# Micromechanical deformations in particulate filled thermoplastics: volume strain measurements

# B. PUKÁNSZKY

Central Research Institute for Chemistry, Hungarian Academy of Sciences, H-1525 Budapest, PO Box 17, Hungary

M. VAN ES, F. H.J. MAURER DSM Research BV, 6100 MD Geleen, PO Box 18, The Netherlands

G. VÖRÖS Institute for General Physics, Eötvös University Budapest, H-1445 Budapest, PO Box 323, Hungary

Volume strain measurements were carried out on PP composites containing different CaCO<sub>3</sub> fillers. During deformation, a volume increase was detected which could be divided into two linear sections as a function of elongation. Comparison of data with existing theories has shown that in the first part, mostly elastic deformation takes place and the slope can be related to the Poisson's ratio of the composite. Scanning electron microscopy revealed that in the second stage, the dominating micromechanical deformation process is debonding. Void formation is initiated at a certain stress which approximately corresponds to the yield stress of the composites, but data in the literature and model calculations indicate that separation of the matrix/filler interface may start at lower stresses. Initiation stress depends on the particle size of the filler and on interfacial interactions. The rate of volume increase has non-linear dependence on the volume fraction of the filler. Volume strain measurements reflect micromechanical deformations well, but further study is needed to explain contradictions between experimental results and theoretical predictions.

#### 1. Introduction

In heterogeneous polymer systems, external load can initiate several micromechanical deformation processes [1]. The character and extent of these deformations play a crucial role in the energy absorption, macroscopic deformation and failure of the material [1, 2]. The prevailing micromechanical deformation mechanism is determined by the inherent properties of the matrix polymer and by local stress distribution. Magnitude and distribution of local stresses are determined by three factors: stress concentration, thermal stresses and interaction of the components [3, 4].

In such systems the two basic micromechanical deformation processes of polymers — shear yielding and crazing — might be replaced or accompanied by several others, the most important of which are debonding and cavitation. Micromechanical deformations are competitive processes, initiated under certain conditions. The criteria for initiation are known for some of them, e.g. for shear yielding and to some extent for crazing [2, 5, 6]; much less is known, however, about the conditions for the others.

During shear yielding, the volume of the specimen remains constant, while crazing, debonding and cavitation are accompanied by volume increase. Measurement and analysis of volume change during the deformation of specimens may lead to a better understanding of the micromechanical deformation processes taking place in heterogeneous polymer systems [1, 7-9]. The dominating deformation mechanism and the factors influencing it must be determined in order to be able to predict and modify the behaviour of the material and to develop composites of improved properties.

In the present study, the deformation behaviour of polypropylene PP composites containing different  $CaCO_3$  fillers was investigated and the volume strain during their deformation was determined. An attempt was made to relate this volume change to the underlying micro-mechanical deformation processes, to analyse volume strain quantitatively, and to find a correlation between the deformation processes and component interaction.

#### 2. Experimental Procedure

An injection moulding grade PP homopolymer (Tipplen H 531, TVK, Hungary) was used as matrix polymer (density: 0.903 g cm<sup>-3</sup>, MFI: 4 g per 10 min). Four different CaCO<sub>3</sub> fillers were studied in two series. The most important characteristics of the fillers are listed in Table I. In the first series, the effect of composition was studied; composites were prepared with Durcal 2 in the 0–0.3 volume fraction ( $\phi_f$ ) range. Composition was changed in 0.05 volume fraction steps. In the second series, fillers with a different particle size (see Table I), i.e. different specific surface area and contact surface, were introduced into the PP matrix in 10 vol % composition.

Homogenization was carried out in a Brabender DSK 42/7 type twin-screw compounder with an L/D ratio of 6. The samples were extruded twice at 70 r.p.m. to assure sufficient homogeneity. The temperatures of the two cylinder zones were 210 and 215 °C, respectively, and that of the head, 220 °C. The homogenized composites were injection moulded into dog-bone-shaped tensile specimens with a  $10 \times 4$  mm cross-section in the testing area.

Volume strain measurements were carried out on a Zwick 1474 tensile tester at ambient temperature. The strain rate was  $9.7\% \text{ min}^{-1}$ . Elongation and decrease of specimen width were measured during deformation. Volume strain was calculated from the recorded changes with a program developed at DSM by assuming that deformation in the two lateral directions is the same.

