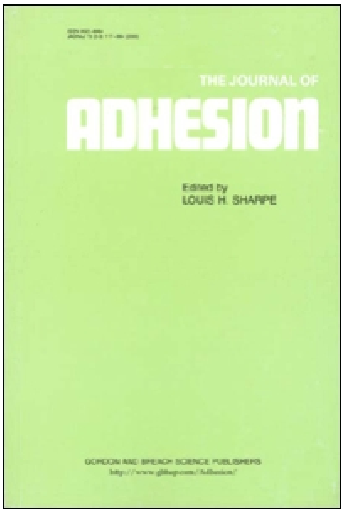

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Pressure Reinforcement of Particulate Polymeric Composites Originated By Adhesive Debonding

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Particulate elastomeric composites exhibit considerable reinforcement when they are extended under moderate superposed pressures. Numerous experiments have shown that this effect is provoked by pore formation and relevant matrix overstraining. The interfacial friction between the debonded matrix and filler has as well been shown to influence this phenomenon markedly. It seemed resonable first to study separately elastic and frictional contributions to reinforcement.

The paper examines the reinforcement effect caused by elastic pore suppression under superposed pressure without taking into account the frictional effect. The structural element has the form of a rubber neo-Hookean cylinder (matrix) with a rigid spherical inclusion (filler) at the center. Quantitative dependence of the reinforcement on the volume suppression, pressure, degree of extension, volume content of the inclusion and modulus of the matrix has been obtained in the framework of large deformation. The analysis of these data has shown that theoretical results were in good agreement with the available experimental evidence.

Some peculiarities of the phenomenon have been established such as the weakening of the extent of reinforcement with the extension, higher reinforcement under negative pressures, two different geometrical modes of the vacuole compression depending on the extension and the range of matrix moduli where the reinforcement effect becomes negligible.

KEY WORDS: Particulate elastomeric composites; porosity; porosity variation; pressure reinforcement; mechanical behavior.

1. INTRODUCTION

Particulate polymeric composites may be regarded as a specific class of materials which is characterized by the appearance of porosity during deformation. In the virgin state these materials are dense. However, they dilate on straining because of numerous microscopic structural failures accompained by pore formation.

This feature imparts some unique mechanical properties to these materials among which the so-called pressure reinforcement is possibly the most outstanding one. This phenomenon was first described about 25 years ago by Oberth[1] and Farris[2,3] who established that moderate external (hydrostatic) pressures superposed on specimens during tensile tests noticeably increased their mechanical stiffness.

The cited experimental investigations have given a general notion of this phenomenon. The main factors contributing to pressure reinforcement were outlined.[1–3] It was demonstrated that pressure influence is intimately related to porosity originating under deformation in the interior of the material. The effect increased with the degree of porosity defined by the deformation of specimens.[1-4] The extent of pressure reinforcement was, however, bounded by some upper limit.

Later, it was found out that pore formation can take place under different modes of deformation not only in simple extension, but also in creep[5] and relaxation.[6] However, the presssure dependence on creep and relaxation did not attract experimentalists' attention for a long time. Only recently the experiments have been carried out, which manifested a strong influence of external pressure on the relaxation and hysteresis loops of damaged particulate composited.[7,8]

The experimental evidence gained has been utilized primarily as a basis for developing phenomenological constitutive relations.[9-11]

Along with these elaborations, studies have been (and are being) carried out directed to development of structural models [12-14] destined for prediction of relations between structural parameters and mechanical behavior of damageable composites. In these works, unit cells of particulate composites are usually examined as some *phenomenological* objects with the imposed set of properties originating from experience and representing, so to say, bulk behavior of cells.

In our opinion, such an approach needs additional investigations oriented to elucidation of processes occurring inside the cell volume. In this case, the unit cell is to be regarded as a certain construction with a well-defined internal geometry, properties of constituent elements, and loading conditions. Methods of *boundary value problems* are then to be used for establishing the stress-strain state of the cell. Such an approach allows one to gain a deeper insight into the inner peculiarities of cells strongly affecting their bulk behavior.

