A contribution from ACI Committee 236, Material Science of Concrete

Uncoupling Modulus of Elasticity and Strength

Effect of small addition of carbon nanotubes on concrete properties

by Surendra P. Shah and Maria S. Konsta-Gdoutos

Our industry has made considerable progress in increasing the compressive strength of concrete. At the time of the first workshop on high-strength concrete, held in Chicago, IL, in 1979,[1] the lower limit for high-strength concrete was defined as 6000 psi (42 MPa). Less than 30 years later, the maximum concrete cylinder strength f_c' specified for Chicago's Trump Tower was 16,000 psi (110 MPa).[2]

While compressive strength is important for minimizing the sizes of compression elements, designers of tall buildings may also specify a high modulus of elasticity (MOE) to limit lateral deformations and ensure occupant comfort. For example, the high compressive strength specified for some elements in the Trump Tower was needed to ensure that the MOE was about 7,000,000 psi (48 GPa)—far greater than the 4,000,000 psi (28 GPa) value that is now routinely possible. In these cases, high strength was not the objective—it was the means to the end. This article summarizes recent research on an alternative way to obtain a high MOE concrete without necessarily increasing the compressive strength.

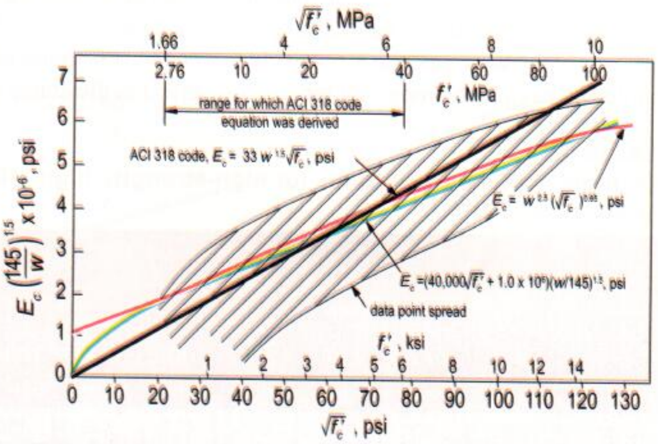

Fig. 1: Secant modulus of elasticity versus concrete strength, based on Reference 3

How Can We Produce a High MOE?

Increasing the compressive strength

While MOE can be raised by increasing the compressive strength, the relationship is weak—many of the empirical relationships used to estimate MOE are functions of the square root of the compressive strength (refer to Fig. 1 and 2). By optimizing mixture proportions and constituents, however, it is possible to make high-strength concrete with an MOE approaching 55 GPa (8,000,000 psi). The data points in Fig. 2, for example, were obtained from tests of high-modulus concrete designed specifically for tall buildings.[4] The mixtures with the highest strength and MOE values comprised ordinary portland cement (OPC), pulverized fly ash (PFA), condensed silica fume (CSF), crushed volcanic rock coarse aggregate in 20 and 10 mm (3/4 and 3/8 in.) maximum size fractions, and river sand (refer to Table 1 for example mixtures). These mixtures, labeled A, B, and C in Table 1 and Fig. 2, demonstrate the importance of water-cementitious materials ratio (w/cm) on both strength and MOE.

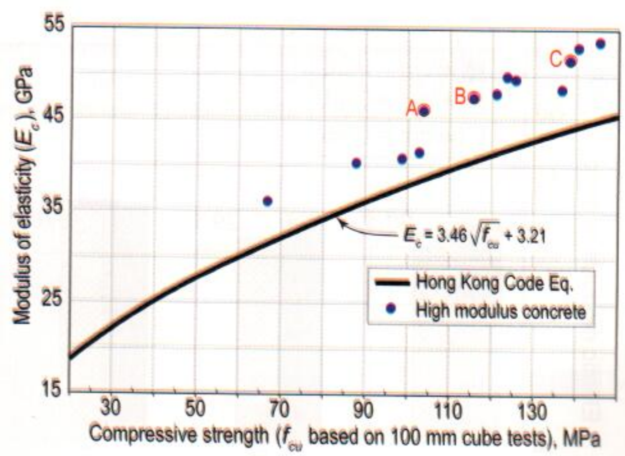

Fig. 2: Compressive strength versus modulus of elasticity (based on References 4 and 5). Mixture proportions for A, B, and C are listed in Table 1 (Note: 1 GPa = 145,000 psi; 100 mm = 4 in.; 1 MPa = 145 psi)

