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SYMPOSIUM PAPER

Tensile, flexural and compressive strength studies on natural and artificial phosphate urinary stones

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Abstract Mechanical properties of renal calculi dictate how a stone interacts and disintegrates by shock wave or intracorporeal lithotripsy techniques. Renal stones of different compositions have large variation in their mechanical strength and susceptibilities to shock waves. Operated urinary stones and artificially developed stones using pharmaceutical methods, composed of phosphates were subjected to tensile, flexural and compressive strength studies using universal testing machine. The infrared spectra confirmed the presence of hydroxyapatite in both the natural stones and struvite with calcium oxalate trihydrate in one stone and struvite with uric acid in the other. The X-ray diffraction analyses confirmed their crystalline nature. It has been observed that the flexural properties depend on the size of the sample even for the samples cut from a single stone. The compressive strengths were almost 25 times larger than the tensile strengths of the respective natural stones as well as the artificial stones prepared.

Keywords Urinary stones · Struvite · Uric acid · Mechanical properties · Infrared spectra · X-ray diffraction

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Introduction

Urinary stones have afflicted human kind since antiquity. A number of materials can form urinary stones in the urinary tract and are highly variable in their composition, structure and susceptibility to shock waves in lithotripsy due to the presence of calcium, magnesium and ammonium phosphates, urates, cystine and proteins [1, 2]. Different phosphates namely hydroxyapatite, carbonate apatite, brushite, struvite and whitlockite, individually or in a mixture, have been detected in renal calculi [3]. Phosphate stones account for 12–20% of all urinary stones and rank first in the list of recurrent calculi [4]. Trace amount of magnesium (0.4–0.5%) was found in all the types of stones [5]. The most important phosphate-containing calculi involved in urinary stone disease are carbonate apatite, brushite, and struvite [6]. The first kidney stone was successfully disintegrated in Munich by extracorporeal shock wave therapy and become the number one choice in the treatment of kidney and ureter stones [7] and is used to treat the majority of simple renal calculi (about 80–85%) satisfactorily [8]. Currently there is a great interest in the treatment of kidney stones by in vivo fragmentation using non-invasive sonic methods as well as invasive ultrasonic and laser techniques [9, 10].

Despite the rapid spread of endourology and extracorporeal lithotripsy, there are several questions still to be answered towards alleviating the agony due to kidney stones [9]. Because of the difference in chemical compositions and structural features of renal calculi, the efficacy of stone fragmentation may vary significantly [11]. The ability to predict how easily a renal stone will break by these methods in vivo would be advantageous and hence the in vitro assessment of the different types of renal stones and the devices used provides important information for

Fig. 1 Surgically removed uric acid with struvite stone (031)

selecting appropriate treatment modalities [9, 10, 12]. Acoustic and mechanical properties of these renal calculi dictate how a stone interacts and disintegrates with mechanical forces produced by shock wave and laser lithotripsy techniques [13]. The mechanical properties of materials such as elastic constants, plasticity and fracture behavior provides useful information on the strength and deformation characteristics of the material [14]. The use of natural stones in experiments to device the treatment modalities and also for the assessment of various stone fragmentation devices is problematic as it is very difficult to procure natural calculi which are identical in their chemical composition and physical properties. The employment of artificial stone models is a reliable alternative and represents a solution to these problems. The substance-specific, standardized, reproducible investigations can be done using these artificial stone models [10, 12, 15]. It is apparent

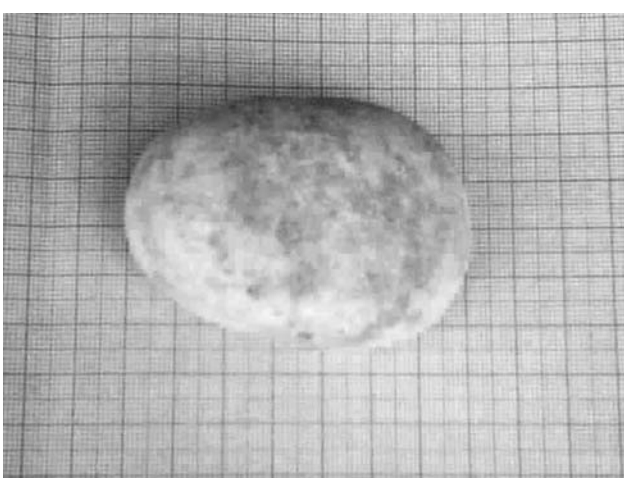


Fig. 2 Surgically removed struvite stone (0902)

