



# Effect of Styrene–Butadiene Rubber Latex on Mechanical Properties of Cementitious Materials Highlighted by Means of Nanoindentation

R. Wang<sup>\*†</sup>, R. Lackner<sup>‡</sup> and P.-M. Wang<sup>\*</sup>

<sup>\*</sup>Key Laboratory of Advanced Civil Engineering Materials (Tongji University), Ministry of Education, 1239 Siping Road, Shanghai 200092, China

<sup>†</sup>Institute for Mechanics of Materials and Structures, Vienna University of Technology, Karlsplatz 13/202, 1040 Vienna, Austria

<sup>‡</sup>Material-Technology Unit, University of Innsbruck, Technikerstraße 13, 6020 Innsbruck, Austria

**ABSTRACT:** In this paper, micro-mechanical properties of styrene–butadiene rubber (SBR) latex-modified cement pastes identified by means of the nanoindentation (NI) technique are related to macro-mechanical properties of SBR latex-modified mortars obtained from standard test methods, considering an SBR latex/cement ratio varying from 0% to 20%. For this purpose, the average value of the hardness and the so-called indentation modulus of the different material phases of the cement paste, i.e. calcium–silicate–hydrate (CSH), portlandite, anhydrous cement, etc., obtained from NI are compared with the compressive and flexural strengths, on the one hand, and the dynamic elastic modulus of SBR latex-modified mortars, on the other hand. This comparison revealed a linear correlation between the dynamic elastic modulus and the indentation modulus and between the compressive strength, flexural strength and hardness. Thus, the obtained results clearly indicate the finer-scale origin of the macroscopic elastic and strength properties, linking the mechanical properties at the so-called *mortar* scale to the *cement-paste* scale.

**KEY WORDS:** *macro-mechanical properties, micro-mechanical properties, nanoindentation, polymer-modified cementitious materials, styrene–butadiene rubber latex*

## Introduction

In order to improve the performance and durability of concrete, the allowance of polymer was introduced in the 1920s [1] and optimized as regards the type and amount of the employed polymers since then [2]. From the mechanical point of view, polymer latexes bridge microcracks in the latex-modified mortar and concrete under stress by the formation of polymer films, which prevents crack propagation. Moreover, it provides a strong calcium–silicate–hydrate (CSH) aggregate bond, leading to increased tensile strength and fracture toughness [3–5]. On the other hand, the sealing effect due to the polymer films also provides a considerable increase in waterproofness or watertightness, resistance to moisture or air permeation [6, 7], chemical resistance and freeze–thaw durability [8, 9]. Recent research results [10, 11] revealed an increase in both flexural strength and tensile bond strength by the allowance of styrene–butadiene rubber (SBR) latex. The toughness was significantly improved [12].

While the macro-mechanical properties of different polymer latex-modified cementitious materials

are reported in the literature, little is known on the impact of polymer latexes on the micro-mechanical properties of cement paste and its effect on the macroscopic properties. Nanoindentation (NI) is employed in this paper to highlight the micro-mechanical properties of SBR latex-modified cement pastes. Originally, NI has been developed to determine the mechanical properties of homogeneous materials, such as metallic alloys and polymer materials, at the nano- and micrometre range.

More recently, NI was applied to cementitious materials for the determination of elastic properties and the hardness of the major clinker phases of Portland cements ( $C_3S$  and alite,  $C_2S$  and belite,  $C_3A$  and  $C_4AF$ ) [13]. The elastic modulus of these phases was found to range from 125 to 145 GPa. The hardness of the calcium aluminate ( $C_3A$ ) is around 10 GPa, while those of the silicates are lower (8–9 GPa). While the existence of two types of CSH (low-density and high-density CSH) was derived from NI-test data on non-degraded and calcium-leached cement paste in Refs [14, 15], three categories of CSH (high, medium and low stiffness) were introduced in

Ref. [16]. The NI results suggest that the elastic properties of the CSH phase are intrinsic properties, with mean values for the elastic modulus of 38.0 GPa for portlandite (CH) and 21.7 and 29.4 GPa for low-density and high-density CSH, respectively. The properties of the clinker phases and cement paste constituents obtained from NI reported in the literature are summarised in Table 1.

While the backcalculation of finer scale properties of cement-based materials from NI test data was developed very recently and is a topic of ongoing research [14, 17–19], little is known on micro-mechanical properties of cementitious materials containing additives. In Ref. [20], e.g. NI was applied to three types of cement paste, the unmodified cement and two cement pastes containing additives, i.e. polypropylene (PP) fibres and SBR latex, heated to different temperatures.

This paper focuses on the correlation between micro-mechanical properties of SBR latex-modified cement pastes and macro-mechanical properties of SBR latex-modified mortars considering SBR latex/cement ratios (P/C ratio) of 0%, 5%, 8%, 10%, 15% and 20%. For this purpose, NI and standard test methods for the determination of macro-mechanical properties are employed. Based on the experimental results, the influence of P/C ratio on the mechanical properties, especially the micro-mechanical properties of cementitious materials considering a constant water/cement ratio (W/C ratio) is investigated.

**Table 1:** Properties of clinker phases and cement paste constituents obtained from nanoindentation reported in the literature (B = Berkovich, C = Cube corner)

Constituent	<i>E</i> (GPa)	<i>H</i> (GPa)	Indenter	Ref.
C <sub>3</sub> S	135	8.7	B	[13]
C <sub>2</sub> S	130	8	B	[13]
C <sub>3</sub> A	145	10.8	B	[13]
C <sub>4</sub> AF	125	9.5	B	[13]
Alite	125	9.2	B	[13]
Belite	127	8.8	B	[13]
Clinker in paste	45.3	2.75	C	[34]
LD-CSH	23.0	0.88	C	[34]
	21.7		B	[14]
HD-CSH	25.7	0.88	C	[34]
	29.7		B	[14]
High-stiffness CSH	41.5	1.43	C	[16]
Medium-stiffness CSH	31.2	1.22	C	[16]
Low-stiffness CSH	22.9	0.93	C	[16]
CH	29.1	1.00	C	[34]
	38.0		B	[14]
CSH-clinker compound	46.1	2.08	C	[34]
CH-clinker compound	26.6	1.04	C	[34]
CH-CSH compound	26.5	0.91	C	[34]
Edge CSH-CH compound	30.8	1.52	C	[34]

Moreover, the relationship between the micro- and macro-mechanical properties of concrete at different length scales, i.e. the *cement-paste* scale and the *mortar* scale, is discussed.

