not diffuse to an appreciable extent away from the fibre into the thermoplastic matrix.

In general, the mechanical properties of the short fibre reinforced compounds improve with higher fibre-matrix adhesion (except for the modulus). A proper choice of the film former chemistry and structure, based on the type of matrix and silane, is thus of critical importance for optimum fibre-matrix adhesion and compound and composite properties.

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