Mechanical behaviors of individual core-shell microspheres and their polymeric composites under different strain rates

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**MECHANICAL BEHAVIORS OF INDIVIDUAL CORE-
SHELL MICROSPHERES AND THEIR POLYMERIC
COMPOSITES UNDER DIFFERENT STRAIN RATES**

ZHANG XIN

INTERDISCIPLINARY GRADUATE SCHOOL

NANYANG ENVIRONMENT & WATER RESEARCH INSTITUTE (NEWRI)

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ZHANG XIN

Interdisciplinary Graduate School

Nanyang Environment & Water Research Institute (NEWRI)

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Abstract

Core-shell microspheres and their polymer composites are widely used in environment and water areas for anticorrosion, self-cleaning, waste absorption, antibacterial and deep sea exploration purposes due to the capability of core-shell structure to carry functional agents. It is also used in aerospace industry and automobile industry due to their lightweight and energy absorption capacities. In order to provide useful information to researchers for optimized design of core-shell microspheres filled polymer composite during application, it is significant to investigate the mechanical response of individual core-shell microsphere and their polymer composite.

Core-shell microsphere with void core was firstly investigated. The mechanical properties of Hollow Glass Microspheres (HGM) filled polymers were studied at different strain rates for tensile and compressive behaviors. HGM filled polymers showed strong strain rate effect and the strain rate sensitivity factor increased with the increased strain rate while decreased when filler volume fraction increased. HGM filled polymer absorbed more energy at volume fraction around 7.5% under low strain rate compression.

The effect of shell material on the core-shell structures was also investigated. Different shell materials based microcapsules were fabricated through different processes. Quasi-static and dynamic compression setups for individual microcapsule were established. The quasi-static and dynamic properties of individual microcapsule were systematically investigated for the first time. The result indicated that the strength of nickel shell based microcapsules were two orders higher than that of the other two microcapsules at different strain rates. Microcapsule modified epoxy resins were manufactured and evaluated with different weight fractions.

The core material may also influence the properties of core-shell structure. Since Shear thickening fluid (STF) can transfer from liquid state to solid state during impact, it can diversify the application of core-shell microspheres. As a result, STF was fabricated and encapsulated successfully by using three different methods for the first time to investigate the influence of core material in a core-shell structure. The mechanical properties of STF capsules were studied to obtain optimized encapsulation process. The introduction of ultraviolet curable resin significantly improved the strength of STF capsule. Repeated loading has been applied on the STF capsules with elastic shell fabricated through a two-step method. The STF capsule using two-step method improved the energy absorption capacity and was reused after each impact. Different deformations and fracture modes of different STF capsules were observed. The importation of STF capsules can improve the impact resistance of silicone gel dramatically since it can improve the energy absorption capacity of matrix material up to 70.16%.

Furthermore, the mechanical models of individual microcapsules and their modified polymer composite were studied to further understand their properties. Cowper-Symonds model was employed to predict the strength of microcapsule at specific strain rate. A linear relationship between strain rate and strength was obtained for all the microcapsule modified epoxy resin. The strain rate sensitivity index of nickel shell based microcapsules modified epoxy resin was higher than the other two polymers. A convenient generalized model was proposed to depict the compressive strength of HGM filled polymers. Numerical simulation was employed to study the mechanical modeling of HGM filled polymer by using hexagonal unit cell and periodical boundary condition.

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List of Abbreviations and Symbols

CAD	computer aided design
CAE	computer aided engineering
CCD	charge-coupled device
CFD	computational fluid dynamics
CFRP	carbon fiber reinforced plastic
CT	computed tomography
C-S	Cowper-Symonds
DMA	dynamic mechanical analysis
DBTDL	dibutyltin dilaurate
EMA	ethylene maleic anhydride
FESEM	field emission scanning electron microscope
GFRP	glass fiber reinforced plastic
HGM	hollow glass microsphere
HDI	hexamethylene diisocyanate
MTTS	trimethoxymethylsilane
NIJ	national institute of justice

OM	optical microscope
PU	polyurethane
PUF	poly(urea-formaldehyde)
PCM	phase change material
PEI	polyethylenimine
PSt-EA	polystyrene-ethylacrylate
PVDF	polyvinylidene fluoride
PMMA	poly(methyl methacrylate)
SHPB	split-hopkinson pressure bar
STF	shear thickening fluid
TGA	thermogravimetric analysis
TDCB	tapered double-cantilever beam
UV	ultraviolet

A	cross sectional area of the bar
A_s	cross sectional area of the specimen
A_c	material constant

A_f	amplify factor
c	reduced thickness
C_0	sound wave velocity in bar
d	diameter of microsphere
e	deflection of microsphere
E	Yong's modulus
E_r	reduced modulus
F_i	impact force
F_c	contact force
F_{max}	peak load
$f(\dot{\epsilon})$	strain rate expression
G_ρ	density expression
K	dynamic scale factor
k_m	elastic mismatch factor
l_0	initial length of specimen
m	weight of impactor
M_n	molecular weight

n	strain rate sensitivity index
S_{max}	failure displacement
T	corresponding time
V	voltage
V_i	initial compressive velocity
V_f	volume fraction
σ	stress of microsphere
ΔP	differential of pressure
ε_R	reflect strain
ε_T	transmit strain
$\dot{\varepsilon}$	strain rate
ν	Poisson's ratio

Chapter 1 Introduction

1.1 Background

During the past decades, organic or inorganic core-shell fillers have been widely used in polymer composites in environment and water areas such as offshore industry for anticorrosion [1], self-cleaning [2], self-lubricating [3], waste absorption [4], antibacterial [5], and deep sea exploration [6] purposes due to the capability of core-shell structure to carry functional agents. Because of the advantage of light weight, high specific strength, high specific stiffness, energy absorption capacity, and self-healing usage [7], the core-shell microspheres filled composites can also be used in areas such as marine industry [8], aerospace components [9], sports goods [6], self-healing composites [10], and construction industry [11]. The core-shell microspheres usually contain one organic or inorganic sphere shell and one liquid or solid core or void core.

The introduction of core-shell microspheres such as hollow glass microspheres (HGM) can prevent the propagation of crack in the matrix. As a result, it provides enhancement to the mechanical properties of the epoxy resin. Most studies reported effects of concentration and size of encapsulated microcapsules on the healing efficiency and fracture toughness through a tapered double-cantilever beam (TDCB) method [12]. The microcapsules can enhance the fracture toughness of composite and heal the crack to some extent. However, the introduction of both hollow shell microspheres and traditional microcapsule may cause decrease in mechanical properties such as tensile property and

compressive property, which are more important than fracture properties, due to the weak strength of hollow microsphere and microcapsule [13, 14].

Meanwhile, high risk of impact has been found during the practical application of core-shell microsphere filled composite such as bird strike and hail strike in aviation industry, sea wave impact in marine industry, and article strike in sports industry, which make the study of the strain rate effect of core-shell microsphere modified matrix material important. It is vital to investigate both static and dynamic behaviors of core-shell filled polymer composite.

It is well known that the properties of the constituents of a composite may significantly influence the overall properties of the composite. However, the mechanical properties including fracture mechanism of individual core-shell microspheres and their polymer composite have not been studied to quite an extent. The present research involves notable efforts to investigate the mechanical behaviors of individual microspheres and microspheres modified composite in both static and dynamic loadings.

1.2 Objectives

The final objective of this research is to explore the rate effect and fracture mode of individual microcapsules and mechanical behaviors including compressive, tensile, and flexural properties, and fracture mode of core-shell microspheres modified polymer composite at different strain rates. To achieve this target, the detailed breakdowns of objectives are listed below.

- a) To set up testing apparatuses that can perform static and impact test on individual core-shell microspheres.
- b) To explore novel methods that can fabricate microcapsules with high strength.
- c) To investigate the rate effect of single core-shell microspheres with different shell materials and their polymeric composite since they are most widely used in many industries.
- d) To study the fracture mechanism of core-shell microspheres modified polymer and investigate the crack propagation at different strain rates.
- e) To explore novel methods to encapsulated functional liquid such as shear thickening fluid to study the effect of core material on core-shell structure and enhance the energy absorption capacities of core-shell microspheres modified polymer composites.
- f) To establish the strength versus strain rate mechanical models for individual core-shell microspheres and core-shell microspheres modified polymer composite to predict and depict the mechanical properties, like strength and modulus, of microcapsules and their modified polymer composite at different volume fractions and loading conditions.

1.3 Scope of work

The current research is focused on the mechanical properties of functional core-shell microspheres and their polymeric composites under different strain rates. It mainly

includes six steps from the setup establishment to the mechanical analysis. The detailed five consecutive steps are listed as follow.

(a) Exploration of mechanical response of hollow microsphere filled polymer.

Both low strain rate loading and dynamic compression tests were carried out to investigate the compressive, tensile, and flexural properties of HGM filled polymer with different volume fractions of glass microspheres. Different fracture modes were discovered for HGM filled polymers under different strain rate loadings by using Computed Tomography (CT) scan and Field Emission Scanning Electron Microscope (FESEM). Finite element method was carried out to verify the experimental data. An empirical model with easy obtained parameters has been established, which can help to predict the compressive strength of HGM filled polymer

(b) Design quasi-static loading setup and impact setup for individual core-shell microsphere.

In this phase, both quasi-static compression setup and dynamic impact setup will be developed. Both of them can capture the load during quasi-static compression and dynamic impact at long term compression and instant impact. Deflection in quasi-static compression and impact velocity in dynamic compression test can be recorded. The fracture mode can also be captured by using CCD camera and high speed camera with microscope.

(c) Rate dependent behaviors of microcapsules and mechanical properties of microcapsule reinforced polymer

Different microcapsules with different shell material including organic and inorganic material were fabricated. The rate dependent behaviors of fabricated microcapsules were investigated through the developed setups. After that, the microcapsules were mixed into epoxy resin with different weight fractions. Both quasi-static compression and dynamic impact test on fabricated composites were carried out to evaluate their mechanical properties and fracture modes.

(d) Characterization of STF and exploration of encapsulation methods for viscous liquid.

The rheology property of STF was conducted by using a rheometer which indicated a high initial viscosity and significant shear thickening effect. In order to tightly package this highly viscous fluid and form robust capsules, different fabrication processes were attempted to optimize the fabrication process.

(e) Evaluation of STF capsules fabricated and mechanical response of STF capsule filled polymer.

The fabricated STF capsules were tested through correlative equipment developed by ourselves. The energy absorption capacity of STF capsules was evaluated to optimize the STF capsules. Fracture analysis was carried out to investigate the deformation and fracture mechanism of the functional capsules. The optimized STF capsules were introduced into polymer material to study the mechanical properties of STF capsules filled composite.

(f) Building up the mechanical models for individual core-shell microspheres and their polymerized composite.

Last but not least, the mechanical models for individual core-shell microspheres and their polymerized composite were developed. Cowper-Symonds model was employed to predict the strength of microcapsule at specific strain rate. A convenient generalized model was proposed to depict the compressive strength of HGM filled polymers. Numerical method was also employed to investigate the mechanical modeling of HGM filled polymer by using hexagonal unit cell and periodical boundary condition.

1.4 Report outline

This thesis is outlined as follows:

Chapter 1 gives an overall introduction to the background of the proposed research, highlights of the research objectives, and scope of the research.

Chapter 2 provides the literature review on the topic of the research, which includes core-shell microspheres and their mechanical behaviors, polymer composites based on core-shell microspheres and their mechanical behaviors, shear thickening fluid and its applications.

Chapter 3 describes the mechanical property of HGM filled polymer with different volume fractions of glass microspheres under both static loading and dynamic compression tests. Since the mechanical properties and fracture modes of HGM filled polymer with relatively lower volume fraction of HGM has not been investigated sufficiently and very high volume fraction of HGM will cause very low absolute strength, specimens with different volume fractions of glass microspheres are fabricated. Meanwhile tensile properties of HGM filled polymer are also studied.

Chapter 4 comprehensively studies the influence of microcapsules in the matrix. The mechanical properties of not only the individual microcapsule, but also the microcapsules modified matrix are investigated. Three types of microcapsules are fabricated through different methods, in which, two traditional microcapsules with silica shell and PUF shell are investigated while a robust microcapsule with metal shell is fabricated successfully through chemical plating. Microcapsules reinforced epoxy resin is fabricated with the weight fraction of 0%, 5%, and 10%. Both the quasi-static and dynamic impact tests of individual microcapsule and microcapsules reinforced epoxy resin are carried out to investigate their mechanical properties.

Chapter 5 discusses the encapsulation of viscous liquid. Polystyrene-ethylacrylate (PSt-EA) particles with ethylene glycol suspensions are used as the STF since it shows good shear thickening behavior and relatively lower initial viscosity. Three different methods are proposed to encapsulate STF. The first method is interfacial polymerization between ethylene glycol and diisocyanate to form the shell in inverse emulsion. The second method is immersion of STF capsule fabricated through method one into ultraviolet (UV) curable resin to form robust shell. The third method is the rapid formation of shell upon dropping the STF droplets into certain solution. Quasi-static compression setup and dynamic impact apparatus for the capsule are designed and manufactured to characterize both quasi-static and dynamic properties of STF capsules fabricated through different methods. High speed camera and FESEM are employed to characterize the fracture mode and morphology of the STF capsules. The fabricated STF capsules are embedded into silicone gel to investigate the influence of STF capsule in the matrix.

Chapter 6 discusses the mechanical models of individual microcapsules with PUF, silica, and nickel shell by using Cowper-Symonds model. The mechanical models of different core-shell microspheres filled polymer with different filler dosages are also studied. An empirical model with easy obtained parameters is established, which can be used to provide reference for the design of HGM filled polymer. Finite element method is applied to study mechanical properties of hexagonal unit cell of HGM filled polymer.

Chapter 7 gives the conclusions of this thesis and the highlights of the recommended future works.

Chapter 2 Advances in core-shell microspheres and their polymer composites

In this chapter, the previous research work related to current topic was reviewed. Firstly, different core-shell microspheres were introduced based on the different shell and core materials. The mechanical properties of individual core-shell microspheres were also described. Then polymer composite based on the introduced core-shell microspheres and their mechanical properties were reviewed. Finally, microcapsules with functional core material were discussed. As one of the functional material, the properties of STF as well as its applications were described and it was found that the STF can be used as functional material to achieve the encapsulation research. It is of great significance to explore novel techniques to tightly package this highly viscous fluid.

2.1 Core-shell microspheres and their mechanical behaviors

2.1.1 Hollow glass microspheres (HGM)

Hollow glass microsphere, sometimes called glass microballon or glass bubble, shows good performance in low thermal conductivity and high chemical resistance and high strength to density ratio [15, 16]. It consists of outer thin glass shell and inner gas core due to the fabrication process, as shown in Fig. 2.1.

HGM is usually produced by a flame forming process, in which a pre-fabricated glass

Fig. 2.1 SEM image of (a) the overall view of HGMs and (b) the cross section of HGM [17].

frit with blowing agent passing a flame with high temperature [18]. With the decomposition of the applied blowing agents, gases can be generated. After that, the glass shell will be formed as spherical shape because of the surface tension. There are a lot of factors that can influence the shell thickness of HGM such as residence time in the flame, flame temperature, viscosity and blowing agent of the feed material. It can also be fabricated through other methods such as liquid droplet process, sol-gel process, fly ash, rotating electrical arc, argon plasma jet, and so on [19, 20]. It has been fabricated commercially by many corporations such as Trelleborg, 3MTM, and so on.

Because of the wonderful mechanical properties of HGM, many researchers have focused their interests in such promising material during the past decades. Koopman et al. [21] investigated the compression testing of HGM by using a nano-indenter. As shown in Fig. 2.2, the initial loading segment is in linear while a horizontal portion in the curve followed, until the tip contacts the substrate, which shows an almost vertical line in the

Fig. 2.2 Typical curve of load versus displacement for a nano-compression experiment on single HGM of less than 10 μm .

curve. Their results also depicted a direct relation between diameter and load to failure of HGM.

Tryana et al. [22] studied the compressive property on the geometrical features of HGMs utilized a nano-indenter with a spherical tip and finite element method to investigate the development of stresses on a HGM through a uniaxial compression. The maximum principal stress distribution of outer top and inner bottom region has been drawn in Fig. 2.3, which indicated that larger stress was concentrated near the contact region of HGM with the spherical tip and HGM with the substrate. This is of great importance when estimating the HGM with flaw as only the contact area suffering the tensile stress during the compression. Similar findings and conclusions were achieved by Wei et al. through analytical solution of elastic hollow sphere at diametrical point loading [23].

Fig. 2.3 Maximum principal stress distribution in a HGM during the compression. (Units in 1×10^{18} Pa)

Fig. 2.4 Stiffness variations of tested microspheres at different diameters [22].

However, their experimental data such as the measured stiffness (shown in Fig. 2.4) showed large scatter which makes the results not so convinced, although they insisted a linear fitting curve between the stiffness and diameter of microspheres.

Zhang et al. [24] investigated the self-healing resin via epoxy–amine system in hollow glass microspheres. The diameter of used hollow glass bubbles was 63 to 90 μm and the fracture load for the self-healing glass bubble was around 7 mN subjected to a quite low rate loading.

The failure strength of the tested HGM is significant to investigate the mechanical properties of HGM. As the complexity of determine the strength of a single HGM, the crush strength of commercial HGM fabricated from 3M is tested through a isostatic crush test of a large volume of microspheres by using a modified version of ASTM standard D 3102-78, which is a standard testing for determination of isostatic collapse strength of HGM [25]. However, the engineers from 3M emphasized that the isostatic test is more suitable for qualify control than design application [26].

There are many kinds of stress testing for individual HGM. One unique tensile test was conducted at Los Alamos National Labs in the late 1970s [27]. They carefully bond individual HGM to two small brass rods and conducted the test by a dynamometer. Due to the sophisticate testing method, it is not practical to measure the strength of a large number of HGM to prove confidence of the data. A tensile burst test of HGM was also carried out at Los Alamos National Labs in 1978 [28]. They used helium to diffuse through the HGM in a constrained tube pressure vessel in a temperature of 350 $^{\circ}\text{C}$. Then decrease the pressure in the tube until the HGM busted because of the internal pressure. The pressure change is recorded upon the failure of HGM. The maximum tensile stress in the HGM was though the equation below.

$$\sigma = \frac{\Delta P \cdot d}{4t} \quad (2.1)$$

where ΔP is the differential of pressure, d is the diameter, and t is the shell thickness.

Bratt et al. [29] assumed the compression test of HGM a pseudo three point bend test and defined the strain and stress on the surface of tested HGM similar to the ASTM standardized flexure test in the following equation.

$$\sigma = \frac{3F(d/3)}{2(\pi d)t^2} = \frac{F}{2\pi t^2} \quad (2.2)$$

$$\varepsilon = \frac{6et}{(d/3)^2} = \frac{54et}{d^2} \quad (2.3)$$

where F represents the force, d represents the diameter and t represents the shell thickness, e represents the deflection. The Yong's modulus is defined as $E = \sigma/\varepsilon$.