The highest MOE shown in Fig. 2, 53.5 GPa (7,760,000 psi), was obtained for a concrete mixture with a 28-day compressive strength of 146 MPa (21,000 psi). The mixture was produced using the same materials and proportions as Mixture C (Table 1), but the grading of the river sand was modified to provide a well-graded fine aggregate. While it's generally not practical to produce well-graded sand, it is practical to use silica fume and high-range water-reducing admixtures (HRWRAs [surfactants, commonly called superplasticizers]). The former increases MOE by increasing the density of the paste-aggregate interface, and the latter allows very low *w/cm* values and further increases the MOE of concrete by increasing the MOE of the paste. Unfortunately, such concrete is relatively brittle and has a high propensity for autogenous shrinkage cracking, so it's important to investigate alternatives.

The data points for all mixtures developed during the cited research are well above the curve shown in Fig. 2, which represents the design equation in the Hong Kong Code of Practice for Structural Use of Concrete.[5] While the equation is valid only for normalweight concrete with cube strengths between 20 and 100 MPa (2900 and 14,500 psi), it also provides a reasonable lower limit for higher-strength concretes. Later in this article, we will use this curve and set of data points for comparison with strength and MOE values for an alternative mixture.

Using stiffer aggregates

Another way to boost the MOE of concrete is to use stiffer aggregates. This effect is illustrated in Fig. 3.[6] In this case, the researchers tested concrete produced with four different types of aggregates (crushed quartzite, crushed granite, limestone, and marble). While the high modulus of the crushed quartzite (110 GPa [16,000,000 psi]) did allow the production of concrete with an MOE approaching 50 GPa (7,250,000 psi), this also required the use of a very low *w/cm* of 0.26. Again, such a mixture can be expected to exhibit brittle behavior and high autogenous shrinkage.

Table 1:
Example mixture proportions for high-strength, high-MOE mixtures (based on Reference 4)

Mixture	OPC, kg/m³	PFA, kg/m³	CSF, kg/m³	Coarse aggregate, kg/m³ 20 mm	Coarse aggregate, kg/m³ 10 mm	River sand, kg/m³	Water, kg/m³	HRWRA, L/m³	*w/cm**
A	405	90	50	525	425	735	150	12	0.28
B	425	90	50	535	435	745	130	18	0.23
C	435	85	55	545	445	755	115	20	0.20

*Excluding water in HRWRA

(Notes: 1 kg/m³ = 1.7 lb/yd³; 1 mm = 0.04 in.; 1 L/m³ = 0.2 gal./yd³)

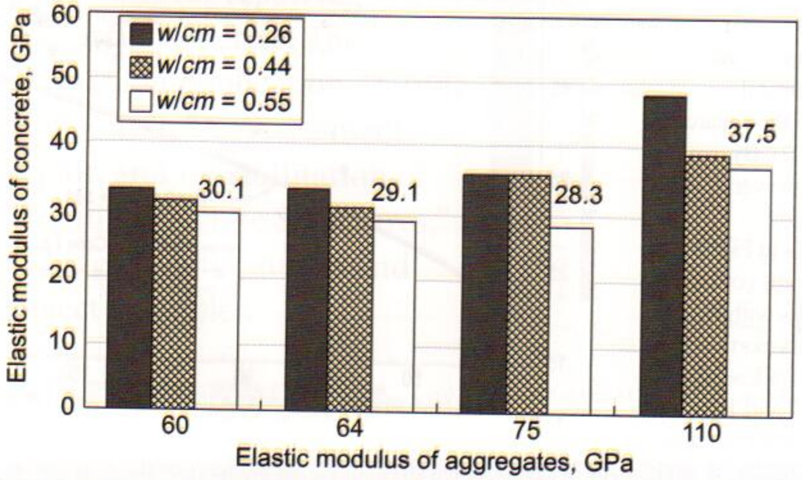

Fig. 3: Relationship between elastic modulus of concrete and elastic modulus of aggregates, for concrete mixtures with *w/cm* values of 0.26, 0.44, and 0.55[6] (Note: 1 GPa = 145,000 psi)

