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LETTERS IN FRACTURE AND MICROMECHANICS

STRESS DISTRIBUTIONS AROUND RIGID NANOPARTICLES

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Abstract. A closed form solution for the stress fields around a rigid nanoparticle under uniaxial tensile load is provided. The work explicitly accounts for the presence, around the nanoparticle, of an interphase of thickness comparable to the particle size and different elastic properties from those of the matrix. The solution allows one to determine, in closed form, the stress concentration around nanoparticles relevant for fracture and strength assessments of polymer nanocomposites.

Keywords: nanoparticles, stress concentration, interphase.

1. Introduction

In nanomodified polymers, as the filler size is decreased to the nanoscale, intra- and supra-molecular interactions lead to the emergence of an interphase whose properties differ from those of both constituents and whose thickness may be comparable to the particle size. Sevostianov and Kachanov (2006, 2007) showed that the effect of such interphase on the overall properties may be substantial, the controlling parameters being the ratio of the interphase thickness to the particle size and the variability of the properties across the interface thickness.
The calculation of the stress concentration around a particle embedded within a matrix has been dealt with by many authors, but there are only few works considering interphases. The aim of the present work is to fill this gap and to determine the stress fields around a rigid nanoparticle under uniaxial tensile load. The work explicitly accounts for the presence of an interphase around the nanoparticle, of thickness comparable to the particle size and whose elastic properties differ from those of the matrix. The solution allows one to determine, in closed form, the stress field around the nanoparticle.

2. Analytical framework

2.1 Stress field solution

Let consider a rigid spherical nanoparticle of radius r_0 embedded by a spherical shell-shaped interphase of radius a, both of them being enveloped into a infinite matrix

(figure 1a). The matrix and the interphase are elastic, homogeneous and isotropic materials and the interphase has elastic properties different from those of the polymer matrix. This system is loaded by a remotely applied uniaxial tension along direction X_2 (figure 1a).
The solution for the displacement field around a particle embedded in an infinite and elastic body loaded by axisymmetrical loads was derived by Goodier (1933) and Oldroyd (1953). Lauke *et al.* (2000) later analysed the problem of a coated particle embedded within a matrix and noted that, with reference only to the deviatoric part of the elastostatic solution, the displacement fields for each sub-dominion of such a problem can be sought in the following form (Lauke *et al.*, 2000):

$$u_{r,k} = \left[\frac{r^3}{14}a_k + \frac{3\lambda_k + 5G_k}{12\lambda_k r^2}b_k + rc_k - \frac{3d_k}{2r^4}\right]\left(3\cos^2\theta_2 - 1\right) \tag{1a}$$

$$u_{\theta,k} = -\left[\frac{5\lambda_k + 7G_k}{14\lambda_k}r^3 a_k + \frac{G_k}{2\lambda_k r^2}b_k + 3rc_k + \frac{3d_k}{r^4}\right]\cos\theta_2\sin\theta_2 \tag{1b}$$

where subscript k=m,a,p denotes the sub-domain (matrix, interphase and nanoparticle) and r and θ_2 are coordinates shown in figure 1b; G_k is the shear elastic modulus and λ_k is Lame's constant.