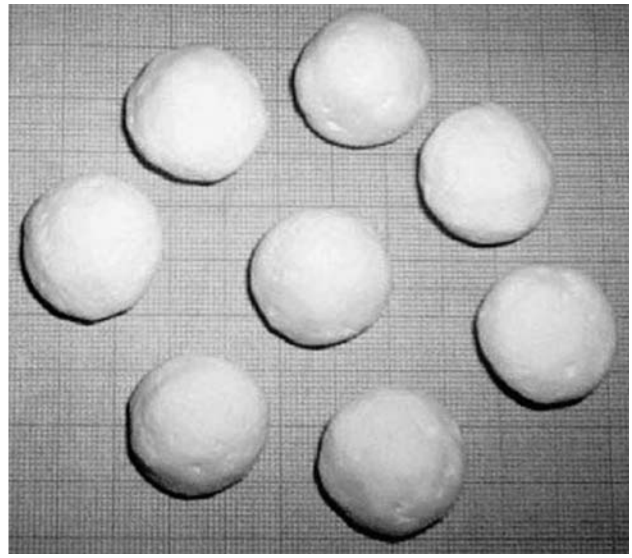


Fig. 3 Artificial Whitlockite stone

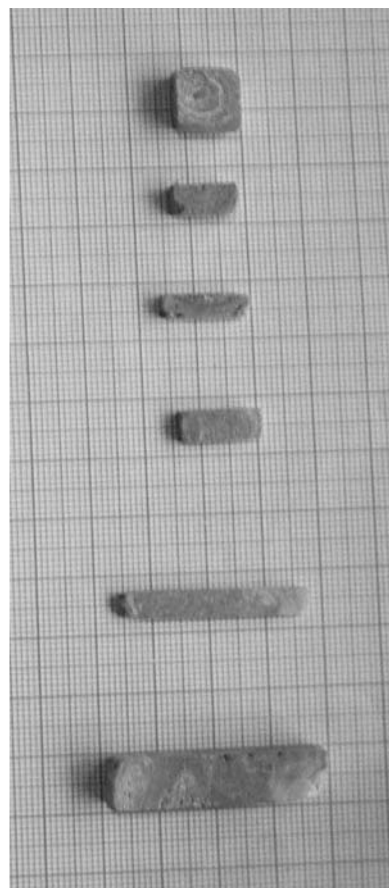


Fig. 4 Machined uric acid with struvite stone

from several studies that stone fragility during lithotripsy depends on the chemical composition, the crystalline structure, flaw size and distribution, microhardness and elasticity, stone volume and shape as well as gas content [16]. Mechanical properties of renal calculi dictate how a stone interact and disintegrate with mechanical forces produced by shock wave and laser lithotripsy techniques [17]. It was also found that both stress waves and cavitation play critical roles in the comminution of kidney stones; they act synergistically rather than individually to ensure an effective and successful fragmentation of renal calculi in shock wave lithotripsy [18]. Tensile stresses may be more effective in some instances in disrupting material because most materials are weaker in tension than compression [19]. Hence, the tensile, flexural and compressive strength studies were performed on natural and artificial phosphate urinary stones using universal testing machine in the present study.

