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Composition dependence of tensile yield stress in filled polymers

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Filled polymers are the simplest type of composite polymeric materials, which consist of a matrix polymer as a continuous phase and a generally inorganic filler dispersed in the matrix. These materials are practically isotropic, if the geometry of the filler particles is isotropic too, or if no orientation of anisotropic fillers occurs during processing.

Fillers are applied to modify various properties (mechanical, electrical, etc.) of polymers or, simply as extenders for lowering the price/volume ratio of the material. In any case, it is essential to know the dependence of the properties on the composition (i.e. on the filler content expressed as volume fraction, φ) in order to achieve an optimum with respect to the desired objective.

Among the mechanical properties yield stress of the composite (σ_{yc}) has primary importance, giving information on the maximum allowable load without considerable plastic deformation. The yield stress of a composite depends, however, in a very complex way on the microstructure (including the interfacial structure), since the load transfer between the phases and also the stress concentration is determined by structural factors (form and size distribution of the filler, its spatial distribution in the matrix, thickness of the interface etc.). It is not surprising that theoretical analysis of simple models gives no satisfactory description of the yield stress as a function of the composition.

In the case of zero adhesion between the filler particles and the continuous polymer phase there is no load transfer to the filler and the total load is carried by the matrix. The composite yield stress depends on the effective load bearing cross-section $1 - \psi$, which is the minimum value of matrix area in the cross-section perpendicular to the load direction:

$$\sigma_{yc} = (1 - \psi)\,\sigma_{yp} \qquad (1)$$

The yield stress of the matrix – as there is no interaction between the two phases – is the same as that of the unfilled polymer, σ_{yp}.

Clearly, the integral mean value of the filler area fraction in the cross-sections, $\bar{\psi}$, is equal to the filler volume fraction φ. The maximum value, ψ, can be given only in probability terms which, however, cannot be expressed easily in an explicit form. To avoid this, simple models were developd. Nicolais and Narkis [1] assumed that in a probe of unit length and cross-section, containing n^3 evenly distributed spherical particles of the same size, the maximum area of filler in the sections containing the centres of n^2 particles,

$$(1 - \psi) = 1 - \left(\tfrac{3}{4}\right)^{2/3} \pi^{1/3} \varphi^{2/3} = 1 - 1.21\,\varphi^{2/3} \qquad (2)$$

This model, however, includes the assumption that the matrix cross-section is zero at a filler volume fraction less than 1, justified by the fact that at a certain filler content, where the matrix loses its continuity (at the maximum packing fraction, φ_{max}) the strength of the composite becomes very low. Still in reality, the cross-section of the matrix can be zero only at $\varphi = 1$.

To avoid such contradictions, we have chosen a simple hyperbolic function, going through the points $\varphi = \psi = 0$ and $\varphi = \psi = 1$ to describe the change of the effective cross-section as a function of filler content:

$$(1 - \psi) = \frac{1 - \varphi}{1 + A\,\varphi} \qquad (3)$$

Equation 3 contains the adjustable parameter A. The value of A may be determined for systems with known φ^* and ψ^* values, according to the following expression:

$$A = \frac{\psi^* - \varphi^*}{(1 - \psi^*)\,\varphi^*} \qquad (4)$$

Values of φ^* and ψ^* are available for various close packings of spherical particles. In the case of hexagonal close packing the volume fraction φ^* is equal to 0.740 and the maximum filled area in a plane section ψ^* is 0.907, corresponding to the hexagonal close packing of circles in a plane. The values of A is then 2.427. For a face centred cubic packing the corresponding values are $\varphi^* = 0.524$, $\psi^* = 0.785$ and $A = 2.318$.

Since the packing of the fillers depends on both particle shape and particle size distribution and can vary from sample to sample, we have chosen $A = 2.5$ as an approximate upper limit. Thus, the composite yield stress can be given in the form:

$$\sigma_{yc} = \frac{1 - \varphi}{1 + 2.5\,\varphi}\,\sigma_{ym}(\varphi) \qquad (5)$$

where $\psi_{ym}(\varphi)$, which formally corresponds to the matrix yield stress, is a function of the filler volume fraction.