The stress is actually calculated as the average pressure applied at the cross-section of the HGM in the equator. They also pointed out that the initial failure in the HGM occurred from the tensile force on the equator rather than from the point of contact of the

Fig. 2.5 Two dimensional representation of a thin walled microsphere illustrating stresses [25].

force, as can be seen in Fig. 2.5. That reveals when the force exceeds tensile strength of glass shell, a circumferential crack may happens around the equator of the single HGM, which is different from the failure pattern of solid or thick walled spheres.

Beside the quasi-static tensile, tensile burst, and quasi-static compressive tests, the dynamic responses of individual HGM were rarely been studied. Adel and Maurizio [30] theoretically discussed the static and dynamic buckling of HGM by using Donnell, Sanders-Koiter, and Teng-Hong nonlinear shell theories. Results indicated that Sanders–Koiter theory provides accurate estimates of the static critical load and dynamic buckling for a wide set of particle wall thicknesses while Donnell and Teng-Hong theories are only valid for very thin wall particles.

2.1.2 Other microballoons

Other hollow microspheres such as carbon microballoon are also widely used in forming synthetic foam. It is crucial to study the individual constituents to utilize them in design. Carlisle et al. [31] studied the compressive properties of individual carbon microballoon by using a modified nanoindenter. Compression curve for single wall carbon microballoons can be found in Fig. 2.6, which performs a similar trend with the compression of HGM. They insisted that the failure load was liner with pseudo-stiffness of carbon microballoon. Meanwhile, they found the flaw in the wall of microballoon may affect the compressive strength of microballoon, although the influence on compressive property is hard to be determined precisely. The compressive properties of carbon microballoon coated with bismaleamid were also carried out [32]. The results suggested

that the coating performed little influence on the compressive properties of carbon microballoons.

Other researchers investigated the compressive behavior of carbon microballon through finite element method [33]. Average stress distributions were calculated to provide a reasonable failure values for carbon microcapsules. They found the maximum bending stress occurred at the equator of microballoon. Carbon microballoon with hole in the wall was also studied which described that the hole acted as the stress riser and the stress concentration becomes more severe with the increase of wall thickness, as shown in Fig. 2.7.

The ceramic hollow spheres are also developed by many researchers [34]. Compressive properties of porous SiC hollow spheres with relatively thicker wall are tested using an in-house developed setup. The diameter and wall thickness for S1 type of specimens are 0.4 mm and 36.1 μm , respectively, while 0.51 mm and 81.6 μm for S2 type of particles. The load-deflection curve can be seen in Fig. 2.8, in which a sudden drop in the force can be found after the fracture of hollow spheres, which is different from that of HGM.

Silica nanoparticle-shelled hollow microspheres were generated by a microfluidic technique. Vertical crack can be found during the compression of the hollow spheres, as shown in Fig. 2.9. They also concluded that after the sintering, the strength of fabricated bubble increased more than one order of magnitude than no sintering samples. Different functional nanoparticles such as magnetic and semiconducting nanoparticles can be

introduced into the bubble shell to form functional light-weight material with tunable mechanical properties [35].

Fig. 2.6 Sample compression curve for a single wall carbon microballoon.

Fig. 2.7 First principal stress distribution around the hole in the shell of carbon microballoon.

Fig. 2.8 Representative load-deflection curve for SiC hollow spheres under compression [36].

The dynamic responses of other hollow microspheres were also rarely discussed. Few investigations are found from the dynamic response of big thin-walled hollow spheres. Dong et al. [37] investigated the dynamic response of hollow spheres with thin wall. Their results suggested that the buckling and deformation mode of spheres were sensitive to the strain rate as five-lobe polygonal dimpling at quasi-static loading and four-lobes polygonal dimpling under strike loading, as shown in Fig. 2.10. They also generate simple model to predict the relation between the applied forced and the deflection.

$$\frac{\delta}{t} = \frac{FRc}{8Dt} \quad (2.4)$$

where D is the plate bending stiffness, δ is the deflection, t is the shell thickness, c is the reduced thickness which can be obtained from $c/t = [12(1 - \nu^2)]^{-0.5}$. By using the generated model, the load-deformation curve was successfully predicted. However, the

predicted curve was not so accurate due to the large deformation and visco-elastic property of ball material in real application.

Zhang et al. [38] studied the dynamic behaviors of viscoelastic thin-walled hollow spheres. It was found that the input kinetic energy was approximately 2.5 to 3 times the deformation energy in quasi-static compression.

Dynamic compressions of big metallic thin-walled hollow spheres were carried out with finite element modelling. Apparent buckling during the impact can be observed due to imperfection of hollow sphere and friction effect during impact, as can be seen in Fig. 2.11a. The predicted deformation history of single hollow spheres can be found in Fig. 2.11b. It showed that local plastic deformation occurred near the impact point that resulted in the wall buckling failure close to the center line which indicated that the initial contact changed from point contact to circular contact. The ratio of wall thickness to diameter significantly affected the maximum stress. Moreover, higher impact velocity caused the crushing occur in the wall close to the impact side. Numerical data showed good uniformity with experimental results.

The contact between non-rigid sphere and flat rigid indenter was studied according to a fully elastic response assumption [39]. A convenient model was established to predict the compliance curve for elastic response of spherical specimen, as can be seen in the following equation.

$$\delta^3 = \left(\frac{4k_m}{3E}\right)^2 \frac{F^2}{R} \quad (2.5)$$

where k_m is the elastic mismatch factor that can be calculated through Young's modulus

Fig. 2.9 Fracture mechanism of characteristic silica nanoparticle-shelled hollow microspheres [40].

Fig. 2.10 Dimple profiles of hollow spheres at quasi-static and dynamic loadings.

and Poisson's ratio of indenter and specimen. Experimental test, simulation, and model analysis were carried out on compression of the unfired glass-ceramic elastic sphere. As can be seen from Fig. 2.12, the response from generated model fitted well with both experimental and finite element results.

Fig. 2.11 (a) Deformation of big metallic hollow sphere and (b) predicted deformation history of single hollow spheres at $v=8$ m/s impact [41].

Fig. 2.12 Compressive curves for generated model (solid line), experimental result (circle), and finite element result (cross).

2.1.3 Microcapsules

During the past decades, microcapsule was widely used to engage self-healing functionality into composites such as self-healing fiber-reinforced composite and self-

healing concrete [10, 42]. Self-healing enables repair of damages in materials partially or even completely without external intervention [43]. In order to fabricate healant-loaded microcapsules, different approaches and different materials have been investigated [44-48]. It is usually consisted of a single core and a layer of solid wall material in spherical shapes, as shown in Fig. 2.13.

Most researchers studied the quasi-static compressive behavior of the microcapsule [49]. Maximum load of microcapsules at quasi-static compression varied from 1 μ N to 60mN with the diameters varied from 40 μ m to 400 μ m [49-52]. Yang et al. [51] studied the polyurethane shell microcapsule used in self-healing area. By adjusting agitation rate, they can generate microcapsules with diameter of 40 to 400 μ m. The maximum load of fabricated microcapsules varied from 2 mN to 50 mN. Kim et al. [52] presented investigations on the mechanical performance of alginate-chitosan microcapsules, which had a diameter of 20 μ m. The applied force varied from 1 μ N to 10 μ N. Dintwa et al. [53] established numerical model to investigate compression test of individual cells. Their numerical model can be used to simulate single cell by adjusting the experimental variables and relevant parameter. Generally, the peak load of microcapsules under

Fig. 2.13 Typical schematic of microcapsule [54].

quasi-static compression varied from 1 μN to 60 mN with the diameters varied from 40 μm to 400 μm . The strength of individual microcapsule was quite weak due to the use of organic polymer or silica as capsule shell which would reduce the overall mechanical properties of composite.

The mechanical properties such as failure stress and load were found to vary with reaction time during the fabrication and the size of microcapsule and [55]. Keller et al. [49] studied mechanical properties of microcapsules using a capsule compression apparatus as shown in Fig. 2.14a. Although the peak load of tested microcapsule with larger diameter is higher than the smaller microcapsule (Fig. 2.14b), the smaller microcapsule has higher normalized failure strength, or more robust, in other words. The images during their tests were obtained which indicated that the shell wall of the capsule did not buckle during compression and the capsule remained effectively intact after failure, as shown in Fig. 2.14c.

However, the strength of individual microcapsule was still quite weak due to the use of organic polymer or silica as capsule shell which would reduce the overall mechanical properties of composite. A double-walled microcapsule fabrication method was developed, which consisted of one polyurethane (PU) shell and one poly(urea-formaldehyde) (PUF) shell [56]. A limited increase in compressive load of double-walled microcapsule than single wall microcapsule can be observed. As a result, a novel inorganic microcapsule should be developed which is much more robust than other traditional microcapsules.

Fig. 2.14 (a) Photograph of experimental setup; (b) typical load-displacement curves for microcapsules with 169 μm and 61 μm diameters; (c) images of a capsule during compression [49].

The dynamic responses of big solid spherical particles were studied by many other researchers [57-59]. Some of them insisted that there was no obvious difference in the failure patterns between static compression and dynamic impact for sphere samples, as samples fail either in three "orange-slices" or in two halves, as can be seen from Fig. 2.15. Meanwhile some researchers [57] concluded that different failure modes of different spherical particles fabricated from different materials were observed. More failure modes at low velocity loading were found when comparing with high velocity impact.

However, the dynamic properties of microcapsules have not been studied sufficiently. Wang et al. [60] and Li et al. [61] conducted high speed compression on single alginate and tomato mesocarp microcapsules by using self-developed micro-compression testers (Fig. 2.16). The maximum velocities of their high speed compressions were 0.2mm/s and 4.9mm/s, respectively, which were both far from enough to investigate the dynamic response of individual microcapsule. As a result, the investigation on the dynamic response of microcapsules is in great need.

The core-shell microspheres have been applied into matrix to obtain multifunctional purposes, such as light weight, good toughness, excellent impact resistance, etc. It is of great importance to discuss the polymer composites based on core-shell microspheres.

Fig. 2.15 Typical failure modes of solid spheres with different diameters [58].

Fig. 2.16 Sketch for micro-compression setup with high strain rate loading [60].

2.2 Polymer composites based on core-shell microspheres and their mechanical behaviors

2.2.1 HGM filled polymer

Fiber reinforced plastics have been developed rapidly because of their prominent mechanical properties. In which, glass fiber reinforced plastic (GFRP) and carbon fiber reinforced plastic (CFRP) have been regarded as the most prominent materials. Many researchers focus on developing stronger fiber layers to enhance the mechanical properties of composite. While others pay more attention on the possibility of modifying matrices by using inorganic fillers. In which syntactic foams and microsphere modified resin are well developed [62-64]. The difference between syntactic foams and microsphere modified resin is that syntactic foams have dramatically high content of microsphere.

In order to develop better particulate composites, a variety kind of inorganic filler materials have been tried, including rubber particles [65, 66], thermoplastic particles [67, 68], as well as hard particles [69, 70]. For all the filler materials, hollow microspheres have been investigated widely during recent years. That is because of its high specific strength, high specific stiffness, relatively high thermal stability, low thermal conductivity, and light weight, which are all important to enhance the mechanical properties of composites [71, 72]. As early as in the 1960s, particulate composites have been developed as buoyancy-aid materials in deep-sea industry [73].

After the initial development, HGM filled polymer has been widely used in many industries, like marine [8, 74], aerospace [9], and sports [6] industries. HGM filled polymer is comprised of hollow glass microsphere and polymer matrix. It has been widely investigated during recent years due to its high specific strength, stiffness, thermal stability, low thermal conductivity, and light weight, which are desirable properties of composites [71, 75]. Syntactic foam is one of such HGM filled polymer which has relatively high volume fraction of HGM [76].

2.2.1.1 Mechanism of improvements by glass microspheres

The introduction of glass microspheres can prevent the propagation of crack in the matrix, as a result, it will provide enhancement to the mechanical properties of the epoxy resin. There are basically five different failure mechanisms for composite with nano-fillers. They are crack bowing, crack deflection, debonding, pull-out, and fiber bridging, respectively [77]. The various toughening mechanisms was shown in Fig. 2.17. In

Fig. 2.17 Toughening mechanisms in composites: (a) crack bowing; (b) crack deflection; (c) debonding; (d) pull-out; (e) fiber bridging.

which, crack bowing, crack deflection, and debonding may be operative in a syntactic foam.

Crack deflection

The hollow microspheres disturb the crack front propagation and results in special propagations of the cracks, as shown in Fig. 2.17(b).

Crack bowing

Crack bowing mechanism is quite similar to crack deflection, as the microspheres may hinder the propagation of the crack to a non-linear crack front, as shown in Fig. 2.17(a). The crack bowing acts in a more indirect manner by decreasing stress intensity of the matrix, while intensifying the stress on the microspheres. The crack cannot propagate unless the microspheres have been crushed.

Debonding

The crack propagation between facial of resin matrix and glass microspheres will cause energy dissipation, which is similar to Fig. 2.17(c). The plastic dilation in the matrix will generate gaps around the debonded microspheres [78].

Crack Propagation via crushing of microspheres

When composite was suffered dynamic impact, it is possible that there is not enough time for the crack to seek paths that require lower energy, but to propagate by crushing the glass microspheres. This phenomenon is like fiber bridging, the crack propagates through glass microspheres and crushes them, as shown in Fig. 2.17(e).

2.2.1.2 Surface treatment of glass microsphere

The interface between glass microspheres and epoxy resin will weaken the whole properties of the composite. As a result, it is important to enhance the interfacial bonding by surface treatment of glass microspheres. Otherwise, the microspheres may act as flaws if they are not adequately secured in the matrix [79]. Furthermore, it is well known that the interaction between glass microspheres and epoxy resin is important in evaluating mechanical properties of the glass microsphere modified resin. 3M Corporation also

investigate the influence of surface treatment on mechanical properties of modified resin, as shown in Fig. 2.18 [80]. They obtain relatively modification under some specific conditions.

2.2.1.3 Compressive properties of HGM filled polymer

Gupta et al. investigate compressive failure features in syntactic foam material under 0.01s^{-1} strain rate, which can be regarded as quasi-static loading condition. Three regions have been divided. They are elastic region, plateau region, as well as densification complete, respectively, as shown in Fig. 2.19 [81].

Studies have showed that the deformation of syntactic foam is bending dominated no matter it is open or closed, which is to say, the topology of the cells causes the cell edges to bend during the application of force, which may make the HGM filled polymer

Fig. 2.18 Effect of surface treatment on mechanical properties.

compliant and slightly weaker, but has the capacity to absorb more compressive energy during testing [82].

Li et al. [83] studied the mechanical response of syntactic foam under different strain rates. Fig. 2.20(a) showed the deformations of syntactic foam at quasi-static compression. The loading tend to generate a shear deformation of the specimen with an approximate 45° shear direction. Meanwhile, Fig. 2.20(b) illustrates recorded deformation of syntactic foam under dynamic compression. Two obvious shear bands appear along the diagonal towards the inside of the specimen. Zone A exhibits property of plastic while zone B exhibits property of elastic, which are different with the phenomenon of specimen under quasi-static loading conditions.

An empirical constitutive model was established to describe the relationship between the peak stress and strain rate,

$$\sigma = \sigma_0(1 + C \log \dot{\epsilon}) \quad (2.6)$$

where σ_0 and C are material constants. A linear relation between the stress and the logarithm of strain rate was observed at specific volume fraction of glass microspheres. The respective parameters were also calculated by using the empirical model with high confidence bounds, as listed in Table 2.1.

Table 2.1 Estimated parameters for peak stress.

	Strain rate (s ⁻¹)	σ_0 (MPa)	C (s ⁻¹)	R^2
Peak stress	0.001-4000	28.42±1.19	0.0702±0.0093	0.94

With the aim of obtaining dynamic response of such porous material, Split-Hopkinson Pressure Bar (SHPB) can be used to apply high strain rate loading [84-86]. The Hopkinson Pressure Bar was first introduced by Bertram Hopkinson in 1914. He only used one metal bar to measure the stress pulse propagation [87]. Thirty years later, in 1949, Kolsky advanced two combined bars to test the dynamic response of specimens, which was well known as the SHPB [88]. SHPB mainly consists of a gas gun, a striker bar, an incident bar and a transmitter bar. Strain gauges are adhered to both incident bar and transmitter bar and linked to an oscilloscope to record the history of stress wave introduced strain in the bars [89]. Stress-strain curves of samples at dynamic loading can be calculated by using the wave theory in solids [90].

Fig. 2.19 Typical curve of stress versus strain for syntactic foam sample with high aspect ratio.

Fig. 2.20 Deformation of specimens at strain rates of (a) 0.001 s^{-1} and (b) 3500 s^{-1} .

Gupta et al. also used SHPB system to test failure mechanisms and mechanical properties of syntactic foams. They found the compressive strength in dynamic impact is usually higher than the quasi-static strength. The SHPB used was exhibited in Fig. 2.21. Basic mechanical properties such as engineering strain, engineering stress, and strain rate can be calculated by using the strain signal collected from the incident and transmitter bars and assuming 1-D elastic wave propagation in the bars.

$$\varepsilon_s(t) = -\frac{2C_0}{l_0} \cdot \int_0^t \varepsilon_R dt \quad (2.7)$$

where C_0 is the velocity of sound wave in the bars, ε_R represents the reflect strain and l_0 represents the initial length of tested specimen.

$$\sigma_s = E \cdot \frac{A}{A_s} \cdot \varepsilon_T \quad (2.8)$$

where A and E represent the cross sectional area of system bar and the modulus respectively, while A_s is the cross section of sample, and ε_T represents transmit strain.

$$\dot{\varepsilon} = -\frac{2C_0}{l_0} \cdot \varepsilon_R \quad (2.9)$$

2.2.1.4 Tensile properties of GMMR

There is a lack of studies focus on the tensile properties of HGM filled polymer, especially on epoxy glass micro-sphere composite. That may due to the neglect effect on mechanical properties when samples stand tensile loading. Gupta et al. [91] have tested sixteen different kinds of syntactic foams and adopted four kinds of hollow glass microspheres. They found that tensile strength decrease with the increasing volume fraction of hollow microspheres. There are 60-80% reductions in the tensile strength for all kinds of syntactic foams. They also observed the tensile modulus exhibit similar trend comparing with tensile strength. While the pure epoxy resin exhibits higher tensile modulus than the ones with hollow microspheres, there are some cases that tensile moduli show some increase for the HGM filled polymer, comparing with the pure epoxy resin.

Fig. 2.21 Split-Hopkinson Pressure Bar Equipment Setup [92].