Materials and methods

The surgically removed urinary stones (Figs. 1, 2) with phosphates were dried in room temperature. Artificial stones composed tri-calcium phosphate (whitlockite) (Fig. 3) and calcium hydrogen ortho phosphate dihydrate (brushite) prepared using the standard pharmaceutical operations of granulation, tableting and coating [10, 12, 20] were used for comparing the results. The stones machined in to rectangular shapes (Figs. 4, 5) with dimensions 43 mm × 19 mm × 6.3 mm (struvite) and 38 mm × 8.95 mm × 6.4 mm, 3.3 mm × 4.7 mm × 2.67 mm (uric acid with struvite) were used in the flexural test. Natural and artificial stones with cross sectional area ranging from 0.892×10^{-5} m^2 to 1.94×10^{-5} m^2 were used for tensile tests while samples with cross sectional area ranging from 1.37×10^{-5} m^2 to 17.48×10^{-5} m^2 were used for compression tests. Tests were performed using the test system Tinius Olsen, Model H5KS, UK with the 50 N load cell for tensile and flexural tests and 5 kN load cell for the compression test with the standard grips provided with cross-head speed of 0.5 mm min^{-1}.

The load at the fracture point for the flexural test was determined with 30 mm support span and hence the flexural strength σ was found using the formula, $\sigma = \frac{3FL}{2bd^2}$ where F is the load (force) at the fracture point, L is the length of

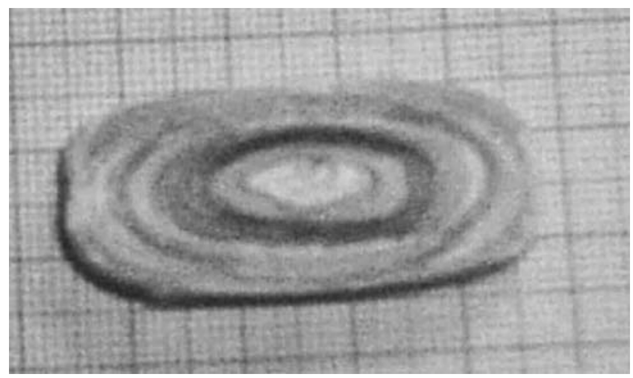


Fig. 5 Machined struvite stone

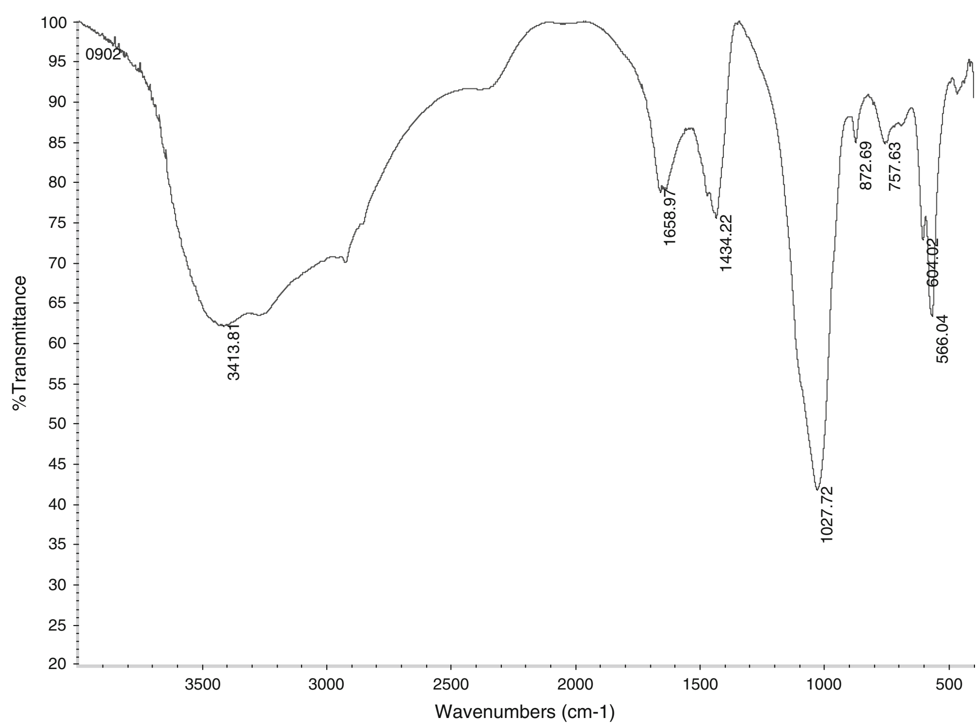


Fig. 6 FTIR spectrum of struvite stone (0902)

