JOURNAL OF MATERIALS SCIENCE 28 (1993) 6605–6610

# Influence of interactions on the tensile behaviour of polystyrene filled with calcium carbonate

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Mechanical properties of filled polymers are dependent on a lot of parameters: matrix properties, particles characteristics (nature, size, shape, size distribution), constituent volume fraction and particle–particle and matrix–filler interactions. In this work, mainly devoted to polymer–filler interactions, the tensile behaviour of calcium carbonate-filled polystyrene is examined for different kinds of filler surface modification: carboxylic acid adsorption and polystyrene or polybutyl acrylate grafting. Experimental relative tensile strength of the composite varies mainly with the matrix proportion in the fracture surface and with the matrix–filler interactions: adhesion level and matrix–particle stress transfer. The model enables the calculation of dewetting angles which are a very good representation of the filler–matrix adhesion level.

## 1. Introduction

Many mineral fillers are used in various polymer systems to enhance physical or mechanical properties. There is a lot of scientific literature on the properties of filled polymer properties and especially on their tensile behaviour [1–40]. Most of these results concern systems with weak adhesion strength or none at all between a polymer matrix and filler particles. In this case, the tensile strength decreases with increasing particle volume fraction. At higher adhesion levels, two behaviours can be observed [12, 13, 18, 24]. The first one is a less important decrease of the strength followed by an increase above a critical particle fraction, whereas the second one is a continuous increase as a function of the filler volume fraction.

The interpretation of these behaviours requires models taking into account various parameters. Mechanical properties of filled polymers are indeed dependent on many parameters: matrix properties, particle characteristics (nature, size, shape, size distribution), constituent volume fraction and particle–particle and matrix–filler interactions.

In a previous study [41] about the mechanical behaviour of low density polyethylene filled with calcium carbonate, we demonstrated the major influence of matrix–filler adhesion energy. In the present study, we report the effect of polymer–filler interactions on the tensile behaviour of filled polystyrene. From the analysis of the tensile strength at break as a function of the particle volume fraction, we developed a semi-empirical model and we have tried to determine the parameters of this model by using different calcium carbonate-filled polystyrene obtained by varying the volume fraction and the surface treatment of the filler.

From other experimental approaches (fracture surface observation by SEM, glass transition temperature by DSC), we have tried to validate the physical significance of the parameters that arise from the model. To take into account the matrix–filler interaction influence, we also performed contact angle measurements and we interpreted them with the Lee unified theory of adhesion [42, 43] to determine spreading coefficients and adhesion energies for the various systems studied.

## 2. Experimental procedure

### 2.1. Materials

The polystyrene used in this work is a commercial product manufactured by BP Chemicals under the trade name HF 555. The average molecular weights in number and in weight are, respectively, 25 000 and 200 000. The Young modulus is equal to 1230 MPa.

The filler used in this study is a natural calcium carbonate ($CaCO_3$) commercially known as Hydrocarb 90 (OMYA S. A.). The main characteristics of this inorganic filler are a density at 25 °C equal to 2.7, a BET surface of 10.23 $m^2 g^{-1}$ and an average particle size, measured in a Sedigraph, equal to 1.2 μm.

The particles were surface treated before incorporation into the matrix. Most of the surface treatment was chosen for its similarity with polystyrene. So, the following coatings were used [44]:

(i) a stearic acid monolayer (ref: 1 ACST) by chemisorption from solution;
(ii) half a stearic acid monolayer (ref: 1/2 ACST) by chemisorption from solution;
(iii) a benzoic acid monolayer (ref: 1 ACBZ) by chemisorption from solution;

(iv) a statistical styrene–maleic anhydride copolymer (ref: SMJ1) supplied by Aldrich (viscometric average molecular weight of 3850 determined from viscometry in MEK at 25 °C using the Mark Houwink relationship: $[\eta] = 1.274\ 10^{-4}\ M_v^{0.662}$).

