The impact of nanoparticles on matrix properties in PMCS

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Abstract

The method of movable cellular automata (MCA) was applied to simulate the stress-strain behaviour of a nanocomposite consisting of an epoxy matrix and 5 vol.% silica nanoparticles and for samples of pure components. The size of the elements used for modelling was fixed at 10 nm, corresponding approximately to the diameter of the filler particles. Modelling results were compared with tensile test results of both, pure epoxy as well as the epoxy-5 vol.% SiO_2 composite. Since assuming bulk properties of the two constituents did not yield satisfactory results, slight modifications of the nanoparticle response functions and nanostructures were tested numerically. Finally, slightly increased strength properties of both constituents had to be taken into account for obtaining good correlation between experimental and modelling results. The tendency of model parameter adjustments corroborate expected changes of composite constituents compared to their respective bulk structures.

1 Introduction

The effect of considerably improving of mechanical as well as tribological properties of conventional polymer matrix composites (PMCs) by adding of silica nanoparticles was shown in [1, 2]. The explanation of this influence seems to be quite clear. It is expectable that Youngs modulus and strength increases if the epoxy matrix is filled with particles which are much harder than the polymer. On the other hand, it is not easy to estimate this effect quantitatively, especially if the concentration of SNP volume fractions is less than 10% (sometimes no more than 1%) and the particles are very small. The latter circumstance rules out an efficiency of finite element modelling (FEM). In the paper a method of discrete approach - movable cellular automata (MCA) method [3] was used to simulate the mechanical behavior of multi-component nanostructured samples. Within this approach a modelled composite is considered as linked nanoparticles bearing the properties of the different constituents. By introducing criteria for link-breaking and relinking, fracture mechanisms and granular flow can be simulated on the nanoscopic scale. The MCA method have no restriction of particles size, therefore it is especially suitable for modelling the mechanical behaviour of nanocomposites. In the paper the most significant results of our recent research works is presented. More detailed information is summarized in [4].

Within the MCA model the mechanical properties of the nanoconstituents are defined by the corresponding response functions in the form of stress-strain curves. Usually such data are available only for bulk materials. It is not really clear yet, to what extend bulk properties can be used to characterize nanoparticles. Although there are innumerable papers describing the size, shape and surface functionalities of silica nanoparticles, only very few information on the mechanical properties of such nano-sized objects is available in the literature. Yan et al. have shown that it is in principle possible to determine the elastic modulus of soft and hard nanoparticles embedded in a polymeric matrix by nanoindentation in combination with finite element modelling [5]. Basu et al. have shown that not only elastic properties, but also stress-strain curves can be derived from nanoindentation tests [6]. A great advantage of modelling is that we can vary material parameters hypothetically in a wide range. Thus it is possible to assess the impact of material properties and volume fractions of constituents of a composite material by a series of parameter studies in a theoretical way. The objective of this paper was to find the right range of material parameters in order to reproduce experimental stress stain curves with our model.

2 Experimental data

The raw materials used for preparation of the EP + 5% SiO_2 composite were: a standard diglycidil ether of bisphenol A (DBEBA) offered by DOW as DER331, a cycloaliphatic amine hardener HY 2954 from Huntsman and a colloidal silica masterbatch with a concentration of 40 mass % and a nominal particle diameter of 20 nm in DGBEBA offered as Nanopox F400 from Evonik. A thin slice was prepared from the EP + 5% SiO_2 composite by microtomy and investigated in a Scanning Transmission Electron Microscope (STEM) of type JEOL 2200FS.

Dumbbell-shaped specimens, 4 mm thick, were machined from casted plates and tested according to DIN EN ISO 527 using universal testing machine (Zwick 1474) at room temperature and at a crosshead speed of 0.5 mm/min. The displacement of each specimen during tension was accurately measured by an extensometer with an initial gage length of 20 mm.

3 Numerical model

3.1 A general formalism

The MCA method is based on conventional concept of cellular automata [3, 7]. It is an extension of cellular automaton approach achieved by incorporating some basic postulates and relations of particle-related methods. The movable cellular automaton is an object of finite size, possessing translational and rotational degrees of freedom. Interaction between automata is defined by normal (acting along the line connecting the mass centers) and tangential forces, each of which is the sum of the corresponding potential and the dissipative component. The principles of writing the equation of motion for a system of movable cellular automata and prescribing

interactions between them are described in [7].

3.2 Model description

The modelling setup was designed as shown schematically in figure 1a. Two types of the sample were considered: homogeneous sample like pure epoxy and nanocomposite on the basis of epoxy as a polymer matrix filled with silica nanoparticles. Their assumed mechanical properties at room temperature, which are needed to define their stress-strain behavior, are depicted in figure 1b. Actually, the stress-strain curve for bulk silica was derived from nanoindentation measurements [6], whereas the corresponding dependence of the epoxy matrix was derived experimentally. The significant input parameters to define the mechanical properties of each material are: Youngs modulus, Poisson ratio, elastic limit, yield strength, fracture strength, strain at yield strength and strain at fracture.

