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An investigation on the tensile strength of particulate filled polymeric composites

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The validity of a semi-empirical equation previously developed for the yield strength evaluation of particulate composites is extended to predict the ultimate tensile strength of composites that do not show large macroscopic plastic behaviour. A good correlation is obtained between the theoretical values derived from the equation proposed and the experimental results from composites filled with both surface treated and untreated particles. A dimensionless parameter related to the filler–matrix interface is obtained and used to judge how effective a surface treatment is in order to enhance the mechanical properties of several particulate filled composites. © *1998 Chapman & Hall*

1. Introduction

Particulate filled polymeric composites are extensively used in many industrial applications. From a technological point of view these composites are well established because they are easy to fabricate. Nevertheless, prediction of the resulting properties of the composites can be a very complex problem, due to the many variables that play definite roles upon the mechanical behaviour of these materials [1]. In order to predict their mechanical behaviour not only the intrinsic properties of the resin and filler and the volume fractions of both constituents are important, but geometrical factors such as filler aspect ratio, particle size and mean interparticle distance are also important parameters to be taken into account [2].

Many authors have dealt with this problem and two recent articles review, respectively, the existing theories to predict the mechanical properties [3] and the effects of the above-cited geometrical parameters [4] on the mechanical behaviour of particulate filled resin matrix composites.

The existent theoretical models provide quite satisfactory bounds for the composite modulus [3]. Ultimate strength predictions are less rigorous, in part due to the role played by filler–matrix adhesion [3]. Although interfacial adhesion between the matrix and filler is of primary importance for load transfer between these phases, it is a parameter difficult to measure. In that way, filler–matrix adhesion is often inferred only qualitatively by examining the interfacial aspects at fracture surfaces or simply by measuring whether or not the mechanical properties of the composite are greater than those of the matrix.

In an attempt to obtain a more rigorous approach to describe quantitatively the compositional dependence of tensile yield stress in filled polymers, Turcsányi *et al.* [5] proposed a semi-empirical relationship that successfully fits the experimental data of many different composites. Their equation is particularly interesting due to a dimensionless parameter, B, which is directly related to filler–matrix adhesion and can be used to characterize the interfacial adhesion in a more quantitative way [5].

In this paper it is shown that the relationship obtained by Turcsányi *et al.* [5] can be also extended to describe the ultimate tensile strength of a series of particulate composites. Values of the B parameter were obtained for the composites tested and used to judge whether or not a surface treatment efficiently enhanced filler–matrix adhesion.

1.1. Strength of particulate filled polymers

The semi-empirical equation derived by Turcsányi *et al.* [5] is

$$\sigma_{yc} = \frac{1-\Phi}{1+A\Phi}\,\sigma_{ym}\exp\{B\Phi\} \qquad (1)$$

were σ_y is the yield stress and Φ the filler volume fraction. The subindexes c and m stand for composite and matrix, respectively. A is a shape parameter, related to the packing distribution of the filler and can be calculated by [5]

$$A = \frac{\psi-\varphi}{(1-\psi)\varphi} \qquad (2)$$

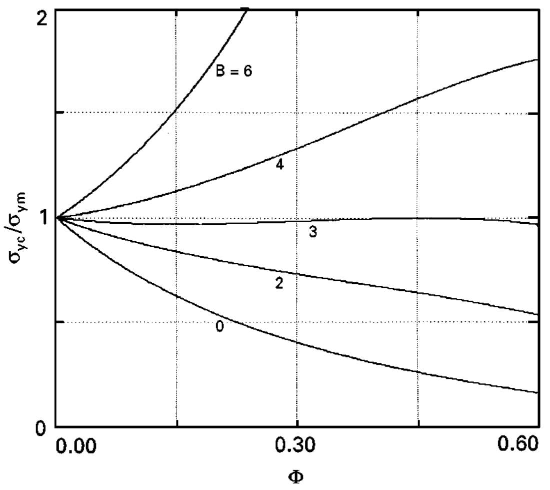

Figure 1 Variation of the yield stress ratio as a function of volume fraction for different values of B. The value of the shape parameter, *A*, was taken to be 2.5 [5].

where ψ and φ are, respectively, the maximum area and volume fractions that can be filled by the particles. For spherical particles the value of *A* is close to 2.5 for both hexagonal closed packed and face centred and simple cubic structures [5].