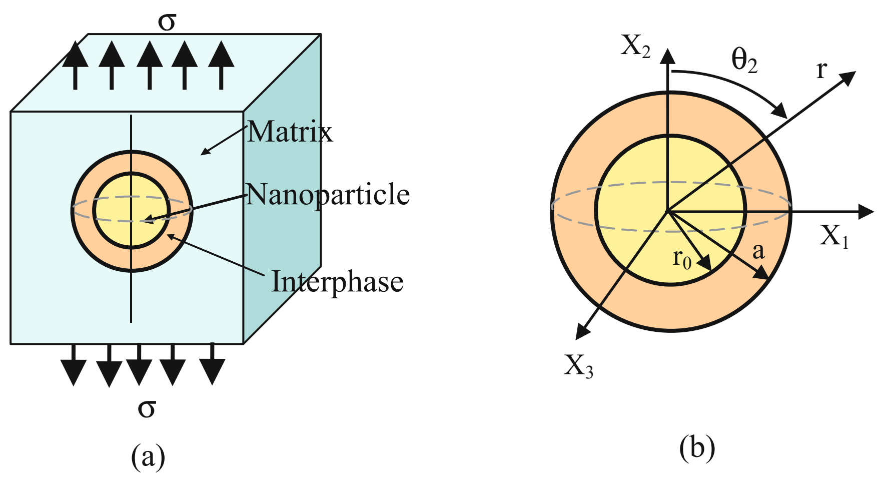

Figure 1. Spherical nanoparticle embedded in a shell-shaped interphase zone under unidirectional load (a). Polar coordinate system used to describe the stress field around the nanoparticle (b).

Hence the components of stresses due to the deviatoric part of the remotely applied uniaxial stress can be written as:

$$\sigma_{rr,d,k} = 3G_k\left[-\frac{r^2}{14}a_k - \frac{9\lambda_k + 10G_k}{6\lambda_k r^3}b_k + 2c_k + 12\frac{d_k}{r^5}\right]\cos^2\theta_2 - G_k\left[-\frac{r^2}{14}a_k - \frac{9\lambda_k + 10G_k}{6\lambda_k r^3}b_k + 2c_k + 12\frac{d_k}{r^5}\right] \quad (2)$$

$$\sigma_{\theta\theta,d,k} = G_k\left[-\frac{5\lambda_k + 4G_k}{2\lambda_k}a_k r^2 + \frac{G_k}{2\lambda_k}\frac{b_k}{r^3} - 6c_k - 21\frac{d_k}{r^5}\right]\cos^2\theta_2 + G_k\left[\frac{15\lambda_k + 14G_k}{14\lambda_k}a_k r^2 + \frac{G_k}{6\lambda_k}\frac{b_k}{r^3} + 4c_k + 9\frac{d_k}{r^5}\right] \quad (3)$$

$$\sigma_{\varphi\varphi,d,k} = G_k\left[-\frac{25\lambda_k + 14G_k}{14\lambda_k}a_k r^2 + \frac{3}{2}\frac{G_k}{\lambda_k}\frac{b_k}{r^3} - 15\frac{d_k}{r^5}\right]\cos^2\theta_2 - G_k\left[-\frac{5}{14}a_k r^2 + \frac{5}{6}\frac{G_k}{\lambda_k}\frac{b_k}{r^3} + 2c_k - 3\frac{d_k}{r^5}\right] \quad (4)$$

$$\tau_{r\theta,k} = -G_k\left[\frac{8\lambda_k + 7G_k}{7\lambda_k}a_k r^2 + \frac{3\lambda_k + 2G_k}{2\lambda_k}\frac{b_k}{r^3} + 6c_k - 24\frac{d_k}{r^5}\right]\cos\theta_2\sin\theta_2 \quad (5)$$

Unknown coefficients a_k, b_k, c_k, and d_k can be determined from the equilibrium and compatibility conditions:

At $r=r_0$ $\quad u_{r,p} = u_{r,a} \quad u_{\theta,p} = u_{\theta,a} \quad \sigma_{rr,d,p} = \sigma_{rr,d,a} \quad \tau_{r\theta,p} = \tau_{r\theta,a}$ (6)

At $r=a$ $\quad u_{r,a} = u_{r,m} \quad u_{\theta,a} = u_{\theta,m} \quad \sigma_{rr,d,a} = \sigma_{rr,d,m} \quad \tau_{r\theta,a} = \tau_{r\theta,m}$ (7)

At $r \to \infty$ $\quad \sigma_{rr,d,m} = \frac{\sigma}{3}\left(3\cos^2\theta_2 - 1\right) \quad \tau_{r\theta,m} = -\sigma\cos\theta_2\sin\theta_2$ (8)

Noting that displacement singularities in the nanoparticle can be avoided if and only if $b_p=d_p=0$, boundary conditions result in a system of 10 equations, providing the 10 unknown constants a_p, c_p, a_a, b_a, c_a, d_a, a_m, b_m, c_m, d_m.