A last series of coatings was done in two steps: chemisorption of acrylic acid, then copolymerization of the acid with styrene or butylacrylate following the procedure described in [45–47]. The molecular weights of these various coatings are given in Table I. Calcium carbonate-filled polystyrenes were studied using various filler weight fractions in the range 5–60% by weight.

### 2.2. Procedures

Compounds were prepared by mixing on a two-roll Troester WNU1 mill for 15 min at 190 °C. The compound was then pressed into the form of a moulded plate by a compression press under a pressure of 60 MPa for 5 min at a temperature of 210 °C. The moulded plate of 0.2 cm thickness was quenched in a cold press.

Samples for tensile tests were cut following the ISO R 527 type I 1/2 method. The testing was performed after ageing first at 80 °C for 24 h and then at 23 °C and 50% RH for 48 h. The tensile test was carried out on an Instron 4301 model at 23 ± 1 °C using a speed of 5 mm/min.

Glass transition temperatures were determined by differential microcalorimetry. The calorimeter is a Perkin Elmer DSC 2 working at a heating rate of 20 °C/min. To avoid the influence of the thermal history of the sample, the measurement is taken after a first heating up to 180 °C followed by cooling at a rate of 10 °C/min.

Fracture surfaces, obtained at room temperature, were observed using a scanning electron microscope JEOL JSM 35.

Contact angle determination was conducted using either the filler column method based on liquid capillary rise and developed by Cheever and Ulicmy [48] or the drop test where 1 µl of liquid is placed on a calcium carbonate pellet obtained by moulding at room temperature and under vacuum [49, 50]. An external pressure of $0.75 \times 10^6$ kN/m$^2$ was applied to obtain a perfectly smooth surface. The various liquids used were heptane, hexane, α-bromonaphthalene, diiodomethane, formamid, distilled water, benzilic alcohol and aniline.

## 3. Results and discussion

### 3.1. Tensile behaviour

Fig. 1 gives the variation of the relative resistance at break ($\sigma_{uc}/\sigma_{um}$) as a function of the filler volume fraction $\phi_f$, for the various systems. It can be observed that the experimental results closely follow continuous curves calculated from the equation

$$\sigma_{uc}/\sigma_{um} = 1 - a\phi_f^{2/3} \qquad (1)$$

This result is consistent with most of the observations mentioned in the literature for brittle polymers filled with spherical particles [8–13].

For all the compounds, a decrease of the resistance at break with respect to the resistance of the matrix is observed. Nevertheless, the importance of this effect is strongly dependent on the nature of the coating and on the particle volume fraction. The surface coatings can be classified into three groups depending on the value of the $a$ parameter (Table II):

(i) high $a$ value when calcium carbonate is treated with stearic acid or polybutylacrylate;
(ii) weak $a$ value for untreated calcium carbonate and for styrene–maleic anhydride copolymer and high molecular weight polystyrene;
(iii) weak $a$ value but an increasing resistance at break at high $\phi_f$ for calcium carbonate coated with benzoic acid or low molecular weight polystyrene.

TABLE I Molecular characterization of various polymer coatings

| Coating nature | Ref. | $M_n$ | $M_w$ |
|---|---|---|---|
| Polystyrene | PS40 | 45 500 | 111 000 |
| Polystyrene | PS100 | 88 000 | 212 000 |
| Polybutylacrylate | PAB | | 20 500 |

