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# Energy Dissipation and Stiffness of Polymeric Matrix Composites with Negative Stiffness Inclusions

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# ENERGY DISSIPATION AND STIFFNESS OF POLYMERIC MATRIX COMPOSITES WITH NEGATIVE STIFFNESS INCLUSIONS

by

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## Energy Dissipation and Stiffness of Polymeric Matrix Composites with Negative Stiffness Inclusions

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Typical structural materials have high stiffness to support a static load but offer low damping capacity. These materials easily transmit vibrations that can propagate through the structure, inducing fatigue and premature failure. Thus, structural materials with enhanced damping would increase the operating life of the structure and improve its performance. Here, we study a new class of metamaterials that exhibits simultaneously high damping and stiffness through the use of negative stiffness structures (NSS) embedded into a polymer matrix.

Traditional materials have positive stiffness behavior, meaning that the stress increases monotonically with the strain. Similarly, structures made from traditional materials exhibit a positive stiffness, so that the load increases monotonically with displacement applied. NSS structures, however, exhibit a region of negative slope in the force versus displacement response. It has been predicted that the incorporation of these mechanically activated NSS into a polymer matrix would improve the damping behavior, but this has not previously been demonstrated experimentally.

A significant part of this work was aimed at determining the geometry of the NSS and the material properties of the NSS and matrix required to achieve high damping. Thus several combinations of NSS geometries, matrix stiffnesses and NSS properties were considered. Analytical and numerical models were developed to guide the design of specimens. Experiments were aimed at producing specimens where damping performance was measured for NSS embedded in a polymer matrix. To conduct these experiments, macro-scale NSS were produced from stainless steel 17-4PH and the properties of the NSS and the NSS embedded in matrices were measured. Results showed that both the design of the NSS and the ratio of the stiffness of the NSS to that of the matrix are important for producing composites that offer simultaneously high damping capacity and high stiffness.

Another key challenge is producing NSS at a fine enough scale so that they can be incorporated into a polymer matrix to produce a composite damping material. Amongst potential manufacturing techniques, the multi-filament co-extrusion (MFCX) was selected because it has the potential to produce ceramic, metal or polymer micro-configured geometries in large quantities, quickly and at low cost. This process uses combinations of ceramic-polymer or metal-polymer compounds to reduce an initially macroscopic structure to the microscale while preserving the geometry of the cross-section. When the viscosities of the compounds are ideally matched, co-extrusion is capable of reducing the cross-section by a factor of up to 1000 times (e.g. well into the microscale). However, extensive characterization of the rheology of the compounds is required to achieve very large reductions for complex cross-section such as these. Preliminary results with co-extruded materials were presented to demonstrate the feasibility of this approach.

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#### **CHAPTER 1: INTRODUCTION**

Structural components that have high stiffness and that can simultaneously damp vibrations [1] [2] [3] have many practical applications [4] [5] [6] [7]. For example, helicopter rotors produce severe vibrations that must be damped to avoid fatigue and improve stability of the aircraft [1]. In this application, materials with enhanced damping performance reduce the required volume they occupy and therefore, the aircraft's overall mass. There are many other applications where the volume available for damping is restricted and both high damping and high stiffness are required [1] [3] [6] [7].

Polymeric materials exhibit the highest damping available in natural materials, whereas metals and ceramics exhibit the highest stiffness. Materials with a combination of moderate stiffness and damping performance can be achieved by producing a composite material made from mixtures of ceramics and polymers, but there is unavoidable trade-off in conventional composites between stiffness and damping performance, as shown in Figure 1.1. Lakes *et al.* [8] [9] and Haberman [10] have shown that this inevitable trade-off between stiffness and damping in conventional composites could be overcome by producing composites that incorporate negative stiffness (NS) structures into a matrix.



Figure 1.1. Young's modulus versus loss factor showing that NS composite materials (circled in red) allow combinations of stiffness and damping performance that cannot be achieved by natural or composite materials. [11]

The main objective of this research is to study the mechanisms that generate a simultaneous increase in both stiffness and energy dissipation when a NSS is embedded into a polymeric matrix. To understand this, important background information is presented in Chapter 2 that explains: two types of negative stiffness mechanisms; previous research confirming that macro-NSS can indeed damp vibrations and absorb impacts; detailed description of the specific objectives and a proposed manufacturing method to produce micro-scale NSS.

#### CHAPTER 2: BACKGROUND

#### 2.1 Thermally activated negative stiffness

Natural and conventional composite materials exhibit positive stiffness behavior, meaning that the force or stress increases monotonically with the displacement or strain. NS structures, in contrast, are designed to exhibit a region of negative slope in their force versus displacement response. Lakes *et al.* produced such composites by embedding  $VO_2$ inclusions into a Sn matrix and subsequently measured the properties of these composites as a function of the external temperature [12]. The negative stiffness behavior in these materials occurs because VO<sub>2</sub> undergoes a thermally activated phase transformation that results in a volume change. This alters stiffness, and thus, by controlling the temperature, the inclusions exhibit the desired behavior. Their experiments showed that, extremely high damping behavior was observed, in the strain range where the inclusions exhibited negative stiffness behavior. Figure 2.1 shows the response of the composite where the tan  $\delta$ parameter is a measure of the damping capability of a material and corresponds to the ratio between the loss modulus, E'' and the storage modulus, E'. Although this is a promising demonstration of the use of NS composite materials, there are practical issues with employing thermally activated phase transformation to achieve high damping. Alternative mechanisms for achieving negative stiffness are therefore desirable.



Figure 2.1. Damping response of a Sn matrix with VO<sub>2</sub> inclusions. Note the damping peak at the phase transformation temperature between 65°C and 66°C. Taken from [12]

#### 2.2 Mechanically activated negative stiffness

Structures containing monostable beams with reversible behavior, such as those shown in Figure 2.2, are a strictly mechanical alternative for achieving NS behavior. When a displacement-controlled force is applied perpendicularly to the beam, the force increases until reaching point (II). Beyond configuration (II), the beam then becomes unstable and buckles to the configuration (III) [13]. The region of the curve where this "snap-through" occurs is encircled in the figure and corresponds to the region where NS behavior is observed. Further compression of the NSS (at displacements greater than 2.6 mm) results in a force versus displacement response typical of a solid beam of the material selected, e.g. a return to the positive stiffness behavior. In Figure 2.2, the region where the NSS is defined to be "activated", is observed between a displacement of 1.2 mm and 2.6 mm (i.e. region where the NS behavior is obtained).



Figure 2.2. (a) Monostable beam with reversible behavior, redrawn from [13]. (b) NSS force-displacement response. Region where the NS behavior is activated is encircled.

Macro-scale NS structures that utilize the concept of monostable beams with reversible behavior have been modeled and experimentally demonstrated to damp vibrations and to absorb energy from impulsive loading [14] [15]. Correa *et al.* [16] [17] has manufactured macro-scale honeycomb structures that display regions of NS behavior and elevated energy absorption capabilities, as shown in Figure 2.3. Unlike conventional honeycombs that showed little recovery after their initial plastic collapse, NS honeycomb structures exhibited reversible behavior that allowed them to be used multiple times.



Figure 2.3. NS honeycomb manufactured using laser selective sintering. Taken from [16]

Kashdan *et al.* [15] demonstrated that NSS can be used dynamically to isolate vibrations. These authors fabricated the macro-scale structure shown in Figure 2.4, which allowed the compression and buckling of the horizontal beam by displacing the left wall inwards. The structure was placed on a shaker table and sensors were used to compare the

input and output accelerations, confirming that the structure was able to damp vibrations effectively.



Figure 2.4. Negative stiffness structure fabricated using nylon. Taken from [15]

Research on NSS was extended to composites by Klatt *et al.* [13] where structures containing 4 NS elements each, were modeled to understand their behavior inside a matrix and the overall composite response. The NS behavior was modeled assuming a structure that contained two materials with different thermal expansion coefficients. Partial buckling was predicted when the in-plane compressive residual stresses induced on the beam during cooling after the sintering process was sufficiently large. Figure 2.5 shows the proposed inclusion and FEA predictions showing the buckling of the beam.



Figure 2.5. NSS to be placed in a matrix. as proposed by Klatt et al. Taken from [13]

The main objectives of the current study include: (I) Using analytical and numerical models to study the combinations of NSS, specimen geometries and material properties that result in large energy absorption. To accomplish this, a model system consisting of a single mechanically activated NSS is considered. (II) Experimentally validate this approach by testing specimens quasi-statically with the NSS placed in parallel with the matrix. (III) Extending the modeling and experimental validation to samples where the NSS is fully embedded in the matrix and (IV) demonstrating the viability of manufacturing micro-scale NSS using MFCX with a design similar to the one proposed by Klatt. [13]

#### 2.3 Micro-filament co-extrusion, MFCX

To manufacture micro-scale NSS, the MFCX process was selected, which typically has been employed with compounds consisting of ceramic powders contained within a polymeric binder. Several compounds, each containing the desired powder composition, are then assembled into a square-section feed rod, as shown in Figure 2.6.



Figure 2.6. MFCX flow diagram.

Regions of the structure that are to remain hollow are produced using a compound containing carbon powder (shown in black) and the region that makes up the structure is made from the powder of the desired material and is shown in gray. The feed rod is then heated to reduce its viscosity and then extruded through a die that reduces the cross sectional area while retaining a self-similar cross-sectional geometry The parts are subsequently sectioned, heated to pyrolyze the polymer, and then heated further to sinter the powder into a solid object to produce large quantities of miniaturized parts that retain the cross-sectional geometry of the original part.



Figure 2.7. Schematic of the extrusion chamber used for capillary rheometry and MFCX.

A schematic illustration of the extruder is shown in Fig. 2.7. It consists of steel extrusion chamber and steel extrusion die. The feed rod is placed inside of the extrusion chamber and a brass piston is used to force the feed rod through the die. The extrusion die is heated to melt the polymer and produce a viscous compound. The extrusion chamber is cooled using a copper coil connected to a heat exchanger. Experiments confirmed that cooling of the chamber is required to prevent distortion of the feed rod prior to the entrance into the die.

After extrusion, the extrudate is cut into shorter sections and reassembled into a square that has the same dimensions as the extrusion chamber to make a new feed rod, which is then extruded again. This process can be repeated several times to obtain the desired size scale. The minimum feature size in the extrudate is limited by the grain size of the powder, as shown in Figure 2.8. The typical minimum feature size that has been demonstrated in the literature is close to 10  $\mu$ m. Smaller features could in principle be obtained if finer powders were used and deagglomeration issues were resolved, which is not a trivial task.



Figure 2.8. a) Extrudate die cross section showing the MFCX flow pattern. b) Example of the cross-section of an extrudate after 1 and 2 reduction steps. Taken from [18]

Once the desired cross-section reduction is obtained, the polymer and carbon black are removed through pyrolysis by heating the specimens in air to  $600^{\circ}$ C, producing water, CO and CO<sub>2</sub> as byproduct gases. The structures are then sintered directly to produce specimens with high density features, while retaining the void space left by the carbon black compound.

It is important to note that MFCX has been previously used mainly to coextrude ceramic microstructures since metal-polymer compounds can in some cases cause catalytic decomposition of the polymer during debinding or during compounding [19], which can result in the release of toxic vapors and/or cause fires. Halloran *et al.* used an alternative method to produce metal structures by coextruding NiO and then reducing the ceramic in a hydrogen atmosphere in order to obtain metallic nickel structures with large ductility [20], as shown in Figure 2.9.



Figure 2.9. Example of structures produced by MFCX from NiO after reduction to Ni. Taken from [20]

Crumm *et al.* [21], showed that is also possible to directly co-extrude mixtures containing metallic powders by coextruding silver-palladium electrodes inside of a ceramic body. The metallic electrodes where shown to be stable during the whole process.

Compounds loaded heavily with stainless steel powder have been used previously in other manufacturing techniques such as metal injection molding (MIM). For example, Khalil *et al.* [22] accomplished this using a binder mixture composed mainly of paraffin wax with ethylene vinyl acetate (EVA), high-density polyethylene (HDPE) and stearic acid (SA) as surfactant. Li *et al.* [23] used a similar mixture for their study. The MIM technique typically uses low viscosity waxes that can be removed easily later. This contrasts with MFCX, since the later requires more viscous polymers that do not leak through the extrusion chamber or during the pre-molding process when compressed. To the knowledge of the author, there has not been previously published work that demonstrates that it is possible to directly coextrude structures containing stainless steel powders, and thus this demonstration is one of the goals of this work.

#### 2.3.1 Rheology

Beeaff *et al.* [24] showed that MFCX requires careful control of the rheological properties of the compounds, which are influenced by the polymer selected, powder size, powder morphology, powder surface chemistry, use of dispersants, mixing rate and temperature. Also, the flow of multilayer structures is affected by the extrusion rate and macro-scale extrusion flaws such as: stick-slip, melt fracture and interface instability. If viscosity mismatch exists between the compounds, additional micro-scale defects are possible such as encapsulation, which results in a loss of the self-similarity in the cross-

sectional geometry. This occurs when low viscosity compound migrates towards the region of highest shear and surrounds the high viscosity compound as shown in Figure 2.10.



Figure 2.10. Coextrusion defects due to viscosity mismatch of the compounds. Taken from [24]

#### 2.3.1.1 Torque rheometry

An approximate match in the viscosity of the different compounds is required for successful MFCX. High shear mixers control the rotational speed and therefore the shear rate during blending of the polymers and powders. In addition, the mixers are equipped with thermocouples and a force transducer that allow the temperature and torque to be measured in real time during blending. The torque can be used to estimate the shear stress if the geometry of the mixing heads and chamber are known. The rheology of most polymer melts can be modeled using a power-law relation between the shear stress  $\tau$ , the shear rate  $\dot{\gamma}$ , the power law index *n*, and a rheological constant *K*, as shown in Eq 1.

$$\tau = K \dot{\gamma}^n \tag{1}$$

Beeaff *et al.* [24] showed that the shear rate can be related to the mixing torque  $M_t$  and the volume of the mixture *V*, through the following relation,

$$M_{\rm t} = \frac{3}{2} V K \dot{\gamma}^n \tag{2}$$

The shear strain rate,  $\dot{\gamma}$ , is calculated using the velocity of the mixing blade edge, *u*, and the distance between the blade and the mixer wall, *h*. In this case, *u* is determined from the rotational speed given in units of revolutions per minute, *R*, and the diameter of the blade, *d*, which is assumed to be a cylindrical approximation to the actual complex blade geometry.

$$\dot{\gamma} = \frac{u}{h} = \frac{\mathrm{d}\pi\,R}{60h} \tag{3}$$

Substituting equation (3) into (2), taking the logarithms of the values of both sides of the equation, and rearranging, the following equation is obtained,

$$\log M = n \log R + C_{\rm m} \tag{4}$$

where  $C_m$  is given by,

$$C_{\rm m} = \log\left(\frac{3}{2}VK\right) + n\log\left(\frac{\pi d}{60h}\right) \tag{5}$$

From equation (4) it can be seen that the slope on a plot of log(M) versus log(R) is the power law index *n* and  $C_m$  is the intersection with the ordinate axis. Thus, from measurements taken during blending and appropriate calculations, it is possible to obtain *K*,  $\dot{\gamma}$ ,  $\tau$  and finally the apparent viscosity,  $\eta_a$ , from the following relationship,

$$\eta_{a} = \tau / \dot{\gamma} \tag{6}$$

These relationships are valid for both pure polymers and polymers with solid loadings of ~50 vol.%, but they break down for extremely high solid loadings (> 60 vol.%) where significant particle-particle interactions occur and therefore different models must be applied.

