

Research Article

Impact Fracture of Composite and Homogeneous Nanoagglomerates

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It is not yet clear on whether the fracture characteristics of structured composite capsules and homogeneous nanoagglomerates differ significantly under impact loading conditions. Experimental measurement of impact fracture properties of such small agglomerates is difficult, due to the length and time scales associated with this problem. Using computer simulations, here we show that nanoagglomerates are subjected to normal impact loading fracture within a few nanoseconds in a brittle manner. The restitution coefficient of the nanoagglomerates varies nonlinearly with initial kinetic energy. The fracture of nanoagglomerates does not always happen at the moment when they experience the maximum wall force, but occurs after a time lag of a few nanoseconds as characterised by impact survival time (IST) and IST index. IST is dependant on the initial kinetic energy, mechanical and geometric properties of the nanoagglomerates. For identical geometries of the capsules, IST index is higher for capsules with a soft shell than for these with a hard shell, an indication of the enhanced ability of the soft nanocapsules to dissipate impact energy. The DEM simulations reported here based on theories of contact mechanics provide fundamental insights on the fracture behaviour of agglomerates—at nanoscale, the structure of the agglomerates significantly influences their breakage behaviour.

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1. INTRODUCTION

Studies on the mechanical strength characteristics of assemblies of discrete nanoparticles assume significance in several applications, for example, in aerospace, civil, pharmaceutical, nuclear, materials engineering, and nanotechnology sectors. A few examples are nanocomposites (capsules) that could induce self-healing in materials, coated particles in which their conductivity could be linked to control light emission and manufacturing of hard-to-flow or easy-to-flow composite powder beads and capsules. Predictions on the impact strength of particulate agglomerates in terms of their single-particle properties are required in several industries. For example, the fracture strength and fragment-size distribution are used as an assessment criterion for quality control of agglomerates at production sites in the powder processing industries. Assemblies of particulate materials exhibit unusual and unpredictable characteristics under mechanical loading [1]. Even structurally homogeneous particulate assemblies under uniform loading could exhibit heterogeneous distribution of forces across interparticle contacts. This makes it difficult to predict their

bulk behaviour as macroscopic strength related to the induced heterogeneities in particulate systems [2, 3]. Though some experimental studies attempted to study the fracture properties of individual nanoparticles, for example, using transmission electron microscopy (TEM) [4], the current level of experimentation is not well advanced to capture the dynamic fracture behaviour of nanoassemblies under more commonly encountered loading conditions such as impact loading. The recent surge of activities in fabricating functional nanoassemblies makes modelling as an alternative route to obtain fundamental understanding on their fracture behaviour in terms of their particle-scale properties. In the present paper, using discrete element modelling (DEM) [5, 6], we present the fracture behaviour of composite and homogenous nanoagglomerates subjected to normal impact loading. Computer simulations offer the ability to create identical initial assemblies for testing, hence advantageous to maintain perfect control during testing. The constitutive relations at element scale (interparticle force-separation relations) are governed by theories of contact mechanics (e.g., JKR (Johnson, Kendall, and Roberts) theory [7] for cohesive particles as described later).

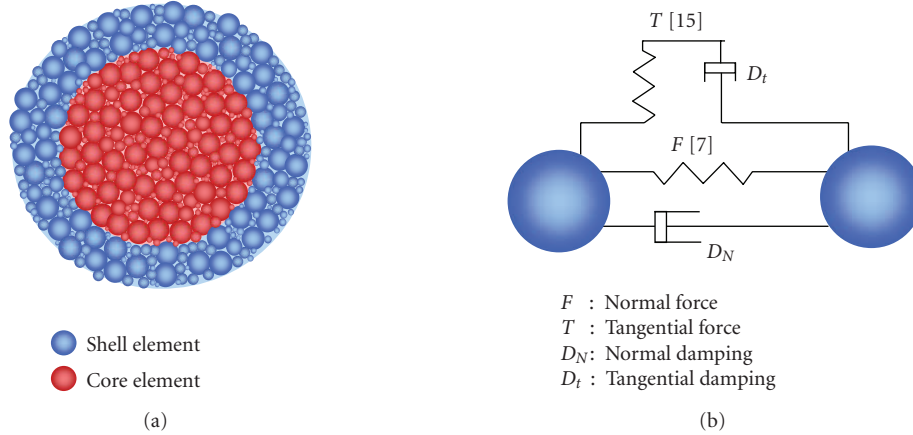


FIGURE 1: Schematic diagram of composite agglomerate idealised as an assembly of discrete (spherical particle) elements.

