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Strengthening of foamed composite materials

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Résumé :

Cette étude porte sur le renforcement de matériaux moussés par des inclusions rigides. Pour cela nous avons mesuré le module de cisaillement d'une mousse de polymère chargée avec des sphères rigides. Nous montrons que le renforcement est fortement dépendant de la taille de ces inclusions. En contrôlant précisément le paramètre géométrique λ qui compare la taille des particules à celle des constrictions dans le réseau de la mousse, nous avons mis en évidence une transition des propriétés mécaniques autour de λ ≈ 1. Pour λ <1, toute charge particulaire renforce la mousse et l'ampleur de ce renforcement dépend directement de la concentration en particules. A l'inverse, pour λ >1, ce renforcement diminue rapidement avec λ et on observe même un ramollissement lorsque λ ≳10. En partant d'une approche de milieu effectif pour décrire l'élasticité d'une matrice élastique avec inclusions rigides, nous proposons un modèle phénoménologique pour les comportements asymptotiques λ <<1 et λ >> 1 et nous obtenons un bon accord avec nos données expérimentales.

Abstract:

We consider the strengthening of foamy materials by hard inclusions. We investigate the shear elastic modulus of soft polymer foams loaded with hard spherical particles and we show that strengthening is strongly dependent on the size of those inclusions. Through an accurate control of the ratio λ that compares the particle size to the thickness of the struts in the foam structure, we evidence a transition in the mechanical behavior at λ≈1. For λ<1, every particle loading leads to a strengthening effect whose magnitude depends only on the particle volume fraction. On the contrary, for λ>1, the strengthening effect weakens abruptly as a function of λ and a softening effect is even observed for λ≳10. From an effective approach which describes the elastic moduli of an elastic matrix loaded with rigid inclusions, a phenomenological model is proposed to describe each asymptotic behavior λ <<1 and λ >> 1 and which is in good agreement with our experimental data

Mots clefs : mousse ; composite ; particule ; module élastique ; polymère

1 Introduction

The incorporation of particles into materials is a well-known strategy to improve their mechanical behavior. When dealing with foamy materials, one has to consider the typical size of the struts that form the solid skeleton compared to the filler size. Several studies have been devoted to the reinforcement of such foams. For example, polyurethane foams or aerated cementitious materials were loaded with different kind of fillers [1,2]. In the current climate of sustainable development, those foam-based materials are destined to expand and in certain cases to replace advantageously conventional building materials. Numerous works were focused on those materials in order to improve

their mechanics. One of the essential features of foamy composite materials is that the filler size has to be fine enough for strengthening to be observed, and it has been shown that reinforcement is not efficient if the added particles are bigger than the bubbles [1]. Surprisingly, whereas this filler size effect is expected to be based on geometry only, it has never been studied from the purely geometrical point of view. Indeed, the bubble size and the gas volume fraction cannot be kept constant when studying the effect of the loading, which increases the difficulty to disentangle all types of effect.
In this study, we propose a generic approach to better understand the subtle interplay between the complex geometry of particulate foams and their mechanics. We investigate the shear elastic modulus of systems which consist of soft polymer foams loaded with hard spherical particles. The experimental study is conducted in such a way that monodisperse precursor foams are unaltered by the loading process, allowing us to assess the strengthening effect due solely to the presence of the particles.

2 Materials and methods

Our model system is a soft polymer foam loaded with hard spherical inclusions. The soft polymer is a gelatin. Above $T_{gel} \approx 29°C$ gelatin is a liquid solution and below it becomes a soft elastic solid. The inclusions are polystyrene beads characterized by a week polydispersity.
Inside a box above T_{gel}, the liquid gelatin solution is mixed with nitrogen in order to produce a precursor monodisperse foam. The gas fraction of this foam is set by controlling the flow rates of the liquid and the gas. In a second step, a suspension of particles in liquid gelatin is pushed and mixed to the precursor foam. The resulting particulate foam is pushed in a transparent shear cell and we rapidly quench the system at a temperature T = 5°C.
In the present study, the gas volume fraction of the particle-laden foam and the bubble diameter are kept constant with respective values: $\phi = 0.8$ and $D_b = 400$ µm. The particle size d_p varies from 6 to 500 µm. Their volume fraction in the whole foam ϕ_p varies from 0 to 6%, which gives with respect to the foam skeleton: $\varphi_p = \phi_p/(1- \phi) = 0 - 30\%$.
Mechanical properties of our samples are characterized by the shear elastic modulus measured in a plane shear test. All the results presented in this paper are performed at the constant shear rate $\dot{\gamma} = 1.3 \cdot 10^{-3}\ s^{-1}$. Thanks to the transparent cell, we measure the surface area of each sample, allowing for the stress to be plotted as a function of the strain. We remain in the linear elastic regime and the shear modulus $G(\phi_p, d_p)$ can be simply deduced from the slope of the linear fit over a strain of 2.6 %.

3 Results and discussions

The influence of the particle loading is characterized by normalizing the shear modulus of particle-laden foams by the value for the corresponding particle-free foam, i.e. $G^*=G(\phi,\varphi_p)/G(\phi,0)$. Fig 1 shows the evolution of the normalized shear modulus as a function of the particle volume fraction for several particle sizes, where two behaviors can be distinguished. The shear moduli of foams loaded with particles of diameter below 40 µm follow the same increasing function of ϕ_p. When the particle size increases, the stiffening can become negligible, as observed for the 250 µm particles. We can even notice a weak softening effect for the 500 µm particles. For that case, note that the particle size becomes comparable to the bubble size.

