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Interfacial design in fiber reinforced polymers

Edith Mäder*, Elena Pisanova

Institute of Polymer Research, Hohe Str. 6, 01069 Dresden, Germany

SUMMARY: Different interphases have been created with different film formers and coupling agents on glass and carbon single filaments embedded in thermoplastic and thermosetting matrices. Three micromechanical procedures (pull-out test, fragmentation test and a version of microbond test in which crack propagation was continuously monitored by optical microscopy) were used to measure fiber/matrix interfacial bond strengh. The effect of interphase microstructure, transcrystallinity as well as matrix molecular weight on the measured bond strength, failure mode, and local properties of the interphase was examined. The possibilities of controlling bond strength between fiber surface and polymer matrix are discussed.

Introduction

Mechanical properties of the fiber reinforced composites are strongly influenced by the properties of the interfacial region between the fiber and the matrix. The interphases comprise a significant part of the matrix phase even in the moderately filled composites 1), so specific properties of the boundary layers should be taken into account by modeling and designing advanced materials. Recently new non-destructive methods have been developed to characterize physical properties of the interphases. It was demonstrated by means of atomic force microscopy 2, 3), dynamic mechanical analysis 4, 5), scanning electron microscopy 6, 7), inverse gas chromatography 8, 9) that the properties of the polymer in the vicinity of the fiber can change drastically. The reasons for this may be restricted segmental mobility, transcrystallinity, selective adsorption of a component of polymeric composition, changed curing, specific interaction between the fiber surface and the matrix polymer. These processes lead to creation of an interphase giving gradient of the matrix properties at the interface. On the other hand, interphases can be designed between fiber and matrix to control composite properties, first of all, stress transfer through the interface.

The theoretical consideration has shown that the stress distribution at the fiber-matrix interface can be considerably changed depending on interphase elastic modulus and thickness 4, 10). That means, interfacial design should be based on foregoing analysis of all possible interactions for a given polymer-fiber pair. It is important that the goals of the design may be opposite for different classes of composites. Indeed, for many thermoplastic polymers, especially when they are the

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non-polar, the main issue is an increase in interfacial adhesion. On the contrary, most thermosetting polymers possess very good adhesion to carbon and glass fiber surface, what results in brittle fracture and low impact resistance. In this case interphases should be created, for example, by introducing a ductile or flexible material between the fiber and the matrix 4).

The interfacial design can be performed when a composite is being formed, or in part before that (matrix modification, fiber surface treatment). But the effectiveness of these can be proved only after the composite formation. Two research directions are of great importance on this stage: first, direct measurements of the interphase properties, and second, micromechanical experiments aimed at examining the ability of the boundary layer of stress transfer. Recently developed micromechanical techniques that provide simultaneous observation of crack initiation and propagation 11–14) deliver necessary information on the interfacial strength as well as on the failure location. This makes possible a separate analysis of the adhesion and friction contributions into measured bond strength. Such an information is a necessary basis for further target-oriented interfacial design.

In this work, various approaches were used to control the structure and properties of the interphases between glass and carbon fibers and polymer matrices of different nature: polar and non-polar thermoplastics as well as thermosetting resins.

Experimental

Materials

E-glass fibers with a diameter of 12 μm and PAN-based carbon fibers with a diameter of 7 μm were used for the experiments. As matrix material, we used granules of thermoplastic polymers — polypropylene homopolymer (PP) and maleic anhydride grafted (PPM), high density polyethylene homopolymer (PE) and maleic anhydride/styrene grafted (PEMS), poly(vinylidene fluoride) (PVF), poly(acrylonitrile butadiene styrene) (ABS), polyamide 6 (PA), polycarbonate (PC), polystyrene (PS) and polyphenylene sulphide (PPS). As thermosetting polymers, vinyl ester resin and DGEBA-based epoxy resin were taken.

Sublayer formation

— *From solution*: different sizing agents were applied from an aqueous solution or polymer dispersion within the continuous spinning process, immediately after cooling glass fibers down. Following model sizings were used: γ-aminopropyltriethoxysilane (APS), methacrylsilane (MAS), APS/polyurethane dispersion (APS+PU), MAS/unsaturated polyester resin dispersion (MAS+UPE), polyvinylalcohol (PVA) and polyvinylacetate dispersion (PVAc).

— *By electrodeposition*: sublayers on carbon fibers were obtained by depositing powdered polymer onto continuous fibers in the chamber of electrostatic fluidized bed coater [15].

Micromechanical tests

— *Pull-out test*: this test was carried out using a pull-out apparatus which allows high precision fiber displacement and force measurement as well as data management [16]. Single fibers were embedded in matrices in a separate micro-oven at a heating/cooling rate of about 50 °C/min. The pull-out test was performed at a crosshead displacement rate of $1.2 \cdot 10^{-2}$ mm/min. From each force-displacement curve, the maximum force F_{max}, and the embedded length, l_e, were determined, and the apparent shear strength τ_{app}, for each specimen was calculated from the equation

$$\tau_{app} = \frac{F_{\max}}{\pi d l_e},$$

where d is fiber diameter.

— *Fragmentation test*: single-fiber composites in the form of a dumbbell, with the fiber running along the specimen axis, were prepared as described elsewhere [15]. The specimen stretching was performed on a tension testing machine at a strain rate of 0.2 mm/min until a neck of maximum possible length was reached. After that specimen was examined in an optical microscope. The interfacial bond strength was calculated from Kelly's formula

$$\tau_{app} = C\frac{\sigma_l d}{2l},$$

where σ_l is the strength of the fiber of the mean fiber length l, and C is correction factor [15].

— *Microbond test*: specimens for this test were prepared on thin cover glass plates as described elsewhere [11, 14]. A mini tensile machine was used to produce tensile load. The free fiber end was glued to the metallic bar attached to the force sensor. The free fiber length was 0.2–2 mm. The testing rate was 0.25 μm/s to ensure slow crack propagation. The testing device was placed on the stage of an optical microscope equipped with a video camera connected to a computer, which made possible to record the picture of crack propagation in step with the applied force. Thus, the crack length was obtained as a function of the applied external force, F. Three characteristic forces — the maximum force F_{max}, the debond force F_d, and the friction force F_f, — were determined for each trial. The debond force was obtained as a limit of the function $F(l_{cr})$, where l_{cr} is the experimentally measured crack length [14]. The local adhesion strength, τ_{ult}, the adhesional pressure, σ_{ult}, and the work of adhesion, W_A, were calculated according to the algorithm proposed in Ref. 14.