## Experiments

### Materials

During the preparation of the cement pastes, ordinary Portland cement (OPC) provided by LAFARGE CTEC (Mannersdorf, Austria) was used. The chemical composition of the cement is given in Table 2. Polymer-modified cement pastes were prepared with Styrofan D623 SBR latex (solids content: 50%; pH 9.5; viscosity: approximately 35–150 mPa·s; minimum film-forming temperature (MFFT): 15–21 °C; average particle size: 0.2 μm).

Portland cement type PII 52.5R, complying with the Chinese standard GB175-1999 [21], and standard sand, according to ISO679 1989 [22], were used for preparing the mortar specimens. The chemical composition of the employed cement is listed in Table 2. Styrofan SD622S SBR latex (solids content: 47%; pH 9.5; viscosity: approximate 30 mPa·s; MFFT: 15–21 °C; average particle size: 0.2 μm), which is similar to Styrofan D623 SBR latex as regards composition, the ratio of the monomers (styrene : butadiene) in the content of comonomers, the MFFT and the particle size, was used during the preparation of the polymer-modified mortars. The observed difference in viscosity between the SBR latexes considered is explained by a slight variation in the solids content.

**Table 2:** Chemical composition of OPC and PII 52.5R Portland cement used in this paper

Component	Mass fraction (%)	
	Ordinary Portland cement	PII 52.5R Portland cement
SiO <sub>2</sub>	20.27	21.3
Al <sub>2</sub> O <sub>3</sub>	4.48	5.1
Fe <sub>2</sub> O <sub>3</sub>	2.19	2.9
CaO	61.37	65.1
MgO	1.46	1.1
SO <sub>3</sub>	0.90	1.8
K <sub>2</sub> O	0.76	0.7
TiO <sub>2</sub>	0.22	0.2
Na <sub>2</sub> O	0.25	–
P <sub>2</sub> O <sub>5</sub>	0.27	–
Cr <sub>2</sub> O <sub>3</sub>	0.01	–
MnO	0.05	–
BaO	–	0.3

## Specimen preparation

### Polymer-modified cement pastes

A constant W/C (as opposed to constant flow) was considered in the experimental programme. All cement pastes were prepared with a W/C ratio of 0.42 and P/C ratio of 0%, 5%, 8%, 10%, 15% and 20% respectively. The cement pastes were cast in cylindrical moulds of diameter 20–30 mm and length 300 mm, and then sealed and cured at 20 °C. After curing, the cylindrical samples were cut into slices of about 10-mm thickness. The surfaces of the so-obtained slices were ground and polished with silicon carbide papers and diamond particles. This was carried out in six stages of decreasing fineness with the last one being in the range of 0.25  $\mu\text{m}$ . After polishing, the specimens were placed in an ultrasonic bath to remove the dust and diamond particles left on the surface or in the porous structure. The curing age at the time of NI testing was 70 days. Before NI testing, the roughness (average of heights) of the samples was checked by the Hysitron Triboindenter, (Hysitron Incorporated, Minneapolis, MN, USA), which is capable of scanning probe microscopy (SPM) imaging. For all samples, the roughness was found to be in the range of 15–20 nm.

### Polymer-modified mortars

The mortar specimens were prepared with a P/C ratio from 0% to 20%, a constant W/C ratio of 0.40 and an aggregate/cement ratio (A/C ratio) of 3. First, the SBR latex was added to the water. Then, the specimens with the dimension of 40 mm  $\times$  40 mm  $\times$  160 mm were prepared according to ISO679 [22]. The specimens were demoulded after 1 day and then cured for 2, 6 or 27 days immersed in 20 °C water.

## Test methods

### Nanoindentation testing program

Nanoindentation tests were carried out using a Hysitron Triboindenter, employing a Berkovic tip. Each indent was characterised by a loading, dwelling and unloading phase, lasting 7, 10 and 7 s, respectively. The maximum load, which remains constant during the dwelling phase, was set equal to 700  $\mu\text{N}$ , giving a loading rate of 100  $\mu\text{N}\cdot\text{s}^{-1}$ . In order to cover the heterogeneity of the cement pastes, the so-called grid-indentation technique [14] was employed. Each grid is characterised by 15  $\times$  15 indents, with spacing between adjacent indents of 10  $\mu\text{m}$ . The distance between adjacent indentation points was chosen in a way to avoid interaction

between the indents. For the determination of the indentation modulus and the hardness, the Oliver and Pharr method [23] was used. Hereby, the hardness  $H$  is determined by

$$H = \frac{P_{\max}}{A_c}, \quad (1)$$

where  $P_{\max}$  is the maximum indentation force and  $A_c$  represents the projected contact area at that load.

For the determination of the indentation modulus  $M$ , the initial slope of the unloading curve,  $S$ , is employed, using the so-called BASH equation [24], with

$$S = \frac{2}{\sqrt{\pi}} M \sqrt{A_c}. \quad (2)$$

With the value of  $M$  at hand, Young's modulus  $E$  is determined from

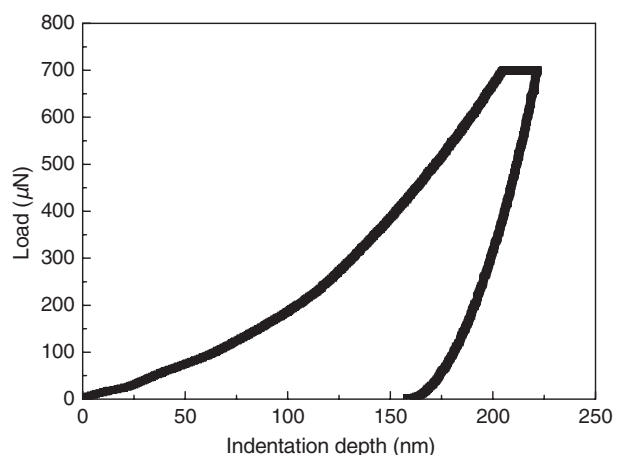
$$\frac{1}{M} = \frac{1 - \nu^2}{E} + \frac{1 - \nu_i^2}{E_i}, \quad (3)$$

where  $\nu$  is Poisson's ratio of the tested material;  $E_i$  and  $\nu_i$  are Young's modulus and Poisson's ratio of the non-rigid indenter.