Typical log(torque) versus log(RPM) curves obtained during compounding by Beeaff *et al.* [24] are shown in Figure 2.11. However, although torque rheometry is useful in part because it is a quick and simple measurement, it is not an ideal method for matching the viscosities of the compounds used in MFCX. A major challenge for obtaining the correct viscosities for MFCX from torque rheometry is that the typical strain rates that are used for MFCX are quite different from those that are possible during torque rheometry. Thus, it is necessary to extrapolate the shear stress to ranges of strain rate where no data exists. Since the power-law relationship between shear stress and shear strain rate may not be valid at these extrapolated strain rates, other methods for measuring viscosity at the strain rates appropriate for MFCX are needed.



Figure 2.11. Typical torque rheometry results for ceramic-polymer compounds with varying solids loadings. Taken from [24]

#### 2.3.1.2 *Capillary rheometry*

A capillary rheometer allows the determination of the apparent viscosity of a polymer melt at a specific temperature and at a strain rate appropriate for MFCX. The same extrusion chamber used for MFCX, shown in Figure 2.7, can be used as a capillary rheometer. The melt reservoir is filled with a pre-compressed feed rod of a specific compound and then is heated to the same temperature used for the torque rheometry. A brass piston pushes the compound melt through a capillary die while the extrusion force is recorded. The compression speed and extrusion force curves are obtained and from them, the shear stress and shear strain can be calculated.

Some of the limitations regarding this method are: 1) long heating and cooling times are required in order to obtain a polymer melt with a uniform temperature; 2) in practice, only one data point is obtained per sample, which further slows the measurement process. Another undesirable effect is that wall slip is a significant factor that affects the viscosity measurements and depends on: additives used, surfaces characteristics, the physicochemical properties and cleaning processes used on the barrel and die surfaces [25]. Also, Syrjälä *et al.* [26] have shown that the uniform temperature profile that is assumed may not be valid, especially close to the die, where viscous flow produces local heating that results in erroneously high measurements of viscosity. This is accentuated for low thermal conductivity polymers that are extruded at high strain rates. Another factor that has to be monitored is the thermal degradation of the polymer and its adhesion to the chamber walls, which increases friction and also results in erroneously high viscosity measurements.

Despite the challenges, Son [27] has shown how the viscosity of a compound can be obtained using capillary rheometry. Rheometry data are obtained from the geometrical dimensions of the die, the pressure drop and the volumetric flow. Corrections are applied to the apparent viscosity and shear stress when a rectangular or square die is used as it was in the current measurements, instead of the circular cross-sectioned dies that are typically used for capillary rheometry. The shear stress at the wall,  $\tau_w$  is calculated from the pressure drop,  $\Delta P$ , the length of the die, *L*, the height and width of the die, *H* and *W*, the volumetric flow rate, *Q*, and the geometric parameters  $a^*$ ,  $b^*$  and  $f^*$  (See Table 2.1) using the following expressions:
$$\tau_{\rm w} = \left(\frac{\Delta PH}{2L}\right) \left(\frac{1}{H/W+1}\right) \tag{7}$$

$$\dot{\gamma}_{a} = \left(\frac{6Q}{WH^{2}}\right) \left(1 + \frac{H}{W}\right) f^{*}\left(\frac{H}{W}\right)$$
(8)

$$\dot{\gamma}_{\rm w} = \dot{\gamma}_{\rm a} \left(\frac{2}{3}\right) \left(\frac{b^*}{f^*} + \frac{a^*}{f^*}\frac{1}{n}\right) \tag{9}$$

$$\mu = \tau_w * \dot{\gamma}_w \tag{10}$$

where,  $\dot{\gamma}_w$  is the shear strain at the wall and  $\dot{\gamma}_a$  is the apparent shear strain rate and *n* is the power law index.

H/W	<i>a</i> *	$b^*$	$f^*$	H/W	<i>a</i> *	$b^*$	$f^*$
0.00	0.5000	1.0000	1.0000	0.55	0.2360	0.7163	0.6348
0.05	0.4535	0.9513	0.9365	0.60	0.2297	0.7065	0.6242
0.10	0.4132	0.9098	0.8820	0.65	0.2248	0.6985	0.6155
0.15	0.3781	0.8745	0.8351	0.70	0.2208	0.6921	0.6085
0.20	0.3475	0.8444	0.7946	0.75	0.2178	0.6870	0.6032
0.25	0.3212	0.8183	0.7597	0.80	0.2155	0.6831	0.5991
0.30	0.2991	0.7954	0.7297	0.85	0.2139	0.6803	0.5961
0.35	0.2809	0.7750	0.7040	0.90	0.2129	0.6785	0.5942
0.40	0.2659	0.7571	0.6820	0.95	0.2123	0.6774	0.5931
0.45	0.2538	0.7414	0.6634	1.00	0.2121	0.6771	0.5928
0.50	0.2439	0.7278	0.6478				

Table 2.1. Geometrical parameters a\*, b\* and f\* values. Taken from [27].

Typical data obtained using capillary rheometry are shown in Figure 2.12. Here each point corresponds to an individual test while recording the force at a constant strain rate. In total, this figure requires 9 separate experiments, each of which are quite time consuming, especially for those data obtained at the lowest strain rates.



Figure 2.12. Typical capillary rheometry data. Taken from [24]

# **2.3.2** Thermal treatments

The different thermal treatments required to pyrolyze, reduce and sinter the extruded structures are very important to produce high quality metals or ceramics. Poor practices result in distortion of the shapes and/or weak structures that do not support the stress imposed on the beam during the buckling required to show negative stiffness behavior. Potential defects include cracks and voids that occur during the pyrolysis process due to gas bubbles being produced too quickly inside the polymer during decomposition. If the heating rate is reduced, the gas can diffuse to the surface and escape leaving the specimens unharmed. This is especially important for thick specimens that have a longer diffusion path and therefore require slower heating rates to avoid cracking [28] [29]. Typical problems caused by fast polymer debinding are shown in Figure 2.13.



Figure 2.13. Defects caused during polymer debinding. a) blistering b) superficial cracks b) internal cracks. Taken from [28]

After polymer debinding, the ceramic can be reduced to a metal by exposing it at high temperature in a reducing atmosphere such as hydrogen atmosphere. This process was used by Crumm *et al.* [20] to manufacture negative Poisson's ratio structures, where NiO was reduced into Ni by heating the specimens in a 10%  $H_2 - 90\%$  N<sub>2</sub> atmosphere at 600 °C. This procedure was confirmed by using thermogravimetric analysis (TGA) that showed that most of the weight loss occurs below 600 °C, as shown in Figure 2.14.



Figure 2.14. TGA data for hydrogen reduction of nickel oxide. Taken from [20]

This procedure works for small objects with large pores that allow for fast  $H_2$  diffusion, but for large specimens, the  $H_2$  flow needs to be increased or pure hydrogen atmospheres must be used; otherwise, the specimens will have different volumetric shrinkage which creates cracks or warpage of the specimens, as shown in Figure 2.15. The heating rate is also important since high rates will accentuate these defects. [30]



Figure 2.15. Typical defects produced during hydrogen reduction. a) NiO-3YSZ flat plate b) Warped plate after reduction in hydrogen. Taken from [30]

The metal or ceramic parts are subsequently sintered so that the walls of the structures obtain high density and therefore high stiffness and strength. Sintering temperatures depend on the composition of the material, powder size, surface area, and green density, but typically are 50-90% of the melting temperature of the material. The green density is controlled during the compounding process and typical formulations include a minimum of 50 vol.% solids loading [18]. Another important factor is the sintering atmosphere, since, depending on the material used, vacuum may be desired to prevent oxidation of the specimens.

## CHAPTER 3: EXPERIMENTAL PROCEDURES

This chapter describes the procedures used to manufacture and test the specimens required for this research. These include the methods used to produce the model NSS structures, the polymeric resins used to test the energy dissipation behavior of the NSS when embedded into a matrix, and the ceramic and metal processing for MFCX. The material characterization procedures used such as: compressive and bending tests; density measurements and scanning electron microscopy (SEM) methods are also described.

# 3.1 NSS in parallel with polymeric matrix

Testing of the NSS when compressed uniaxially in parallel with a polymeric matrix provides basic understanding of the energy dissipation mechanisms and stiffness behavior of the system. This section explains the design methodology, manufacture and the testing procedures used to study these specimens.

### **3.1.1** Design and modeling

In order to understand the improvements in energy dissipation when embedding NSS into a matrix, as predicted by previous models [8] [9] [10] [13], a macro-scale structure was used in order to facilitate and improve quality of the energy dissipation measurements of each specimen. The maximum strain encountered during a bi-stable snap-through event occurs at the fixed ends of the beam. Equation (11) allows the estimation of the maximum strain for a bi-stable beam, which was used to estimate the maximum allowable strain for a monostable beam. Here, t is the beam thickness, l is the beam length and h is its initial apex height. [31]

$$\varepsilon_{max} \approx 2\pi^2 \frac{th}{l^2} + 4\pi^2 \frac{t^2}{3l^2}$$
 (11)

An additional practical constraint is that to ensure that snap-though is reversible, the maximum strain encountered anywhere in the negative stiffness structure (NSS) during loading must be less than the yield strain. Fabrication of reversible NSS that can achieve a significant displacement range in the NS regime therefore requires the choice of base materials that have high yield strain. For the design of the NSS considered in this study, equation (1) was solved numerically, iterating over different beam parameters to ensure that the maximum strain encountered during snap-through was less than the yield strain of the material used to construct the NS structure. The design of choice was the one that was predicted to result in substantial negative stiffness behavior without significant yielding when using a specific stainless steel alloy. A slightly larger apex than the original design was selected because preliminary testing revealed that more significant NS behavior was obtained with small amounts of plastic deformation as a trade off during the initial loading cycles. The force versus displacement responses for subsequent loading cycles of the NSS are shown in Figure 3.1. Here, the NS behavior is circled in red and only appears after some plastic deformation is observed. The total amount of plastic deformation can be determined by calculating the difference between the loading and unloading curves. For this image, the amount of plastic deformation was approximately 1.6 mm.



Figure 3.1. Response for the NSS showing plastic deformation during the initial loading cycles. The plastic deformation is the difference between the loading and unloading responses in the displacement axis. (i.e. from 0 to 0.16 mm.)

Figure 3.2 shows the force versus displacement response of the NSS for several loading-unloading cycles. Loading and unloading to a peak displacement of 0.8 mm results in primarily an elastic response (blue curve) although some hysteresis is apparent along with a small amount of plastic deformation. A subsequent load-unload cycle to the same peak displacement (red curve) exhibits a nearly identical response to the first load-unload cycle. The third load-unload cycle to a peak displacement of 1.1 mm (green curve) exhibits more plastic deformation upon unloading but the fourth cycle, also to a peak force of 1.1. mm (purple curve), is virtually identical to the third cycle. From this data, it can be concluded that after an initial loading-unloading cycle, for subsequent loading-unloading cycles, the NSS experiences primarily elastic deformation as long as the peak displacement for the subsequent cycles is equal or less than the peak displacement for the initial cycle.



Figure 3.2. Force versus displacement response for subsequent cycles showing elastic deformation for the fourth loading-unloading cycle.

The response of the NSS was then modeled using finite element analysis (FEA) to determine the complete force versus displacement response. Figure 3.3 shows a comparison of FEA predictions with experimentally obtained data.



Figure 3.3. a) Finite element analysis (FEA) of NSS without deformation. b) FEA of NSS after the beam was buckled. c). Experimental versus predicted NS response.

# 3.1.2 Matrix selection

From the work of Lakes [8] and Klatt. [13], it has been suggested that energy absorption is maximized when the moduli of the matrix and an embedded NS inclusion are carefully selected such that the amplitude of the stiffness of the NS inclusion is matched by a positive stiffness of similar magnitude in the matrix. This ensures the composite's force-displacement performance is constant when the NSS enters the NS regime. When an NS inclusion is entirely embedded within a polymer and the specimen is loaded in uniaxial compression, a complex stress state arises in the specimen. By analogy with conventional composite theory, the behavior of the *NS inclusion* + *matrix* can be approximated by considering the NS inclusion and the matrix to be simultaneously loaded in parallel and series. Even for this simplified configuration, superposition cannot be applied and thus, modeling of the behavior of the specimen requires extensive FEA simulation due to: large strain gradients that occur near interfaces, non-linear behavior of the matrix at large strains, and non-linearities that occur during the buckling of the beam in the NS inclusion. For these reasons, accurate modeling of the system requires extensive FEA analogous to the work of Fritzen and Kochmann [32].

A simpler configuration that can be modeled analytically is shown in Figure 3.4(b) in which the NS inclusion and matrix are placed in parallel relative to the axial loading direction by removing the matrix material that lies above and below the NS inclusion and only placing the matrix on the sides of the NS inclusion. This configuration allows the polymer and clear the NSS to be treated independently and the behavior of the sample to be determined by superposition. Such an analysis allows an estimate of the required matrix modulus to produce the expected overall (NS inclusion + matrix) flat force-displacement response.



Figure 3.4. a) Stainless steel NSS b) NSS with a resin matrix on the sides of the NSS which results in a configuration in which the NSS is in parallel with the matrix. (Picture was enhanced to distinguish the resin faces).

Three polymers with a range of modulii were selected to validate this approach. One matrix was selected with a modulus equal in magnitude to the NSS, the second matrix had a modulus slightly larger than the NSS, and the third one was much stiffer than the NSS. The three matrices were classified as L for the low modulus matrix, M for the moderate modulus matrix, and H for the high modulus matrix.

## 3.1.3 Materials

The NSS were produced from sintered 17-4 PH stainless steel powder (174AR-AAAN, LPW Inc., Pittsburgh, Pennsylvania). with a particle size below 50  $\mu$ m, as determined from SEM (JEOL JSM – 5610 SEM) micrographs and shown in Figure 3.5.



Figure 3.5. SEM of SS17-4PH powder.

The powder was loosely compacted inside of an alumina crucible and then sintered at 1300°C for 3 hours under vacuum that was maintained using a mechanical roughing pump. For this NSS application, this alloy has the advantage that it can be heat treated to tailor the yield stress, tensile strength and ductility. To maximize the yield strain, the sintered plate was solution-treated for 2 hours at 1038°C, then cooled in still air [33].

Two plates were produced for this study using the above methods. The first plate was machined for measurement of the relative density using a helium pycnometer and using Archimedes' method. These two methods for measuring density showed good agreement and both indicated that the relative density of the plate was approximately 95% following sintering. The material from this plate was also used to measure the Young's modulus and yield strength using a three-point bending configuration with a span of 40 mm, as shown in Figure 3.6. Specimens with length, height and width of 45.6 mm, 0.97 mm and 7.69 mm were machined from the plate and the force versus displacement response was measured. The yield strengths and moduli were determined using standard equations from Eulerian beam theory. The experimentally determined Young's modulus of the stainless steel was 150 GPa and the yield strength was approximately 1 GPa. Both of these values are consistent with expected values for this grade of sintered stainless steel with a relative density of 95%. [33] [34] [35].



Figure 3.6. Three-point bending test configuration.