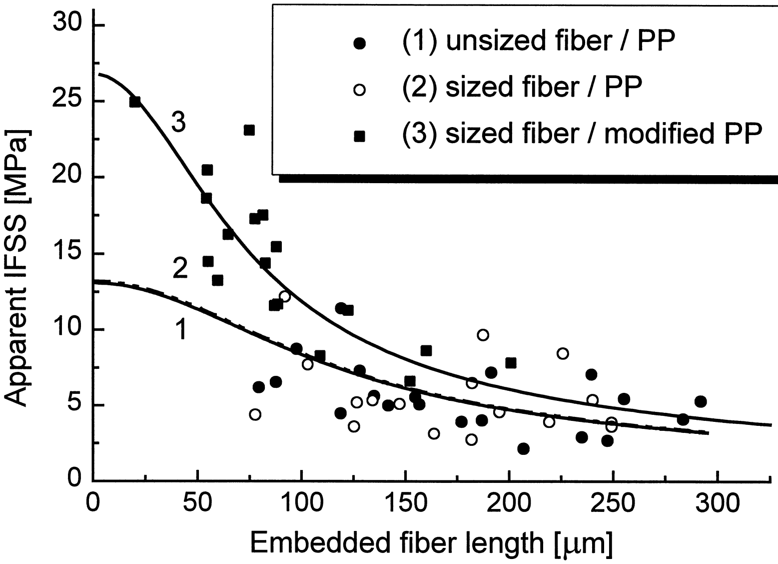

Fig. 1: Apparent interfacial shear strength in glass fiber–polypropylene systems plotted versus the embedded length: (1, 2) PP, (3) PPM. Results of the pull-out test; fiber sized with APS. Lines are approximations of experimental data according to shear lag analysis [21] using the least-squares method.

Micro-thermal analysis

Micro-thermal analysis μTA 2990 (TA Instruments) combines a scanning force microscope with the thermomechanical analysis. The experiments were made on the polished samples in the vicinity of the fiber-matrix interface. The glass transition temperatures were detected at the distances 2, 4 and 20 µm from the glass fiber surface.

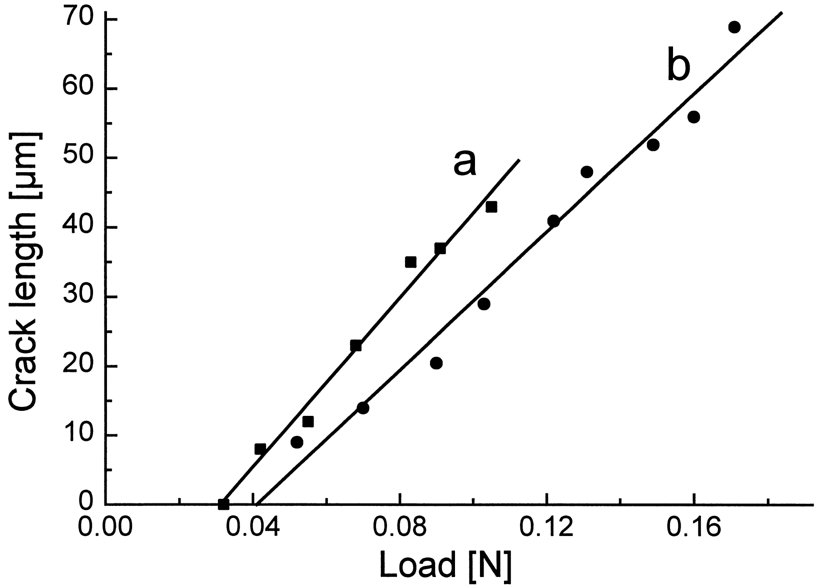

Fig. 2: Experimental relationships between applied load and the crack length from microbond test: (a) PP, (b)PPM; fiber sized with APS.

Results and Discussion

Non-polar polymers

The main problem of fiber reinforced non-polar polymers is low adhesion between the fiber and the matrix. Due to the lack of reactive groups in the polymer chains, the polymer adhesion to fiber surface is provided only by van der Waals forces that can hardly be influenced by means of interfacial design. Indeed, as was shown by pull-out 17) and push-out 18) experiments as well as by testing macrocomposites 19, 20), any treatment of the fiber surface did not result in the improvement of the bond strength or composite properties in the case of PP or PE matrices.

Table 1. Effect of fiber coating on interfacial characteristics of the polypropylene/glass fiber system.

Matrix	Fiber coating	τ_{ult} (MPa)	σ_{ult} (MPa)	W_A (mJ/m^2)
PP	—	13.1	98	69
PP	APS	13.2	100	70
PPM	—	12.8	97	68
PPM	APS	26.8	147	91

The only possible way to improve adhesion of non-polar polymers is simultaneous modification of both fiber surface and the matrix in such a way that reactive acidic and basic groups are created on the contacting surfaces. This approach appeared very effective for PP composites: sizing of

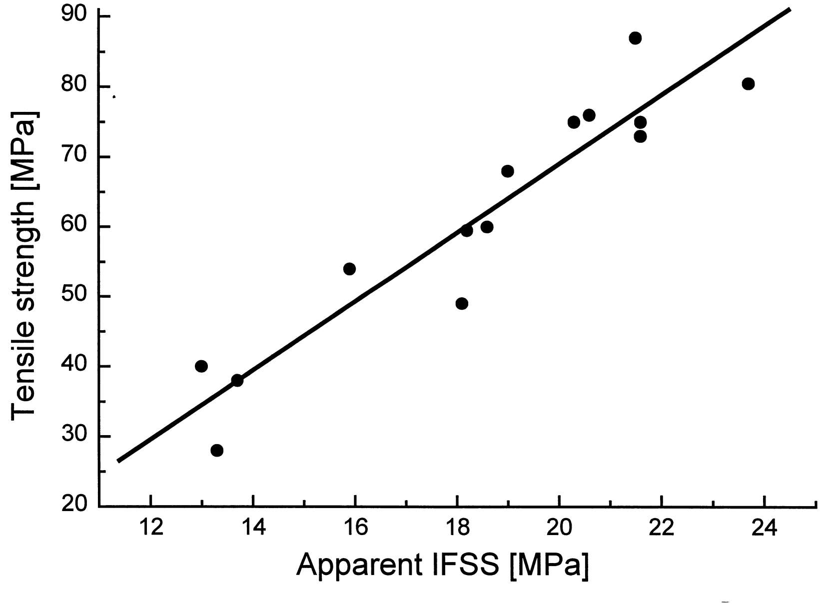

Fig. 3: Tensile strength of PP/glass fiber composites versus interfacial shear strength from pull-out test.

glass fibers by basic APS and simultaneous introducing acidic groups into the matrix resulted in considerable increase in the strength of composites with continuous [17] and short [2] glass fibers as well as in the bond strength from push-out test [18].

As can be seen from the results of pull-out test presented in Fig. 1, the interfacial shear strength is markedly greater for modified PP as compared to unmodified matrix in the whole range of embedded lengths. A crack between modified PP and sized fiber is initiated at considerably greater applied external force (Fig. 2). Interfacial characteristics for PP–glass fiber systems calculated from pull-out and microbond data are summarized in Table 1. It should be mentioned that the work of adhesion between PP and glass fiber surface estimated from micromechanical testing is in a good agreement with the value obtained from wetting and inverse gas chromatography [21]. An increase in the work of adhesion for modified PP–sized fiber system up to 91 mJ/m^2 can be attributed to the acid-base interactions between amino groups on the fiber surface and acidic groups in the polymer chains. A strong correlation between the strength of micro- and macrocomposites (Fig. 3) is an additional evidence for the fact that adhesional interaction is of key importance in the interfacial design in the case of non-polar polymers like PP.

