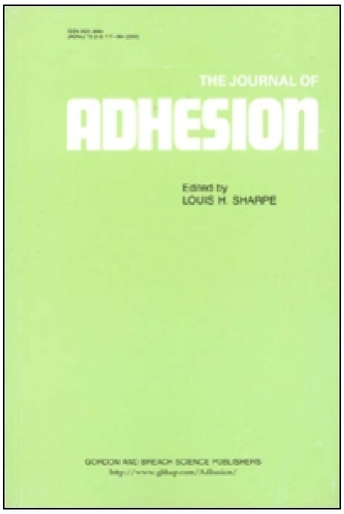

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An Interphase with Changing Properties and the Mechanism of Deformation in Particulate-Filled Polymers*

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The comparison of the results of calculations based on experimental data with those derived from a simple, two phase, elastic model proved the existence of a hard interphase in particulate-filled composites. Moreover, beside elastic properties, also other mechanical characteristics of the interphase, including yield stress, are different from those of the components. An energy analysis showed that the relationship between the yield stress of the matrix and the debonding stress determines the mechanism of deformation. Strong adhesion leads to matrix yielding, while decreased interaction leads to debonding, with a corresponding dependence of composite yield stress on filler content. Particle size, interaction and interphase properties determine the stress necessary to separate the matrix/filler interface. The thickness of the interphase depends on the strength of the interaction; a linear correlation was found between the size of the interlayer and the reversible work of adhesion.

Keywords: Particulate filled polymers; stress analysis; interphase with changing properties; tensile yield stress; composition dependence; debonding; matrix yielding; interfacial interaction; particle size dependence

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*One of a Collection of papers honoring Yuri S. Lipatov on the occasion of his 70th Birthday, 10 July 1997.

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INTRODUCTION

In heterogeneous polymer systems the mechanism of micromechanical deformations and, consequently, the macroscopic properties of the polymers are determined by the local stress distribution around the inclusions [1,2]. With the exception of reactive coupling, the dominating deformation mechanism is debonding in particulate-filled polymers [3–5]. Besides stress concentration and thermal stresses, debonding is also influenced by interfacial interaction, which is determined by the strength of the interaction and the size of the inclusions [4,6–8].

Stress distribution around the inclusions is determined by stress analysis; the traditional approach of Goodier [9] is the most often applied for the calculation of the main stress components. This approach, however, leaves numerous questions open [6,10,11]. In heterogeneous polymer systems interaction of the components leads to the development of an interphase, which has properties different from those of both components [12,13]. The development of such an interphase is not taken into account by Goodier's analysis [9].

Several attempts have already been made to predict the elastic properties of composites by introducing an interphase layer of definite thickness and properties, which are independent of the position inside the layer [14–15]. These models assume isotropic properties of the matrix and the interlayer. In the case of a spontaneously-formed interphase, a continuous change of elastic properties must occur in the interlayer, from a higher value at the surface to the matrix characteristics at a certain distance from the particle.

In an earlier paper, the existence of such an interlayer was assumed and with the help of a first-order perturbation calculation an approximate analytical solution was given for the stresses inside and outside the particles [16]. The results of the analysis were used in a simple averaging procedure and composition dependence of tensile yield stress was predicted by choosing the proper dependence of elastic properties on the distance from the particle. Although relatively good correlation was found between prediction and experimental results, the model possessed several contradictions. It considered changing elastic properties in the interphase, but assumed a constant yield stress, which is probably not true. Since the model was used for the prediction of yield stress, the eventual change of this property in the interface must also be studied. This issue is addressed in the present paper. The effect of changing interphase yield stress on debonding is investigated by stress analysis and the averaging techniques developed earlier.

PRELIMINARY CONSIDERATIONS, EXPERIMENTAL EVIDENCE

Although it seems to be obvious that not only elastic properties (modulus, Poisson's ratio), but also other mechanical properties, including yield stress, of the interphase change with the distance measured from the particle surface, it is worthwhile to consider some experimental evidence which may support this assumption. Comparison of the yield stress and modulus of unmodified polymers indicate a very close correlation between the two quantities [17]. This correlation is presented in Figure 1, where the corresponding properties measured by us [10] are compared with values taken from the literature [17]. The close correlation leads to the obvious conclusion that the increase of modulus due to adsorption on the filler surface and decreased mobility are accompanied by similar changes in yield stress, *i.e.* the correlation presented in Figure 1 for virgin polymers is valid also in the interphase. This assumption is corroborated by the strong correlation between the debonding and yield stresses in particulate-filled composites [5] and by the fact that larger yield stresses than that of the matrix can be achieved with fillers having high specific surface area leading to the formation of considerable interphase.

The composition dependence of yield stress for PVC/$CaCO_3$ composites is presented in Figure 2. The data were taken from previous studies [10, 11]. Two different $CaCO_3$ fillers were used with average particle diameters of 3.6 and 58.0 μm. Composite yield stress decreases with increasing filler content in both cases, indicating that debonding is the dominating deformation mechanism. Debonding occurs before reaching the yield stress of the polymer; most of the load is carried by the matrix. Similar correlations are observed also in polypropylene (PP)/$CaCO_3$ composites [5].

