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Effects of crystallinity and supermolecular formations on the interfacial shear strength and adhesion in GF/PP composites

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ABSTRACT

Aim of this study was to screen the morphological effects on the interfacial shear strength (τ_i) in glass fibre (GF) reinforced isotactic polypropylene (iPP) model composites. τ_i was determined by a modified single fibre pull-out technique. It was established that the relation between τ_i (5 - 6 MPa) and the yield stress of the iPP ($\sigma_y \approx 30$ MPa) is at about 1 : 6 and that the τ_i values were not influenced by the mophological superstructure set under isothermal crystallization conditions. Increased τ_i was only observed when specimens were produced non-isothermally, by quenching ($\tau_i \approx 9$ MPa). This improvement could not be related to thermal shrinkage stresses. The enhancement in τ_i was attributed to better wetting and improved adhesion due to the enlarged amorphous PP (aPP) - phase. A schematic adhesion model considering the wetting behaviour of aPP and iPP was proposed.

1 INTRODUCTION

The interface between reinforcing fibres and matrix in composite materials is widely regarded as an important factor determining their mechanical property profile. Especially when processing of semicrystalline thermoplastic materials is considered, changes in the matrix morphology around the fibres are to be taken into account. These microstructural changes may affect the fibre/matrix adhesion and can thus be treated as additional interphase parameters. It is not clear yet how different morphological structures induced by processing in thermoplastic composites are really essential in respect with the interfacial shear strength (τ_i) and the related failure. So, e.g. transcrystalline superstructures developed around the reinforcing fibres are reported both to promote interfacial shear strength of GF/PP [1] or not to influence it at all [2]. The effects of thermal shrinkage stresses acting perpendicular to the fibre surfaces (i.e. in radial direction of the fiber) and thus increased interfacial friction are emphasized by various authors in analogy to thermoset curing.

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2 EXPERIMENTAL

2.1 Testing Method

A modified pull-out technique first described in [2] was used. This technique allows both to modify the interface morphology and matrix microstructure and to determine interfacial shear strength and failure mechanisms easily.

Fig. 1 shows the specimen set-up and loading mode of a specimen in the modified pull-out testing technique, schematically.

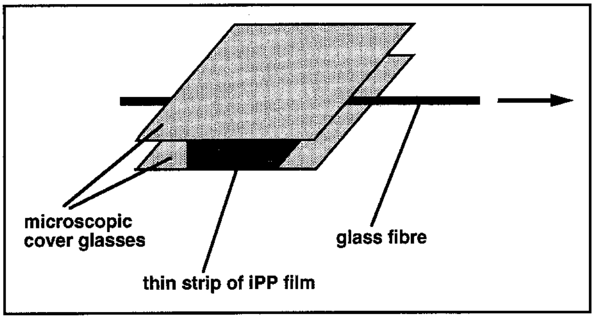

Figure 1
Modified single fibre pull-out testing technique

Samples were prepared either in a thermostatic chamber followed by quenching in iced water or in a hot stage of a Leitz transmitted light microscope during isothermal crystallization conditions. Crystallization was carried out either with or without (quiescent melt) shearing of the melt to be applied by pulling the fibre partly from the melt. The embedded fibre lengths varied in a range from 500 to 1500 µm, according to the sample preparation. As iPP is a ductile material uniform shear yielding of the interface is assumed, i.e. the shear-stress-criterion is used for data reduction. The interfacial shear strength (τ_i) value was simply calculated by:

$$\tau_i = \frac{F_{max}}{\pi D L}$$

where F_{max} is the maximum tensile load, D and L are fibre diameter and embedded glass fibre (GF) length, respectively.