The modification of the whole matrix material is not the only possibility to affect the adhesional interaction at the interface. Another way is introducing a layer of polar polymer between the fiber and the non-polar matrix. The interphase plays a key role in stress transfer, therefore a thin layer

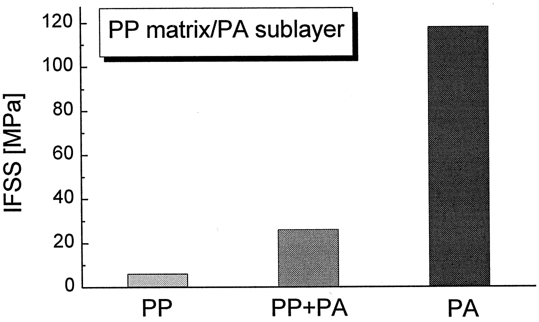

Fig. 4: Interfacial shear strength in carbon fiber / electrodeposited sublayer / polymer matrix systems. Results of the fragmentation test; left bar shows results for only matrix material, right bar, for only sublayer material.

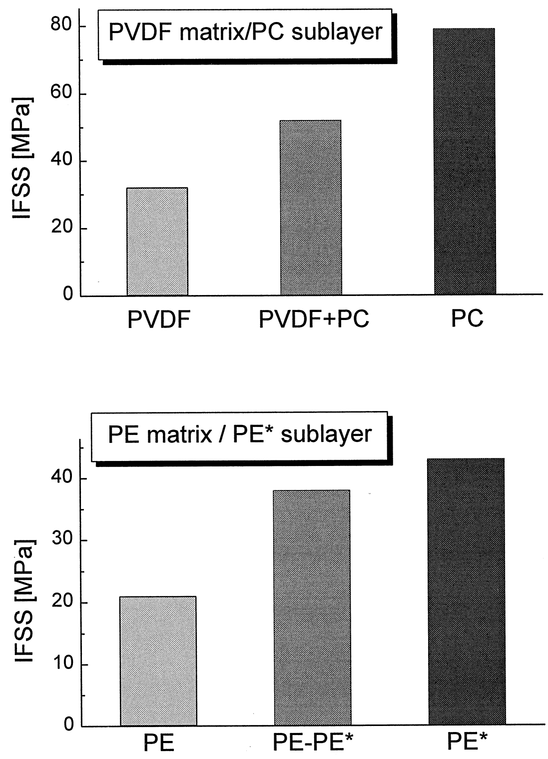

Fig. 4 (continued): Interfacial shear strength in carbon fiber / electrodeposited sublayer / polymer matrix systems. Results of the fragmentation test; left bar shows results for only matrix material, right bar, for only sublayer material. PE* is PE modified by gamma radiation in air.

of another polymer with good adhesional ability could be very effective for improving composite strength. In the case of continuous fibers such a layer can be applied by deposition of the powdered polymer onto fibers in an electric field [15)]. This operation can be easily combined with the deposition of main matrix material used in dry technologies of composite fabrication.

When creating interphases using this technique, interdiffusion of the sublayer and the matrix polymer is facilitated by the fact that the process of interphase formation takes place for a sufficiently long time and at the temperature which is above melting points of both polymers. Bond strength measurement for various carbon fiber/sublayer/ matrix systems showed that in all cases it was intermediate between corresponding values for the matrix and sublayer materials

(Fig. 4). By using sublayers or interphases, two mechanisms of bonding should be taken into account: good adhesion to fiber surface is due to presence of active groups involved in acid-base interaction at the interface, while at the sublayer-matrix boundary interdiffusion plays the main part [20–22].

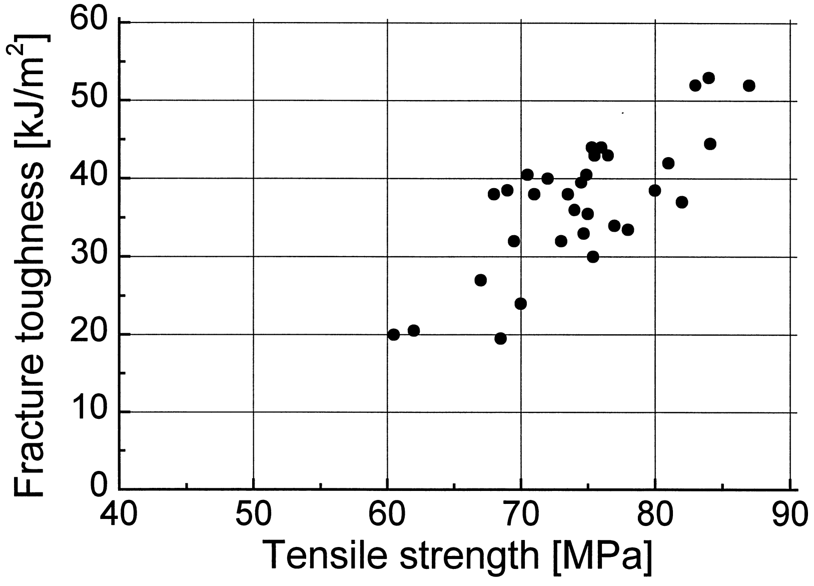

Fig. 5: Impact toughness versus tensile strength of PP/glass fiber composites with different fiber coatings.

The sublayers can also be applied from solutions or polymer dispersions; this procedure can be done immediately after the continuous fiber spinning process [16]. Having varied the chemical composition of film formers, we showed that it affected to a great extent the strength of PP-glass fiber composites [2, 17]. It should be mentioned that thickness of a sublayer and interdiffusion play a great part in such interphases [23]. When the sublayer is too thick, it becomes the "weak point" of the system, and the failure process occurs within it. Washing off the excessive sublayer material results in an increase of the bond strength [23]. According to recent investigation, the optimum interphase thickness for different polymer-fiber pairs is about 0.1–0.2 μm [4, 24]. Proper interfacial design should take into account not only acid-base interactions at the interface, but also thickness of the interphase and interdiffusion with bulk matrix material. Under these conditions, simultaneous increase in impact resistance and tensile strength of the composites can be achieved (Fig. 5).

To activate PE powder surface, maleic anhydride and styrene monomers were grafted onto it. The presence of oxygen-containing functional groups was determined using XPS. ToF-SIMS investigations were carried out to obtain information about the molecular build-up of the grafted polymers. The spectra gave evidence of polymer chains with alternating maleic anhydride and styrene units (Table 2).

Table 2. Some properties of modified polyethylene (PEMS) and its interface with glass fibers.

