Adhesion between fillers and matrices in composite materials

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Summary

In this paper, the applicability of mixing rules for the mechanical properties of particulate filled energetic composite materials and the role of the surface properties of the single constituents is discussed. A novel structure of mixing rules for the breaking behaviour of the composites is proposed.

1. Introduction

Many modern energetic materials, especially solid rocket propellants, propellant powder grains and PBX explosives have the same structure as composite materials used for engineering construction needs. These materials are a combination of different constituents: a relatively “soft” matrix in which a relatively “hard” filler is dispersed, combining the advantages of the single components in view of the mechanical properties of the composite. In polymeric composites, fillers or reinforcing materials are mainly used for stiffening of the matrix polymer. In energetic materials, the role of the fillers is different. They are used in order to achieve a certain combustion behaviour and to provide the energy content. Of course, they also influence the mechanical behaviour of the composite, but not always in the desired direction.

One main source of problems in composite materials is the interface between the matrix material and the filler surface.

During production of the composites, a good adhesion between the surfaces of the components must be assured, for which a good wetting of the filler surface with the matrix material is an indispensable prerequisite. A weak adhesion between matrix and filler can lead to a detachment of the matrix from the filler surface (dewetting) which can result in a rising sensitivity of the energetic material to shocks and impacts by the formation of “hot spots”.

The breaking behaviour of composites is also strongly influenced by the filler content. High filler contents lead to a severe decrease in the elongation at break. A weak adhesion between matrix and filler can additionally decrease the elongation at break. Cracks in energetic materials however can lead to a catastrophic failure of the whole system.

Adhesion between matrix and fillers is not only dependent on the single material components but also on additives used during production like processing aids, initiators or catalyst, but is also influenced by many production parameters (mixing times, temperatures, curing times and conditions, humidity, shrinkage of the matrix,…).

The adhesion between the matrix material and the filler surface in composites is a central point of interest though very difficult to handle due to the high amount of influencing factors.

The starting point of the ongoing investigation whose so far obtained results are presented in this poster was the question, whether it exists a possibility for the development of a simple measuring method for the prediction of positive or negative effect of parameter changes during the production of composites on the matrix-filler-adhesion by a correlation of mechanical properties of the composites by using the surface properties of the single constituents of the composite.

2. Theoretical Background

As already mentioned, the production process of composite materials must assure a good adhesion between the matrix and the filler surface. The adhesion is dependent on the chemical properties of the partners and the physics involved in the wetting process. Wetting is controlled by the surface properties of the partners and rheology of the mixing process .

2.1 Wetting and Adhesion

The first approach to describe wettability by the macroscopic observable contact angle ϑ as a function of the involved interfacial tensions has been provided by the empirical equation of YOUNG: $\cos \vartheta = (\gamma_{SV}-\gamma_{SL})/\gamma_{LV}$. Here γ_{LV} denotes the surface tension at the interface of liquid and vapor phase, γ_{SL} at the solid-liquid and γ_{SV} at the solid-vapor interface (Figure 1:).

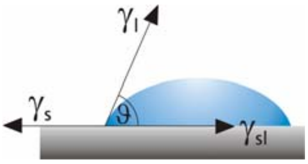


Figure 1: Liquid drop on an ideal flat solid

Since real surfaces are not plane, attention must be paid to the influence of surface roughness on apparent contact angles [Wenzel 1936, Cassie 1944]

Adhesion means the phenomenon when two (e.g. solid) surfaces are held together by interfacial forces (specific adhesion), chemical bonds (chemical adhesion) or interlocking action (mechanical adhesion), or a combination of them. In the case of specific adhesion the forces are of the same type as those which give rise to cohesion.

The thermodynamically derived equation by DUPRÉ introduces the reversible work of adhesion w_a of two phases 1 and 2 and its relation to interfacial tensions: $w_a = \gamma_1+\gamma_2-\gamma_{12}$.

It expresses that the reversible work of separating phase 1 and phase 2 must be equal to the change in the free energy of the system (γ_{XY} are free energies per unit surface area of X-Y interfaces). Under idealized conditions (e.g. ideal flat surfaces, no contributions from chemical or mechanical adhesion, equilibrium conditions, ...) the adhesion force is therefore directly correlated with the contact angels of the materials involved.

In these equations no attention is paid to mechanical and chemical adhesion). Both of them can be influenced by wetting agents and bonding agents which make chemical bonds between the matrix and the filler surface possible.

2.2 Mixing Rules for Mechanical Properties

The bulk properties of the composite materials are the result mainly of the bulk properties of the single constituents and their respective surface properties. Furthermore they depend on the filler content, the shape of the filler particles, the total interfacial area, the presence of processing aids, wetting and bonding agents and the processing parameters.