To observe if large porosity defects or impurities were present in the SS specimens, a SS plate was fractured and the SEM was used to observe the fracture surface. The SEM images shown in Figure 3.7 reveal small amounts of segregated porosity that is consistent with highly dense parts.



**100** µm





Figure 3.7. SEM pictures of the sintered material at different magnifications.

The second plate was used to manufacture the NS inclusions by water-jet cutting, as shown in Figure 3.4(a). The expanding conical shape of the water jet results in an increase in the cutting kerf with depth into the material. Thus, the width of the beams in the NS inclusion were slightly thicker at the top of the plate where the jet entered and thinner at the bottom of the plate. The effects of the thickness variations of the beams on the behavior of the inclusions was considered in the FEA model.

Two- or three-part elastomeric urethane resins (Clear Flex 30 resin, Smooth-On Inc., Macungie, Pennsylvania) were used to manufacture the matrix. This specific resin system was used because the Young's modulus is adjustable by varying the composition and because the cured polymers are transparent. The latter attribute allows for direct observation of the NS inclusion within the matrix while the specimens are being tested. To define the compositions of the matrices, it was necessary to determine the required matrix moduli and since these depended on the stiffness of the NS inclusion, the force versus displacement response of the NS inclusion was measured first. The required matrix Young's modulus was then determined from equation (12), simplifying the calculations by assuming simple uniaxial response

$$k \approx \frac{A * E}{L} \tag{12}$$

where k is the stiffness of the matrix, A is the area of the matrix, E is the Young's modulus of the matrix and L is the height of the matrix, which is the same as the height of the NSS. Experiments were also performed to confirm that the resin exhibited approximately linear behavior in the deformation range of interest for these studies. The resins were mixed and then placed in a vacuum for 2 minutes using a mechanical roughing pump to remove air bubbles from the mixture; this process was repeated twice. The resin was then poured into acrylic molds and cured at room temperature for 24 hours and then cured at 75 °C for 48 hours. Three specimen geometries were tested to compare energy absorption: (1) a solid rectangular prism of the neat matrix material, (2) a rectangular prism of the matrix material containing a void with the same volume and geometry as the NS inclusion, and (3) a rectangular prism of the matrix containing the stainless steel NS inclusion, as shown in Figure 3.4(b). The void for specimen geometry (2) was produced by casting the resin around a rectangular plate with the same dimensions as the NS inclusion that was suspended by 3 pins. Once the resin was cured, the plate was removed but the support pins were left inside the resin. In total, nine specimens were prepared when taking into account the variations in matrix stiffness and configuration. The three resin formulations used were labeled *low, medium* and *high* stiffness and are shown below in Table 3.1.

	Resin A (wt. %)	Resin B (wt. %)	So-Flex® Resin (wt. %)	Young's modulus E (kPa)
High E	51.5	48.5	0	968
Medium E	41	38.5	20.5	310
Low E	34.7	32.6	32.6	9.38

Table 3.1. Matrix formulations and properties

### 3.1.4 Quasi-static uniaxial testing

For quasi-static testing, the force and displacement were monitored while the specimens were compressed uniaxially using a screw-driven test frame at a constant displacement rate of 1 mm/min. The origin in displacement was defined relative to the top of the NS inclusion and loading-unloading cycles were performed from the origin. Plastic deformation of the NSS was observed during the initial 3 loading cycles such that the height of the NSS decreased 0.3 mm permanently. For subsequent cycles, the maximum compressive elastic range, as measured from the top of the NSS, was 1.4 mm.

The NSS was then placed in the matrix, where multiple cycles were conducted to a displacement of 1.4 mm. The energy and stiffness calculations presented in this dissertation correspond to the cycles 2 - 7. The first cycle was omitted because anomalously large energy absorption was observed, mainly due to stress relaxation in the matrix. The energy dissipated per cycle (related to the damping capacity) was determined from the hysteresis during a load-unload cycle and was calculated by integrating numerically the area within the force-displacement curve. For the matrix materials, the nominal engineering stress and strain were calculated from the force and displacement and the Young's moduli were calculated for each matrix material from the slopes of stress versus strain, in the linear regions. The specimen containing the NSS was slightly shorter in height (approximately 0.1 mm) than the other specimens, which resulted in a small but noticeable disparity when comparing specimens; this disparity was largest at small displacements and diminished as the force increased.

# **3.2** NSS embedded within a polymeric matrix

In order to study the energy dissipation mechanisms when the NSS was completely embedded in the matrix, different model specimens were designed, manufactured and tested. This section explains the relevant experimental procedures that were followed.

## **3.2.1** Design and modeling

For this section, a different NSS was cut from a fully dense SS 17-4 plate with a Young's modulus of 196 GPa and a yield strength of 1.1GPa in its annealed condition (AMS 5604, supplied by Online Metals [33] [36]). This NSS exhibited a small amount of plasticity during the first cycle (0.2 mm of height change), but a larger negative stiffness region was obtained when compared to the previous structure. The NSS measured 57.8 mm long, 2.15 mm thick and 15 mm tall and was labeled NSS#2 in order to differentiate it from the one mentioned in the previous section. To model the predicted response of the NSS#2 using FEA, the thickness was taken to be 0.55 mm instead of 0.5 mm and the beam apex was reduced slightly by 0.34 mm. These corrections are consistent with the observed manufacturing defects caused by the water jet cutting process and the plastic deformation observed during the first cycle of the beam, which corresponded to 0.2 mm. With these corrections, the predicted and experimental response are shown in Figure 3.8 for a displacement load of 2.2 mm.



Figure 3.8. FEA and experimental results of NSS#2.

Although the FEA predictions do not match the experiment exactly, the important features of the experimental curve are successfully predicted. In particular, the following are features are predicted: an initially linear response and a peak force followed by a negative stiffness regime that eventually saturates.

## **3.2.2** Matrix selection

In order to determine the required matrix stiffness, FEA modeling with ABAQUS<sup>®</sup> was performed<sup>1</sup>. The corrected NSS#2 model was placed inside a matrix with the following dimensions: 65 mm long, 11 mm thick and 25 mm tall. It is important to note that the matrix had a void where the NSS#2 was placed without leaving gaps with the surroundings. To assure interaction between the matrix and the NSS#2, global frictionless interaction

<sup>&</sup>lt;sup>1</sup> The FEA models were conducted by Nuria Cobo-Losey with assistance from Clint Morris. The author guided this work.

boundary condition was applied and a hard contact interface was utilized between the top face of the NSS#2 and the matrix. The model, constrains and boundary conditions used in the FEA are summarized in Figure 3.9. Different Young's moduli were used to model the matrix in order to determine the matrix modulus that predicted an overall flat force versus displacement response when the NSS was activated.



Figure 3.9. Constraints and boundary conditions used for the FEA model of the NSS#2 embedded in a matrix.

## 3.2.3 Materials

A similar procedure to the one mentioned in the previous section was used to manufacture the polymeric matrices (Clear Flex 30 resin, Smooth-On Inc., Macungie, Pennsylvania) for the embedded NSS model specimens. The resins were degassed, molded and cured in a similar way as mentioned before. The main differences compared to the specimens used for the NSS in parallel with the matrix were: (I) These specimens had a section of the matrix in series with the NSS allowing for compression of the matrix before the buckling of the beam. (II) The void was placed at the bottom of the matrix, so the NSS#2 could slide in and out of it, allowing for testing of the same NSS#2 with other matrices with different stiffness. (III) A solid brass plate, with the same outer dimensions as the NSS#2, was machined and used to determine the behavior when a stiff inclusion is placed inside the matrix. In order to study the importance of matching the stiffness of the matrix to the one of the NSS, three resin formulations were used and were labeled L for the low modulus matrix, M for the moderate modulus matrix and H for the high modulus matrix as shown below in Table 3.2.

	Resin A (wt. %)	Resin B (wt. %)	So-Flex® Resin (wt. %)	Measured Young's modulus E (kPa)
High E	51.5	48.5	0	968
Medium E	41	38.5	20.5	617
Low E	34.7	32.6	32.6	327

Table 3.2. Matrix formulations and properties

It is important to note that small variations during the preparation of the specimens were observed to result in significant Young's modulus differences. This was most evident for the low and medium stiffness specimens.

For each of the three different stiffness resins, four specimens were tested, corresponding to: 1) the neat matrix, 2) a matrix containing a void, 3) a void filled with a solid brass plate and 4) a void filled with the NSS#2, as shown in Figure 3.10. This resulted

in a total of twelve specimens when the different matrices and specimen geometries are included.



Figure 3.10. Specimens used for testing of NSS embedded in a matrix. a) Neat matrix. b) Matrix containing a void. c) Solid brass plate. d) NSS #2.

Figure 3.11 illustrates how the NSS#2 completely fills the space available inside the void matrix. The brass plate also resulted in a completely filled void.



Figure 3.11. Specimen containing NSS #2 embedded within a matrix.

## 3.2.4 Quasi-static uniaxial testing

During the first compression cycle, the NSS#2 exhibited plastic deformation such that the height of the NSS decreased 0.2 mm, permanently. In this case, the plastic deformation, and subsequent effects on force threshold and displacement range, were small enough that they did not significantly affect the results of subsequent compression cycles.

A similar compression testing procedure to the one described for the NSS loaded in parallel with the matrix was used for the NSS#2 which was embedded in a resin matrix. However, for the embedded specimen, it was tested to a constant force rather than to a constant displacement for reasons that will be discussed in the chapters that follow. Also, the displacement rate was set to 10 mm/min instead of 1 mm/min. A faster displacement rate was used to reduce the testing time, since the displacements were much larger for these specimens than when the NSS was placed in parallel only with the resin. This makes a significant difference in the time required for measuring the twelve specimens, with 7 testing cycles per specimen. Because the energy and stiffness measurements were compared at the same strain rates for all of the specimens used in this part of the study, differences in the viscoelastic response of the matrix would be expected to affect each of the specimens in the same way and thus not be a factor in making relative comparisons. Furthermore, experimental testing was performed on all the M stiffness specimens at 1 mm/min and 10 mm/min to assess how the strain rate affected the results.

The NSS#2 was placed in the L stiffness matrix, where it was compressed until the NSS#2 buckled completely, which was verified visually through the transparent resin. The force required to achieve complete buckling was measured to be 35 N and it was selected as the constant maximum force to be used for further testing in order to be able to compare the different specimens under the same conditions. It is important to note that since the stiffness of the matrices is different and the tests were performed at a constant maximum force, buckling did not occur at 35 N for the M and H stiffness resins. This is because the stiffer resins were able to support a higher force and they therefore transmitted less force to the NSS#2. In order to compare the behavior before buckling and after buckling of the NSS#2 for the *M* stiffness matrices, these specimens were compressed to 45 N, which was the force required to completely buckle the NSS#2. The H stiffness specimens were compressed to 70 N in order to activate the NSS#2. Furthermore, in order to compare the pre-buckling and post-buckling behavior of the L matrix+NSS#2 specimen, a series of tests were conducted where it was also compressed to a peak force of 30 N, which was insufficient to activate the structure.

Seven cycles were conducted for each of the specimens to the peak force and the force versus displacement responses presented here are for cycles 2 - 7. The data of the first cycle was omitted again because of excessive stress relaxation in the matrix. The energy dissipated per cycle was determined from the hysteresis during a load-unload cycle and was calculated by integrating numerically the area within the force-displacement curve. For the matrix materials, the nominal engineering stress and strain were calculated from the force and displacement and the Young's moduli were calculated for each matrix material from the slopes of stress versus strain in the linear regions. For the NSS#2+*L* stiffness resin, it was necessary to provide a range of stiffness values, since it varied greatly depending if the linear region during the loading response was used or the overall response was selected.

# 3.3 MFCX

This section describes the different materials, processes, characterization methods and testing procedures used to perform the MFCX successfully for this study. The main purpose of the coextrusion study was to demonstrate that microstructures with a similar design of the NSS presented previously can be manufactured with MFCX.

## 3.3.1 Materials

The materials used to make the feed rods for the MFCX process are the following:
 Steel powder: 17-4 PH stainless steel (SS) powder with maximum particle size of 50 μm (174AR-AAAN, LPW Inc., Pittsburgh, Pennsylvania).

- Binder: poly(ethylene-co-butyl acrylate) (PEBA-35, 430773, Sigma-Aldrich, St. Louis, MO).

- Plasticizers: heavy mineral oil (HMO) (O122-1, Fisher Scientific, Hudson, New Hampshire) and polyethylene glycol (PEG 6000 A17541, Alfa Aesar, Ward Hill, MA).

- Filler: carbon black (CB) (Black Pearls 120 VP-6752, Cabot, Billerica, MA).

- The gases used for the thermal processes were: argon gas (UN 1006, industrial grade 99.995% pure, Praxair, Danbury, CT) and hydrogen gas (UN 1049, industrial grade, 99.95% pure, Praxair, Danbury, CT)

#### **3.3.2** Metal-polymer compatibility

In order to test the compatibility of the powder with the binder and plasticizers, a 10 g batch of SS 17-4 powder was compounded manually with the binder PEBA-35, HMO and PEG 6000. The batch was heated to 300°C, where it was evident that the polymer started to pyrolyze. Since this temperature is much higher than the required for compounding (135°C) and the polymer did not react violently with the metal, the compound was considered safe for the process.

## **3.3.3** Compounding and rheometry

The SS 17-4 powder was compounded with PEBA-35, HMO and PEG 6000. To improve the compound homogeneity, the mixture was compounded three times, 1 hour each, using a Brabender shear mixer (EPL-V5501, Plasti-corder, C.W. Brabender, Hackensack, N.J.) at 135°C. A separate batch of compound was made with CB, PEBA and HMO to be used as filler for the empty spaces in the structure. The formulations used for the compounds are shown in Table 3.3.

	Volume percent of material used					
Compound	PEBA-35	SS 17-4	Carbon Black	PEG-6000	Heavy mineral oil	
SS compound	38.22	54.99		0.37	6.42	
CB compound	59.60		33.24		7.16	

Table 3.3. MFCX compound formulations

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To be able to successfully coextrude the micro-scale NSS, it was necessary to match the viscosity of the two composites at the desired extrusion strain rate. A first approximation was made with the Brabender mixer using torque rheometry, where the rotational speed (RPM) was varied while monitoring the torque required to shear the compound. The whole measuring process was performed in about 5 minutes, after recompounding the mixture three times, with the chamber fully loaded. The data for the SS compound was obtained first and plotted as log(torque) versus log(RPM) [24]. The compounding data for the CB compound was plotted in the same way and compared to that for the SS. The two curves were linearly extrapolated to lower shear rates to predict the behavior at the equivalent shear rate for the coextrusion process. The coextrusion shear rate is approximately 0.59 s<sup>-1</sup> which corresponds to 0.1 RPM (-1 on the log scale). After some iteration, while varying the composition of the CB, the two curves matched their viscosity at low strain rates. It is important to note that the extrapolation was needed since the Brabender mixer cannot operate at the low shear rates used for MFCX.

