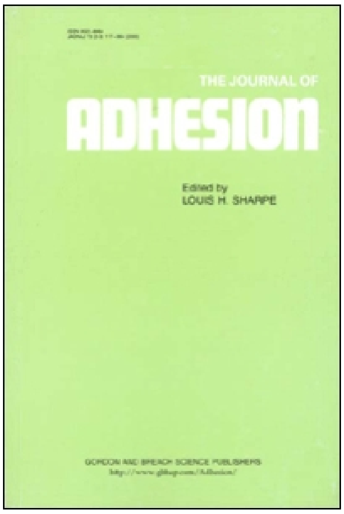

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Unit Cell Evolution in Structurally Damageable Particulate-Filled Elastomeric Composites under Simple Extension

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A special form of the unit cell is offered for investigation of matrix separation in particulate composites. The threshold tear strength of the matrix is used as a basis for the strength-of-cell estimations. Numerical experiments have been performed within the bounds of large deformation theory.

A weak dependence of the ultimate strength on the filler content as well as the extensive plateaus on tensile elongation have been revealed. The latter are due to the slow and stable character of matrix detachment from filler particles.

These results have proved to be in a good agreement with the available experience.

KEY WORDS: Cell model of filled rubbers; structural damage; matrix-filler detachment; large deformation theory; comparison of theory and experiment; mechanical behavior; adhesion; boundary value problem; finite element method.

1 INTRODUCTION

Elastomeric particulate composites are so-called damageable or degradable materials. Under working conditions they often exhibit considerable stress softening retaining, nonetheless, their service performance.

Mullins, the pioneer investigator of the problem, clearly demonstrated that the softening is the phenomenon of the structural damage, which takes place at various scale levels including both the injuries of chemical and physical links within the matrix molecular network and the alterations of larger order such as matrix-filler separations and internal matrix tearing.[1]

Although stress softening has been the object of numerous investigations for about 40 years,[1–17] many particular problems remain to be solved.[18]

Experiments testify that the separation of matrix from filler particles during deformation is, possibly, the most dramatic phenomenon among other damage mechanisms. Especially, it is characteristic of highly-filled composites, based on well vulcanized rubber matrices, such as, for instance, those reported in Schwarzl's[3,7] and Farris'[5,6] papers.

Studies have been and are being carried out directed to development of structural models[9–17] destined for prediction of relations between structural features and mechanical behavior of damageable composites. Some of them examine a single sphere in an infinite matrix[9-11] that is far from actuality. The other works[12-17] assume the unit cells to be 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 the *boundary-value problems* are then to be used for establishing the stress-strain state of the cell. Such an approach allows one to get a deeper insight into the inner peculiarities of cells strongly affecting their bulk behavior.

The investigation of the phase separation mechanism is exactly the topic of our paper. It was felt that the problem could be best conceived if a properly chosen unit cell was used as the basis for an analysis. The choice of the shape and the loading conditions for the unit cell are the first points examined in the paper. An attempt to describe the separation phenomenon in simple tension, as some evolutionary process, was then undertaken. The analysis was applied to various volume contents of the solid phase in the unit cells.

2 THEORETICAL BACKGROUNDS

2.1 Shape of the Model Element

The choice of an appropriate structural element arises from the general notion of structural specificity of particulate composites. These materials may be regarded as systems of randomly-spaced, rigid spherical particles imbedded into a soft, highly-resilient elastic matrix forming the continuum part of the material. Originally, particles are assumed to be perfectly bonded to the matrix. However, on extension, detachment of the matrix from filler occurs leading to formation of cavities (vacuoles) oriented along the direction of the extension. After complete matrix separation from filler particles, structural elements continue resistance for some time, although with strongly decreased stiffness. Finally, they break down and become incapable of resisting elastically.

The task was to pick the unit cell geometry as close to that of real materials as possible. The isometric configuration, allowing rather close packings, was regarded as the most suitable for representing properties of particulate composites. With this in mind, the isometric hexagonal bee cells (honey-comb) seemed to be the most desirable. However, restricted possibilities of present-day computing techniques have not permitted calculations with such a shape. So, we were forced to choose a simpler shape, namely that of the cylinder (matrix) containing a rigid spherical inclusion (filler particle) at the center (Fig. 1). The height of the cylinder was taken equal to its diameter.

