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ASSESSMENT OF MECHANICAL PROPERTIES OF PARTICULAR POLYMER COMPOSITES BY WAY OF MICROHARDNESS MEASUREMENTS

HODNOCENÍ MECHANICKÝCH VLASTNOSTÍ PARTIKULÁRNÍCH POLYMERNÍCH KOMPOZITŮ POMOCÍ MĚŘENÍ MIKROTVRDOSTI

Jiří Minster[1], Ladislav Berka[2], Julia Hristova[3]

The applicability of Vickers microhardness measurements for mechanical assessment of filled polymer composites and heterogeneous polymer concretes is discussed in the paper. Two types of composites based on epoxy and polyester matrices were investigated. The epoxy polymer concrete and filled epoxy composite were fabricated by curing a low molecular epoxy resin Diepox 450 at room temperature with an aliphatic polyamide (diethylentriamine). The post-cure process involved heating (6 h T=80°C) with slow quench to laboratory temperature. The measured polyester composites were prepared by unsaturated polyester resin (Jotun ChS Polyester 122), and were cured at normal temperature and pressure according to the conventional curing system. The post-curing process involved post-heating (6 h at T=80°C) with the aim of stabilising the structure and properties. Two types of finely dispersed fillers were used: hard (marble powder) and soft (powdery PVC). The volumetric concentration of the individual fillers was 20%. Experimental indentation tests were performed with an Anton PAAR (MHT 10V) Vickers microhardness tester with a video measuring system. The loads were from 5 to 300 [gf]. They were applied at a constant loading rate during a time interval of 10 s and maintained in contact with the sample surface for another 5 s. The applied forces and the diagonal lengths are coupled by the Mayer power law, very sensitive and convenient for identifying individual phases of a heterogeneous material. More than two hundred indentations were performed altogether. Since the physical parameters of the Mayer power law of all measured phases were close to two, a simple dependence was defined of MHV values on strength parameters. The reinforcing effect of the hard filler and changes in the microhardness (i.e, in the yield strengths and moduli) in the neighbourhood of filler micrograins were also substantiated.

Keywords

Vickers microhardness; Particular polymer composites; Mechanical characterisation

Vickersova mikrotvrdost, částicové polymerní kompozity, mechanická charakterizac

[1] Institute of Theoretical and Applied Mechanics, Czech Academy of Sciences, Prosecká 76, 190 00 Prague, Czech Republic; E-mail: minster@itam.cas.cz, Website: http://www.itam.cas.cz

[2] Czech Technical University in Prague, Faculty of Civil Engineering, Thakurova 7, 166 29 Prague, Czech Republic; E-mail: berka@fsv.cvut.cz

[3] Central Laboratory of Physico-Chemical Mechanics, Bulgarian Academy of Science, Acad. G. Bontchev St. Bl.1, Sofia 1113, Bulgaria; E-mail:juli@clphchm.bas.bg

Introduction

The Vickers hardness test is commonly used to characterize the hardness of materials. Microhardness is understood as the hardness of a small volume of material, determined through measurements on special apparatus under very low loadings [1]. It is defined as the ratio of the used load to the indent area. Microhardness values are generally higher than macrohardness values. Modern apparatus for microhardness measurements reduce the influence of various disperse factors resulting from the construction of the apparatus and the technique that is used. The apparatus enables the load, the rate of loading and maintenance of full contact to be programmed. The experiments are simple to perform, need only a small quantity of material (the samples have to be polished and cleaned), are generally non-destructive, and can easily be repeated many times. This makes it possible to design a measurement for any desired confidence level, and to distinguish between the precision of the result and the hypothetical heterogeneity of the sample [2]. The localised nature of the microhardness test allows information to be obtained regarding the definite heterogeneity of the measured surfaces, for example from different phases of filled polymer matrices and polymer concretes.

Microhardness values are influenced by factors, dependent both on structural and physical-mechanical properties of tested materials. Among structural the anisotropy of hardness of crystalline materials is the most important. The anisotropy is indicated [1] either polar (structural, I. order anisotropy – different lengths of indent diagonals are a characteristic demonstration) or reticular (II. order anisotropy, caused by different density of crystal particles in different directions – indents have a perfect form, but their dimensions are dissimilar). During the indentation cycle four deformation processes must be distinguished: (i) elastic recovery beneath the indentation upon removal of the load, (ii) permanent plastic deformation (measure of hardness – material can sink-in or pill-up along the contact boundary), (iii) creep during loading and (iv) visco-elastic relaxation after the load is removed. Since the elastic effects are negligible, the hardness of the rheonomic materials is measured for short loading times in order to minimize creep, and immediately after the load is removed, in order to minimize relaxation [3].