B is the parameter involved with the filler–matrix interface properties and is particular to each filler–matrix pair. If B = 0 the filler acts as as void. No adhesion and no stress transfer take place at the filler–matrix interface. The influence of the B parameter can be best visualized by rearranging Equation 1 and plotting the yield stress ratio, σ_{yc}/σ_{ym}, as a function of the volume fraction, Φ. The variation obtained is shown in Fig. 1. For values of $B \leqslant 3$ the filler–matrix interface is weak and no reinforcing effect is obtained.

Equation 1 is also believed to be applicable to model the ultimate tensile strength, σ_u, of the composites if σ_u is used instead of σ_y. Such an approach can be looked upon as valid whenever the composite does not show a gross macroscopic yield deformation. That is, the composite fails in a brittle manner without a definite yield point or it shows small plastic deformation. This approach is, in reality, much the same of that used for the Tsai–Hill failure criterion [6], which is an extension of the Hill yielding criterion for metals. In the former criterion the yield strengths used for the latter one are skillfully replaced by the ultimate strengths of the more brittle composite materials.

In order to verify the above-mentioned statement, composites with four different polymer matrices and with several fillers were tested in tension.

2. Experimental procedure

The composites were made with volume fractions of filler ranging from 4 to 25%. Four thermoplastic polymers were used as a matrix, namely, polypropylene (PP) and low (LDPE), medium (MDPE) and high density (HDPE) polyethylene. The fillers used were calcium carbonate, atapulgite, sepiolite and short length sisal fibres. The fibres had a mean length of 3 mm. The other fillers were sieved and only the fraction under mesh 200, i.e. with a mean size less than 75 μm, were used.

TABLE I Composites analysed

Matrix	Filler
PP	Atapulgite, atapulgite + KRTTS
LDPE	Atapulgite, $CaCO_3$, atapulgite + silane, sepiolite + HA
MDPE	Atapulgite
HPDE	Atapulgite, $CaCO_3$, atapulgite + silane, sisal

In order to vary the adhesion between filler and resin, atapulgite filled composites were also made with surface treated particles. The surface treatment agents employed were γ-aminopropilmetoxysilane and isopropil-triisoestearoil titanate (KRTTS). Both were used at a concentration of 1% by weight. The sepiolite particles were treated with a solution of hydrochloric acid (HA). Table I shows the complete set of composites produced.

Before their incorporation in the matrix, the fillers were dried for 48 h at 110 °C. The composite formulations were tumble mixed for 45 min at room temperature before being compounded at 180 °C using a roll-mill with a 1 : 1 : 2 friction ratio. The material was ground and dog-bone tensile specimens having, on average, 3.2 mm thickness, 12.6 mm width and a gauge length of 70 mm, were compression moulded.

The specimens were tested according to the ASTM D638 standard, on a mechanical driven testing machine operating at a constant crosshead velocity of 50 mm min^{-1}. With that velocity of testing the strain rate initially imposed on the specimens was of the order of $10^{-2}\,\text{s}^{-1}$. As shown by contours of constant strain rate [7] for similar thermoplastic polymers, the strain rate used seems to be high enough to suppress, at least partially, the plastic deformation ability of the resin matrices used in this work. In that manner the specimens will fail preferably on a brittle mode, satisfying the boundary condition set in Section 1.1.

The morphological aspects of the filler–matrix interface of each particular composite were observed by scanning electron microscopy (SEM). The fracture surfaces analysed were gold or carbon sputtered and observed with secondary electrons imaging at 15–20 kV.

3. Results and discussion

The experimental values obtained for the tensile strengths of all the composites tested are shown in Tables II–V. As can be seen, a wide range of filler–reinforcement behaviour and filler–matrix interaction was obtained.