This appears to be even more necessary when one intends to understand and describe the combined response of the elastic and frictional forces in unit cells towards the action of the external pressure.[7,8] As a first step, it seems expedient to investigate separately the contribution of elastic and frictional factors. At this time, the accounting for elastic effects appears quite feasible. This paper is focussed on the solving of this problem.

2. THEORETICAL BACKGROUND

The composites in question are materials of the matrix type. Their structure represents closely-spaced, rigid, spheroidal particles embedded into the soft, elastic matrix forming the continuum part of the system. Pore initiation and progression in such strongly heterogeneous materials is the result of numerous microscopic internal failures provoked by high local matrix stressing. In polymeric composites, these microfailures usually represent interfacial separation of matrix from filler and take the form of ellipsoid cavities (vacuoles) around particles.[1,2,15]

For the elucidation and exploration of the mechanism of pressure reinforcement, a representative unit cell of composite material has been adopted in the form of an isometric, elastic, incompressible cylinder (matrix) in which a rigid sphere (filler particle) is placed (Fig. 1(a)). It is assumed that in this cell the matrix is not bonded to the inclusion and is ready for immediate pore generation after the extension has begun. Previous history of the structural element is not examined, being beyond the scope of the subject matter of this paper.

It can be easily imagined that when the ends of the model are pulled apart without superposing hydrostatic pressure the matrix starts detaching from the poles of the sphere, its equatorial part retaining contact with the sphere (Fig. 1(b)). No friction forces between matrix and sphere surface in this locality are assumed.

From general considerations, one may suppose that superposing pressure on the elongated model must shrink the vacuole and somewhat augment the elastic energy of the matrix above that already stored by stretching. This must entail corresponding increases in the retractive effort, F_p, to keep up a constant level of stretching (Fig. 1(c)).

The additional growth of the effort at the same stretch is exactly the pressure reinforcement effect that is the subject of our investigation.

Our task was to obtain a quantitative relationship between the elongation and superposed hydrostatic pressure as external actions, on the one hand, and elastic resistance and pore volume changes as the responses of the model, on the other hand.

The computations were performed within the framework of large deformation theory by a procedure reported in Reference 16, where triangular, cylindrical finite elements with a square approximation to the displacement field and linear functions for the mean pressure were used in calculations of the stress and strain fields. Condensation of the elements was made near the localities of high stress gradients.

The behaviour of the matrix was assumed to be that of an incompressible, neo-Hookean material characterized by an elastic potential of the simplest form

$$W = C(I_1 - 3),$$

where C is a constant equal to 0.05 MPa, which is equivalent to the shear modulus, G, of 0.1 MPa for the range of small deformations; I_1 is the first main invariant of the

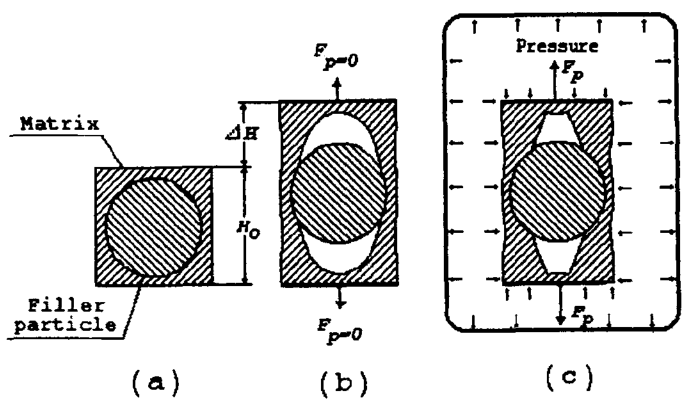

FIGURE 1 Unit cell construction and modes of loading: (a) initial state; (b) only stretching; (c) stretching with superposed hydrostatic pressure. Sphere radius: 0.84 cm. Cylinder length: 2 cm.

Cauchy–Green deformation measure tensor. The filler particle being rigid, all the energy of deformation is stored within the matrix volume.

The loading of the model has been performed in two stages. The first one represented the extension of the model to a prescribed level at zero external pressure. The second stage involved the incrementally-increasing pressurization that was continued until vacuole volume became zero or negligibly small. In both cases: (1) the pressure inside the vacuole has been retained at zero level; (2) the vertical displacements of the ends of the model have been taken constant while the radial ones were without restriction.