From a macroscopic point of view, hardness (*MHV*) is correlated to the yield stress, σ_y, of the material (according to Tabor [4] $MHV \approx 3\ \sigma_y$). Tabor's relation is well substantiated for both amorphous and crystallized unoriented polymers. Brittle materials (i.e. mineral fillers, quartz river sand and gravel) have a tendency to crack during and after indentation. Cracks of different origin and form [5] deteriorate the measurements and assessment. A possible solution of the trouble is to change the way of loading. The applicability of Vickers microhardness measurements for mechanical assessment of filled polymer composites and heterogeneous polymer concretes is discussed in the paper.

Materials

Two types of composites based on epoxy and polyester matrices were investigated. The epoxy polymer concrete (EPC) and filled epoxy composite (EC) were fabricated by curing a low molecular epoxy resin Diepox 450 (D 450) at room temperature with an aliphatic polyamide. The post-cure process involved heating (6 h, T=80^{o}C) with slow quench to laboratory temperature. The investigated EPC consists (by weight) of 12.5 % epoxy matrix, 0.9 % hardener, 0.9 % thinner and particulate fractions of marble flour (15 %), quartz river fine sand (30.2 %) and crushed diabase stone of the size 10-20 mm (40.5 %). The EC contains (by volume) 20% marble powder ($CaCO_3$). The D 450 specimens were tested after a period of 14

years physical aging in room environment. A part of the D 450 specimens was after physical aging reheated to 80°C (Tg+10°C) and quenched to room temperature. This is classified as rejuvenation.

The measured polyester composites were prepared by unsaturated polyester resin (Jotun ChS Polyester 122) (Chs 122), and were cured at normal temperature and pressure according to the conventional curing system: cobalt naphthenate (accelerator) cyclohexanon peroxide (initiator). The post-curing process involved post-heating (6 h at T=80°C) with the aim of stabilising the structure and properties. Two types of finely dispersed fillers were used: hard (marble powder) and soft (powdery PVC). The volumetric concentration of the individual fillers was 20%. The modulus of elasticity of the hard filler is higher by one order than that of the matrix, and the modulus of elasticity of the soft thermoplastic filler is commensurate with that of the matrix. The volumetric concentration of the individual fillers was 20%.

Experiments

Experimental indentation tests were performed with an Anton PAAR (MHT 10V) Vickers microhardness tester with a video measuring system. The loads were from 5 to 300 [gf]. They were applied at a constant loading rate during a time interval of 10 *s* and maintained in contact with the sample surface for another 5 *s*. More than two hundred indentations were performed altogether. Both diagonal lengths of each indentation were optically measured in the hardness apparatus with a magnification of 500, using zoomed fields. For the recommended diagonal lengths of 20 μm (indentation depth *h* is then approximately 3 μm) the estimated precision of the optical diagonal length measurement is in the range of two percent.