The treated and untreated atapulgite acts effectively as a reinforcement in LDPE and MDPE matrix composites. Only a second-order reinforcement effect, if any, is seen with PP and HDPE matrices. Sepiolite treated particles also act as an effective reinforcement for the LDPE matrix, but with a slighter effect than that of atapulgite. The calcium carbonate filler showed

TABLE II Tensile strength (MPa) of PP composites

Volume fraction	Atapulgite	Atap. + KRTTS
0	29.7	29.7
4.2	32.4	33.1
8.9	31.0	32.2
14.4	31.7	31.6
20.7	30.9	30.6

TABLE III Tensile strength (MPa) of LDPE composites

Volume fraction	Atapulgite	Atap. + silane	Sepiolite+ HA	Volume fraction	$CaCO_3$
0	10.3	10.3	10.3	0	10.3
4.3	11.0	11.8	10.9	3.7	11.0
9.1	12.4	13.6	12.0	8.0	10.9
14.7	14.3	15.0	14.4	12.9	11.1
21.1	15.5	16.8	–	18.7	11.8

TABLE IV Tensile strength (MPa) of MDPE composites

Volume fraction	Atapulgite
0	13.6
4.3	14.0
9.2	15.1
14.8	15.9
21.3	16.7

TABLE V Tensile strength (MPa) of HDPE composites

Volume fraction	Atapulgite	Atap. + silane	Volume fraction	$CaCO_3$	Volume fraction	Sisal
0	30.4	30.4	0	30.4	0	30.4
4.4	28.5	29.1	3.8	26.7	6.8	25.8
9.3	31.0	31.0	8.2	23.2	10.4	25.0
15.0	32.2	32.8	13.2	20.2	14.1	24.3
21.6	31.4	32.3	19.2	18.0	24.7	20.6

little reinforcement effect with LDPE and has, really, a void-like effect in the HDPE composite. Sisal fibres had a deleterious effect upon the tensile strength of HDPE composites.

The experimental results were fitted with the modified Equation 1, allowing the shape parameter, A, the B parameter and also the ultimate matrix strength, σ_{um}, to be the adjustable variables. The results obtained with the fitting procedure are shown in Figs 2–5. The values obtained for the parameters adjusted, as well as the correlation coefficients, r, are shown in Tables VI–VIII. As shown in Fig. 2, the adjusted curve for the PP matrix composites do not match with the experimental data. Therefore, the parameters adjusted to the modified Equation 1 for the PP matrix composites are not shown in Tables VI–VIII.

As is shown in Figs 2–5 the assumption that Equation 1 could be rearranged in order to model the ultimate tensile strength is valid when the composite

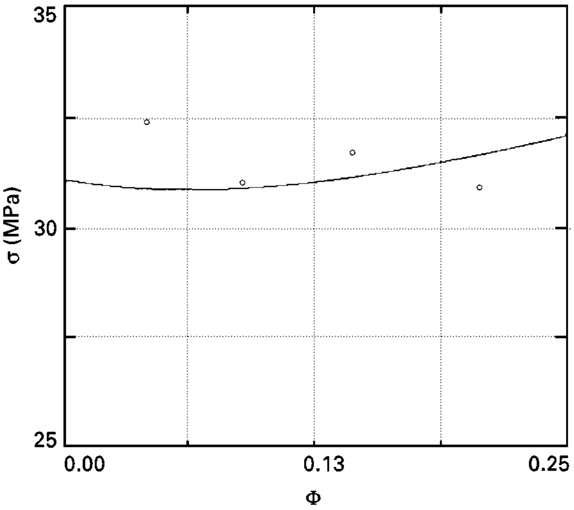

Figure 2 Fitting procedure for PP composites exhibiting macroscopic plastic deformation (there is no correlation between the experimental points and the modified Equation 1; the experimental points for both composites tested are very close and merge together at the scale used).