2.2 Variation of the matrix microstructure

Different matrix microstructures were set by the crystallization conditions. Crystallizing the GF/iPP sample isothermally at T_c = 140°C resulted in a coarse α-spherulitic structure, whereas quenching the specimens in iced water led to a finely dispersed morphology. The microstructure of the pure PP-matrix is not influenced by the GF present, no transcrystallization occured. Contrary to this, the cooling rates and crystallization temperatures affected the matrix morphology: higher T_c originated larger and structurally more perfect spherulites, and increasing cooling rates reduceed the degree of crystallinity (T_c = 140°C: X_c = 52,5%, $\varnothing_{spher.} \approx$

200-300 μm; T_c = 135°C: X_c = 46,4%, Øspher. ≈ 120-200 μm; quenched: X_c = 42,5%). The apparent crystallinity was established by differential scanning calorimetry (DSC) measurements using a Mettler TA 4000 thermoanalytical system ($\Delta H_{c,100\%}$ (iPP) = 190 J/g).

Transcrystalline-like superstructures in GF/iPP can be achieved by melt shearing, e.g. by pulling the GF partially in the isothermally crystallizing iPP melt. This melt shearing generates a layer containing oriented polymer chains along the fibre length. This layer exhibits a strong nucleation ability for homogenous crystallization. Therefore, this phenomenon should be called row-nucleated cylindritic crystallization rather than transcrystallization [3]. Fig. 2 demonstrates schematically that "transcrystallization" appears when the spherulite growth is restricted to one direction, i.e. perpendicular to the fibre surface.

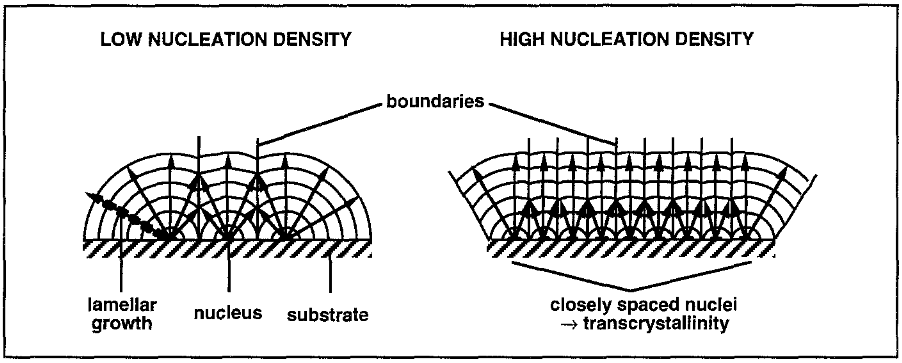

Figure 2 Influence of nucleation density on supermolecular structure formation

As pointed out schematically in Fig. 2, "transcrystallization" is strictly related with spherulitic one. In particular, the growth rates and lamellar orientations of three-dimensionally growing spherulites and in the corresponding cylindrites and transcrystalline layers are similar. It should further be mentioned that there was no significant difference in the degree of crystallinity between the samples with spherulitic and cylindritic matrix morphologies.

3 RESULTS

The interfacial strength values obtained by the modified pull-out testing technique on GF/iPP-samples of varying matrix microstructure/morphology are summarized in Fig. 3.

It is very striking that even the highest τ_i-values, i.e. ~ 9 MPa for the quenched specimens, are far below the shear yield strength of the neat iPP (~ 30 MPa). This indicates clearly an insufficient level of adhesion between GF and iPP. Furthermore, changes in the supermolecular structures around the GF (spherulite/cylindrite) seem not to enhance the adhesion at all (τ_i ~ 4...6 MPa), only rapid cooling proved to be beneficial. The shear strength values obtained in the present work (4.8 - 9.0 MPa) fit well in the τ_i-range (4.5 - 8.4 MPa) published in the lierature for GF / iPP by using various micromechanical testing methods [4-6].