Reinforcing with carbon nanotubes

There has been considerable recent interest in applying nanotechnology to concrete. Researchers have studied incorporating nanoparticles such as nanosilica and nanolimestone as well as nanofibers such as carbon nanotube (CNT), graphene, and graphene oxide.[7] CNTs show great promise for enhancing the MOE of concrete, as they possess MOE values on the order of 1 TPa (1000 GPa [145,000,000 psi]), and they have very large surface areas.[8] Many researchers have studied cement paste reinforced with CNTs[9]; however, deterrents to commercial application have included the high cost of CNTs, problems with workability, and the practical difficulty of achieving uniform dispersion throughout the cementitious matrix. We believe that we have solved these problems by devising a method to disperse CNTs through the application of HRWRAs and ultrasonication (refer to Fig. 4). When well-dispersed, a very small amount of CNTs can substantially improve mechanical properties of concrete and reduce autogenous shrinkage.[10-12] In addition, because CNTs are highly conductive, they also offer the opportunity to create mixtures with self-sensing ability, expressed as piezoresistivity.[13]

Investigations using Dispersed CNTs

The results of flexural strength tests of control specimens (*w/cm* of 0.485 in pastes and mortars) and specimens made with 0.1% CNTs by weight of cement are shown in Fig. 5. Flexural strength was measured according to ASTM C348,

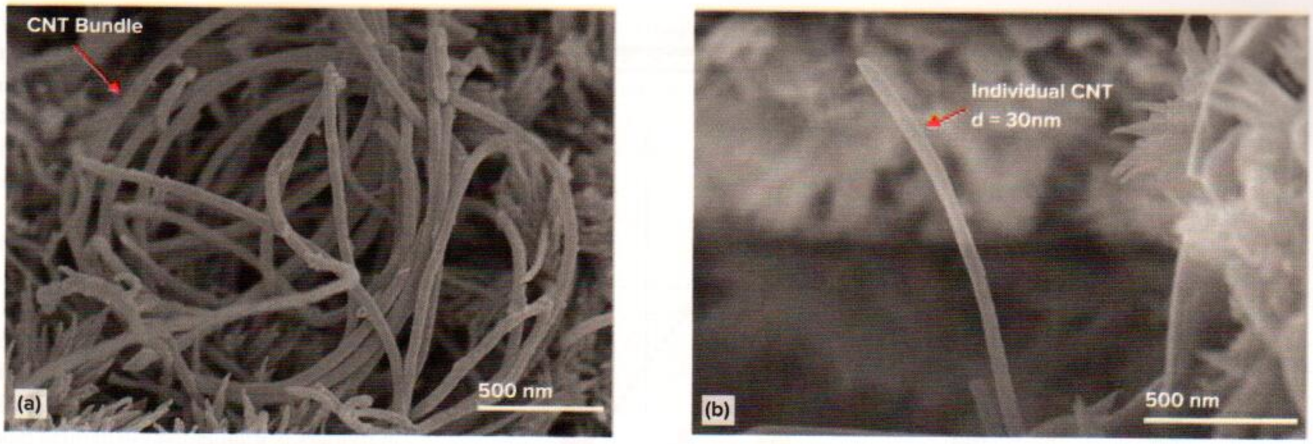

Fig. 4: SEM image of cement paste nanocomposites reinforced with CNTs: (a) produced without ultrasonication procedure; and (b) produced using an HRWRA (surfactant) and ultrasonic energy[10]

"Standard Test Method for Flexural Strength of Hydraulic Cement Mortars," on beams with dimensions 40 x 40 x 160 mm (1.6 x 1.6 x 6.3 in.). For all CNT specimens, well-dispersed CNTs were added in an aqueous solution. Additional tests were conducted using notched flexural specimens in three-point bending. Six prismatic 20 x 20 x 80 mm (0.8 x 0.8 x 3.2 in.) notched specimens (Fig. 6) were tested using a 25 kN (5600 lbf) MTS servo-hydraulic, closed-loop testing machine under displacement control. The crack mouth opening displacement (CMOD) was used as the feedback signal to produce stable crack propagation at the rate of 0.008 mm/min (0.0003 in./min), such that the peak load was reached about 5 minutes after the test started.

Both compressive strength and MOE were measured on 100 x 100 mm (4 x 4 in.) cubes and 100 x 200 mm (4 x 8 in.) cylinders, following ASTM C39/C39M, "Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens," and ASTM C469/C469M, "Standard Test Method for Static Modulus of Elasticity and Poisson's Ratio of Concrete in Compression." Following the ASTM C293/C293M, "Standard Test Method for Flexural Strength of Concrete (Using Simple Beam with Center-Point Loading)," procedure ensures that the variations of the test results are not significant and will not affect the conclusions.