Micromechanical deformations and the structure of the undeformed and deformed composites generally were studied by scanning electron microscopy (SEM). Deformed composites were prepared by extending the specimen up to a certain deformation in the tensile testing machine, and then removing it from the grips. After removal elastic deformation relaxes and only plastic deformation remains. Micrographs were taken from fracture surfaces prepared at liquid nitrogen temperature.

#### 3. Results

# 3.1. Micro- and macromechanical deformations, mechanism

Stress against strain curves of the composites were registered up to 25% elongation. All composites showed the behaviour typical for most thermoplastics; the  $\sigma$  against  $\varepsilon$  curves exhibited a maximum at a certain deformation usually associated with yielding  $(\sigma_y)$ , or more generally with plastic deformation.

Both the initial slope of the stress against strain curves and the absolute value of the stress change with increasing filler content (Fig. 1). The maximum becomes more pronounced and shifts to lower deformations. Much smaller changes were observed in the shape of the curves when the type, i.e. specific surface

TABLE I Characteristics of the CaCO<sub>3</sub> fillers

Trade name	Producer	Density (g cm <sup>-3</sup> )	Particle size (µm)	Specific surface (m <sup>2</sup> g <sup>-1</sup> ) 0.5	
Calcilit 100	Alpha	2.71	58.0		
Millicarb	Omya	2.65	3.6	2.2	
Durcal 2	Omya	2.65	3.6	3.3	
Polcarb	ECC	2.64	1.3	5.0	

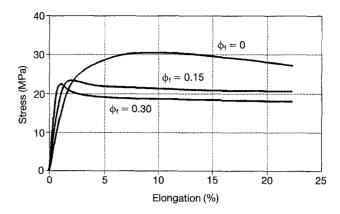


Figure 1 Stress against strain curves of PP/CaCO<sub>3</sub> composites of different filler content

area of the filler, was varied, although the value of yield stress also showed characteristic changes in this case.

Fig. 2 presents the composition dependence of the yield stress. Indeed, yield stress decreases with increasing filler content as indicated by Fig. 1. The observed tendency is the result of the combined effect of decreasing effective load-bearing cross-section and matrix/filler interaction [10, 11]. Composition dependence of yield stress can be expressed as

$$\sigma_{y} = \sigma_{y0} \frac{1 - \varphi_{f}}{1 + 2.5 \varphi_{f}} \exp(B\varphi_{f})$$
(1)

where  $\sigma_y$  and  $\sigma_{y0}$  are the yield stresses of the composite and the matrix, respectively,  $\varphi_f$  is the volume fraction of the filler, and *B* is a parameter related to the matrix/filler interaction. As shown earlier the influence of decreasing load-bearing cross-section can be eliminated

$$\sigma_{\rm yred} = \sigma_{\rm y} \frac{1 + 2.5 \,\varphi_{\rm f}}{1 - \varphi_{\rm f}} = \sigma_{\rm y0} \exp\left(B\varphi_{\rm f}\right) \tag{2}$$

and the linearized plot of the reduced yield stress makes possible an evaluation of the interaction, and of structural effects, which are even more important in the present case [11, 12]. The very good linear fit of Fig. 3 indicates a homogeneous distribution of filler particles in the matrix; structure related phenomena (change of matrix properties by the introduction of the filler, aggregation, and segregation of particles during flow) seem to be absent in the composites studied.

Volume change measured during the deformation of the matrix polymer and a composite containing 0.30 volume fraction filler is presented in Fig. 4. Both materials show some volume increase, although that of the composite is significantly larger than the change observed in the case of the filler-free PP. Moreover, the volume increase of the composite appears to proceed in two steps with increasing elongation.

Further volume strain curves are shown in Fig. 5. All the curves have a similar character, increasing more or less linearly with deformation. The linear deformation dependence is divided into two stages with different slopes, which seems to indicate two filler-related micromechanical deformation processes. A significant volume increase, however, starts only in

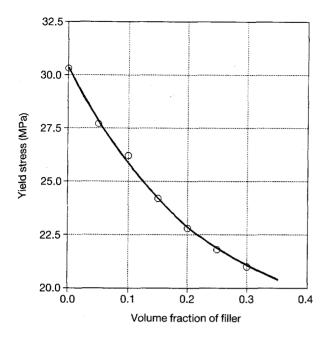


Figure 2 Composition dependence of tensile yield stress of PP/CaCO<sub>3</sub> composites. Filler: Durcal 2,  $A_f = 3.3 \text{ m}^2 \text{ g}^{-1}$ .