A different composition dependence is observed in a low density polyethylene (LDPE) matrix, when the filler with the smaller particle

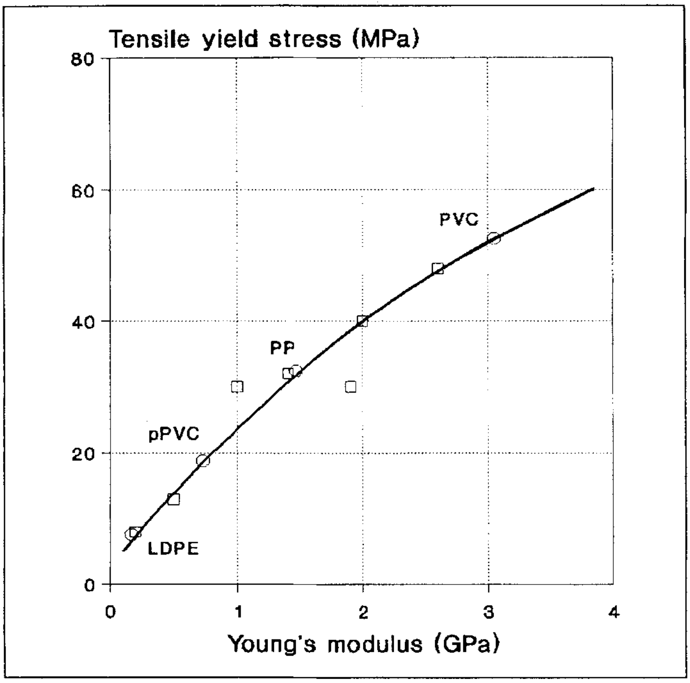

FIGURE 1 Correlation of Young's modulus and tensile yield stress of neat polymers, (□) literature data [17], (○) own measurements [10].

size is added (Fig. 3). The yield stress of the composite increases monotonically with increasing filler content, *i.e.* the filler carries a part of the external load. The composition dependence of yield stress is similar in plasticised PVC (pPVC) composites as well (Fig. 4). Yield stresses which exceed that of the neat matrix polymer indicate the presence of larger than the average stresses around the inclusions and, possibly, the formation of a hard interlayer with increased modulus and yield stress.

A simple model was used for the determination of the average stresses in the polymer and in the inclusions. We assume that at the composite yield stress the polymer has undergone plastic deformation, *i.e.* yielded. Moreover, the load carried by the components corresponds to their effective cross-sections occupied in the specimen, *i.e.* $(1-1.21\varphi^{2/3})$ for the matrix and $1.21\varphi^{2/3}$ for the inclusions, where φ

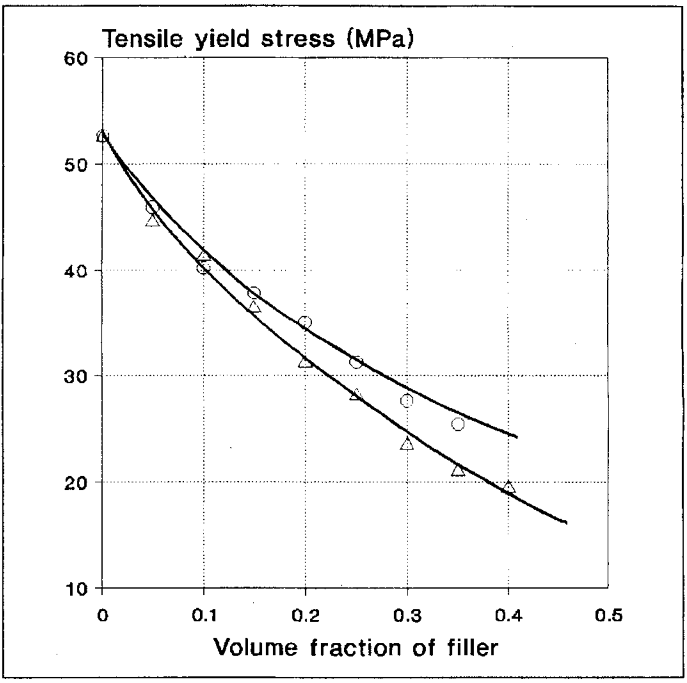

FIGURE 2 Tensile yield stress of PVC/$CaCO_3$ composites plotted against their filler content. Particle size: (Δ) 58.0 μm, (○) 3.6 μm.

is the volume fraction of the inclusions in the composites [18]. If we assume that the average stress acting across the surface of the particles is σ^*, the following equivalence must be valid:

$$\sigma_y = \sigma_y^0(1 - 1.21\,\varphi^{2/3}) + \sigma^* 1.21\,\varphi^{2/3} \tag{1}$$

where σ_y and σ_y^0 are composite and matrix yield stresses, respectively. These two values can be determined by fitting Eq. (1) to the experimental data; the results of the calculations are collected in Table I. The load carried by the filler (σ^*) is always smaller than the matrix yield stress when the filler with the large particle size is used, *i.e.* debonding takes place. When the specific surface area of the filler is larger (smaller particles), σ^* can significantly exceed the yield stress of