Material	MAH (wt%) /ST (wt%)[a]	Gel content (%)	τ_{app} (MPa)	τ_f (MPa)	σ_{ult} (MPa)	[C–O]/ [C=O][b]
PEMS1	5/0	0.5	4.5	2.7	53.6	0.497
PEMS2	5/2.5	4.1	27.6	12.3	126.3	0.853
PEMS2T	5/2.5[c]	11.8	30.0	20.0	152.8	—
PEMS3	5/5	5.5	28.9	4.7	171.0	0.610
PEMS3T	5/5[c]	11.0	31.0	17.5	135.8	—

[a] MAH — maleic anhydride; ST — styrene.
[b] From Ref.[25].
[c] Heat treatment for 10 min at 250°C.

The monomers grafted onto the PE surface increased its polarity. To investigate the effect of different chemical composition on the adhesion strength, single APS-sized glass fibers were embedded in their melts. The force-displacement curves showed significant changes of the interphase behavior (Fig. 6). First, the adhesion of all modified matrices was considerably greater than the adhesion of non-modified matrix. The subsequent thermal treatment caused, in all probability, cross-linking within the interphase and further increase in the number of local bonds at the interface. The increased degree of cross-linking was confirmed by greater gel content (Table 2). As a result, the interphase for thermally treated samples was much stronger, and the failure mechanism was quite different. As can be seen in Fig. 6, these samples failed through matrix yielding rather than brittle interfacial crack propagation.

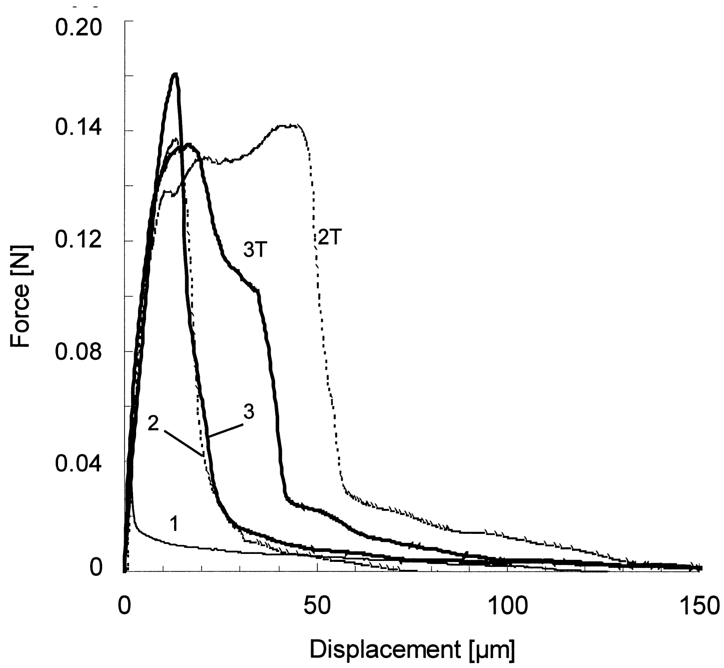

Fig. 6: Pull-out force-displacement curves for PEMS matrices / APS-treated glass fibers. Matrix designations (1, 2, 2T, 3, 3T) are the same as in Table 2.

Polar thermoplastic polymers

As was shown by recent research, acid-base interaction plays an important part in adhesion of polar polymers to reinforcing fibers; its contribution to the total bond strength and work of adhesion can be greater than the contribution of dispersion forces [21, 26)]. Thus, the creation of complementary donor or acceptor groups on the fiber surface should be a basis of interfacial design in this case. Indeed, it was demonstrated for many polar thermoplastic polymers that the bond strength of polymer-fiber joints was proportional to such thermodynamic parameters as the surface free energy or the reversible work of adhesion estimated from wetting [16, 27, 28)] or inverse gas chromatography [21, 26)].

Thus, a change of the work of adhesion after fiber treatment can be used to predict the trend for interfacial bond strength. For example, W_A between glass fiber surface and ABS decreases after fiber sizing with APS (Table 3). The reason for this is a suppression of donor-acceptor interaction between acidic hydroxyl groups on the unsized glass surface and donor groups (nitrile, vinyl, phenyl) of the polymers. The sizing alters substantially the chemical nature of glass fibers: basic amino groups cover the acidic hydroxyl groups of the glass fiber surface [16, 17]. As a result, the interfacial bond strength also decreases upon fiber sizing (Fig. 7). The strength of macrocomposites made from ABS and aminosilane sized glass fibers was lower as compared to that of the composites with unsized fibers (Table 3, [29]).

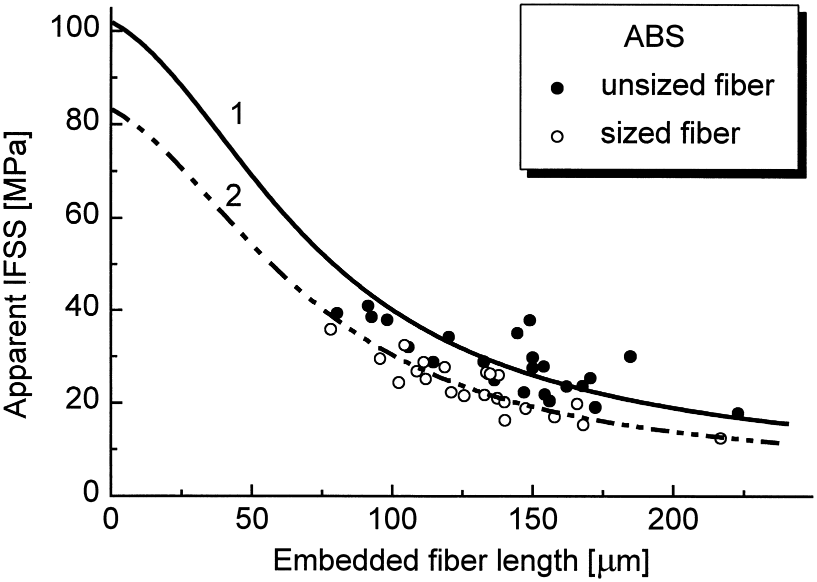

Fig. 7: Apparent interfacial shear strength in glass fiber–ABS systems plotted versus the embedded length: (1) unsized, (2) APS sized fiber. Results of the pull-out test. Lines are approximations of experimental data according to shear lag analysis [21] using the least-squares method.

Molecular weight of the polymer is also very important for interfacial design. In PS/glass fiber systems, the increase in average molecular weight led to enhanced adhesion strength. In contrast to previously reported decrease of adhesion strength when APS-sizing was used [21], already at moderate molecular weights an increase in adhesion strength was found (Table 4). This can hardly be explained by changes in polarity, however, could be due to creation of stronger interphases. Low molecular weight polymers usually fail through brittle cracks. In high molecular weight polymers, this mechanism is inhibited by interdiffusion of chains.

Table 3. Effect of the sizing on the work of adhesion, interfacial bond strength, and strength of short-fiber reinforced composites.