A typical load versus indentation-depth curve obtained from the performed NI testing of a cement paste with a P/C ratio of 10% is shown in Figure 1.

### Macro-mechanical properties

The compressive strength and flexural strength were determined according to ISO 679 [22]. The dynamic elastic modulus was determined according to GBJ 82-85 [25].



**Figure 1:** Typical load versus indentation-depth curve obtained from the performed nanoindentation testing of a cement paste with a P/C ratio of 10%

## Presentation of Results

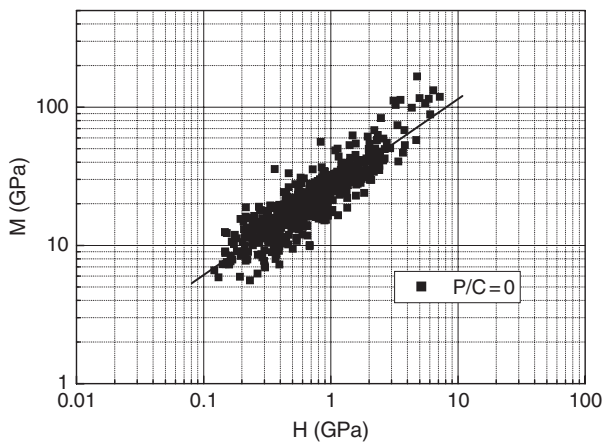
Micro-mechanical properties of SBR latex-modified cement pastes

Combining Equations (1) and (2), the indentation modulus  $M$  should scale with the hardness  $H$  according to:

$$M \propto H^\alpha \text{ with } \alpha = 0.5. \quad (4)$$

Relation (4) holds strictly only for indentation in a homogeneous half-space. Any deviation from this relation can be attributed to errors in the determination of  $M$  and  $H$  that could be caused by the surface conditions (surface roughness, material imperfections, heterogeneities of similar length scale as the depth of indentation, etc.), leading to an improper estimation of the contact area.

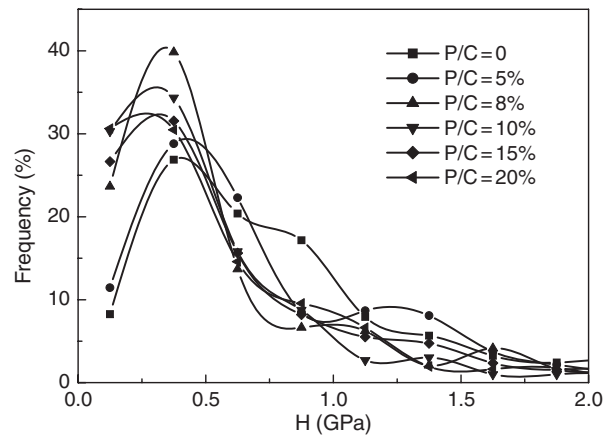
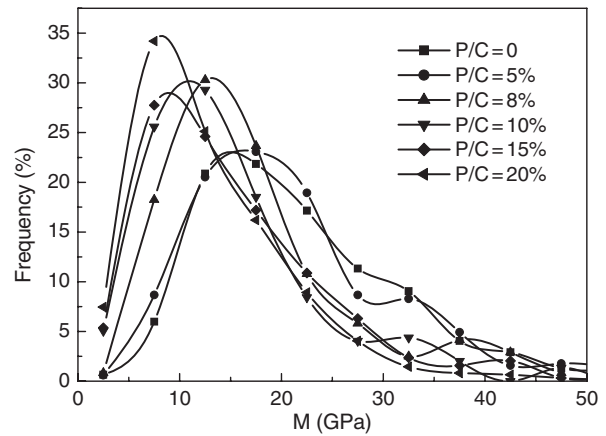
Figure 2 shows the indentation modulus with respect to the hardness obtained from NI testing of a cement paste with no SBR latex, from which  $\alpha$  is obtained as the slope of the approximation line. Table 3 contains the values for  $\alpha$  for all investigated types of cement paste. Similar to the microindentation results reported in Ref. [26] the values of  $\alpha$  are higher than the expected value of 0.5. However, as the values of



**Figure 2:** Indentation modulus ( $M$ ) versus hardness ( $H$ ) obtained from nanoindentation testing of a cement paste with no styrene-butadiene rubber latex