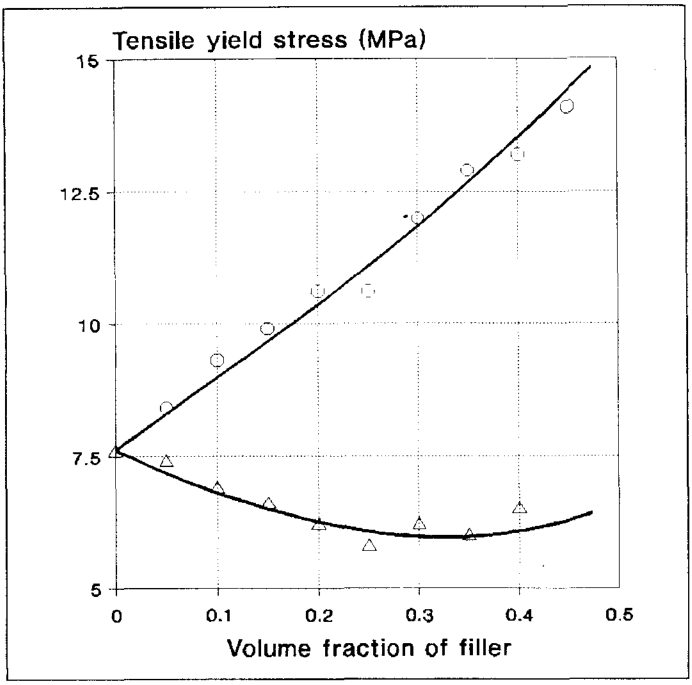

FIGURE 3 Composition dependence of the tensile yield stress of LDPE/$CaCO_3$ composites. Particle size: (Δ) 58.0 μm, (○) 3.6 μm.

the matrix (LDPE, pPVC). Assuming that the matrix does not yield around the particle and that Goodier's prediction is valid, stresses in the interphase should be larger than $2\sigma_y^0$. However, if we do not allow for the formation of a hard interlayer, the yield stress of the interphase equals that of the matrix and stresses larger than σ_y^0 could not develop around the particles. Two explanations can be given for the large σ^* values:

a) An interphase does not form or its properties are the same as that of the matrix, but large local deformations lead to the strain hardening of the polymer.

b) An interphase forms with changing properties, and modulus and yield stress are larger than that of the matrix. The material adsorbed in the interphase deforms elastically; it does not yield.

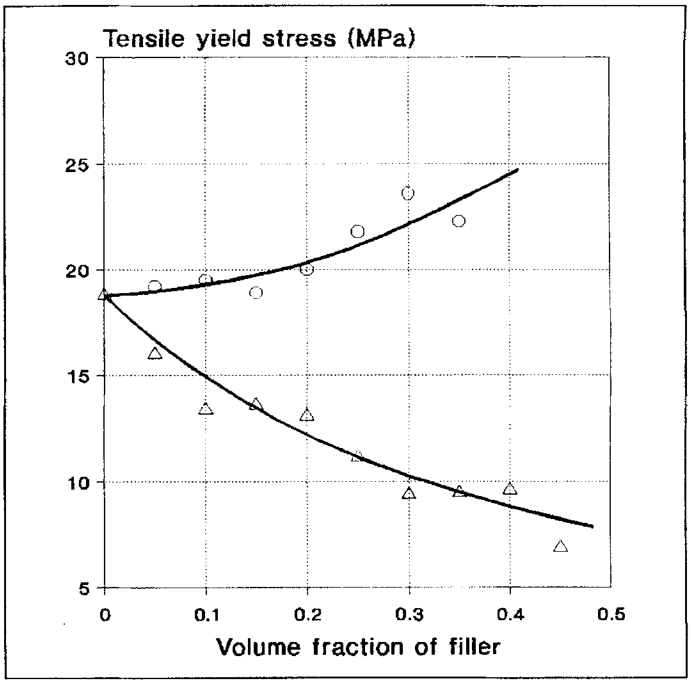

FIGURE 4 Effect of filler content and particle size of the filler on the tensile yield stress of pPVC/$CaCO_3$ composites. Particle size: (Δ) 58.0 μm, (○) 3.6 μm.

TABLE I Calculated matrix yield stress and average stress induced in the particles

Matrix	*$D_f = 3.6\ \mu m$* σ_y^0 *(MPa)*	σ^* *(MPa)*	*$D_f = 58\ \mu m$* σ_y^0 *(MPa)*	σ^* *(MPa)*
PVC	53.5	5.2	53.5	1.6
PP	33.1	9.7	33.1	3.3
pPVC	**18.7**	**21.8**	18.7	4.4
LDPE	**7.1**	**16.1**	7.8	4.0

STRESS ANALYSIS

In order to find the proper explanation for the above presented question, a simplified stress analysis was carried out and the conditions for debonding were determined.

Existence and Properties of the Interphase

Assuming that, due to stress concentration, stresses larger than σ_y^0 can develop in the vicinity of the particle, the average tensile stresses in the particle can be determined from the stress components. Stress distribution around the particles embedded in an elastic matrix can be described by the σ_{rr}, $\sigma_{\theta\theta}$ and $\sigma_{r\theta}$ stress components superposed on the σ^e external stress. It can be simply shown (Fig. 5) that only the σ_{rr} and $\sigma_{r\theta}$ components lead to forces, which act in the same direction as the external stress. In a homogeneous material at a given σ^e external tensile stress a force $A\sigma^e$ acts in the direction of the stress, where A is the cross section of the specimen perpendicular to the direction of the external stress. In the presence of a filler, a three-dimensional stress field develops around the particles. Stresses inside the particles will be different from those in the matrix. Averaging must be carried out both for the cross section of the particles and the matrix. Thus, by taking