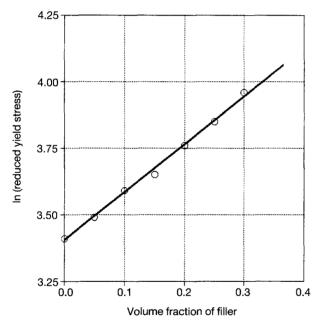


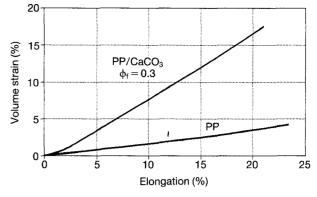
Figure 3 Reduced tensile yield stress of  $PP/CaCO_3$  composites plotted against composition in the linearized form.

the second stage; i.e. the intersection of the two straight lines can be regarded as an initiation deformation or stress value, which triggers off a certain micromechanical deformation process. In connection with Fig. 5 and the volume strain correlations, two questions arise:

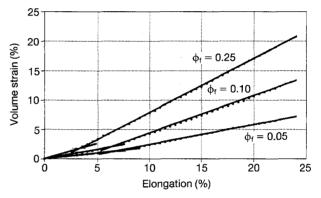
1. What is the relation of the initiation point to the stress against strain curve, i.e. to yield properties?

2. What kind of micromechanical deformation process is initiated at this point?

In order to answer the first question, elongation and stress measured at the initiation point were collected in Table II, together with yield properties ( $\sigma_y$ ,  $\varepsilon_y$ ). Comparison of the data shows that initiation ( $\sigma_i$ ) and yield stress ( $\sigma_y$ ) are similar. This observation is further



*Figure 4* Volume strain of PP and a PP composite as a function of elongation.



*Figure 5* Dependence of volume strain of PP composites on deformation. Effect of filler content.

corroborated by Fig. 6, which shows that the correlation of the two quantities yields a straight line with zero interception. Fig. 6 and its correlation indicates that the micromechanical deformation process, which results in the strong volume increase, starts at or in the close vicinity of the maximum of the stress against strain curve, i.e. at the yield point. Similar results were obtained from the comparison of initiation and yield strain. These observations differ from those of Vollenberg and Heikens [3, 13]. They found a characteristic kink in the stress against strain curve and assigned it to the debonding stress. The relation of this kink, and the separation of the matrix/filler interface, were also verified by microscopy. The debonding stress values determined by them are much lower than the initiation or yield stresses measured in this work.

In order to identify the dominating micromechanical deformation mechanism as well as to check the above findings on initiation, SEM micrographs were taken from the fracture surface of samples deformed to different extents. Elongation of the samples was carried out in a wide range; micrographs were taken from the fracture surface of samples deformed up to 0,  $0.25\varepsilon_y$ ,  $0.5\varepsilon_y$ ,  $0.75\varepsilon_y$ ,  $\varepsilon_y$ ,  $2\varepsilon_y$  and  $5\varepsilon_y$  elongations. In the last case, significant necking was observed; samples were taken both from the uniformly deformed and from the necked area. The study was made on the PP containing no filler and the composites prepared with 0.1 volume fraction of Durcal 2. Selected samples of

TABLE II Comparison of yield properties and volume strain characteristics

Filler type	$\boldsymbol{\phi}_{f}$	σ <sub>y</sub> (MPa)	ε <sub>y</sub> (%)	ΔV <sub>y</sub> (%)	σ <sub>i</sub> (MPa)	ε <sub>i</sub> (%)	ΔV <sub>i</sub> (%)	d∆V/dε
_	0	30.3	8.9	1.47			_	0.18
Durcal 2	0.05	27.7	6.9	1.58	27.6	7.8	1.84	0.40
Durou. 2	0.10	26.2	5.2	1.67	26.1	5.4	1.76	0.55
	0.15	24.2	3.8	1.49	23.2	4.4	1.75	0.67
	0.20	22.8	2.4	1.05	22.5	2.6	1.22	0.73
	0.25	21.8	1.5	0.70	21.8	1.9	0.88	0.85
	0.30	21.0	1.0	0.35	21.4	0.9	0.26	0.88
Calcilit 100	0.10	24.3	5.8	1.81	24.0	5.5	1.67	0.53
Millicarb	0.10	25.3	5.5	1.63	25.4	6.1	1.81	0.53
Polcarb	0.10	27.3	5.2	1.58	27.3	5.5	1.63	0.50