Most of our investigations on the benefits of CNTs (as well as almost all

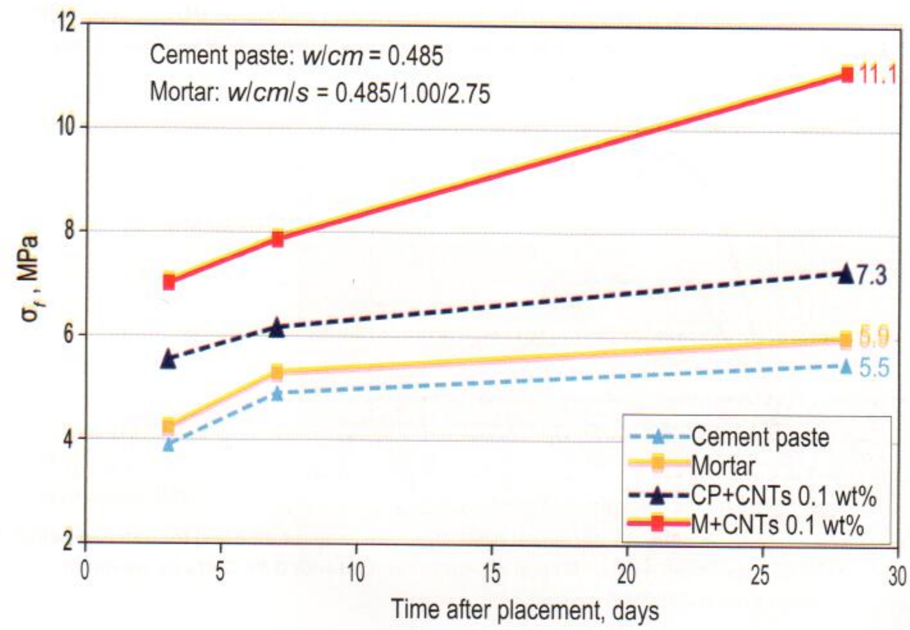

Fig. 5: Rate of development of flexural strength σ_f of the control cement paste (CP) and mortar (M) specimens and cement pastes and mortars reinforced with 0.1% CNTs by weight of cement (based on References 14 and 15) (Note: 1 MPa = 145 psi)

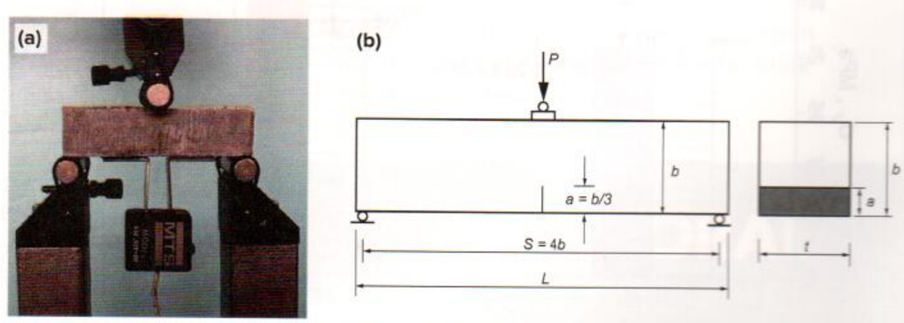

Fig. 6: Notched specimen tests: (a) three-point bending test setup with gauge used to measure crack mouth opening displacement (CMOD); and (b) geometry of notched specimens[16]