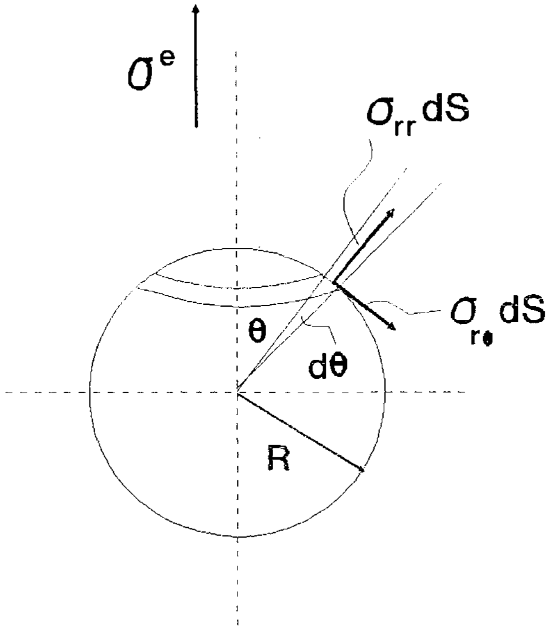

FIGURE 5 Stress components initiating debonding.

into account the stresses acting on the particles and the matrix, respectively, and by using the corresponding surfaces, an average force is determined, which acts against the external force. The $\langle\sigma_{rr}\rangle + \langle\sigma_{r\theta}\rangle + \langle\sigma_{\theta\theta}\rangle$ equivalent "tensile stress" multiplied by the cross-section of a particle gives a force, which is equal to that caused by the complicated three-dimensional stresses around the particle. $\langle\sigma_{\theta\theta}\rangle$ does not contribute to the average force acting in the direction of the external stress. As a consequence, the surface average of stresses can be calculated as:

$$\langle\sigma_{rr}\rangle + \langle\sigma_{r\theta}\rangle = \frac{1}{R^2\pi}\int_0^{\pi/2} \sigma_{rr} 2\pi R^2 \sin\theta\cos\theta\, d\theta - \frac{1}{R^2\pi}\int_0^{\pi/2} \sigma_{r\theta} 2\pi R^2 \sin^2\theta\, d\theta \tag{2}$$

By using the explicit form of the stress components [9] we arrive at

$$\sigma_{rr} = \alpha + \beta\cos 2\theta \quad \text{and} \quad \sigma_{r\theta} = \gamma \sin 2\theta \tag{3}$$

Substituting these into the average stress we obtain

$$\langle\sigma_{rr}\rangle + \langle\sigma_{r\theta}\rangle = \alpha - \gamma \tag{4}$$

α and γ can be given as three-parameter functions, *i.e.*

$$\alpha = 2G\left(\frac{2A}{R^3} - \frac{2\nu}{1-2\nu}\frac{C}{R^3} + \frac{12B}{R^5}\right)$$

$$\gamma = G\left(\frac{24B}{R^5} - \frac{2(1+\nu)}{1-2\nu}\frac{C}{R^3}\right) \tag{5}$$

In the above correlations G is the shear modulus of the matrix and ν its Poisson's ratio. If the particles are much stiffer than the matrix A,

B and C can be expressed as

$$A=\frac{\sigma^0 R^3}{4G}\left(\frac{1-\nu}{1+\nu}+\frac{3}{16-20\nu}\right)$$

$$B=-\frac{\sigma^0 R^5}{8G}\frac{1}{8-10\nu} \tag{6}$$

$$C=-\frac{\sigma^0 R^3}{8G}\frac{5(1-2\nu)}{8-10\nu}$$

and the average stress is given as

$$\sigma^*=\langle\sigma_{rr}\rangle+\langle\sigma_{r\theta}\rangle=\sigma^e\left(\frac{1-\nu}{1+\nu}+\frac{2}{8-10\nu}\right) \tag{7}$$

The value of σ^* can be determined from Eq. (7), which is the Goodier [9] solution for the elastic case, if σ^e is equaled to σ_y^0 and the appropriate Poisson's ratio is substituted. The calculation was carried out for the two matrices and the filler with the small particle diameter, where debonding did not occur; the results are collected in Table II. Comparison of the data calculated by the model presented above (σ^*_{calc}) and those obtained directly from the experiments (σ^*_{meas}) leads to the conclusion that the simple, two-phase, elastic model yields lower average stresses than the values calculated by Eq. (1). The difference verifies our assumption about the formation of a hard interphase with changing properties, which makes possible the development of the high σ^* stresses actually measured in the material. The remaining

TABLE II Comparison of interphase stresses determined from experimental data and theoretical prediction

Matrix	σ^*_{meas} (MPa)	σ^*_{calc} (MPa)	ν	σ_y^0 (MPa)
LDPE	16.1	15.1	0.43	16.1
pPVC	21.8	17.5	0.46	18.7

σ^*_{meas} was derived from Eq. (1)
σ^*_{calc} was calculated from Eq. (7)

question is the mechanism of stress transfer and debonding, as well as the parameters influencing them.