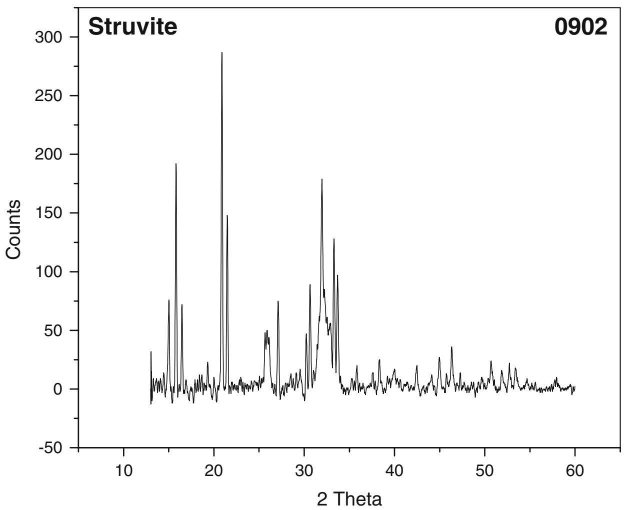


Fig. 7 X-ray diffraction pattern of struvite stone (0902)

the support span (30 mm), b is width, d is thickness of the sample. The flexural modulus Y was calculated using the formula, $Y = \frac{FL^3}{4bd^3\delta}$ where δ is the mid span deflection for the breaking load F [21]. The tensile strength was determined by the force at which tensile break occurs. The compressive strength was determined by the collapse of the material due to compression by minimum of 10% force change in natural stones and apparent change in compression in artificial stones.

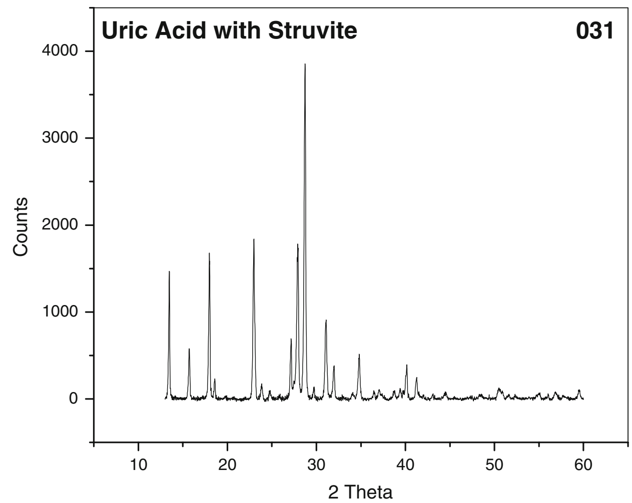


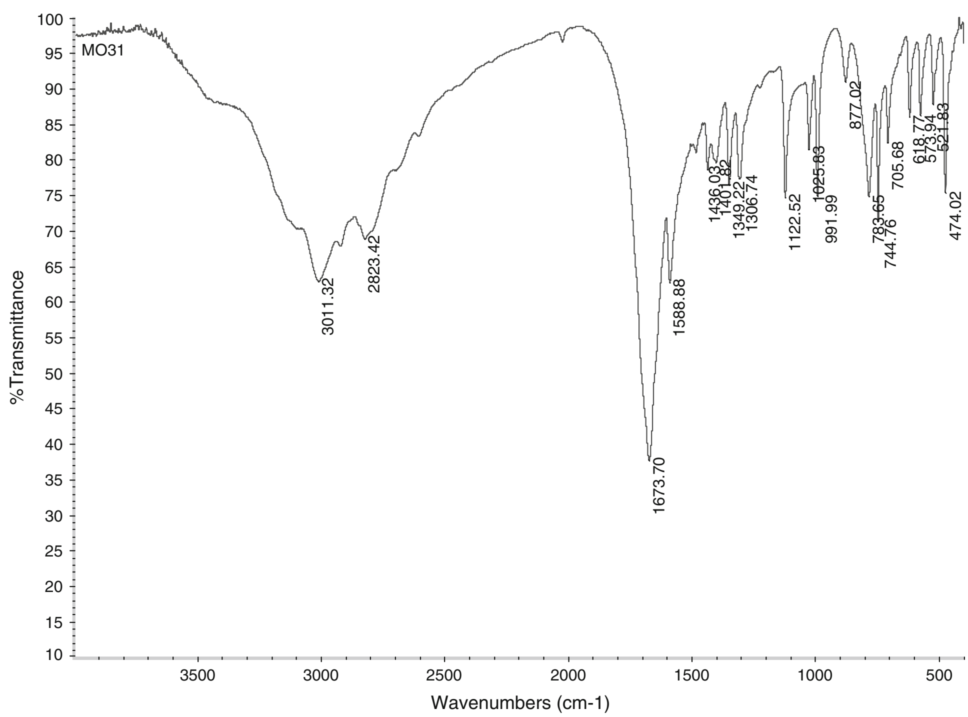
Fig. 9 X-ray diffraction pattern of uric acid with struvite stone (031)