The volume content (fraction) of inclusions in this configuration has been varied from zero to a maximum of 0.67, when the surface of the inclusion touches the boundaries of the cylinder. This value is not far from the actual ultimate random packing of uniform spheres (0.63–0.64).[19]

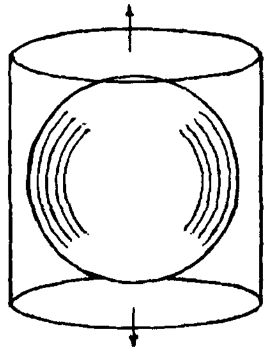

FIGURE 1 Unit cell geometry with 40% inclusion content.

A constant value, namely 2 cm, was assigned to the diameter of the cylinder, D, and its height, H. The diameter of the inclusion was adopted as a varying parameter that took the values corresponding to prescribed volume fillings of 0.1, 0.2, 0.3, 0.4 and 0.5.

In all instances, the life cycle of the unit cell started from the unstressed state with the inclusion bonded to the matrix.

Only coarse filler particles have been examined. That means that no surface tension effects were taken into consideration.

2.2 Loading Conditions

The cell was tested in simple tension. Cylinder ends were moved apart, vertical displacements being constant and radial ones not constrained. No lateral stresses were applied. In actual composites, this stress state is characteristic of cells located at or near the free surfaces of the specimens.

No surface tractions were applied to the surface of the detached portion of the cell.

The resistance of the model has been expressed through reduced stress, σ, defined as

$$\sigma = F/S_o,$$

where F is the force of extension and S_o is the initial cross-section of the cell. The strain, ε, of the cell was defined as

$$\varepsilon = \Delta H/H,$$

where ΔH is the relative displacement of the ends.

In all the numerical experiments the maximum straining of the model was assumed to be 50 per cent.

2.3 Mechanical Properties of Constituent Materials

The approach adopted in this paper is purely elastic, with no time dependency being taken into account. Therefore, only an equilibrium elastic process was examined.

The properties of the matrix have been supposed to be that of neo-Hookean material. They are characterized by the elastic potential, W_{el}, of the simplest form

$$W_{el} = C(I_1 - 3).$$

Here C is a constant equal to 0.05 MPa, which corresponds to the shear modulus, G, of 0.1 MPa for the range of small deformations; I_1 is the first main invariant of Cauchy-Green deformation measure tensor.

The inclusion is assumed to be a perfectly rigid solid.

2.4 Matrix Detachment Condition

During extension, the cell stores elastic energy that is embodied exclusively in the matrix phase, the inclusion being perfectly rigid. It is of importance that the matrix has a *restricted* volume. Hence, one may expect that the total elastic energy release, after bond fracture onset has occurred, might be profound enough to stop the initial, possibly inevitable, catastrophic crack fomation. A stable crack propagation is thought to be quite plausible with ever-continuing extension. This is what differentiates our statement from the others that have been examined earlier[9,10] for conditions of constant strain energy density in the surrounding matrix.

Whether or not the crack growth is stable is determined by the balance between the amout of the elastic energy accumulating within the matrix during extension and the releasing capability due to dilation after detachment has taken place.

The following scheme of calculation was adopted. For a given inclusion size, a set of tensile curves was calculated where each calculation was made for an imposed area, S, of debond that was kept constant. These calculations provided two relationships characterizing cell behavior, namely, force, F, as a function of ε and S

$$F = \phi_1(\varepsilon, S) \tag{1}$$

and the elastic energy, W, of the cell as function of ε and S

$$W = \phi_2(\varepsilon, S). \tag{2}$$

The magnitude of the imposed debonded area, S, has been varied from zero to some maximum value defined by the inclusion diameter. As an illustration, the data obtained for the cell with the 40 per cent solid filling are shown in graphic form in Figures 2 and 3. From Figure 2, it is seen that the resistance of the cell with increasing S falls from some initial highest stiffness at S equal to zero to the minimum stiffness where debonding reaches its ultimate value. A like interrelation is kept for the strain energy, W, of the cell (Fig. 3).