It is worth mentioning here that in his work Lauke *et al.* (2000) did not solved in closed form the problem but stated that the solution of the system of 10 equations for the 10 unknown coefficients was only possible numerically.

The system of boundary conditions is solved in closed form in this work, assuming the particle is much stiffer than the matrix and the interphase (as in the case of polymers modified by nanoparticles). After some algebraic manipulations the following solution for unknown coefficients can be given:

$$a_a = \frac{\omega}{\Omega}\frac{\sigma}{r_0^2} \qquad b_a = \frac{\xi}{\Omega}\sigma r_0^3 \qquad c_a = \frac{\eta}{2\Omega}\sigma \qquad d_a = \frac{\kappa}{2\Omega}\sigma\ r_0^5 \qquad a_m = 0$$
$$c_m = \frac{\sigma}{6G_m} \qquad b_m = \sigma r_0^3 \lambda_m \times \frac{G_a G_m\left(3\bar{a}^5\omega + 8\xi\right) + \lambda_a\left[3G_m\left(\bar{a}^5\omega + \xi\right) - 5\bar{a}^3\Gamma\right]}{G_m \Omega \lambda_a\left(8G_m + 3\lambda_m\right)} \tag{9}$$
$$d_m = \sigma r_0^5 \times \frac{7\bar{a}^2 G_a G_m\left[5\bar{a}^5\omega G_m + 3\lambda_m\left(\bar{a}^5\omega + \xi\right)\right] + \lambda_a \times \Psi}{42 G_m \Omega \lambda_a\left(8G_m + 3\lambda_m\right)}$$

where σ is the remotely applied stress while, denoting with $\bar{a} = a/r_0$, other auxiliary parameters are defined as:

$$\begin{aligned}\alpha = {} & 28G_a^4 \cdot (8G_m + 3\lambda_m)(28 + 50\bar{a}^3 - 36\bar{a}^5 + 25\bar{a}^7 + 8\bar{a}^{10}) + \\ & 12G_m^2 \cdot \lambda_a^2 \cdot (14G_m + 9\lambda_m)(\bar{a} - 1)^4 \cdot (4 + 16\bar{a} + 40\bar{a}^2 + 55\bar{a}^3 + 40\bar{a}^4 + 16\bar{a}^5 + 4\bar{a}^6)\end{aligned} \tag{10}$$

$$\begin{aligned}\beta = {} & 4G_a^3\Big\{2G_m\big[7G_m(-224 - 25\bar{a}^3 + 18\bar{a}^5 + 75\bar{a}^7 + 156\bar{a}^{10}) + \\ & 4\lambda_a \cdot (182 + 400\bar{a}^3 - 504\bar{a}^5 + 350\bar{a}^7 + 97\bar{a}^{10})\big] + \\ & 3\lambda_m \cdot \big[7G_m(-76 + 25\bar{a}^3 - 18\bar{a}^5 + 25\bar{a}^7 + 44\bar{a}^{10}) + \\ & \lambda_a(182 + 400\bar{a}^3 - 504\bar{a}^5 + 350\bar{a}^7 + 97\bar{a}^{10})\big]\Big\}\end{aligned} \tag{11}$$

$$\begin{aligned}\chi = {} & G_a G_m \lambda_a\Big\{112G_m^2(37 - 100\bar{a}^3 + 126\bar{a}^5 - 100\bar{a}^7 + 37\bar{a}^{10}) + \\ & 9\lambda_a\lambda_m \cdot (-96 + 100\bar{a}^3 - 168\bar{a}^5 + 75\bar{a}^7 + 89\bar{a}^{10}) + \\ & 6 \cdot G_m\big[\lambda_a(-304 - 100\bar{a}^3 + 168\bar{a}^5 - 25\bar{a}^7 + 261\bar{a}^{10}) + \\ & 12\lambda_m(37 - 100\bar{a}^3 + 126\bar{a}^5 - 100\bar{a}^7 + 37\bar{a}^{10})\big]\Big\}\end{aligned} \tag{12}$$