Once the two compounds were obtained, capillary rheometry was performed. This is in principle the most relevant viscosity characterization available since it uses the same hardware and extrusion parameters required for the MFCX process. To make the extrusion feed rod, each compound was compressed in a hydraulic laminating press into a 2 mm thick plate, then, cut, stacked and compressed two more times to remove air bubbles from the compound. The plate was then cut into pieces, placed into open aluminum molds and compressed at 140°C. The excess material flowed through the open ends of the molds allowing complete filling. The feed rod obtained was a square prism with dimensions of

14.7 mm  $\times$  14.7 mm  $\times$  100 mm. The feed rod was inserted into the same extrusion chamber used for the MFCX process, heated to 135°C at the die and the main body was kept at 67°C with a water cooling unit to reduce polymer sticking to the walls. To perform the extrusion, a brass plunger was used to reduce friction and the displacement rate was controlled with a universal test frame (Sintech 2/G, MTS Systems, Triangle Park, NC), while the forces were monitored with a load cell (100 KN maximum range). The force versus crosshead displacement curves for both composites were obtained at the desired extrusion speed.

## **3.3.4** Coextrusion process

Aluminum molds were machined to create each section of the NSS as shown in Figure 3.12(a). The same process used to remove the air bubbles from the feed rod was applied to ensure that each molded part was practically void-free. To promote compound release from the mold, the aluminum molds were covered with aluminum foil which was peeled off easily once the molded parts cooled down. The molded parts were assembled as shown in Figure 3.12-b, forming a feed rod with dimensions of 14.7mm×14.7mm×100mm.



Figure 3.12. Feed rod assembly used for MFCX. a) Molded individual parts. b) Assembled feed rod.

Two geometries were extruded, the geometry corresponding to the NSS#2 and a modified version that had three main differences: (I) a shorter top beam, (II) an increased window clearance and (III) a taller base as shown in Figure 3.13. The shorter top beam facilitated mechanical testing. This is because when the top beam is coextruded, it can deform and interfere with the free movement of the beam during buckling. The increased window clearance facilitates complete beam buckling by mitigating small geometry variations that are expected from the coextrusion process. The taller base increased the stability of the NSS when handled and during testing of the specimens.



Figure 3.13. (a) First coextruded geometry based on the NSS#2. (b) Second coextruded geometry with: (I) a shorter top beam (II), increased window clearance and (III) with a taller support base.

Due to the fact that the PEG 6000 plasticizer has a low melting temperature of 60°C [37] and because it is not miscible in the PEBA binder, a two phase mixture results [28]. Thus, it was observed that the SS compound that utilized the PEG plasticizer melted at lower temperatures than the CB compound. Because of this, it was necessary to seal the ends of the feed rod with the CB compound. If this was not done, the SS flowed more readily than the CB compound, resulting in distortion of the desired structure. The sealing process was done by heating a solid piece of CB compound in a hot plate, then sticking the ends of the feed rod into it and removing the feed rod from the hot plate to allow it to cool down. Later, the excess material was removed with a sharp blade.

Before the coextrusion process, voids were removed from the feed rod by compressing it in the extrusion chamber by placing a cap in place of the extrusion die to block the flow. The chamber was heated to 140°C and the feed rod compressed up to a pressure of 2.2 MPa at 1 mm/min. The pressure was maintained for 1 hour, and then the chamber was allowed to cool down, the pressure was released and the cap was replaced by the extrusion die.

To perform the MFCX, the extrusion die was heated to  $135^{\circ}$ C and the extrusion chamber was maintained at 67°C. Once the temperatures were stable, the MFCX process was performed at a constant strain rate of 0.59 s<sup>-1</sup>.

The minimum feature size for the extruded geometry corresponds to the beam thickness and after the coextrusion process, this dimension was approximately  $50 - 60 \,\mu\text{m}$ . As shown previously in Figure 3.8, the SS maximum particle size is close to  $50 \,\mu\text{m}$ . Therefore, the coextrusion process could only be performed once, otherwise, the beam

thickness would have been smaller than the maximum particle size, creating voids in sections of the beam.

## **3.3.5** Thermal processing

In order to remove the polymer and produce a dense structure with minimal oxidation, the specimens were subjected to three thermal processes: 1) thermal debinding, 2) hydrogen reduction and 3) high temperature vacuum sintering.

The extrudate was manually cut with a sharp blade into thin slices under 0.5 mm thick. This is important since if the slices were too thick, the structures would have a large aspect ratio and collapse when the support provided by the polymer surrounding them was removed. Also, the structures could not be oriented in other directions, otherwise the beam would collapse under its own weight during high temperature sintering. The placement and orientation of the extrudate slices is shown in Figure 3.14.

The slices were placed inside a tube furnace without sealing the tube ends to allow for natural convective air flow. The following heating schedule was used to debind the polymer: heating from 24°C to 130°C in 1 hour, from 130°C to 300°C in 90 hours, from 300°C to 400°C in 20 hours, from 400°C to 600°C in 13 hours, soaked for 1 hour at 600°C and cooled down to room temperature in 4 hours.





Afterwards, without moving the specimens, the tube ends were sealed and argon gas was introduced for 15 minutes to remove the air and create an inert atmosphere. Afterwards, hydrogen gas with a 50 SCCM flow was introduced into the system and maintained during the reduction process. The temperature was increased from room temperature to 800°C in 7 hours, soaked for 1 hour at 800°C and cooled down to room temperature in 4 hours. This pre-sintering step increased the strength of the specimens sufficiently to allow them to be transferred to the vacuum furnace. The specimens were carefully removed from the tube furnace and moved to the vacuum furnace (Model 144, The Furnace Source, Terryville, CT). It is important to note that the vacuum furnace was needed since the available tube furnace couldn't reach the required sintering temperature. Despite the care in handling the specimens, some of the specimens broke during the transition from one furnace to the other and had to be discarded. Once inside the vacuum furnace, the remaining specimens were heated from room temperature to 1300°C in 2 hours, soaked at 1300°C for 3 hours and cooled down at room temperature in 6 hours (cooling limited by thermal inertia of the furnace). Afterwards, the Archimedes' density of the micro-scale NSS was determined indirectly by measuring a large specimen that was placed in the same batch and subjected to the same conditions; this specimen was found to be 92% dense.

## 3.3.6 Testing

The micro-scale NSS specimens were manually compressed under an optical microscope as a first verification of the elasticity of the beam. Afterwards, this approximate specimen geometry was modeled in Comsol Multiphysics to predict its force versus displacement response and verify if they were suitable for uniaxial compression testing in a nanoindenter (Agilent Nanoindenter model XP). The specimens were then compressed at a constant displacement rate of 1 nm/second to produce pseudo-static loading at a low

strain rate<sup>2</sup>. The displacement range was dependent on the structure being tested since all the specimens had geometrical variations.

In order to test the compression behavior of the micro-scale NSS, an aluminum base was made with the following dimensions:  $10 \text{ mm} \times 10 \text{ mm} \times 3 \text{ mm}$ . A thermoplastic adhesive (Crystalbond®, Aremco, Valley College, NY) was used to fix the NSI to the base. Also, two 0.2 aluminum plates were glued to the base surrounding the NSI to provide additional support. A diagram of the testing setup is shown in Figure 3.15



Figure 3.15. Support base used for NSI compression testing with nanoindenter.

A summary of the MFCX processes, processing parameters, material characterization techniques and possible defects is attached in the appendix in Table 9.1as a guide for future testing.

<sup>&</sup>lt;sup>2</sup> The nano indentation tests were performed by Chenglin Wu from Dr. Liechti's group in the Department of Aerospace Engineering and Engineering Mechanics Department at the University of Texas at Austin.

# CHAPTER 4: QUASI-STATIC TESTING OF NSS IN PARALLEL WITH A POLYMERIC MATRIX

# 4.1 Overview

As shown in section 2.2, NSS embedded in a matrix have been predicted to offer enhanced combinations of stiffness and energy absorption capacity compared to conventional composites. Understanding the complex interactions that occur when an NSS is completely embedded in a matrix and loaded cyclically is challenging. In this chapter a simplified architecture is studied in which the NSS is placed in parallel with the matrix in an effort to understand these interactions and use this information to design effective NSS/polymer matrix composites.

# 4.2 Procedures

As discussed in Chapter 3.1, specimens made of a NSS placed in parallel with a polymeric resin were tested under uniaxial compression. Three specimen geometries were tested to compare the energy absorption: (1) a solid rectangular prism of the neat matrix material, (2) a rectangular prism of the matrix material containing a void with the same volume and geometry as the NS inclusion, and (3) a rectangular prism of the matrix containing the stainless steel NS inclusion, as shown in Figure 4.1. These three specimens were made with three variations of resin stiffness providing a total of nine specimens. The three stiffness matrix were labeled *low* (*L*), *medium* (*M*) and *high* (*H*) stiffness to facilitate their identification.


Figure 4.1.Specimens manufactured. a) NSS by itself. b) NSS + matrix. c) matrix. d) matrix + void. Specimens b), c) and d) were made with a low (L), medium (M) and high (H) stiffness resin.

## 4.3 Results

The force versus displacement responses are shown in Figure 4.2 for four different samples: the isolated NSS, the isolated matrix, the matrix containing a void with the same volume of the NSS (*matrix* + *void*), and the NSS in parallel with the polymer matrix (*matrix* + *NSS*). Matrices with three different Young's moduli were selected with low stiffness (L *matrix*), medium stiffness (M *matrix*), high stiffness (H *matrix*). Figure 4.2 a), b), and c) show the four force versus displacement responses for the four specimens and for each of the three matrix materials.

The force versus displacement responses for the neat matrices all show approximately linear responses during loading and the moduli were measured from this linear region. The measured moduli are 9.38, 310, and 968 kPa for the L, M, and H matrices respectively The curves all exhibit a concave curvature upon unloading. This response is expected for an elastomeric polymer that exhibits some degree of viscoelasticity.

The addition of a void in the matrix alters the force-displacement response by reducing the effective modulus and thus, at a given displacement, the force is lower for the matrices containing a void compared to the corresponding matrix that does not contain a void. The addition of an NSS further alters the force versus displacement response. Both the loading and unloading curves are convex for each of the three combinations of *matrix* + *NSS*. This behavior is most pronounced for the specimens with the *L* and *M* matrices, where the force versus displacement response has a slope near zero for an extended displacement range from approximately. 0.8 mm to 1.4 mm.



Figure 4.2. Force versus displacement response for the NSS, *matrix*, *matrix* + *void*, and *matrix* + NSS for (a) the *L* matrix, (b) the *M* matrix, and (c) the *H* matrix.

The energies dissipated during a load-unload cycle from 0 to 1.4 mm of displacement are shown in Table 4.1 for the isolated NSS, the *matrix* + *void*, and the *matrix* + *NSS* for specimens prepared with the *L*, *M*, and *H* matrices. The values of the energy absorption that are reported are an average and standard deviation measured from cycles 2 - 7 during repeated cyclic loading.

Specimen	Energy dissipation (mJ/cycle)	Specimen	Energy dissipation (mJ/cycle)
L matrix	$1.51\pm0.46$	M matrix + NSS	$3.64\pm0.35$
L matrix + void	$1.17\pm0.39$	H matrix	$11.52 \pm 0.23$
L matrix + NSS	$1.9\pm0.18$	H matrix + void	$7.67\pm0.14$
M matrix	$4.23\pm0.18$	H matrix + NSS	$8.52\pm0.18$
M matrix + void	$2.93 \pm 0.26$	NSS	$0.85\pm0.09$

Table 4.1. Energy dissipated per cycle for each specimen.

As expected based on the force versus displacement response of the neat matrices and the condition of displacement controlled loading, the energy absorbing capacity of the specimens increase with the stiffness of the matrix.

By calculating the difference between the energy dissipated by the *matrix* and the *matrix* + *void* specimens, one can determine the energy dissipated by a section of the matrix that has the same dimensions as the NSS. If this region of the matrix had an L stiffness, it would dissipate 0.34 mJ of energy, which is much less than the 0.85 mJ corresponding to the NSS. In this case, replacing the matrix with the NSS results in a significant increase in

energy dissipation. If this region of the matrix had an M stiffness, it would dissipate 1.3 mJ of energy, which is more than the 0.85 mJ corresponding to the NSS. In this case, replacing the section of the matrix by the NSS has a negative effect on the energy dissipation. If this section of the matrix had an H stiffness, it would dissipate 3.85 mJ of energy, which is much more than the 0.85 mJ corresponding to the NSS. In this case, replacing this section of the matrix with the NSS has a large negative effect in the energy dissipation.

Comparing the *matrix* + *NSS* specimens, it is apparent that the energy dissipated increases with the matrix stiffness. Again, this is because the contribution to the energy absorption from the matrix increases with matrix stiffness, as observed from the neat matrices. More importantly, when comparing the energy absorbed for the *matrix* + *NSS* specimens for the *L*, *M*, and *H* matrices, it is apparent that for each of the matrices, the energy dissipation is approximately a sum of the energy dissipated by the *matrix* + *void* and the isolated NSS. This result is expected because, for these specimens, the NSS was placed in parallel with the matrix. The total load capacity of the specimen in this configuration is thus a superposition of the load bearing capacity of the matrix and NSS.

For the samples containing the NSS, it is not straightforward to define a representative stiffness because of the significant non linearity when the NSS is activated. The stiffness reached a maximum in the initial loading range but can drop to zero when the NSS is being compressed in the negative stiffness region. To address this issue, a nominal stiffness was defined by calculating the slope of a straight line connecting the origin to the measured force at 1.3 mm of displacement.

The nominal stiffness values versus energy dissipated during the load-unload cycles from 0 to 1.4 mm of displacement are plotted in Figure 4.3a-c for the isolated *matrix*, the *matrix* + *void*, and the *matrix* + *NSS*, for specimens prepared with the *L*, *M*, and *H* matrices. Error bars in Figure 4.3 represent the standard deviation from 6 measurements in both the energy dissipation per cycle and the stiffness measured during loading of the specimens. The error bars for the stiffness are present but are too small to be observed in these graphs.

For the specimens prepared using the *L* matrix (Figure 4.3a), both the highest stiffness and the highest energy absorption are observed for the specimen containing the *matrix* + *NSS*. For the specimens prepared with the *M* matrix (Figure 4.3b), the neat matrix absorbs more energy than either the *matrix* + *void* or the *matrix* + *NSS*. However, the neat matrix has a lower stiffness than the *matrix* + *NSS*, but a higher stiffness than for the *matrix* + *void*. The neat matrix also absorbs more energy than either the *matrix* + *NSS*, but a higher stiffness than for the *matrix* + *void* or the *matrix* + *void*. The neat matrix also absorbs more energy than either the *matrix* + *void* or the *matrix* + *void*. The neat matrix also absorbs more energy than either the *matrix* + *void* or the *matrix* + *NSS* for the specimens prepared with the *H* matrix (Figure 4.3c). These results confirm that both higher energy dissipation and higher stiffness relative to the neat matrix alone can be achieved with composites containing NSS, but only when the stiffness of the NSS and the matrix are matched (e.g. for the *L* matrix in this case).



Figure 4.3. Stiffness versus energy dissipation for the *matrix*, *matrix* + *void*, and *matrix* + *NSS* for (a) the *L* matrix, (b) the *M* matrix, and (c) the *H* matrix. Note the differences in scales between (a), (b), and (c). Error bars represent the standard deviation from 6 measurements.

### 4.4 Discussion

Two significant results are demonstrated in this work. First, as shown in Figure 4.2a, a plateau in the force versus displacement behavior was achieved in a composite structure consisting of a matrix containing a NSS. Such a plateau is advantageous in structural design, since the behavior can be programmed to isolate objects from forces above a specified threshold based on application requirements. This benefit has a direct application for shock absorption applications where this behavior can be used to reduce the acceleration during impact [14].