The results of these calculations have provided data necessary for the ensuing estimation of the tensile curves with the matrix naturally separating from the inclusion during the process of extension.

To describe the debond's origination and progression, Griffith's approach has been used in much the same way as it has been done in other publications.[9,10,20] A small precursor circular debond has been assumed to exist at the poles of the sphere. The

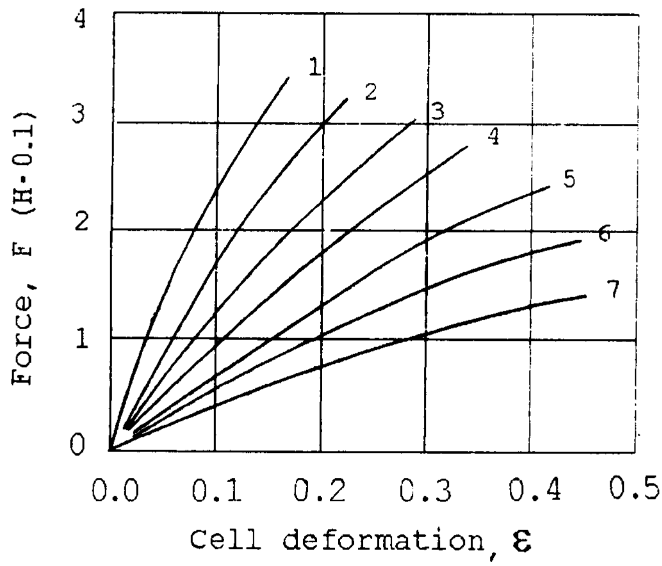

FIGURE 2 Force of extension, F, *versus* cell deformation, ε, for a series of debonds, S. Numbers on the curves indicate the areas of detachment in cm^2: 1-0.0; 2-0.416; 3-1.05; 4-1.48, 5-2.28; 6-3.20; 7-4.43.

energy, T_d, required for further matrix detachment has been defined as

$$T_d = \left(\frac{\partial W}{\partial S}\right). \tag{3}$$

Here, ∂W is the energy increment of the given system needed to increase crack area by ∂S, T_d being the characteristic property of the pair "matrix-inclusion".

In our case, the only energy source for debonding is the strain-energy, W_m, accumulated in the matrix that, according to expression (2), depends both on the current cell deformation, ε, and on the current crack area, S.

The condition (3) may be rewritten as

$$T_d = \frac{\partial \phi_2(\varepsilon, S)}{\partial S} = \vartheta(\varepsilon, S). \tag{4}$$

Having assumed T_d to be some characteristic property of the cell system and having assumed its value to remain constant during the entire process of the matrix detachment from the inclusion, we open the opportunity to establish an explicit interrelation between ε and S by means of expression (4). For a number of growing S_i values, beginning with the small initial one, corresponding ε_i values are calculated from (4). Then, after having substituted relevant ε_i, S_i pairs into expression (1), the $F \sim \varepsilon$ correlation characterizing tensile behavior of the cell under imposed T_d can be obtained.

Therefore, the process of detachment may be regarded as that of the transfer of the cell from the initial state of the nearly-perfect bond to the final one of complete separation.

