POLYMER COMPOSITE WITH INHERENT FUNCTION OF DAMAGE VISUALIZATION: MECHANICAL PROPERTIES OF MICROCAPSULES

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Abstract

The new concept of structural health monitoring for polymer composites is presented by bio-inspired "bruisable" GFRP composite with inherent function of damage visual indication. Concept is undertaken by smart sensitive layer, based on fabric impregnated with a mixture of two suspensions — microcapsules with a leuco dye and microcapsules dye developer. The mechanical properties of the microcapsules were studied out to evaluate their effect on mechanical properties of the composite. During the work the results of the direct measurement of the microcapsule by AFM and effective properties of the microcapsules obtained by reverse calculations were compared.

1. Introduction

Polymer composites are widely used in various industries due to specific combination of properties. While the main scientific challenges are related with polymer composites, especially, glass fibre reinforced plastics (GFRP) used as structural elements. Structural health monitoring and damage diagnostics are most topical for aviation and aerospace, boats and marine, automobile and wind power industries, where constructions are subjected to high loads and have high costs.

The new concept of structural health monitoring for polymer composites is presented by bio-inspired "bruisable" GFRP composite with damage visualization capability. Visualization of damaged place is provided by colour changing in the place of applied load like a bruise in the human body. The approach is undertaken by integrating microencapsulated leuco dye and dye developer into the glass fabric layer, which will be used as a part of the composite. The chemical reaction between microencapsulated leuco dye and dye developer is possible when mechanical load brings to the burst of capsule shell, dye is released, and get into the contact with colour developer [1]. Obviously, embedding foreign objects with lower mechanical characteristics in comparison with polymer system will lead to the degradation of the mechanical properties of the polymer system. Thus, some compromise is required when choosing between mechanical properties and the ability to detect the destruction of the material at an early stage [2].

The general aim of the study was to improve the exploitation safety of polymer composites in constructions by using material with damage visual indication ability. The specific aim of the study was to determine mechanical properties of microcapsules for the GFRP composite with damage visualization capability. For this purpose, the following tasks were formulated.

- Determine the size of microcapsules and shell thickness.

- Determine the elastic modulus of single microcapsules by atomic force microscopy (AFM) method.
- Calculate elastic properties of single microcapsule applying analytical model.
- Determine mechanical properties of a set of polymer films filled with microcapsules and calculate the effective elastic modulus of microcapsules.

2. Sizes of microcapsules and shell thickness

Microcapsules (m/c) with leuco dye and m/c with dye developer, as water based dispersions were supplied by *Papierfabrik August Koehler Ag.*, *Germany*. The microcapsules are made from melamine-formaldehyde resin.

The microcapsules were examined by a scanning electron microscope (SEM) Hitachi S - 4100. The capsules destruction process was studied, and microcapsules shell thickness was measured using micro photo of damaged capsules, see Fig. 1.

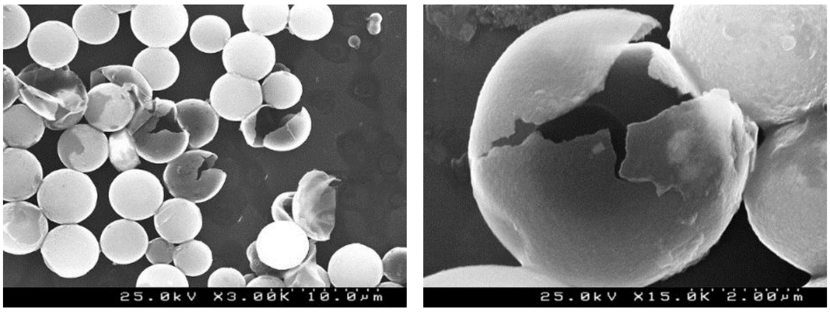

Figure 1. Microphoto of damaged microcapsules.

Microcapsules size was measured and its size distribution was calculated from the microscope images using ImageJ software, see Fig. 2, and by dynamic light scattering (DLS).

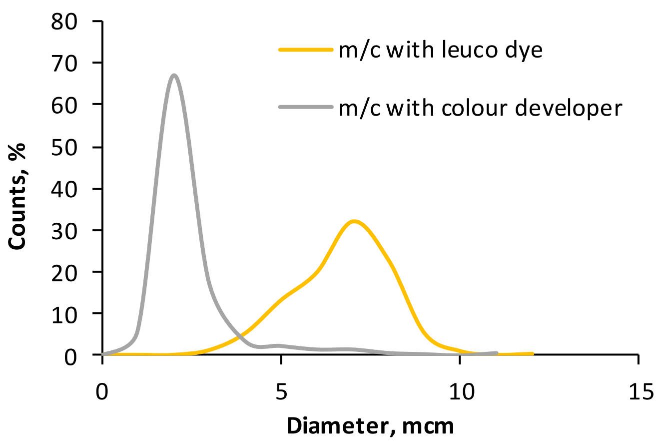

Figure 2. Microcapsules size measuring with the size distribution.