The dependence of σ_{ym} on φ is often neglected, but in most cases deviations occur from the simple equation of Nicolais and Narkis [1], which takes into consideration only the decrease of the effective load bearing cross-section. These deviations were explained by stress concentration effects [2], by the reinforcing effect of anisotropic filler particles [3], or by other factors [4]. To study the dependence of $\sigma_{ym}(\varphi)$ on the filler content the quantity $\sigma_c\,(1 + 2.5\varphi)/(1 - \varphi)$ was plotted as a function of φ for 25 different polymer/

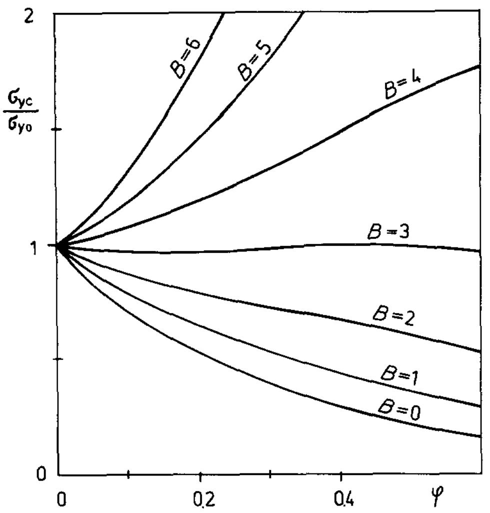

Figure 1 The change of relative composite yield stress as a function of filler volume fraction calculated for various values of the parameter *B*.

filler systems. Both literature data and results of our own measurements were included. It was found, that in many cases an approximate linearity exists, but generally a linear dependence of σ_m on φ can be observed. Somewhat unexpectedly this dependence was best described by the exponential function, resulting in the following general expression:

$$\sigma_c = \frac{1-\varphi}{1+2.5\,\varphi}\,\sigma_0 \exp\{B\varphi\} \qquad (6)$$

Fig. 1 shows the calculated relative composite yield stress σ_{yc}/σ_{yo} as a function of the filler volume fraction for various values of the constant *B*.

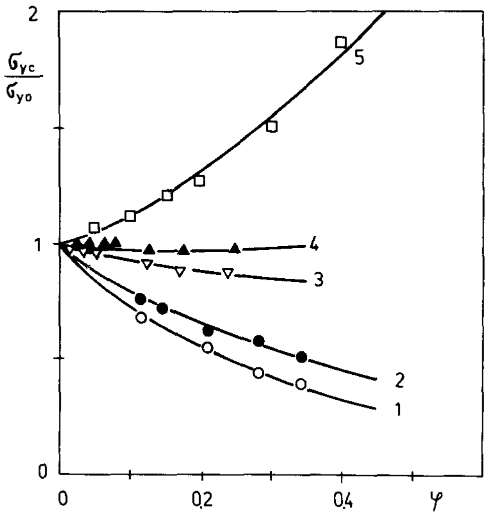

Figure 2 Normalized yield stress values, σ_{yc}/σ_{yo} as a function of the filler volume fraction φ for different polymer/filler systems. (1) ABS/glass beads [5], (2) ABS/glass beads, surface treated [5], (3) polypropylene/wollastonite [3], (4) polypropylene/talc [3], (5) LDPE/$CaCO_3$. Full lines were calculated with the following values of the parameter B = 0.246, 1.059, 2.537, 3.010 and 4.512.

Equation 6 was fitted to the experimental data by minimizing the sum of squared relative differences in σ_{yc}, giving an estimation for the parameters σ_{yo} and *B*. The fit was generally very good, the mean value of relative differences between measured and computed values of composite yield stress being typically 1 to 2%. In most cases, the parameter σ_{yo} was equal to the yield stress of the pure polymers σ_{yp} within the experimental error.