**Table 3:**  $M$ - $H$  scaling relation parameter  $\alpha$  for styrene-butadiene rubber latex-modified cement pastes

P/C (%)	$\alpha$
0	0.66
5	0.59
8	0.60
10	0.65
15	0.65
20	0.61

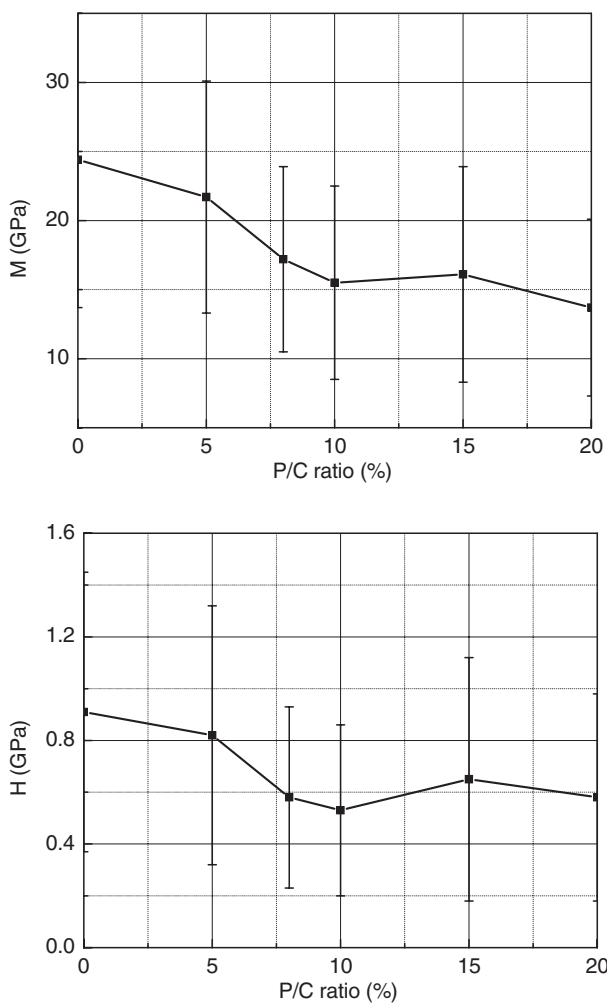


**Figure 3:** Frequency graph of indentation modulus ( $M$ ) and hardness ( $H$ ) obtained from nanoindentation testing of styrene-butadiene rubber latex-modified cement pastes

$\alpha$  remain relatively constant for the cement pastes characterised by a different P/C ratio, the addition of SBR latex affects only the mechanical properties, with no significant changes in the surface conditions, with the latter explaining the deviation of  $\alpha$  from 0.5.

The indentation modulus and hardness frequency distributions for all investigated cement pastes are given in Figure 3. In order to relate the frequency plots, representing the micromechanical response of the material phases of the cement pastes, to material properties (Young's modulus, compressive and flexural strength) of the investigated types of the mortar, the average value of the experimentally obtained frequency plots for the indentation modulus and hardness was determined<sup>1</sup> (see Figure 4). Hereby, the average value of the indentation modulus decreases by 10% with 5% SBR latex addition, and then

<sup>1</sup>It will be shown in the following section (Discussion) that the determination of elastic properties of the mortar on the basis of the average value of the indentation modulus gives very good agreement between the predicted and measured elastic properties of mortars. Thus, for the present study, a distinction of different material phases at the cement paste scale, as reported in Refs [14–16], is not performed.



**Figure 4:** Dependence of average value of indentation modulus ( $M$ ) and hardness ( $H$ ) on the P/C ratio for styrene-butadiene rubber latex-modified cement pastes obtained from nanoindentation test data

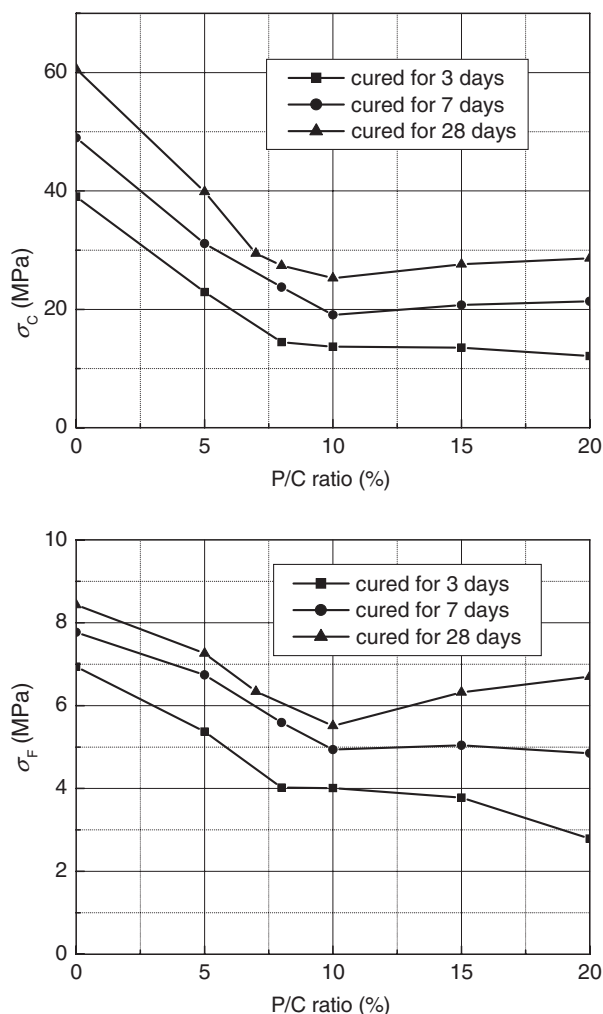
decreases sharply to about 64% of that of the control cement paste when the P/C ratio reaches 10%. When the P/C ratio increases from 10% to 15%, the indentation modulus increases slightly, and then decreases gradually with the P/C ratio increasing from 15% to 20%. The change in the indentation modulus with the P/C ratio between 10% and 20% is not significant.

The change in the average values for the hardness of SBR latex-modified cement pastes with an increasing P/C ratio is slightly more pronounced than the change of the corresponding indentation modulus.

### Macro-mechanical properties of polymer-modified mortars

#### Compressive strength and flexural strength

The compressive strength and the flexural strength of SBR latex-modified mortars with a different P/C ratio and curing ages are illustrated in Figure 5. The com-



**Figure 5:** Compressive strength ( $\sigma_c$ ) and flexural strength ( $\sigma_F$ ) of polymer-modified mortars as a function of the P/C ratio

pressive strength decreases with an increase in P/C ratio up to 10%, and then increases slightly for those cured for 7 and 28 days, and declines slightly for that cured for 3 days. The longer the curing ages, the higher is the compressive strength.