The force response of the model was expressed through the stress, σ, reduced to the initial cross-section, S_0

$$\sigma = F_p/S_0 - P,$$

Where F_p is the resulting force at the end of the model and p is the applied external pressure. The value of σ represents "pure" retractive stress, free of the superposed pressure component.[2,3]

The extension of the model, ε, has been expressed simply as the ratio of the length increment of the model, ΔH, to its initial length, H_o (Fig. 1).

3. RESULTS OF CALCULATIONS

3.1 The Influence of Pressure on the Mechanical Resistance of the Model

The detailed investigation of the problem has been performed for the geometry of a model shown in Figure 1, corresponding to a rather high filler content of about 40% by volume.

In the work descibed in References 1 and 2 it was common practice to present the pressure influence by a set of tensile and dilation curves obtained under various superposed pressures. To make comparison with their experimental data more evident, it seemed reasonable to retain the same procedure for the presentation of the results of our calculations.

Therefore, tensile and dilation curves for the unit cell have been calculated at various extensions, ε (from 0,01 to 0.5), and pressures, p (from 0 to 5 MPa). These are given in Figure 2. The calculated relationships closely resemble the experimental ones demonstrated in References 1 and 2. Considering that our simulation approach takes into account only the elastic properties of the model, one may conclude that pressure reinforcement of actual composites is controlled primarily by the elastic response of the matrix inside the composite system. The upper envelope in Figure 2(a) represents ultimate pressure reinforcement corresponding to complete, or nearly complete, pore suppression.

Figure 3 depicts stress reinforcement as a function of pressure for various extensions. It can be seen that the resistance of the model rises with pressure and extension. In the region of small extensions, the attainment of ultimate reinforcements occurs at low pressures.

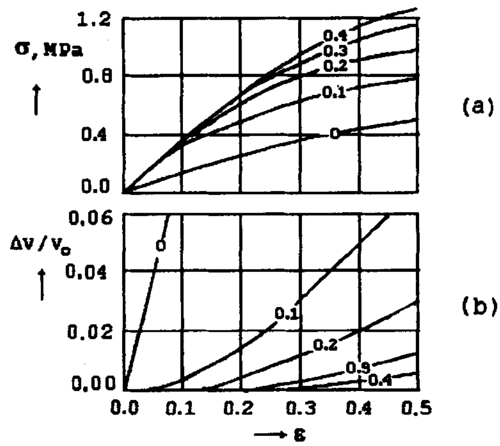

FIGURE 2 Tensile (a) and dilation (b) curves under various pressures indicated on the curves in MPa.

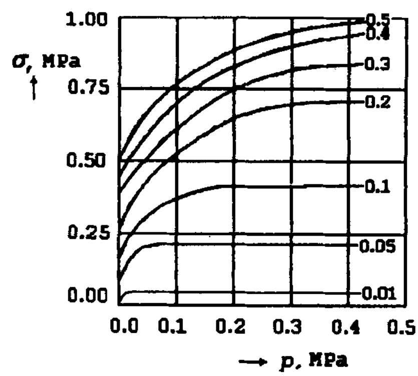

FIGURE 3 Stress increase as a function of pressure for various extensions indicated near the curves.

Another feature of this phenomenon is revealed when the *relative* pressure sensitivity, R_f, instead of the *absolute* one, is used in the analysis of the pressure reinforcement mechanism, the R_f value being defined as

$$R_f = \sigma_p/\sigma_{p=0} - 1, \qquad (1)$$

where σ_p is the stress in the stretched model at a given pressure p and $\sigma_{p=0}$ is the stress at zero pressure at the same stretch.

The results of calculations are shown in Figure 4, from which one may conclude that, for the geometry of Figure 1, there exists some maximum R_f value (close to 2.0) characteristic of lower extensions (up to about 10%). At higher extensions, the maximum relative reinforcement beigins to diminish, tending, presumably, to zero. Thus, the pressure sensitivity weakens with extension. Incidentally, this explains the nonlinear character of the upper envelope in Figure 2(a).