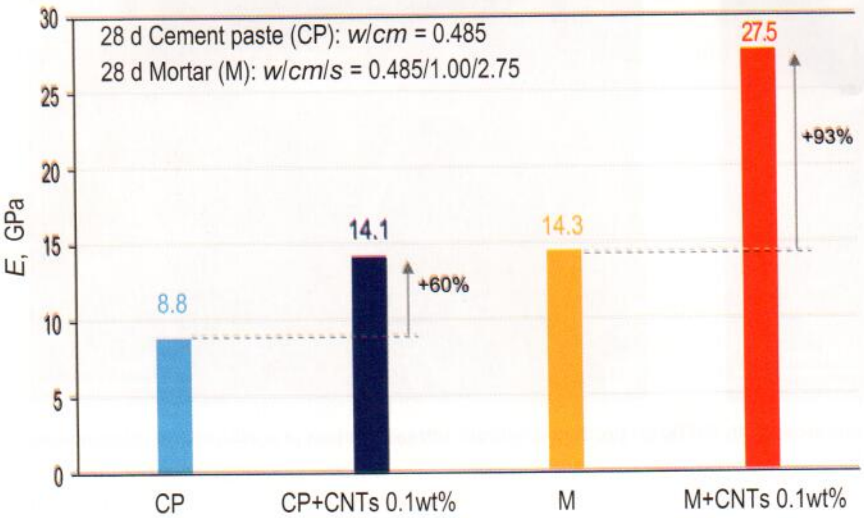

Fig. 7: Modulus of elasticity E (at 28 days) for cement paste (CP) and mortar (M) reinforced with 0.1% CNTs by weight of cement (based on References 15 and 16) (Note: 1 GPa = 145,000 psi)

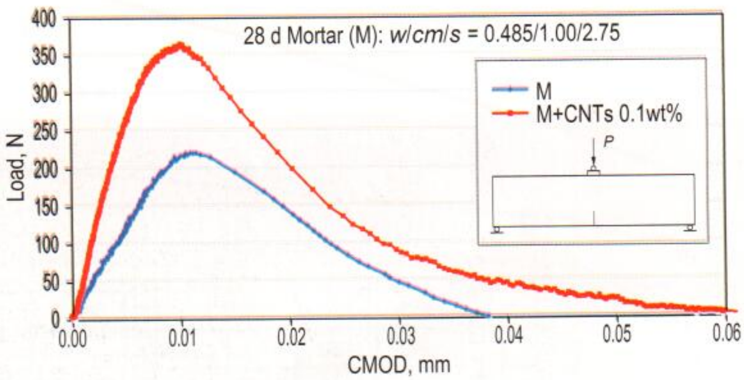

Fig. 8: Crack mouth opening displacement (CMOD) versus load (at 28 days) for notched beam specimens fabricated from mortar (M) and mortar reinforced with 0.1% CNTs by weight of cement[15] (Note: 1 N = 0.225 lbf; 1 mm = 0.04 in.)

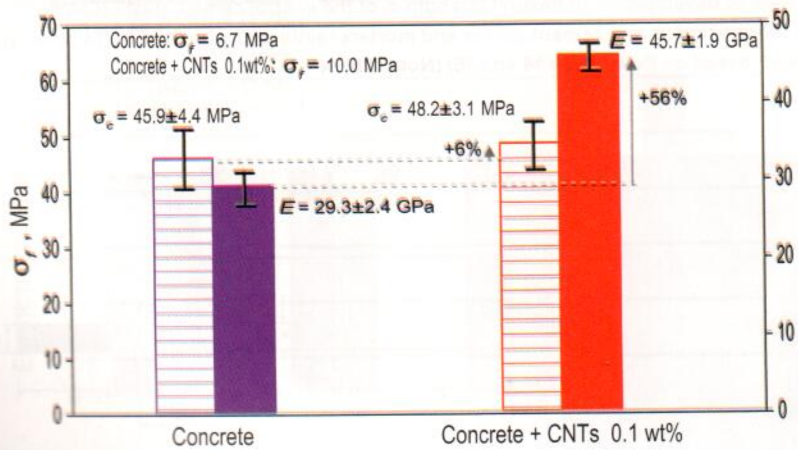

Fig. 9: Compressive strength at 28 days, σ_c, and MOE for concrete and concrete reinforced with 0.1% CNTs by weight of cement (Note: 1 MPa = 145 psi; 1 GPa = 145,000 psi)

other published work) have been conducted using cement paste. Nanoscale fibers will influence primarily the cement paste; therefore, one might expect that benefits would be less pronounced for mortar and concrete. However, this has not been the case. The substantial enhancement of MOE associated with CNT additions are shown in Fig 7. The figure also shows that the benefits associated with the addition of CNTs are much greater for mortars than for cement pastes, even though the portion of CNTs in mortars is smaller than in cement pastes (in both mixture types, the addition rate was 0.1% by weight of cement).