The compositions of these stones were analyzed using Fourier Transform Infrared (FTIR) Avatar 330 spectrometer. The powdered samples were also subjected to X-ray diffraction analysis using PANalytical X'per PRO X-ray diffractometer with CuK radiation source.

Results and discussion

For the natural struvite urinary stone (0902), the absorptions at 566 and 872.69 cm^{-1} indicate the presence of

Fig. 8 FTIR spectrum of uric acid with struvite stone (031)



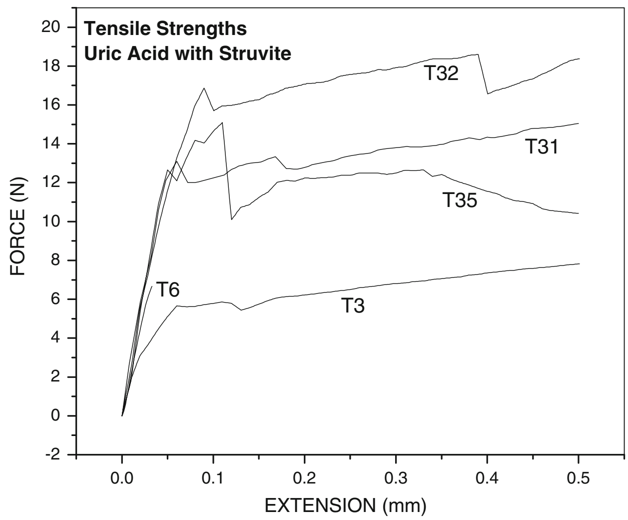


Fig. 10 Tensile strength graph of uric acid with struvite stone (031)