$$\begin{aligned}\delta = {} & G_a^2\Big\{392G_m^3(16 - 25\bar{a}^3 + 18\bar{a}^5 - 25\bar{a}^7 + 16\bar{a}^{10}) + \\ & 9\lambda_a^2\lambda_m \cdot (48 + 200\bar{a}^3 - 336\bar{a}^5 + 225\bar{a}^7 + 38\bar{a}^{10}) + \\ & 4 \cdot G_m^2\big[\lambda_a(-2492 - 400\bar{a}^3 + 504\bar{a}^5 + 525\bar{a}^7 + 1863\bar{a}^{10}) + \\ & 63\lambda_m(16 - 25\bar{a}^3 + 18\bar{a}^5 - 25\bar{a}^7 + 16\bar{a}^{10})\big] + \\ & 6G_m\lambda_a\big[4\lambda_a(48 + 200\bar{a}^3 - 336\bar{a}^5 + 225\bar{a}^7 + 38\bar{a}^{10}) + \\ & \lambda_m(-808 + 400\bar{a}^3 - 504\bar{a}^5 + 325\bar{a}^7 + 587\bar{a}^{10})\big]\Big\}\end{aligned} \tag{13}$$

$$\begin{aligned}\xi = {} & -75\bar{a}^3\lambda_a(2G_m + \lambda_m)\Big\{14G_a\big[G_a \cdot (4 + \bar{a}^7) + 4G_m(\bar{a}^7 - 1)\big] + \\ & \lambda_a \cdot \big[G_a(16 + 19\bar{a}^7) + 16 \cdot G_m(\bar{a}^7 - 1)\big]\Big\}\end{aligned} \tag{14}$$

$$\omega = 6300\,\bar{a}^3(\bar{a}^2 - 1)\,\lambda_a(G_a - G_m)(G_a + \lambda_a)(2G_m + \lambda_m) \tag{15}$$

$$\eta = 5\bar{a}^3(2G_m + \lambda_m)\left\{28G_a^2\left[G_a\cdot(25-9\bar{a}^2+4\bar{a}^7)+G_m(-25+9\bar{a}^2+16\bar{a}^7)\right]+ 2\lambda_a G_a\cdot\left[G_a(400-252\bar{a}^2+97\bar{a}^7)+4\cdot G_m(-100+63\bar{a}^2+37\bar{a}^7)\right]+ 3\lambda_a^2\cdot\left[G_a\cdot(100-84\bar{a}^2+19\bar{a}^7)+4G_m\cdot(-25+21\bar{a}^2+4\bar{a}^7)\right]\right\} \quad (16)$$

$$\kappa = -15\bar{a}^5(2G_m+\lambda_m)(G_a+\lambda_a)\left\{14G_a\cdot\left[G_a(4+\bar{a}^5)+4G_m(\bar{a}^5-1)\right]+ \lambda_a\cdot\left[G_a(16+19\bar{a}^5)+16G_m(\bar{a}^5-1)\right]\right\} \quad (17)$$

$$\Omega = \alpha+\beta+\chi+\delta \quad (18)$$

$$\Gamma = \Omega - 3\eta G_m \quad (19)$$

$$\Psi = G_m\left[G_m\left(19\bar{a}^7\omega - 21\bar{a}^2\xi + 168\kappa\right) - 21\bar{a}^5\Gamma\right] + 3\lambda_m\left[G_m\left(5\bar{a}^7\omega + 21\kappa\right) - 7\bar{a}^5\Gamma\right] \quad (20)$$