The flexural strength decreases with an increasing P/C ratio until it reaches 10%. The tendency of the flexural strength is similar to that of the compressive strength. The decrease until a P/C ratio of 10%, however, is smaller. For a P/C ratio above 10%, the flexural strength decreases for 3 days, hardly changes for 7 days, and increases for 28 days curing time.

#### Toughness

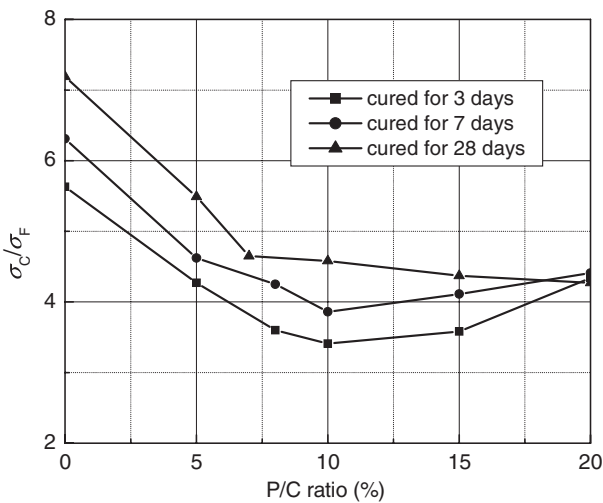
The ratio of compressive strength to flexural strength of the mortar is an important factor to judge its toughness. The smaller the ratio, the better is the toughness. Figure 6 shows the ratio of the compressive strength to flexural strength of SBR latex-modified mortars for a different P/C ratio. The ratio drops sharply with the P/C ratio increasing up to 10%. For higher P/C ratios, the change in the ratio of



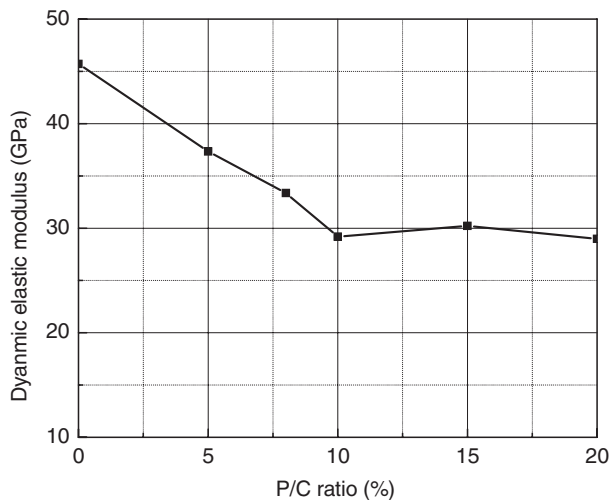
compressive strength to flexural strength with P/C ratio is less pronounced. When the P/C ratio is above 10%, the ratio of the compressive strength to flexural strength rises slightly for the polymer-modified mortars cured for 3 and 7 days, but declines for the mortar cured for 28 days. The above results suggest that the toughness of the polymer-modified mortars improves with an increasing P/C ratio. The higher the P/C ratio, the better is the toughness for P/C ratio smaller than 10%. When the P/C ratio is higher than 10%, the beneficial effect of the increase in the P/C ratio on the toughness is not significant.

*Dynamic elastic modulus*

The dependence of the dynamic elastic modulus on the P/C ratio of SBR latex-modified mortars cured for 28 days is shown in Figure 7. The dynamic elastic modulus decreases with an increase in P/C ratio up to 10%. For a P/C ratio higher than 10%, on the other



**Figure 6:** Ratio of compressive strength to flexural strength ( $\sigma_c/\sigma_F$ ) of styrene-butadiene rubber latex-modified mortars as a function of the P/C ratio



**Figure 7:** Dynamic elastic modulus of styrene-butadiene rubber latex-modified mortars cured for 28 days as a function of the P/C ratio

hand, it has no significant effect on the dynamic elastic modulus.

**Discussion**

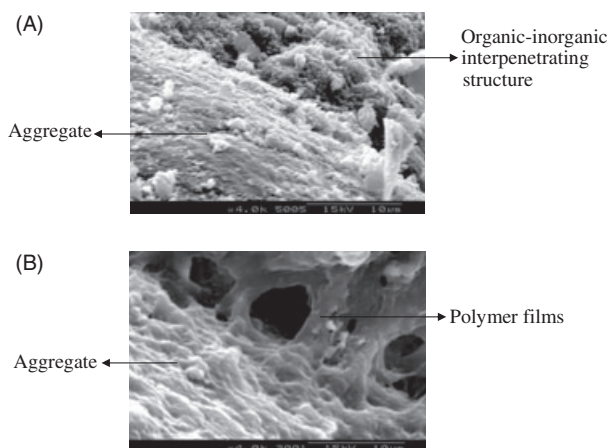
Discussion on mechanical properties

On the one hand, SBR film is very tough as a rubber for comprising both the flexible butadiene chains and the rigid styrene chains, and thus the addition of SBR latex improves the toughness of the rigid mortar. On the other hand, SBR latex has lower strength compared with the cement mortar and results in an increased porosity of cementitious materials [12, 27] and, thus, decreased bulk density (see Table 4, containing the bulk density of the SBR latex-modified mortars). The relative low modulus of the polymer phase and the increased porosity explain the observed decrease in the indentation modulus of SBR latex-modified cement pastes and the dynamic elastic modulus of SBR latex-modified mortars with an increasing P/C ratio.