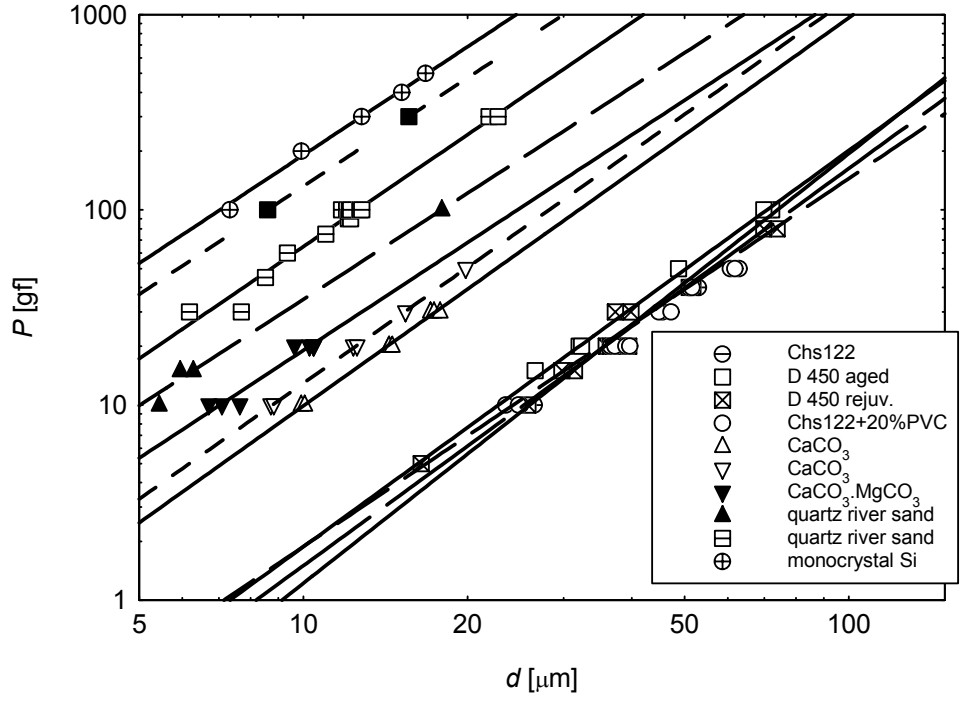

Fig.1 Mayer lines $P = a * d^n$ of measured materials and minerals

The Vickers microhardness (*MHV*) was calculated with the equation

$$MHV=k*P/d^2 \quad (1)$$

where k is a constant depending on the indenter geometry and on the units chosen (here $k=1.8185*10^4$), P is the applied force (in gf) and d is the diagonal length (in μm). The Vickers

microhardness unit then corresponds to MPa. The applied force P and the diagonal length d are coupled [6] by the Mayer power law

$$P=a*d^{n} \quad (2)$$

where a and n are physical parameters corresponding to strength and plastic material properties. The value of n gives the trend of *MHV* with a change in the diagonal length d, proportional to the applied force P. When n=2, *MHV* is constant for increasing P, for n<2 it decreases and for n>2 it increases, respectively. Mayer lines are very sensitive and convenient for identifying individual phases of a heterogeneous material (see Fig.1).

Results

Values of the physical parameters a and n corresponding to the Mayer power law and Vickers microhardness values of measured materials and minerals are summarized in Table 1. Since the physical parameters n of all measured phases were relatively close to two, a simple linear dependence was defined of *MHV* values on strength parameters a (see Fig.2).

Both types of anisotropy were recorded, the second order anisotropy typically in single micrograins of marble filler. For this material the best confidence levels of microhardness were achieved. Two kinds of quartz river sand were identified to produce specimens.

Tab. 1 Values of the physical parameters a and n and microhardness values of the measured materials and minerals

a [gf/μm^n]	n	*MHV* [MPa]	material
0.0138	2.04	285±14 (4.9 %)	Chs 122
0.0174	2.03	343±32 (9.3 %)	D 450 rejuvenated
0.0214	1.89	357±29 (8.2 %)	D 450 aged
0.0244	1.89	297±29 (9.9 %)	Chs 122 + 20 % PVC
0.102	1.99	1798±59 (3.3 %)	$CaCO_3$
0.138	1.97	2338±41 (1.7 %)	$CaCO_3$
0.279	1.83	3544±336 (9.5 %)	$CaCO_3$. $MgCO_3$
0.542	1.81	6931±782 (11.3 %)	quartz river sand
0.845	1.89	11585±1146 (9.9 %)	quartz river sand
1.90	1.90	23500±1555 (6.1 %)	mineral
2.74	1.84	34301±2106 (6.1 %)	crystal Si

The microhardness values of the pure D450 matrices do not differ significantly. The reinforcing effect of the hard filler and changes in the microhardness (i.e, in the yield strengths and moduli of the polymer matrices) in the neighbourhood of filler micrograins in relatively dilute compositions can be seen in Figs. 3 and 4.

There is not substantial difference in operation between aged and rejuvenated D450 epoxy matrices (see Fig.3). In both cases the asymptotic microhardness values of the composite matrices are lower in comparison with the values of their pure forms given in Tab.1. Dependence of time-age shift on aging time, defined for the investigated materials ([7],[8]), accounts for the possibility of measuring momentary characteristics for longer time intervals than commonly expected. Conversely, the character of the polymer matrix-hard mineral filler cooperation in the composites is rather different for the used low molecular weight resins

(oligomers) (contrast Figs. 3 and 4). Higher cure shrinkage of the polyester matrix, comparing to the epoxy resin, may be a reason for higher hardness values in a larger region of a micrograin neighbourhood and a slower lag phenomenon of the filler reinforcing effect for the polyester composite.