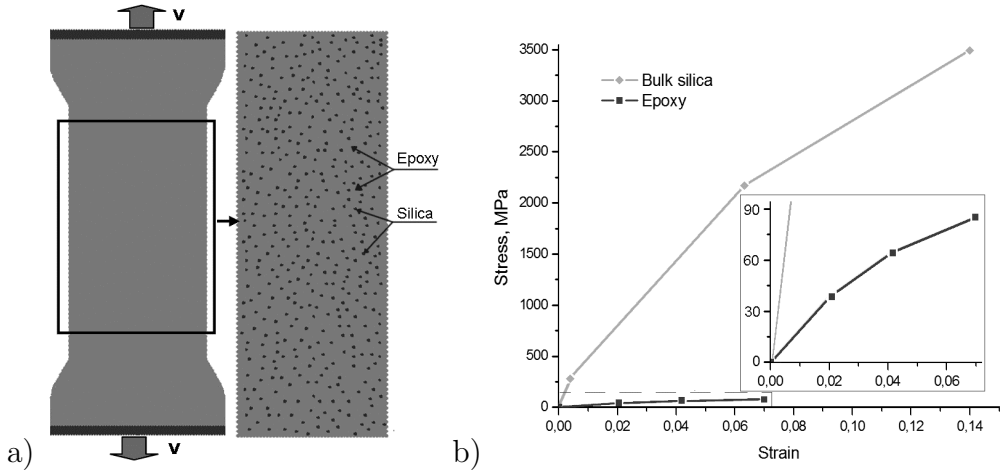


Figure 1: The initial structure of modeled composite and a loading scheme (a); the model response functions of the constitutive elements (b).

The automata size was adjusted to 10 nm according to the smallest size of silica nanoparticles, which are currently used experimentally for polymer matrix composites. A constant velocity (V) equal to 0.2 m/s was applied on all automata of the top and bottom layers of the sample in opposite directions. The geometry of the sample was: 15 µm along loading direction and 3 µm in transvers direction. Thus, the loading conditions similar to uniaxial tension test was reproduced for a small fragment of the real sample. For the composite sample the concentration of silica inclusions embedded in epoxy was kept constant at 5 vol.%. The distribution of silica inclusions in modeled setup was adjusted in a way to achieve best similarity with the real nanostructure. The total number of particles was more than 8000.

4 Results of modelling

4.1 Modelling the stress-strain behavior of pure material

First the uniaxial tensile test of the sample in which the model parameters of all particles were corresponding to the mechanical properties of the pure epoxy was investigated. Verification of the parameters was carried out by comparing the resulting loading diagram with the available experimental data for the similar sample. Figure 2a shows the results of calculations for the homogeneous sample of pure epoxy. The curve marked by filled circles is the experimental stress-strain dependency which was also used as a target response function for defining the behaviour of each element in the setup. Curve no. 1 depicts the stress-strain behaviour resulting from a modelling effort based exactly on this assumption. The resulting curve has the same fracture strain but lower ultimate tensile strength. Curves no. 2 and 3 correspond to the modeled samples in which slightly increased strength properties had to be attributed to the nano-scale elements of the pure epoxy in order to obtain the desired fit with the experimental data. This can be interpreted in terms of a size effect of mechanical properties, i.e. we should assume higher elastic, yield and strength properties for nanoparticles, compared to bulk properties of the same material. In fact, increased Youngs modulus and fracture strength was observed experimentally for silicon as well as silica nanowires [8].

From figure 2b it is clear that the character of the main crack formed when the deformation is about 7% is different from the fracture pattern of the real sample (figure 2c). This distinction can be caused due to the two-dimensional formulation of the numerical model or by the presence of imperfections such as voids or microcracks which are not considered in the model.