The properties of polymer-modified cementitious materials are influenced by its microstructural compositions, composed of polymer films, cement hydrates, combined structures between organic and inorganic phases, etc. The combined structures develop when the coherent polymer films form at a P/C ratio of  $\approx 8\%$  (Figure 8). The coherent polymer films reduce interfacial weakness, prevent extending of microcracks and drop the rigidity of mortars [28]. As a result, the polymer takes good effect in improving the toughness. A further increase in the polymer content, after the interpenetrating structure was formed, results in an increase in the thickness of the already formed polymer films. Even though the increase in the Aft content and the decrease in the  $\text{Ca(OH)}_2$  content for a P/C ratio higher than 10% [29] would result in an increase in the strength of the cement paste, the strength may still decrease as a result of structural changes in the material, such as increased porosity [30] and thickening polymer films. These two counteracting impacts on the material properties resulted in an overall marginal effect on

**Table 4:** Bulk density of styrene-butadiene rubber latex-modified mortars ( $\text{g cm}^{-3}$ )

	P/C (%)					
	0	5	8	10	15	20
Cured for 3 days	2.36	2.10	1.97	1.94	2.09	2.21
Cured for 7 days	2.34	2.11	1.97	1.96	2.14	2.24
Cured for 28 days	2.34	2.12	1.95	2.00	2.05	2.15



**Figure 8:** Microstructure of styrene-butadiene rubber latex-modified mortar cured for 28 days with a P/C ratio of 8%: (A) untreated sample and (B) sample treated with 1% HCl for 5 min before observation [28]

the mechanical properties for a further increase in the P/C ratio above 10%.

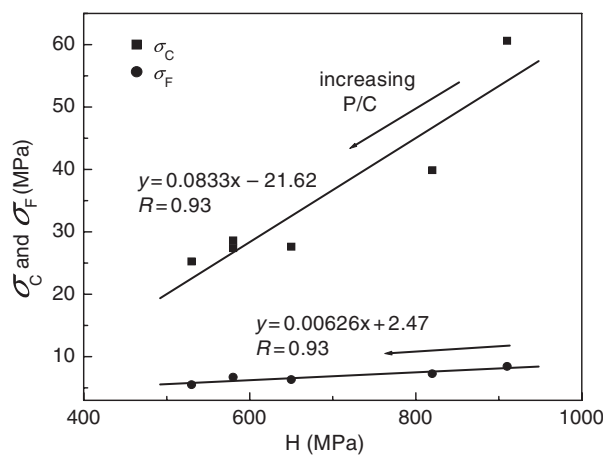
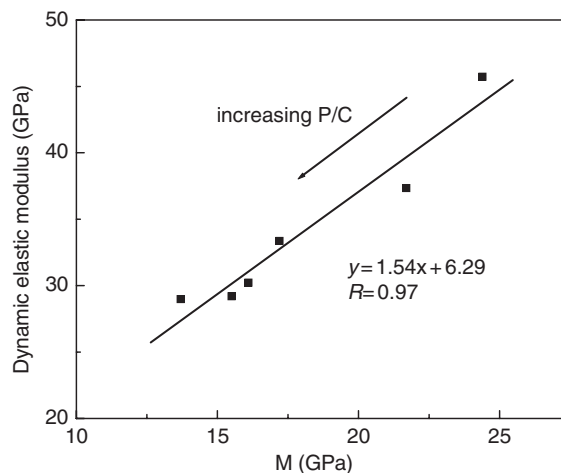
### Discussion on the correlation between micro- and macro-mechanical properties

Figure 9 shows the macro-mechanical properties (dynamic elastic modulus, compressive strength and flexural strength) of SBR latex-modified mortars plotted with respect to the micro-mechanical properties (indentation modulus and hardness) of SBR latex-modified cement pastes. The relationship between the dynamic elastic modulus and the indentation modulus is approximated using a linear function, giving a relative coefficient of 0.97. The observed correlation between the elastic modulus and the indentation modulus may be explained exclusively by the presence of the aggregates. This assumption is assessed by estimating Young’s modulus of the mortars by means of a continuum micromechanics approach considering a two-phase (aggregate and cement paste) composite (Mori–Tanaka scheme with spherical inclusions, see, e.g. Refs [31–33]):

$$\mu_{\text{eff}} = \frac{(1 - f_A)\mu_M + f_A\mu_A[1 + \beta(\mu_A/\mu_M - 1)]^{-1}}{(1 - f_A) + f_A[1 + \beta(\mu_A/\mu_M - 1)]^{-1}} \quad (5)$$

$$k_{\text{eff}} = \frac{(1 - f_A)k_M + f_Ak_A[1 + \alpha(k_A/k_M - 1)]^{-1}}{(1 - f_A) + f_A[1 + \alpha(k_A/k_M - 1)]^{-1}}, \quad (6)$$

with  $\alpha = 3k_M/(3k_M + 4\mu_M)$  and  $\beta = [6(k_M + 2\mu_M)]/[5(3k_M + 4\mu_M)]$ . In Equations (5) and (6), indices M and A refer to the cement paste matrix and the aggregates respectively. The volume fraction of the aggregates,  $f_A$ , is determined from the mix design (W/C = 0.4, A/C = 3) as



**Figure 9:** Correlation between macro- and micro-mechanical properties of styrene-butadiene rubber latex-modified cementitious materials

$$f_A = \frac{\frac{A/C}{\rho_A}}{\frac{1}{\rho_C} + \frac{A/C}{\rho_A} + \frac{W/C}{\rho_W} + \frac{P/C}{\rho_P}}, \quad (7)$$

where  $\rho_A = 2.65 \text{ g cm}^{-3}$ ,  $\rho_C = 3.15 \text{ g cm}^{-3}$ ,  $\rho_W = 1 \text{ g cm}^{-3}$  and  $\rho_P = 1.02 \text{ g cm}^{-3}$  refer to the density of the aggregate particles, cement, water and SBR latex respectively. The so-obtained ratio between dynamic elastic modulus  $E$  of the investigated mortar and the indentation modulus  $M$  is given in Table 5, ranging from  $E/M = 1.72$  for the unmodified sample to  $E/M = 2.04$  for a P/C ratio of 20%. This trend is well captured by the linear function shown in Figure 9, with  $E/M \approx 1.75$  in the low P/C ratio regime and  $E/M \approx 2.0$  in the high P/C ratio regime. Thus, SBR latex modification mainly affects the elastic properties of the cement paste identified from NI, with the increase from the indentation modulus  $M$  to the dynamic elastic modulus  $E$  of the mortar explained exclusively by the addition of aggregates. A similar impact of aggregates on the elastic properties of the mortar was reported in Refs [31, 32].