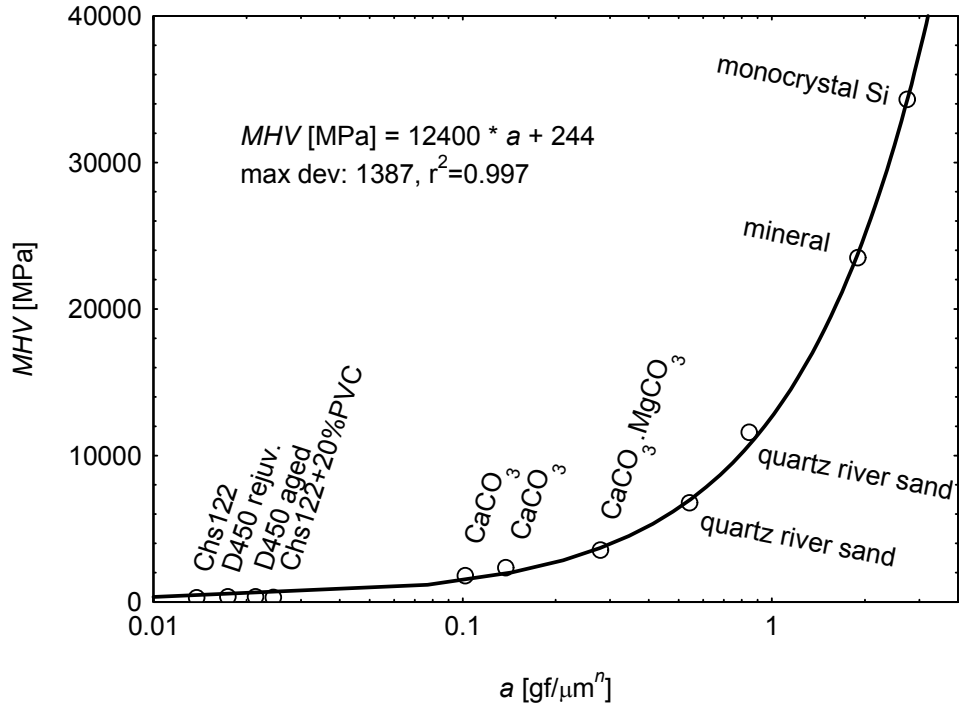

Fig.2 *MHV* of the measured materials and minerals as a linear function of the strength parameter *a*

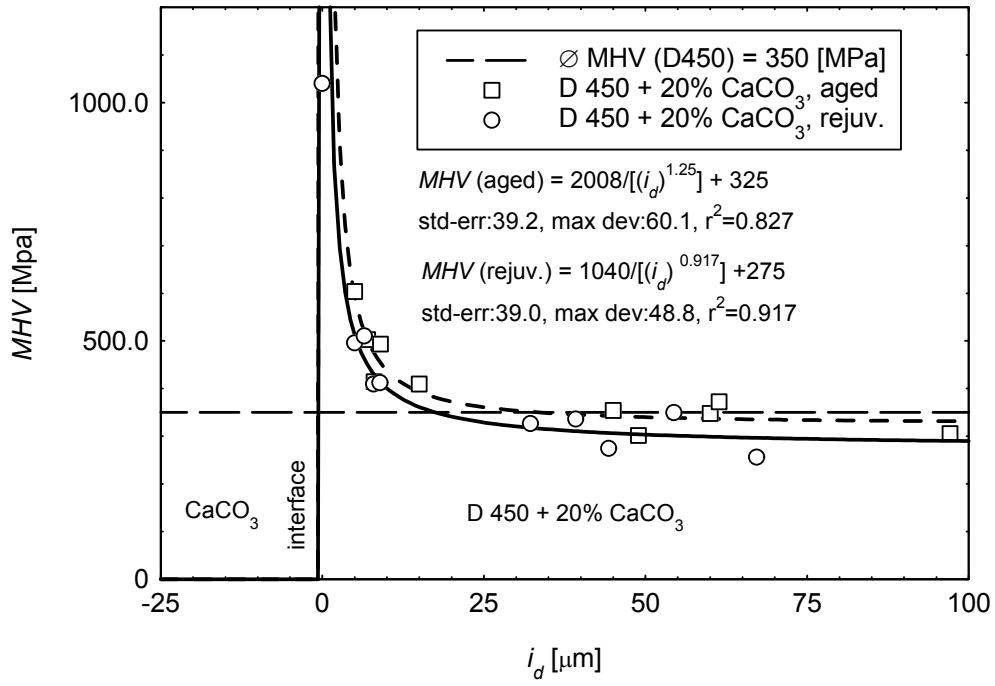

Fig.3 Vickers microhardness in the neighbourhood of $CaCO_3$ micrograins in the D450 aged and D450 rejuvenated epoxy matrices. i_d defines the normal distance between the grain boundary and indent mid points.