2. SIMULATION EXPERIMENTS

The impact characteristics of composite and homogeneous agglomerates presented here are generic in nature. However, at the present time, the physical properties and the structure of the composite agglomerates considered here correspond to idealised functional agglomerates, such as capsules used in self-healing applications [8]. Although human-intervened repairing of engineering materials exists for several centuries, the concept of designing self-healing materials is at its infancy and a current topic of interest among researchers [e.g., [8–10]. Though the intention of the current paper is not to address the issues related with fabrication of composite matrix and diffusion properties of the healing capsules, we wish to point out that fracture strength of self-healing nanocomposite capsules is estimated (e.g., diametrical compression test [11]) to characterise their strength at the production stages. However, to the best of our knowledge, impact fracture characteristics of such nanocomposite capsules (particularly with frictionless core) are not yet known, an aspect considered in the present work. Assessment of the impact properties of capsules in terms of discrete particle-scale properties, a priori, would help to optimise the production of such capsules at the manufacturing sites. Experimental methods to study the dynamic fracture of nanoagglomerates under impact loading have not advanced sufficiently at the present time due to the small length and time scales associated with this problem, as shown later.

In the present study, we focus on the normal impact fracture properties of composite (Figure 1), as well as homogeneous nanoagglomerates. The composite agglomerate is made of an outer shell and inner core having thickness ratio (ratio of thickness of the shell to the diameter of the core) equal to 0.2. The shell is idealised as bonded discrete assemblies of sphere elements (Figure 1) and the mechanical properties of the individual elements correspond to the outer wall of the UF self-healing capsule [11]. The inner part of the composite agglomerate is idealised as “fictitious” core elements (spheres), that could represent the soft healing agent present in self-healing capsules [11]. The core elements

are frictionless, incompressible and the equivalent density and weight of the core represents that of encapsulated dicyclopentadiene (DCPD) [12]. The core elements support only the hydrostatic self-weight of DCPD. This approach, though a simplified one, accounts the contribution of the weight of DCPD present in the core of capsules during impact. The simulations are performed using discrete element method (DEM) [5], a technique well-established to study the strength characteristics of particulate assemblies in terms of their single-particle properties [e.g., [1–3, 5, 6]. We created two types of agglomerates: (i) “solid” agglomerate (homogeneous) and (ii) composite agglomerate (Figure 1), referred to as “capsule.” The agglomerates have the following properties: diameter of the agglomerate 2120 nm, packing fraction 0.73, number of particles in the agglomerate c.a. 6000, average diameter of individual particles 100 nm (80–120 nm with a normal size distribution), density of particles 1600 kg/m³, Young’s modulus 10 GPa, Poisson’s ratio 0.35, interparticle friction 0.3, restitution coefficient of individual particles 0.6, and two cases of surface energy (cohesive particles) 3.5 J/m² (“strong”) and 0.35 J/m² (“weak”). The “strong” and “weak” agglomerates are considered with the view to study the role of interface energy between the particles that form the agglomerate on their breakage characteristics at macroscopic level. Hence, in total, we considered four different combinations of agglomerates: “solid-strong,” “solid-weak,” “capsule-strong,” and “capsule-weak.”

DEM models the interactions between discrete (sphere particle) elements as a dynamic process, and the time evolution of the elements are advanced using an explicit finite difference scheme. More details on the DEM methodology can be found elsewhere [5]. In the present simulations, the interactions between the elements are governed by theories of contact mechanics (nonlinear) as briefly summarised below. For JKR theory-based contact model [7], the normal incremental normal stiffness can be computed as follows [13]:

$$k_N = \frac{2E^* a [3 - 3(a_C^3/a^3)^{1/2}]}{3 - (a_C^3/a^3)^{1/2}}, \quad (1)$$

in which, a is the contact radius between particles [13] and a_C is defined as

$$a_C^3 = \frac{3P_{ADH}R^*}{4E^*}, \quad (2)$$

where R^* and E^* are the reduced particle radius and elastic modulus are function of the individual particle radii, R_1 and R_2 , and elastic moduli, E_1 and E_2 , of the (two) particles in contact as follows:

$$\frac{1}{E^*} = \frac{(1 - \nu_1^2)}{E_1^*} + \frac{(1 - \nu_2^2)}{E_2^*}, \quad (3)$$

$$\frac{1}{R^*} = \frac{1}{R_1^*} + \frac{1}{R_2^*},$$

where ν_1 and ν_2 are the Poisson's ratio of the (two) particles in contact. P_{ADH} is the adhesion force and is equal to the negative of the pull-off force, P_{OFF} , that is, force required to break a contact. According to the JKR model [7], the pull-off force is given by

$$P_{OFF} = -P_{ADH} = -3\pi\gamma R^*, \quad (4)$$

where γ is the surface energy of particles [14]. The tangential force (T) exerted at the contact between contiguous particles is related to the pull-off force and applied normal contact force F_N [15] as a result of decrease in contact area due to peeling of contacts as [13]:

$$P_{EFF} = F_N + 2P_{OFF} \pm \sqrt{4(F_N P_{OFF} + P_{OFF}^2) - \frac{1}{4} \frac{T^2 E^*}{G^*}}, \quad (5)$$

where G^* is the reduced shear modulus of the two particles in contact and is defined as

$$\frac{1}{G^*} = \frac{(2 - \nu_1)(1 + \nu_2)}{E_1} + \frac{(2 - \nu_2)(1 + \nu_1)}{E_2}, \quad (6)$$

where the subscript 1 and 2 correspond to the (two) particles in contact.

This peeling of contiguous particles continues until the tangential force reaches a certain value, T_{peel} [7]:

$$T_{peel} = 2\sqrt{(4F_N P_{OFF} + P_{OFF}^2) \frac{G^*}{E^*}}. \quad (7)$$

If the value of the tangential force is larger than the peeling force, T_{peel} , gross sliding occurs [16]. At this stage, if the normal force is larger than the value of $-0.3P_{off}$, the tangential traction is related to the friction coefficient μ as follows [16]:

$$T = \mu(F_N + 2P_{ADH}). \quad (8)$$

For normal force less than $0.3P_{off}$, the sliding criterion becomes [16]

$$T = \mu F_N \left(\frac{2P_{EFF} + F_N}{3P_{EFF}} \right)^{3/2}. \quad (9)$$

It is worth noting that in absence of adhesion, $P_{ADH} = 0$ and $P_{EFF} = F_N$. Hence, (8) and (9) reduce to the well known Amonton's law.

Different cases of nanoagglomerates were initially created for the specifications presented above (the procedure to create the agglomerates is similar to those presented in a previous work) [6]. The agglomerates were then subjected to normal impact [6, 13] against a rigid nonsticky wall (surface energy of the rigid wall material is kept as 0 J/m^2). Impact tests were performed for a range of initial kinetic energy assigned to the agglomerates. The motion of the agglomerates was carefully tracked down, and the wall force and breakage pattern of the agglomerates were carefully examined during and after the impact of nanoagglomerates with the wall.

3. RESULTS AND DISCUSSION

Here, we present the breakage characteristics of composite (capsule) and homogenous (solid) agglomerates impacting against a wall for a range of initial kinetic energies (Figure 2) assigned to them. We analysed the evolution of the wall force during impact, and present its maximum value as a function of initial kinetic energy of the assemblies, as presented in Figure 3.

Figures 2–3 show that breakage pattern of nanoagglomerates strongly depends on their initial kinetic energy. From Figure 3, we observe that the capsules tested here are more fragile than the solid agglomerates (compare Figure 2(iii) and (iv) for an identical value of initial kinetic energy). In Figure 3, we identified two indicators, namely, the “ i ” and “ j ” points. The “ i ” points correspond to the lowest values of initial kinetic energy at which minor redistribution of contacts (i.e., loss/gain of contacts) were noticed. For values of kinetic energy below point “ i ,” no change in contact positions was observed within the agglomerates. The “ j ” point corresponds to the lowest value of initial kinetic energy for which fragmentation is observed in the agglomerates.