The second important result is shown in Figure 4.3-a where a simultaneous improvement is demonstrated in both the stiffness and the energy dissipation in a composite material containing an NSS relative to the same neat matrix. This result is important because it clearly demonstrates that the tradeoff between stiffness and energy absorption that occurs in conventional composites can be decoupled by incorporating NSS. Note that the overall stiffness and energy absorption for the L matrix + NSS is lower on an absolute basis than the neat H matrix. However, further refinements to the NS structure to better match its stiffness to the H matrix (e.g. by adding beams in series or by changing the material used to manufacture the NSS) should allow the H matrix + modified NSS composite to improve the stiffness and energy absorption relative to the H matrix.

Previous work performed by Dixon *et al.* [17] demonstrated a large energy dissipation by the NSS when it is manufactured with polymeric materials such as nylon 11. For polymeric NS structures, energy dissipation occurs through viscoelastic relaxation of the polymer chains in the NS structure itself and provides a large dissipation with full

recovery after the load is removed. However, when the NSS is made of a metal, as in this research, the stiffness is greater, but the energy dissipation is reduced since metals are not viscoelastic at cold working temperatures and therefore energy dissipation mechanisms for metallic NSS are limited to internal friction and small amounts of plasticity.

For the configuration used in the current study, where the metallic NSS was placed in parallel with a polymer matrix, the total energy dissipated by the *NSS+matrix* is a simple addition of the energies dissipated by the NS and the matrix, as summarized in Figure 4.4.



Figure 4.4. Energy dissipated for the *matrix*, and *matrix* + *void*, and *matrix* + *NSS* for the L matrix, the M matrix, and the H matrix.

Further improvements in the energy absorption could be achieved with a configuration where the NSS is completely embedded into a resin. In this case, the extra energy dissipation would come from the localized strain in the vicinity of the NSS when the beam buckles. Also, this localized strain could be further enhanced during dynamic loading since polymers have non-linear damping behavior [38]. This is the subject of Chapter 5 and will be explored in detail there.

# 4.5 Conclusions

A composite consisting of a metallic NSS in parallel with a polymeric matrix was modeled, manufactured and experimentally tested under quasi-static, uniaxial, compressive loading. The behavior of the NSS modeled using FEM was found to be in good agreement with the experimentally measured force versus displacement response. Experimental testing of composites demonstrated that when the stiffness of the matrix and NSS is matched, both the stiffness and energy absorption are increased relative to the neat matrix. It was also demonstrated that this matching of the stiffnesses is critical, since the benefits to the stiffness and/or the energy absorption of the composite are lost when the matrix is either too stiff or too compliant when compared to the NSS.

# CHAPTER 5: UNIAXIAL TESTING OF NSS EMBEDDED WITHIN A POLYMERIC MATRIX

In Chapter 4, it was shown that, if the matrix stiffness is properly matched to that of an NSS, it is possible to produce a composite that has both higher stiffness and higher energy absorption than a neat matrix. However, the architecture studied in Chapter 4 was an idealized structure in which the NSS was placed in parallel with the matrix. This configuration limits the energy absorption of the composite to a linear superposition of the energy absorption of the matrix and NSS. In this chapter, a realistic composite architecture in which the NSS is embedded in a matrix is studied. The goals are to determine the conditions under which both stiffness and energy absorption are simultaneously maximized.

#### 5.1 Procedures

The detailed procedures used to perform FEA and the experiments related to this chapter are presented in Section 3.2, and thus are only summarized here. The Young's modulus and yield strength of fully dense SS17-4 were used to design an improved negative stiffness structure which was labeled NSS#2. This structure was modeled using FEA and the predicted force versus displacement response was obtained. Using a plate of fully dense SS17-4, a NSS#2 specimen was manufactured with water jet cutting. The NSS#2 structure showed a larger negative stiffness behavior with a small amount of plastic deformation, when compared to the NSS used in the previous chapter. To model the predicted response of the NSS#2 using FEA, the beam thickness was increased by 0.05

mm and the beam apex was reduced slightly by 0.34 mm. Both of these changes were consistent with the observed manufacturing defects and initial plastic deformation after the first compression cycle. The experimental and predicted force versus displacement responses agreed very well, validating the FEA models. Using the updated NSS#2 model, FEA simulations were performed to match the stiffness of the structure to the polymeric matrix. The criterion for matching the NSS#2 and matrix stiffness was that the predicted force versus displacement response in the model exhibited a region with a flat response.

In order to study the importance of matching the stiffness of the matrix to the one of the NSS#2, three resin formulations were used and were labeled L for the low modulus matrix, M for the moderate modulus matrix and H for the high modulus matrix. For each of the three different stiffness resins, four specimens were tested, corresponding to: 1) a completely filled matrix, 2) a matrix containing a void, 3) a void filled with the NSS#2 and 4) a void filled with a solid brass plate, as shown in Figure 5.1.

The specimens then were compressed at 10 mm/min uniaxially in a universal testing frame. The force versus displacement response was recorded for seven loading-unloading cycles. The average energy dissipated per cycle and the average stiffness was calculated from the cycles 2 - 7. The first cycle was ignored because it exhibited abnormally large energy dissipation due to stress relaxation of the matrix.



Figure 5.1. Specimens manufactured. a) Neat matrix. b) Matrix + void. c) Matrix + NSS. d) Matrix + brass plate. Each specimen was manufactured for the *L*, *M* and *H* stiffness matrix.

# 5.2 Finite modeling of Embedded NSS in Matrices

As discussed previously, FEA was performed to determine the influence of matrix stiffness on the overall response of the NSS + matrix composite. The main objective was to use the FEA to then select the composition of the matrix to obtain a region with a flat force versus displacement response during compression of the specimen. Figure 5.2 shows the results of a representative FEA model for the NSS#2 embedded within the *L* stiffness matrix. The FEA simulations predicted that it should be possible to activate the NSS structure when it was embedded in the *L*, *M*, and *H* matrices, without exceeding stresses to fracture the beam in the NSS.



Figure 5.2. FEA results of NSS#2 embedded in the L matrix. a) cross-section at a force sufficient to activate the NSS#2. b) Isometric view. Colors indicate the von Mises stress.

Figure 5.3 shows the predicted force versus displacement responses for the embedded NSS#2 in the *L*, *M*, and *H* matrices. From this plot, it is seen that for NSS#2 + L matrix, there is significant non-linearity that is predicted to begin at a displacement of approximately 2.2 mm and a force of 32 N. The onset of this non-linearity corresponds to the force and displacement where the NSS activates. After the onset of the non-linearity, the stiffness is predicted to slightly decrease until the displacement is large enough to completely buckle the beam in the NSS#2. At still larger displacements, the stiffness is predicted to become positive again at a displacement of approximately 2.5 mm, when the NSS#2 is fully compressed.



Figure 5.3. Predicted force versus displacement responses for the *L*, *M* and *H* stiffness matrices + NSS#2.

Comparing the NSS#2 + L matrix to NSS#2 + M matrix, it is apparent that as the matrix stiffness is increased, the non-linear region of the force versus displacement response is pushed to higher forces. Also, the NSS#2 is activated at a smaller displacement, since the matrix on top of the NSS#2 is stiffer and transmits the force more directly to the NSS#2. It is also notable that the degree of nonlinearity decreases as the matrix stiffness is increased from *L* to *M*. For the *NSS#2* + *M* matrix, the stiffness, although decreased when the NSS activates, it is never predicted to fall to zero or become negative.

Comparing, the NSS#2 + H matrix to the samples with the lower stiffness matrices, it is observed that the force predicted to activate the NSS#2 is even greater. Also, the displacement required to activate the NSS#2 is smaller than in the other two cases. More importantly, the decrease in stiffness that occurs upon activation of the NSS#2 is very small when compared to the NSS#2 + L matrix and NSS#2 + M matrix.

# 5.3 Comparisons between FEA simulations and experiments

The predicted FEA force versus displacement responses from Figure 5.3 are replotted and compared in Figure 5.4 a-c against the experimentally measured force versus displacement responses for the NSS#2 in the L, M, and H matrices.



Figure 5.4. Comparison of predicted and experimental force versus displacement responses for: a) *NSS#2+L matrix*. b) *NSS#2+M matrix*. c) *NSS#2+H matrix*.

From this figure it is apparent that the FEA results predict an initial stiffness that is greater than the measured initial stiffness. A careful examination of the experimental data reveals an initial non-linearity for all three samples in the first 0.5 mm of displacement. This is a typical response in compression tests and likely due to the inevitable slight misalignments between the compression platens and the specimen surfaces. This is responsible for most of the discrepancies between the predicted and measured initial stiffnesses. Comparing the predicted and measured force-versus displacement responses for the *NSS#2* + *L* matrix, it is apparent that the general trends in the experimental data are correctly predicted by the FEA model. However, the predicted change in stiffness is greater and the displacement range over which the activation of the NSS occurs is smaller than that observed experimentally.

Similar trends are observed for the predicted and measured NSS#2 in M matrix and the NSS#2 in H matrix. The likely causes of the discrepancies between the FEA predictions and experimental results are: 1) material properties of the NSS#2 and in particular, the matrix properties may differ slightly between the predictions and the experiments. 2) The FEA simulations assume that there is bonding between the NSS and the matrix. In reality, there is no bonding and only frictional tractions resist slipping. 3) Geometrical variations in the dimensions of the beam are present due to manufacturing errors from the water jet cutting process. These errors include a conical taper due to the kerf during the cutting process and also variations along the beam due to the precision of the machine.

# 5.4 Effects of strain rate on the energy dissipation

#### 5.4.1 Testing of *L* matrix specimens to displacements of 4 mm

The measurement of the energy dissipated by the specimens is an important part of understanding the behavior of NSS-based composites. Because viscoelastic polymers, such as those used here, exhibit a strain rate dependence to their energy absorption, the effect of the strain rate on the energy absorption of the NSS#2 in the L, M, and H matrices were studied. It is important to note that the tests were performed to a fixed displacement, instead of a fixed force. This was done to keep the strain constant in both cases and thus only the nominal strain rate was changed.

The force versus displacement responses to a fixed displacement of 4 mm are shown in Figure 5.5. This data corresponds to the L matrix at displacement rates of 1 and 10 mm/min. From this plot, it is apparent that increasing the strain rate causes an increase in stiffness, as expected for a viscoelastic material. The Young's modulus measured from the slopes in the linear regions of the force versus displacement plots were determined to be 260 kPa at a displacement rate of 1 mm/min and 307 kPa at 10 mm/min.

The energy absorption was calculated during a load-unload cycle from the hysteresis. The energy absorption was 7.89 mJ at a displacement rate of 1 mm/min and 12.7 mJ at a displacement rate of 10 mm/min. This confirms that, in the measurement range selected, larger strain rates increase the energy dissipation for the L matrix.



Figure 5.5. Response of the *L* stiffness matrix at displacement rates of 1 mm/min and 10 mm/min.

#### 5.4.2 *M* matrix testing to peak forces of 45 N

In order to test even further the behavior of the specimens at different strain rates, more detailed strain rates studies were performed for a). the isolated *M matrix*, b). the *M*-*matrix* +*void*, c). the *M matrix* + *NSS*#2 and the *M*-*matrix* + *plate*. In each case, the specimens were compressed to a fixed force of 45 N during 7 load-unload cycles at displacement rates of 1 mm/min and 10 mm/min. The resulting plots for individual specimens comparing both displacement rates are shown in Figure 5.6. With the exception of the first cycle which likely exhibits stress relaxation, the force versus displacement data in each case are very repeatable for cycles 2-7.



Figure 5.6. Plots of force versus displacement for 7 successive cycles for the *M* matrix specimens at displacement rates of 1 mm/min and 10 mm/min. (a) *M matrix*. (b) *M matrix* + void. (c) *M matrix* + NSS (d) *M matrix* + plate.



Figure 5.6. Continued. Plots of force versus displacement for 7 successive cycles for the *M* matrix specimens at displacement rates of 1 mm/min and 10 mm/min. (a) *M matrix*. (b) *M matrix* + void. (c) *M matrix* + NSS (d) *M matrix* + plate.

From Figure 5.6. it can be seen that any of the cycles from 2-7 is representative of the others and therefore, to reduce the clutter in the data and facilitate analysis, the force versus displacement responses were replotted in Figure 5.7 and Figure 5.8 with one loading-unloading cycles at displacement rates of 1 mm/min and 10 mm/min.



Figure 5.7. Force versus displacement responses for all *M* stiffness specimens tested to a peak force of 45 N at a displacement rate of 1 mm/min.

In Figure 5.7, it is apparent that adding a solid plate to the isolated matrix increases the stiffness of the composite but does not otherwise significantly alter the shape of the force versus displacement response. Similarly, adding a void to the isolated matrix reduces the stiffness, but also does not qualitatively change the force versus displacement response. In contrast, the addition of the NSS#2 results in a significant change in the forcedisplacement response compared to the neat matrix. Upon activation of the NSS#2, a significant decrease in stiffness occurs in the sample containing the NSS#2.

Comparing the data in Figure 5.7 at a displacement rate of 1 mm/min to the data in Figure 5.8 at a displacement rate of 10 mm/min, there are many qualitative similarities. For example, the effects of adding a solid plate or adding a void to the matrix are similar at the higher strain rate to what was observed at the lower strain rate. The shape of the force versus displacement response for the *matrix* + *NSS#2* is, however, qualitatively different

at the higher strain rate. At a strain rate of 1 mm/min, the resin has a lower stiffness and the NSS#2 is activated approximately in between 2 mm and 3.2 mm, where a small flat region is observed. After this displacement, the NSS#2 is completely compressed and it behaves similarly to a solid metal plate with a similar slope to the *M matrix* + *plate* specimen. It is also noted that further displacement is required to reach the specified 45 N force. The response is very different at a strain rate of 10 mm/min. In this case the resin has a higher stiffness and the NSS#2 is activated at a slightly smaller displacement, approximately between 1.8 mm and 3 mm, which is more evident from Figure 5.6-c. Furthermore, the specified 45 N force is reached as soon as the NSS#2 is completely compressed and no flat region is observed.



Figure 5.8. Force versus displacement response for all *M* stiffness specimens tested to a peak force of 45 N at a displacement rate of 10 mm/min.

The average energy dissipation versus stiffness for the M stiffness specimens at both strain rates are presented in Figure 5.9, where the circles correspond to a displacement rate of 1 mm/min and the squares correspond to a displacement rate of 10 mm/min. The arrows indicate the direction of increased strain rate and the dashed lines connect the minimum and maximum stiffness values for the matrix containing the NSS#2. The maximum stiffness value for the *L matrix*+*NSS#2* was calculated from the slope in the linear loading range. The minimum stiffness value was calculated by taking the slope of a line drawn from the origin to the force corresponding to the maximum displacement obtained for each specimen.

Comparing the samples measured at a displacement rate of 1 mm/min (the circles), it is apparent that there is a distinct trend. Increasing the stiffness of the composite by adding the plate decreases the energy absorption, whereas decreasing the stiffness by adding a void increases the energy absorption. Thus, for these samples there is a natural trade-off between stiffness and energy absorption that is typical of composites and which can be represented by a monotonically decreasing curve. The data for the *NSS#2* + *matrix* specimen at both, a displacement rate of 1 mm/min and 10 mm/min appears to lie slightly above the curve that defines the stiffness versus energy dissipation trade-off for specimens that do not contain an NSS. Nevertheless, these experiments show that, although changing the strain rate alters the absolute stiffnesses and energy absorption results, it does not significantly alter the relative differences between the different specimen architectures (e.g. neat *matrix*, *matrix* + *void*, etc.).