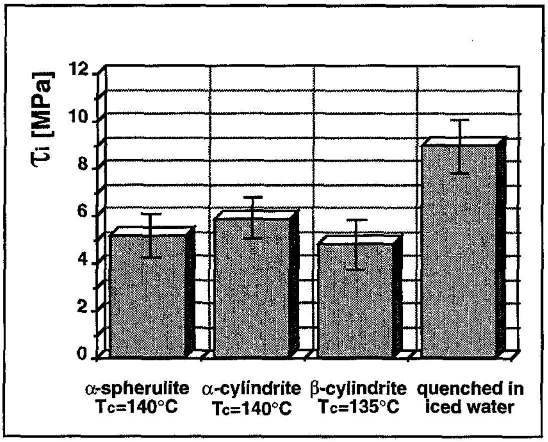

Figure 3

Interfacial shear strength as a function of matrix microstructure for GF / iPP

4 DISCUSSION

4.1 Identical Shear Strength for Spherulitic and Cylindritic Crystallization

As α-cylindrites and α-spherulites are of the same nature, their supermolecular structures should not affect much the adhesion to GF. On the other hand, they certainly differ in nucleation density on and near the glass fibre surface. This may promote adhesive friction between matrix and reinforcing fibre by increased radial compressive stresses [7]. It was demonstrated [3] that the β-cylindritic structure consists of two layers. In the vicinity of the pulled glass fibre α - row nuclei of higher thermal stability develop due to melt shearing. These α - row-nuclei exhibit a selective β - nucleation ability at Tc = 135°C which results in the growth of β-cylindrites. Thus, again an α-spherulitic structure is relevant for the adhesion to the GF, even then when a β-cylindrite formed around the GF.

4.2 Increased Interfacial Shear Strength for the Quenched Samples

There are, on principle, two possible effects that may explain the improved adhesion observed between GF and iPP: a) higher interfacial strength due to matrix thermal shrinkage and thus increased interfacial friction at failure initiation and during pull-out and b) enhanced adhesion due to better wetting of the enlarged amorphous PP (aPP) - phase.

Referring to the thermal shrinkage, several authors, e.g. [8], developed theoretical models in order to estimate frictional effects by considering the residual stresses and thus the "overall" adhesion between the matrix and the fibre. Although these models were worked out for thermoset matrix composites (given ΔT: curing temperature - room temperature), attempts have been made to modify them for thermoplastic matrix composites as well, e.g. [9]. Inspite of the fact that terms related with effective temperature differences, material properties (viscositiy, morphology) are very uncertain, some of these models (e.g. [10]) estimate τ_i quite well. Since the cited mechanical models base on differences in thermal expansion between fibres and matrices, tests with polyacrylonitrile (PAN) - based high-tenacity carbon fibres (CF) were also conducted. The interfacial shear strength was not expected to increase in CF/iPP due to enlarged compressive residual stresses since $\alpha_{th,rad}$ (CF) $\approx$ $\alpha_{th,rad}$ (GF) which was found, indeed (Fig. 4)

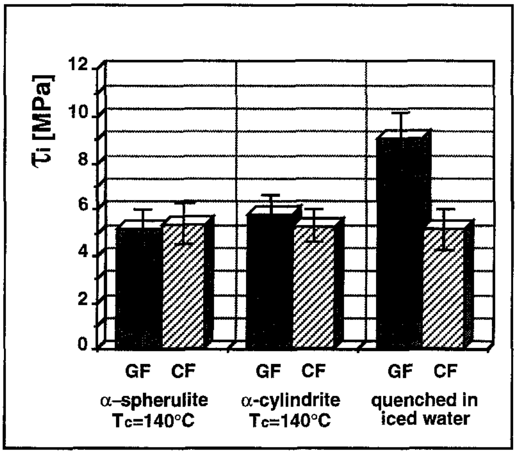

Figure 4
Interfacial Shear Strength for GF/iPP and CF / iPP model composites

Again, it is striking that both combinations GF/iPP and CF/iPP exhibit a poor adhesion and an almost constant shear strength value. For CF/iPP even quenching the sample in iced water had no beneficial effect, the interfacial shear strength in CF/iPP was influenced neither by the matrix morphology nor by the cooling rates. For the quenched modifications τ_i-values of GF/iPP are even higher than those for CF/iPP. This fact indicates that mechanical friction is definitely not the relevant factor to improve fibre/matrix adhesion for the used GF/iPP-material. Furthermore, no significant deviations in the dynamic interfacial friction (while pulling the fibre through the matrix after interface failure) were observed in the load-displacement curves registered.