Matrix	Fiber$^{a)}$	W_A (mJ/m^2)$^{b)}$	τ_{app} (MPa)	Tensile strength (MPa)	Flexural strength (MPa)	Impact strength (kJ/m^2)
ABS	unsized	102	31.8	68	101	6.8
ABS	APS	83	22.7	48	81	8.6
PA	unsized	83	24.6	101	172	7.1
PA	APS	73	33.6	128	224	11.2
PA	APS+epoxy	94	51.0	132	231	12.1

$^{a)}$ Fiber content: ABS, 15% [28]; PA, 30% [16, 29].
$^{b)}$ From IGC (ABS), from wetting data (PA) [16].

Table 4. Effect of fiber sizing and molecular weight distribution of the matrix polymer on adhesion strength between polystyrene and glass fibers.

Matrix		Sizing	τ_{ult} (MPa)	τ_{app} (MPa)
M_n (g/mol)	M_w (g/mol)			
20,000	20,000	—	62.4	15.2
140,000	280,000	—	85.9	22.3
140,000	280,000	APS	91.0	23.5
1,800,000	1,800,000	—	96.5	26.1

A further effect of artificially created interphases could be studied by applying a sublayer of acid-terminated polystyrene (TEMPO-method after Fukuda et al. [30]) of different molecular weight onto aminosilane sized glass fibers from 3 wt.% solutions of tetrahydrofurane (similarly to application of film formers during glass fiber spinning). Donor-acceptor interaction in this system occurs between COOH-groups of the sublayer and NH_2-groups from aminosilane. Thus, a precondition for covalent bonds formation was achieved, which resulted in a considerable increase in adhesion strength (Table 5). Adhesion strength appeared to be dependent on the molecular weight of the functionalized PS, and at the molecular weight of M_n = 34,700 a clear maximum was detected. This effect can be due to the competition between interfacial adhesion and strength of the interphase. While the cohesive brittle fracture for smaller molecular weights has a greater influence of the adhesion strength than the adhesive acid-base interactions, the reduced adhesion strength with further enhanced molecular weights of the sublayer can be due to decreased number of acidic groups (end-terminated products).

Table 5. Effect of acid terminated PS sublayers on adhesion strength between polystyrene (M_w = 280,000) and aminosilane sized glass fibers.

Sublayer		τ_{ult} (MPa)	τ_{app} (MPa)
M_n (g/mol)	M_w (g/mol)		
—	—	91.0	23.5
8,000	10,500	95.6	24.9
28,400	39,000	116.9	29.5
34,700	44,200	148.0	44.9
47,800	70,000	107.9	27.8

Thus, acid-base interactions are not the only mechanism for controlling interfacial adhesion and bond strength. It can be seen, for example, from the pull-out data obtained by testing joints of PA

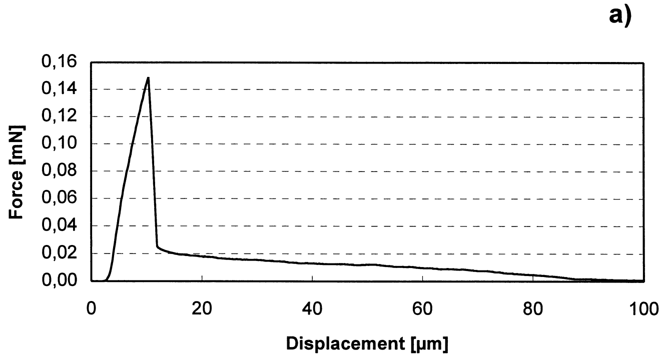

Fig. 8: Typical force-displacement curves from the pull-out test for glass fiber/polymer matrix systems: (a) ABS.

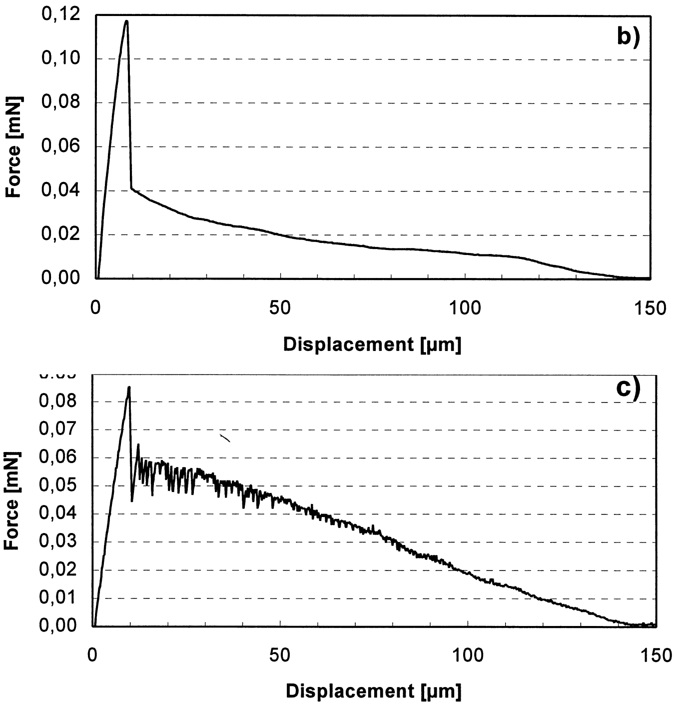

Fig. 8 (continued): Typical force-displacement curves from the pull-out test for glass fiber / polymer matrix systems: (b) PA, (c) PPS.

or PPS with glass fibers. Some reported data on the strength and adhesion in PA-glass fiber systems seem to be contradictory. So, on the one hand, an evident correlation has been found between W_A from wetting data and composite strength for PA with unsized and sized glass fibers [16]. On the other hand, the use of some sizing agents resulted in a decrease of fiber surface energy or W_A, but at the same time the composite strength increased [20, 31]. A similar effect was observed for other thermoplastic polymers [22]. Our experiments have confirmed this discrepancy, which can be seen from Table 3. So, APS sized fiber has lower surface energy as compared to the unsized fiber, while the application of an epoxy-containing layer increases the surface energy drastically [31]. Nevertheless, both treatments improve tensile strength as well as impact resistance of short fiber reinforced PA composites.

The obvious difference in behavior of glass reinforced PA and ABS composites can be explained by the ability of PA of forming transcrystalline region around a fiber when preparing the composites [7, 32]. ABS is an amorphous polymer; in this case, the interfacial bond strength is governed by adhesion, especially by acid-base interactions. Microscopic observations showed that contact failure under loading occurred in adhesional way (through the interface), and post-debonding friction was very low (Fig. 8a). In contrast, transcrystalline layers of PA at glass fiber surface influence the stress transfer, giving rise to composite strength [32]. Adhesion of PA to glass surface is rather high [16, 31], therefore the failure within the transcrystalline interphase is probable. The high post-debonding friction confirms this assumption (Fig. 8b). Sizing glass fiber with APS as well as treatment by epoxy dispersion leads to increase in both interfacial strength and friction (Table 6). As a result, strength of macrocomposites is also enhanced (Table 3).