In practical situations, the accuracy of a hardness measurements consisting of n indentations may be important. Schneider et al. [2] found the number n^* of indentations required to attain the accuracy level α by the equation

$$n^* = \left(\frac{2u_\alpha}{(1-\alpha)} \frac{\sigma_d}{\mu_d} \right)^2 \tag{3}$$

where u_α is the reduced value defining the α-confidence interval in Gaussian statistics (u_α =1.96, 2.33 and 2.56 for α=95, 98 and 99% respectively). The diagonal length d is a Gaussian distribution parameterized by its mean μ_d and its variance σ_d^2. A given set (e.g. 5x2) of diagonal lengths has first to be recorded and estimates of the average diagonal length and variance can be defined from the measurements. Using Eq. (3) the numbers n^* indentations required to reach a 95% confidence level for some common values of the ratio $\sigma_{d/} \mu_d$ are presented in Table 2.

Table 2. Number of indentation required to reach 95% confidence level for some common values of the ratio $\sigma_{d/} \mu_d$

$\sigma_{d/} \mu_d$	0.01	0.02	0.03	0.04	0.05	0.06	0.07
$n^*_{95\%}$	1	3	6	10	16	23	31

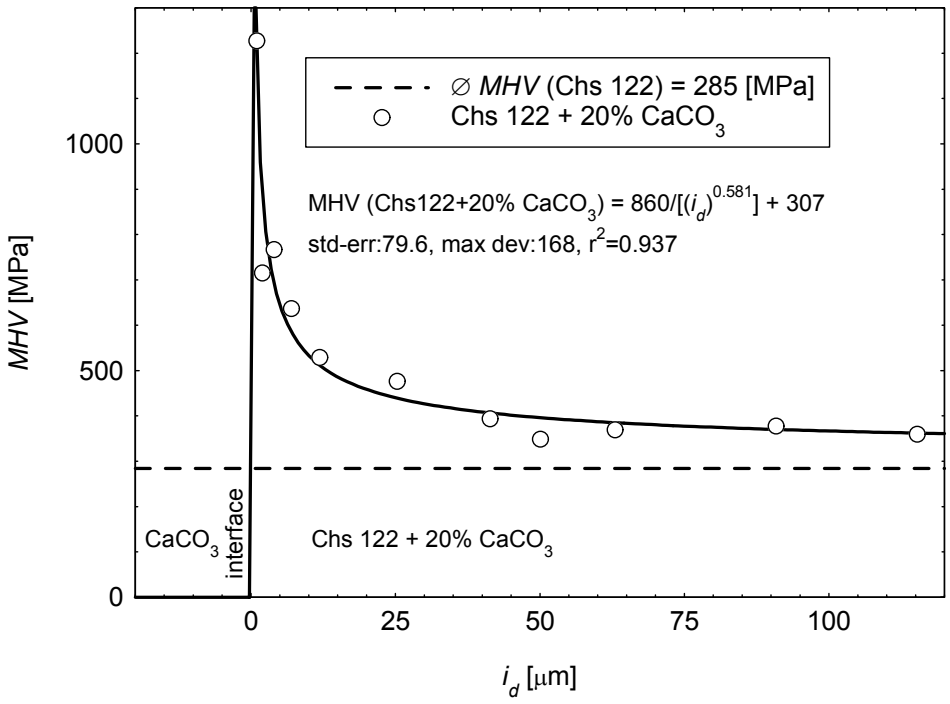

Fig.4 Vickers microhardness in the neighbourhood of a $CaCO_3$ micrograin in the Chs 122 polyester matrix. i_d defines the normal distance between the grain boundary and indent mid points.

Conclusion

Microhardness measurements offer possibilities for the mechanical characterization of specific parts of the common particular polymer composites on a micrometer scale. The information can be used as a bridging parameter between microstructure and macroscopic mechanical properties.

Acknowledgement

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