Stress Transfer, Debonding

We assume that the elastic properties of the matrix change according to a single $\alpha(|\underline{r}|)$ function, *i.e.*

$$E = E^0\alpha(|\underline{r}|); \quad G = G^0\alpha(|\underline{r}|) \tag{8}$$

where E^0 and G^0 are the corresponding properties of the matrix. The origin of our coordinate system is placed in the center of a particle and $|\underline{r}|$ is the absolute value of the distance measured from this point. The matrix deforms under the effect of σ^e external load and the deformation field around the particle is superposed on this deformation. Displacement and stress components are noted by $u_i^e(\alpha, \underline{r})$, $u_i^c(\alpha, \underline{r})$ and $\sigma_{ik}^e(\alpha, \underline{r})$, $\sigma_{ik}^c(\alpha, \underline{r})$, respectively. Since the modulus of the particles is about one order of magnitude larger than that of the matrix, they are completely rigid, *i.e.* they do not deform. For particles embedded in an infinite matrix the following boundary conditions apply:

$$\lim_{|\underline{r}|\to\infty} \sigma_{ik}^c(\alpha, \underline{r}) = 0$$

$$\underline{u}^e(\alpha, R) + \underline{u}^c(\alpha, R) = 0 \tag{9}$$

$$\lim_{|\underline{r}|\to\infty} \varepsilon_{ik}^c = 0$$

$$\lim_{|\underline{r}|\to\infty} \underline{u}^c = 0$$

where $\underline{u}(\alpha, R)$ is the displacement field on the surface of the particle with a radius of R. The energy of elastic deformation for the matrix is

$$2U(\alpha) = \int_V \sigma_{ik}^e(\underline{r})[\varepsilon_{ik}^e(\underline{r}) + \varepsilon_{ik}^c(\alpha, \underline{r})] + \sigma_{ik}^c(\alpha, \underline{r})[\varepsilon_{ik}^e(\underline{r}) + \varepsilon_{ik}^c(\alpha, \underline{r})]\,dV \tag{10}$$

The volume integral must be calculated only for the matrix, since the particle is completely rigid. The last three terms of Eq. (10) are transformed into surface integrals according to Figure 6, where S^k is the external surface of the sample and S^F is the surface of the particle. Taking into account that the σ^e_{ik} stress field is free of divergence and that at the S^k surface u^c_i disappears, the second term of Eq. (10) can be expressed by using the Gauss theorem

$$\int_V \sigma^e_{ik}(\underline{r})\varepsilon^c_{ik}(\alpha,\underline{r})]\,dV = \int_V [\sigma^e_{ik}u^c_i(\alpha,\underline{r}))_{,i} - \sigma^e_{ik,k}(\underline{r})u^c_i(\alpha,\underline{r}))]\,dV$$

$$= \oint_{S^F} \sigma^e_{ik}(\alpha,R)u^c_i(R)\,dS_k$$

The third and fourth terms of Eq. (10) can be transformed in a similar way, *i.e.*

$$\int_V \sigma^c_{ik}(\alpha,\underline{r})\varepsilon^e_{ik}(\alpha,\underline{r})\,dV = \oint_{S^F} \sigma^c_{ik}(\alpha,R)u^e_i(R)\,dS_k \tag{12}$$

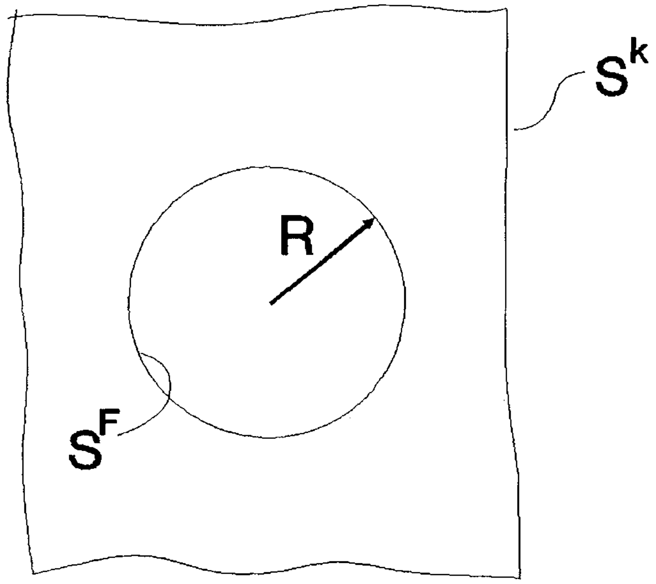

FIGURE 6 Calculation of elastic energy by surface integrals; representative surfaces.

and

$$\int_V \sigma_{ik}^c(\alpha, \underline{r})\,\varepsilon_{ik}^c(\alpha, \underline{r})\,dV = \oint_{S^F} \sigma_{ik}^c(\alpha, R)\,u_i^c(\alpha, R)\,dS_k \tag{13}$$

The sum of the last two terms is zero because of the second boundary conditions of Eq. (9), thus the total elastic energy of the matrix can be expressed as

$$2U = \int_V \sigma_{ik}^e \varepsilon_{ik}^e\,dV + \oint_{S^F} \sigma_{ik}^e(R)\,u_i^c(R)\,dS_k \tag{14}$$

In the above presented calculation we assumed that the particle is attached to the matrix by its whole surface. If the external stress is further increased, debonding occurs at a certain σ^{eD} stress. The total elastic deformation energy of the matrix can be calculated in this case, too. The stress in the matrix takes the form:

$$\sigma_{ik}^D = \sigma_{ik}^{eD}(\underline{r}) + \sigma_{ik}^{cD}(\underline{r}) \tag{15}$$

where σ_{ik}^{cD} is the stress concentration remaining around the particle after debonding, which takes place suddenly on a sufficiently large area after initiation. At the moment of debonding, the interaction of the filler and the matrix is disrupted, the conformational freedom of the molecules increases, and the elastic properties no longer change in the vicinity of the particle. The displacement field consists of two terms as well:

$$u_i^D(\underline{r}) = u_i^{eD}(\underline{r}) + u_i^{cD}(\underline{r}) \tag{16}$$