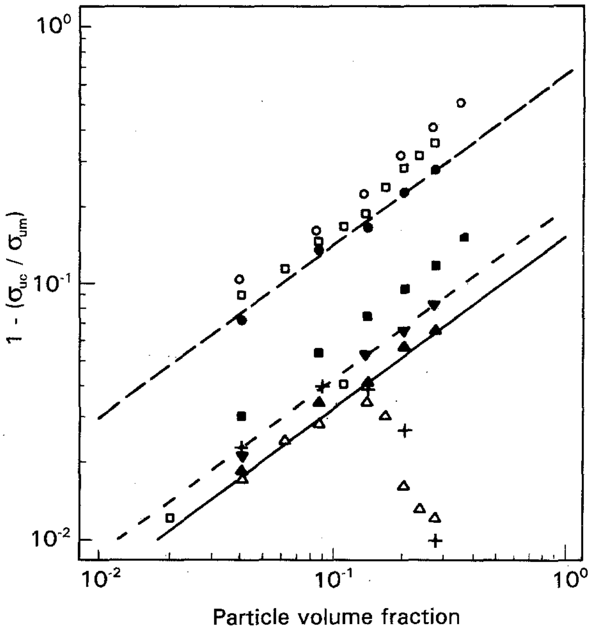

*Figure 1* Logarithmic representation of relative resistance at break as a function of the particle volume fraction for filled polystyrene. Influence of the surface treatment. Relationship: $\sigma_{uc}/\sigma_{um} = 1 - a\phi_f{}^{2/3}$. ○ 1 ACST; □ 1/2 ACST; ● PAB; ■ unmodified; ▼ SMJ 1; ▲ PS 1 0 0; + PS 4 0; △ 1 ACBZ.

TABLE II Values of parameters $a$ and dewetting angles $\Theta_1$ and $\Theta_2$

| Coating | $a$ | $\Theta_1$ | $\Theta_2$ |
|---|---|---|---|
| 1 ACST | 1.04 | 90° | 90° |
| 1/2 ACST | 0.90 | 65.5° | |
| PAB | 0.67 | 53.5° | |
| Untreated | 0.30 | 32.5° | 45° |
| SMJ1 | 0.20 | 25.5° | 34.5° |
| PS 100 | 0.15 | 22.5° | 30° |
| PS 40 | 0.20 | 26° | 35° |
| 1 ACBZ | 0.17 | 23.5° | 31.5° |

TABLE III Contact angle values between various liquids and treated or untreated calcium carbonates

| Coating | Benzilic alcohol | Aniline | α-Bromonaphtalene | Diiodomethane | Formamid | Distilled water |
|---|---|---|---|---|---|---|
| 1 ACST | 66° | 71.8° | | 79.7° | 90.5° | 106° |
| 1/2 ACST | 51.7° | | | 71.0° | 79.4° | |
| PAB | | | 32.5° | 55.5° | 76.5° | 100° |
| Untreated | | | 0° | 39.2° | 53.5° | 80.9° |
| SMJ 1 | | | 39.6° | 54.8° | | 88.9° |
| PS 100 | | | 14.5° | 38.5° | | 95° |
| PS 40 | | | 15° | 38° | | 104° |
| 1 ACBZ | | | | 51° | 68.5° | 85.6° |

## 3.2. Matrix–filler interactions

Contact angle value of a series of liquids deposited on treated and untreated calcium carbonates are noted in Table III.

Employing the Lee unified theory of adhesion [42, 43], we calculated Harkin's spreading coefficient $\lambda_{LS}$, the adhesion work $W_{SL}$, the wetting parameter $M$ and the failure parameter $B$. Both parameters are important because knowledge of them makes it possible to predict the wettability and the type of failure. An $M$ value higher or lower than 1 means that the particle surface is or is not wetted by the polymer. A $B$ value higher or lower than 1 means that the failure is cohesive or adhesive. Table IV gives these calculated parameters.

The negative values obtained for $\lambda_{LS}$ in the case of stearic acid coatings mean that polystyrene does not wet the filler spontaneously; therefore, an adhesive type failure should normally occur. In contrast, for the other coatings the filler is wetted by the polymer and from the Lee model, due to the low but positive $\lambda_{LS}$ values, the failure should be just at the limit of the cohesive and adhesive types. Wetting and failure parameters accord very well with this interpretation.