The well known mixing rules for the estimation of the mechanical properties of composite materials only consider the bulk properties of filler and matrix and the volume fraction of the filler. Mixing rules exist and are commonly used for the prediction of the young´s modulus of composites. For other properties, as the especially for enegetic materials very important breaking behaviour, mixing rules are existing, but they are not really reliable and therefore of no practical importance. The mixing rules describe the properties of the composite as linearly dependent on the filler content. They vary between the properties of the pure matrix and those of the pure filler.

- Explanation of mixing rules and their philosophy

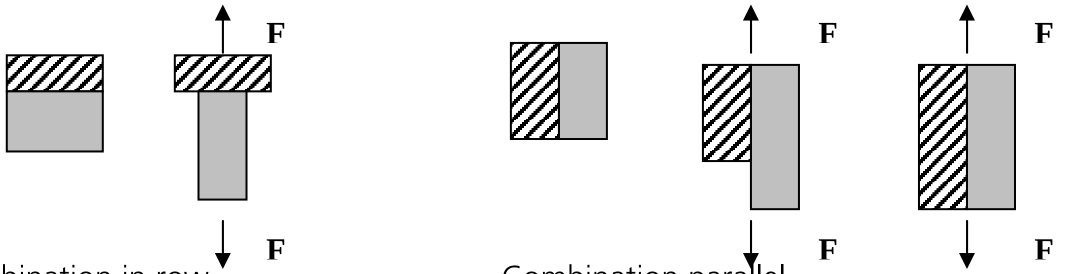
The mixing rules regard the composite as a combination of the constituents of the composite as pure materials as blocks in parallel or in a row. (Figure 2) They are leading to the simple equations [Schmitz 1994, Bourban 1997, Menges 1990]:

Parallel: in case of ideal adhesion $E_C = (1 - V_F) \cdot E_M + V_F \cdot E_F$

in case of non-adhesion $E_C = (1 - V_F) \cdot E_M$

Row: in case of ideal adhesion $E_C = \frac{1}{(1 - V_F)} \cdot E_M$

with E_C: young’s Modulus of compound, E_M: young’s modulus of matrix, E_F: young’s modulus of fiber, V_F: volumetric content of fiber



Combination in row Combination parallel

non-adhesion ideally adhesive

Figure 2: Models for the composites

Due to the fact that the shape of the fillers have a major influence on the mechanical properties of the compound, several authors have extended the simple rules in this respect by introducing shape factors [Takayanagi et al. 1963, Bai 1992, Taprogge 1971, Greco 1994]. For energetic materials, spherical or nearly spherical filler particles are of main interest.

Our intention to carry out this work was to extent the existing mixing rules with respect to surface properties of the constituents.

3. Experimental

The known mixing rules were mainly made for the development of engineering materials with filler contents of technical interest. In order to test the newly developed integration of the surface properties of the constituents of the composite, engineering plastics were used as a starting point for the investigation. Therefore, the following materials were chosen as matrices:

- PP with and without bonding agent
- PC
- HTPB/IPDI

PP and PC were chosen due to their pronounced difference in surface energy. HTPB was chosen as an example for a rocket propellant binder.

As fillers were used

- Glass beads with and without bonding agents
- Glass fibers with and without bonding agents

The thermoplastic composite materials were produced by compounding in an extruder and subsequent injection moulding into dog bone shaped samples. The

HTPB composites were produced by mixing in kneader and subsequent vacuum casting into dog bone shaped samples.

The mechanical properties of the composites were derived in a tensile test. The quality of the matrix-filler-adhesion was observed by SEM of the broken surfaces of the samples.

The surface tensions of the thermoplastic matrix materials were obtained by contact angle measurements and by the pendant drop method.

Some results of contact angle measurements on different glass fibres and matrix materials at room temperature are shown in Table 1 and Table 2:

Table 1: Contact angle measurement

Material	Contact angle [°]		Surface energy [mN/m]		
	water	benzyl alcohol	γ_S^d	γ_S^p	γ_S
Glass fibre PPG 3780 13µm	39,8±3,5	0	10,5	46,5	57,0
Glass fibre PPG 3780 13µm (coated)	55,0±1,4	2,0±2,8	16,8	28,6	45,4
Glass fibre PPG 3299 17µm	63,2±3,0	21,2±9,1	18,2	21,6	39,8
Glass fibre PPG 3242 17µm	57,9±6,6	25,7±5,9	14,0	28,6	42,6
Glass fibre PPG 3242 10µm	61,9±3,1	30,3±4,4	14,4	25,2	39,6
Polypropylene (Dow 705-44)	96,7±1,2	35,9±1,6	37,1	0,6	37,7
Polybond 3200	103,9±0,9	27,4±3,1	49,9	0,2	50,1
Polycarbonate (Makrolon 3208)	84,3±4,7	32,0±1,0*	41,6	1,8	43,4