Table 6. Effect of the fiber sizing on the interfacial shear strength and frictional strength

Matrix	Fiber	τ_{mean} (MPa)	τ_f (MPa)
PA	unsized	24.6	12.2
PA	APS	33.6	18.5
PA	APS+epoxy	51.0	24.2
PPS	unsized	11.8	9.0
PPS	APS	17.5	12.7
vinyl ester	MAS+UPE	67.4	4.2
vinyl ester	PVA	22.5	9.5

Very high post-debonding friction was characteristic of PPS-glass fiber system (Fig. 8c). Sizing the fibers by APS resulted in slight enhancement of bond strength and interfacial friction (Table 6). This effect can not be explained by an increase of adhesion. Indeed, both ABS and PPS possess pronounced donor nature, thus their adhesional interaction with glass surface must decrease after aminosilane fiber sizing. This is the case for ABS, but not for PPS. The reason for this can be the same as for PA composites - namely, formation of a transcrystalline layer around the fibers. Recently, Meretz et al. [33] have shown that the bond strength between PPS and carbon fiber varied in a wide range depending on the thermal conditions of the contact formation. The failure mode changed from ductile to brittle indicating different structures of PPS layers adjacent to fiber surface. It should be mentioned that no fiber sizing was used in that work, so it can be regarded as an example of controlling "natural" interphases between a fiber and a thermoplastic polymer. Similar results were obtained for other thermoplastic polymer joints with carbon and glass fibers: the bond strength and the failure mode appeared to depend considerably on the conditions of adhesional contact formation [27, 34–37].

Table 7. Effect of the fiber sizing on the interfacial characteristics and strength of longitudinal glass fiber/epoxy composites. Fiber content is 50 %.

Fiber	τ_{ult} (MPa)	σ_{ult} (MPa)	Tensile strength (MPa)	Tensile modulus (GPa)	ε (%)	Shear strength (MPa)
unsized	59.7	153	27.3	8.7	0.3	55.2
APS	160.7	326	72.9	8.9	1.0	62.0
APS+PU	84.3	232	49.2	9.3	0.6	55.3
PVAc	51.0	185	24.1	8.2	0.3	54.7

Taking into account good interfacial adhesion of most polar thermoplastic polymers to the glass and carbon surfaces, we can define the aim of interfacial design for this case to be creation of sufficiently thick and strong boundary layers between the fiber and the matrix. Varying temperature and time during the contact formation can be a powerful tool of controlling structure and strength of interphases. In the case of designed interphases introduced between the fiber and the matrix, interdiffusion and post-debonding friction are very important. The friction after debonding plays a great part in the dissipation of the fracture energy preventing a composite from brittle fracture and providing high impact resistance [4].

Thermosetting polymers

Most thermosetting polymers possess very good adhesion to glass and carbon fiber surface, what results in the brittle fracture and low impact resistance of the composites [4]. The increase in interfacial bond strength upon fiber sizing is often followed by deterioration of the strength of macrocomposites [2, 4, 38]. Therefore, the objective of interfacial design in this particular case is different from that for thermoplastic polymers. Interphases are created in epoxy and other thermosetting polymers in a specific way: preferential adsorption on the fiber surface of one component of matrix composition [1, 3, 39, 40] and possible chemical bonding at the interface [1, 39–41] are very important. Control over these processes assumes knowledge of the structure and properties of the formed interphase. Drzal et al. [40] have demonstrated that preferential adsorption and higher diffusivity of amine as compared to epoxy monomer leads to creation of brittle interphases with high modulus at the carbon fiber surface. Recent direct measurements by AFM gave similar result also for glass [2] and copper [3] fibers: the modulus of the interphase was markedly higher than that of the bulk matrix.

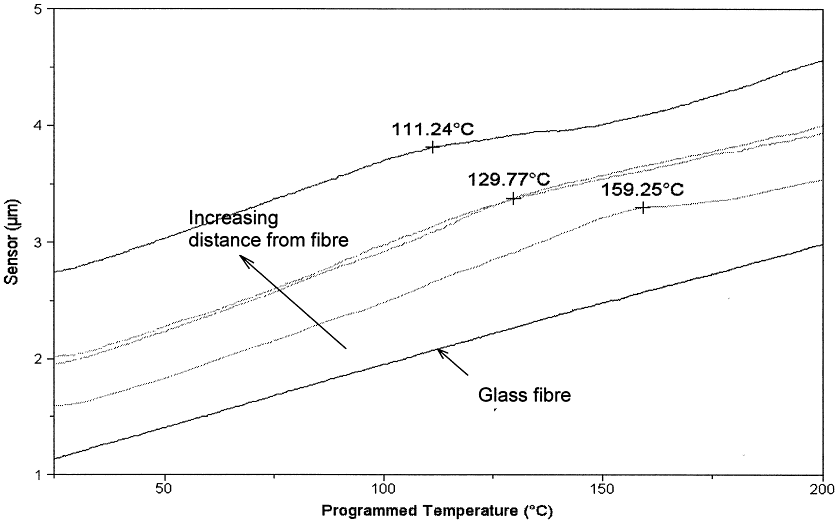

Fig. 9: μTA results for epoxy matrix at the following distances from glass fiber surface: (a) 2 μm, (b) 4 μm, (c) 20 μm.

Sizing of the glass fibers by aminosilane results in a considerable enhancement of interfacial strength [21, 42]. Transverse tensile strength and shear strength of long-fiber composites are also increased (Table 7). The possible reason for this can be covalent bonding between epoxy groups and amino groups on the fiber surface which can act as additional curing agent. Such a chemical interaction at the interface can contribute very much to bond strength: as was shown by Drzal et al. [41], a low (about 3%) chemical bonding increased interfacial strength between epoxy resin and carbon fiber by 34%.

Nevertheless, such an interphase remains very thin (APS does not cover the fiber surface) and brittle [2]. The introduction of designed ductile and flexible interphases which could dissipate fracture energy seems to be more appropriate. With this aim, we used the combined APS + PU coating which could provide good adhesion and is rather ductile under loading. As was shown in our previous work [2], the interphase formed between the epoxy matrix and the sized glass fiber was sufficiently stiff, thus providing good stress transfer through the interface. On the other hand, it appeared to be more uniform and ductile as compared to "natural" interphase for unsized glass fiber, with nearly linear gradient in nano stiffness and in friction coefficient [2].