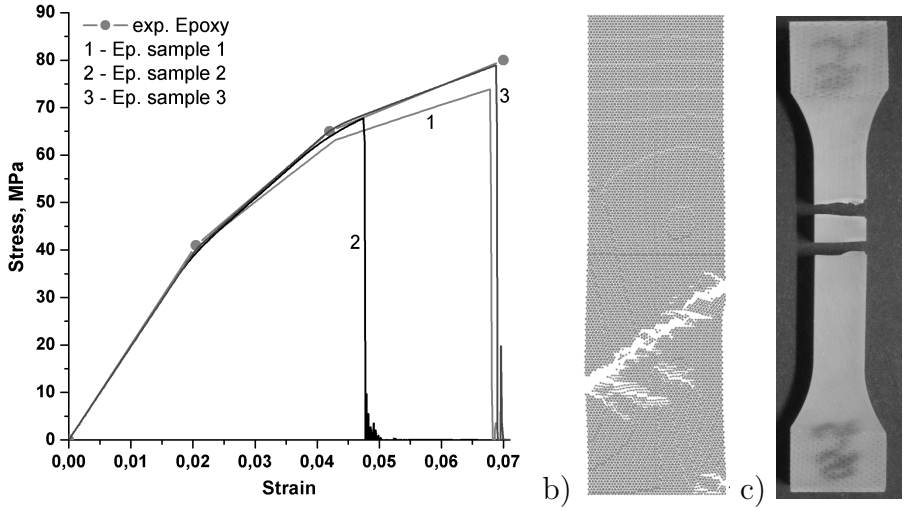


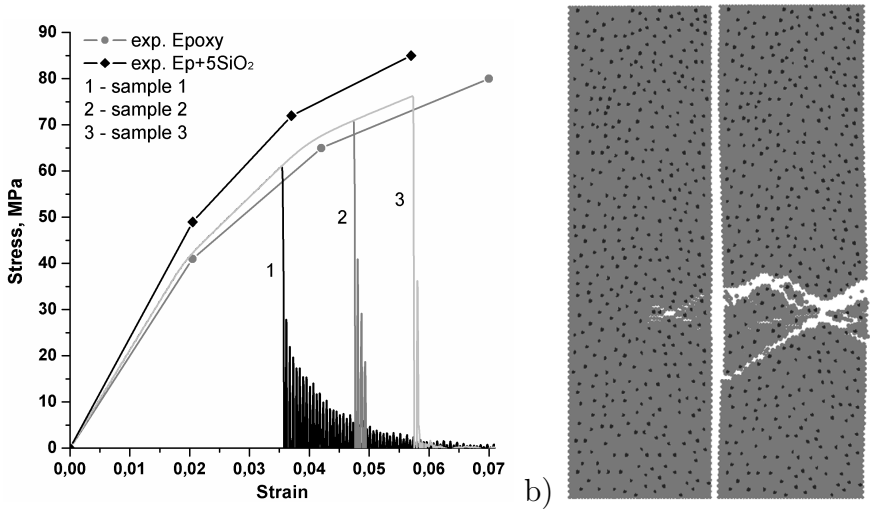
Figure 2: Results of calculation for the pure epoxy sample: resulting loading diagram (a), modeled (b) (sample 3 on fig. 2a) and a real (c) sample after generation of crack.

Similar calculations of the uniaxial tensile tests were carried out for the homogeneous samples in which the model parameters of the response functions for each element were corresponding to the properties of silica nanoparticles. The resulting

values for both components were used to generate the composite sample based on the polymer matrix, as described in the next section.

4.2 Modelling the stress-strain behavior of the composite

On the next stage of the investigation the uniaxial tensile test for a composite sample consisting of epoxy matrix filled with 5 vol.% silica nanoparticles was simulated. An attempt to generate a sample, using the previously fitted model parameters of the response functions for both constituents, did not give the expected result. Due to the introduction of the silica nanoparticles the resulting curve shows an increase of stiffness of the composite sample within $7-8\%$ in comparison with the pure epoxy sample (curve no.1 in figure 3a), while the experimental curve corresponds to an increase in stiffness of the composite samples over 20% (filled diamond symbols in figure 3a). At the same time the modeled composite sample (curve no. 1) demonstrates very low fracture strain which can be interpreted as weak adhesion properties between matrix and hard inclusions.



a) b)

Figure 3: Results of calculation for the composite sample: resulting loading diagrams (a), two consecutive snapshots of the structure evolution of the modeled sample 3 during a generation of the main crack (b).

Attempting to achieve a better fit to experimental results, the procedure of the adhesive properties modification at the interface between soft matrix and rigid inclusion was used. For this purpose the parameter which corresponds to the von Mises fracture criterion and controls the conditions of the linked to unlinked state transition in the pair of elements of two materials was increased. Other curves depicted in the figure 3a show that the increasing of fracture criterion up to 98 MPa (curve of the sample 2) and 108 MPa (curve of the sample 3) change only the deformation properties of the resulting composite sample, while the slope of the curve is not changed. The resulting structures of the modeled sample 3 at the time of main crack nucleation and propagation are shown in the figure 3b.