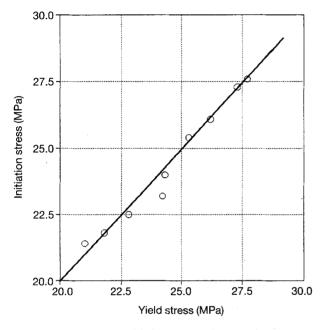


Figure 6 Correlation of initiation and yield stress of  $PP/CaCO_3$  composites.

the composites containing the large (Calcilit 100) and the small (Polcarb) particles were also investigated.

Despite the fact that the PP matrix polymer has also shown some volume increase during deformation, no observable change could be detected in the structure of the deformed samples. No sign of the elongated polymer fibres characteristic of crazing could be observed on the fracture surfaces, thus the observed volume increase must be determined by the Poisson's ratio of the polymer. Indeed from the slope of the  $\Delta V/V_0$  against  $\varepsilon$  correlation, a Poisson's ratio of 0.41 could be calculated for PP which agrees well with values determined by other techniques.

On the micrographs of the filled composites, no significant change can be observed up to the yield strain. As Fig. 7a shows, good contact exists between the filler and the matrix in the case of both large and small particles. The micrograph taken at the yield point  $(\varepsilon_y)$  shows more or less the same picture, although a slight debonding can be observed around the larger filler particles (Fig. 7b). No change could be detected on the micrographs taken from samples of intermediate deformations either. Fig. 7c, a micro-

graph of a specimen deformed up to  $2\varepsilon_y$ , clearly shows that the dominating micromechanical deformation process is debonding. A separation of the interface can be observed on the figure around the large and small particles alike. Good adhesion of the matrix can be detected only in the case of very small particles.

From these results, it is clear that the main micromechanical deformation process leading to the observed significant volume increase is debonding. Similarly to the matrix PP, the first, much smaller volume increase is related to the elastic deformation of the material and it is associated with the Poisson's ratio of the composite. The volume increase measured at the initiation point  $(\Delta V_i)$  decreases with increasing filler content (Fig. 8). Attention must be called, however, to the fact that the total amount of volume increase is very small in this first stage. If we compare these numbers to the significant volume increase measured in the second stage, the dominating character of debonding becomes clear.

#### 3.2. Analysis of the debonding process

The above results have proved that the dominating micromechanical deformation process leading to volume increase is debonding in the particulate-filled composites investigated. The main characteristics of debonding are the existence of a threshold or initiation stress and a subsequent, linear increase of volume during further deformation. Initiation, i.e. separation of the matrix/filler interface, must depend on interfacial adhesion; Figs 7a-d also indicated the effect of particle size.

In order to determine the influencing factors and establish the criteria for debonding, the local stress distribution around the particles must be analysed. Such an analysis was carried out earlier for a single particle embedded in an infinite matrix [14]. Stress concentration, thermal stresses and adhesion were taken into consideration during the analysis [4].

In the determination of debonding stress, it was assumed that debonding takes place when the energy resulting from the change of elastic deformation is equal or larger than the work necessary to create new surfaces (Fig. 9), i.e.

$$\Delta U = U^0 - U^D - W_{AB} \Delta S \ge 0 \tag{3}$$

where  $U^0$  and  $U^D$  are the elastic energies before and after debonding,  $W_{AB}$  is the reversible work of adhesion, and  $\Delta S$  is the size of the new surfaces. After carrying out the necessary calculations, the final result for the debonding stress is given by Equation 2

$$\sigma_{i} = -\frac{\sigma_{T}}{2} + \left(\frac{\sigma_{T}^{2}}{4} + \frac{2W_{AB}G_{0}}{C_{1}R}\right)^{1/2}$$
(4)

where  $\sigma_i$  is the initiation stress for debonding,  $\sigma_T$  thermal stress,  $G_0$  the shear modulus of the matrix, R the radius of the particles, and  $C_1$  is a constant containing the characteristics of the components. Model calculations and an analysis of some experimental data have shown that in the composites investigated  $|\sigma_T| \ge 2W_{AB}G_0/C_1R$ , thus Equation 4 can be expressed as

$$\sigma_{\rm i} = -\sigma_{\rm T} + \frac{2W_{\rm AB}G_0}{|\sigma_{\rm T}|C_1} \frac{1}{R}$$
(5)

The correlation reflects both the expected influence of interaction and the observed particle size dependence.