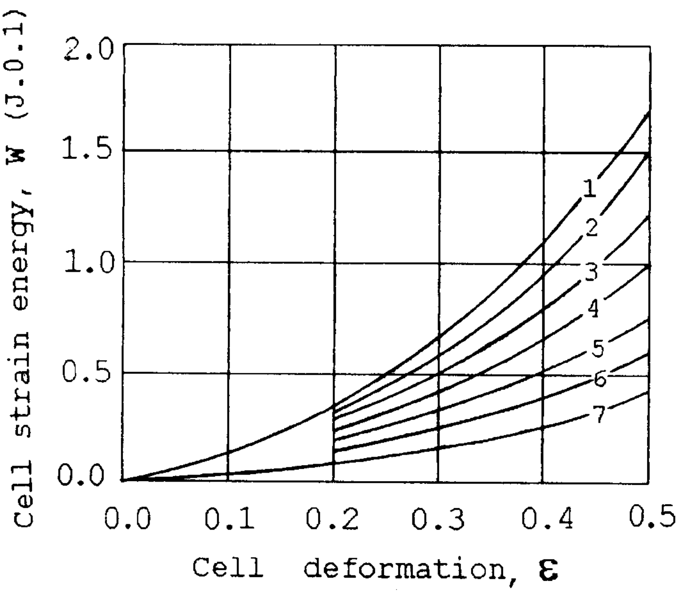

FIGURE 3 Strain energy, W, *versus* cell deformation, ε, for a series of debonds, S. Numbers on the curves indicate the areas of detachment in cm^2: 1-0.0; 2-0.416; 3-1.05; 4-1.48; 5-2.28; 6-3.20; 7-4.43.

It may be expected that the shape and spread of the transition zone might depend on the volume content of the inclusion in the cell. At low solid contents (small sphere diameters) the detachment process will affect the resistance of the cell slightly. In contrast, at high solid contents, when the matrix volume and the amount of stored strain energy become moderate, the influence of detachment must turn out to be considerable.

Properly speaking, the aim of the paper is just that of quantitative prediction of the process examined above as a qualitative one.

2.5 Method of Solution of Boundary Value Problem

The solution has been found within the framework of large deformation theory.

The mathematical statement of the problem has been described in detail elsewhere.[21] Briefly the method consists in using a function, $He(H,\bar{u})$, developed especially for incompressible or nearly incompressible materials:

$$He(H,\bar{u}) = \int_{V_0} (AH(I_3-1) - A^2\frac{\alpha}{2}(H-\chi^*)^2 + W(I_1,I_2) + \frac{1}{2}(k_1+k_2)((I_1-1) - A\alpha(H-\chi^*))^2 - \rho^0\bar{K}\bar{u})\,dV_0 - \int_{S_p^0} \bar{p}\bar{u}\,dS_p^0.$$

Here, $A = 2(k_1 + k_2)/(2 - \alpha(k_1 + k_2))$ and α are generalized elastic moduli; $\bar{u}$ is the displacement vector; V_0 and S_p^0 are, respectively, the unstrained volume with volume forces, $\bar{K}$, and density, ρ^0, and the surface where forces, $\bar{p}$, are applied. For an incompressible material, the generalized modulus of elasticity, α, is equal to zero. Then the incompressibility condition ($I_3 = 1$) is satisfied automatically during variation of the function with H. The function is varied in H and $\bar{u}$. Minimizing $He(H, \bar{u})$ on $\bar{u}$ and H produces a set of variational equations that is equivalent to all the differential equations of continuous media mechanics.

The finite element method was used for calculations. A typical sketch of the adopted finite element grid is shown in Figure 4 for a solid volume content of 40%. Considering the geometry of the cell, a condensation of elements near the inclusion was performed.

Displacement vector components and mean stress function in n and m nodes were approximated by the shape functions ψ_P and ϕ_N. Then, the displacements are $u_P = \psi_P u_P^n$, $u^k = \psi_m u^{mk}$, and the mean stress function $H = \phi_N H^N$. Here, u_P^n, u^{mk} are covariant and contravariant displacement vector components.

A program was developed for the incremental load procedure, using triangular cylindrical finite elements with a square approximation to the displacement field, and linear fnctions for the mean pressure. In contact zones, the conditions of non-penetration and non-positiveness of normal pressure have been introduced.

The initial small debond, in the form of disconnected matrix nodes at the poles and at their nearest interfacial neighbors, was introduced to make feasible the Griffith approach. The area of such bebond was of only about 1% of the total interface area. The calculations have shown that $F \sim \varepsilon$ and the strain $W \sim \varepsilon$ curves obtained for the perfectly-bonded system and those with the initial debond present are very close to each other. So, when, in extension of the debonded sample, the critical condition (3) is reached at some point on the $F \sim \varepsilon$ curve, this point (taking into account the above reasoning) without appreciable error may be considered as that belonging also to the