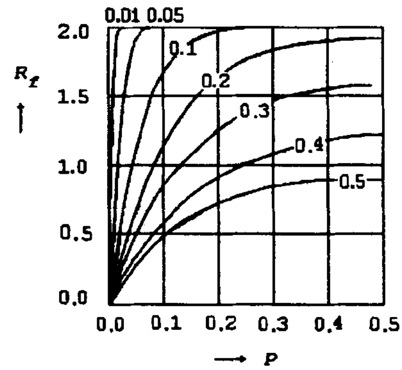

FIGURE 4 Relative reinforcement *versus* pressure at various extensions indicated on the curves.

Evidently, pressure reinforcement must be influenced strongly by the modulus of matrix. The greater the modulus, the lesser the suppression of the pore volume and the weaker the reinforcement effect. The analysis of tensile curves as functions of P and G, the latter varying from 0.05 to 8.0 MPa, has shown these functions to be relatively invariant with P/G ratios for a given stretch.

These calculations have also permitted the determination of the value of the matrix modulus, G, that makes the resistance of the unit cell insensitive to hydrostatic pressure. The analysis has shown that the pressure reinforcement effect can be neglected when the modulus of matrix become 100–200 times greater than the operating pressure, the effect turning out, in that case, to be less than one percent. Hence, considering that atmospheric pressure is close to 0.1 MPa one may conclude that atmospheric reinforcing action, as such, should be taken into account only when one has to deal with soft matrices having moduli less than 0.001 MPa. If the operating pressures for a given composite are of the order 10 MPa, then the pressure effects will be "felt" with matrix moduli of the order of 0.1 MPa.

Figures 3 and 4 demonstrate the reinforcement *versus* P dependence for the particular case where the filler content in the unit cell is 40 percent by volume. The changing of the unit cell filling will, naturally, affect the form of the $R_f \sim P/G$ curves. One may expect that diminishing the sphere size, that is the hard-phase content, will lead to a decrease in the pressure sensitivity of the model due to decrease of the vacuole volume. Calculations corroborate this assumption (Figure 5). Two limiting cases can be foreseen without recourse to calculations. The first characterizes the cell that does not contain inclusion (zero filler content). It must be insensitive to pressure action, its R_f function representing a straight line at zero level. The second case corresponds to the ultimate filler content which (caused by the geometry of the unit cell) is close to 66.7%. Here the radius of the sphere is nearly equal to the radius of the cyclinder. Only a very thin matrix layer surrounds the equatorial part of the sphere. This cell must exhibit the highest pressure sensitivity.

It seemed of interest to evaluate the behavior of the model under negative pressures, that is under superposition of hydrostatic extensions. In contrast to the case previously studied, here nothing impedes the volumetric expansion of the model in the initial

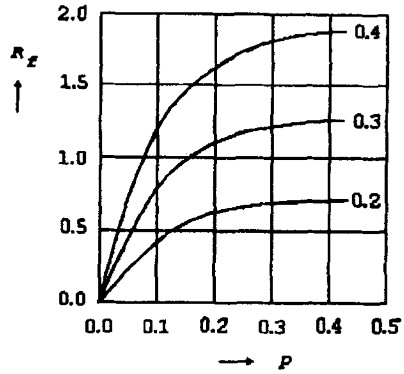

FIGURE 5 Influence of the volume filling of the unit cell on the relative reinforcement at 20% stretching. Volume fillings are indicated near the curves.

(non-stretched) state after applying the negative pressure. This leads to the appearance of a retractive force at the ends of the model even at zero elongation. Figure 6 demonstrates the difference between the tensile curves obtained under positive (0,1 MPa) and negative (−0.1 MPa) superposed pressures. It is seen that reinforcement under negative pressures is higher than that under positive pressures. Thus, the extension under zero superposed pressure provides the least possible mechanical resistance of the model.

A poorly-studied point is the mechanical resistance and porosity characterization of the model under the action of compressive forces. Figure 7(a) depicts the typical shape of the cavity appearing during compression at zero external pressure. Its form resembles an empty flattened tear around the equatorial part of the sphere. Figure 7(b) reveals the pressure resistance of the debonded model to compression to be significantly greater than that to extension. This distinction is evidently caused by the peculiarity of the geometrical structure of the model.