2.2.1.5 Flexural properties of GMMR

Similar to the studies on the tensile properties of HGM filled polymer, there is only few studies focus on flexural properties of HGM filled polymer. As presented in Fig. 2.22 [74], the flexural strength generally decreases with the increase of glass microsphere volume fraction. This shows that the matrix plays most significant role in the flexural testing, which leads to reduction in flexural strength. The decrease of flexural strength is independent of the wall thickness of the glass microspheres. They also found that the moduli of all composites are higher than that of pure resin.

2.2.1.6 Unit cell in finite element method for HGM filled polymer

Many researchers conducted micromechanical analysis of particle-reinforced and fiber-reinforced composites based on unit cell [93-95]. Unit cell packing has been developed to simulate micromechanical property by using periodically boundary

Fig. 2.22 Experiment results of flexural strength of syntactic foams.

condition. Different periodic elements and unit cells (as shown in Fig. 2.23) were considered, such as diamond element, rectangle element, square element, and hexagonal element. A sharp corner in diamond element is not ideal and suitable for finite element calculations. Meanwhile it is not helpful to apply rectangle element of spheres with high volume fraction. Therefore, the hexagonal particle-matrix layout can be selected to conduct the finite element simulation, as shown in Fig. 2.24.

2.2.2 Other systems

Many other hollow microspheres filled in matrix were also developed for applications. Hollow carbon microsphere syntactic foam has attracted the interests of many researchers due to its thermal insulation, impact absorption and gas filtration properties [96, 97]. They found that the compressive and flexural strength of hollow carbon microspheres

Fig. 2.23 Various periodic elements and unit cells for hexagonal packing [98].

Fig. 2.24 A Voronoi cell for a close packed hexagonal packing [94].

syntactic foam decreased with the increasing hollow carbon microsphere content, which was attributed to the increasing void space from the introduced fillers [14]. The influence of coupling agent was also discussed which revealed that the coupling agent could increase the fracture toughness and maximum fracture toughness values at specific filler content.

The mechanical performances of ceramic hollow microspheres syntactic foam (usually with aluminium matrix) were investigated due to their potential in energy absorption applications [99, 100]. During the compression, linear elastic region, plateau region, and densification region have also been observed just as the HGM filled polymer, as shown in Fig. 2.25. The results revealed the ceramic hollow microspheres syntactic foam have the advantages of high strength, a flat plateau regime, and good ductility. Meanwhile, because of the high strength of individual ceramic microcapsule, the compressive strength of tested syntactic foam can increase up to 80% at low weight

fraction of hollow ceramic microspheres as shown in Fig. 2.26. However, a decrease trend was observed at high weight fraction of the ceramic fillers.

Fig. 2.25 Representative compressive stress-strain curve of fabricated ceramic hollow microsphere filled foam with 70% filler volume fraction [101].

Fig. 2.26 Compressive strength of hollow ceramic microspheres filled foam at quasi-static loading [102].

Fly-ash cenospheres are usually fabricated in thermal power plant from coal burning or heavy fuel oil combustion. It is byproduct from residual waste which can save cost and solve major disposal problems [103, 104]. The cenosphere can be mixed into polymers and metals to form cenosphere filled syntactic foam [105]. The compressive strength decreased with the increasing size and volume fraction of cenosphere at quasi-static loading [106, 107]. The fabricated foam exhibited distinct strain rate sensitivity which led to significant increase in energy absorption in high strain rate compression [108, 109]. However, Goel et al. insisted that the energy absorption and compressive strength achieved to maximum value at strain rate around 750 s^{-1} and come to decrease with strain rate further increase [110]. An empirical equation was obtained to predict the dynamic compressive property of fabricated foam.

2.2.3 Microcapsules modified polymers

Microcapsules are a kind of micro-containers with organic polymeric or inorganic shells, and various functional agents including solid agents, liquid agents or gas agents that can all be encapsulated by various methods [111]. During the past decade, microencapsulation techniques have achieved great development and have been applied widely to polymeric materials and cements for the preparation of intellectual materials [112, 113]. Self-healing concept was inspired by simulating the biological healing process once wounded. The encapsulated self-healing material can cure the cracks after the cracks break the microcapsule, as shown in Fig. 2.27a. The stress distribution close to a crack near the sphere mixed in a matrix and subjected to a tensile loading was

investigated through numerical method, as shown in Fig. 2.27b. The stiffness of the microcapsule may significantly influence the stress state and crack propagation. E^* is defined as the stiffness of microcapsule divided by the stiffness of the matrix. The crack is attracted by the microcapsule when $E^* = 1/3$, which is beneficial to the rupture and the healing process, while asymmetry stress distribution can be observed which can lead to an undesirable tendency of the crack to apart away from the microcapsule when $E^* = 3$.

Due to the wide application of microcapsules and microspheres reinforced polymers, researchers have studied the mechanical response of them with great interests. A lot of scientists [12, 43, 114] investigated the effects of concentration and size of the microcapsules on healing efficiency and fracture toughness through a tapered double-cantilever beam (TDCB), as can be seen in Fig. 2.28.

The addition of microcapsule can significantly toughen the pure epoxy and increase the absorbed energy to failure, as shown in Fig. 2.29. The fracture toughness increases with the increase of microcapsule concentration which indicates that the microcapsule can heal the fracture cracks dramatically.

Blaiszik et al. [115] reported the tensile properties of microcapsule (diameter around 1 μm) filled epoxy. A significant decrease trend in the tensile strength was observed with increasing capsule fill content. Rzeszutko et al. [13] also investigated the effect of microcapsule concentration on tensile properties of microcapsule filled polymer. The microcapsules fabricated had diameters of 180 μm . Both the strength and modulus of

Fig. 2.27 (a) The autonomic self-healing system; (b) Stress distribution in the areas surrounding a crack as it approaches a sphere mixed in a matrix with tensile loading [45].

polymer decreased with the capsule fill content. They also revealed that the behavior followed the model assuming the microcapsules behaved as voids.

However, in most cases, the importation of self-healing microcapsule may affect the basic mechanical properties (like tensile and compressive properties) of matrix

Fig. 2.28 Schematic of TDCB geometry (dimensions in mm) [114].

Fig. 2.29 Virgin and healed fracture toughness at different capsule concentrations [114].

material. Moreover, the microcapsule modified matrix material may suffer from impact from hail, dropped tools during maintenance, ballistic impact etc. in the application [116, 117], which makes the study of the strain rate effect of microcapsule modified matrix

material urgently. Nevertheless, the dynamic properties of microcapsule filled polymer have rarely been discussed.

2.3 Microcapsules with functional core materials

2.3.1 Functional microcapsule

Besides the above mentioned microcapsule with self-healing material, there are many other functional materials as the core material of microcapsule to achieve multi-functional properties in practical application.

Phase change material (PCM) is widely used in energy storage in many industries [11] due to its capacity to release and absorb the heat through the phase change process (e.g. absorbing heat from solid state to liquid state). Since the traditional microencapsulation technology requires hydrophobic core material, paraffin waxes are selected as the appropriate material to fit the role. Paraffin with different melting points can be used as the core material. Many scientists studied the thermal properties of PCM microcapsule filled in matrix [118-120]. The fabricated microcapsule with paraffin core can be mixed in the slurry, paint, or concrete as the matrix with different volume fraction. Results indicated that PCM microcapsule showed effective potentials for unused heat energy storage and latent heat storage.

Lubricant materials can also perform as the core material to enhance tribological property of polymer matrix. Yang et al. [121] and Li et al. [122] investigated tribological behaviors of polymer with ionic liquid core microcapsules. The polymer with

microcapsules showed much lower wear and friction coefficient than that of pure polymer.

Moreover, different drug material can be encapsulated in biology field as the drug delivery [123, 124]; fire retardants and fire extinguishers can be encapsulated as fire proofing microcapsule in building materials [125]; anticorrosive materials can be encapsulated as anticorrosion coatings in many fields [126, 127], and so on.

All the different core materials mentioned above can attribute the fabricated microcapsules to multi-functional materials. It is significant to investigate the mechanical properties of core shell structures with different core materials, especially for the liquid core which behaves good strain rate sensitivity, such as shear thickening fluid.

2.3.2 Shear thickening fluid and its applications

Shear thickening fluid (STF) is a non-Newtonian fluid as its viscosity increases with the shear load, which is also called a dilatant [128]. It was first developed by the mixture of cornstarch and water and described in Doctor Seuss's children's book series, as a magic object which can be transferred from stable liquid state to solid like state [129]. The properties of shear thickening fluid depend on Hamaker theory and Van der Waals force, and the shear thickening effect can exist stably. Shear thickening phenomenon occurs when the fluid transfer from stable liquid state to flocculation state.

Wagner et al. [129] investigated the shear thickening in colloidal dispersions. It was found that the hydrodynamic force decreased with increasing distance between particle surfaces. When the shear stress increases, the particles are organized in parallel flows, which will reduce its viscosity. But when the shear stress rises up to a specific value, the

hydrodynamic interactions between particles become dominate factors, which will lead to a difficulty in particles flowing and increase its viscosity in turn, as shown in Fig. 2.30. Because of the novel behaviors it can provide, shear thickening fluid has attract interest of many researchers and scientists [130, 131]. Also many companies and armies are investigating such material to develop body armor applications [132, 133].

It has been observed that there are many parameters that influences the properties of shear thickening materials, such as particle volume fraction, size, shape, distribution, material and interaction [134]. From Fig. 2.31, it is clear that the required critical shear rate increases with the increasing volume fraction of particles.

The particle shape can also influence the viscosity of suspension. The rod shape particle tend to exhibit more obvious shear thickening property, while sphere shape is considered difficult to form shear thickening phenomenon, as shown in Fig. 2.32.

Fig. 2.30 The state change of typical colloidal dispersion.

The dynamic response of STF in a restrained space has been tested by using a modified SHPB [135]. An obvious energy dissipation capacity of STF has been observed. Based on this distinct sensitivity to strain rates, STF has been applied to many different fields. It can be used in sandwich structures and foam materials to improve their impact resistance [136]. It can also be introduced as damper material [137] to investigate the vibration control, noise reduction, and fatigue endurance. Most researchers focused this novel material on body armors because of its promising impact resistance during impact and flexibility without impact load [138]. It has potential to balance the flexibility of the armor for normal body movements and the protectiveness of the armor upon high speed impacts. Plenty of investigations have been done and have demonstrated the feasibility about the application of STF in this area [139, 140]. Many researchers [141-143] studied the stab resistance of STF treated Nylon and Kevlar fabrics, and found that dramatic

Fig. 2.31 Viscosity vs. shear rate for 2:1 aspect ratio CaCO_3 -STF at various particle volume fractions [144].

Fig. 2.32 Influence of particle shape on shear thickening for particle volume fraction of 0.2 [128].

Fig. 2.33 (a) Knife impactor, (b) spike impactor, and (c) foam backing [141].

improvements in puncture resistance have been observed under both quasi-static spike penetration and high and low speed spike penetration tests. National Institute of Justice

Fig. 2.34 Quasi-static spike test results.

(NIJ) standard for stab testing was adopted which required standard knife, spike, and foam backing placed behind the tested target, as shown in Fig. 2.33.

Rosen et al. [145] fabricated shear thickening fluid by dispersing kaolin particles and silica particles in glycerol to prepare K-STF and S-STF shear thickening fluid. As seen in Fig. 2.34, fabrics with shear thickening fluid can support much bigger load compare with the pure fabrics and pure NIJ foam backing, even at quasi-static conditions.

Beside the quasi-static spike test, drop spike test has also been investigated by Decker et al. [141]. Dramatic improvements have been obtained in drop spike test under both high and low speed drop velocities. The modified Kevlar fabric exhibits significant improvement in puncture resistance over pure Kevlar fabric, as shown in Fig. 2.35. Moreover, significant energy dissipation in the damaged zone has been found.

The ballistic impact test on Kevlar woven fabrics infiltrated with colloidal STF has also been carried out by Kartsonakis [146] and Lee et al. [147, 148] through a fixture presented in Fig. 2.36. In order to demonstrate the property of such novel material, 244m/s penetration velocity was adopted. There is a dramatic enhancement for the modified Kevlar fabric in ballistic penetration resistance, since the penetration depth of impregnated target has been decreased so much, as shown in Fig. 2.37. The fabric with shear thickening fluid can dissipate much more energy than the pure fabric. Kalman et al. [149] used Poly(methyl methacrylate) (PMMA) particle to fabricate shear thickening fluid, which is softer than silica. They found that both kinds of shear thickening fluids can dramatically enhance the puncture resistance of Kevlar fabrics under high velocity

Fig. 2.35 Spike drop tests for pure Kevlar fabric and Kevlar with STF fabric.

ballistic testing (shown in Fig. 2.38), but relatively less improvement under low speed testing. Their conclusions are similar with research work from Park et al. [150].

The previous studies about the application of STF for body armors were achieved by directly immersing the fabrics into bulky STF [151]. However, this direct application of STF is restricted by its intrinsic properties. Firstly, the viscosity of STF is very high, which varies from several Pa s to several tens Pa s [128, 152, 153]. The high viscosity makes the direct application of it very difficult. Secondly, STF is colloidal suspension of highly concentrated nanoparticles dispersed in medium, and the shear thickening effect is very sensitive to the compositions. The direct infusion of STF into the fabrics will influence the local composition and the stability of the suspension attributed to the mutual interaction between the fabrics and the ingredients in the suspension with different physical and chemical properties. Besides that, the evaporation of the medium,

Fig. 2.36 Fixture for STF impregnated target in ballistic test [154].

Fig. 2.37 Comparison of front Kevlar layers for (a) unimpregnated, (b) impregnated target after ballistic test, and (c) penetration depth of two targets [147].

Fig. 2.38 Single-layer ballistic V50 results of fabric samples [149].

like ethylene glycol, will dramatically influence the rheological behavior, or even lead to the solidification of the mixture. And finally, due to the high hydroscopicity of ethylene glycol in STF, it is prone to be negated by the moisture in the surroundings if it is not well sealed. Although these factors will inevitably deteriorate the performance of the STF in the fabrics, especially for the long term, the principal purpose of previous investigations is to explore feasibility of using STF for impact resistant material. Very

few studies have been focused on how to increase the stability of the STF in the fabrics. Polyethylene film pouches were applied by Egres et al. [133] to seal fabric impregnated with STF to avoid the influence from external, this approach cannot prevent the influence of the fabric on the stability of the impregnated STF.

In order to overcome the above-mentioned disadvantages and increase the stability of STF during its service life when STF is used for the impact resistant materials, it is of great significance to explore the techniques to tightly package this highly viscous fluid. Encapsulation of the targeting materials is among one of the most promising technique to achieve this, because it cannot only solidify the substances for easy handling, but also isolate them to minimize the mutual influence with the surrounding environment. However, because of the high viscosity, the shear thickening effect, and the feature of multiple ingredients of STF, it is a big challenge for its encapsulation. Although the techniques are diversified for the encapsulation of solids and liquids with low viscosity [155], till now there are no investigations about the encapsulation of liquids with high viscosity like STF.

2.4 Summary and current issues

2.4.1 Summary

In this chapter, the research work by other researchers related to the current topic was reviewed. It was found that the core-shell structure microspheres and their polymeric composites were widely used in many fields. Core-shell structure microspheres were

introduced based on different shell and core materials. The mechanical properties of hollow glass microspheres, other microballoons, and microcapsules were investigated. The HGM filled polymer, microcapsules modified polymer, and other systems were reviewed. Many efforts were found focused on the HGM filled polymer or called synthetic foam due to its light weight, high specific strength, high specific stiffness, low thermal conductivity, etc. The mechanical properties of single microcapsule and microcapsules filled polymer were investigated by many researchers. The core material will also influence the properties of the core-shell structure. As one of the functional material, the properties of STF as well as its applications were described and it was found that the STF can be used as functional material to achieve the encapsulation research. As a result, the mechanical properties and the application of STF were reviewed in this chapter.

2.4.2 Summary and current issues

- Because of the technique limitation of testing setups, almost all the researches only focused on the low speed and quasi-static compression test on different core-shell microspheres. The development of relative mechanical testing apparatus is in great need. Meanwhile, the results were not convinced because of the large scatter due to the large variations of the obtained data [22]. Since the load capacity of single capsule is often very small, it is of great challenge to acquire the valid experimental data under both quasi-static and dynamic loadings.

- The fracture mechanism of HGM filled polymer should be investigated adequately. Moreover, there is a lack of studies focus on tensile and flexural performances of HGM filled polymer.
- Most of the researchers concentrated on the size effect and filler concentration effect of microcapsules filled polymer on the fracture toughness and healing efficiency by using TDCB. Few works have been found focused on other mechanical properties of microcapsules filled polymer. The introduction of traditional microcapsules in epoxy resin may decrease the mechanical properties such as strength and modulus due to the weakness of individual microcapsules. As a result, more studies should be carried out on the above mentioned issue.
- The fracture mechanism and mechanical model of core-shell microspheres modified polymer have not been studied sufficiently. It is significant to investigate the two factors to further understand the mechanism and provide recommendations of the design of such novel materials for other researchers.
- In order to increase the stability of STF during its service life when STF is used for the impact resistant materials, it is of great significance to explore the techniques to tightly package this highly viscous fluid. Encapsulation of the targeting materials is among one of the most promising technique to achieve this, because it cannot only solidify the substances for easy handling, but also isolate them to minimize the influence with the surrounding environment. However, due to the high viscosity, the shear thickening effect, and the feature of multiple ingredients of STF, it is a big challenge for the encapsulation. Although the techniques are diversified for the encapsulation of solids and liquids with low

viscosity [155], till now there are no investigations about the encapsulation of liquids with high viscosity like STF.

- Most of the simulation work was only focused on the mechanical properties of macro hollow spheres and solid spheres during their elastic deformation stage in two-dimensional and three-dimensional categories. Microcapsule with liquid core should also be investigated during the whole loading stage in both quasi-static and dynamic loadings using numerical method.
- Mechanical modeling on the core-shell microsphere was mostly constrained in hollow sphere and solid sphere while most of the mechanical modeling of particle reinforced composite was only focused on glass bubble reinforced polymer. The mechanical modeling of both individual core-shell microcapsules and their reinforced polymer at different loading conditions should be investigated adequately.

Chapter 3 The strain rate effect on the mechanical properties of hollow glass microsphere modified polymer

3.1 Introduction

Hollow Glass Microspheres (HGM) filled polymer were developed as buoyancy-aid materials in deep-sea industry as early as 1960s [73]. The introduction of glass microspheres can prevent the propagation of crack in the matrix. As a result, it provides enhancement to the mechanical properties of the epoxy resin. The crack bowing, crack deflection, and debonding are three different failure mechanisms for syntactic foam [14, 77]. Studies have implied that deformation mechanism of syntactic foam is bending dominated, in another word, the topology of the cells causes the cell edges to bend during the application of force, which may make the HGM filled polymer compliant and slightly weaker, but absorb more compressive energy during static testing [82].