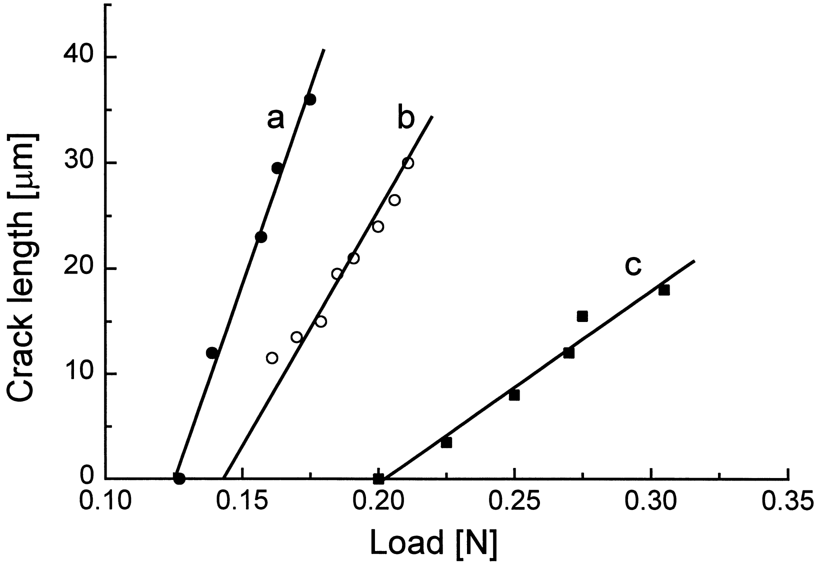

Fig. 10: Experimental relationships between applied load and the crack length from microbond test for glass fiber/epoxy matrix systems. (a) PVAc sizing, (b) unsized fiber, (c) fiber sized with APS.

The particular properties of this interphase can be confirmed by μTA results. Great local differences in the glass transition temperature were found between the interphase (at the distances 2μm and 4μm) from the fiber surface and bulk matrix (Fig. 9). The increase of T_g was 48^0C which is in good agreement with the results obtained by Thomason [5]. He has shown by DMA technique that T_g in thin epoxy layers on the glass fiber is by 44^0C greater than in bulk matrix.

This effect was also described by Lipatov: T_g of PS estimated from IGC data was by 30^{0}C greater in thin layers on the glass surface than in the bulk [8]. This effect is due to interaction between the fiber surface and polymer macromolecules leading to a decrease of segmental mobility and thus to an increase in T_g. In the case of epoxy resin, an additional reason for this is enhanced cross-linking density at the fiber surface.

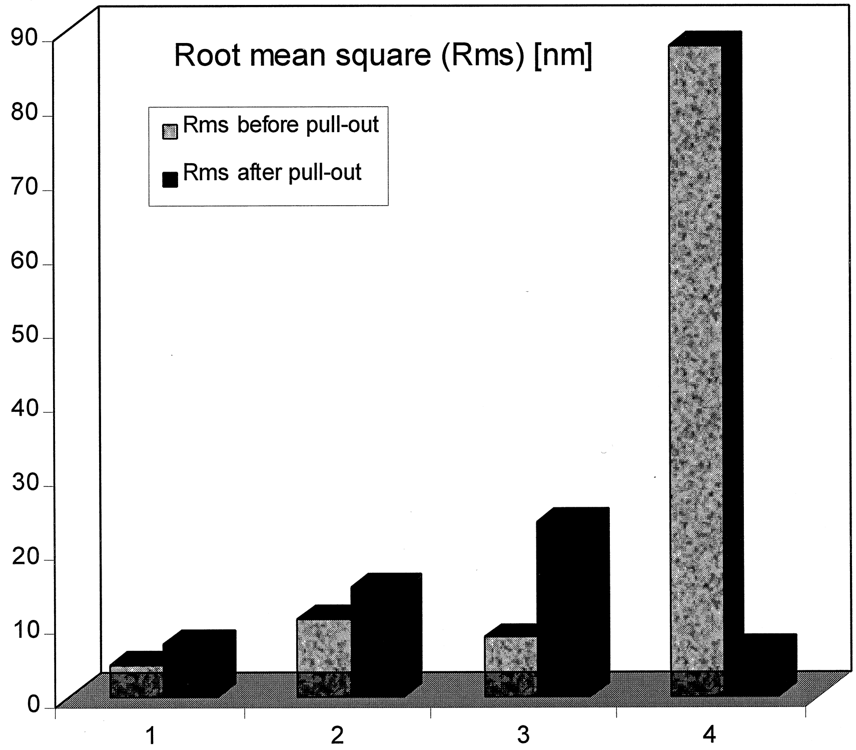

Fig. 11: Roughness parameters (nm) as root mean square (R_{ms}) $R_{ms} = \sqrt{\sum (Z_i - Z_{ave})^2 / N}$ of the glass fiber surface before and after the pull-out test: (1) unsized fiber, (2) APS, (3) APS+PU, (4) PVAc.

It is well known that fiber surface treatments affect the cure kinetics of anhydride- and amine-cured epoxy systems [43, 44]. A similar effect was recently described for the curing of vinyl ester resins on the surface of carbon [39] and glass [1] fibers. It was found that preferential adsorption of some constituents led also in this case to the creation of a "natural" interphase having properties different than the polymer bulk properties. This resulted in low mechanical properties of the composites due to low fiber-matrix adhesion. Application of fiber sizings was found to improve the level of adhesion between the carbon fiber and the matrix 39).

The results of our pull-out experiments also demonstrated the strong dependence of the interfacial strength on the fiber sizing (Table 6). MAS sized glass fibers possess good adhesion to vinyl ester matrix, what can be explained by the ability of silane sizing to accelerate significantly the cure of vinyl ester 1). This cured layer at the fiber surface has evidently a high elastic modulus and thus provides an effective stress transfer. In contrast, application of PVA coating led to decrease in interfacial strength between vinyl ester and glass fiber (Table 6). It should be noted that the failure occurs in this case through the interface; the crack initiation can be seen by a clear kink on the force-displacement curve.

Also a PVAc coating seems to have low adhesion to glass surface; it can be confirmed by the results of pull-out and microbond tests for epoxy matrix (Table 7, 21)). The bond strength between PVAc sized glass fiber and the epoxy resin is low; the crack is initiated at smaller applied force (Fig. 10). Another possible reason for this can be weakness of the formed interphase itself - the ductile PVAc polymer cannot support a sufficiently high level of stress transfer.

The post-debonding friction is low for PVAc sized fibers. The application of APS sizing leads to an increase in the friction after pulling the fiber out from epoxy resin. It can be explained by the changed failure mechanism from pure interfacial debonding to plastic yielding of the matrix followed by cohesive failure within the interphase. This can be confirmed by the roughness parameters of glass fibers determined by AFM in tapping mode before and after pull-out test (Fig. 11). The roughness of APS and APS+PU sized fibers increased after pulling out from the epoxy matrix, what is evidence of a cohesive failure in the interphase. On the contrary, the roughness of the PVAc sized fibers was markedly greater before the test, and than it decreased to the level which was characteristic of unsized glass fibers. Therefore, the failure occurred through the fiber-coating interface.

Hence, in the case of thermosetting polymers particular mechanisms of the interphase formation, especially chemical reactions at the interface, should be taken into account. The introduction of "artificial" interphases is essential for preventing brittle failure. Such interphases should be sufficiently stiff, possess good adhesion to the fiber surface and provide the interdiffusion between matrix and coating.