It is supposed, therefore, that the increase of the shear strength is related with the feature and the location of the amorphous phase. The increased amorphous fraction (lower degrees of crystallinity, Xc, in the quenched specimens) is believed to promote the interfacial shear strength by improved surface wetting. In order to check this hypothesis, similar pull-out tests were performed on GF/aPP (atactic or amorphous polypropylene) whereof the results are summarized in Fig. 5. It is obvious that the GF/aPP specimen exhibit very low interfacial shear strength values and that there is no dependence on cooling conditions to be detected. It should be noted here that τ_i agrees wit the yield strength of the used aPP fraction (~ 1 MPa).

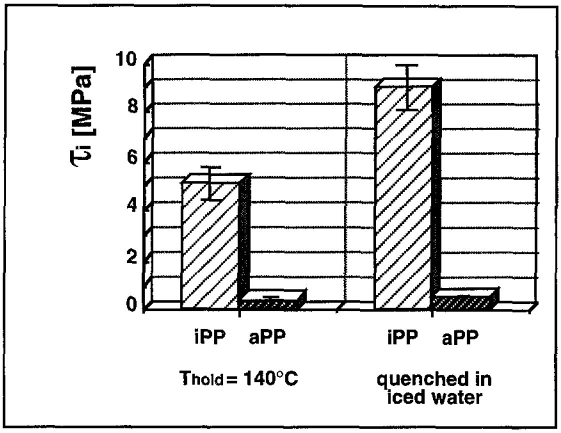

Figure 5
Interfacial shear strength for GF/iPP and GF/aPP model composites

SEM - fractographs of the failed GF/aPP interfaçes (see Fig. 7) show that - in contrary to poor adhesive-type interfacial failure of GF/iPP (see Fig. 6) - cohesive matrix failure occured that clearly indicates both good wetting and insufficient matrix shear strength.

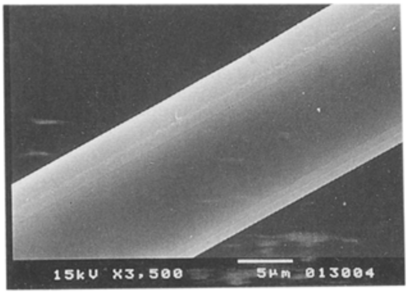

Figure 6
Adhesive-type interfacial failure in GF/iPP

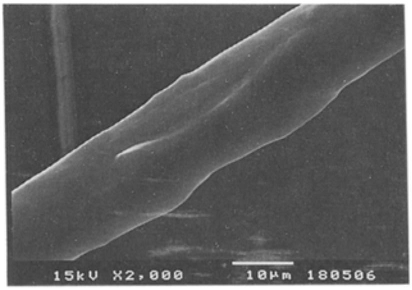

Figure 7
Cohesive matrix failure in GF/aPP

The superior wetting properties of aPP could be proved by measuring the apparent contact angle of iPP and aPP on a glass plate (GP) whose surface tension was determined to be ~25 mN/m following the Zisman method [11]. Samples were molten up to 200°C, isothermally crystallized (140°C, 30min) in a hot stage and subsequently measured at room temperature using a Ramé-Hart contact angle tele-goniometer. The contact angle of iPP/GP was 55° whereas the aPP/GP sample exhibited a lower one of 35° what reveals better wetting of the glass plate by aPP. In addition, the iPP droplets were - in contrary to the aPP ones - fully debonded from the glass plate after cooling down. This "de-wetting" - phenomenon was attributed to different volume changes in iPP and aPP during crystallizationand subsequent cooling (see Fig. 8). Due to the volume change by crystallization and thermal shrinkage in iPP high shear forces emerge in the iPP/GP interface, resulting in easy detaching.