2.2 Closed form solution for the stresses around the nanoparticle

The maximum concentration of stresses within the interphase always takes place around the nanoparticle, at $r=r_0$. The deviatoric components of stresses can be re-written as:

$$\bar{\sigma}_{rr,d,a} = \sigma\left(\bar{A}_a\cos^2\theta_2 + \bar{B}_a\right) \qquad \bar{\sigma}_{\theta\theta,d,a} = \sigma\left(\bar{C}_a\cos^2\theta_2 + \bar{D}_a\right)$$
$$\bar{\sigma}_{\varphi\varphi,d,a} = \sigma\left(\bar{E}_a\cos^2\theta_2 + \bar{F}_a\right) \qquad \bar{\tau}_{r\theta,a} = \sigma\bar{H}_a\cos\theta_2\sin\theta_2 \quad (21)$$

where:

$$\bar{A}_a = \frac{3G_a}{\alpha+\beta+\chi+\delta}\left[-\frac{\omega}{14} - \xi\frac{9\lambda_a+10G_a}{6\lambda_a} + \eta + 6\kappa\right] \quad (22)$$

$$\bar{B}_a = -\frac{G_a}{\alpha+\beta+\chi+\delta}\left[-\frac{\omega}{14} - \xi\frac{9\lambda_a+10G_a}{6\lambda_a} + \eta + 6\kappa\right] \quad (23)$$

$$\bar{C}_a = \frac{G_a}{\alpha+\beta+\chi+\delta}\left[-\omega\frac{5\lambda_a+4G_a}{2\lambda_a} + \xi\frac{G_a}{2\lambda_a} - 3\eta - \frac{21}{2}\kappa\right] \quad (24)$$

$$\bar{D}_a = \frac{G_a}{\alpha+\beta+\chi+\delta}\left[\omega\frac{15\lambda_a+14G_a}{14\lambda_a} + \xi\frac{G_a}{6\lambda_a} + 2\eta + \frac{9}{2}\kappa\right] \quad (25)$$

$$\bar{E}_a = \frac{G_a}{\alpha+\beta+\chi+\delta}\left[-\omega\frac{25\lambda_a+14G_a}{14\lambda_a} + \frac{3}{2}\xi\frac{G_a}{\lambda_a} - \frac{15}{2}\kappa\right] \quad (26)$$

$$\bar{F}_a = -\frac{G_a}{\alpha+\beta+\chi+\delta}\left[-\frac{5}{14}\omega + \frac{5}{6}\xi\frac{G_a}{\lambda_a} + \eta - \frac{3}{2}\kappa\right] \quad (27)$$

$$\bar{H}_a = -\frac{G_a}{\alpha+\beta+\chi+\delta}\left[\omega\frac{8\lambda_a+7G_a}{7\lambda_a} + \xi\frac{3\lambda_a+2G_a}{2\lambda_a} + 3\eta - 12\kappa\right] \quad (28)$$

To obtain the complete stress components, $\bar{\sigma}_{ij,a}$, the stress fields due to deviatoric part of remote uniaxial stress has to be superimposed to stress components due to the hydrostatic part of the remote uniaxial stress, which can be determined as (Zappalorto *et al.*, 2011):

$$\bar{\sigma}_{rr,h,a} = \frac{\sigma}{3C_h} \qquad \bar{\sigma}_{\theta\theta,h,a} = \bar{\sigma}_{\varphi\varphi,h,a} = \frac{\sigma}{3C_h}\frac{3K_a - 2G_a}{3K_a + 4G_a} \tag{29}$$

where:

$$C_h = \frac{\frac{3K_a}{G_m} + 4 - 4\cdot(1 - \frac{G_a}{G_m})(r_0/a)^3}{(\frac{3K_a}{G_m} + 4\frac{G_a}{G_m})\left(\frac{3(1-\nu_m)}{1+\nu_m}\right)} \tag{30}$$