Figure 5.9. Comparison of stiffness versus energy dissipation per cycle between specimens with *M matrix* at 1 and 10 mm/min. Arrows connect the data for the same specimens at different strain rates. Dashed lines connect minimum and maximum stiffness values for the NSS#2+M matrix.

# 5.5 Uniaxial testing to peak forces of 35 N

In this section, the force versus displacement responses for the L, M and H stiffness matrix specimens is compared for a displacement rate of 10 mm/min. Also, the energy dissipation versus stiffness is included in order to compare the overall behavior of the different specimens.

#### 5.5.1 *L* matrix specimens

Figure 5.10 shows the force versus displacement responses for all the *L* stiffness matrix specimens that were compressed at a displacement rate of 10 mm/min up to a peak force of 35 N. As was observed for the *M*-matrix specimens, the addition of a stiff plate increases the stiffness of the composite and the introduction of a void decreases the stiffness of the composite. However, the shapes of the force versus displacement plots are not strongly affected by these changes to the neat matrix. The *L matrix* + *NSS#2*, however, shows a distinct change in stiffness upon activation of the NSS#2 at a force of approximately 32 N, corresponding to a displacement of approximately 3 mm.



Figure 5.10. Response of *L* stiffness matrix specimens compressed at a displacement rate of 10 mm/min.

The *L* stiffness specimens where also compressed at a force of 30 N to compare the behavior before and after activation of the NSS#2 inside the matrix as shown by Figure 5.11. This figure shows that when the *L matrix* + *NSS#2* specimen is loaded to a force-displacement that is too low to activate the NSS#2, it behaves similarly to the neat matrix or to a traditional composite, e.g. there is a nearly constant stiffness during loading. However, upon activation of the NSS#2, there is a dramatic change in slope.



Figure 5.11. Force versus displacement response of the *L matrix+NSS#2* tested to a peak force of 30 N and 35 N at a displacement rate of 10 mm/min.

Figure 5.12 shows the calculated average energy dissipations and stiffness values for six compression cycles (the first cycle was omitted) for the *L* matrix materials. The dashed line connects the minimum and maximum stiffness values that were measured for the *L* matrix+NSS#2 specimen before and after the beam of the NSS#2 was completely compressed. Two regions are shaded to show the trends in the positions of the data for the

specimens that do not contain the NSS#2, e.g. conventional materials. The grey shaded region shows the approximate trade-off between stiffness and energy dissipation for a peak force of 30 N. The pink shaded region shows the approximate trade-off between stiffness and energy dissipation for a peak force of 35 N. It is clear from this plot that when the NSS#2 is activated in the L matrix, the combination of stiffness and energy absorption is outside of the bounds of what is observed in neat matrices or matrices containing conventional reinforcements.



Figure 5.12. Energy dissipated per cycle versus stiffness of L matrix specimens. Circles correspond to the data measured with a peak force of 30 N and squares to the data measured with a peak force of 35 N.

#### 5.5.2 *M* matrix specimens

Figure 5.13 shows the force versus displacement response of all the *M* stiffness matrix specimens when compressed at a displacement rate of 10 mm/min up to a peak force 35 N. As was observed for the *M*-matrix materials, the addition of a stiff plate results in a stiffer composite and the addition of a void decreases the stiffness of the composite. A notable difference is that, at the same force that was observed to result in significant non-linearity in the force versus displacement response of the *L*-matrix + *NSS#2*, no discrete non-linearity is observed in the force versus displacement plot for the *M* matrix + *NSS#2*. Observations of the specimens during testing revealed that the NSS#2 was activated in the *L* matrix + *NSS#2* but not in the *M* matrix + *NSS#2* specimen.



Figure 5.13. Responses of *M* stiffness matrix specimens compressed at a displacement rate of 10 mm/min to peak force of 35 N.

Figure 5.14 shows the calculated average energy dissipation versus stiffness for load-unload cycles 2 - 7. Only one stiffness value is shown for the *M matrix* + *NSS#2* specimen, since the NSS#2 was not completely activated and the stiffness therefore was nearly constant with force. This plot shows that when the NSS#2 is not activated the composite follows the same stiffness versus energy dissipation trade-off as neat materials or conventional composites.



Figure 5.14. Energy dissipated per cycle versus stiffness of *M* stiffness matrix specimens.

#### 5.5.3 *H* matrix specimens

Figure 5.15 shows the force versus displacement responses for the *H* stiffness matrix specimens when compressed at displacement rate of 10 mm/min to peak force of 35 N. The observed force versus displacement responses are similar to those observed for the *M*-matrix specimens, e.g. the addition of a solid plate increases the stiffness relative to the neat matrix and the addition of a void decreases the stiffness relative to the neat matrix. Unlike the *M matrix* + *NSS#2* specimen, which was stiffer than the *M* matrix, the *H matrix* + *NSS#2* exhibits a force-displacement response that is nearly identical to that of the neat matrix. This is due to the fact that the stiffness of the matrix is comparable to that of the NSS#2 when it is in its positive stiffness regime.



Figure 5.15. Response of H -matrix specimens when compressed at a displacement rate of 10 mm/min to a peak force of 35 N.

Figure 5.16 shows the calculated average energy dissipation versus stiffness for load-unload cycles 2 - 7 for the *H* matrix specimens when compressed at a displacement rate of 10 mm/min to a peak force of 35 N. Only one stiffness value is shown for the *H* matrix + *NSS#2* specimen, since the NSS#2 was not activated and the stiffness therefore it was nearly constant during loading. The results are similar to that observed for the *M* matrix samples in that all of the specimens lie at or below the trade-off curve between the stiffness and energy dissipation for neat materials and conventional composites.



Figure 5.16. Energy dissipated per cycle versus stiffness of *H*-matrix specimens.

# 5.6 *M* matrix specimens tested to peak forces of 45 N

In Figure 5.8 it was shown that a peak force of 35 N was not sufficient to activate the NSS#2 when it was embedded in the M matrix and that under these conditions the specimen behaved like a conventional composite. This section presents a comparison of the behavior of the M matrix+NSS#2 tested to a peak force of 35 N and 45 N. The larger force is sufficient to activate the NSS#2 structure when it is embedded in the M matrix. The force versus displacement responses are shown Figure 5.17 for the NSS#2 embedded in the M matrix to peak forces of 35 and 45 N. The displacement rate in both cases was 10 mm/min



Figure 5.17. Response of *M matrix*+*NSS#2* tested to a peak force of 35 N and 45 N.

The force versus displacement response for when this sample was tested to a peak force of 45 N exhibits the classical non-linearity associated with the activation of the NSS#2. However, compared to L Matrix + NSS#2 specimen, the reduction in slope upon activation of the NSS#2 was not as great. Nevertheless, when comparing the responses for the *M* Matrix + NSS#2 specimen tested to 30 and 45 N, it is clear that significantly more hysteresis occurs at a peak force of 45 N, when the NSS is activated.

Figure 5.18 shows the variations in stiffness and energy dissipation for the M matrix specimens at forces of 35 N and 45 N. The lower force is not sufficient to activate the NSS#2 when it is embedded in this matrix, but the higher force does cause activation. The data for the other M matrix specimens are also included to compare the relative behavior of the specimens containing the NSS#2.

The regions containing the *M* matrix, *M* matrix + plate and *M* matrix + void specimens are shaded because they represent the behavior of conventional materials and provide a basis for comparison with the behavior of the *M* matrix+NSS#2 specimen. A dashed line is used to connect the minimum and maximum stiffness values obtained for the *M* matrix + NSS#2 specimen when the structure was activated. Arrows are used to connect each specimen from its 35 N (region in gray) to its corresponding 45 N measurement (region in pink).

It is clear from the plot that higher energy absorption occurs for all specimens when the peak force is increased from 35 N to 45 N, as expected for viscoelastic materials. It is also apparent that the *M matrix* +*NSS#2* sample exhibits behavior is that is slightly above the trade-off curve between stiffness and energy absorption for conventional materials, but only when the NSS#2 is activated. Comparing the behavior for the *M* matrix +NSS#2 to that for the *L* matrix +NSS#2 sample shown in Figure 5.12, it is clear that the data point for *M* matrix +NSS#2 specimen lies more closely to the trade-off curve than the data point of the *L* matrix +NSS#2 specimen.



Figure 5.18. Energy dissipated per cycle vs stiffness for *M* matrix specimens when tested to peak forces of 35 N (circles) and 45 N (squares) at a displacement rate of 10 mm/min.
#### 5.7 *H* matrix specimens tested to peak forces of 70 N

From Figure 5.15, it is clear that a peak force of 35 N is not sufficient to activate the NSS#2 when it is embedded in the H matrix. Further testing indicated that a force of 70 N was required to activate the NSS#2 when it was embedded in this matrix.

Figure 5.19 shows a comparison of the *H matrix+NSS#2* tested to peak forces of 35 N and 70 N at a displacement rate of 10 mm/min. Although the NSS#2 was confirmed to activate at a force of 70 N by observing the NSS#2 through the transparent matrix during testing, the force versus displacement response at 70 N did not show a strong non-linearity and it is therefore difficult to distinguish where activation of the NSS occurred from the force versus displacement response.



Figure 5.19. Response of *H matrix+NSS#2* tested to peak forces of 35 N and 70 N at a displacement rate of 10 mm/min.

Comparing the force versus displacement responses for when the NSS#2 was embedded in the *L*, *M*, and *H* matrices (Figure 5.11, Figure 5.17, and Figure 5.19), it is clear that the largest hysteresis increase occurs when the NSS#2 is placed in a matrix whose stiffness is well-matched to the NSS#2 and activation of the NSS occurs.

Figure 5.20 shows the force versus displacement responses for all the *H* matrix specimens tested at a displacement rate of 10 mm/min to a peak force of 70 N. The force versus displacement responses are qualitatively similar that observed at the lower force of 35 N, despite the fact that the large force is sufficient to activate the NSS. At both forces, all of the specimens exhibit nearly constant stiffnesses with increasing displacement. One subtle difference between the response of the *H matrix* + *NSS#2* specimen is that, when it was tested at 70 N, its stiffness was slightly lower than when compressed at 35 N.



Figure 5.20. Response of *H* matrix specimens tested to a peak force of 70 N at a displacement rate of 10 mm/min.

Figure 5.21 shows the variations in stiffness versus energy dissipation for the H matrix specimens at forces of 35 N and 70 N. The lower force is not sufficient to activate the NSS#2 when it is embedded in this matrix, but the higher force does cause activation. The data for the other H matrix specimens are also included to compare the relative behavior of the specimens containing the NSS#2. The regions containing the H matrix, H matrix + plate and H matrix + void specimens are shaded because they represent the behavior of conventional materials and provide a basis for comparison with the behavior of the H matrix + NSS#2 specimen. In this case, the minimum and maximum stiffness values for the H matrix + NSS#2 overlapped, therefore the minimum value was removed from the graph.

Arrows are used to connect each specimen from its 35 N (region in gray) to its corresponding 70 N measurement (region in pink). Because there is a large increase in force between the lower and higher forces, there is a significant increase in energy dissipation as the force is increased. However, the most important point is that unlike the L matrix + NSS#2 and M matrix + NSS#2, the H matrix + NSS#2 does not exhibit behavior above the trade-off curve, even when the NSS is activated. This shows that two conditions are required in this class of composite to achieve large combinations of stiffness and energy absorption: 1) the force must be sufficient to activate the NSS and 2) the matrix stiffness must be matched to the stiffness of the NSS in the region where it is activated.



Figure 5.21. Energy dissipated per cycle vs stiffness of *H* matrix specimens when compressed at 35 N (circles) and 70 N (squares)

The results obtained in this section including average energy dissipation and stiffness values for all the specimens are summarized in the appendix in Table 9.2.

#### 5.8 Discussion

In this section the results are analyzed in order to highlight significant findings.

#### 5.8.1 Effects of strain rate on the energy dissipation

In Figure 5.5 the influence of strain rate on the cyclic behavior of the *L* matrix materials was explored while keeping the peak displacement fixed. The increase in strain rate was observed to increase the energy dissipation for the neat *L* matrix. This is an important observation since it shows that strain rate can be one of the factors that influence the energy dissipation in neat viscoelastic specimens. Both the strain and strain rate would be larger in a localized region adjacent to the stiff inclusion, as shown in Figure 5.2. In addition, as shown in Figure 5.9, the localized increases in strain and strain rate that occur in the vicinity of the *M matrix* + *plate* specimen resulted in an even greater increase in energy absorption than what was observed in the neat polymer matrix.



Figure 5.22. Increased strain rate of the polymer at the top of the specimen.

It is important to note that the above tests were performed to study the differences in energy dissipation with variations in strain rate, while keeping a fixed peak <u>displacement</u>. Subsequent testing was performed at a fixed peak <u>force</u> were additional complications arise. In this case, the localized higher strain rate increases the energy dissipation, but on the other hand, the higher strain rate stiffens the polymer matrix and the force is achieved with a smaller displacement, reducing the hysteresis and hence reducing the energy dissipation. Because of this, the specimens were tested under fixed peak force conditions to observe the relative behavior between them.

The influence of varying the displacement rate, for the M matrix specimens, is also representative of the behavior that would be obtained for the L and H specimens. When these specimens were tested to a peak force of 45 N, it was observed that higher strain rates resulted in a stiffer matrix, reaching the specified force faster. This affected the M matrix + NSS#2 specimen the most as shown in Figure 5.6(c). Here, it was observed that higher strain rates reduced the force transmitted to the NSS#2. Even when complete compression of the NSS#2 was achieved in both cases, more deformation was observed at the slower displacement rate of 1 mm/min. This is very important for design purposes since it illustrates that changes in the strain rate will affect the force threshold where the NSS activates. Also, if the strain rate is too large, the NSS may not activate at all, meaning that there will be a maximum window of operation for the NSS inside a polymeric matrix. In such a case, FEA studies that include non-linear models for the matrix should be used to predict the behavior as a function of strain rate and the desired application. Figure 5.9 confirms that for the M matrix specimens, although the stiffnesses increase with strain rate (particularly for the specimen containing the stiff plate inclusion), the energy dissipation is decreased for all the specimens, with the exception of the specimen containing the NSS#2, where the energy dissipation increased slightly. As mentioned before, this occurs because the matrix becomes stiffer at larger strain rates, reducing the hysteresis during the load-unload cycle. Also from this plot, it can be observed that even though the results for all of the specimens are sensitive to strain rate, it is possible to compare samples with different architectures if the strain rate is fixed. For example, the trends observed between the different architectures was similar at displacement rates of 1 mm/min and 10 mm/min.

#### 5.8.2 Uniaxial testing to peak forces of 35 N

#### 5.8.2.1 L matrix specimens

Figure 5.10 shows the response of the *L* stiffness matrix specimens. Here, it can be seen that, as expected, the specimen containing the plate has the highest stiffness. Also, the *L* matrix+NSS#2 specimen shows the desired flat response at a force of approximately 32N (between 3 to 4 mm of displacement).