Elongation dependence of volume strain can be divided into two linear sections which have different slopes. If it is assumed that only elastic deformation takes place in the first section and deformation is sufficiently low, the rate of volume increase can be expressed as [7, 9, 15, 16]

$$\frac{\mathrm{d}(\Delta V/V_0)}{\mathrm{d}e_3} = 1 - 2\nu_\mathrm{e} \tag{6}$$

where  $e_3$  is the relative elongation in the longitudinal direction and  $v_c$  is the Poisson's ratio of the composite. The slope of the first part of the  $\Delta V/V_0$  against *e* correlation is related to  $v_c$ ; in other words v can be determined by volume strain measurements.

Considerable effort has been made to analyse the second part of the volume strain curve, where significant volume increase is observed. The slope of the straight line was extensively used to characterize the micromechanical deformation processes taking place during uniaxial loading of a specimen. Basically, two approaches can be distinguished. In his analysis Bucknall [1, 17, 18] considered only crazing as the micromechanical process causing volume increase. He assumed that volume change consists of only the elastic part and crazing

$$\Delta V(t) = \Delta V(0) + \Delta V(\text{crazing})$$
(7)

He expressed the deformation dependence of volume change

$$\Delta V = \frac{V}{V_0} - 1 = \lambda_1 \lambda_2 \lambda_3 - 1 = (1 + e_3)(1 + e_1)^2 - 1$$
(8)

where  $e_1$  is the deformation in the lateral direction. After carrying out the necessary operations and neglecting secondary terms, he obtained

$$\Delta V = e_3 + 2e_1 \tag{9}$$

From Equation 9 it is obvious that the slope of the volume strain curve, i.e.  $d\Delta V/de_3$ , is 1 if only crazing takes place during deformation and zero if shear

yielding is the exclusive micromechanical deformation. If both mechanisms are present, the slope is somewhere between 0 and 1.

While Bucknall [1] and also Sjoerdsma [16] assumed that the only process leading to volume increase is crazing, Farris [19] considered only dewetting. He developed a stochastic model for the description of the dilatation of particulate filled elastomers. The three basic assumptions of his model are that (i) cavities can form at any deformation; (ii) the cavities are rotational ellipsoids and their two short axis are equal to the diameter of the particles; and (iii) the long axis increases as a function of deformation with a rate proportional to the diameter of the particle. Taking into account that some of the particles do not debond, he obtained the correlation

$$\frac{d\Delta V}{de_3} = \sum_{i=1}^{n} \frac{dV_i}{de_3} + \sum_{n+1}^{N} \frac{dV_i}{de_3}$$
(10)

where n is the number of cavities and N the total number of particles. As the second part of the equation is zero, the correlation can be expressed as

$$\frac{\mathrm{d}(\Delta V/V_0)}{\mathrm{d}e_3} = C\varphi_\mathrm{f} \tag{11}$$

where C is a constant. The equation allows also partial dewetting (cavitation around only a part of the particles). Farris observed, however, that in most cases all the particles debonded and the value of C was very close to 1. On the other hand, in the case of a wide particle size distribution, cavities formed only around large particles.

A comparison of the two theories reveals that both predict a slope between 0 and 1 for the volume strain against elongation correlation. Indeed, in most cases the slope is in this range. The maximum slope measured by Bucknall [1] was 0.95, although a value of 1.14 was published by Coumans and Heikens [7]; the difference is, however, inside the standard deviation of the measurement. Farris's [19] approach, on the other hand, predicts a slope which is proportional to, but always smaller than the volume fraction of the filler.

#### 3.3. Verification of the analysis

The analysis has revealed the most important factors influencing the initiation of debonding and the further increase of volume strain with deformation. Some parts of the analysis were already directly or indirectly verified by the experimental data and by electron microscopic investigations. Linear dependence of volume strain on elongation justified the analysis, as well as the particle size dependence of debonding in Fig. 7a-d.