**Table 5:** Micromechanics-based determination of effective Young's modulus for styrene-butadiene rubber latex-modified concrete (employed aggregate properties:  $E = 65$  GPa,  $\nu = 0.23$ ; employed cement paste properties:  $\nu = 0.24$ ,  $E = (1-\nu^2)M$ ;  $\mu = E/(2 + 2\nu)$ ,  $k = E/(3-6\nu)$ ,  $E = 9\mu k/(\mu + 3k)$ )

P/C (%)	Cement paste				$f_A$ (-)	Concrete			
	$M$ (GPa)	$E$ (GPa)	$\mu$ (GPa)	$k$ (GPa)		$\mu_{\text{eff}}$ (GPa)	$k_{\text{eff}}$ (GPa)	$E_{\text{eff}}$ (GPa)	$E_{\text{eff}}/M$ (-)
0	24.4	23.0	9.3	14.7	0.61	17.0	26.1	42.0	1.72
5	21.8	20.5	8.3	13.2	0.60	15.8	24.3	39.0	1.79
8	17.3	16.3	6.6	10.5	0.59	13.8	21.1	34.0	1.96
10	15.5	14.6	5.9	9.4	0.58	12.8	19.6	31.6	2.04
15	16.1	15.2	6.1	9.7	0.57	12.9	19.7	31.7	1.97
20	13.8	13.0	5.2	8.3	0.55	11.5	17.5	28.2	2.04

Within the investigated range of strength properties, the compressive strength and the flexural strength correlate linearly with the hardness. The strength of the investigated mortars is much lower than the hardness of the respective cement paste, which is explained by the different stress situations encountered during macroscopic testing and NI: whereas the specimen is loaded uniaxially during the testing of the mortar, high hydrostatic stress states develop under the indenter tip during NI.

The decrease in the compressive strength and hardness with increasing polymer content is explained by the constant W/C ratio considered the experimental programme, giving a higher porosity as the polymer content increases [30]. Obviously, this change in porosity has a higher impact in case of uniaxial loading situations as encountered during testing of mortar specimens, resulting in a faster drop of the compressive strength for increasing polymer content when compared with the change in hardness obtained from NI.

Similar to the compressive strength, the constant W/C ratio considered in the experimental programme resulted in a decrease in the flexural strength with increasing polymer content. However, the slower decrease in the flexural strength when compared with the decrease in the hardness with increasing polymer content indicates the improvement in the interface properties by the addition of SBR latex. Obviously, these interface properties have a significant effect on the tensile-loading performance of mortars.

## Conclusions

The mechanical properties of SBR latex-modified cementitious materials at different length scales, i.e. mortar and cement paste, were investigated, showing a good correlation between the dynamic elastic modulus of the mortars with the indentation modulus of the

cement pastes, and the strength properties of the mortars with the hardness of the cement pastes. Based on the test results obtained from NI and standard methods for the determination of macro-mechanical properties, the following conclusion can be drawn:

- The toughness of SBR latex-modified mortars is improved markedly at SBR latex/cement ratio (P/C ratio) of 10%. When the P/C ratio is higher than 10%, the beneficial additional effect of the SBR latex on both the micro- and macro-mechanical properties is not significant.
- The dynamical elastic modulus of SBR latex-modified mortars was directly related to the indentation modulus obtained from NI testing of the respective cement paste. The employed correlation model was formulated in the framework of continuum micromechanics, considering aggregate particles as spherical inclusions.
- The strength of SBR latex-modified mortars is much lower than the hardness of SBR latex-modified cement pastes, explained by the different stress situations during macroscopic testing and NI testing. The encountered linear relations between the hardness and macroscopic strength properties highlight the finer scale origin of the performance of SBR latex-modified mortars. In addition to that, the increased porosity associated with the addition of SBR latex had a large impact on the compressive strength and a rather low impact on the flexural strength, indicating the beneficial effect of SBR latex on the interface properties, with the latter mainly controlling the flexural strength of the considered types of mortar.
- For the P/C ratio increasing up to 10%, the beneficial effect of the P/C ratio was significant, showing a continuous reduction in the ratio between the compressive and flexural strengths. Accordingly, a P/C ratio of 8–10% was found as the optimal SBR latex content in practical applications.



## ACKNOWLEDGEMENTS

We thank LAFARGE CTEC Mannersdorf (Mannersdorf, Austria) and BASF (BASF Aktiengesellschaft, Germany) for providing the cement and Styrofan D623 SBR latex for this work. We are grateful for helpful support during NI testing by Andreas Jäger (Vienna University of Technology, Austria). The research is supported by the National Key Project of Scientific and Technical Supporting Programs Funded by Ministry of Science & Technology of China (2006BAJ05B03) and Program for Young Excellent Talents in Tongji University (2006KJ050). Financial support by EURASIA-PACIFIC UNINET is also gratefully acknowledged.