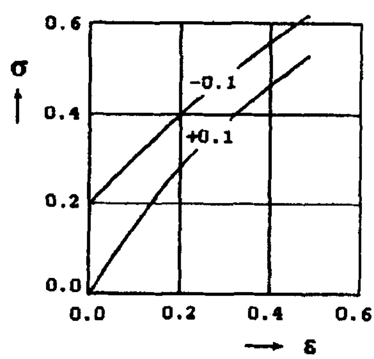

FIGURE 6 Tensile curves under positive and negative pressures which are indicated on the curves in MPa.

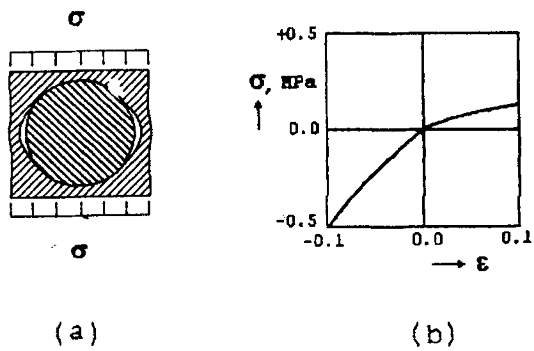

FIGURE 7 The pattern of the detachment under compressive stess with zero superposed pressure (a) and the curves of one-directional extension and compression (b) of the unit cell under zero external pressure.

3.2 Dilation ~ Pressure Effects

It is obvious that the volume change of the model under compressing external pressure is the sum of the volume change of the condensed part of this system and the vacuole volume suppression. In a rigorous approach, the retention of the first item must be taken into account. However, in the present analysis, where the condition of the incompressibility of the matrix and the sphere has been adopted, the actual compressibility of the condensed part of the model will be ignored.

The porosity of the unit cell, V_r, has been expressed as the ratio of the current vacuole volume to the initial cell volume. A set of curves of V_r *versus* P, shown in Figure 8, has been calculated for various elongations, ε, (from 0.1 to 0.5) and pressures (from 0.0 to 0.5 MPa). In the framework of the conditions adopted, if the extension is zero, no volume change takes place on applying hydrostatic pressure. The greater is the extension of the model the greater is the vacuole volume appearing without hydrostatic

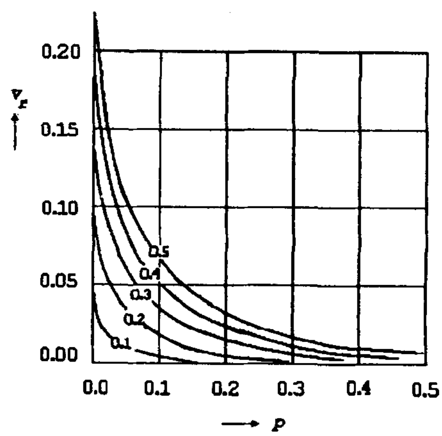

FIGURE 8 Porosity of the unit cell as a function of pressure for various extensions indicated on the curves.

pressure and the greater becomes its diminution after the appplication of the external pressure.

A steep fall of pore volume is characteristic of the lower pressure region. The magnitude of V_r becomes negligibly small when the pressure is 5 to 10 times greater than the shear modulus of the matrix.

The calculations have shown that there exist two geometrical modes of vacuole shrinking under pressurization. The first one, characteristic of lower deformations (up to 10 percent), represents simple and complete closure of the narrow curvilinear gap between the matrix and the sphere's surface. The second mode, depicted in Figure 9, occurs at higher deformations. In this case, complete pore suppression seems to be hardly possible because of the extreme stiffness of the dome-like part of the vacuole.

4. DISCUSSION

Several points seem to merit consideration. First, it may be stated that purely elastic effects play an important, possibly leading, role in the phenomenon of pressure reinforcement. The effect is caused by the shrinking of pores under the action of external pressure. In this conncetion, the direct juxtaposition of the relative pressure reinforcement, R_f, and the relative pore compression, R_v, is of interest.