From 6 measurements of broken microcapsules, the average wall thickness of the capsules was defined 0.103 ± 0.014 μm.
From the SEM images and DLS test results was defined that microcapsules have some evident distribution by size. Average diameter of m/c with leuco dye is 7 μm while m/c with developer is 2 μm (both results of SEM photo). Automatic counting and results of light scattering measurements give essential errors in the case of incorrect development of microcapsule agglomerates.

3. AFM and nanoindentation

The topography of the dried microcapsules was monitored by AFM ICON, Bruker on the mica as the substrate. The separated microcapsules kept their original almost spherical character after drying with the height 1.6 μm and the width 1.8 μm, see Fig. 3.

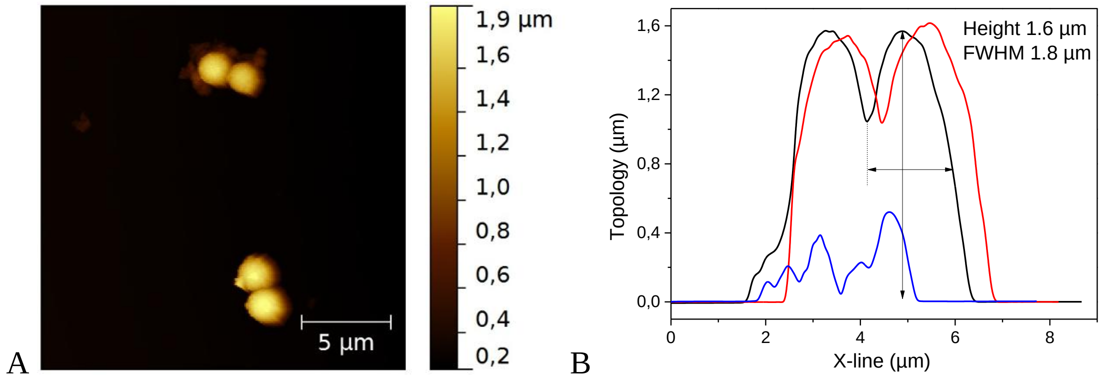

Figure 3. Topological image (A) and corresponding topological profile (B) of microcapsules.

Nanoindentation measurement were carried out at room temperature with an NEXT AFM (NT-MDT, Russia) equipped with nanoindentation set-up and acoustic shelter. The indenter was a diamond Berkovich tip having a spring constant 10.2 ± 0.3 kN·m^{-1} (three-sided pyramid with a half angle of 30° with nominal tip apex radius of curvature less than 30 nm).
The nanoindentation measurement was used for both the maximal force loading necessary for rupture and the real quantification of elastic modulus. Typical nanoindentation curve loaded until rupture of the microcapsule is illustrated in Fig. 4. The force decreased quickly as microcapsule is broken (ruptured) as it was observed on the microscope. The mean load necessary for rupture was determined as 107 ± 10 μN.
The value of the modulus was calculated according thin shell theory. Close to the pole, the modulus was calculated applying equation found for shallow spheres by *Reissner* [3] The normal displacement of the pole *d* under point loading with force *F* is given by Eq. (1):

$$d = \frac{\sqrt{3(1-\nu^2)}}{4} \cdot \frac{FR}{Eh^2} \quad (1)$$

where *E* is elastic modulus of microcapsules, *h* is the shell thickness, *R* is the radius of capsule, *ν* the Poisson ratio. For utilization of thin shell theory, two assumptions are necessary to be fulfilled: the shell thickness needs to be less than 1/10 of microcapsule radius and low forces (deformation) can be applied.

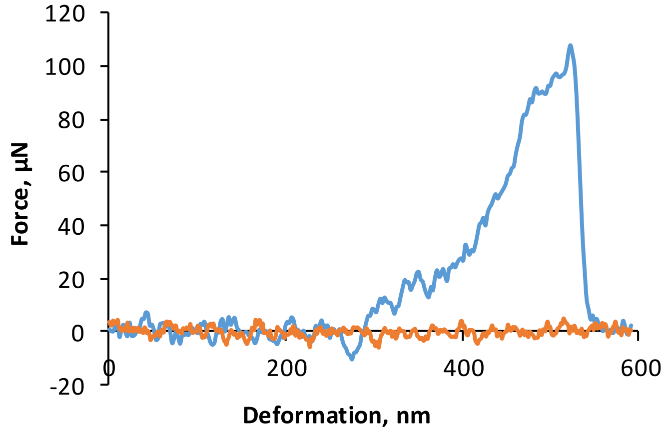

Figure 4. Deformation vs. applied force until the rupture of the microcapsule on AFM. Loading (blue line) and unloading (orange line).