This latter, qualitative evidence is further corroborated by the particle size dependence of the initiation stress presented in Fig. 10. In the figure, particle size is expressed in terms of specific surface area according to the correlation of  $R = 3/(A_f \rho_f)$ , where  $A_f$  is the specific surface area and  $\rho_f$  the density of the filler. According to Equation 5, initiation stress should depend linearly on reciprocal particle size. Fig. 10 strongly corroborates the results of the analysis and proves the effect of



Figure 7 SEM micrographs taken from the fracture surface of PP/CaCO<sub>3</sub> composites deformed to different extents. Deformation: (a) 0%, (b)  $\varepsilon_y$ , (c)  $2\varepsilon_y$ , (d)  $5\varepsilon_y$  (necking region). Magnifications (a) 10000, (b) 6000, (c) 4000 and (d) 3000.

the size of the interface on the debonding process. Although good correlation exists between the prediction and experimental data, the analysis does not resolve the contradiction between the observation of Vollenberg [3] and our measurements, namely that debonding starts at a lower stress ( $\sigma_D$ ) than the value initiating the observable increase of volume ( $\sigma_i$ ).

Equation 11, on the other hand, suggests a linear dependence of the rate of volume increase on filler content. According to Fig. 11, however, the correlation does not correspond to the prediction at all. In the figure the predicted linear correlation is also presented. Even if we shift the straight line higher to take into account the volume strain of PP, the deviation of

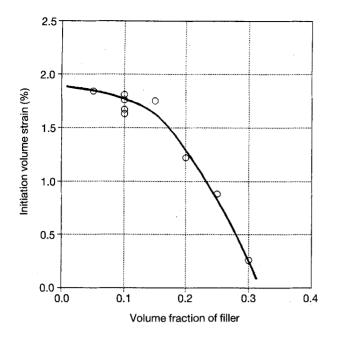


Figure 8 Composition dependence of the initiation volume strain of  $PP/CaCO_3$  composites.

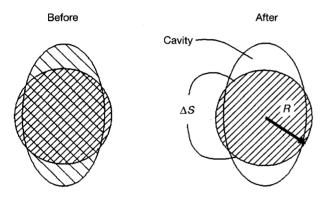


Figure 9 Schematic representation of debonding and subsequent volume increase.

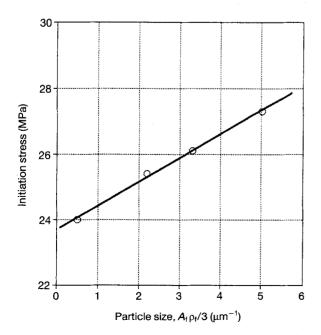


Figure 10 Particle size dependence of the debonding (initiation) stress of  $PP/CaCO_3$  composites.

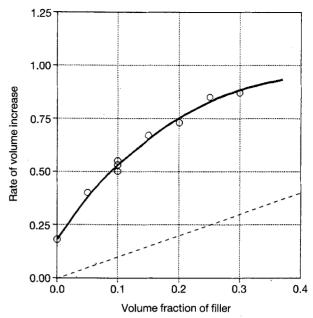


Figure 11 Effect of composition on the rate of volume increase in  $PP/CaCO_3$  composites; (---) predicted by Equation 11 at C = 1.

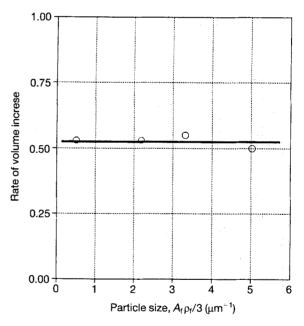


Figure 12 Rate of volume increase plotted against particle size.

the line and the measured values is strong. Equation 11 indicates also that the rate of volume increase is independent of particle size. According to Fig. 12 the slope of the  $\Delta V/V_0$  against  $\varepsilon$  correlation is really independent of particle size, at least in the studied particle size range.

Although some parts of the analysis presented above proved to be correct (e.g. linear dependence of volume increase on elongation, dependence of initiation stress on particle size, and independence of the rate of volume increase from particle dimensions), in some cases contradictions were observed between data in the literature and our findings, as well as deviations from theoretical predictions. These contradictions merit further consideration. Nevertheless, the analysis and its comparison with the experimental data have proved that in the particulate filled composites investigated, the dominating micromechanical deformation process is debonding; in other words, the volume strain measurement is a convenient tool for the study of micromechanical deformation processes in heterogeneous polymer systems.