The universality of Equation 6 is remarkable if one

TABLE I Matrix type, filler characteristics and parameters (σ_0, *B*) of composite yield stress calculated from Equation 6

Polymer type	Filler				σ_0 ($N\,mm^{-2}$)	*B*	$\bar{\Delta}$* (%)	Reference†
	Type	Shape	Size (μm)	Specific surface ($m^2\,g^{-1}$)				
ABS	Glass beads	Sphere	12.7–38.1		29.76	0.246	1.17	5
PP	$CaCO_3$	Sphere	58.4	0.5	33.26	0.791	0.70	
ABS	Glass, treated	Sphere	12.7–38.1		29.20	1.059	1.28	5
PP	$CaCO_3$	Sphere	3.6	2.2	33.12	1.189	0.17	
PP	Glass	Sphere	105		39.42	1.351	1.16	6
PP	$CaCO_3$	Sphere	8.6	2.4	30.79	1.610	2.93	
PP	Glass	Sphere	< 15		29.46	1.708	0.53	3
PP	$CaCO_3$	Sphere	1.1	8.1	32.97	1.859	0.33	
PP	$CaCO_3$	Sphere	0.08	16.5	33.44	1.859	0.81	
PP	$CaCO_3$	Sphere	1.6	5.0	33.02	1.932	0.56	
PP	Silica	Sphere	0.6	18.4	32.84	2.073	0.43	
PP	Wollastonite	Fibre	length < 10		30.32	2.537	0.28	3
PP	Talc	Plate	13.6	3.0	33.62	2.566	0.91	
PP	Talc	Plate	5.7	5.9	34.06	2.692	1.08	
PP	Talc	Plate	2.8	8.4	33.66	2.753	0.69	
PP	Talc	Plate	12/1–4‡		32.14	3.010	0.77	3
HDPE	$CaCO_3$	Sphere	3.5	1.2	26.18	3.348	0.25	
HDPE	Talc	Plate	13.6	3.0	25.88	3.926	0.44	
LDPE	$CaCO_3$, treated	Sphere	1.1		8.14	4.249	2.10	
LDPE	$CaCO_3$	Sphere	3.6	3.3	8.17	4.345	1.28	
LDPE	$CaCO_3$	Sphere	3.5	1.2	7.83	4.477	0.62	
LDPE	$CaCO_3$	Sphere	3.5	1.2	8.21	4.512	0.72	
LDPE	$CaCO_3$	Sphere	3.6	2.2	7.91	4.525	1.23	
PP	SiO_2	Sphere	0.04		42.62	5.702	1.07	6
PP	SiO_2	Sphere	0.007		44.6	6.474	2.37	6

*Mean value of relative differences between measured and computed values.
†Our own results, where no reference is given.
‡Length 12 μm, thickness 2–4 μm.

takes into account the diversity of the composites investigated. The polymers were various types of polyethylene, polypropylene and ABS thermoplastics, the yield stress, σ_{yp} ranging from 8 to 40. Even more diverse were the fillers: many types of $CaCO_3$ differing mainly in the particle size, particle size distribution and specific surface; silicas (some of them having very small particle sizes), but also spherical glass beads, acircular wollastonite fibre and lamellar talc. Some of the curves calculated with fitted parameters are shown in Fig. 2 together with the measured values. All the determined σ_0 and B values of the investigated systems as well as the most important characteristics of the fillers are compiled in Table I.

In the validity domain of Equation 6 the polymer/filler pairs are characterized essentially by the value of the parameter B. Although B has no direct physical meaning it is obviously connected with the interfacial properties of the given system and also depends on the yield stress of the matrix. This becomes evident if we study the data of Table I. For the ABS polymer filled with glass beads $B = 0.246$ was determined, approximating the "no adhesion" case. Surface treatment, which increased the adhesion between the phases, resulted in a higher $B = 1.059$ value. In a series of polypropylene composites filled with various types of $CaCO_3$, B varied between 0.791 and 1.932, showing a loose correlation with the specific surface and in another series, where extremely small SiO_2 particles were incorporated into a PP matrix, the B values were higher than 6. It is also very interesting to note that Equation 6 equally applies to composites containing anisotropic particles (see Fig. 2 and Table I). These examples give a hint to the applicability of this parameter in studying interactions at polymer/filler interfaces.

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