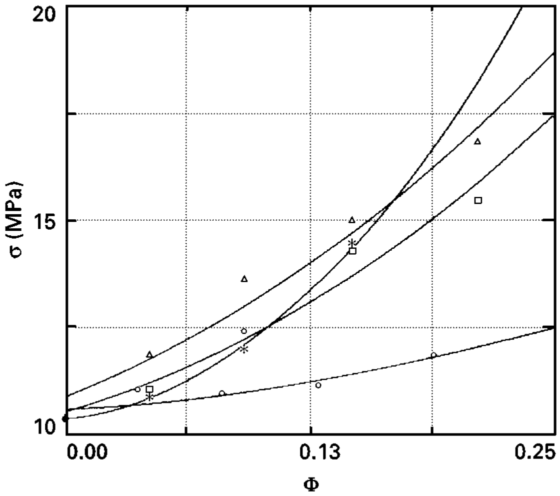

Figure 3 Fitting procedure for LDPE composites (a good correlation was obtained between the experimental points and the modified Equation 1): (□) atapulgite, (△) atapulgite + silane, (○) $CaCO_3$, (∗) Sepiolite + HA.

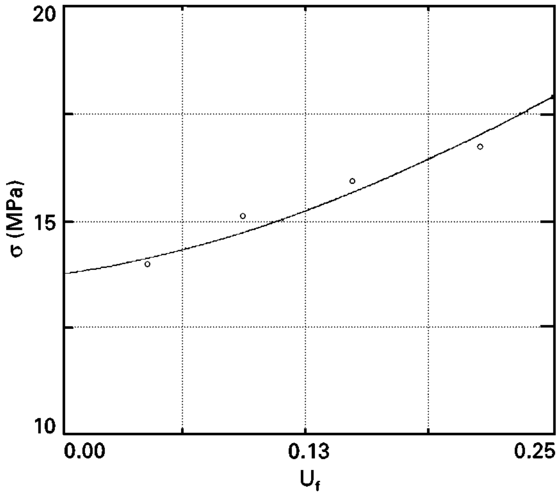

Figure 4 Fitting procedure for an atapulgite filled MDPE matrix composite.

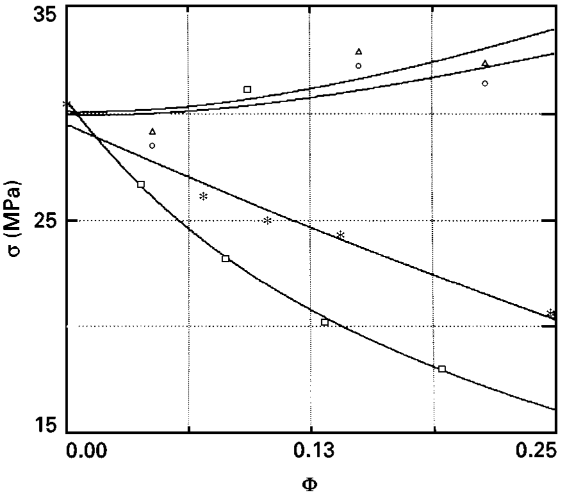

Figure 5 Fitting procedure for HDPE composite (correlation between the experimental results and the modified Equation 1 was good for both particulate filled as well as for short fibre composities): (O) atapulgite, (△) atapulgite + silane, (□) $CaCO_3$, (*) sisal.

TABLE VI Values of the parameters adjusted to the modified Equation 1 for LDPE

Parameters	Atapulgite	Atap. + silane	$CaCO_3$	Sepiolite + HCl
σ_{um}, MPa	10.49	10.85	10.54	10.31
A	3.26	2.66	2.72	6.57
B	5.57	5.41	3.89	7.94
r	0.984	0.983	0.910	0.999