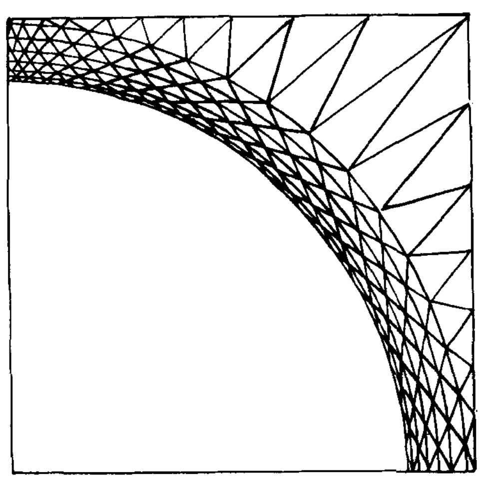

FIGURE 4 Adopted finite element grid, containing 135 triangular elements.

$F \sim \varepsilon$ curve of the perfectly-bonded sample. Hence, this position may be regarded as that where the matrix detachment comes into play.

The computation gives the stress and strain fields that are further converted into F and ε.

3 ANALYSIS AND DISCUSSION

If the filler-matrix bond is high enough then the detachment may occur only through internal tearing of the matrix phase in the most-stressed locality (at the pole region in our case). Therefore, the tear strength of elastomeric materials, T_e, may be considered as the ultimate value of the bond strength. Energies of debond less than T_e may be considered as characteristic of the filler-matrix bond.

With this in mind, data concerning threshold tear strengths of elastomers have been used in the following analysis. According to Gent and Tobias,[22] the threshold tear strength of hydrocarbon elastomer correlates with its Young's modulus. The use of this correlation has permitted us to specify the threshold tear strength for the matrix examined in this paper at the level of 150 J/m^2.

Tensile curves have been calculated for several volume fillings providing that T_d was everywhere taken equal to 150 J/m^2. Figure 5 demonstrates these curves wherein their left sides represent the high stiffness of the still non-damaged cells. A steep drop of stress occurs at the inflection points, where the $\partial W/\partial S$ derivaties reach 150 J/m^2 at the most-strained polar zones. This drop bears evidence of the loss of stability which finally becomes a stable, uneventful fall in stress until the ultimate detachment is reached.

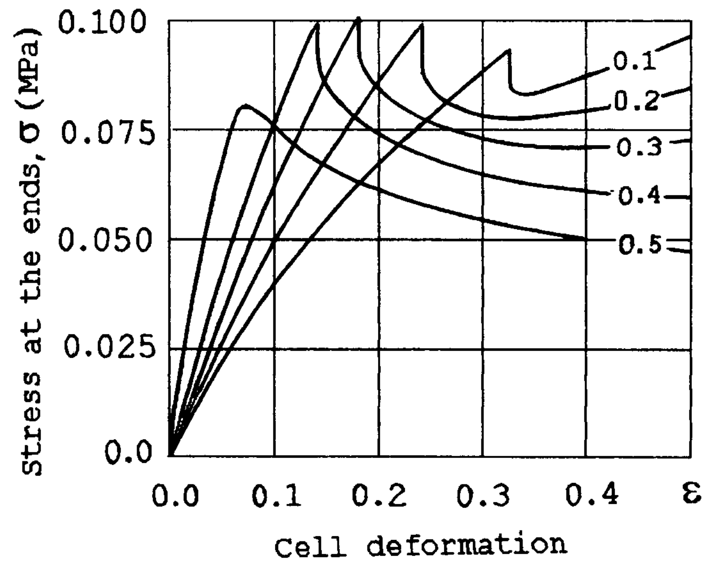

FIGURE 5 Effect of filler content on tensile behavior of the unit cells for T_d = 150 J/m^2. Numbers on the curves indicate fractional filler volume content: 1-0.1; 2-0.2-; 3-0.3; 4-0.4; 5-0.5.

Afterwards, the stress begins to rise according to the lower level of the rigidity characteristic for the totally debonded state. It can be seen that the relative magnitudes of the stress drops diminish with the solid content growth and completely disappear, when the solid volume reaches 50%. It is seen that 50% extension is insufficient for bringing the system to complete debonding. The transition zone has evidenced itself as a more extended one than would be expected before calculations.