The boundary conditions are modified

$$\lim_{|\underline{r}| \to \infty} \sigma_{ik}^{cD}(\underline{r}) = 0$$

$$\lim_{|\underline{r}| \to \infty} \sigma_{ik}^{cD}(\underline{r}) = 0 \tag{17}$$

for the debonded surface

$$(\sigma_{ik}^{eD} + \sigma_{ik}^{cD}) n_k |_{SF} = 0 \tag{18}$$

and for the places where debonding did not take place

$$u_i^{eD}(\alpha, \underline{r}) + u_i^{cD}(\alpha, \underline{r}) = 0 \tag{19}$$

From these conditions the elastic energy of the matrix after debonding can be obtained as

$$2U^D = \int_V \left[\sigma_{ik}^{eD} \varepsilon_{ik}^{eD} + \sigma_{ik}^{cD} (\varepsilon_{ik}^{eD} + \varepsilon_{ik}^{cD}) + \sigma_{ik}^{eD} \varepsilon_{ik}^{eD} \right] dV \tag{20}$$

The three last terms are transformed into surface integrals just as before. In the transformation S' represents the debonded part of the S^F surface (Fig. 7). The second and third terms are transformed

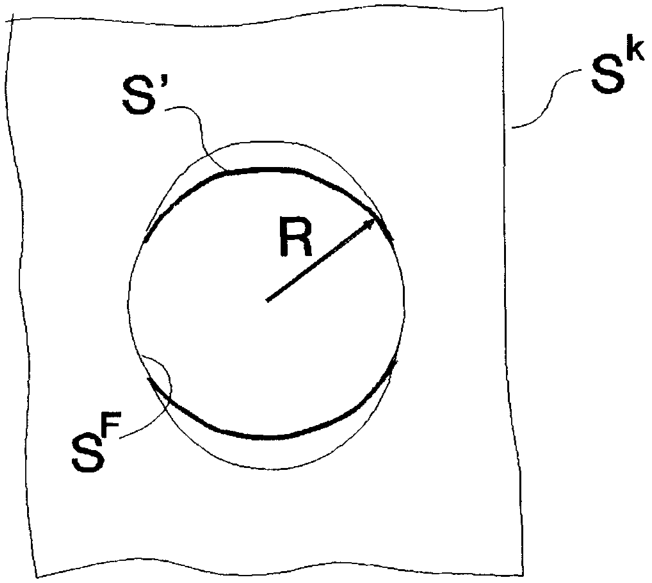

FIGURE 7 Creation of new surfaces in debonding; representative surfaces.

together by using the conditions that

$$\operatorname{div}\hat{\boldsymbol{\sigma}}^{cD} = 0 \quad \text{and} \quad \operatorname{div}\hat{\boldsymbol{\sigma}}^{eD} = 0 \tag{21}$$

thus

$$\int_V \boldsymbol{\sigma}_{ik}^{cD}(\boldsymbol{\varepsilon}_{ik}^{eD} + \boldsymbol{\varepsilon}_{ik}^{cD})dV = \oint_{S^F+S^k} \boldsymbol{\sigma}_{ik}^{cD}(u_i^{eD} + u_i^{cD})\, dS_k \tag{22}$$

Since σ_{ik}^{cD} and u_i^{cD} disappear on the S^k surface, the rest of Eq. (22) can be divided into two parts

$$\oint_{S^f} \boldsymbol{\sigma}_{ik}^{cD}(u_i^{eD}+u_i^{cD})\, dS_k = \int_{S'} \boldsymbol{\sigma}_{ik}^{cD}(u_i^{eD} + u_i^{cD})\, dS_k$$

$$+ \int_{S^F-S'} \boldsymbol{\sigma}_{ik}^{cD}(u_i^{eD} + u_i^{eD})\, dS_k \tag{23}$$

because of the condition of Eq. (19) the second term of Eq. (23) is zero. The first term of Eq. (23) can be tranformed according to the condition expressed in Eq. (18)

$$\oint_{S^F} \boldsymbol{\sigma}_{ik}^{cD}(u_i^{eD}+u_i^{cD})\, dS_k = -\int_{S'} \boldsymbol{\sigma}_{ik}^{eD}(u_i^{eD} + u_i^{cD})\, dS_k \tag{24}$$

thus the total energy of the matrix can be given as

$$2U^D = \int_V \boldsymbol{\sigma}_{ik}^{eD}\boldsymbol{\varepsilon}_{ik}^{eD}dV - \int_{S'} \boldsymbol{\sigma}_{ik}^{eD}(u_i^{eD} + u_i^{cD})dS_k + \oint_{S^F} \boldsymbol{\sigma}_{ik}^{eD}u_i^{cD}\, dS_k \tag{25}$$