Moreover, as Fig. 8 indicates, the increase in modulus is associated with increased flexural strength and is not accompanied by a decrease in ductility or fracture toughness.[13-16]

Compressive strength and MOE values for concrete specimens are shown in Fig. 9. Mixture proportions (*w/cm/s/CA*) were 0.51/1.00/2.63/2.04. Mixtures with CNTs had 0.1% CNTs by weight of cement. The compressive strength of the control concrete mixture was found to be 45.9 MPa (6660 psi), while the compressive strength of the concrete reinforced with CNTs was 48.2 MPa (6990 psi). Interestingly, while the addition of CNTs resulted only in a slight increase in the compressive strength, it provided a substantial increase in MOE—almost 56%. MOE was also calculated from flexural tests, conducted according to ASTM C293/C293M on beams with dimensions 70 x 80 x 380 mm (2.8 x 3.2 x 15 in.), and was found in perfect agreement with the MOE values found using concrete cylinders and cubes. Further, the addition of CNTs also enhanced flexural strength by about 50%.

Why Do CNTs Boost the MOE of Concrete?

There has been some indication that addition of CNTs alters the nanostructure of calcium silicate hydrate (C-S-H).[11,17] Researchers have also suggested that CNTs provide a massive surface area for the precipitation of cement hydrates, conceivably in a well-packed format that could contribute to the formation of denser

C-S-H agglomerates with higher stiffness.[18] This effect is shown in Fig. 10, where the results of nanoindentation tests on control paste specimens and specimens reinforced with 0.08% CNTs by weight of cement are presented as frequency plots of the calculated MOE values. The shift in the plots indicates that the addition of CNTs has increased the stiffness of the C-S-H.

If one assumes that the increase in the MOE of the concrete associated with the addition of CNTs is solely due to the increase in the MOE of the cement paste, the experimental results far exceed the values that can be inferred from the normal rules of composite materials. Therefore, the increased MOE must be the result of other factors. It is possible that CNT additions modify the interface between aggregates and cement matrix at a nanoscale level similarly to silica fume additions. However, the increase in MOE due to CNT additions is not associated with increased compressive strength and decreased ductility.

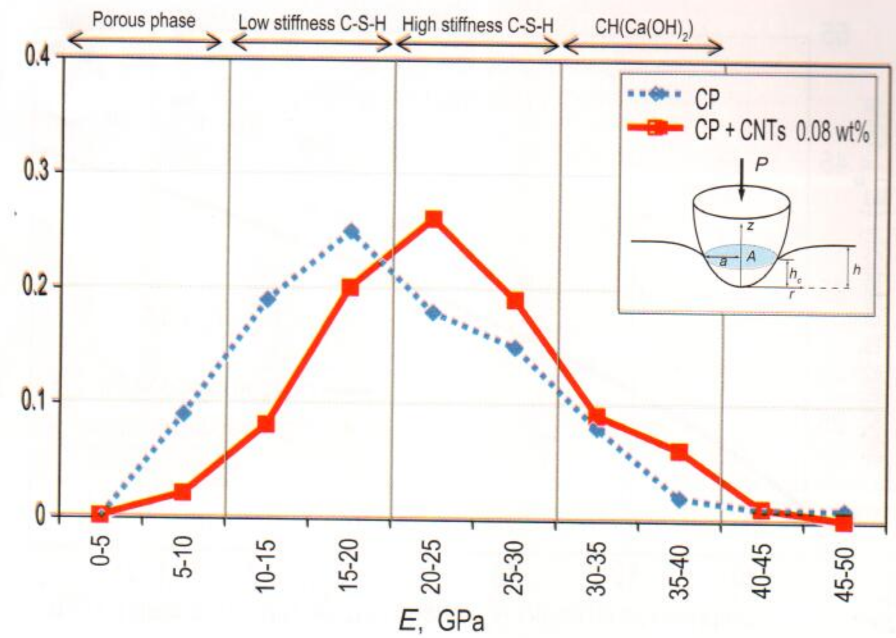

Fig. 10: Probability plots of the MOE for 28-day cement paste (w/cm = 0.485) and cement paste reinforced with 0.08% CNTs by weight of cement[11] (Note: 1 GPa = 145,000 psi)

Concluding Remarks

Figure 11 provides an update of Fig. 2 to include the data point for our concrete mixture reinforced with 0.1% CNT by weight of cement. The data point is well above the design curve provided in the Hong Kong Code. Compared with data for mixtures with similar MOE values, this was achieved at almost half of the compressive strength. This shows that small CNT additions are capable of greatly enhancing MOE of concrete, without increasing its compressive strength or brittleness. The approach therefore deserves deeper investigation.