TABLE VII Values of the parameters adjusted to the modified Equation 1 for MDPE

Parameter	Atapulgite
σ_{um}, MPa	13.78
A	2.95
B	4.39
r	0.976

TABLE VIII Values of the parameters adjusted to the modified Equation 1 for HDPE

Parameters	Atapulgite	Atap. + silane	$CaCO_3$	Sisal
σ_{um}, MPa	29.91	30.09	30.48	29.45
A	2.49	2.85	4.73	0.58
B	3.45	3.78	1.70	0.21
r	0.630	0.786	0.999	0.978

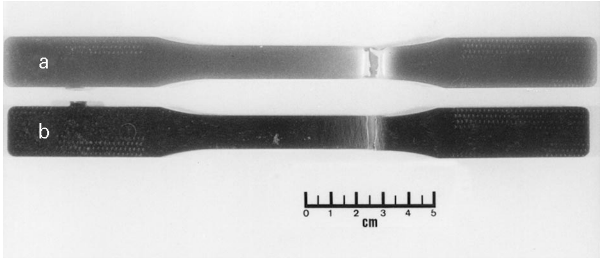

Figure 6 Macroscopic aspects of fractured specimens: (a) typical polypropylene failure, showing large macroscopic plastic deformation; and (b) polyethylene failure, where the specimens do not show large plastic deformation.

does not show a gross yield behaviour. Under the test conditions used in this work, the PP based composites were the only ones that showed large plastic deformation. Fig. 6 shows the average macroscopic aspect of the test specimens for the polypropylene matrix composites and for polyethylene matrix composites. Therefore, as expected, the experimental data obtained for the PP composites could not be fitted with the model proposed, as the primary boundary condition sat is not satisfied.

Other interesting results can be drawn from Tables VI–VIII. First, the matrix ultimate strength was left as a free adjustable variable at the fitting procedure. Nevertheless, all the adjusted values obtained for σ_{um} were close to the experimental ones (cf. Tables II–V with Tables VI–VIII). This implies that the basic boundary condition for the modified Equation 1, that is $\sigma_{uc} = \sigma_{um}$ if $\Phi = 0$, is obeyed, indicating that the semi-empirical Equation 1 realistically describes the behaviour shown by the composites.

Another result obtained from Tables VI–VIII refers to the shape parameter. The limiting value of 2.5 proposed by Turcsányi *et al.* [5], is a very good approximation whenever the reinforcement can be treated as regularly arranged rounded equiaxial particles of the same size. But, as well as the morphology, the size distribution of the particles is also important in determining the shape parameter. For example, with a bigranulometric distribution, the volume effectively occupied by the spherical particles can attain 82% compared with 74% for a monogranulometric distribution [8]. Quantitatively, for a bigranulometric distribution where the smaller particles totally occupy the interstitial hole located at the centre face position of a simple cubic arrangement, $\psi = 0.920$ and $\varphi = 0.636$. For such a distribution the value of *A* calculated from Equation 2 is 5.56. Therefore, values of *A* higher than 2.5 indicate that a non-monogranulometric distribution of particles was used. This is indeed true, because the composites tested here were fabricated with the total sieved material under mesh 200, as already cited in the experimental procedure. According to the values shown in Tables VI–VIII the atapulgite particles have a more closed size distribution than sepiolite particles. Fig. 7 shows the fracture morphology for the atapulgite filled polypropylene matrix composite with 20.7% volume fraction. It can be seen that the atapulgite particles can be treated as roughly spherical elements with a tight size distribution. The very different values obtained for the shape parameter of the calcium carbonate composites may indicate that the raw material used was not homogeneously prepared.

It is clear that the shape parameter for the sisal fibres had to be considerably different from those obtained for the particulate reinforcements. For that