4.3 Introduction of additional interface particles

Within the framework of the most recent MCA modelling scheme, the existence of a transition layer can change the response of the system, as shown in [9]. In order to take into account the presence of the interface layer around each hard inclusion additional elements with intermediate mechanical properties defined by the rule described in cited paper were introduced. Briefly the main algorithm to define the certain parameter of intermediate particles can be formulated as

$$P_{new} = P_A C_A + P_B C_B \tag{1}$$

where P_{new} calculated value of the selected parameter for the intermediate particle, P_A and P_B corresponding value of the same parameter for materials A and B (for, example matrix and inclusion as in our case), C_A and C_B corresponding concentration of materials A and B in the intermediate particle. The fracture criteria can be found in the same manner using the rule 1. Simultaneously with the introduction of interphase particles, the absolute number of nanoinclusions was also reduced in order to keep the total volume concentration of silica about the same amount in comparison with the previous calculations.

The detail information about the results of calculations with introducing of additional interface particles is given in [4]. In short, the resulting loading diagrams demonstrate that the used technique allowed one to change the angle of slope of the curves in the right direction, while the deformation capacity of the composite sample declined sharply. None of the modifications was capable of describing the experimental curve EP + $5SiO_2$ in respect of predicting the right strain at fracture.

4.4 Modification of the mechanical properties of the matrix

The next step towards defining modelling parameters which should finally enable us to simulate the stress-strain behaviour of the real nanocomposite was a modification of the mechanical properties of the particles of the matrix material, i.e. the epoxy. To go into this direction is justified by the finding that cross-linking of the epoxy molecules is considerably increased in the presence of silica nanoparticles [1, 10].

The result of modifications of epoxy mechanical properties for the satisfying variant of modeled composite sample is shown in Table 1. Numbers in parentheses denote the deviation of given parameter in comparison to the similar bulk epoxy properties. The resulting response function for the considered example is depicted in figure 4.

5 Conclusion

It has been demonstrated that the MCA-model, has the ability of simulating the tensile properties of a polymer matrix composite filled with silica nanoparticles. Although only a two-dimensional structure was considered, representing a micron-sized flat sample with a thickness corresponding to the element size (10 nm), it was possible to simulate the same stress-strain behaviour and fracture pattern as observed for a macroscopic tensile specimen.

Table 1: Adjustment of epoxy properties in comparison to bulk one

	bulk(Epoxy)	Epoxy in modeled composite
Youngs modulus, GPa	2	2
Elastic limit (Y_1), MPa	41	45(10%)
Yield strength (Y_2), MPa	68	73(7%)
Strain at Y_2	0.042	0.042
Ultimate tensile strength (UTS), MPa	88	96(9%)
Ultimate strain	0.075	0.075

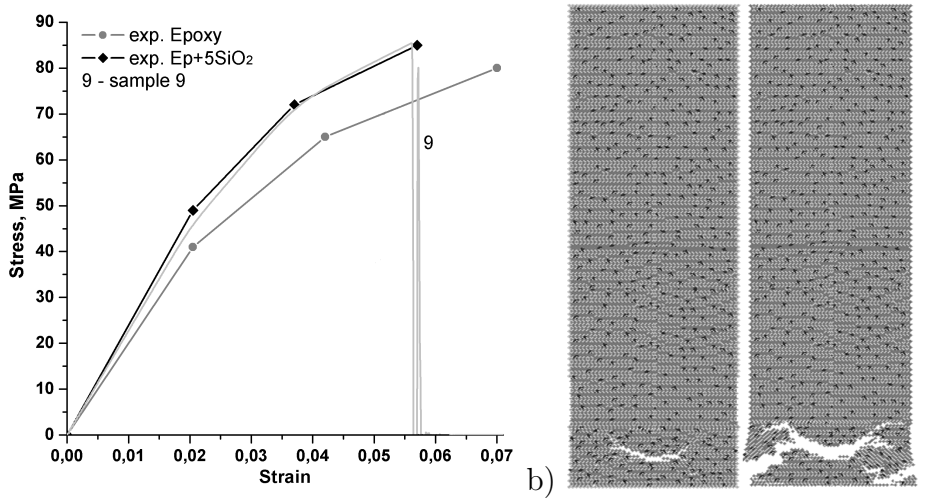


Figure 4: Resulting loading diagrams for the modeled samples (a), two consecutive snapshots of the structure evolution of the modeled sample 9 during a generation of the main crack (b).

In order to obtain the desired fit between experimental data and modelling results, several modifications of input parameters, which were not a priori obvious, had to be tested numerically. The parameter studies did not only finally provide the best modelling values, but they also shed light on the issue how certain parameters affect the mechanical behaviour of both monolithic as well as composite nanostructures.

The refined response functions obtained by comparison with experimental tensile tests are not only useful for simulating the stress-strain behaviour of a wide range of EP-SiO_2 nanocomposites, but they will also be used in the future for simulating the sliding behaviour of hybrid nanocomposites with exceptional tribological properties [2], as already mentioned in the introduction.

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