We observe that, in the case of homogeneous solid agglomerates, the relation between the maximum wall force (F) and initial kinetic energy (E_{in}) follows power law in the form:

$$F = A \left(\frac{1}{2} m \right)^{3/5} V^{6/5}, \quad (10)$$

where m is the mass of the agglomerate, and V is the impact velocity. Note that (10) has the same form as that of single elastic particle [17]. According to Johnson [17], an expression for the maximum wall force for an impact of a single particle against a flat target can be obtained in the form:

$$F = 3.029 R^2 E^{*2/5} \rho^{3/5} V^{6/5}, \quad (11)$$

where E^* is the reduced elastic modulus of the particle and the target, ρ the particle density, and R the particle radius. Combining (10) and (11) and substituting the values of the parameters in the above expressions, we obtain the effective reduced elastic modulus of the assemblies as 0.7 GPa

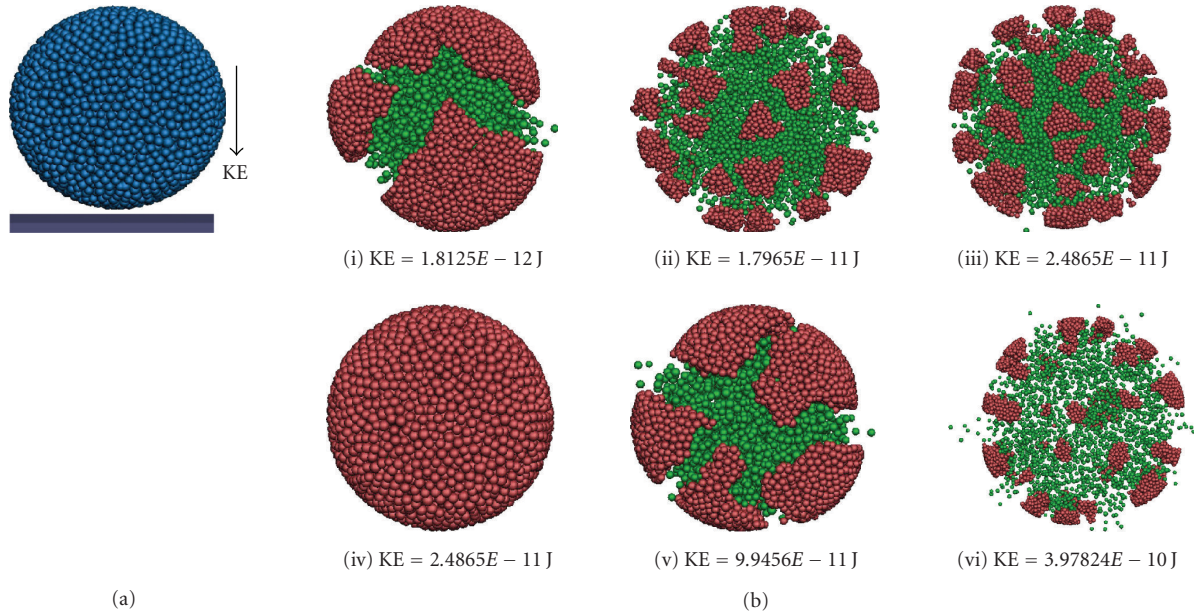


FIGURE 2: (a) Solid agglomerate (homogeneous) approaches the wall with an initial kinetic energy KE. (b) Fragmentation patterns in weak capsules (i)–(iii), and strong capsules (iv)–(vi) for different values of initial kinetic energy (top view). Red: fractured outer shell elements. Green: core elements.

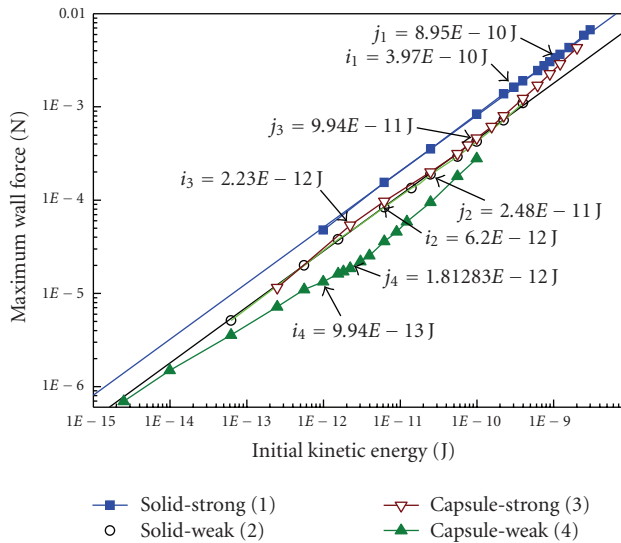


FIGURE 3: Maximum wall force as a function of initial kinetic energy.