Figure 5.12 summarizes the overall response of the specimens and clearly shows that when the NSS#2 is embedded into the matrix and activates so that the beam buckles completely, a large increase in the energy dissipation and stiffness occur simultaneously. These results are in agreement with the predictions of Lakes [8] [9] and Haberman [10],

which are summarized in Figure 1.1. This figure also shows the importance of completely buckling the beam in the NSS for increasing the energy absorption per cycle.

The results for peak forces of 35 N for the *L* matrix+NSS#2 shown in Figure 5.12 include a dashed line that indicates the measured stiffness range. This range corresponds to the minimum and maximum measured stiffness and it is important to clarify the difference. The minimum stiffness is calculated from the slope computed by drawing a line between the origin to the force when the displacement reaches the maximum (4.2 mm in this case). The maximum stiffness corresponds to the linear portion of the loading curve (between displacements of 0 and 3 mm) and does not include the flat response from the force vs displacement curve when the NSS is activated.

In order to compare which stiffness value is relevant for each application, 3 cases are described: (I) If the NSS#2 is not activated when embedded inside the matrix, then the maximum stiffness value shown in Figure 5.12 should be used. (II) If the NSS#2 is completely buckled when embedded inside the matrix, then the minimum stiffness value shown in Figure 5.12 should be considered. This case, for example, could correspond to an impact where the peak force was greater than 35 N. (III) If the NSS#2 is barely activated by a static load but not completely buckled inside the resin matrix and a vibration is applied, then two stiffness values could be observed, one for the static load and another one for the dynamic load. In the case of the dynamic load, the stiffness value would approach zero in the flat range of the force versus displacement curve. This scenario is very interesting since it could be applied, for example, for isolation of vibrations. If this material was used in a structural application such as to damp vibrations from a helicopter rotor, the helicopter's

weight could be supported by the maximum stiffness of the specimen, while the vibrations would be damped by a soft material capable of dissipating large amounts of energy with minimum stiffness.

#### 5.8.2.2 *M matrix specimens*

Figure 5.13 shows the force versus displacement behavior of specimens with the M stiffness matrix. Here it can be seen that the stiffness of the M matrix+NSS#2 specimen is slightly lower than that of the M matrix + plate, even when the NSS#2 is not completely activated. This means that the NSS#2 does not behave as a completely rigid inclusion, even when it is compressed in its positive stiffness range. This causes small changes in the force-displacement behavior even when the inclusion does not exhibit negative stiffness behavior.

Figure 5.14 shows that when the NSS#2 is embedded into the matrix and only compressed in its positive stiffness regime, the typical trade-off behavior is obtained. In this case, the *M* matrix + plate shows the largest stiffness but lowest energy dissipation, the *M* matrix has larger energy dissipation but less stiffness, and the *M* matrix + *NSS#2* is located in between the two data points (typical trade-off). This is especially interesting if the results are compared against Figure 5.12. It can be seen that the relative position for the specimen containing the NSS#2 changes completely when the structure exhibits negative stiffness behavior. The stiffness is not affected much, but the relative energy dissipation is increased greatly when the NSS#2 is activated. By comparing the *L* and *M* matrix specimens, the extra energy dissipation that was observed for the *L* matrix+*NSS#2* can be attributed to: larger localized strain rate, increased localized strain, and larger overall

deformation under the same force (i.e. the flat region of the force displacement curve results in large displacements at a fixed force).

#### 5.8.2.3 *H matrix specimens*

The responses of the *H* matrix specimens, presented in Figure 5.15 and Figure 5.16 show similar results to those observed for the *M*-matrix specimens, when the NSS#2 was not activated. In this case, the relative positions of the NSS#2 in the stiffness versus energy dissipation trade-off are very similar, and embedding the NSS#2 into the matrix does not produce significant improvements in the stiffness versus energy dissipation trade-off.

#### 5.8.3 M matrix specimens tested to peak forces of 45 N

A peak force of 45 N was used to determine the differences before and after the NSS#2 was activated in the *M* stiffness matrix. Figure 5.17 shows that once the NSS#2 is activated, non-linear behavior is clearly obtained in the force versus displacement curve for the *M* matrix + NSS#2.

In Figure 5.18 it can be seen that when the force is large enough to allow for complete buckling of the NSS#2, a large energy dissipation is observed relative to the other specimens tested under the same conditions. It can also be observed that if compared against Figure 5.12, the energy dissipation and stiffness benefits are not as significant. This is a strong indication that matching the stiffness of the matrix and the NSS#2 is very important in order to improve the benefits in the stiffness versus energy dissipation trade-off.

#### 5.8.4 *H* matrix specimens tested to peak forces of 70 N

Figure 5.19 shows that when the NSS#2 is embedded into the *H* matrix, its contribution to the force versus displacement response is so small that it is barely noticeable. Also, Figure 5.20 shows that the *H* matrix+NSS#2 specimen is even more compliant than the *H* matrix specimen. Lastly, Figure 5.21 shows that no significant benefits were observed when the NSS#2 was embedded into the *H* stiffness matrix. A slight improvement in the energy dissipation was observed but at a cost of reduced stiffness. Combined, these three plots (Figure 5.12, Figure 5.18 and Figure 5.21) clearly show that matching the stiffness of the NSS#2 and the stiffness of the matrix is critically important to obtain the benefits desired when embedding NSS into a polymeric matrix.

#### 5.9 Conclusions

FEA simulations were used to predict the force versus displacement responses when the NSS#2 was embedded in different matrices where the stiffness values of the matrices varied substantially compared to the stiffness of the NSS#2. For these simulations, the actual dimensions of the NSS#2 and the elastic properties of the matrices and NSS#2 were used. Upon testing, it was found that experimental behavior of the test specimens matched the predictions reasonably well. This provided a validation for the models and the specified boundary conditions used.

Subsequent tests showed that three mechanisms contribute to enhanced energy dissipation when the NSS#2 was embedded into a polymeric matrix. These include: 1) increased localized strain rate, 2) increased localized strain and pronounced deformation

due to the flat response obtained in the force versus displacement curve for the L matrix+NSS#2 specimen. These data confirmed the hypothesis that a flat response in the force versus displacement curve produces the highest energy absorption and is able to achieve an increase of both the stiffness and energy dissipation relative to the trade-off that is observed in neat materials and in conventional composites.

It was suggested that these materials may be ideal for applications where a large load needs to be statically supported while vibrations are damped with low dynamic stiffness. Most importantly, it was shown that to achieve simultaneous increases in stiffness and energy absorption both of the following conditions must be met: 1) the NSS#2 stiffness in the activated state must be closely matched to that of the matrix, 2) the force on the composite must be sufficient to activate the NSS when it is embedded in the matrix. Furthermore, it is important to design the NSS in order to be able to activate it depending on the expected strain rates that the application may require. Failing to do this could result in a matrix that would not activate the NSS at the expected force threshold.

# CHAPTER 6: MICROMANUFACTURE BY CO-EXTRUSION OF NEGATIVE STIFFNESS INCLUSIONS

This chapter focusses on preliminary research aimed at using micro-co-extrusion to reduce the dimensions of NSS to the microscale to enable a polymer-matrix, NSSparticulate composite. As discussed in Chapter 2, successful micro-co-extrusion requires that the shape of the macroscale feed rod structure be maintained during the extrusion process. Thus, much of this chapter is focusses on the conditions required to successfully co-extrude NSS structures.

Van Hoy *et al.* have shown that the principle factor that controls the success in coextruding polymer-ceramic compounds is that the viscosities of all of the compounds in the feed rod must be matched [18]. Thus, after performing the compounding procedures described in Chapter 3, the stainless steel- (SS) and carbon black- (CB) containing compounds were first characterized using torque rheometry, which is the standard characterization for MFCX procedures. In the first section of this chapter, the log(torque) vs log(RPM) plots obtained through torque rheometry for each of the compounds used in the feed rod are analyzed to predict the viscosity behavior at low strain rates.

Additional rheological characterization was performed through capillary rheometry at much lower strain rates. The geometry and strain rates used for capillary rheometry are very similar to that used in co-extrusion and thus this testing methodology was believed to be the most direct measurement of the properties of interest. However, capillary rheometry is a very time-consuming measurement technique compared to torque rheometry. Thus, one goal of this work is to determine if correlations can be made between the viscosities determined from torque rheometry at high strain rates and the viscosities measured using capillary measurements at strain rates appropriate for co-extrusion.

Even with the two previous rheological characterization techniques, a small viscosity mismatch between the compounds was observed after studying the geometry of the extruded specimens. Because of this, parallel plate viscometry was selected as a third rheological characterization method. It was hypothesized that this technique is not as strongly affected by friction at the interface between the polymer and surfaces of the testing equipment when compared to capillary rheometry.

The second section of this chapter describes the production of the feed rods used for the coextrusion process. This includes the manufacture of a structure based on the NSS#2 and a modified version with a larger base, smaller top beam and wider window gap. SEM images of the extrudates are included to characterize the distortions of the structure that occurred during extrusion and to observe manufacturing defects such as: voids, geometrical variations and broken beams sections.

Following production of the micro-scale NSS, preliminary tests were conducted on the structures by manually loading the NSS under an optical microscope to determine if the NSS could be activated. Nanoindentation studies were also performed in an attempt to measure the force versus displacement response of the micro-scale NSS. These preliminary measurements showed anomalous behavior that requires further study.

### 6.1 Rheology

#### 6.1.1 Torque rheometry

Torque rheometry measurements were obtained during the compounding process, as explained in detail in Chapter 3. The results of the measurements were extrapolated to low strain rates for both the SS- and the CB-containing compounds. This allowed the compositions of the compounds to be adjusted until the viscosities extrapolated to low strain rates appropriate for co-extrusion were matched, as shown in Figure 6.1. In this figure, the experimental data is presented as filled circles and the projected trends are shown as dashed lines.



Figure 6.1. Torque rheometry results and extrapolation of the torque to low strain rates. There is a linear relationship between the log(torque) and log(viscosity).

#### 6.1.2 Capillary rheometry

After the compounding process was completed, the behavior of the polymers was measured using capillary rheometry with the same extrusion chamber used for coextrusion, as detailed in Chapter 3. The measured force to extrude the compound is related to the shear stress and the crosshead displacement is related to the shear strain [24]. The results are shown in Figure 6.2 and include four tests at two different displacement rates for the SS- and CB-containing compounds. Although the forces at a particular displacement for the CB- and SS-containing compounds do not match exactly (which would be an indication that the viscosities were completely matched) they were similar enough to conclude that a successful coextrusion should be possible. [18]



Figure 6.2. Capillary rheometry results for CB- and SS-containing compounds at two different displacement rates.

#### 6.1.3 Parallel plate rheometry

The parallel plate rheometer was used to characterize the rheological behavior of the SS- and CB-containing compounds. Figure 6.3 shows the piece of equipment used and its principal components (AR2000 ex, TA Instruments, New Castle, DE). This technique was selected because it reduces measurement errors due to interactions with the walls (i.e. friction) by using two parallel plates with the compound heated and compressed in between them. The sample is loaded in between the plates, heated to melt the compound and compressed by lowering the top plate. The excess material that flows radially out of the plates is removed manually to reduce measurement errors. Afterwards, the top plate rotates at a controlled speed and the equipment measures the torque versus revolutions per minute.



Figure 6.3. Parallel plate rheometer. The top plate can rotate and adjust the distance between the plates.

Figure 6.4 shows the results obtained for both, the SS- and CB- containing compounds. From this plot, it can be observed that at the strain rate used for coextrusion  $(0.59 \text{ s}^{-1} = -0.23 \text{ in log scale})$ , the SS compound exhibited a lower viscosity than the CB compound, despite the fact that the usual methods for measuring viscosity (torque and capillary rheometry measurements) indicated that the SS and CB compounds exhibited similar viscosities. The viscosity difference is much greater at smaller strain rates corresponding to those used for co-extrusion. This explains why some extruded micro-scale NSS exhibited large distortions during co-extrusion, since the strain rate is not uniform across the extrusion chamber. A hypothesis for the cause of this discrepancies between the viscosities obtained using different techniques is presented in the discussion.



Figure 6.4. Parallel rheometry results for the neat PEBA polymer, the SS compound and the CB compound.

It is also important to observe that the SS compound exhibited a large non-linearity above 0.4 s<sup>-1</sup>. Above this value, the measurements were not valid since wall-slip occurred

for this specific specimen, generating the flawed data. Comparison in this region between the SS and the CB compounds demonstrates that a significant difference in the compoundwall interaction exists between the two materials.

#### 6.2 Coextrusion and thermal treatments

Since the capillary rheometry results confirmed the viscosity match for the SS- and CB-compounds, the parts were molded and assembled as explained in Chapter 3. The resulting macro-scale feed rods are shown in Figure 6.5. The regions with the darker contrast are the regions consisting of the CB-containing compound and the regions with the lighter contrast consist of the SS-containing compounds. For both of the feed rods the NSS structure is wholly encapsulated within the CB-containing compound so that the SS-containing compound does not contact the die surface during co-extrusion.



Figure 6.5. Feed rods assembled for MFCX: a) geometry for NSS#2 and b) modified geometry with larger base, larger window clearance and shorter top beam.

After assembly, the feed rods were extruded at a displacement rate of 1 mm/min and a temperature of 135°C as explained in detail in Chapter 3. The overall reduction in size scale during extrusion was approximate a factor of 4. To characterize the extrudate it was cut manually at room temperature using a razor blade into thin slices about 0.3 mm thick and studied using an optical microscope. The images of the extrudate cross-sections are shown in Figure 6.6. The images show that there is clearly some distortion that occurs during the extrusion, despite the apparently matched viscosities of the compounds. The distortion of the structures is greatest near the edges of the feed rods. A comparison of the structures before and after extrusion shows that after extrusion the structures are no longer completely encapsulated within the CB-containing compound and that they touch or nearly touch the edges of the die surfaces. This is an indication that the flow through the dies was not uniform and that the die wall friction was slowing the CB-containing compound and causing the SS-containing compound to move towards the edges of the die. Additional distortion was observed from bulging of the extrudate. This arises from die swelling when viscoelastic recovery occurs as the extrudate experiences the sudden loss of pressure upon exit from the die.



Figure 6.6. Optical micrographs of extrudates. a) Geometry based on NSS#2. b) NSS with modified geometry.

The micro-scale features of the extrudates were studied using a scanning electron microscope (SEM), as shown in Figure 6.7 and Figure 6.8. These images show that the speckled appearance of the NSS that was apparent at low magnifications in Figure 6.6 is

the result of the individual SS particles. Figure 6.7-b and Figure 6.8-b show that the beam section is only one or two particles thick.



Figure 6.7. a) SEM images of the extrudate with the NSS#2 structure. b) Higher magnification image of the beam connection from the NSS shown in a).



Figure 6.8. a) SEM images of the extrudate from the modified NSS#2 (shorter top beam, wider window gap and larger base). b) Higher magnification image of the beam connection from the NSS shown in a).

Figure 6.9 shows a magnified view of the beam section, which has an approximate thickness of 70  $\mu$ m. This image shows more clearly this geometry could not be further reduced in size because, since any further reduction would result in gaps in the beam wherever the beam was less than one particle thick.



50 µm

Figure 6.9. Magnified view of the beam section of NSS#2.