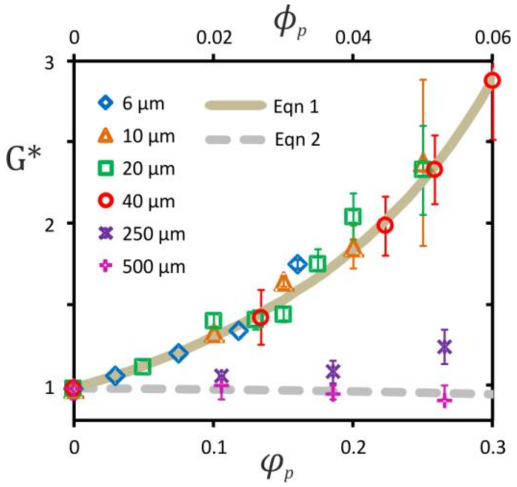

Fig. 1: The shear modulus of particle-laden foams normalized by the modulus of the corresponding particle-free foam as a function of the particle volume fraction φ_p in the interstitial volume or the corresponding fraction ϕ_p in the whole sample volume.

To understand this stiffening-softening transition, it is necessary to consider the foam at the scale of the solid skeleton, or foam network. The size of interest is d_c, the size of passage through constrictions within the foam pore space. In order to compare the particle size with d_c, we will use the so-called confinement parameter $\lambda=d_p/d_c$. From [3] and for $\phi=0.8$, $\lambda \simeq 8.5\ d_p/D_b$. When $\lambda < 1$, particles can explore freely the whole interstitial space whereas when $\lambda \gtrsim 1$, they have to be forced to enter the constrictions in deforming the bubbles surface. One can also imagine that for $\lambda \gg 1$ the particles cannot be included anymore in the space defined by the foam network but instead the network is restructured around them. Thus, for a given particle volume fraction, the resulting particle configuration in the foam network depends crucially on λ, which is expected to have a significant influence on the mechanical behavior.

To quantify this influence, let's first consider the asymptotic case of small particles, i.e. $\lambda \ll 1$. The corresponding shear modulus will be called G^*_{max}. In one hand, the elastic modulus of solid foams normalized by the modulus of the solid skeleton is a decreasing function of the gas volume fraction: $G(\phi)/G(0) = f(\phi)$. On the other hand, the modulus of an elastic matrix with rigid inclusions normalized by the modulus of the matrix is an increasing function of the particle fraction $g(\varphi_p)$. Thus, when the particles are small enough, the stiffness of the elastic skeleton is set by the particle volume fraction it contains and the reduced shear modulus of particulate foams can be written as a combination of those two functions and one finally obtains: $G^*_{max}= g(\varphi_p)$. We make use of the Krieger-Dougherty equation to fit our data as suggested by previous studies on the elastic modulus of yield stress fluids loaded with particles [4]:

$$G^*_{\max}(\varphi_p) = g(\varphi_p) \approx \left(1-\varphi_p/\varphi_p^*\right)^{-2.5\varphi_p^*} \qquad (1)$$

where $\varphi_p^* \approx 0.6$. This phenomenological function can be used to estimate $G^*_{max}(\varphi_p)$, which is found to be in good agreement with experimental data for particles smaller than 40 µm, i.e. $\lambda \leq 0.84$, as shown in Fig 1.

Let's now consider the case of G^*_{min}, which corresponds to the case of very large particles compared to the size of constrictions, i.e. $\lambda \gg 1$. That situation should be understood as particles large enough to be fully excluded from the space defined by the solid network. In such a case, the system is composed of particle-free foam that embeds large inclusions. As the particles no more contribute to the volume of the network, the gas fraction of the embedding foam, ϕ', is therefore increased with respect to the gas fraction in the whole system, ϕ. The relation between ϕ' and ϕ is: $\phi'=\phi/(1-\phi_p)$. In combining the effect of ϕ_p on ϕ', with the effect of gas fraction on the shear modulus of foams, i.e. $f(\phi)$, one can deduce that the shear modulus of the embedding foam decreases as ϕ_p increases. Consequently, two opposing effects interact for particle-laden foams characterized by $\lambda \gg 1$: the particles stiffen the embedding foam whose shear modulus is decreased with respect to the corresponding unloaded foam. The global behavior of G^*_{min} depends on the magnitude of those two effects. Similarly to what has be done for G^*_{max}, one can write: $G(\phi,\phi_p)/G(\phi,0) = G(\phi,\phi_p)/G(0,\phi_p)\cdot G(0,\phi_p)/G(0,0)\cdot G(0,0)/G(\phi,0)$. Therefore, the corresponding global shear modulus is:

$$G^*_{\min}(\phi_p) = g(\phi_p)\cdot \frac{f\left(\frac{\phi}{1-\phi_p}\right)}{f(\phi)} \qquad (2).$$

The function *f* has been determined from measurements on particle-free gelatin foams. Fig1 illustrates that eqn 2 predicts the global softening of the foamy material, in spite of the presence of solid inclusions.

4 Conclusion

We have addressed the issue of the strengthening of foamy materials by hard inclusions. The shear elastic modulus of particle-laden polymer foams has been measured as a function of the particle loading, in such a way that the ratio λ of particle size to the foam network typical size was controlled. This geometric parameter was found to have a crucial influence on the mechanical behavior. For $\lambda<1$, every particle loading leads to a strengthening effect whose magnitude depends only on the particle volume fraction. On the contrary, for $\lambda>1$, the strengthening effect weakens abruptly as a function of λ, and a softening effect was even observed for $\lambda \gtrsim 10$. This transition in the mechanical behavior of foamy composite materials has been interpreted in terms of the evolution for the particles configuration in the foam network.

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