Acknowledgments

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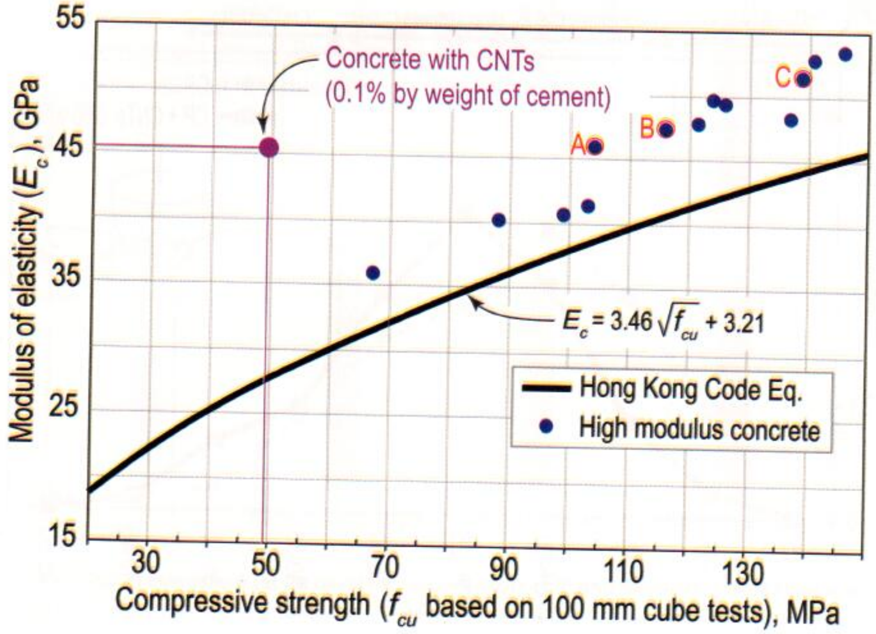

Fig. 11: Updated version of Fig. 2, showing the increase in MOE due to using CNTs in concrete (Note: 1 GPa = 145,000 psi; 100 mm = 4 in.; 1 MPa = 145 psi)

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Note: Additional information on the ASTM standards discussed in this article can be found at **www.astm.org**.

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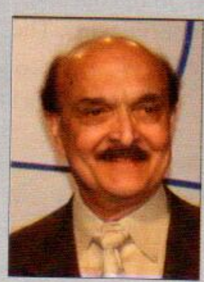

ACI Honorary Member **Surendra P. Shah** is Walter P. Murphy Professor of Civil Engineering (Emeritus) at Northwestern University, Evanston, IL. He is a member of ACI Committees 215, Fatigue of Concrete; 239, Ultra-High Performance Concrete; 241, Nanotechnology of Concrete; 544, Fiber-Reinforced Concrete, 548, Polymers and Adhesives for Concrete; and 549, Thin Reinforced Cementitious Products and Ferrocement. He is also a member of Joint ACI-ASCE Committee 446, Fracture Mechanics of Concrete.

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[illegible] the Institute through future [illegible]nts within the industry.

[illegible], Kleinhans began at CRSI as a staff Structural/Bridge Engineer before assuming the Managing Director role of the Epoxy Interest Group (EIG). During that time, she received the 2015 ACI Young Member Award for Professional Achievement. She was awarded "for contributions to the design and use of concrete in bridges, serving as a liaison with concrete industry institutes, and for her service on ACI technical committees."

Kleinhans has 15 years of experience in structural engineering and bridge design. She began her career at Modjeski and Masters, Inc., and she has held positions at National Steel Bridge Alliance (NSBA) and CTLGroup. She received her bachelor's degree in civil engineering from the University of Alaska-Fairbanks, and her master's degree and PhD in civil engineering from the University of Missouri-Rolla. Kleinhans is a licensed professional engineer.

Errata

In the article "Uncoupling Modulus of Elasticity and Strength," November 2017 issue, page 37, a clarification has been added as follows:

- "For example, the high compressive strength specified for some elements in the Trump Tower was needed to ensure that the MOE was about 6,200,000 psi (43 GPa)—far greater than the 4,000,000 psi (28 GPa) value that is now routinely possible with conventional mixtures."

In the article "Evolution of ACI 562 Code – Part 3," April 2016 issue, the following corrections have been made:

- On page 64 in equation R4.5.2a, U_o should be U_c; and
- On page 68 in Table 2, the Baseline σ at $\beta = 3.0$ (col.) for the D/L of 8 (row) should be 0.073 and not 0.73.

The online archived versions of these articles have been updated.