The difference in elastic energy before and after debonding is

$$2(U - U^D) = \int_V (\boldsymbol{\sigma}_{ik}^{e}\boldsymbol{\varepsilon}_{ik}^{e} - \boldsymbol{\sigma}_{ik}^{eD}\boldsymbol{\varepsilon}_{ik}^{eD})dV + \oint_{S^F} [\boldsymbol{\sigma}_{ik}^{e}u_i^{c}(\alpha, R) -$$

$$-\sigma_{ik}^{eD}(R)u_i^D(R)dS_k] - \int_{S'} \sigma_{ik}^{cD}(u_i^{eD} - u_i^{cD})dS_k \tag{26}$$

The volume integral can be transformed again

$$\int_V (\sigma_{ik}^e \varepsilon_{ik}^e - \sigma_{ik}^{eD}\varepsilon_{ik}^{eD})dV = \int_{S^F} (\sigma_{ik}^e u_i^e - \sigma_{ik}^{eD}u_i^{eD})dS_k$$

$$+ \int_{S^k} (\sigma_{ik}^e u_i^e - \sigma_{ik}^{eD}u_i^{eD})dS_k \tag{27}$$

The last integral of Eq. (27) is zero, because $\sigma_{ik}^e = \sigma_{ik}^{eD}$ before and after debonding and if debonding takes place on a particle somewhere in the matrix far from the S^k surface it does not influence its value, *i.e.*

$$\lim_{|\underline{r}| \to \infty} \underline{u}^e = \lim_{|\underline{r}| \to \infty} \underline{u}^{eD} \tag{28}$$

thus only the integral calculated on the surface of the particle remains from Eq. (27)

$$2(U - U^D) = \oint_{S^F} [\sigma_{ik}^e(u_i^e + u_i^c) - \sigma_{ik}^{eD}(u_i^{eD} + u_i^{cD})]\,dS_k$$

$$- \int_{S'} \sigma_{ik}^{eD}(u_i^{eD} + u_i^{cD})dS_k \tag{29}$$

By dividing the S^F surface into debonded and adhering parts and using the boundary conditions, the first term can be simplified to the integration according to S'. The total deformation energy in this case is

$$U - U^D = -\int_{S'} \sigma_{ik}^{eD}(u_i^{eD} + u_i^{cD})dS_k \tag{30}$$

When debonding occurs the deformation field of the matrix is modified, thus also the elastic energy of deformation changes. A new surface is formed at the same time, which occurs only if the energy gained by the modification of the deformation field is sufficient to create the new surface. Thus, the condition of debonding can be expressed as

$$|U - U^D| \geqslant \int_{S'} W dS \tag{31}$$

where W is the reversible work of adhesion. Introducing Eq. (30) into Eq. (31) we obtain

$$\int_{S'} \boldsymbol{\sigma}_{ik}^{eD}(u_i^{eD} + u_i^{cD}) dS_k - \int_{S'} W dS \geqslant 0 \tag{32}$$

Debonding is initiated at the pole of the particle ($\theta = 0$, see Fig. 5) on a small $\Delta S'$ surface, where stresses and deformations can be regarded as constant, thus the local condition of debonding is

$$\boldsymbol{\sigma}_{ik}^{eD}(u_i^{eD} + u_i^{cD}) n_k - W \geqslant 0 \tag{33}$$

In the condition expressed by Eq. (33), $u_i^{eD} + u_i^{cD} = \Delta_i$ represents a small change of displacement. The first term of Eq. (33) expresses the work done by the external load if the displacement of a unit surface is Δ_i. If Δ_i is sufficiently large at a given $\boldsymbol{\sigma}^{eD}$ stress, debonding occurs. The critical displacement can be created by thermal fluctuation. At the pole of the particle only $\boldsymbol{\sigma}_{rr}^{eD}$ differs form zero, thus Δ_i must be taken into account only in the r direction. The probability difference between the formation and disruption of one interaction point depends on the external stress and it is proportional to Δ_r, *i.e.*

$$\Delta_r \sim (e^{-U - \sigma^{eD} V/kT} - e^{-U + \sigma^{eD} V/kT}) \tag{34}$$

where U is the adsorption energy, V the activation volume and $\sigma_{rr}^{eD} = \sigma^{eD}$. If $\sigma^{cD} V \ll kT$, then Eq. (34) can be expressed as a series and

Δ_r takes the form

$$\Delta_r \sim \frac{\sigma^{eD} V}{kT} e^{-U/kT} \tag{35}$$

It can be shown by dimensional analysis [6] that

$$\Delta_r = \frac{1}{A_0} \frac{R}{E(\alpha, R)} \frac{\sigma^{eD} V}{kT} e^{-U/kT} \tag{36}$$

where $E(\alpha, R)$ is the Young's modulus measured on the surface of the particle and A_0 is a constant. Normally the expression could be written as

$$\Delta_r = \frac{1}{A_0} \frac{R}{E} \sigma^{eD} \tag{37}$$

However, in our case the Δ_i displacement must take place before debonding, when the properties of the interphase are determined by the interaction. As a consequence, $E(\alpha, R)$ must be substituted into Eq. (36) instead of E. If the released strain energy is sufficiently large, debonding occurs and the modulus decreases to the matrix value. Introduction of Eq. (36) into Eq. (33) leads to

$$\frac{(\sigma^{eD})^2 R V}{E(\alpha, R) A_0} \frac{e^{-U/kT}}{kT} - W \geqslant 0 \tag{38}$$

which, after expressing σ^{eD}, gives the condition of debonding

$$\sigma^{eD} = \sqrt{A_0 \frac{W E(\alpha, R)}{R V} kT e^{+U/kT}} \tag{39}$$

CONSEQUENCES

Eq. (39) clearly shows that in the case of changing interphase properties the relationship of σ^{eD} and σ_y^0 can change with the particle size of the filler. If the particle size is large, $\sigma^{eD} < \sigma_y^0$, debonding takes place and composite yield stress (σ_y) continuously decreases with increasing filler content. If the particles of the filler are small, the relationship of the two quantities changes and the correlation will be reversed as is shown in Figures 3 and 4.