Moreover, the examination of micrographs provided by SEM analysis confirms the contact angles and deductions from Lee's theory. Failure surfaces are classified into two groups. Fig. 2 shows the failure surfaces in the case of a stearic acid monolayer coating [Fig. 2(a)] representative of the first group (stearic acid and polybutylacrylate coating) and of a benzoic acid monolayer coating [Fig. 2(b)] representative of the other types of coating. In the first case decohesion between filler and matrix is observed, whereas in the other one the particles are surrounded by the matrix and practically not apparent on the micrograph.

A last series of experiments was performed by measuring the $T_g$s of the compounds containing 40% by weight of filler. The $T_g$ of the pure polystyrene used was $361.6 \pm 0.2$ K. Table V gives these measurements.

No significantly important modification of $T_g$ is observed. Nevertheless, except for the stearic acid coating, the particles give rise to a small $T_g$ increase.

## 3.3. Tensile behaviour interpretation

### 3.3.1 *Volume effect*

The tensile behaviour of the various systems clearly shows that the relative resistance at break obeys Equation 1. A more or less important decrease in the filler volume fraction is well observed. This behaviour can be attributed first to a 'volume effect'. The strength of the filled polymer is determined by the effective decrease in the cross-sectional area of the load-bearing polymer matrix due to the presence of the filler. For brittle materials, the fracture path follows the stress concentration zones [1, 5, 20, 51, 52]. In the case of spherical particles without adhesion, the fracture path deviates through the equatorial plane of all the spheres which are encountered [51, 52]. The power 2/3 in Equation 1 is then justified [7].

TABLE IV $\lambda_{LS}$ coefficient, adhesion work $W_{SL}$, Lee wetting parameter $M$ and failure parameter $B$ [42, 43]

| Coating | $\lambda_{LS}$ (mJ/m$^2$) | $W_{SL}$ (mJ/m$^2$) | $M$ | $B$ |
|---|---|---|---|---|
| 1 ACST | − 41.8 | 49.1 | 0.46 | 0.43 |
| 1/2 ACST | − 26.3 | 61.8 | 0.67 | 0.59 |
| 1 ACBZ | + 11.1 | 86.1 | 1.12 | 0.93 |
| Untreated | + 21.4 | 93.0 | 1.24 | 1.03 |
| SMJ 1 | + 3.6 | 81.6 | 1.04 | 0.86 |
| PAB | + 22.6 | 91.0 | 1.22 | 1.00 |
| PS 40 | + 10.5 | 88.4 | 1.14 | 0.96 |
| PS 100 | + 11.6 | 88.6 | 1.15 | 0.96 |

The value of factor $a$ depends on the packing geometry. It can be divided into two terms, a volume packing factor $\phi_M^{-2/3}$, depending on the maximum packing fraction ($\phi_M$) and a second one $A_M$ representing the maximum surface concentration in particles in their maximum density plane. When the fracture plane passes through the particle equators (case without adhesion) it can be written that

$$a = A_M/\phi_M^{2/3} \tag{2}$$

Table VI gives the calculated $a$ values for various packing geometries.

It can be observed that the value of $a$ of 1.21, generally mentioned in the literature, corresponds to a simple cubic packing. In this case $\phi_M = 0.52$ and not 0.75 as calculated without taking into account $A_M$ [5, 7, 22]. For a random packing, $\phi_M = 0.635$ and a value for $a$ of 1.06 is found, close to the value reported by Ramsteiner *et al.* [4].

For the particles coated with a stearic acid monolayer we found an experimental value of $a$ equal to 1.04 (Table II), corresponding, in the case of perfect dewetting, to a $\phi_M$ value of 0.66, consistent with the random packing geometry.