### 4. Discussion

Our measurements, as well as data in the literature, show that volume increases during the deformation of the composites investigated, and this volume change takes place in two steps with increasing elongation. SEM studies have shown that significant volume increase occurs only in the second step of the deformation process. Assuming that mostly elastic deformation takes place in the first stage, the rate of volume increase can be related to the Poisson's ratio of the composite according to Equation 6.

Poisson's ratio of the composites investigated were calculated; these are listed in Table III. The values calculated at large filler content are extremely low. Extrapolation of the data to  $\varphi_f = 1$  (Fig. 13) yields an unreal Poisson's ratio for the filler. The strong composition dependence of v and the calculated low values may have several reasons. Uncertainty of the determination is relatively large, and the first elastic region of deformation is very short, especially at high filler content. As a consequence, determination of the slope is difficult, the curve turns into the second part, accompanied by considerable volume strain, at very low elongations. The observations of Vollenberg and Heikens [3, 20] also merit some consideration. They assigned debonding to a kink on the stress against strain curve, but this stress value is lower than the initiation stress observed in our experiments. Although the slope of the first section is unambiguously related to the Poisson's ratio of the composite, the considerable experimental error and the possibility of separated interfaces warrant caution in using volume strain measurements for the determination of this quantity in heterogeneous polymer systems.

The main factors influencing initiation stress are given by Equation 5 and the particle size dependence of  $\sigma_i$  completely corresponds to the prediction. Vollenberg's data and model calculations [3], however, show that debonding occurs at a considerably lower stress than the initiation of volume increase. This indicates the possibility of two separate processes. Stress analysis has shown that debonding is

TABLE III Poisson's ratios calculated from the first part of the volume strain curve for PP and for  $PP/CaCO_3$  composites

Filler type	$\phi_{\rm f}$	ν
_	0	$0.41 \pm 0.01$
Durcal 2	0.05	$0.40 \pm 0.01$
	0.10	$0.35 \pm 0.01$
	0.15	$0.33 \pm 0.01$
	0.20	$0.29 \pm 0.04$
	0.25	$0.27 \pm 0.04$
	0.30	$0.27\pm0.02$
Calcilit 100	0.10	$0.37 \pm 0.02$
Millicarb	0.10	$0.37 \pm 0.01$
Polcarb	0.10	$0.37 \pm 0.02$

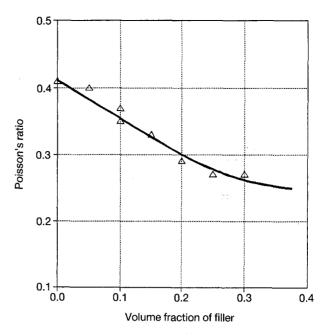


Figure 13 Composition dependence of Poisson's ratio (v) calculated from the first part of the volume strain curve.

initiated at the pole of the particle, as because of stress concentration, local stresses reach a maximum here. With increasing elongation, the debonded surface proceeds along the surface of the particle from the pole towards the equator. Because of constantly changing stress distribution, a deformation is reached where extension of the debonded surface stops and void formation starts. The stress values characterizing the two processes must be proportional to each other, as they can be predicted by the same correlations. More theoretical and experimental work need to be done, however, to determine their exact values and find the correlation between them.

The rate of volume increase, i.e. the slope of the  $\Delta V/V_0$  against  $\varepsilon$  lines and its relation to the underlying micromechanical deformation process, is very contradictory. Both theories presented above [1, 19] predict linear dependence of volume increase on elongation. Experimental data obtained in this work correspond to these predictions (Figs 4 and 5). The contradiction lies in the rate of volume increase and in its dependence on composition. In his analysis Bucknall [1, 17, 18] neglects to take into account the number of initiation sites during the crazing of HIPS, although 10 cavities do not yield the same volume increase as 10<sup>6</sup>. Farris [19] predicts linear dependence of the slope on the volume fraction of the particles (initiation sites) with a slope of  $\leq \varphi_{f}$ . The present results, however, indicate non-linear dependence of the rate of volume increase on filler content.