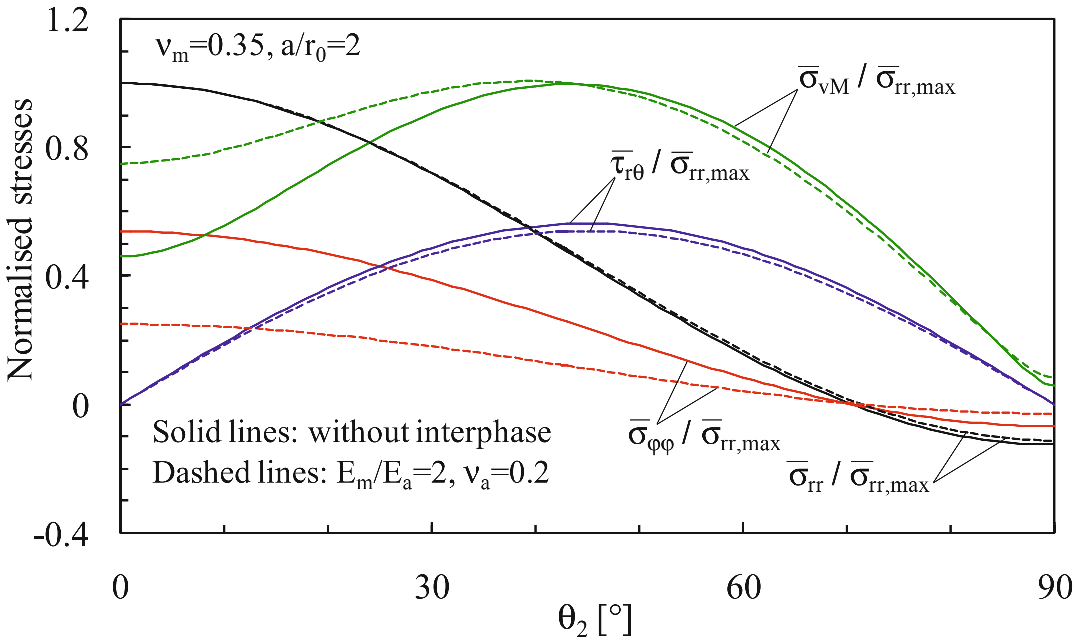

Figure 2. Plots of the stress components along the nanoparticle periphery. Softer interphase.

As it can be seen from figures 2 and 3, the normalised stress distributions around the periphery of the nanoparticle is largely influenced by the interphase elastic properties, both in the case of softer (figure 2) or harder (figure 3) interphases. It is interesting to note that, in all cases, the maximum radial stress occur at the pole of the particle (θ_2=0) while the maximum von Mises stress (σ_{vM}) occurs approximately at θ_2= 40 degrees. The elastic properties of the interphase affect not only the stress distributions, but, especially, the maximum values of the von Mises stress (figure 4) around the nanoparticle. It can be seen indeed that the stiffer the interphase the higher the maximum von Mises stress, which reaches an almost asymptotic value for a/r_0 higher than 2.

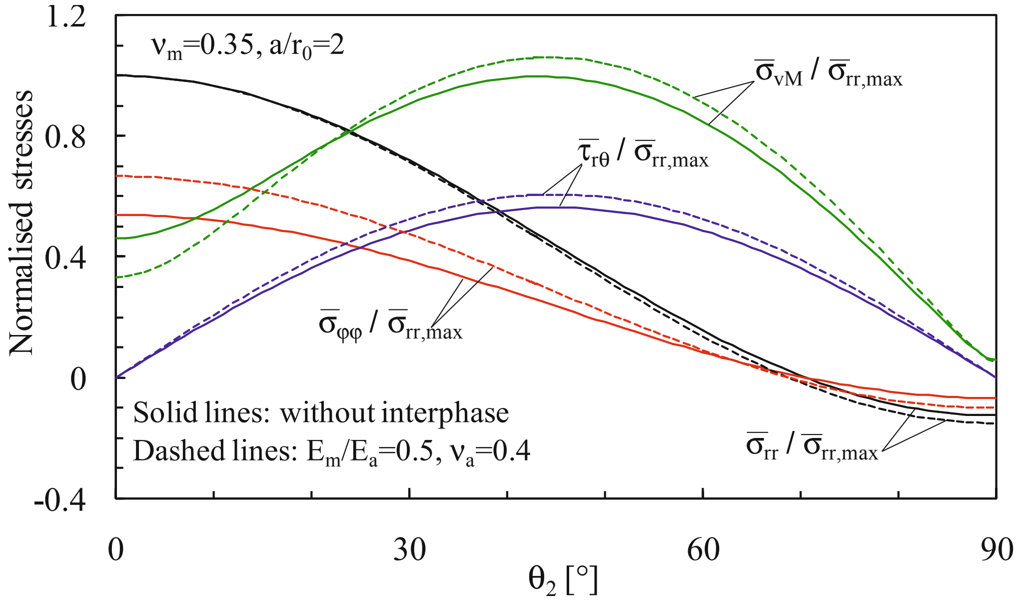

Figure 3. Plots of the stress components along the nanoparticle periphery. Harder interphase.