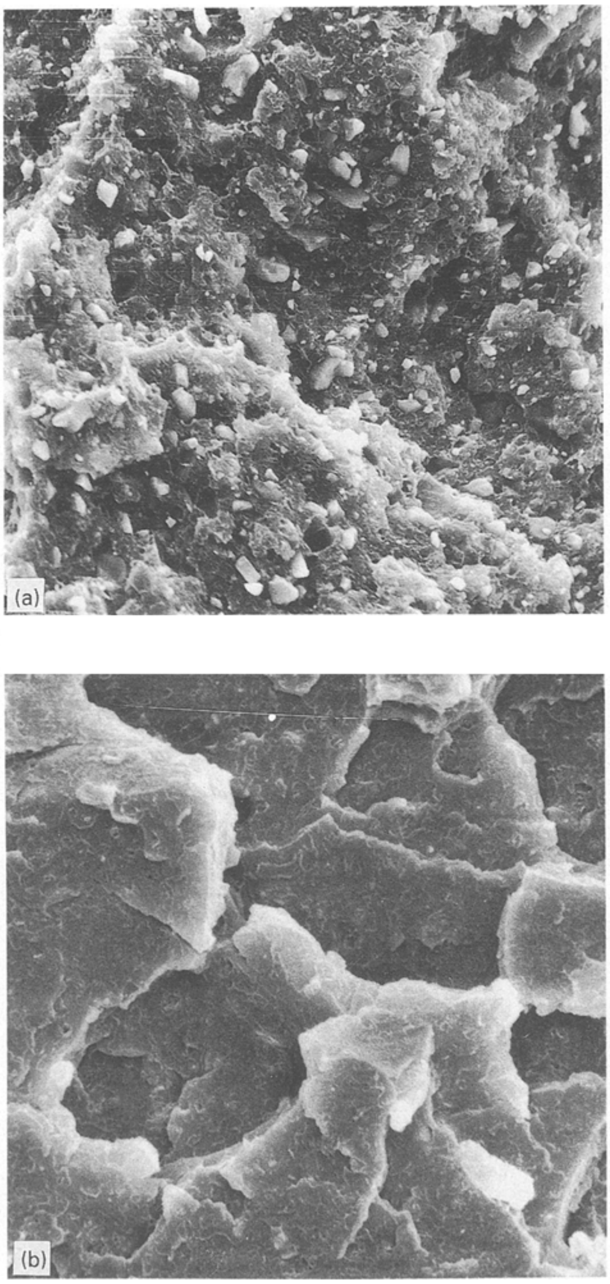

*Figure 2* Fracture surfaces of calcium carbonate filled polystyrene. (a) Particles coated with a stearic acid monolayer (magnification × 1000). (b) Particles coated with a benzoic acid monolayer (magnification × 2000).

TABLE V Polystyrene $T_g$s in compounds filled with 40% by weight of untreated or treated calcium carbonate

| Coating | $T_g$ (K) |
|---|---|
| 1 ACST | $360.8 \pm 0.3$ |
| 1/2 ACST | $362.0 \pm 0.7$ |
| 1 ACBZ | $362.9 \pm 0.4$ |
| Untreated | $363.0 \pm 0.8$ |
| SMJ1 | $364.6 \pm 0.7$ |
| PAB | $363.0 \pm 0.9$ |
| PS 40 | $365.4 \pm 1.3$ |
| PS 100 | $365.7 \pm 0.6$ |

TABLE VI $a$, $\phi_M$, $A_M$ parameters for various packing of spherical particles

| Packing | $\phi_M$ | $A_M$ | $a$ |
|---|---|---|---|
| Simple cubic | 0.52 | 0.785 | 1.21 |
| Random | 0.635 | 0.785 | 1.06 |
| Face centered cubic | 0.74 | 0.785 | 0.96 |

### 3.3.2. Adhesion effect

In addition to this 'volume effect', an adhesion effect has to be taken into consideration. The level of the matrix–filler adhesion can be defined as the stress to be applied to the interface for dewetting. It has been shown that in the case of excellent interfacial adhesion, crazes or shear bands are formed near the poles of the particles [53–56]. The $a$ factor is then equal to zero and the relative resistance at break attains an upper limit equal to 1 [1, 6, 12, 57].