It is of great importance to systematically investigate the mechanical response of HGM filled polymer with different volume fractions tests subjects to both low strain rate loadings and dynamic compressions. Specimens with glass microspheres of 0%, 5%, 7.5%, 10%, 15%, and 20% by volume have been fabricated. The optimized volume fraction of glass microspheres with better energy absorption capacity has been explored. The mechanism of fracture modes and crack propagations of HGM filled polymer under compression has been observed by using CT scan and Field Emission Scanning Electron Microscope (FESEM, Jeol, Model: JSM-7600F). Meanwhile tensile property and flexural property of HGM filled polymer were also been studied.

3.2 Materials and method

3.2.1 Materials and samples

The epoxy and hardener used were Epolam 5015 resin and hardener, manufactured by Axson Technologies. K1 glass microspheres, supplied by 3M Corporation, were selected and its basic properties can be found in Table 3.1 [156]. The ratio between epoxy resin and hardener was 100 to 30. As suggested by the manufacture, the pot life for 500g of mixed epoxy resin was 135 minutes at 25 °C and the cured density was 1.10g/cm³. The debris and broken glass microspheres were filtered out with water sink to guarantee integrity of spheres before usage. The mixture of glass microspheres and resin were stirred continuously but slowly by hand to ensure uniform dispersion of glass microspheres. After which, the suspension was put into a vacuum oven (MRC, Model: 1410-DIG) and a connected rotary vane vacuum pump (Vacuubrand, Model: RZ-2.5) were used to remove air bubble from the mixture. And it was stirred intermittently and slowly to avoid glass microspheres from floating to the top of the mixture.

Table 3.1 Properties of K1 glass microspheres.

Type	Crush Strength (MPa)	Density (g/cm ³)	Outer Diameter (µm)	Wall thickness (µm)	Radius ratio
K1	1.724	0.125	65	0.58	0.991

Fig. 3.1 (a) Aluminium molds and (b) silicone molds used for fabricating tensile, compressive, and flexural specimens.

In order to develop appropriate mold to fabric different shapes of specimens, Computer Aided Design (CAD) design has been applied by using AUTOCAD software. Eventually, different aluminium molds have been manufactured according to the details designed, as shown in Fig. 3.1a. Liquid state silicone was poured into the aluminium mold. After that, the aluminium mold together with the silicone gel liquid was kept in the oven for two hours under 60 °C. The tensile mold, compressive mold, flexural mold can all be seen in Fig. 3.1b.

The well dispersed suspension was poured to silicone gel molds which have been applied release agent (Pol-Ease 2300 Release Agent) on the surface to facilitate removal of solidified specimens. For the molds to fabricate tensile and flexural specimens, another

silicone cove plate was used to guarantee the planeness of the specimens. The specimens were cured for 24 hours in atmospheric temperature. After which, the specimens were heated in an oven (Binder, Model: ED-240) under 80 °C for 16 hours. Specimens with glass microsphere volume fraction of 0%, 5%, 10%, 15%, and 20% have been fabricated.

3.2.2 Experiments

3.2.2.1 Low strain rates testing

The compression specimens had a height of about 22mm and a diameter of about 9.9mm which were prepared by using cylindrical mold. The low strain rate specimens were then machined to a height of 15mm, while the dynamic specimens were machined to 6mm by using a lathe machine. The tensile specimens were in dog bone shape with a dimension of 4mm in width, 3mm in thickness, and 30mm in length in the center of the specimens. The flexural specimens were cut to 70mm×15mm×3mm by using a diamond cutter (Yasuda Plastic Sample Cutting Machine). The surfaces of all specimens were polished to guarantee the planeness. Instron 5569 Universal Testing Machine was carried out to process quasi-static compression tests, tensile tests, and flexural tests in accordance to the ASTM D695 standard, ASTM D638 standard, and ASTM D790 standard respectively, as shown in Fig. 3.2a, b, and c. An extensometer (Instron, Model: 2630-105, Static Extensometer GL) with gage length of 25mm was used to carry out the tensile tests. Three strain rates at 0.0005s^{-1} , 0.01s^{-1} , and 0.2s^{-1} have been applied for both low strain rate compression tests and tensile tests.

3.2.2.2 High strain rates testing

For the apparatus to process dynamic compression test, SHPB equipment was carried out, as shown in Fig. 3.2d. Two different lengths of aluminium bullets, 40mm and 82mm, were used for the tests. The strain rates that can be obtained from dynamic tests were approximately $1,250\text{s}^{-1}$ and $2,750\text{s}^{-1}$.

Basic mechanical data such as engineering strain, engineering stress, and strain rate can be calculated by using the strain signal collected from the incident and transmitter bars as shown in Equations 3.1 to 3.3. 1-D elastic wave propagation is assumed in the bars.

Fig. 3.2 Testing apparatuses of (a) low strain rate compression test, (b) tensile test, (c) flexural test, and (d) dynamic compression test.

$$\varepsilon_s(t) = -\frac{2C_0}{l_0} \cdot \int_0^t \varepsilon_R dt \quad (3.1)$$

$$\sigma_s = E \cdot \frac{A}{A_s} \cdot \varepsilon_T \quad (3.2)$$

$$\dot{\varepsilon} = -\frac{2C_0}{l_0} \cdot \varepsilon_R \quad (3.3)$$

where C_0 represents the sound wave velocity in the bars, ε_R represents the reflect strain and l_0 is the initial length of the specimen. A and E are the cross section of bar material and the modulus respectively, while A_s represents the cross section of the sample, and ε_T represents the transmit strain.

Dynamic equilibrium state was regarded as a significant factor to evaluate the reliability of SHPB testing method. Stress applied to the front end of the sample can be determined by the summation of stresses introduced by the incident and the reflection waves, while stress applied to the rear end of the sample is the stress introduced by the transmitted wave. Fig. 3.3 shows the rear end and front end stress during the process. As can be seen, force equilibrium is largely achieved which implies the data collected from SHPB is valid.

3.3 Results and discussion

3.3.1 Compression properties

Fig. 3.4a shows the typical curves of compressive stress versus strain for samples with different volume fractions at low rate loading with strain rate of 0.01s^{-1} . The compression process can be divided into three stages. The first stage has a linear

Fig. 3.3 Stress propagation during SHPB test.

relationship until an apex appears, corresponds to elastic behavior of HGM filled polymer. The second stage contains a drop followed by a plateau due to stable crack propagation or crash of glass microspheres, which contributes to energy dissipation. The third stage appears when a significant fraction of glass microspheres are collapsed and the composite is condensed until the final crush failure of the matrix.

Fig. 3.4b reveals the typical compressive stress versus strain curves for samples with different volume fractions at dynamic loading with strain rate of $2,750\text{s}^{-1}$. The process can also be divided into three stages just as the partition of process at low strain rate loading.

3.3.1.1. Volume fraction effect

It can be observed from Fig. 3.5a, the compressive strength of specimens decreases

Fig. 3.4 Typical curves of compressive stress versus strain for HGM filled polymer under strain rate of (a) 0.01 s^{-1} and (b) 2750 s^{-1} .

with the increase of V_f , which agrees well with the result from Bunn et. al [157]. Many researchers found that there is a liner relationship between compressive strength and V_f [158, 159]. Similarly, the results of this study indicate a strong linear relationship ($R^2 > 0.91$) for all the conditions as shown in Table 3.2.

Table 3.2 Analysis of linear relationship between compressive strength and V_f for specimens at low strain rates.

Strain Rate (/s)	Slope	Intercept	R^2
0.0005	-2.2859	93.081	0.94168
0.01	-2.5027	102.560	0.95576
0.2	-2.7956	115.320	0.91555

The theory for the decrease in compressive strength when the V_f increases is that the decrease of V_f of matrix will weaken the overall strength of samples as matrix is regarded as the main strained component. This theory is also suitable for the decrease of sample density with increasing V_f , as exhibited in Fig. 3.5b. It also indicates a linear relationship between density ρ and V_f , the relationship can be expressed as below. This shows that the strength of specimen is related to their densities. This phenomenon creates a possibility to take specimen density as one factor to analyze the strength of HGM filled polymer when comparing similar HGM filled polymer specimens under loading with similar strain rate, as shown in Fig. 3.5c. This proxy reduces complicated testing.

$$\rho = -1.6122V_f + 1.1641 \quad (3.4)$$

3.3.1.2 Strain rate effect

It can be observed from Fig. 3.6a, with the same V_f , the compressive modulus generally increases as the increasing strain rate ranges from $0.0005s^{-1}$ to $2,750s^{-1}$. However, such trend becomes weaker when the V_f has a larger value. Meanwhile, the

Fig. 3.5 (a) Compressive strength for HGM filled polymers at various V_f under low strain rates, relationship between (b) density of HGM filled polymer specimens with V_f and (c) compressive strength with density of HGM filled polymer specimens.

compressive moduli reduce with the increase of V_f under same strain rate. Similar to the results of low strain rate test, compressive strength of samples at dynamic loading decreases with the increase of V_f , which can be found in Fig. 3.6b.

The results of this study also indicate a strong linear relationship as $R^2 > 0.97$ for both conditions, as shown in Table 3.3, which is analogous to the trend from low strain rate tests. The strain energy per unit density can be achieved by integrating strain energy until

destructive failure strain and dividing it with specimen density. Fig. 3.6c reveals that in most cases the specimens with HGM can absorb more strain energy at low strain rate loadings (0.0005s^{-1} , 0.01s^{-1} and 0.2s^{-1}). Due to the relatively higher values of strain energy observed around V_f of 5% and 10%, meticulous V_f should be applied. As a result, specimens with V_f of 7.5% have been fabricated. Eventually samples with V_f of 7.5% show stronger capacity of stain energy absorption. That is due to microspheres absorb more energy during the compression but decrease the absolute strength of material. 7.5% can be regarded as an optimized volume fraction for energy absorption under low rate loading.

Compared to dynamic loading and low rate loading, as seen in Fig. 3.4a, higher peak load and plateau load are observed at high strain rate impact, which improves the strain energy absorbing capacity when HGM filled polymer subjected to high strain rate loading.

During low strain rate loading, the specimen suffers both hydrostatic pressure and shear stress, which cause localized damage in the specimen. The CT scan can detect the density variation of the material. However, the compression of the specimen may cause the failure of the filled hollow glass microsphere which can reduce the existed hollow

Table 3.3 Analysis of linear relationship between compressive strength and V_f for specimens at dynamic strain rates.

Strain Rate (/s)	Slope	Intercept	R^2
1250	-5.5170	205.38	0.98130
2750	-6.0936	217.51	0.97511

Fig. 3.6 (a) Compressive modulus at various V_f under different strain rates, (b) compressive strength at various V_f under dynamic strain rates, and (c) strain energy per unit density at various V_f and low strain rates.

area in the epoxy resin. Under such circumstance, the CT scan may not detect the microstructure of the crushed hollow glass microspheres. The HGMs can be seen as black dots in CT scan image, which are well distributed in original specimen as depicted in Fig. 3.7a. After the crush of microspheres and densification of the specimen, the black dots will shrink or disappear in CT scan image. Localized stress concentration will cause damage in the specimen during the loading, as shown in Fig. 3.7b. The damage zone is indicated by dash line and the shape is similar with the simulated results of Li et al. [83].

Fig. 3.7 Profiles of (a) original specimen and (b) tested specimen with V_f 5% at $0.0005s^{-1}$ strain rate loading from CT scan, (c) profile of specimen with V_f 5% at $2750s^{-1}$ strain rate loading from CT scan, (d) mechanism of the crack propagation in the specimen at (d) high strain rate loading and (e) low strain rate loading.

The hydrostatic pressure is the domain factor in the center area while the shear stress concentrates in the corner areas. Moreover, four shear bands with approximate 45° to the loading direction have been observed as indicated by four solid lines. The shear bands are similar with the theoretical analyses by Balch et al. [160] and Gupta et al [161].

The rate sensitivity of the matrix material is the determining factor of the rate sensitivity of the HGM filled polymer. During high strain rate loading, the crack is forced to propagate through the HGM, as shown in Fig. 3.7c (red arcs represent the debris of glass microspheres). The mechanism of crack propagation during high strain rate loading

has been explained in Fig. 3.7d. The energy will dissipate in the process, which can be regarded as one contributing factor to influence the energy absorbing capability of HGM filled polymer. That means, larger strain rate allows less time for the crack to seek low impedance paths which consumes less energy. Oppositely, the crack tends to bypass the HGM during low rate loading which will cause more glass microspheres debonding compare with the crack propagations under dynamic impact, as shown in Fig. 3.8a, b, and c. The mechanism of crack bypasses the HGM can be seen in Fig. 3.7e. On the other hand the crack passing through HGM will cause extensive crushing of HGM under dynamic impact, as shown in Fig. 3.8d, e, and f.

3.3.2 Tensile properties

HGM filled polymer has been regarded as an energy absorbing material under compression loading. However, its tensile properties have rarely been investigated. Fig. 3.9 reveals tensile strength of HGM filled polymer at three different low strain rates. As shown in Fig. 3.9, the tensile strength also exhibits strain rate sensitivity as the larger the strain rate, the higher the strength. This trend has also been observed in compressive strength, which reveals an overall improvement of strength. Meanwhile, it must be noted that the tensile strengths drop rapidly as the increase of V_f , which indicates that the introduction of glass microspheres dramatically deteriorates the tensile strength of epoxy resin.

The tensile modulus obtained was captured by using an extensometer. It can be seen from Fig. 3.10a, for most of the specimens with same V_f , the tensile moduli rise with the increase of strain rates, although they are all low ones. This trend is similar with that of

tensile strength. On the other hand, the tensile moduli decrease smoothly with the increase of V_f . Moreover, the tensile moduli do not show apparent reductions as

Fig. 3.8 FESEM micrograph of fracture surface of specimens with V_f 5% at (a), (b), (c) 0.0005s^{-1} and (d), (e), (f) 2750s^{-1} strain rate loading.

Fig. 3.9 Tensile strength of epoxy specimens modified with various V_f of HGM and tested at low strain rates.

Fig. 3.10 (a) Tensile modulus and (b) specific modulus of epoxy specimens modified with various V_f of HGM and tested at low strain rates.

tensile strengths exhibit. It reveals that the introduction of glass microspheres will not dramatically deteriorate the tensile modulus, and the tensile modulus does not change as much as tensile strength with the increase of V_f .

It must be mentioned that there is a decrease in specimen density as the increase of V_f . As a result, specific moduli of specimens have been drawn in Fig. 3.10b. There is a slight improvement of the tensile modulus for all the specimens with glass microspheres except a small disturbance at 15% V_f . The enhancement can be concluded the introduction will slightly improve the specific tensile modulus at low strain rate loading. That is due to the microsphere can decrease the density of material more than decrease the tensile modulus of material.

3.3.3 Flexural properties

It can be seen from Fig. 3.11a, the flexural strength drops rapidly with the increase of V_f . The relationship between flexural strength and V_f is also quite linear. However, it must be noted that, the deterioration rate for flexural strength is much higher than that for compressive strength and tensile strength, since the slope is more precipitous than that under the other two loading conditions. This may attribute to that flexural strength is more sensitive to the volume fraction of microspheres, which may deteriorate due to that samples under flexural test will take both compressive and tensile stress at the same time. All specimens were broke at the middle. The fracture surface of specimen with higher V_f could be smoother, while it could be rougher and uneven for the specimen with lower V_f and without glass microspheres, which indicates the brittleness of sample increase with increase of V_f , as shown in Fig. 3.12. Meanwhile, there is integrated debris with shapes of

inverted triangle fly off from specimens with lower V_f or without glass microspheres when specimens were fractured. The angle of such inverted triangle is approximately 45 degree for pure specimens and gets smaller with the increase of V_f , which indicates that the epoxy material is more likely to fracture under tensile and shear load instead of compressive load. Both the results of flexural strength and flexural modulus fit well with the conclusion from Tagliavia et al. [74].

As can be seen from Fig. 3.11a, the flexural modulus also decreases gradually with the increase of V_f . This is due to the fall in the content of bearing matrix. When specific modulus is considered, there is a slight increase from 5% to 20% of V_f , as shown in Fig. 3.11b. The specific modulus with 15% V_f is a little higher than that with 20% V_f , which are both larger than that of the pure specimen. As a result, the trade-off between flexural modulus and density is optimal at 15% V_f . Thus, GMMR could possibly offer superior resistance to flexural deformation.

Fig. 3.11 (a) Flexural strength of specimens at various V_f , (b) specific modulus for GMMR specimens at various V_f .

Fig. 3.12 Fractured (a) Pure Epoxy, (b) V_f 5% and (c) V_f 20% specimens.

Fig. 3.13 (a) Flexural modulus and (b) flexural strength of specimens without and with surface treatment.

Specimens with pretreated glass microspheres have also been investigated. As seen in Fig. 3.13(a), there is an increase in the flexural modulus for treated glass microspheres. This highlights that flexural modulus is depend more on the interfacial property. The

surface treatment improves the interfacial properties between glass microspheres and epoxy resin, which has actually improved the specimen's deformation resistance. However, as seen in Fig. 3.13b, a decrease in the flexural strength can be found for the surface treated specimen, this may due to stronger interfacial bond may cause glass microspheres crush in priority to the failure of epoxy resin under flexural loading, which will lead to more stress concentration and lower down the flexural strength of material.

3.4 Summary

HGM filled polymer absorbs more energy at V_f around 7.5% under low strain rate compression. Both specific tensile modulus and specific flexural modulus increase a bit comparing with the pure polymer matrix without the inclusion of HGM. HGM filled polymers exhibit strong strain rate sensitivity, and the sensitivity factor decreases with the increasing V_f . Different failure modes of specimens at lower strain rate compression and dynamic loading were observed. During low rate loading, the hydrostatic compression and shear stress perform as the superposition to cause localized damage in the specimen. The crack tends to pass through glass microsphere at high strain rate loading.

Chapter 4 Rate dependent behaviors of microcapsules and mechanical properties of microcapsule reinforced polymer

4.1 Introduction

During the past decades, microcapsule has been widely used to engage functionality including self-healing, drug delivery, phase change material, etc. into composites to achieve varieties of multifunctional materials during practical applications [10, 42]. However, in most cases, the introduction of microcapsule may decrease the mechanical properties of the composites because the strength of individual microcapsule was quite weak. However, Most researchers studied the quasi-static compressive behavior of the traditional microcapsule [49], few of them discussed the dynamic properties of microcapsules.