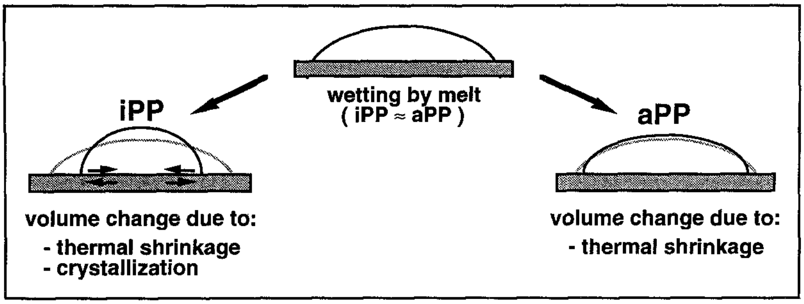

Figure 8 "De-wetting" - mechanism due to crystallization

On the base of both wetting properties and material strength an optimum in terms of adhesion and load transfer capability can be provided by a proper mixture of iPP and aPP. In this case both requirements are met: a) good wetting (by the amorphous PP phase) and b) sufficient material strength (crystalline PP phase) Therefore, if the matrix (or interface) morphology and degree of crystallinity of GF/iPP isothermally crystallized and quenched specimens is considered, the "covered interface"of the fibre by the amorphous fraction is much smaller in a coarse spherulitic structure where the amorphous phase can be found at the spherulite boundaries. Obviously, the geometrical probability that such boundaries lay along the fibre surface is much lower than in a quenched sample of fine texture. In the latter case, the amorphous phase is not be ejected during crystallization and, in addition, due to the rapid cooling its fraction also increases (see Fig. 9). In the quenched samples good wetting is maintained by a large amorphous PP phase and a finely dispersed structure; high matrix strength is supplied by a "close-meshed network" in which crystalline blocks are held together by tie molecules. The proposed adhesion model for GF/iPP suggests some kind of interpenetrating network built up by an amorphous and a crystalline PP phase.

The proposed model could further be confirmed by the fact that quenched and subsequently annealed (140°C, 30min) samples gave τ_i values similar to the isothermally crystallized ones. This was related to the de-wetting mechanism depicted in Fig. 8 under such a post-crystallization process.

5 CONCLUSIONS

Adhesion and thus interfacial shear strength in the examined GF/iPP is not influenced by the matrix microstructure. Furthermore, cooling-caused residual stresses and thus frictional effects hardly effect the interfacial shear strength. Enhanced interfacial strength in the quenched samples can be attributed to better wetting and improved adhesion due to the enlarged amorphous PP-phase. A schematic model considering the wetting behaviour of iPP and aPP was proposed. It was concluded that high interfacial shear strength is related with both wettability and shear strength of the matrix. Since they are changing in the opposite direction in semicrystalline materials, an optimum between them should be targeted.

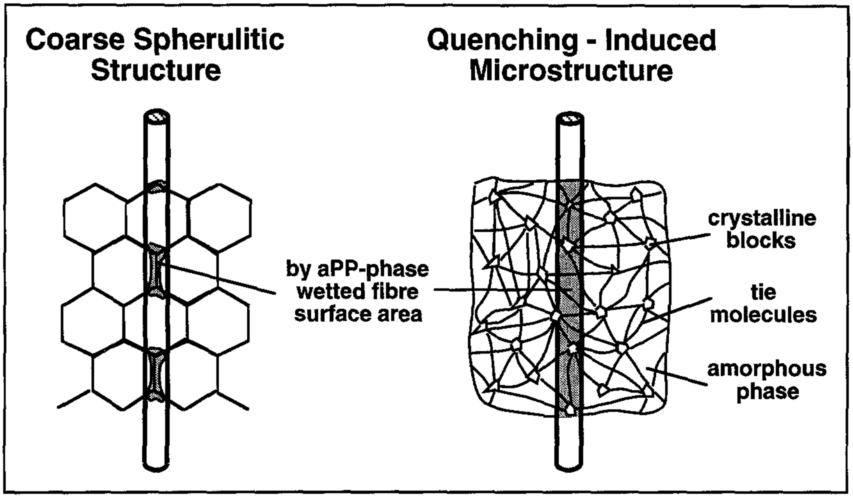

Figure 9 Scheme on the wetting behaviour of iPP in function of the microstructure

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