* Diiodomethane

Table 2: Results of pendant drop measurements at 230°C:

Material	Surface tension [mN/m]*
Polypropylene (Dow 705-44)	20,0
Polybond 3200	21,9

* density at 230°C is circa 0,9 g/cm³

The contact angle measurements were performed at room temperature with at least two pure liquids (e.g. distilled water and benzyl alcohol or diiodomethane). The surface energies were calculated from contact angles using the model of OWENS-WENDT [Owens 1969], which separates dispersive (upper index d) and polar (upper index p) contributions to intermolecular forces:

$$\gamma_{SL} = \gamma_S + \gamma_L - 2\left(\sqrt{\gamma_S^d \gamma_L^d} + \sqrt{\gamma_S^p \gamma_L^p}\right)$$

$$(1 + \cos\vartheta)\gamma_L = 2\left(\sqrt{\gamma_S^d \gamma_L^d} + \sqrt{\gamma_S^p \gamma_L^p}\right)$$

The pendant drop measurements were conducted in a heat chamber at temperatures above the glass transition point of the materials (~250°C). The surface tension of the polymer melt was calculated by analyzing the drop shape with the software DSA II (Krüss).

The surface energies of glass fibers were calculated from contact angle data which were obtained from measurements with a single fiber tensiometer.

The surface energies of the filler particles were calculated as previously describes from contact angle data. The contact angles in turn were calculated by using the WASHBURN equation from sorption measurements with different liquids on the tensiometer K12 (Krüss):

$$\cos \vartheta = \frac{m^2}{t} \cdot \frac{\eta}{\rho^2 \cdot \gamma_L \cdot C}$$

t: time; m: sample weight; η: viscosity of liquid; ρ: density of liquid; γ_L: surface tension of liquid; ϑ: contact angle between liquid and solid surfaces; C: capillarity constant

In this equation η, ρ and γ_L are known parameters, t and m are obtained on measuring and ϑ and C must be determined.

4. Results

- Influence of filler content on modulus / on break

As predicted by the mixing rules, the modulus rises with filler content, whereby the particle size distribution has a severe influence. Bimodal particle size distributions lead to a decrease in modulus at the same filler content compared to a monomodal particle size distribution. For the elongation at break, the same dependencies hold.

- The Influence of shape of filler particles on modulus / on break

The influence of the shape of the filler particles can exemplarily be seen in Figure 3. The glass fibers lead to a severely higher modulus of the composite than the glass beads at the same filler content.