The calculation was done from the linear part of nanoindentation curve (small deformation regime), and values of the force and half of the deformation (2.1 μN and 20 nm – see Fig. 5) and *h* (0.103 μm – defined from SEM image of broken microcapsules).
From the Eq. (1) the elastic modulus of microcapsules, *E* is defined by Eq. (2):

$$E = 0.43 \cdot \frac{FR}{dh^2} \tag{2}$$

where *E* is elastic modulus of microcapsules, *d* is half of the measured deformation, *h* is shell thickness, *R* is radius of capsule, *F* is loading force. For the individual particle the elastic modulus was calculated of *E* = 3.2 GPa. The same estimation was carried out on the 10 individual particles. The mean elastic modulus was determined as E_1 = 3.5 ± 0.3 GPa.

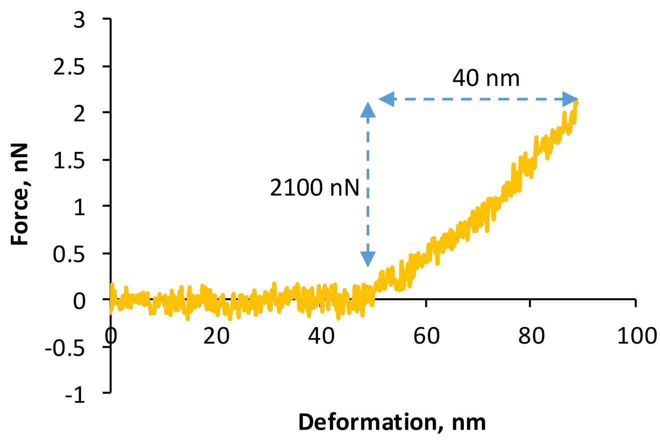

Figure 5. Nanoindentation curve in the small deformation regime.

4. Continuum elastic theory

The microcapsules are considered as shells of radius *R*, thickness *h*, made of an isotropic elastic material with an elastic modulus *E* and Poisson ratio *ν*. In general, a force applied on top of the capsule will induce both bending and in-plane shear and stretch. Considering a small deformation, capsule flattens in the region in contact with the surface. Comparing the total energy to the work $W \sim \int f d\delta$ exerted by the force f this leads to, Eq. (3) and (4):

$$f_{sh} = \frac{\Delta E h^2}{R(1+v)\sqrt{6(1-v)}} \tag{3}$$

for pure shear deformation, and

$$f_{st} = \frac{\Delta E h^2}{R(1+v)\sqrt{6(1+v)}} \tag{4}$$

for pure stretch deformation.

In this form the equation shows that the capsule behaves like a spring with a spring constant proportional to E (elastic modulus), h^2 (square of the thickness) and $1/R$ (inverse of the capsule radius). For the large deformations, dependency of the force on the deformation is not linear [4].

Using force-displacement curve obtained by AFM, exactly the linear part, see Fig. 5, the elastic modulus of single m/c was calculated taking into the account that total force is $f = f_{sh} + f_{st}$. From the calculation the value of elastic modulus of microcapsules E_2 = 0.525 ± 0.025 GPa, most corresponded to the experimental data, see Fig. 6.

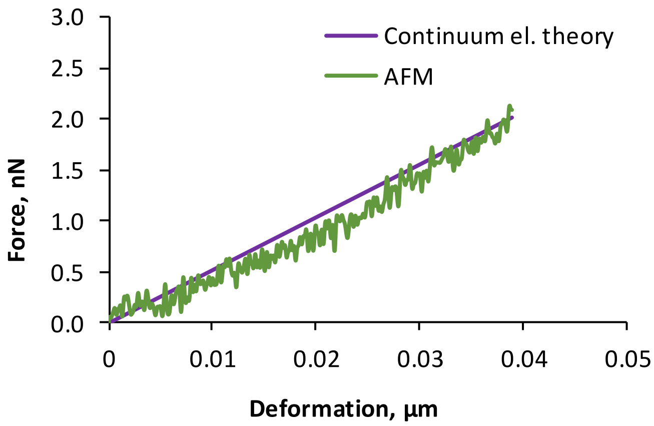

Figure 6. Force vs. deformation of microcapsule during the nanoindentation; AFM experiment and calculation.