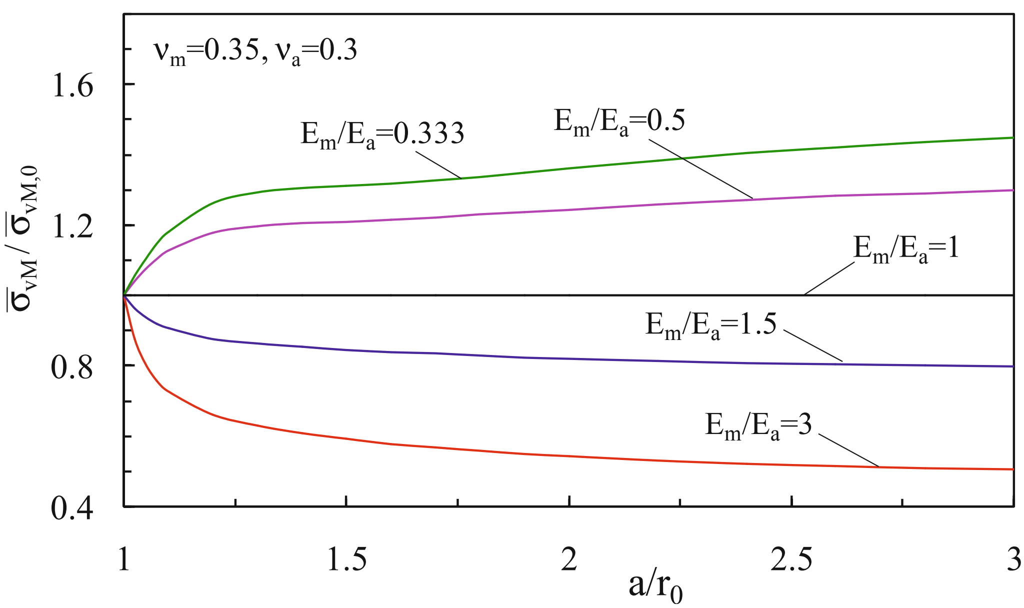

Figure 4. Influence of the interphase elastic properties on the maximum von Mises stress around nanoparticles. $\sigma_{vM,0}$ is the maximum von Mises stress stress occurring in the absence of interphase (a/r_0=1).

3. Conclusions

A closed form solution for the stress fields around a rigid nanoparticle under uniaxial tensile load has been provided accounting for an interphase embedding the nanoparticle. For the case of polymers modified by nanoparticles, this has allowed to determine, in closed form, the stress concentration around the nanoinhomogeneity, such a parameter being strictly related to the fracture toughness and strength of nanocomposites.

References

Goodier, J.N. (1933) Concentration of stress around spherical and cylindrical inclusions and flaws. *Journal of Applied Mechanics* **55** 39-44.

Lauke, B., Schüller, T., Beckert, W. (2000). Calculation of adhesion strength at the interface of a coated particle embedded within matrix under multiaxial load. *Computational Materials Science* **18**, 362-380.

Oldroyd, J.G. (1953) The Elastic and Viscous Properties of Emulsions and Suspensions. Proceeding of the Royal Society A, **218,** 122-132.

Sevostianov, I., and Kachanov, M. (2006) Homogenization of a Nanoparticle with Graded Interface. *International Journal of Fracture* **139**, 121–127.

Sevostianov, I., and Kachanov, M., (2007) Effect of interphase layers on the overall elastic and conductive properties of matrix composites. Applications to nanosize inclusion. *International Journal of Solids and Structures* **44**, 1304–15.

Zappalorto, M., Salviato, M., Quaresimin, M. (2011) Influence of the interphase zone on the nanoparticle debonding stress. *Composites Science and Technology* **72**, 49-55.