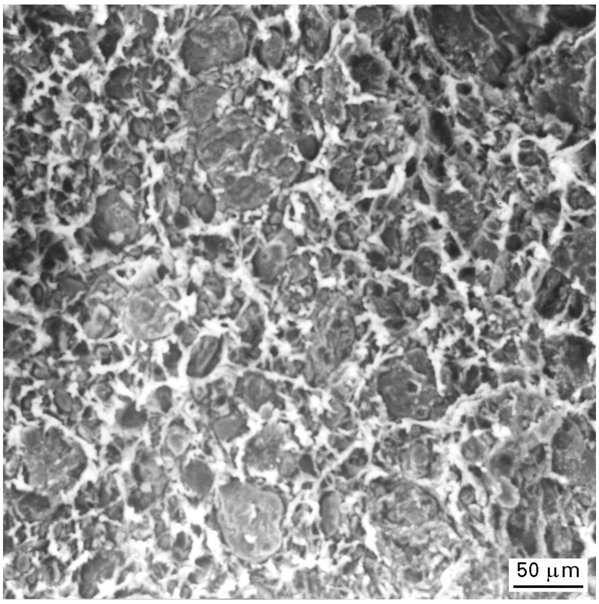

Figure 7 Atapulgite–PP fracture surface (the atapulgite particles have a roughly rounded form).

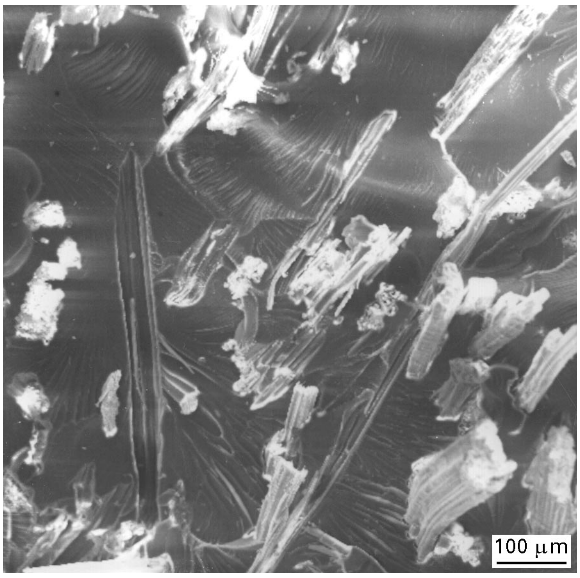

Figure 8 Fracture surface of the sisal–polyethylene composites (the short length sisal fibres are preferably aligned along one axis of the composite specimen).

reason the shape parameter must also be left as an adjustable parameter if the aspect ratio of the reinforcement is different from one. If the fibres are taken as cylindrical elements stacked on a cubic arrangement both the ψ and φ parameters are numerically equal. The shape parameter for such a distribution is zero. The value obtained for the shape parameter for the short length sisal fibres–HPDE composites approaches zero. This result indicates that the fibres are oriented at a preferred direction on the composite. In fact, as shown in Fig. 8 the fibres are preferably aligned along the main axis of the tensile specimens. So, the value encountered for the adjusted A parameter is appropriated for reinforcement elements with an aspect ratio more than one and that are aligned with the axis of the composite.

Finally, as said before, the value of the B parameter taken from Tables VI–VIII is a quantitative measure of each filler–matrix pair interaction. Therefore, by examining the B values, a more systematic analysis of the effect of surface treatment upon filler–matrix adhesion can be made. For example, it can be seen from Tables VI–VIII that, for the composites studied here, treatment of atapulgite particles with a silane coupling agent produced only a secondary effect upon filler–matrix adhesion and, consequently, upon the properties of the composite.

It is worth noting that the approach proposed in this work is able to deal with composites displaying very different performances. The usual models based on the power law [3], for example, have more restrictive boundary conditions, such as poor bond between the fillers and the matrix, to be applied correctly.

4. Conclusions

The tensile strength behaviour of particulate filled composites follows the modified version of the semi-empirical equation proposed by Turcsányi *et al.* [5]. The approach proposed here is valid when the composites have a macroscopic brittle behaviour and no gross yield deformation occurs. The shape parameter must be left as an adjustable variable, because it can be used as an indirect measure of the particle size distribution and of the presence of a preferred fibre orientation. The B parameter can be effectively used as a quantitative measure of the efficiency of surface treatments on each filler–matrix pair. It can also serve as a measurement of the reinforcement efficiency of the filler.

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