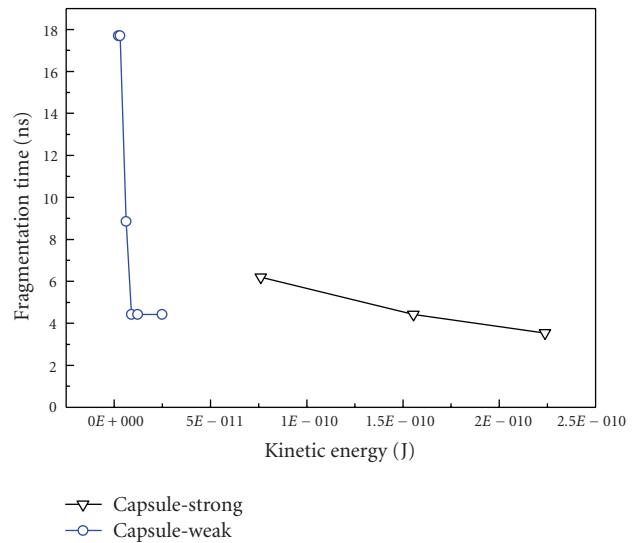


FIGURE 4: Variation of fragmentation time (IST) with initial kinetic energy of the capsules.

and 3.1 GPa for the weak and strong solids, respectively, (which are lower than the elastic modulus of individual nanoparticles). Due to the complex nature of nonlinear variation between maximum wall force and initial kinetic energy, in the case of composite agglomerates (Figure 3) such a simplification (reduced modulus) is difficult to make.

In our simulations, we observed that the fragmentation of the nanoassemblies due to impact loading occurred within a few nanoseconds. However, to investigate the effect of bond strength of the shell (i.e., interface energy of shell elements) on the fracture properties of the capsules, in Figure 4, we show the variation of the impact survival time (IST), that is,

the time elapsed between the stages of attaining maximum wall force and when capsules fragmented (corresponding to their “j” point, Figure 3). It is evident that IST depends on the initial kinetic energy and geometric structure of the assemblies. For an increase in the initial kinetic energy of the capsules, IST decreases. The difference between the maximum and minimum values of IST referred to as IST index (I_{ist}) is about 2 nanoseconds for the strong capsules and about 12 nanoseconds for the weak capsules. At relatively low kinetic energy regimes, the particle contacts in the capsules could sustain the forces for longer period before dissipating them during unloading (post-impact regime).

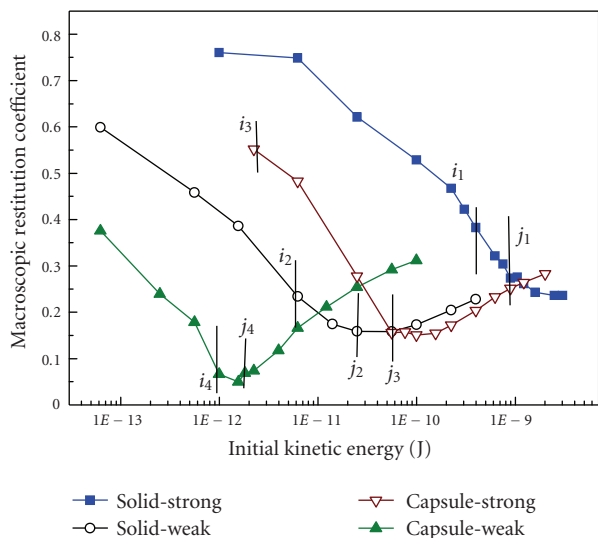


FIGURE 5: Restitution coefficient as a function of initial kinetic energy.

For high values of initial kinetic energies, the unloading of contact forces could occur so abruptly, leading to severe fragmentation/scattering of the capsules within a short duration of IST. Qualitatively, IST index could be considered as a useful indicator of the ability of nanoassemblies to sustain forces in response to the impact energy (time required to self-organise/optimize the force-sharing contacts to sustain forces, and then unload the forces across the contacts during postpeak regime).