The values of stresses at the inflection points may be regarded as the strengths of cells. Evidently, the strength seems to vary only slightly as function of filler content. It remains close to 0.1 MPa in the range of solid concentrations from 0.1 to 0.5. Since this strength value has been obtained from the threshold tear strength of the matrix, one is led to the conclusion that it might characterize the ultimate strength of the system under consideration. The Young's modulus of the matrix being 0.3 MPa, one may conclude that the ultimate strength reaches only about one third of this value. This accords well with some experimental data. In Reference 3, a polyurethane rubber filled with various fractional amounts of sodium chloride was tested. Tensile tests showed that the ratio of ultimate strength to the Young's modulus was 0.33–0.37 at high filler contents. Reference 23 dealt with an ethylene-propylene rubber filled with glass beads. There, the like magnitude of 0.32–0.36 was obtained.

The next distinctive feature worthy of attention is the existence of a considerable transition zone between perfectly-bonded and completely-debonded states of the cell. Figure 5 shows that this zone extends over 50%. This prediction is also rather close to the experimental data cited in References 3 and 17 where plateau regions of the same order had been found. One may conclude that the so-called yield phenomena observed

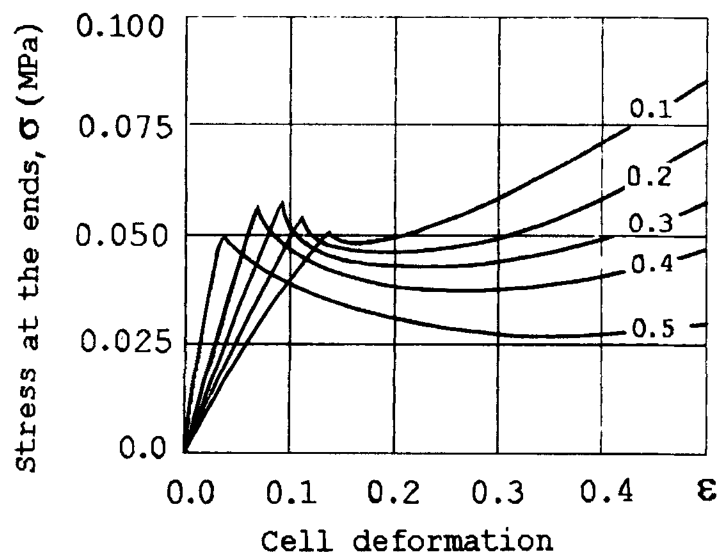

FIGURE 6 Effect of filler content on tensile behavior of the unit cells for $T_d = 50\,J/m^2$. Numbers on the curves indicate fractional filler volume content: 1-0.1; 2-0.2; 3-0.3; 4-0.4; 5-0.5.

in extension of highly-filled particulate polymers arise primarily from the considerable extent and stable character of the debonding phenomenon.

A magnitude of the detachment energy less than the threshold tear strength of the matrix may be considered as the energy of filler-matrix debonding. Taking, for instance, T_d to be equal to 50 J/m^2 one obtains the set of tensile curves shown in Figure 6. It is interesting that the strength of the cell has reduced by only one half, while the energy of separation is taken three times lower. In this figure the transition from the initial high rigidity to the lower final one is seen more clearly than in Figure 5.

4 CONCLUSIONS

1. An isometric cylindrical form of the unit cell has been offered and studied in the characterization of the mechanical behavior of elastomeric, particle-filled composites when the separation of matrix from filler takes place. The calculations were performed within the bounds of large deformation theory on the purely elastic basis, dissipative phenomena not being taken into account.
2. The value of ultimate strength for particulate composites, based on the threshold tear strength of matrix, have been estimated and proved to be in a good agreement with experimental data.
3. A weak dependence of the ultimate strength on the filler content has been revealed which is in agreement with experiments.
4. The extensive plateaus on the tensile curves, often observed in testing highly-filled elastomers, are explained as zones where the matrix gradually separates from the filler in a stable manner.
5. The trustworthy analysis of detachment phenomena in elastomeric, particulate-filled composites strongly calls for the theory of large deformations to be used as a calculation background.

Acknowledgements

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