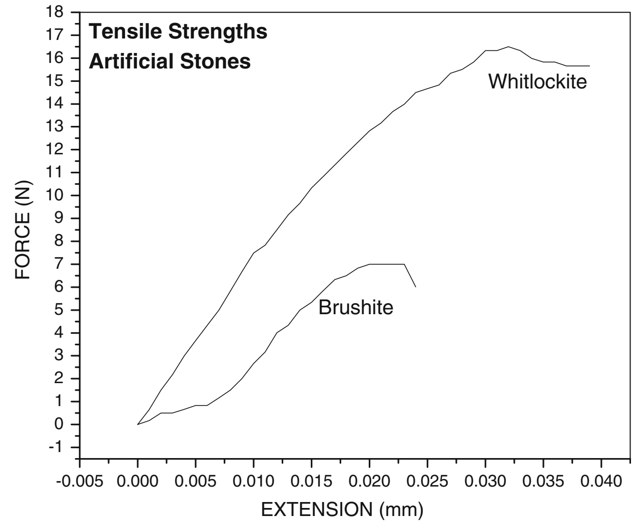


Fig. 12 Tensile strength graph of artificial stones

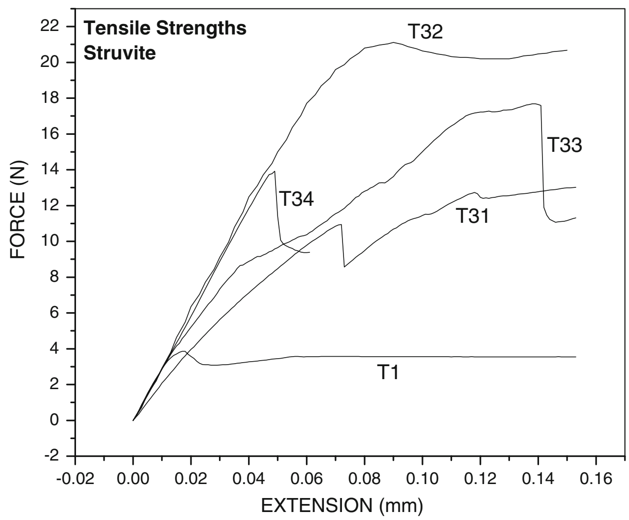


Fig. 11 Tensile strength graph of struvite stone (0902)

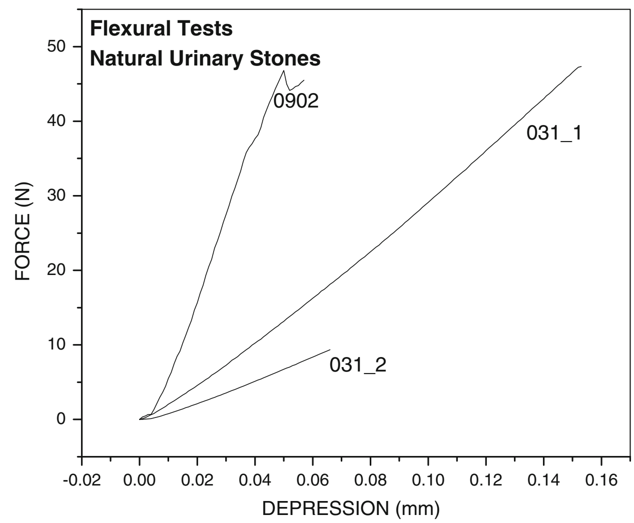


Fig. 13 Flexural strength graph of natural stones

P–O–P asymmetric stretching vibrations while the absorptions at 1,658.97 and 3,413.81 cm^{-1} indicate the presence of NH group [22, 23] (Fig. 6). In the X-ray diffraction pattern (Fig. 7) of this stone, all the peaks very well match with Mg $PO_4(NH_4)\cdot6H_2O$ (JCPDS card no. 20-0665) confirming struvite. A few peaks match with $Ca_5(PO_4)_3(OH)$ (JCPDS card no. 86-0740), indicating the presence of hydroxyapatite. For the other natural urinary stone (031), the absorptions at 991.99 and 877.02 cm^{-1} indicate the presence of P–O–P asymmetric stretching vibrations while the strong absorptions at 573.94 and 521.83 cm^{-1} indicate the presence of acid phosphates [22, 24]. The absorption at 1,588.88 cm^{-1} indicates the asymmetric deformation of NH_3^+ [23] (Fig. 8). In the X-ray diffraction pattern of this natural urinary stone, majority of peaks are matching with uric acid (JCPDS card no. 28-2016) confirming the pattern belongs to uric acid. A few peaks match with $Ca_5(PO_4)_3(OH)$ (JCPDS card no. 86-0740 and there is also a phase of struvite observed (JCPDS card no. 20-0665) (Fig. 9). The FTIR spectra and the X-ray diffraction analyses of the artificial stones also show conformity with their basic chemical substance. Tensile and compressive strengths for all the stones and the flexural strength and flexural modulus for the natural stone samples were determined from the graphs drawn (Figs. 10, 11, 12, 13, 14, 15) and their average values are tabulated (Table 1).