In Figure 5, we present the “macroscopic” restitution coefficient of the nanosolids and capsules, which is the ratio between the rebound velocity and initial velocity of the assemblies (or, the square root of the ratio between final and initial values of kinetic energy). In this plot, we have also marked the positions of “*i*” and “*j*” points (similar to Figure 3).

It is evident that the restitution coefficient of the UF capsules and solids exhibit nonlinear variation with the initial kinetic energy assigned to them. In general, the change of curvature in the restitution coefficient curves interestingly correlates with the “*i*” and “*j*” points. In particular, “*j*” points coincide well with the change in curvature of the restitution coefficient plots after which restitution coefficient increases with initial kinetic energy. The value of the (macroscopic) restitution coefficient of nanoagglomerates at critical regime (time period elapsed between *i* and *j* points) is lower than that of the individual nanoparticles used in the simulations (0.6).

The breakage properties of the agglomerates can be also assessed by studying the damage ratio and the fragmentation size ratio as a function of the initial kinetic energy for the assemblies [6]. The damage ratio is defined as the ratio between the number of contacts either lost or gained in the assemblies at a given stage of impact and the initial number of contacts in the (unbroken) assemblies. At a given time, if contacts are effectively lost in the assembly, then damage ratio will have a positive sign and if contacts are

gained then damage ratio will be negative. Although damage ratio is normally expected to be positive, it is not entirely impossible to have negative damage ratio, in particular, for low impact velocities of structured geometries as they could favour a net gain of contacts as discussed later. The fragmentation size ratio is defined as the number of particles in the clusters (1st and 2nd largest fragments) to the initial number of particles in the assemblies. Figure 6 shows the damage ratio and fragmentation size ratio as a function of wall force. It is evident that the variation in fragmentation size ratio passes through three regimes: minor disintegration, fragmentation, and shattering (fragmentation ratio about 5%) of the particles were observed in these regimes, as marked by I, II, and III, respectively, in Figure 6. These plots (sharp transition of fragment size with wall force at regime II), together with Figure 2 suggest that from the point of view of structural damage, the fracture of nanoagglomerates tends to be brittle in nature. Further, the fracture strength of nanocapsules is about four times lower than that of nanosolid agglomerates (Figure 3). Hence, the capsules are more fragile than the solid agglomerates. Though further experimental research is required to understand the cause of negative damage ratio in nanoagglomerates, the small values of negative damage ratio observed here for the case of strong capsule (at low wall forces) could be attributed to the consolidation of the contacts at low initial kinetic energies of the capsule prior to fracture.

4. CONCLUDING REMARKS

To summarise, we have performed computer-based investigations on the impact fracture characteristics of composite as well as homogeneous nanoagglomerates. Nanoagglomerates tend to produce brittle fracture under normal impact loading. The nanocapsules studied here are observed to be more fragile than nanosolid agglomerates, a desired aspect in designing self-healing applications. The time required to fracture the nanoagglomerates (impact survival time) studied here is in the order of a few nanoseconds, whereas previous studies on the fracture of microparticulate solid agglomerates suggest this as about a few microseconds [6]. This could make it difficult to capture the dynamic fracture behaviour of nanoagglomerates experimentally, at least at the present time. Although the impact fracture strength of the capsules having a strong shell (higher value of interface energy) is higher than for capsules with a weak (soft) shell, IST index for capsules having a soft shell is higher than for capsules with a strong (hard) shell, an indication of the enhanced ability of soft composite agglomerates to dissipate the energy due to impact within the assemblies. We showed that the macroscopic restitution coefficient of the nanoagglomerates vary nonlinearly with the initial kinetic energy. The computer simulations employed here can help us not only to predict the structural damage characteristics of the nanoagglomerates in terms of their properties at the discrete element scale, but also provide valuable information a priori to suitably assess and design the fabrication of these assemblies, an aspect desired in industries. We also wish to point out that the current simulations have employed