For less important interfacial adhesion, crazes or shear bands are initiated at points located between the poles and the equatorial plane [51, 53–55]. In this case, a partial dewetting of the matrix surrounding the particles has to be observed due to the applied load [53–56, 58]. The importance of this 'dewetting effect' depends directly on the level of the matrix–filler adhesion [55, 56]. The fracture path then runs along the particle surface at points situated between the pole and the equator. The polymer proportion in the fracture plane is all the greater if the adhesion level is high and the dewetting weak.

For a known maximum packing fraction $\phi_M$, variations of factor $a$ could represent variations of dewetting angles and thus of filler–matrix adhesion level. From the experimental values of factor $a$, it is possible to calculate dewetting angles $\Theta_1$. Relation (2), only valid for systems without polymer–filler adhesion, can be generalized to systems with various adhesion levels (Relation 3)

$$a = \frac{A_M}{\phi_M^{2/3}} \sin^2 \Theta_1 \tag{3}$$

with $\Theta_1 = 0$ when the failure occurs at the pole and $\Theta_1 = 90°$ when there is no adhesion.

Such a relation is only valid in the absence of any stress transfer. Attention has to be paid to systems with adhesion when they transfer stress from the matrix to the particles [41]. Considering such a transfer, occurring only by shear, Relation 1 has to be written as follows

$$\sigma_{uc}/\sigma_{um} = 1 - 0.585\, a'\, \phi_f^{2/3} \tag{4}$$

Corrected dewetting angles $\Theta_2$ have to be calculated from corrected $a$ values obtained by dividing the experimental value by the constant factor 0.585. $\Theta_1$ and $\Theta_2$ dewetting angles are given in Table II.

When comparing Tables II and IV the fracture surfaces, it is clearly seen that the dewetting angles are a very good representation of the filler–matrix adhesion level.

A weak dewetting is observed when the break occurs at the limit between the cohesive and adhesive failures. Very few particles can be observed in the fracture surface. The calculated dewetting angles around 30° can be compared to values of 37° determined by Wang *et al.* [51].

A strong dewetting is observed when numerous particles are seen on the fracture surfaces. It is consistent with Lee's prediction of adhesive failure. The dewetting angles have typical values around 60° for poor adhesion systems [54, 55].

However, the behaviour of polystyrene filled with polybutylacrylate-coated particles cannot be explained in such a manner. We believe that the unexpected result may be a consequence of the poor resistance of the coating itself, leading, contrary to the predictions of the Lee model, to a failure of adhesive type.

This approach makes possible an understanding of the decrease of the relative resistance at break with the increase of the filler volume fraction. We also observed, above a critical volume fraction, an increase in tensile strength. This could be explained by a modification of matrix properties resulting from the presence of particles [41].

## 4. Conclusions

We have demonstrated that the tensile resistance of a brittle polymer such as a polystyrene can be modelled by a mathematical relationship, considering the resistance as mainly dependent on the matrix proportion in the fracture surface. A parameter depending on the matrix–filler interactions intervenes in this relationship. This parameter can be correlated with the matrix–filler adhesion energy calculated from contact angle measurements.

When stress transfer from the particles to the matrix is taken into consideration the model enables the calculation of dewetting angles with values similar to those reported in the literature for systems with various adhesion levels.

To improve the model validation, the amount of filler in the fracture surfaces must be evaluated.

## Acknowledgements

The authors are indebted to the National Fund for Scientific Research (FNRS) and to the Institut pour la Recherche Scientifique dans l'Industrie et dans l'Agriculture (IRSIA) for their financial support. P. Godard is a Research Associate of the National Fund for Scientific Research (Belgium).

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*Received 2 July 1992*
*and accepted 2 June 1993*