The X-ray diffraction and FTIR patterns of the powdered natural urinary stones are in good agreement with the reported patterns of struvite and uric acid with struvite. The

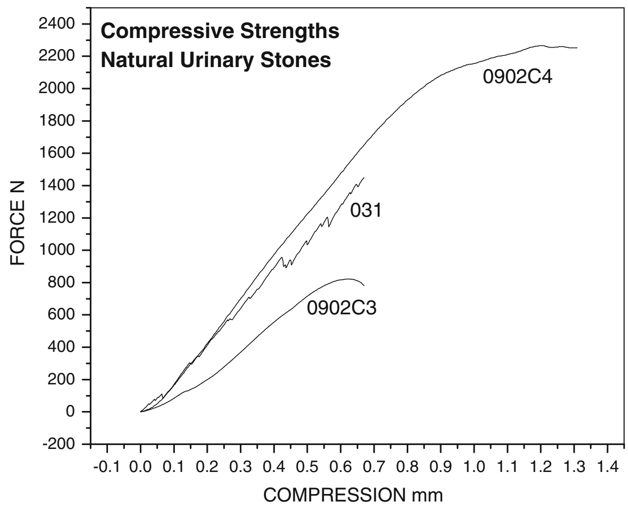


Fig. 14 Compressive strength graph of natural stones

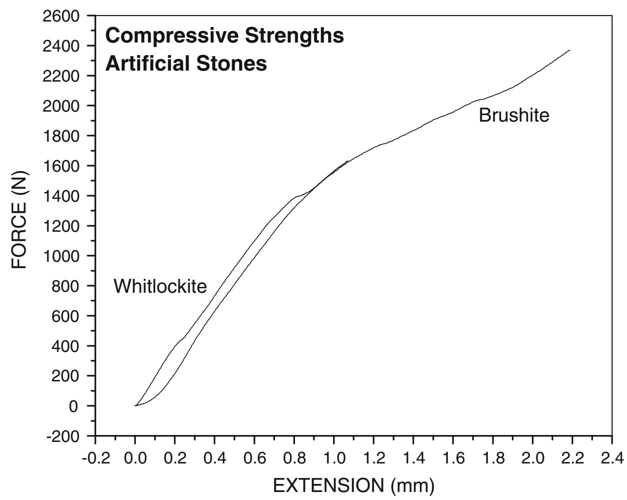


Fig. 15 Compressive strength graph of artificial stones

tensile strengths for the natural stones vary from 0.400 to 1.264 MNm^{-2} while the compressive strengths were found to be varying from 13.77 to 20.41 MNm^{-2} in conformity with the reported values [6, 9, 25]. For the first time, the flexural strength and hence the flexural modulus for the struvite urinary stone was determined and found to be 2.714 MNm^{-2} and 1.133 GNm^{-2} respectively, and for the uric acid with struvite stone samples, the flexural strength and the flexural modulus were found to be varying from 5.81 to 12.55 MNm^{-2} and 0.890 to 10.68 GNm^{-2} respectively. The multiple compressions and tensile breaks observed are due to the layered structure of these urinary stones.

Conclusions

The FTIR spectra confirmed the presence of hydroxyapatite in both the natural stones and struvite with calcium oxalate trihydrate in one stone and struvite with uric acid in another stone. The X-ray diffraction analyses confirmed their crystalline nature. The in-vitro mechanical strength of the urinary stones, the tensile and flexural strength measurements and hence their flexural modulus, were studied directly using universal testing machine. It has been observed that the flexural properties depend on the size of the sample even for the samples cut from a single stone. The compressive strengths were almost 25 times larger than the tensile strengths of the respective natural stones as well as the artificial stones prepared. By correlating these values, it would be helpful in understanding the internal structure of the urinary stones and hence optimizing the treatment parameters of shockwave lithotripsy and other similar non-invasive techniques.

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Table 1 Flexural, tensile and compressive strengths of natural and artificial stones

Material	Flexural strength (MNm^{-2})	Flexural modulus (GNm^{-2})	Tensile strength (MNm^{-2})	Compressive strength (MNm^{-2})
Natural urinary stone-1 [uric acid + struvite (031)]	5.81 (large) 12.55 (small)	0.890 (large) 10.68 (small)	0.812 ± 0.378 (n = 5)	20.4
Natural urinary stone-2 [struvite (0902)]	2.71	1.13	0.749 ± 0.263 (n = 5)	14.4 ± 0.45 (n = 2)
Brushite stone	–	–	0.436	10.42
Whitlockite stone	–	–	1.20	32.85

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