The last term is expressed as follows

$$R_v = 1 - v_p/v_{p=0},$$

where v_p is the vacuole volume at the pressure, P, and $v_{p=0}$ is the vacuole volume at zero pressure.

Figure 10 demonstrates (for construction of Fig. 1) this relation. Close interconnection between two parameters is evident.

Two operating parameters contribute to elastic energy storage in the deformed matrix of the model. The first one is the extension of the model and the second one is the superposing of the pressure on the extended model. The relationship between these contributions depends on the degree of elongation. Relative pressure reinforcement is strongly pronounced at lower deformation levels wherein it can reach several times the

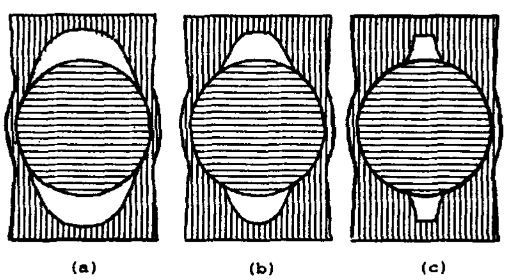

FIGURE 9 Vacuole shapes under different pressures: (a) zero pressure; (b) 0.12 MPa; (c) 0.37 MPa.

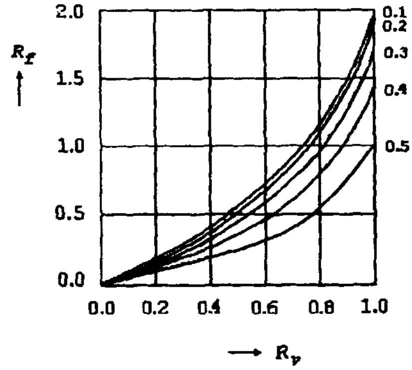

FIGURE 10 Relative pressure reinforcement as a function of the relative pore suppression for various extensions indicated near the curves.

elongation efforts. Its influence drops with imposed stretch, and above 50 per cent model deformations the energy stored from the elongation becomes predominant.

It is well borne in mind that the above analysis has proceeded from the assumption of the frictionless slip of the matrix over the sphere's surface in the region of their contact. In actuality, bonding between the adjacent faces of the sphere and the matrix can take place. Friction forces can appear during the sliding of the matrix along the sphere's surface. These processes, in principle, can somewhat deform the general pattern of pressure reinforcement displayed above. However, we suppose they are of secondary importance in the phenomenon under examination. We intend to continue the studies in this direction.

It is important to keep in mind that all conclusions concerning pressure reinforcement may be extended only to systems with closed porosity.

CONCLUSIONS

1. The theoretical investigation of the phenomenon of pressure reinforcement has been performed on the basis of a unit cell approach. The variant of the unit cell with 40 per cent volume filling was adopted for closer examination. A neo-Hookean elastic matrix, finite deformations and frictionless slippage of the matrix over the inclusion's surface have been assumed in calculations. A series of calculations were performed to obtain the magnitudes of pressure reinforcements and pore volumes as functions of elongation and hydrostatic superposed pressures.
2. The results corroborate, in general, the earlier experimental data so far as they concern the values of reinforcement effects and volume changes.
3. It has been shown:

— The reinforcement effect considerably drops with elongation. It explains the nonlinear character of the limiting envelope observed in experiments;

— Pressure reinforcement effects may be neglected when moduli of matrix become 100–200 times greater than the operating pressure, the effect turning out to be less than one per cent;

— Superposing of negative hydrostatic pressure provokes the pressure reinforcement of the model even at zero elongation. Moreover, during stretching, the negative pressure effect is even greater than that generated by the usual positive pressurization. From this it is inferred that the least mechanical resistance of the model to extension takes place under zero superposed pressure;
— Volume change under the action of superposed pressure takes two different geometrical modes depending on the current value of stretch. At lower deformations (up to 10 per cent), a simple and complete closure of the narrow curvilinear gap between the matrix and the sphere occurs. However, at higher deformations, complete pore suppression seems to be hardly possible because of the extreme stiffness of the dome-like part of the vacuole to compression.

4. The results obtained can be regarded as a sound basis for the development of constitutive relations in continum mechanics of damageable composite materials.

Acknowledgment

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