Conclusion

The possibilities of controlling bond strength between fiber surface and polymer matrix are discussed. The principles of interfacial design are different for the polymers having different chemical nature. Thus, the main issue in the case of non-polar polymers is an increase in the interfacial adhesion. This can be achieved by a chemical modification of the non-polar matrix, what provides acid-base interaction at the interface. Another possibility is the introduction of a reactive polymer sublayer between non-polar matrix and fiber surface.

For polar thermoplastic polymers the interfacial design is based on the controlling over acid-base interactions between fiber and matrix. The morphology of the "natural" interphases plays a great part in these systems. The varying temperature and time of contact formation can change drastically the structure of the boundary layer and affect the interfacial bond strength. The possible formation of a transcrystalline interphase should be taken into account.

In the case of thermoset polymers, preferential adsorption of one component of polymer composition and chemical reactions at the interface are of great importance. The "natural" interphases are often too brittle, therefore an introduction of ductile and flexible sublayers can be regarded as an important tool of the interfacial design. The thickness of the interphase and the possibility of interdiffusion at the matrix/sublayer interface should be taken into account by a fiber coating selection. An acceleration of the curing at the interface and possible chemical reactions between coating and matrix material result in improving interfacial bond strength.

References

1. G. R. Palmese, O. A. Andersen, V. M. Karbhari, *Composites* **A30**, 11 (1999)
2. K. Mai, E. Mäder, M. Mühle, *Composites* **A29**, 1111 (1998)
3. M. R. VanLandingham, R. R. Dagastine, R. F. Eduljee, R. L. McCullough, J. W. Gillespie Jr, *Composites* **A30**, 75 (1999)
4. M. Labronici, H. Ishida, *Composite Interfaces* **2**, 199 (1994)
5. J. L. Thomason, *Composites Sci. Technol.* **44**, 87 (1992)
6. P. F. M. Meurs, P. J. G. Schreurs, T. Peijs, H. E. H. Meijer, *Composites* **A27**, 781 (1996)
7. R. L. Clark Jr, R. G. Kander, B. B. Sauer, *Composites* **A30**, 27 (1999)

8. Y. S. Lipatov, *Physical Chemistry of Filled Polymers,* engl. transl. by R. J. Mosely, Internat. Polym. Sci. and Techn. Monograph No 2 (1977), Moscow
9. V. I. Irzak, L. I. Kuzub, *Composite Interfaces* **4**, 45 (1996)
10. L. E. Asp, L. A. Berglund, R. Talreja, *Composites Sci. Technol.* **56**, 657 (1996)
11. A. Hampe, C. Marotzke, *J. Reinf. Plastics and Compos.* **16**, 341 (1997)
12. M. R. Piggott, Y. Xiong, *Composites Sci. Technol.* **52**, 535 (1994)
13. M. C. Andrews, R. J. Young, J. Mahy, *Composite Interfaces* **2**, 433 (1994)
14. S. Zhandarov, E. Pisanova, K. Schneider, *J. Adhesion Sci. Technol.,* **14**, 381 (2000)
15. S. Zhandarov, V. Dovgyalo, E. Pisanova, *J. Adhesion Sci. Technol.,* **8**, 995 (1994)
16. E. Mäder, K. Grundke, H.-J. Jacobasch, G. Wachinger, *Composites* **25**, 739 (1994)
17. E. Mäder, H.-J. Jacobasch, K. Grundke, T. Gietzelt, *Composites* **27A**, 907 (1996)
18. G. Kalinka, A. Leistner, A. Hampe, *Composites Sci. Technol.* **57**, 845 (1997)
19. J. M. Felix, P. Gatenholm, H. P. Schreiber, *Polymer Composites* **14**, 449 (1993)
20. I. Ulkem, H. P. Schreiber, *Composite Interfaces* **2**, 253 (1994)
21. E. Pisanova, E. Mäder, *J. Adhesion Sci. Technol.,* **14**, 415 (2000)
22. P. H. Harding, J. C. Berg, *J. Adhesion Sci. Technol.,* **11**, 471 (1997)
23. E. Mäder, E. Pisanova, *Polymer Composites,* in press
24. E. Pisanova, E. Mäder, S. Zhandarov, *ICCM-12: Proc. 12 Int. Conf. Composite Interfaces,* paper 419, ISBN 2-9514526-2-4, Paris (1999)
25. S. Schneider, PhD thesis, Technical University Dresden, Germany, 1997.
26. M. Nardin, J. Schultz, *Composite Interfaces* **1**, 177 (1993)
27. P. Bourgeois, T. Davidson, *J. Adhesion* **45**, 73 (1994)
28. Y. L. Zou, A. N. Netravali, *J. Adhesion Sci. Technol.,* **9**, 1505 (1995)
29. S. Y. Fu, B. Lauke, *J. Mater. Sci. Technol.* **13**, 389 (1997)
30. H. Malz, PhD thesis, Technical University Dresden, Germany,1999.
31. H.-J. Jacobasch, K. Grundke, E. Mäder, K.-H. Freitag, U. Panzer, *J. Adhesion Sci. Technol.,* **6**, 1381 (1992)
32. R. L. Clark Jr, M. D. Craven, R. G. Kander, *Composites* **30A**, 37 (1999)
33. S. Meretz, W. Auersch, C. Marotzke, E. Schulz, A. Hampe, *Composites Sci. Technol.* **48**, 285 (1993)
34. E. Pisanova, S. Zhandarov, V. Dovgyalo, *Polymer Composites,* **15**, 147 (1994)

35. M. C. Waterbury, L. T. Drzal, in: *Controlled Interfaces in Composite Materials,* H. Ishida (Ed.), Elsevier Science, New York 1990, p. 731

36. M. C. Paiva, M. Nardin, C. A. Bernardo, J. Schultz, *Composites Sci. Technol.* **57**, 839 (1997)

37. J. Denault, *Composite Interfaces* **2**, 275 (1994)

38. L. Ye, A. Afgani-Khatibi, G. Lawcock, Y.-W. Mai, *Composites* **29A**, 1525 (1998)

39. M. J. Rich, S. Corbin, L. T. Drzal, *ICCM-12: Proc. 12 Int. Conf. Composite Interfaces,* paper 772, ISBN 2-9514526-2-4, Paris (1999)

40. L. T. Drzal, M. Rich, M. Koenig, P. Lloyd, *J. Adhesion,* **16**, 133 (1983)

41. L. T. Drzal, N. Sigura, D. Hook, *Composite Interfaces* **4**, 337 (1997)

42. F. M. Zhao, N. Takeda, K. Inagaki, N. Ikuta, *Advanced Composites Letters,* **5**, 113 (1996)

43. G. R. Palmese, R. L. McCullough, *J. Adhesion,* **44**, 29 (1994)

44. A. Garton, W. T. K. Stewenson, *J. Polym. Sci. Polym. Chem.,* **26**, 541 (1988)