The contradiction between Farris's theory [19] and the present experimental data may have several reasons. In the present experiments, only one lateral dimension was measured and equality of deformation in the other direction was assumed. On the other hand, the assumptions made by Farris [19] in his analysis might not hold in all cases. He assumed that the cavities formed are rotational ellipsoids with short axis which are equal to the diameter of the particles. Fig. 7d seems to contradict this, showing irregular holes significantly larger than the diameter of the particles form. This may explain the larger slopes at low volume fractions. With increasing filler content the probability of aggregation increases and neighbouring cavities might hinder each other in growth. As a result, the rate of volume increase slows down with increasing filler content of the composite. Although this tentative explanation seems to be in accordance with the experimental observations, more research has to be done to prove its validity and explain the discrepancy between the theoretical predictions and practice.

## 5. Conclusions

These studies carried out on particulate filled PP composites have proved the importance of micromechanical deformation processes in the deformation and failure behaviour of polymers. Introduction of filler into PP leads to a change in the mechanism of micromechanical deformations. In the filled system, the dominating process is debonding, i.e. the separation of the matrix and filler surfaces under external stress. Considerable volume increase is initiated around the deformation where maximum is observed on the stress against strain curve, i.e. yield stress is an indicator of the prevailing micromechanical deformation process.

An analysis of the conditions for debonding showed that interfacial interactions play an important role in the mechanism of deformation and generally in the mechanical behaviour of composites. The rate of volume increase depends strongly on the volume fraction of the dispersed component, but it is independent from its size, properties or adhesion to the matrix. The analysis was strongly corroborated by a number of independent data. Additional experiments are needed in order to obtain more precise correlations and further verify these results.

# Acknowledgements

The financial support of the National Scientific Research Fund (OTKA 1789) is gratefully acknowledged.

#### References

- 1. C. B. BUCKNALL, "Toughened Plastics" (Applied Science, London, 1977).
- A. J. KINLOCH and R. J. YOUNG, "Fracture Behaviour of Polymers" (Elsevier, London, 1983).
- 3. P. H. T. VOLLENBERG, PhD Thesis, University of Eindhoven, 1987.
- 4. B. PUKÁNSZKY and G. VÖRÖS, Compos. Interfaces 1 (1993) 411.
- 5. H. BREUER, NATO ASI Ser. E 89 (1985) 375.
- 6. Idem. Ibid. 89 (1985) 383.
- 7. W. J. COUMANS and D. HEIKENS, Polymer 21 (1980) 957.
- 8. V. P. CHACKO, R. J. FARRIS and F. E. KARASZ, J. Appl. Polym. Sci. 28 (1983) 2701.
- 9. E. A. A. HARTINGSVELDT, PhD Thesis, Technical University of Delft, 1987.
- 10. B. TURCSÁNYI, B. PUKÁNSZKY and F. TÜDÓS, J. Mater. Sci. Lett. 7 (1988) 160.
- B. PUKÁNSZKY, B. TURCSÁNYI and F. TÜDÓS, in "Interfaces in Polymer, Ceramic and Metal Matrix Composites", edited by H. ISHIDA (Elsevier, New York, 1988) p. 467.
- 12. B. PUKÁNSZKY, K. BELINA, A. ROCKENBAUER and F. H. J. MAURER, *Composites* (in press).
- 13. P. H. T. VOLLENBERG and D. HEIKENS, J. Mater. Sci. 25 (1990) 3089.
- 14. N. J. GOODIER, J. Appl. Mech. 55 (1933) 39.
- 15. R. J. FARRIS and R. FALABELLA, Sagamore Army Materials Research Conference Proceedings, Vol **32** (1987) 199.
- 16. S. D. SJOERDSMA, PhD Thesis, Eindhoven University of Technology, 1981.
- 17. C. B. BUCKNALL, Adv. Polym. Sci. 27 (1987) 121.
- C. B. BUCKNALL, in "Polymer Blends", edited by D. R. Paul and S. Newman (Academic Press, New York, 1978) p. 91.
- 19. R. J. FARRIS, Trans. Soc. Rheol. 12 (1968) 315.
- 20. P. VOLLENBERG, D. HEIKENS and H. C. B. LADAN, Polym. Compos. 9 (1988) 382.

Received 29 April and accepted 6 October 1993