In this chapter, in order to comprehensively understand the influence of microcapsules in the matrix, the mechanical properties of not only the individual microcapsule, but also the microcapsules modified matrix should be investigated. In this chapter, three types of microcapsules have been fabricated through different methods, in which, two traditional microcapsules with silica shell and PUF shell were investigated while a robust microcapsule with metal shell has been fabricated successfully through chemical plating. Microcapsules reinforced epoxy resin was fabricated with the weight fraction of 0%, 5%, and 10%. Both quasi-static compression and dynamic impact tests of individual microcapsule and microcapsules reinforced epoxy resin were conducted to investigate their mechanical properties. Charge-Coupled Device (CCD) camera, high

speed camera, optical microscope (OM) and Scanning Electron Microscope (SEM, JEOL JSM-5600LV) were used to characterize the fracture mechanism of microcapsule and their reinforced epoxy resin.

4.2. Materials and method

4.2.1 Materials and samples

4.2.1.1 Synthesis of nickel-P shell-based liquid wax microcapsules

Nickel-based microcapsules with liquid core were fabricated successfully through electroless plating approach. Firstly, palladium particles were absorbed on the surface of emulsified liquid wax monodisperse droplets as catalyst (Fig. 4.1a). Secondly, metal alloy shell was generated through the chemical plating. The fabricated nickel shell microcapsules were washed and collected after 24 hour air-dry.

4.2.1.2 Synthesis of SiO₂ shell-based heptadecane microcapsules

The aqueous solution of Arabic gum was diluted with deionized water and the solution was kept in a beaker with a mechanical stirrer (Caframo, Model: BDC6015). Then heptadecane and Hexamethylene diisocyanate (HDI) were added into the solution to generate emulsion at 50 °C. After that Polyethylenimine (PEI, Mw~1300) solution was added into the emulsion system for two hours' agitation. Then the precursor microcapsules were dispersed into deionized water. Meanwhile, the hydrolysis of Trimethoxymethylsilane (MTTS) was carried out in hydrochloric acid solution (HCl, 0.1N) for 1h. The hydrolysis of MTTS was mixed in the system for 24 h. Finally, the

fabricated Silica microcapsules were washed and collected after 24 hours' air-dry for further study. The schematic process can be found in Fig. 4.1b.

4.2.1.3 Synthesis of poly (urea-formaldehyde) (PUF) shell-based heptadecane microcapsules

Microcapsules were prepared through in-situ polymerization in an oil-in-water emulsion, as shown in Fig. 4.1c. Some amount of aqueous solution of ethylene maleic anhydride (EMA) copolymer in a beaker was placed in a temperature controlled water bath. The solution was then stirred by the mechanical stirrer. Some amount of urea, ammonium chloride and resorcinol were dissolved in the solution. Heptadecane was added into the prepared solution to form an emulsion at 55 °C. After 4 hours reaction, the suspension with microcapsules was separated under vacuum environment. The separated PUF microcapsule were rinsed and dried for 24 h before testing.

Fig. 4.1 Schematic process of (a) nickel shell, (b) Silica shell, and (c) PUF shell based microencapsulation.

4.2.1.4 The fabrication of microcapsule modified polymers

Epoxy resin and hardener (Epolam 5015/5015) purchased from Axson Technologies were mixed together with a ratio of 100 to 30, as suggested by the manufacturer. The fabricated microcapsules were mixed into the resin with the mechanical stirrer until the viscosity of the resin is relatively high, which can prevent the sinkage of nickel shell microsphere and the floatage of Silica and PUF shell microcapsule. The suspension was degassed by using the vacuum oven which connected to the vacuum pump. The suspension was poured into cylindrical silicone gel mold with release agent and cured for 24 hour under ambient temperature. Then the suspension with the silicone gel mold was placed into an oven with temperature of 60 °C for 16 hours. Specimens with microcapsule weight fraction of 0%, 5%, and 10% were fabricated to investigate the influence of weight fraction of microcapsules. The cured cylindrical shape specimen had a height of about 25 mm and a diameter of about 7 mm. In order to keep relatively constant weight fraction of testing specimen, only the center part of the cylinder will be cut into two specimens with diameters of 7 mm and heights of 5mm by using a diamond cutter (Yasuda Plastic Sample Cutting Machine). Two end surfaces were polished using a polish machine before testing.

All the chemical materials used in the reaction process were purchased from Sigma Aldrich and used as received unless been clarified.

4.2.2 Experiments and testing

4.2.2.1 Quasi-static speed loading for microcapsule

As can be seen in Fig. 4.2a, the quasi-static loading setup is consisted of one load cell to measure the load during the compression. The punch head is connected to an actuator which can drive it with a constant velocity. Three constant test speeds at 1 $\mu\text{m/s}$, 10 $\mu\text{m/s}$, and 100 $\mu\text{m/s}$ were applied. A CCD camera with a stereo microscope (Zeiss, Stemi 2000-C) was used to take the images during the compression. The strain rate can be calculated by dividing the velocity of the punch head by the diameter of the microcapsule. The nominal strength can be defined as the measured load divided by the cross section area at the equator of the microcapsule, while the nominal strain is defined as the deflection of the punch head divided by the diameter of the microcapsule.

4.2.2.2 Impact testing of microcapsule

Fabricated impact loading setup contains one impactor which can drop freely in a transparent slide guide, one high sensitive quartz-piezoelectric force sensor (Kistler 9217A) with charge amplifier (Type 5015A1000) which can record the precise load during the impact, one high speed camera (Fastcam SA4, Photron) with the stereo microscope recording at 10^5 frames per second to capture the deformation and damage mode during the impact, as shown in Fig. 4.2b. Two impact velocities at 0.3 m/s and 2.2 m/s were applied to conduct the impact test by adjusting the drop height of the impactor. From the conservation of momentum we can assume that the velocity of the impactor is a constant value during the impact since the load during the impact is very low. This phenomenon was also confirmed as there was no obvious change of the velocity of the

impactor during the impact. As a result, the nominal strain can be calculated by dividing the diameter of the microcapsule from the initial impact velocity of the impactor. Meanwhile the strain rate is defined as the initial velocity of the impactor divided by the diameter of the microcapsule. The nominal strain is defined the same with that at the quasi-static loading. More than 10 samples were tested for each loading condition. An impactor stopper with a thickness of 170 μm and a 500 μm hole in the centre was used in the direct impact apparatus to ensure all samples can have the same deformation of approximately 100 μm and to avoid complete crushing of the microcapsules for further microstructural examination.

The calculations of the strain rate, the nominal strength, and the integrated failure strain followed the following equations,

$$\dot{\varepsilon} = \frac{V_i}{D} \quad (4.1)$$

$$\sigma = \frac{F_{max}}{A} = \frac{4F_{max}}{\pi \cdot D^2} \quad (4.2)$$

$$\varepsilon = \frac{S_{max}}{D} \quad (4.3)$$

where $\dot{\varepsilon}$ is the strain rate of specimen, V_i is the initial compressive velocity, D represents diameter of microcapsule, σ represents the nominal strength of microcapsule, F_{max} represents the peak load, ε is the integrated failure strain, and S_{max} is the failure displacement of microcapsules which is regarded as the displacement at peak load. From the pictures captured by high speed camera, it is found that the velocity of impactor in the micro impact apparatus remains constant during the compression of microcapsules.

Therefore, it is reasonable to assume that the microcapsules are subjected to constant strain rates both at the low and the high speed impacts [162].

4.2.2.3 Low strain rates testing of composite

Instron 5569 Universal Testing Machine was used to conduct the low strain rate compression, as can be seen in Fig. 4.2c. Two strain rates were applied which were 0.0067 s^{-1} and 0.2 s^{-1} . Grease was applied on both two surface of testing specimen to diminish the influence of friction between sample and Instron machine. Stress versus strain curve of tested sample was generated from the deflection and load captured by Instron machine. Four samples were applied for all low strain and high strain loading conditions.

4.2.2.4 Dynamic impact testing of composites

SHPB was carried out to process the dynamic loading, as shown in Fig. 4.2d. To amplify the captured signal from SHPB, aluminum bars were used. In order to form longer impact stress wave, the length for striker bar was 50 cm. Two pressures for the gas gun which were 40 psi and 100 psi were established to achieve lower strain rate loading and higher strain rate loading. The relative applied strain rates were 1100 s^{-1} and 3200 s^{-1} respectively. As described in Chapter 3, section 3.2.2.2, dynamic equilibrium state has to be achieved before processing the obtained data. The stress applied to the front end of the specimen can be calculated through the incident and reflection stress waves. The stress applied to the rear end can be obtained from the transmitted wave. As shown in Fig. 4.3, force equilibrium is largely achieved which indicates that the data collected from SHPB

is valid to use. All the data was proved to come to equilibrium state before further investigations.

Fig. 4.2 (a) Quasi-static compression setup and (b) dynamic impact setup for microcapsules and (c) quasi-static compression machine and (d) SHPB for microcapsules modified epoxy resin.

Fig. 4.3 Stress propagation during dynamic compression test.

4.3 Results and discussion

4.3.1 Characterization of fabricated microcapsules

The morphology of three types of microcapsule was studied through FESEM. All of them are in regular sphere shape as shown in Fig. 4.4a1, b1, c1. Meanwhile, smoother surface has been observed for nickel shell based microcapsule and relatively coarse

Fig. 4.4 (a1) nickel based microcapsule and (a2) its shell structure, (b1) silica based microcapsule and (b2) the shell structure, (c1) PUF based microcapsule and (c2) the shell structure.

Fig. 4.5 Size distributions for (a) nickel based, (b) silica based, and (c) PUF based microcapsules; (d) thermogravimetric analysis of three different microcapsules.

surface for silica microcapsule and PUF microcapsule due to different fabrication process.

The diameters of the microcapsules were measured by using the optical microscope. The size distribution of them can be found in Fig. 4.5a, b, and c. The average diameters of nickel, silica, and PUF based microcapsules are 236.6 μm, 226.6 μm, and 222.9 μm, respectively. The average diameters of them are relatively similar with each. Microcapsules with diameter from 210 μm to 290 μm were selected by the optical

microscopic to conduct the individual microcapsule tests, which can be regarded as spheres with similar size. The thickness for nickel, silica, and PUF shell based microcapsule are approximately 6.7 μm , 2 μm , and 3 μm , respectively, which are measured through SEM.

The Thermogravimetric Analysis (TGA) test has also been conducted. Fig. 4.5d shows the TGA curves for three types of microcapsules by using a TGA instrument (TGA, Hi-Res Modulated TGA 2950) with a nitrogen atmosphere. The temperature rise rate for all types of microcapsules is 10 $^{\circ}\text{C}/\text{min}$ till 350 $^{\circ}\text{C}$ and stop heating thereafter. It can be found that the inner wax core material will be burned up after 250 $^{\circ}\text{C}$ for both silica and PUF shell microcapsules. However, the metal shell will protect the core material since a decrease trend of weight loss of core material still remains at 250 $^{\circ}\text{C}$. This phenomenon indicates that the nickel shell encapsulates the core material well and protects the core material effectively. In other words, nickel shell based microcapsule shows good thermal stability. The weight fraction of the microcapsule is also investigated by analyze the weight loss of break microcapsule by using TGA. After analysis, the core material weight fractions for nickel based microcapsule, silica based microcapsule, and PUF based microcapsule are 30.01%, 88.02%, and 88.95%, respectively.

4.3.2. Mechanical properties of individual microcapsules

4.3.2.1 Strain rate effect

The mechanical property of individual microcapsule was investigated through dynamic and quasi-static setup for microcapsules. In order to obtain steadier testing result,

Fig. 4.6 Nominal strength of microcapsules as a function of strain rate.

more than 10 repeated tests were carried out and more than 8 valid data points are analyzed for each loading condition.

As can be seen from Fig. 4.6, the nominal strength for nickel based microcapsule is two orders higher than that of silica based microcapsule and PUF microcapsule, which indicate that the strength for nickel microcapsule is much higher than traditional microcapsules. For the nominal strength of all the three types of microcapsules, an increase trend can be observed with the increase of strain rate, especially at high strain rate. The nominal strength silica microcapsule is slightly higher than that of PUF microcapsule, also their absolute value is close to each other.

The integrated failure strain has been illustrated in Fig. 4.7. For all the three microcapsules, the integrated failure strain remains relatively constant at different strain rates. Meanwhile, the PUF microcapsule shows the highest failure strain while the nickel microcapsule shows the lowest, which reveals that the PUF material may provide higher

Fig. 4.7 integrated failure strains for three types of microcapsules at different strain rates.

Fig. 4.8 Failure images of (a) nickel, (b) silica, and (c) PUF shell based microcapsule during quasi-static compression; Failure progress of (d1-d4) nickel, (e1-e4) silica, and (f1-f4) PUF shell based microcapsule during the dynamic impact; Schematic of failure morphology and FESEM images of (d5, d6) nickel, (e5, e6) silica, and (f5, f6) PUF shell microcapsules.

toughness for the microcapsule filled polymer than the chemical synthesized silica and nickel material.

4.3.2.3 Fracture modes

The fracture images can be obtained by using the CCD camera. The results can be found in Fig. 4.8a, b, and c. A single macro crack from top surface to the end surface can be found in the nickel shell microcapsule at static loading. A similar crack that occurs from top to end can also be observed in the silica shell microcapsule. However, no obvious overall crack can be found in the PUF shell microcapsule due to better ductile properties of PUF material than silica and nickel materials. The dynamic failure process can be captured by the high speed camera with a time interval of 20 μ s, as shown in Fig. 4.8d, e, and f. The failure schematics are illustrated in Fig. 4.8d5, e5, and f5. The nickel shell based microcapsule may break into two main parts and several small pieces and cracks are also generated. The silica shell microcapsules may also fail into several parts. However, the PUF shell based microcapsule performs more concentrated failure area. These phenomena can be proved through FESEM images in Fig. 4.8d6, e6, and f6. Moreover, the failure for microcapsule under quasi-static loading is more uniform than that under dynamic loading for all the microcapsules. That is because the initial crack may not have enough time to response during high strain rate impact which can make the failure more localized. Meanwhile, the failure region is larger for nickel microcapsule than the region in Silica and PUF based microcapsule. The liquid inside microcapsule can eject out during the impact as shown in the figures.

Fig. 4.9 Typical compressive stress versus compressive strain curves of different microcapsules modified epoxy resin at (a), (b) quasi-static loading and (c), (d) dynamic loading.

4.3.3 Mechanical properties of microcapsule modified polymer

The typical compressive stress and strain curve at quasi-static compression can be found in Fig. 4.9a. The stress-strain curve at quasi-static compression can be divided into three stages. The first stage contains a linear relationship between stress and strain until an apex occurs. The second stage starts from a drop and remains a plateau thereafter. The drop is due to the stable crack propagation and the rupture of microcapsule. As shown in

Fig. 4.9b, the stress drops for pure resin sample and nickel microcapsule are quite similar, which are much higher than that in silica and PUF based microcapsules. It can be explained as nickel based microcapsule is much stronger than silica and PUF based microcapsule, which means that the fracture of nickel based microcapsule may cause more strength decrease of the overall epoxy composite than the other two kind's microcapsules. The third stage is the condensation stage till a catastrophic failure for the pure resin specimen, while only partial failure has generated for the nickel based microcapsule and the stress rises up again thereafter. However, for both silica and PUF based microcapsule, no obvious failure can be observed from the curve, the stress keeps rising only with small variations. This is because the introduction of microcapsules may reduce the propagation of macro cracks which may cause catastrophic failure during the compression.

Although the stress-strain curve obtained at dynamic impact can also be split into similar three stages, some differences can be observed from that of quasi-static compression, as shown in Fig. 4.9c. The drops for all specimens during the second stage are relatively smaller than that at quasi-static compression due to more tiny cracks may occur during impact which may reduce the strength loss than that of larger cracks. During the last stage, pure resin sample shows catastrophic failure as in quasi-static compression, while nickel, silica, and PUF based microcapsule samples show assuasive failures, especially nickel shell based microcapsule sample exhibits larger failure strain under impact.

Fig. 4.10 Elastic moduli of microcapsules modified epoxy resin.

The elastic modulus of specimen under quasi-static compression can be found in Fig. 4.10. As can be seen, the moduli will increase for all the specimens if the strain rate rises from 0.0067 s^{-1} to 0.2 s^{-1} . The modulus of nickel microcapsule specimen will increase with the increase of weight fraction. Different from the increase of nickel based microcapsule, a decline trend can be observed for moduli of silica and PUF based microcapsule specimen with the increase of weight fraction. The moduli are close to each other for silica and PUF based microcapsule specimen with same weight fraction and strain rate. As a result, the formula of adding nickel based microcapsule can increase the modulus of matrix resin material while silica and PUF based microcapsule can decrease the modulus and will deteriorate it if more silica or PUF based microcapsule has been introduced.

Fig. 4.11 Fracture surfaces of (a) nickel shell, (b) silica shell, and (c) PUF shell based microcapsules reinforced epoxy resin after dynamic loading.

4.3.4 Fracture mechanism

The fracture surface of three different microcapsule modified epoxy resin can be found in Fig. 4.11. Fig. 4.11a1 shows the OM images of the fracture surface of nickel shell microcapsule modified epoxy resin. Although obvious cracks can be observed in most of the microcapsules at the fracture surface, the break microcapsules remain integral shape. It indicates that the nickel shell based microcapsules can provide support even after their breakages, because the high strength of nickel shell may bear the load in a

restrained space condition during the impact. Fig. 4.11a2 and a3 show distinct partial breakage of the microcapsules as indicated by yellow arrows. However, microcapsule with no obvious breakage from the front view has also been found as indicated by blue arrow. Fig. 4.11b1 shows the OM images of fracture surface of silica shell microcapsule modified epoxy resin. Comparing with Fig. 4.11a1, different fracture scene can be observed as all the silica shell based microcapsules at the fracture surface have been broken since only part of the shell has been left. Fig. 4.11b2 and b3 illustrate that some of the cracks pass through the silica shell based microcapsule and break them into pieces, as indicated by the dash lines and red arrows, respectively. This phenomenon can be explained as during the impact test, the crack propagates to the microcapsule and passes through the microcapsule due to the lower strength of silica microcapsule than that of the matrix material. Similar phenomenon can be observed in the fracture surface of PUF shell based microcapsule modified epoxy resin. Cracks passing through the microcapsule and multiple breakages of microcapsules can be seen in Fig. 4.11c. As a result, the introduction of nickel shell may not reduce the load bearing capacity of epoxy resin too much while the introduction of silica and PUF shell based microcapsules may decrease the strength of the matrix material significantly.

4.4 Summary

One metal shell based microcapsule and two traditional shell based microcapsules have been fabricated successfully in the lab. Both quasi-static compression and dynamic impact on individual microcapsule has been carried out. The results indicate that the

strength of nickel shell based microcapsule is much more robust than the PUF and silica shell based microcapsules at different strain rates. More debris and cracks can be observed at dynamic impacts than that at quasi-static compressions, which indicates more energy can be dissipated during the impact.