5. Polymer films filled with microcapsules

Mechanical properties of a single microcapsule obtained during AFM tests could be used in further calculation and modelling, but it doesn't represent the real situation; microcapsules in composite are used in large quantities and possible interaction or agglomeration of the capsules should be taken into account, and they have wide size distribution. Mechanical properties of the heterogeneous polymer blends depend on its composition and structure. In addition to the colloidal structure of the mixture, properties are determined by parameters such as the ratio of the elastic moduli of the phases, adhesion between the phases, and the particle diameter of the dispersed phase. The *Rule of mixture* (ROM) [5] as a simple model (adhesion and particle size are not considered) could be used for an approximate result. For the evaluation of the effective mechanical properties of microcapsule the indirect method was applied. Properties of composite (films with integrated microcapsules made from CHS 200 V 55 epoxy and Telalit 180 hardener) with known concentration of microcapsules were measured. Effective properties of microcapsules were calculated from the data applying ROM. An example of the specimens for a tensile test is shown in Fig. 7. The concentration of microcapsules in specimen was recalculated, taking into account coefficient 0.4 (microcapsules are presented as 40% suspension in water).

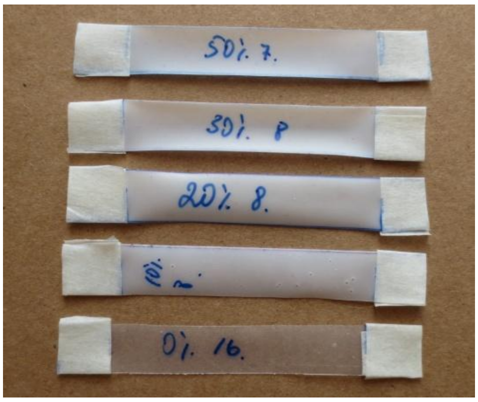

Figure 7. Polymer matrix with integrated microcapsules.

Data of the tensile tests (stress vs. strain) were used in further calculations. For the determination of elastic modulus of microcapsules, the *Voigt* Eq. (5) and *Reuss* Eq. (6) approximations, known as the "rule of mixtures" and the "inverse rule of mixtures", respectively, were applied:

$$E_c = E_f \cdot V_f + E_m \cdot V_m \tag{5}$$

$$E_c = \left[\frac{V_f}{E_f} + \frac{V_m}{E_m}\right]^{-1} \tag{6}$$

where E_m is elastic modulus of matrix and E_f is the one of filler, V_m is volume fraction of matrix and V_f is the one of filler, $V_m + V_f = 1$. Applying *Voigt* and *Reuss* approximations for the experiment results, the effective elastic modulus of microcapsules was defined as $E_3 = 0.2$ GPa, Fig. 8.

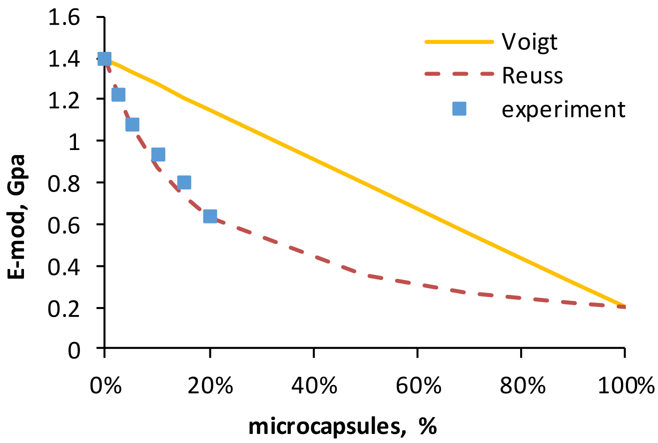

Figure 8. Elastic modulus of polymer with m/c vs. concentration of m/c; experiment and calculation.

Conclusions

In the present work mechanical properties of single microcapsules were studied out by AFM nanoindentation measurements and applying different analytical models for the calculation of the elastic modulus. Effective mechanical properties of the bunch of microcapsules were calculated by applying *top-bottom* approach, namely by approximation of experimental dependences of polymer films moduli vs. content of microcapsules. The value of the elastic modulus obtained for the single microcapsule E_1 = 3.5 GPa by *Reissner*, E_2 = 0.5 GPa by continuum elastic theory, and for the group of microcapsules E_3 = 0.2 GPa differ significantly. This can be explained by the fact that the microcapsules have some variation in size, and the value of the modulus is directly related to the value of the size of the microcapsule. The applied analytical models were formulated for solid elastic inclusions. The behaviour of the microcapsules with the liquid inside substantially differs from the behaviour of the solid inclusions, therefore, further modelling is necessary.

Acknowledgments

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