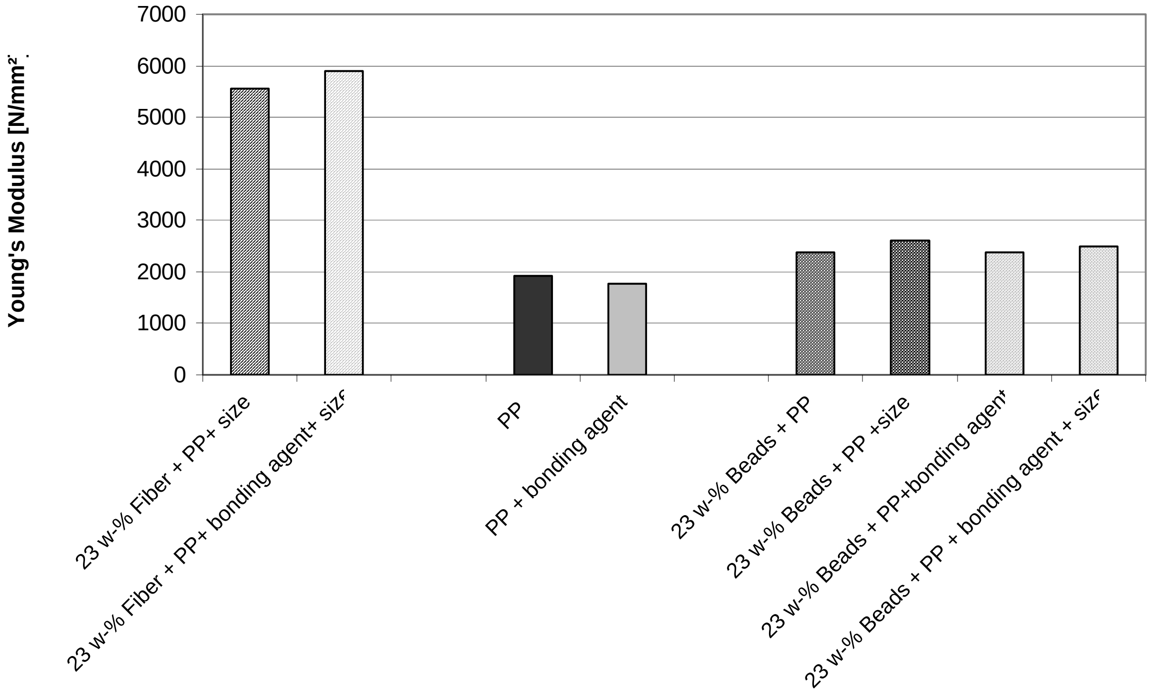


Figure 3: Young´s Modulus of different PP composites

- Influence of bonding agents on modulus / on break

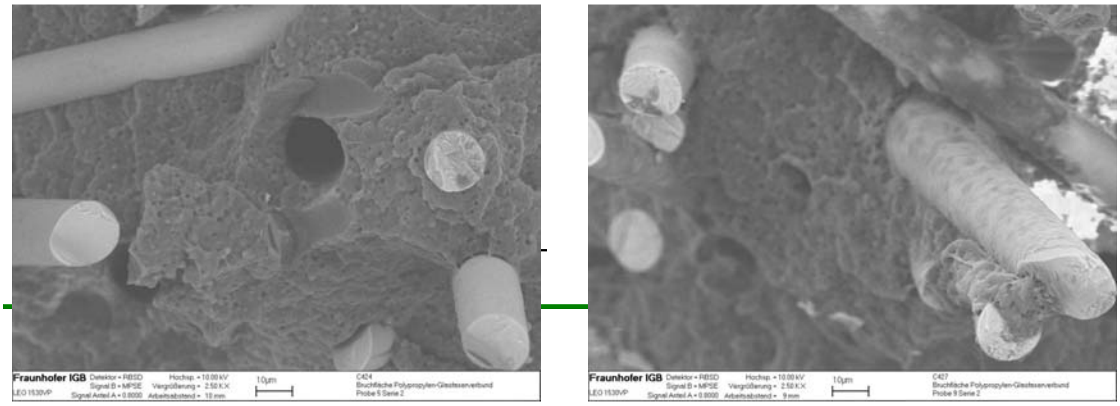
The modulus of the composites appeared to be minor changed with the use of bonding agents. This can be explained with the fact, that the modulus is determined at low elongations where the detachment of the matrix from the filler surface plays no important role even at higher filler contents. In this area of elongations, the compressional forces of the matrix on the filler surface, due to shrinking processes during the production of the material (curing and cooling) may be essential in view of a hindering of detachment processes.

The force and the elongation at break are strongly dependent on the adhesion of the matrix to the filler surface (Table 3,

Figure 4). The better the adhesion, the higher the breaking forces and the breaking elongations.

Table 3: Break properties of PP-composites

Material	ε_{Br} [%]	σ_{Br} [N/mm²]	Adhesion SEM-picture
PP	19,2	7,9	
PP + bonding agent	21,7	9,0	
23 w-% fiber + PP + size A	1,8	38,4	no adhesion



23 w-% fiber + PP + size A

23w-% fiber + PP + bonding agent+ size A

Figure 4: SEM pictures of fibers with and without bondig agent

- Correlation between surface properties and mechanical properties

As explained above, the modulus is mainly affected by the shape of the filler particles and therefore by the specific surface area of filler. The surface properties and the adhesion between matrix and filler surface influences mainly the breaking properties of the composite.

5. Modelling

A mixing rule for the modulus comprising the specific surface area and a shape factor of the filler is sufficient for an estimation of the modulus of a compound in the case of a monomodal size distribution of the filler particles. For bi- or multimodal size distributions, a special attention must be paid to the distribution of coarse and fine particles.

In this work, an advanced mixing rule for breaking properties of particle filled composites comprising the specific surface area of the filler and the surface properties of the constituents of the composite is proposed. This rule has the form:

$\sigma_{Break.C} = f(\sigma_{Break.M}$; filler content; filler shape; γ_M ; γ_F)

$\varepsilon_{Break.C} = f(\varepsilon_{Break.M}$; filler content; filler shape; γ_M ; γ_F)

6. Conclusions

In this investigation, the structure for an advanced mixing rule for the breaking properties of a composite material consisting of a relatively weak matrix with relatively strong filler particles was developed, that takes the surface energies of the constituents and therefore the adhesion between them into account.

The main problem with the application of the new mixing rules is the proper determination of the surface properties of the fillers and a proper correlation between the surface energies and the quality of adhesion.

Further work remains to be done in view of an improvement of the measurement methods for the determination of the surface properties of the fillers and a broader data base must be established for a verification of the new mixing rules.

7. Literature

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