Microcapsules modified epoxy resin with weight fractions of 0%, 5%, and 10% were manufactured and tested at quasi-static and dynamic compression loading. Nickel shell based microcapsules modified epoxy resin showed close mechanical strength to the pure epoxy even at different strain rates while both PUF and silica shell based microcapsules modified epoxy resin performed dramatic decreases in the strength comparing with the pure polymer. The nickel shell based microcapsule may remain a relatively integral sphere shape although most of them fractured at the fracture surfaces of the composite epoxy resin. However, a catastrophic failure of PUF and silica shell based microcapsule can be found at the fracture surfaces. Meanwhile, the cracks may propagate through the fractured PUF and silica shell based microcapsules during the crack propagations.

Chapter 5 Optimization of shear thickening fluid encapsulation technique and dynamic response of encapsulated capsules

5.1 Introduction

Shear thickening fluid (STF) is a colloidal suspension of nanoparticle, medium, and other necessary additives. It is a non-Newtonian liquid, and its viscosity increases rapidly when the shear rate increases, especially after a threshold shear rate. [129, 163] Attributed to this unique property, it has been adopted as the impact resistant material for body armors to balance the flexibility of the armor for normal body movements and the protectiveness of the armor upon high speed impacts. [139, 143, 164] However, the practical applications are restricted by its own physical and chemical properties, such as high viscosity, hygroscopicity, hard to handle or integrate into structures, etc. In order to overcome these disadvantages and increase the stability of STF during its service life, it is of great significance to explore the techniques for the packaging of this highly viscous fluid.

In this chapter, polystyrene-ethylacrylate (PSt-EA) particles with ethylene glycol suspensions are used as the STF since it shows good shear thickening behavior and lower initial viscosity during our past researches [165, 166]. Three different methods are proposed to encapsulate STF. The first method is interfacial polymerization between ethylene glycol and diisocyanate to form the shell in inverse emulsion. The second method is immersion of STF capsule fabricated through method one to form robust shell. The third method is the rapid formation of shell upon dropping the STF droplets into

certain solution. Quasi-static compression setup and impact apparatus for fabricated capsule were manufactured to characterize both quasi-static and dynamic properties of STF capsules fabricated through different methods. High speed camera and FESEM were employed to characterize the fracture mode and morphology of the STF capsules. The fabricated STF capsule has also been embedded into silicone gel to investigate the influence of STF capsule in the matrix. A drop weight setup was also manufactured to study the mechanical property of the STF capsule reinforced silicone gel.

5.2 Materials and experiments

5.2.1 Materials and samples

All the chemicals used in fabrication of original STF were purchased from Sinopharm Chemical Reagent Co., Ltd. Suprasec 2644, which is a diisocyanate pre-polymer based on methylene diphenyl diisocyanate, was obtained from Huntsman. The ultraviolet (UV) curable resin, NOA 61, was purchased from Edmund Optics. The other chemicals, including ethylene glycol, anhydrous toluene, anhydrous chloroform, dibutyltin dilaurate (DBTDL), and polyethyleneimine (PEI) with molecular weight (M_n) of about 600 (PEI-600), were supplied by Sigma-Aldrich, and were used as received.

5.2.1.1 The preparation of PSt-EA particles

Styrene, ethyl acrylate, acrylate, and distilled water were mixed and stirred for 30 min in a 500 mL flask. Potassium persulfate was added 10 min before the reactor was heated to 75 °C in a water bath for 6 h under a nitrogen atmosphere protection. After that, the

Fig. 5.1 PSt-EA nanoparticles in the original STF.

resultants were collected through centrifugation. Eventually, the PSt-EA nanoparticles were rinsed in ultrasonic cleaner and then dried in a vacuum oven at 50 °C.

5.2.1.2 The preparation of PSt-EA colloidal suspensions

The collected PSt-EA nanoparticles were mixed into ethylene glycol to prepare the STF. The mixed colloidal suspension was milled and rubbed for 24 h in a ball crusher to prevent the aggregation of the particles. The volume fraction of particles is 57.2%. Fig. 5.1 shows the nanoparticles in the original STF. The average diameter of the PSt-EA is about 350 nm.

5.2.1.3 Fabrications of STF capsule

Fabrication of STF capsule by a single step

The fabrications of the STF capsules can be found Fig. 5.2a. Briefly, the diluted STF containing 85 wt% original STF, 10 wt% ethylene glycol, and 5 wt% PEI-600, were instilled into the reaction solution containing 4.0g Suprasec 2644, 4.0ml toluene and

5.7ml chloroform, using a syringe with a needle of inner diameter of 0.61 mm. Later, the mixture was placed onto a shaker (Heidolph, Unimax 1010) and shaken gently for 60 min. After that, the capsules were rinsed with pure toluene for 3-4 times, and collected after the evaporation of the toluene for further treatment.

Coat the STF capsules with NOA 61

To enhance the robustness of the STF capsules, the collected STF capsules were further coated with another layer of UV curable resin, NOA 61, as shown in Fig. 5.2b. The obtained STF capsules described above were added into 25 wt% and 50 wt% NOA 61 solution in toluene to soak the resin monomers at the outer surface. After being immersed for about 5-10 min, the capsules were moved out from the soaking solution, and dried in the open air for the evaporation of the absorbed toluene. To avoid the agglomeration of the STF capsules after the curing of NOA 61, the STF capsules were separated from each other and placed on a Teflon substrate. Finally the treated STF capsules were subjected to UV exposure in an UV oven (UVF-chamber, Techno-digm) under 80% intensity for 60s.

Fabrication of STF capsules by a two-step method

The original STF capsules were synthesized using a two-step method by firstly instilling the diluted STF into immersion solution to stabilize the STF droplets, and then transferring to other reaction solution for the growth of the shell, as can be seen in Fig.

5.2c. In the first step, the diluted STF, containing 70 wt% STF, 25 wt% ethylene glycol, and 5 wt% PEI-600, was instilled by a syringe into an immersion solution containing 4.0g Suprasec 2644, 4 ml toluene and 1.7 ml chloroform, to stabilize the STF droplets by the instant reaction between PEI-600 and Suprasec 2644 to form the polyurea shell at the interface. After being gently shaken about 5-10 min, the immersion solution was removed and the stabilized STF droplets were rinsed with pure toluene to remove the residual chloroform. Later the stabilized STF droplets were transferred into 40 ml of toluene with 5.0g Suprasec 2644 and 0.01 wt% catalyst DBTDL in a 250 ml beaker on a programmable hotplate. Under gentle agitation of 150 rpm using a three-blade propeller, the system was heated up with a heating rate of 120 °C/h with targeting temperature of 40 °C, and further reacted for 2h. The STF capsules were rinsed with pure toluene for 3-4 times and collected for further treatment.

The reason why a two-step method is desired is to minimize the influence of chloroform on STF and increase the thickness of the shell by the reaction of ethylene glycol with Suprasec 2644. In the first step, the STF droplets were stabilized by the formation of the preliminary membrane around the droplets by the instant reaction between PEI-600 and Suprasec 2644 at the interface. In the second step, the shell was thickened by the reaction of ethylene glycol and Suprasec 2644 at elevated temperature under the catalysis of DBTDL.

The major function of chloroform in this study is to adjust the density. The usage of less amount of chloroform can minimize its influence on STF. The immersion solution with this combination have density very close to that of the diluted 70 wt% STF, so that

the instilled STF droplets can suspend in it, rather than float at the top nor deposit to the bottom, for the uniform growth of the preliminary polyurea shell.

5.2.1.4 Fabrications of STF capsule reinforced silicone gel

First of all, the silicone gel (Sylgard 527, Dow Corning, Midland, MI, USA) material part A (gel base) and part B (catalyst) were mixed adequately through a mechanical stirrer. And then the gas bubbles were removed from the mixed liquid in a vacuum oven

Fig. 5.2 Fabrication process for (a) single step method, (b) coat the STF capsules with NOA 61, and (c) two-step method.

(MRC, Model: 1410-DIG). After that, the STF capsules were dispersed into the prepared liquid material and the mixture was poured into a cylindrical mold with 13mm inner diameter. Eventually the STF capsules and liquid mixture with the plastic mold was heated at 100 °C for 30 minutes in an oven (Binder, Model: ED-240) to cure the silicone polymer. The height of the fabricated samples is about 5 mm. The volume fraction of the STF capsule is about 13.9%.

5.2.2 Experiments

5.2.2.1 Rheological measurements

A rheometer (AntonPaar MCR 301) with two flat plates was used to study rheological properties of fabricated STF with a constant shear rate increase at room temperature of 25 °C. The gap between the two plates is 0.3mm. The viscosity versus shear rate of fabricated PSt-EA suspension can be found in Fig. 5.3. The initial viscosity of the suspension is about 8 Pa s. The viscosity of the STF decreases a little bit with increasing shear rate at the early stage. However, a dramatically increase of the viscosity can be observed when the shear rate comes to 550 s⁻¹. Eventually the viscosity can rise up to 115 Pa s when the shear rate increases to 680 s⁻¹, which indicates a good shear thickening properties for the fabricated PSt-EA suspension.

Fig. 5.3 Viscosity of PSt-EA suspension as a function of shear rate.

5.2.2.2 Low strain rate compression testing

A punch head connected to a load cell was used to carry out the low strain rates compression of fabricated STF capsules, as depicted in Fig. 5.4a. The loading speed was controlled by an actuator with a controller which can record the accurate deflection of the specimen. The compression velocity is controlled as $10\mu m$ per second. Since the strain rate is defined as the compression velocity divided by the diameter of the tested specimen, the corresponding strain rate of the low strain rate testing is about $0.005 s^{-1}$. The nominal stress is defined as the measured load divided by the cross section area at the equatorial position of the capsule, while the nominal strain is defined as the deflection divided by the diameter of the capsule.

5.2.2.3 High strain rates impact testing

In order to evaluate the impact properties of fabricated STF capsules, a high strain rate compression apparatus is established, as shown in Fig. 5.4b. The apparatus consists of one epoxy polymer impactor with a mass of 1.343 g which can be dropped freely in a slide guide to generate different initial impact velocities. A low level force sensor with a charge amplifier was adopted to measure the load during the impact. A high speed camera with super LED lights is used to record the instant images during the dynamic compression. Four different impact velocities are applied, which are 1.5 m/s, 2.1 m/s, 2.55 m/s, and 2.95 m/s, respectively.

By using the momentum conservation equation, the velocity of the impactor during the impact can also be calculated as follow,

$$F_i \cdot T = m \cdot v \quad (5.1)$$

where F_i is the impact force, T is the corresponding time, m represents the weight of impactor, and v represents the impactor velocity.

Fig. 5.5a shows the calculated velocity variation of the impactor during a typical impact test. The velocity decreases during the impact due to the resistance of the capsule. At last the velocity diminishes to zero with small vibrations since the impactor stops at the holder. Meanwhile the deflection of the capsule can be integrated from the impactor velocity.

5.2.2.4 Drop weight testing

After the characterization of single capsule, it is necessary to evaluate the mechanical properties of STF capsule embedded in the matrix. As a result, a T-shape impactor made of aluminum material was manufactured which has a mass of 149 g, as shown in Fig. 5.4c. The aluminium plate with a diameter of 50 mm was fixed on an aluminium bar with a diameter of 12.7 mm. The impactor can be dropped freely through a plastic slide guide to guarantee the vertical impact. The drop velocity of the impactor is approximately 1.4 m/s. One polyvinylidene fluoride (PVDF) piezoelectric film with a dimension of 50 mm by 50 mm by 0.1 mm was placed on the surface of the holder to measure the impact

Fig. 5.4 (a) Low rate loading apparatus, (b) high rate loading apparatus, (c) drop weight setup, and (d) SHPB for the calibration of PVDF films.

Fig. 5.5 (a) Velocity of the impactor during one typical impact test and (b) calibration results of PVDF film by using SHPB.

loading during the test. The start point can be obtained by using the high speed camera. The lower PVDF film captured the whole loading history during the impact. The high speed camera was settled to capture all the information during the drop weight test as well.

The load can be calculated from the voltage obtained by the PVDF film in equation 2.

$$F = A_f \times V \quad (5.2)$$

where F represents the loading force, A_f represents the amplify factor, and V represents the voltage obtained from the PVDF film.

Fig. 5.6 Typical nominal stress versus nominal strain curve of STF capsule with different reaction time at (a) quasi-static loading and (b) dynamic loading.

The lower PVDF film was calibrated by using the SHPB. The PVDF film was placed between the incident and transmitted bars with no gap distance, as can be seen in Fig. 5.4d. The contact force between the incident and the transmitted bar was measured by the strain gauge adhered to the transmitted bar and the PVDF film. The loads captured by SHPB and PVDF film are shown in Fig. 5.5b. After the comparison, the amplify factor A_f of the PVDF film is calculated as 126. Moreover, different impact velocities of the striker are applied, which insists that the calculated value of factor A_f , 126, is suitable for all the applied cases.

5.3 Results and discussion

5.3.1 Influence of reaction time and the NOA 61

The impact resistance of STF capsule with different reaction time by using the single step method has been investigated. Fig. 5.6a shows the typical curve of nominal stress versus nominal strain of STF capsule with different reaction time at quasi-static compression loading. Fig. 5.6b illustrates typical stress strain curve of STF capsule under dynamic loading condition. The results indicate that the capsule with one hour reaction time shows good impact resistance and relatively higher quasi-static strength. In order to improve the easy handling of fabricated capsules, the influence of UV curable resin has been studied.

The typical nominal curves of stress-strain for different STF capsules at quasi-static loading can be found in Fig. 5.7a. A continuous rise of nominal stress can be observed

Fig. 5.7 (a) Typical nominal stress- nominal strain curves and (b) nominal strength of STF capsules with different content of UV curable resin in the shell and different reaction time at quasi-static loading condition; (c) typical nominal stress- nominal strain curves of STF capsule with different reaction durations and optimized content of NOA 61 in the shell and (d) typical nominal stress- strain curves of STF capsule with different content of NOA 61 in the shell and optimized reaction duration at impact loading condition.

during the quasi-static loading and a sudden crack occurred which caused the sharp decline of the stress. As described in Fig. 5.7b, the quasi-static strength of fabricated STF

capsule increases dramatically with the rise of the fraction of the NOA 61, which indicates that the introduction of NOA 61 can improve the basic strength of capsule that can make it easier to be handled. The nominal strength increases with the increase of the content of NOA 61. Especially, the peak stress almost rises 10 times when the content is 50% for samples with one hour reaction. The raise for samples with 30 minutes reaction is also significant although not as high as that with one hour reaction. That is because the capsules with 30 minutes reaction is still quite weak because the shell of the capsule is very thin comparing with the samples with one hour reaction. The thin shell capsule may absorb less NOA 61 during the infiltration which can weaken the strength of fabricated capsule.

Fig. 5.8 Strain energy density for STF capsules with different reaction durations and contents of UV curable resin at impact loading.

The typical strain stress curve of STF capsule with 50% NOA 61 with different reaction time at dynamic loading is manifested in Fig. 5.7c. The stress in the early stage increases dramatically with increasing reaction time. The peak stress will become lower if the reaction time increases. With the increase of reaction time from 5 minutes to 1 hour, the energy absorption capacity will increase from 0.095 MPa to 0.396 MPa (Fig. 5.8), which reveals that the 5 minutes reaction may not be sufficient to generate a functional liquid with strong shear thickening effect while 1 hour reaction time is able to generate good shear thickening fluid which absorbs more energy during the impact. Meanwhile, the dynamic responses of STF capsule with different dosages of NOA 61 have also been studied. It can be seen in Fig. 5.7d that the stress raises after the impactor contact the capsule. After that, the capsules are crushed and an obvious peak stress occurs due to the densifications of the capsules. The capsule with 25% NOA 61 shows similar peak stress with capsule without NOA 61 while the capsule with 50% NOA 61 shows lower peak stress. The 50% NOA 61 capsule can absorb a little bit more energy than capsule with no NOA 61 and capsule with 25% NOA 61 as shown in Fig. 5.8 due to the higher strength of the shell.

5.3.2 STF capsules with elastic shell

Although the polyurea/NOA-STF capsule performs good shear thickening behavior and good handling capacity. It still can be improved by forming an elastic shell capsule with higher quasi-static strength.

Fig. 5.9 (a) Repeatabile tests for STF capsule, (b) typical nominal stress versus nominal strain curves and (c) related strain energy density for STF capsule fabricated through two-step method at static and dynamic loading conditions, (d) strain energy density for STF capsule with different fabrication method, and (e) rebound velocities of the impactor at different drop velocities.

The STF capsule fabricated through the two-step method can recover completely after the impact since the nominal stress-strain curves of the same capsule under 1.5 m/s impacts fit well with each other, as depicted in Fig. 5.9a. Meanwhile, Fig. 5.9b illustrates nominal stress-strain curves of the capsules under different loading conditions. Under quasi-static loading, a catastrophic failure will happen after a steady increase of nominal stress. The strength of the capsule is about 160 KPa which is three times higher than that of capsules with NOA 61 resin. During the impact loadings, the peak stress will increase with the increase of impact velocity. However, the STF capsule can recover after every impact. The strain energy absorption capacity can be found in Fig. 5.9c. The strain energy absorption of STF capsule at impact loading increases dramatically, comparing with the capsule at quasi-static loading. It may increase almost 20 times for the capsule at 2.95 m/s drop comparing with quasi-static loading. Meanwhile the absorbed strain energy increases with the increasing impactor drop velocity.

The hardened UV curable resin increases the catastrophic failure strength significantly. However, it may not influence the strain energy absorption capacity so much since the strain energy density of hardened capsule is quite close to the original STF capsule, as shown in Fig. 5.9d. However, the STF capsules fabricated through two-step method absorb more strain energy since almost all the impact energy is absorbed by the capsule.

The impactor stopped at the holder immediately after the impact for the unhardened and hardened shell because the breakage of the shell will cause the leakage of high viscosity liquid. However, the impactor rebounds after the impact for the STF capsule

fabricated through two-step method. The rebound velocity increases as increase of initial drop velocity while the increase trend decreases, as shown in Fig. 5.9e.

5.3.3 Deformation and fracture modes of STF capsules

The impact process of STF capsule with 5min reaction and 50% UV curable resin can be found in Fig. 5.10a. The interval times for the pictures in the first three columns are all $400\mu\text{s}$. An apparent unstable state can be seen in Fig. 5.10a2 as the top and end surfaces of the capsule are not symmetrical. After the breakage of the shell of the capsule, the core liquid will spray out as illustrated in Fig. 5.10a4, which indicated that the STF suspension may not behave shear thickening effect during the impact loading. However, different

Fig. 5.10 Deformation of STF capsule (a) with 5 min reaction and 50% UV curable resin, (b) with 1 hour reaction and 50% UV curable resin, and (c) with elastic shell at the time interval of $400\mu\text{s}$.

impact process for STF capsule with 1 hour reaction and 50% UV curable resin can be observed. Equilibrium state can be found during the whole impact process. After the fracture of the capsule, the core material remains the solid shape as shown in Fig. 5.10b2 which indicate that the core material can provide sufficient shear thickening effect during impact. After 1.186 second, the STF liquid turned to liquid state and covered the damaged sample. A similar equilibrium state has also been found in elastic shell capsule. However, there is no damage during the impact and the impactor rebounds after the impact. The STF capsule recovers its shape slowly after removing the impact load as shown in Fig. 5.10c4 and eventually returns to its original sphere shape that can be retested.