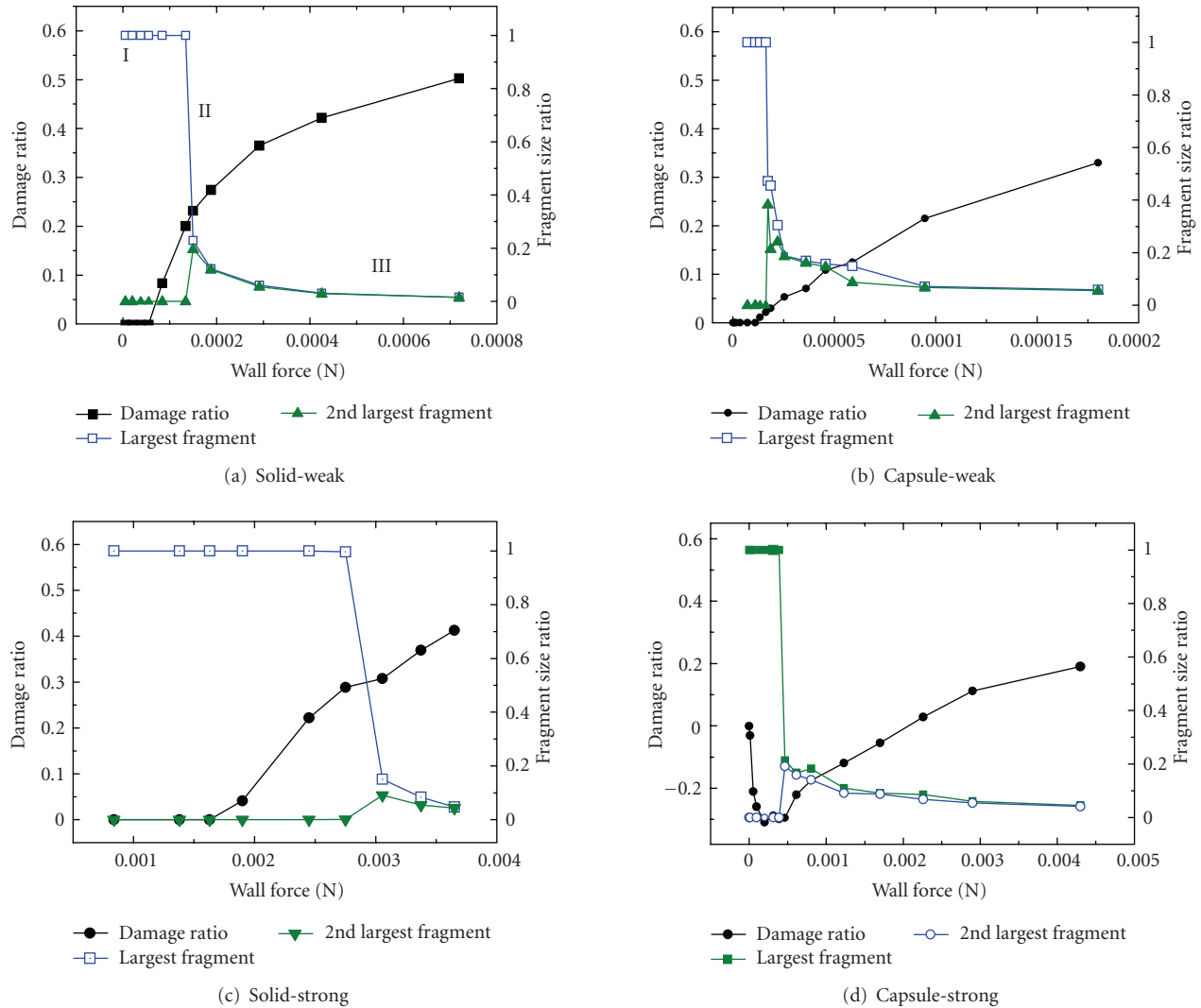


FIGURE 6: Variation of damage ratio and fragmentation size ratio versus wall force.

constitutive relations at nanoelement (particle) scale based on JKR theory of adhesion. Nevertheless, some of the existing studies on different context have supported the applicability of JKR theory for particles at nanoregime (e.g., [18]). However, more realist interaction laws for nanoparticles need to be accounted, preferably based on actual measurements [18]. Further investigations are required to account additional complexities such as variations in particle shape, thickness variations within the shell elements, and other complex loading conditions encountered in real practice. Also, other routes to achieve fracture of nanocapsule may be proposed [19] for new engineering applications, such as a triggered response of some type, but these methodologies are not yet sufficiently developed.

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