## REFERENCES

- Cresson, L. (1923) Improved manufacture of rubber road-acing, rubber-flooring, rubber-tiling or other rubber-lining. *British Patent* 191, 474.
- Ohama, Y. (1997) Recent progress in concrete-polymer composites. *Adv. Cement Based Mater.* 5(1), 31–40.
- Xia, Z. and Luo, L. (2001) The impact of curing conditions on the mechanical properties of modified mortars and cement. *J. South China Univ. Technol. (Nat. Sci. Edn)* 29(6), 83–86 (in Chinese).
- Hu, S. and Luo, L. (2002) Study on mechanical properties of polymer-modified cement mortars. *Technol. Highw. Transp.* (2), 30–34 (in Chinese).
- Schulze, J. (1999) Influence of water-cement ratio and cement content on the properties of polymer-modified mortars. *Cem. Concr. Res.* 29, 909–915.
- Zhong, S. and Chen, Z. (2002) Properties of latex blends and its modified cement mortars. *Cem. Concr. Res.* 32(10), 1515–1524.
- Zhong, S., Shi, M. and Chen, Zh. (2002) The AC response of polymer-coated mortar specimens. *Cem. Concr. Res.* 32(6), 983–987.
- Zhong, S. and Yuan, H. (2003) *Application of Polymer in Concrete*. Chemistry and Industry Publishing Company, Beijing (in Chinese).
- Mirza, J., Mirza, M. S. and Lapointe, R. (2002) Laboratory and field performance of polymer-modified cement-based repair mortars in cold climates. *Construct. Build. Mater.* 16(6), 365–374.
- Wang, P. M., Xu, Q. and Stark, J. (2001) Mechanical properties of styrene-butadiene emulsion modified cement mortar used for repair of bridge surface. *J. Build. Mater.* 4(1), 1–6 (in Chinese).
- Li, F. (2003) Study on properties of SBR-modified cement mortars at different water-cement mass ratio, MSc thesis. Tongji University (in Chinese).
- Wang, R., Wang, P. M. and Li, X. G. (2005) Physical and mechanical properties of styrene-butadiene rubber emulsion modified cement mortars. *Cem. Concr. Res.* 35, 900–906.
- Velez, K., Maximilien, S., Damidot, D., Fantozzi, G. and Sorrentino, F. (2001) Determination by nanoindentation of elastic modulus and hardness of pure constituents of Portland cement clinker. *Cem. Concr. Res.* 31, 555–561.
- Constantinides, G. and Ulm, F.-J. (2004) The effect of two types of C–S–H on the elasticity of cement-based materials – results from nanoindentation and micromechanical modeling. *Cem. Concr. Res.* 34, 67–80.
- Jennings, H. M., Thomas, J. J., Gevrenov, J. S., Constantinides, G. and Ulm, F.-J. (2007) A multi-technique investigation of the nanoporosity of cement paste. *Cem. Concr. Res.* 37, 329–336.
- Mondal, P., Shah, S. P. and Marks, L. (2007) A reliable technique to determine the local mechanical properties at the nanoscale for cementitious materials. *Cement Concr.* 37, 1440–1444.
- Pichler, Ch. and Lackner, R. (2008) Identification of logarithmic-type creep of calcium-silicate-hydrates by means of nanoindentation. *Strain*. In print.
- Ganneau, F. P., Constantinides, G. and Ulm, F.-J. (2006) Dual-indentation technique for the assessment of strength properties of cohesive-frictional materials. *Int. J. Solids Struct.*, 43, 1727–1745.
- Pichler, Ch., Lackner, R. and Ulm, F.-J. (2008) Scaling relations for viscoelastic-cohesive conical indentation. *Int. J. Mater. Res.* 99, 836–846.
- Wang, R. and Lackner, R. (2006) Nanoindentation study on cement pastes containing additives subjected to high temperature. *Proceedings of the EURO-C 2006 Conference on Computational Modeling of Concrete Structures* (G. Meschke, R. de Borst, H. A. Mang and N. Bicanic, Eds). Taylor & Francis Group, London. 27–30 March, Mayrhofen, Austria, pp. 249–261.
- GB175-1999, *Portland cement and ordinary Portland cement*, Chinese standard, SBTS, 1999.
- ISO679 1989, *Methods of Testing Cements – Determination of Strength*, ISO, 1989.
- Oliver, W. C. and Pharr, G. M. (1992) An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments. *J. Mater. Sci.* 7, 1564–1583.
- Borodich, F. M. and Keer, L. M. (2004) Contact problems and depthsensing nanoindentation for frictionless and frictional boundary conditions. *Int. J. Solids Struct.* 41, 2479–2499.
- GBJ 82-85, *Testing methods for long-term and long-lasting performance of ordinary concrete*, Chinese standard, SBTS, 1985.
- DeJong, M. J. and Ulm, F.-J. (2005) *Sources of high temperature degradation of cement-based materials: nanoindentation and microporoelastic analysis*, CEE Report R05-01, Massachusetts Institute of Technology, Cambridge, MA.
- Silva, D. A., John, V. M., Ribeiro, J. L. D. and Roman, H. R. (2001) Pore size distribution of hydrated cement pastes modified with polymers. *Cem. Concr. Res.* 31, 1177–1184.
- Wang, R., Wang, P. M. and Li, X. G. (2004) Microstructural aspects of styrene-butadiene rubber (SBR) latex-modified mortars. *Proceedings of the Research and Application of Green Building Materials*, Shanghai, China: 302–308 (in Chinese).
- Wang, R., Li, X. G. and Wang, P. M. (2006) Influence of polymer on cement hydration in SBR-modified cement pastes. *Cem. Concr. Res.* 36, 1744–1751.

30. Wang, R. and Wang, P. M. (2006) Effect of curing methods and composition on physical properties of SBR latex-modified mortars. *Proceedings of the Fifth Asian Symposium on Polymers in Concrete* (N. Lakshmanan, C. V. Vaidyanathan, Y. Ohama and M. Neelamegam, Eds). Allied Publishers Pvt. Ltd., Chennai, India: 139–145.
31. Bernard, O., Ulm, F.-J. and Lemarchand, E. (2003) A multiscale micromechanics-hydration model for the early-age elastic properties of cement-based materials. *Cem. Concr. Res.* **33**, 1293–1309.
32. Pichler, Ch., Lackner, R. and Mang, H. A. (2006) A multiscale micromechanics model for the autogenous-shrinkage deformation of early-age cement-based materials. *Eng. Fracture Mech.* **34**, 1–25.
33. Pichler, Ch., Lackner, R. and Mang, H. A. (2008) Multiscale model for creep of shotcrete – from logarithmic-type viscous behavior of CSH at the  $\mu\text{m}$ -scale to macroscopic tunnel analysis. *J. Adv. Concr. Technol.* **6**, 91–110.
34. Hughes, J. J. and Trtik, P. (2004) Micro-mechanical properties of cement paste measured by depth-sensing nanoindentation – a preliminary correlation of physical properties with phase type. *Mater. Charact.* **53**, 223–231.