Although changing yield stress of the interphase was neglected previously, a similar solution was obtained for the condition of debonding [16,19]. The previous correlations did not contain the term expressing the changing elastic properties of the interphase. The assumption of a dynamic equilibrium of adsorption and desorption in the absence of an external force made it possible to include this factor into the correlation. The measurement of debonding forces as a function of particle size, strength of interaction and temperature makes possible the determination of the modulus of the interface and the correlation presented in Figure 1 allows us to calculate the interphase yield stress as well.

The experimental evidence and the calculations presented above clearly prove the existence of a hard interphase. The final question is its thickness, which must depend on the strength of the interaction. Interaction is created by secondary, van der Waals forces, but the range of these forces is small, not more than a few nanometers. When the material is deformed, the volume affected by the decreased mobility of the chains attached to the surface is much larger, shown also by the larger interphase thicknesses determined by indirect, mechanical measurements [20]. This volume and the thickness of the interphase can be estimated by a semi-empirical correlation developed earlier for the quantitative description of the composition dependence of tensile yield stress in heterogeneous polymer systems [10]:

$$\sigma_y = \sigma_y^0 \frac{1-\varphi}{1+2.5\,\varphi} \exp(B_y\,\varphi) \tag{40}$$

where the term $(1-\varphi)/(1+2.5\varphi)$ expresses the decrease of effective load-bearing cross-section on filling, while $\exp(B_y\varphi)$ describes the interaction. The parameter B_y contains the thickness of the interphase (l) and its yield stress (σ_{yi})

$$B_y = (1 + l\,\rho_f A_f)\,\ln\frac{\sigma_{yi}}{\sigma_y^0} \tag{41}$$

where A_f and ρ_f are the specific surface area and the density of the filler, respectively. Parameter B_y can be determined from the composition dependence of tensile yield stress and, if the experiments are carried out with at least two fillers of different particle sizes, l can be calculated from the results.

The measurements and the calculation have been carried out and the obtained interphase thicknesses are plotted in Figure 8 for the four matrices studied. The thickness of the interphase linearly changes with increasing adhesion, which is characterized by the reversible work of adhesion in this case. This result further corroborates the validity of the theoretical approach presented in the previous section.

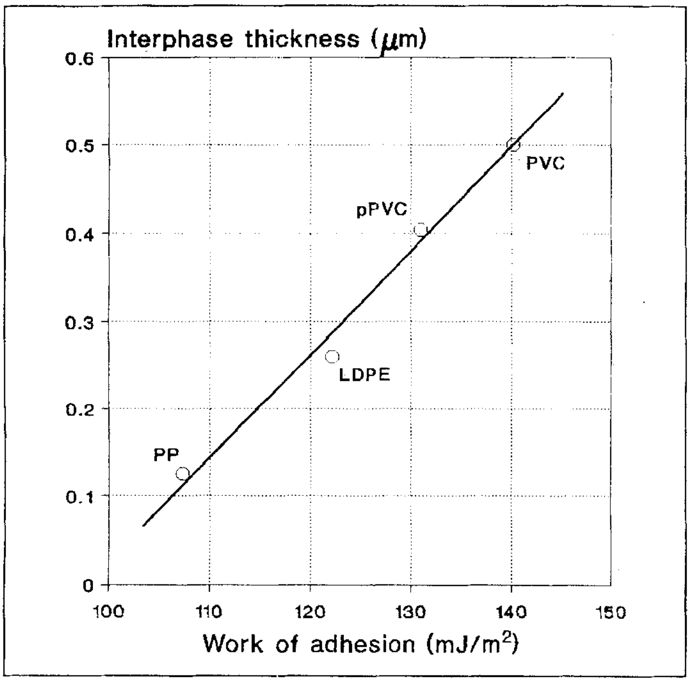

FIGURE 8 Effect of the strength of interaction on the thickness of the spontaneously-formed interphase.

CONCLUSIONS

The comparison of theoretical calculations and experimental data proved again the spontaneous formation of an interphase on the surface of a filler or reinforcement. Besides the elastic properties, the yield stress of the interphase also changes continuously from the surface of the particles to the matrix. In the absence of debonding, the development of this hard interface leads to increased composite yield stress. Debonding starts at the pole of the particles and proceeds catastrophically towards the equator if the elastic deformation energy of the matrix is sufficient for the creation of new surface. By assuming the dynamic equilibrium of adsorption and desorption in the absence of external forces, the parameters influencing debonding stress could be determined. The strength of the interaction, the size of the particles and temperature influence the separation of the matrix/filler interface. In the absence of debonding, tensile yield stress of the composite increases with filler content, while in its presence it decreases with composition. The apparent volume of the matrix influenced by interaction during deformation depends on the strength of interaction, it increases considerably with the reversible work of adhesion between the components. The results of the theoretical calculations make possible the analysis of the debonding process. Further experiments must be carried out to verify the treatment.

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