5.3.4 Impact resistance of matrix with STF capsules

Since the STF capsules fabricated through two-step method shows excellent shear thickening effect. It is of great interests to investigate the impact resistance of STF capsules modified silicone gel. The matrix material with 13.9% STF capsule by volume has been fabricated and tested by using the self-manufactured drop weight setup.

The results can be found in Fig. 5.11a, which depicts the typical stress strain curve of pure silicone gel specimen and STF capsule reinforced silicone gel composite. The impact can be divided into two stages. The first stage is the lasting compression stage which may cause the continuous deformation of the tested specimen. The second stage is caused by the condensation of specimen which behaves a large peak stress. It can be seen

Fig. 5.11 (a) Stress Strain curves of pure silicone gel and silicone gel with STF capsules at drop weight tests; (b) strain energy density absorbed by pure silicone gel and silicone gel with STF capsules.

From Fig. 5.11b that the pure silicone gel exhibits lower first stage stress while the STF capsule reinforced silicone gel behaves significantly higher first stage stress, which indicate that the embedded STF capsule may help improve the impact resistance of matrix material. This phenomenon reveals that the STF capsule is hardened during the impact test. However, lower peak stress has been observed for silicone gel with STF capsule. This can be explained as the STF capsule may absorb more impact energy during the impact which will reduce the residual impact energy which generates peak

stress in the second impact stage. The strain energy density has also been calculated through the integration of the stress till the strain of 0.6. The results that found in Fig. 5.11c indicates that the strain energy density absorbed by the pure silicone gel is only 0.029 MPa while the STF capsule reinforced silicone gel composite absorbs 0.050 MPa strain energy density. In other word, the energy absorption capacity is improved by 70.16% after the introduction of STF capsules fabricated through two-step method which can be regarded as a significant modification in the purpose of impact resistance applications.

5.4 Summary

STF that consists of PSt-EA particles and ethylene glycol was fabricated in the lab to achieve an outstanding shear thickening effect. The STF was encapsulated by using three different methods for easy handling. Quasi-static compression and dynamic impact apparatuses have been established to investigate the strain rate effect on the fabricated STF capsules. The UV curable resin may increase the quasi-static strength and energy absorption capacity of fabricated STF capsules. The STF capsules fabricated through the two-step method show an elastic shell which can stand the multiple impacts without any damage. Meanwhile the related STF capsules exhibit better impact resistance than the STF capsules fabricated through other methods. Different deformation and fracture modes have been found for STF capsules fabricated through different methods. Different from STF capsules fabricated with UV curable resin, no damages can be found in STF capsules with elastic shell even under higher velocity impact. Moreover, the STF capsules can also enhance the impact resistance of silicone gel significantly. The energy absorption capacity has increased 70.16% after the introduction of STF capsules.

Chapter 6 Mechanical models for individual microcapsules and their polymeric composites

6.1 Introduction

Mechanical model is an important approach to evaluate the mechanical properties of materials and structures [167, 168]. The contacts between sphere and plate were discussed by many researchers as early as the 18th century. The elastic deformation and stress distribution of sphere during static compression were developed with many assumptions such as pure elastic deformation, elastical isotropic property, much smaller contact radius than the sphere radius, etc [169]. Mechanical models for individual microcapsules under static and dynamic loading conditions should be investigated systematically. Meanwhile, the mechanical models of core-shell microsphere filled composite are not studied sufficiently.

As a result, the mechanical models of individual microcapsules with PUF, silica, and nickel shell were studied by using Cowper-Symonds model. The mechanical models of different core-shell microspheres filled polymer with different filler dosages were also studied. Moreover, an empirical model with easily obtained parameters has been established, which can be used to provide reference for the design of HGM filled polymer. Besides that, an in-house program was developed to mesh the rhombic dodecahedron unit cell. Finite element method has been applied to study mechanical properties of hexagonal unit cell of HGM filled polymer.

6.2 Mechanical model for individual microcapsule

6.2.1 Cowper-Symonds model for individual microcapsule

The mechanical model of individual microcapsule can be studied through empirical equations. The Cowper-Symonds (C-S model) law is suitable for any set of stress strain data that maintains a shape of consistent curve at different strain rates [170]. Meanwhile, the model is applicable in both compressive and tensile experimental data [171]. It is also available in modeling impact in numerical studies by using commercial finite element software.

The dynamic scale factor K is described here to evaluate the rate dependence of the fabricated microcapsules. The dynamic scale factor K can be deduced from C-S model which can be expressed as the following equation [172],

$$K = 1 + \left(\frac{\dot{\epsilon}}{D}\right)^{1/q} \quad (6.1)$$

where $\dot{\epsilon}$ is the strain rate, D and q are constants for specific material in C-S model.

The compressive strength at loading speed 1 $\mu\text{m/s}$ was used as the reference strength σ_r . The dynamic scale factor under corresponding strain rate can be calculated by the following equation [173],

$$K_c = \sigma_c / \sigma_r \quad (6.2)$$

where σ_c is the strength under corresponding strain rate.

Fig. 6.1 Dynamic scale factors for three types of microcapsules at different strain rates.

Table 6.1 Parameters of C-S model for microcapsules.

Microcapsules	D	q	R^2
Nickel	36595.9	3.19	0.9996
Silica	1547.5	5.16	0.9919
PUF	166.9	5.44	0.9718

As shown in Fig. 6.1, all the curves fit well with the C-S model since all the R square values are greater than 0.97. The PUF shell based microcapsule shows the largest dynamic scale factor followed by the silica shell based microcapsule and the nickel shell based microcapsule behaves the lowest, which indicates the PUF shell based microcapsule behaves the highest strain rate sensitively. Based on the parameters obtained from Table 6.1, it is convenient to predict the dynamic strength of fabricated microcapsules at different strain rates which is of great benefit to practical engineering

applications. Thereafter, the contact force between compactor and microcapsule can be estimated in both dynamic and quasi-static conditions.

6.2.2 Modulus of fabricated microspheres

In order to evaluate the stiffness of fabricated microcapsule, the modulus can be investigated by using Hertz theory [174, 175]. The theory can theoretically analyze the contact force, stress, and deflections for a spherical object. It can also point out the maximum stress in the specimen at the edge of the contact circle between the specimen and the contact plate [39]. The contact force of sphere between two rigid flat plates can be expressed as the following equation,

$$F_c = \frac{4R^{1/2}}{3} \frac{E}{1-\nu^2} \left(\frac{d}{2}\right)^{3/2} \quad (6.3)$$

where F_c is the contact force, R , E , ν , and d are the radius, the modulus, the Poison's ratio, and the deflection of microcapsule, respectively.

The modulus of tested microcapsule can be calculated by using the Hertz model. Particularly, $E_r = E/(1 - \nu^2)$ is defined as the reduced modulus of the microcapsule. The microcapsules can be assumed as incompressible material during the compression [176], which is to say, the value of ν for the whole microcapsule structure can be defined as 0.5. After the calculation from the above mentioned equation, the moduli of nickel, silica, and PUF based microcapsules are 500.25 MPa, 3.52 MPa, and 2.65 MPa, respectively. The modulus of silica shell based microcapsule is a little bit higher than that of PUF shell based microcapsule due to the higher stiffness of silica material. The modulus of nickel shell based microcapsule is two orders higher than the other two

traditional microcapsules, which reveals that the nickel shell based microcapsule behaves dramatically higher stiffness.

6.3 Generalized model for core-shell microspheres filled polymer

6.3.1 Generalized model for microcapsules filled polymer

The strength change rate can be defined as the strength value of microcapsule specimen divided by that of pure resin specimen at the same loading condition. The change rates for microcapsule specimens can be found in Fig. 6.2. An approximate 5% increase can be observed for nickel based microcapsule for both 5% and 10% weight fraction. However, the change rate will decrease after strain rate 0.2 and the decrease values are less than 5% which remains relatively constant. As a result, the introduction of nickel based microcapsule may not influence the strength of matrix resin significantly. For both silica and PUF based microcapsule specimens, the strength will decrease dramatically since some of them are close to 25%. Moreover, decrease trends can be observed for them with increasing strain rate, which indicate that addition of silica or PUF based microcapsule will decrease the strength of matrix resin and its strain rate sensitivity.

As can be seen in Fig. 6.3, linearity between compressive strength and strain rate can be observed for all the specimens. The linearity can be expressed as the equation below,

$$\sigma = n \cdot \log \varepsilon' + A_c \quad (6.4)$$

Fig. 6.2 Variations of strength of different microcapsules modified epoxy resin.

where σ is the material strength, ε' represents the strain rate, n can be regarded as the strain rate sensitivity index, and A_c is the material constants. The parameters of linear models for different specimens are summarized in Table 6.2. Since all the residual squares are larger than 0.98, precise linear models are obtained to predict mechanical properties of microcapsule modified polymer.

The pure resin samples show largest strain rate sensitivity index which indicate that epoxy resin is more sensitive to strain rate than the microcapsules. Although the dynamic scale factor for nickel shell based microcapsule is lower than those of silica and PUF

Fig. 6.3 Relationship for (a) 5% microcapsule samples and (b) 10% microcapsule samples between compressive strength and strain rate (log).

based microcapsule, nickel based microcapsule modified polymer is more sensitive than the other two microcapsule modified polymer specimens. This can be explained as the strengths for silica and PUF based microcapsule are too low which may not influence the strain rate sensitivity as much as the nickel based microcapsule. However, the PUF based microcapsule modified polymer behaves higher strain rate sensitivity than silica based

microcapsule modified polymer sample due to the higher dynamic scale factor of individual PUF based microcapsule as describe in Fig. 6.1. Meanwhile, the introduction of microcapsule will influence the material constant A as the material constant for nickel shell based microcapsule polymer is close to pure resin while it is close for silica based microcapsule modified polymer to PUF microcapsule polymer. In general, the addition of microcapsule will affect both the strain rate sensitivity of resin and its material constant in different manners.

6.3.2 Generalized model for HGM filled polymer

It can be generally observed from Fig. 6.4 that the compressive strength under low strain rate loadings and dynamic loadings increases with the increased strain rate. This phenomenon could be explained with the rate sensitivity of HGM filled polymer material.

Li et al. [83] provided an empirical equation to evaluate the strength of syntactic foams under intermediate strain rates base on limited data. Their model is based on the linear relationship between compressive strength and the log of strain rate.

Table 6.2 Parameters for linear model of microcapsules modified epoxy resin.

Parameters	Pure resin	Nickel		Silica		PUF	
		5%	10%	5%	10%	5%	10%
n	20.20	18.65	18.19	15.54	14.99	16.31	16.39
A_c	137.84	137.94	136.55	121.19	107.36	121.87	109.11
R^2	0.9973	0.9873	0.9856	0.9969	0.9932	0.9847	0.9898

Fig. 6.4 Compressive strength for specimens at various V_f and strain rates.

Table 6.3 Analysis of results from specimens using empirical constitutive model.

V_f (%)	σ_0 (MPa)	C (/s)	R^2
0	150.08	0.1320	0.96987
5	125.48	0.1274	0.95351
10	101.81	0.1209	0.97460
15	87.759	0.1226	0.97940
20	74.264	0.1084	0.98618

$$\sigma = \sigma_0(1 + C \log \dot{\epsilon}) \quad (6.5)$$

where σ_0 and C are constant. Using this empirical equation, the corresponding coefficient of each assembly can be obtained as shown in Table 6.3.

Moreover, it is of practical interest to investigate the characteristics of two constant σ_0 and C . σ_0 exhibits a significant decrease with the increase of V_f , which indicates σ_0 is

very sensitive to V_f while C is less sensitive, which suggests C is an intrinsic material property of HGM filled polymer.

Strain rate sensitivity factor Σ can be defined as [177]:

$$\Sigma = \frac{\sigma - \sigma_q}{\sigma^*} \frac{1}{\log(\dot{\epsilon}/\dot{\epsilon}_q)} \quad (6.6)$$

where σ is the strength at a given strain rate, σ^* is the strength at given strain rate of 0.0005 s^{-1} , $\dot{\epsilon}$ is the strain rate, and the subscript q refers to quasi-static testing. The results for all specimens indicate strong strain rate sensitivity. Σ decreases with the increase of V_f which indicates that the specimens with lower HGM content show stronger strain rate sensitivity. Moreover, for all specimens, Σ becomes larger with the increase of strain rate, which indicates the strain rate sensitivity becomes more obvious when the strain rate is higher.

As described above, Li et al. [83] make the assumption of linearity between compressive strength and strain rate. However, as exhibit in Fig. 6.5, a quadratic model is more suitable to depict the relationship between strain rate and material strength, it can be expressed as $ax^2 + bx + c$, as shown in Table 6.4. As can be seen, such quadratic model could predict the compressive strength more precisely since $R^2 > 0.998$. Nevertheless, because of the decrease of sensitivity factor with the increase of V_f , it can be regarded as a linear model approximately when the V_f rises up to a specific high value. That may explain why Li et al. use a linear model to predict the compressive strength of syntactic foam which has high value of V_f . Moreover, the error bars in Fig. 6.5 are quite small, which indicates consistency and the repeatability of experiment results.

Table 6.4 Quadratic analysis of relationship between Compressive strength and strain rate for specimens at various V_f .

V_f (%)	a	b	c	R^2	Equations
0	2.2929	18.437	133.35	0.99907	$96.289 \times [1 + 0.0478 \times (1 + 0.498 \log \dot{\epsilon})^2]$
5	1.6914	14.965	113.14	0.99803	$80.031 \times [1 + 0.0444 \times (1 + 0.475 \log \dot{\epsilon})^2]$
10	1.3252	11.513	92.141	0.99999	$67.132 \times [1 + 0.0411 \times (1 + 0.480 \log \dot{\epsilon})^2]$
15	1.0383	10.133	80.183	0.99992	$55.468 \times [1 + 0.0413 \times (1 + 0.453 \log \dot{\epsilon})^2]$
20	0.7093	7.8147	69.468	0.99890	$47.953 \times [1 + 0.0347 \times (1 + 0.426 \log \dot{\epsilon})^2]$

Fig. 6.5 Relationship for specimens between compressive strength and strain rate (log) for various V_f .

The quadratic models at different V_f are summarized in Table 6.4. From the equation sets, a generalized quadratic equation can be established as follows,

$$\sigma = A[1 + B(1 + C \log \dot{\epsilon})^2] \quad (6.7)$$

where A is close to the quasi-static compressive strength of material and C is a constant. B can be further related to the volume fraction of glass microspheres as follows,

$$B = -0.0584V_f + 0.0477. \quad (6.8)$$

As a result, the empirical equation can be expressed in a simple form for predicting the dynamic strength of HMG filled polymers.

$$\begin{aligned} \sigma &= \sigma_0 [1 + (-0.0584V_f + 0.0477)(1 + 0.4664 \log \dot{\epsilon})^2] \\ &= \sigma_0 [1 + (0.0942\rho - 0.0619)(1 + 0.4664 \log \dot{\epsilon})^2] \\ &= \sigma_0 [1 + G_\rho \cdot f(\dot{\epsilon})] \end{aligned} \quad (6.9)$$

where G_ρ and $f(\dot{\epsilon})$ are the density and the strain rate related expressions respectively.

Mulliken et al. [178] developed a model to predict the yield stress of polymers over a wide range of strain rates based upon the Dynamic Mechanical Analysis (DMA) test data and many other parameters. Comparing with their model, the model developed in this study is more convenient and efficient since all the parameters used in the studied model are easy to obtain and operate.

6.4 Numerical study for HGM filled polymer

The modulus of core-shell microsphere can be investigated through numerical method. A three-phase rhombic dodecahedron unit cell model with perfect interfaces was developed on the base of the unit cell approach to simplify the simulation process. ABAQUS/Standard was used to simulate the modulus of specimen. Hexagonal unit structure was selected to simulate the overall structure, as shown in Fig. 6.6a. Periodic

boundary conditions was applied on the boundary of unit cell. Displacement equations [98] can be implemented into ABAQUS. The nodes of the original face and the image face were guaranteed the same relative position. An in-house program was developed to mesh the rhombic dodecahedron unit cell, which could ensure a uniform hexahedral mesh generation of the rhombic dodecahedron with a sphere in the center, as shown in Fig. 6.6b. The basic material properties are listed in Table 6.5. A uniform 1MPa tensile stress was applied on the unit cell to carry out the simulation.

Fig. 6.6c reveals the stress distribution after tensile test. As can be seen, the stress distributed on the circumference which is perpendicular to loading direction is much higher than that of the other areas.

Three different types of HGMs were simulated. The first HGM with diameter of 65 μm and thickness of 0.58 μm had the same dimensions with authentic K1 glass microsphere in the experiment. The second HGM (Simulation- 2) with diameter of

Table 6.5 Material properties in the simulation.

Material	Diameter (μm)	Thickness (μm)	Compressive modulus (GPa)	Tensile modulus (GPa)	Poisson ratio
K1 HGM	65	0.58	60	60	0.21
Simulation- 2	65	1.16	\	60	0.21
Simulation- 3	130	0.58	\	60	0.21
Epoxy	\	\	2.492	2.718	0.35

Fig. 6.6 (a) Hollow glass microsphere-epoxy layout and hexagonal unit cell, (b) uniform hexahedral meshes of a unit cell, and (c) stress distribution of hollow glass microsphere.

65 μm and thickness of 1.16 μm had a thicker wall thickness than authentic K1 glass microsphere but had same diameter. The third glass microsphere (Simulation- 3) with diameter of 130 μm and thickness of 0.58 μm had a larger diameter than K1 glass microsphere but same wall thickness.

6.4.1 Simulation of compressive modulus

The compressive modulus has been simulated at quasi-static condition by using unit cell approach. Fig. 6.7 shows the quasi-static compressive modulus of specimens at different volume fractions, a decrease trend can be observed in both experiment and simulation results. The values and trend of simulation result are both similar with the experiment result. Meanwhile simulation result is higher than experiment result, which is due to the perfect bonding between glass microsphere and epoxy in the simulation. In authentic samples, more voids will occur when the volume fraction is very high because the higher the volume fraction, the larger the viscosity, which makes the sample very difficult to be degassed before curing. Moreover, since the HGMs are very easy to be fractured, some of them will be crushed during the fabrication. Both the phenomena can be regarded as the reasons to explain simulation result is higher than experiment result.

6.4.2 Simulation of tensile modulus

The tensile modulus was also simulated at quasi-static condition by using unit cell approach. As shown in Fig. 6.8, both K1 HGM and Simulation- 3 show a decrease trend with the increase of volume fraction. The modulus of Simulation- 3 is smaller than that of K1 HGM under same volume fraction, due to the larger diameter of Simulation- 3

Fig. 6.7 Quasi-static compressive modulus of simulation and experimental results.

Fig. 6.8 Quasi-static tensile modulus of simulation and experimental results at different volume fractions.

will weaken the mechanical properties of both glass microsphere and HGM filled polymer. Oppositely, if the glass microsphere becomes much stronger, such as increase the wall thickness as Simulation- 2, the modulus will almost maintain constant with the increase of volume fraction. The simulation results of K1 HGM fit well with the experiment result and the experiment results are generally a little smaller than K1

simulation results, this is due to the perfect bonding condition in simulation as well as no voids, initial crack of matrix, and crush of glass microsphere.

6.5 Discussion and summary

The mechanical models of different microcapsules were studied. All of the individual microcapsules show significant strain rate effect and fit well with the C-S model. A modulus model was built up to evaluate the modulus of core-shell structure microsphere. The results indicated that the metal shell based microcapsule is two orders higher than that of traditional PUF shell based microcapsule and novel silica shell based microcapsule.

The mechanical models of different core-shell microspheres filled polymer were also discussed. Linearity between compressive strength and strain rate of different microcapsules modified epoxy resin can be observed. Moreover, nickel shell based microcapsule modified polymer is more sensitive than the other two microcapsule polymer specimens. For the HGM filled polymer, an empirical model with easy obtained parameters has been established, which can be used to predict the compressive strength of HGM filled polymer.

Numerical method was employed to investigate the modulus variation of HGM filled polymer with different filler dosage at both compressive and tensile loadings. In order to simplify the simulation process, unit cell approach and periodic boundary conditions were employed. An in-house program was developed to mesh the rhombic dodecahedron

unit cell. Different types of HGMs were simulated which revealed that simulation result fitted well with the experimental result.

Some recommendations for novel materials design:

The introduction of HGM and PUF and silica shell based microcapsules may reduce the absolute mechanical properties such as strength and modulus of the epoxy resin. The reduction of strength and modulus show an increase trend if the filler content keeps increase. Meanwhile, with the increase of filler content, the air bubble may increase due to the mixture process which will perform as the defects in the composite. These defects will reduce the overall performance of the composite. When the filler content increase to a certain level, it will be not easy to fabricate the core-shell microsphere filled polymer which may lead to an even harder process to fabricate the composite such as fiber reinforced plastics. As a result, relatively lower filler content should be applied to fabricate the functional core-shell microspheres reinforced polymer.

However, the importation of robust metal shell based microcapsule may remain or even increase the basic mechanical properties of the epoxy resin. Core-shell microsphere with smaller diameter and thicker wall thickness can increase mechanical properties of microspheres filled composite. As a result, robust metal shell based microcapsules with smaller diameter and thicker wall thickness will be preferable to fabricate the novel material.

The strain rate sensitivity of both the shell and core materials may influence the strain rate effect of fabricated novel materials. Robust shell material with higher strain rate sensitivity can be employed to fabricate the microcapsule which can improve both the

quasi-static and dynamic performance during the application. Moreover, functional core material with higher strain rate sensitivity (e.g. shear thickening effect) could be employed to modify mechanical properties of novel material even further during low velocity impact and ballistic impact.

Chapter 7 Conclusions and future work

7.1 Conclusions

This thesis focuses on the investigation of the mechanical behavior and associated failure mechanism of core-shell microspheres and core-shell microspheres modified polymer composite subjected to different strain rates and conditions, which can contribute to adequately understanding the mechanical mechanism for the different core-shell structures, mechanical properties and failure mode for core-shell microsphere modified polymer composite. Functional microcapsule with a core material of STF was successfully fabricated to diversify the application of microcapsules.

The mechanical properties of HGM filled polymer were studied in the report. HGM filled polymer absorbs more energy at V_f around 7.5% under low strain rate compression. Both specific tensile modulus and specific flexural modulus increase a bit comparing with the pure epoxy. HGM filled polymers exhibit strong strain rate sensitivity, and the strain rate sensitivity factor decrease with the increasing volume fraction. Different failure modes of specimens at low strain rate loading and high strain rate loading were observed. During low strain rate loading, the hydrostatic compression and shear stress perform as the superposition to cause localized damage in the specimen. The crack tends to pass through glass microsphere at high strain rate loading.

In order to investigate the mechanical response of different core-shell microcapsules, one metal shell based microcapsule and two traditional shell based microcapsules have been fabricated in the lab. Both quasi-static compression and dynamic impact on

individual microcapsule has been carried out. The results indicate that the strength of nickel shell based microcapsule is much more robust than the PUF and silica shell based microcapsules at different strain rates. The nickel shell based microcapsules are good to improve mechanical performance of composite structure for both quasi-static and dynamic loadings. More debris and cracks in all the microcapsules at dynamic impacts can be observed through the high speed camera than that at quasi-static compressions, which indicates more energy can be dissipated during the impact.

Besides that, microcapsules modified epoxy resin with weight fractions of 0%, 5%, and 10% were manufactured and tested at quasi-static and dynamic compression loading. nickel shell based microcapsules modified epoxy resin showed close mechanical strength to the pure epoxy even at different strain rates while both PUF and silica shell based microcapsules modified epoxy resin performed dramatic decreases in the strength comparing with the pure polymer. The nickel shell based microcapsule may remain a relatively integral sphere shape although most of them fractured at the fracture surfaces of the composite epoxy resin. However, a catastrophic failure of PUF and silica shell based microcapsule was found at the fracture surfaces. Meanwhile the cracks may propagate through the fractured PUF and silica shell based microcapsules during the crack propagations.

Due to the excellent shear thickening effect of STF which can absorb much more energy during impact than that at static loading. It is of great interests and challenges to encapsulate such viscous liquid. STF that consists of PSt-EA particles and ethylene glycol was fabricated in the lab to achieve an outstanding shear thickening effect and relatively lower initial viscosity. The STF was encapsulated by using three different

methods for easy handling. Quasi-static compression and dynamic impact apparatuses have been established to investigate the strain rate effect on the fabricated STF capsules. The UV curable resin may increase the quasi-static strength and energy absorption capacity of fabricated STF capsules. The STF capsules fabricated through the two-step method shows an elastic shell which can stand the multiple impacts without any damage. Meanwhile the related STF capsules exhibit better impact resistance than the STF capsules fabricated through other two methods. Different deformation and fracture modes have been found for STF capsules fabricated through different methods. Different from STF capsules fabricated with UV curable resin, no damages can be found in STF capsules with elastic shell even under higher velocity impact. Moreover, the STF capsules can also enhance the impact resistance of silicone gel significantly. The energy absorption capacity has increased 70.16% after the introduction of STF capsules.

The mechanical models of different core-shell microspheres and their polymer composite were discussed. All of the individual microcapsules show significant strain rate effect and fit well with the C-S model. Linearity between compressive strength and strain rate of microcapsule modified epoxy resin can be observed. Moreover, nickel shell based microcapsule modified polymer is more sensitive than the other two microcapsule polymer specimens. An empirical model with easy obtained parameters has been established, which can be used to predict the compressive strength of HGM filled polymer. Finite element method was established to investigate modulus of HGM filled polymer under both compressive and tensile loadings. Moreover, several recommendations for novel materials design were provided which can be used to provide reference for other researchers.

7.2 Novelty and Contributions

The contributions of this research are:

1. Traditional PUF shell based microcapsule, novel silica shell based microcapsule, and metal shell based microcapsule were fabricated successfully in the lab. The mechanical properties of these fabricated microcapsules were investigated individually by using the quasi-static compression setup and dynamic impact setup designed and developed in the lab for the first time. The mechanical properties and failure mechanism of microcapsule reinforced epoxy resin was also investigated.
2. The mechanical response of HGM filled polymer with different volume fractions of glass microspheres tests were carried out subjects to both low strain rate loadings and dynamic compressions, tensile tests, and flexural tests. The crack tends to pass through glass microsphere under high strain rate impact while tends to bypass the glass microsphere under relatively low strain rate loading.
3. The encapsulation of STF was successfully carried out for the first time by using three different methods for easy handling. The mechanical response including energy absorption capacity, deformation process, and failure modes of optimized STF capsule and STF capsule filled polymer were studied systematically.
4. Mechanical models of individual core-shell microspheres as well as their modified epoxy resins were discussed. An in-house program was developed to mesh the rhombic dodecahedron unit cell. Unit cell approach and periodic boundary conditions were employed in the numerical analysis to investigate the

modulus variation of HGM filled polymer with different filler dosage at both compressive and tensile loadings. Several recommendations for the design of novel material were provided.

7.3 Recommendations for future work

Although the mechanical properties of individual core-shell microspheres and their modified polymer have been investigated abundantly, further studies are still important and should be performed in the future.

1. Continuum mechanics theory and interaction between core-shell microspheres

The mechanical behavior of accumulated particles is a sophisticated and complicated problem during the practical applications. In 2005, Science journal listed “Can we develop a general theory of the dynamics of turbulent flows and the motion of granular materials?” as one of the 125 most compelling puzzles and questions facing scientists today and over the next quarter-century at the Science Magazine’s 125th anniversary [179]. The mechanical properties of packing microcapsule can be investigated through developed apparatus and finite element method. Continuum mechanics theory, interaction between each core-shell microsphere, and packing style should be taken into consideration.

2. Interaction properties between core-shell microsphere and matrix

As known from the HGM filled polymer, it is important to enhance the interfacial bonding by surface treatment of glass microspheres. Otherwise, the microspheres may act

as flaws if they are not adequately secured in the matrix. The interaction between glass microspheres and epoxy resin plays a key factor in evaluating the mechanical property of glass microsphere modified resin. The interfacial properties between the core-shell microsphere and the matrix will also influence the overall performance of composite dramatically. The interfacial condition between the microsphere and the matrix can be investigated through mechanical methods. Surface treatment of microspheres can be applied to enhance the bonding capacity between the two constituents to evaluate the influence of interfacial properties on the mechanical response of core-shell microspheres modified polymer.

3. Fiber reinforced composite incorporated with robust self-healing microcapsule

The robust metal shell microcapsule has been successfully fabricated through chemical plating method in this thesis. The mechanical strength of nickel shell based microcapsule filled epoxy remains a certain level comparing with the pure epoxy which is different with traditional self-healing microcapsule filled epoxy. Since the self-healing microcapsules are used in fiber reinforced composite, concrete, etc., the mechanical properties of fiber reinforced plastics may influence a lot by importing self-healing microcapsules. The variations on the mechanical properties as well as the self-healing efficiency should be evaluated for fiber reinforced plastics with both traditional self-healing microcapsules and robust metal shell microcapsules at varieties of loading conditions such as quasi-static and dynamic compression, tension, three-point bending, fracture toughness testing, and so on.

4. Optimization on the STF microcapsule and its application

STF with more significant shear thickening effect and lower initial viscosity can be developed by using different particle and solution system with surfactant to increase the interaction force between molecules. After the fabrication of high quality STF, new methods can be employed to synthesize STF capsule with smaller size and higher energy absorption capacity. In the interests of improving the fabrication efficiency and decreasing the diameter of synthesized capsule to micro-level, spray machine can be employed to generate amount of even microsphere shape liquid as the reaction solution. By this mean, the quantity and size of STF microcapsule can be adjusted through spray process instead of generate macro-sphere one by one through a syringe with a needle. The fabricated STF microcapsule can be embedded into many other polymeric systems rather than silicone gel to enhance the energy absorption capacity during impact which can diversify the applications of STF microcapsules.

5. Simulation modeling of individual microcapsule

The dynamic impact of individual nickel shell based microcapsule can be simulated by using ABAQUS/EXPLICIT. The finite element model can be found in Fig. 7.1a, which consists of two rigid plates, one spherical shell, and one spherical core. The quadrilateral shell mesh and hexahedral solid mesh are applied for the nickel shell and wax core materials, respectively, as shown in Fig. 7.1b and c.

Fig. 7.1 (a) Modeling of compression of individual microcapsule, (b) quadrilateral mesh for shell, and (c) hexahedral mesh for liquid core.

The basic mechanical properties of nickel material can be obtained from the literature reviews [180-182]. For the nickel material, the Young's modulus is 100 GPa; the Johnson-Cook hardening factor is 0.025; the fracture strain is 2%. The dynamic viscosity of liquid wax is tested by the rheometer, as can be seen from Fig. 7.2, which shows a relatively constant viscosity of 0.026 Pa s no matter the shear rate. The gap between the two plates is 0.3mm. The “us-up” model in equation of state is employed to study the liquid material. Seven impact velocities are applied which are 0.0001 m/s, 0.001 m/s, 0.005 m/s, 0.025 m/s, 0.25 m/s, 2.5 m/s, and 25 m/s, respectively.

The typical load deflection curves of individual nickel shell based microcapsule under impact at a strain rate around 10^4 s^{-1} and 10^5 s^{-1} can be found in Fig. 7.3a. The result revealed that the contact force between the impactor and the sphere and contact force between the sphere and the holder fitted well with each other at strain rate around 10^4 s^{-1} , which indicated that a stress equilibrium state was achieved during the impact. This phenomenon fitted well with the experimental results from direct impact and Taylor impact. In other words, it is accurate enough to measure the impact force during the

experiment by using the dynamic impact setup for microcapsules developed in the laboratory. However, the equilibrium state was not achieved when the strain rate rised up to 10^5 s^{-1} because of the short time for stress wave propagation in the specimen. The nominal stress was also investigated through FEM. As can be seen in Fig. 7.3b, the nominal stress from the simulation fits well with that from the experiment result. A similar trend is also observed which indicates the reliability of the conducted mechanical model for individual microcapsule.

Fig. 7.2 Rheology property of liquid wax at different shear rate.

Fig. 7.3 (a) typical load versus deflection curve of the compression at strain rate around 10^4 and 10^5 s^{-1} through FEM; (e) nominal stress versus strain rate through experiment and simulation.

Fig. 7.4 Fracture process and stress distribution of individual microcapsule during the (a) quasi-static compression, (b) dynamic impact, and (c) ultrahigh dynamic impact through simulation; fracture image for individual microcapsule after (d) quasi-static compression and (e) impact test.

The fracture processes of individual nickel shell based microcapsule under strain rate of 0.37 s^{-1} compression, $9,000 \text{ s}^{-1}$ impact, and $90,000 \text{ s}^{-1}$ ultrahigh dynamic impact through simulation are shown in Fig. 7.4a, b, and c with a time interval of 0.2s, $8 \mu\text{s}$ and $1 \mu\text{s}$, respectively. The stress concentrated at both top and end surface of the microcapsule at both quasi-static loadings and dynamic loadings. The fracture morphology through the simulation result is quite similar with that of individual microcapsule (FESEM image) after experiment since single overall crack (Fig. 7.4c) of microcapsule from quasi-static loading and many cracks and debris (Fig. 7.4d) from dynamic loading can be observed. Moreover, more cracks could be observed at ultrahigh dynamic loading (Fig. 7.4e) which confirmed our conclusion in the experiment part.

However, the simulation of quasi-static compression test with strain rate lower than 0.37 s^{-1} is not conducted because explicit method may consume too much time while implicit method with more accurate model with coupling effect between liquid and solid in finite element simulation should be established by using co-execution between Computer Aided Engineering (CAE) software and Computational Fluid Dynamics (CFD) software to solve the complex mechanical behavior. A continuous model of individual microcapsule should be established systematically through thorough experiments, finite element method, and mathematical analysis. Since the basic mechanical properties of fabricated nickel-phosphorus alloy are difficult to obtain. Micro-tensile test on such

fabricated material, including traditional shell material and robust metal shell material, could be conducted in both quasi-static and dynamic strain rate by using micro-testing setup that can be designed and developed in the future.

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List of Publications

Journal publications:

1. Zhang H, **Zhang X (Co-first author)**, Chen Q, Li X, Bao C, Sun D, Wang P, Yang J, Yang EH, Gong X. Encapsulation of shear thickening fluid for the application of impact resistant material, Journal of Materials Chemistry A, 2017.
2. Li X, **Zhang X (Co-first author)**, Zhang H, Yang J, Nia AB, Chai GB. Mechanical behavior of Ti/CFRP/Ti laminates with different metal composite interface properties, Composite structures, 163 (2017):21-31.
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4. **Zhang X**, Wang P, Neo H, Lim G, Malcolm AA, Yang EH, Yang J. Design of glass fiber reinforced plastics modified with CNT and pre-stretching fabric for potential sports instruments, Material & Design, 92 (2016): 621-631.
5. **Zhang X**, Wang P, Zhou Y, Li X, Yang EH, Yu TX, Yang J. The effect of strain rate and volume fraction on compressive and tensile properties of hollow glass microsphere filled polymer, Composite part b, 101 (2016): 53-63.
6. Wang P, **Zhang X (Co-first author)**, Hansen RV, Sun G, Zhang H, Zheng L, Yu TX, Lu G, Yang J. Strengthening and failure mechanisms of individual carbon nanotube fibers under dynamic tensile loading, Carbon, 102 (2016): 18-31.
7. Wang P, **Zhang X**, Zhang H, Li X, He P, Lu G, Yu TX, Yang J. Energy absorption mechanisms of the modified double- aluminum layers under low-

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8. Wang P, **Zhang X**, Lim G, Neo H, Malcolm AA, Xiang Y, Lu G, Yang J. Improvement of impact-resistant property of glass fiber-reinforced composites by carbon nanotube-modified epoxy and pre-stretched fiber fabrics, *Journal of Materials Science*, 50. 18 (2015), pp. 5978-5992.
 9. Wang P, Liu W, **Zhang X**, Lu X, Yang J. Enhanced fracture toughness of carbon fabric/epoxy laminates with pristine and functionalized stacked-cup carbon nanofibers. *Engineering Fracture Mechanics* 148 (2015), 73-81.

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1. **Zhang X**, Wang P, Yang EH, Yang J. Strain rate effects of compressive properties of hollow glass microspheres filled polymers, DAPS2015, 19-21 May, 2015, Singapore.
2. **Zhang X**, Wang P, Sun D, Yang EH, Yang J. Rate effect on compressive properties of micro metal alloy hollow spheres with liquid wax inside, ICILSM 2016, 22-26 May, 2016, Turin, Italy.
3. Zhou Y, **Zhang X**, Yang J, Lu G. Dynamic shear test on soft gels to mimic sports injury of human brain tissue, ICSST, 12-13 Dec, 2016, Singapore.
4. Li X, **Zhang X**, Yang J, Chai GB. High-velocity impact behavior of Titanium based fiber metal laminates (FMLS), ESHP2016, 25-28 September, 2016, Beijing, China.