After extrusion, the extrudates were cut and then pyrolyzed to remove the polymer and carbon black and then further heated to 1300°C under vacuum to sinter the SS, as detailed in Chapter 3. The sintered NSS were then observed with an optical microscope and SEM, and the results are shown in Figure 6.10 and Figure 6.11. At this scale, the SS grains can easily be observed within the NSS specimen. The dimensions of the sintered NSS specimens were approximately: 3 mm long x 0.5 mm thick x 0.6 mm tall and the beam thicknesses ranged from between 20 to 40  $\mu$ m, depending on the specimen. Compared to the as-extruded parts, the sintered parts exhibit more distortion of the structure. Some distortion from sintering as was observed here is not unusual, however, for the co-extrusion process. [18]



(b)

Figure 6.10. Optical microscopy of sintered micro-scale NSS. The background was removed to highlight the structure. a) Sintered micro-scale NSS #2. b) Magnified view of the beam section.



Figure 6.11. SEM images of sintered micro-scale NSS. a) Modified micro-scale NSS (shorter top beam, wider window gap and larger base) b) Magnified view of the beam section.

Despite the visible distortions of the structures following co-extrusion and sintering, many of the specimens that were produced had a geometry that approximated the desired structure. However, some also showed defects such as voids, extreme geometry deformation, broken beam sections, an insufficient window to allow for complete buckling of the beam, and superficial defects due to cutting of the extrudate. Examples of these defects are shown in Figure 6.12 and Figure 6.13.



Figure 6.12. Examples of defects during MFCX. a) distortion of the NSS so that there is insufficient window clearance. b) beam with broken connection (highlighted in red)



Figure 6.13. Examples of defects observed in modified NSS structures. a) Void in the main body and beam with broken connection. b) Superficial defects that arose during cutting of the extrudate. Defects are highlighted with red boxes.

## 6.3 Testing of micro-scale NSS

Before subjecting specimens to detailed quantitative mechanical testing, preliminary qualitative tests were conducted to confirm that the NSS would activate. These qualitative tests were conducted manually by compressing the beam under an optical microscope using a blunt aluminum pyramid that was glued to the base of the NSS, as shown in the still images captured from video in Figure 6.14 and Figure 6.15. These images show that despite the imperfect structures, the NSS did activate under an applied load and subsequently elastically recovered when the load was removed.



Figure 6.14. Stills images captured from the video while compressing the NSS manually in an optical microscope. Sequence follows (a), (b), (c), (d) and continues in Figure 6.15.



Figure 6.15. Sequence continues from Figure 6.14. Still images captured from the video while compressing the micro-scale NSS manually under an optical microscope. Sequence follows (e), (f), (g), (h)

Micro-scale NSS specimens were mounted on independent aluminum bases and supported laterally by thin aluminum plates that were also glued to the base as shown in Figure 3.15. In order to confirm that the beam was free to move under compression, the specimens where observed under the optical microscope by rotating the base sideways 90 degrees and observing the front of the micro-scale NSS as shown in Figure 6.16.



Figure 6.16. Diagram showing the direction of observation of the mounted micro-scale NSS under the optical microscope.

A mounted specimen is shown in Figure 6.17 where it can be seen that the top beam does not have interference with the side walls. Also, the window has enough clearance to allow the beam to be compressed with the nanoindenter. Only the micro-scale NSS is shown in focus because of the small depth-of-field of optical microscopes.

# Thin aluminum plates



Figure 6.17. Micro-scale NSS mounted on an aluminum base and supported laterally by aluminum plates prior testing.

There was considerable variation in the specimen geometries for sintered NSS and many of the NSS specimens that were produced did not activate. As an example, Figure 6.18 shows two other specimens that did not activate or did not activate with the desired response because of interference between the top beam and the side walls of the NSS.



Figure 6.18. a) and b) Mounted micro-scale NSS specimens. Both specimens show interference between the top beam and the side walls that prevented activation of the NSS with the desired response.

NSS samples that appeared to have close to the ideal structure were selected for quantitative testing. These specimens were compressed uniaxially in the nano-indenter, as described in Chapter 3 and a representative force versus displacement response is shown in Figure 6.19.



Figure 6.19. Preliminary data obtained by nanoindentation for micro-scale NSS specimens. a) Complete force versus displacement data. b) Magnification of the data showing non-linear behavior in the force versus displacement response.

Figure 6.19(a) shows the complete force versus displacement response, where a large spike in the force is observed at a displacement of about 33,000 nm. Figure 6.19(b) shows a more detailed view of the force versus displacement response prior to the force spike. Here, a non-linear response is observed that resembles the expected negative stiffness behavior.

Figure 6.20 shows an NSS after the indentation and it is clear that as a result of the testing, the NSS has undergone significant plastic deformation and collapse of the structure. Although this is a different specimen than that shown in Figure 6.17, this figure suggests that the large force spike that was observed occurred when the beam completely buckled and the indenter then pushed the beam into the solid steel base of the structure, thereby damaging the NSS.



Figure 6.20. Optical micrograph of NSS after excessive compression during testing.

To determine if the initial response of the NSS before the force spike was a result of activation of the NSS, the micro-scale NSS force vs displacement response was predicted using FEM modeling and compared to the experimental response. To accurately model the response using FEM, it is important that the actual specimen geometry be used in the FEM model. This was challenging because the manufacturing imperfections resulted in geometry non-uniformities that were difficult to capture in the FEM. In an attempt to estimate the response of the micro-scale NSS, the overall NSS thickness was varied between 0.5 mm and 0.08 mm as shown in Figure 6.21.



Figure 6.21. Minimum and maximum thickness of the NSS used for the FEA predictions.
The predicted force versus displacement responses for NSS with thicknesses of 0.08 mm and 0.5 mm are shown in Figure 6.22-a. This figure shows that the predicted displacement range over which the NSS is active (in between a displacement of 0.025 to .075 mm) does not vary significantly, as expected. However, the predicted force required to activate the beam increases linearly with the thickness of the NSS.

A comparison of the experimental data obtained with the nanoindenter and the predicted response from FEM assuming a thickness of the NSS of 0.08 mm is shown in Figure 6.22-b. This comparison shows poor agreement between the predictions and the experiments. In particular, the predicted displacements required to activate the NSS do not agree well with the measured displacements. Potential reasons for this disagreement are discussed in the section that follows.



Figure 6.22. Force versus displacement response for micro-scale NSS. a) FEA prediction for two specimen thicknesses. b) Comparison of experimental and predicted response for a NSS thickness of 0.08 mm.

#### 6.4 Discussion

#### 6.4.1 Matching of Metal-Polymer Compound Viscosities

Considerable effort was made to adjust the compositions of the CB- and SScontaining by adding plasticizer to the compounds so that their viscosities would be matched under the conditions used for co-extrusion. The torque and capillary rheometry where were used to characterize the viscosities of the two compounds. It was found that the viscosities obtained using torque rheometry could be extrapolated to lower strain rates in order to obtain similar results during capillary rheometry. This is important because although capillary rheometry provides similar conditions to the coextrusion process (i.e. strain rates, temperature profile). these tests are considerably more time consuming to perform. The extrapolation of the data during torque rheometry was a very useful first approximation that allowed to have similar force vs displacement behavior during the capillary rheometry testing.

However, even with an approximate match in viscosities of the compounds, distortions of the NSS structure occurred during co-extrusion. To highlight these distortions, images showing a cross-section of the feed rod before and after coextrusion are reproduced in Figure 6.23. It is apparent from this figure that a major cause of the distortion is that the distance between the SS-containing compound and the die wall is dramatically reduced during co-extrusion.



Figure 6.23. Comparison of distance between the SS and the extrusion chamber wall a) For the feed rod before coextrusion. b) For the extrudate after coextrusion.

Two main reasons are suggested for the mismatch in flow, despite the approximate match in viscosities of the compounds. First, the PEG plasticizer that was used to adjust the viscosity of the SS-containing compound may have influenced the behavior of this compound. The grade of PEG used in this research melts at 60°C [37] and is a liquid above that temperature. Furthermore, PEG is not miscible in the PEBA binder and thus, when it melts, it forms a two phase mixture [28], where one of the phases is a liquid and the other is a solid. This would obviously affect the flow behavior of the compound compared to compound containing a single phase binder/plasticizer.

Second, both torque rheometry and capillary rheometry used for this research ignore a critical factor that is believed to be very important for this particular coextrusion, e.g. the friction at the wall [24] [25] [27]. When determining viscosity using capillary rheometry, the force required to produce flow at a specific rate is measured. This force has contributions from both the friction at the wall and the force required to produce flow of the compound through the die. This is apparent from the data in Figure 6.2 because the extrusion force monotonically decreases as the feed rod is reduced in length throughout the test. This occurs because the contact area between the compound and the extrusion chamber is reduced with feed rod length, thus decreasing the contributions to the force from friction.

It is hypothesized that when measuring individual compounds during the capillary rheometry tests, the SS-containing compound exhibits a higher coefficient of friction with the extrusion die than the CB-containing compound. Thus, although the forces to extrude both compounds may have been nearly the same, the contribution to the force for the SS-containing compound from friction was likely higher and the complimentary contribution from flow was therefore likely lower than for the CB-containing compound. Evidence supporting this hypothesis is apparent from comparing the response of the SS compound (blue) and the carbon black compound (black) in Figure 6.2. It is seen that the reduction in force with increased displacement is much larger for the SS-containing compound. This suggests that since the reduction of area was the same in both cases, the friction decreased much faster for the SS-containing compound, implying a higher friction coefficient at the wall.

This effect is more noticeable at the slower displacement rates of 1 mm/min. When the displacement rate increased to 2 mm/min (green and orange responses), a progressive accumulation of SS particles in between the piston and the extrusion chamber was observed that likely influenced these results by increasing the friction even further. The observed distortions of the extrudate match with the expected behavior of a lower viscosity compound encapsulated within in a higher viscosity compound. As shown by Hilmas *et al.* [24], the lower viscosity material flows outwards to the regions of highest shear, which in this case is towards the walls of the extrusion die.

Although an approximate match in viscosities has been used previously as the criterion to establish the conditions for successful extrusion, in the current work this criterion was not sufficient and distortions of the extrudate were observed. One reason why this criterion may have been successful previously but not in the current work may be due to characteristics of the powders used in the compounds. In previous work with ceramics and carbon black, all of the powders used were sub-micron and somewhat irregular in shape. In the current study, the carbon black was similar to previous work, but the SS powder was coarse (maximum grain size was 50  $\mu$ m) and spherical. These differences in powder characteristics, along with the differences in surface chemistries of the powders lead to quite large differences in compositions of the compounds used to achieve similar viscosities. Finer SS powders could reduce this problem, but unfortunately were not available commercially.

Parallel plate viscometry was proposed as a different method to measure the viscosities of both compounds at low strain rates and without the errors caused by wall friction that was observed with capillary rheometry. Parallel plate rheometry was performed with the SS- and CB-containing compounds. These results show that the distortions observed during co-extrusion were likely caused by differences in the viscosities of the compounds that were not detected by torque or capillary rheometry.

Further work is needed to determine if matching the viscosities of compounds using torque rheometry would result in extrusions free of distortions in the cross-section.

From Figure 6.4, it is evident that wall slipping occurred between the SS-containing compound and the parallel plates at large strain rates, which was evidenced by a large drop in in the measured viscosity. The differences in strain rate at the onset of slipping provides further confirmation of the important differences in interaction between the SS- and CB-containing compounds.

#### 6.4.2 Other defects

Extrusion defects such as voids and superficial defects were occasionally observed, but the majority of the micro-scale NSS were successfully extruded and did not show significant defects of this nature. Greater care in removing voids during fabrication of the feed rod could further reduce the incidence of these defects.

Figure 6.9 shows that the beam in the NSS structure consists only one or two grains of SS in the thickness direction. The grain size sets a limit on the magnitude of the reduction in size of the NSS that is possible during extrusion. The reduction from the feed rod to the extrudate was 4×. If a larger reduction was attempted so that a smaller NSS could be produced, it would be likely that gaps would occur in the beam since it is not possible to produce a beam with a thickness smaller than the grain size. Potential solutions to this problem are 1) to use a SS powder with a smaller particle size or 2) redesign the NSS so that the beam dimensions are larger relative to the size of the NSS. Unfortunately, finer SS powders were not available commercially so the only viable option at the current time is to redesign the NSS.

#### 6.4.3 Testing of micro-extruded NSS

Despite the challenges that were encountered with co-extruding NSS, Figure 6.10 showed conclusively that the co-extrusion process is potentially a viable route for producing micro-scale NSS. This figure shows that even when extrusion defects were present, the NSS micro-scale structure was activated by application of a force that was applied manually. However, this preliminary test also showed that the NSS design was not optimal given the distortions in the geometry that occurred during co-extrusion. Figure 6.11 shows the modified NSS design that was produced with a reduced top platen length, increased window clearance, and increased base height.

The nanoindentation results shown in Figure 6.19 corresponded to the micro-scale NSS #2 and due to time constraints the modified version with larger base could not be tested. Even though these results are promising, further work is needed to assess the behavior of the micro-scale NSS.

Figure 6.22-b shows that a significant discrepancy exists between the experimental and predicted response. The predicted and measured force thresholds where the NSS is activated are very similar, but the predicted displacement range for activation of the NSS varies significantly from the experimental data. It is possible that geometry differences between the FEM model and the actual specimen were responsible for this discrepancy. For example, the specimen exhibited a lower beam apex than what was modeled.

As pointed out the in the previous section, the thickness of the beam in this NSS was small enough that it was of order the grain size. This is important, since the predictions

from the FEA modeling were based on the assumption of isotropic elastic materials. Clearly, for an elastically anisotropic material like iron, this assumption would not be valid when the beam thickness consists of only a single grain. Thus, additional errors may arise from this effect. Nevertheless, even with these differences, the preliminary results are encouraging and they lay the bases for future work.

### 6.5 Conclusions

Previous work has shown that co-extrusion can be successfully performed when there is an approximate match in viscosities of the compounds used to produce the feed rod. These measurements of viscosity are typically obtained from torque rheometry during the compounding process. For this reason, the compositions of the metal/polymer compounds and carbon black/polymer compounds used in this work were adjusted so that there was an approximate match in viscosities as measured using torque rheometry. The results were extrapolated to the lower strain rate used for coextrusion and in order to confirm that this extrapolation was valid, capillary rheometry was performed as an additional characterization. Capillary rheometry measurements of the compounds showed good agreement with the torque rheometry and therefore the coextrusion was attempted.

Study of the extrudates revealed that there was significant distortion of the NSS during co-extrusion. It was found that the SS-containing compound was migrating to the edges of the cross-section during extrusion. This suggests that there were wall friction effects in the capillary measurements that resulted in anomalous viscosity measurements.

These frictional effects masked the fact that the intrinsic viscosity for the CB-containing compound was actually higher than the SS-containing compound. In an attempt to determine the cause of this distortion, additional rheological characterization was performed using parallel plate viscometry. This technique confirmed that there were significant differences in viscosities between the CB- and SS- containing compounds, despite the measurements from torque and capillary measurements that indicated that the viscosities were similar. Large differences in the sizes and shapes of the powder particles between the SS an CB created challenges in producing compounds with similar compositions and viscosities.

The coarse SS particle size with respect to the thickness of the beam was also found to limit the reduction in the size of the NSS during co-extrusion. If smaller micro NSS are needed, a SS powder with a finer particle size would have to be used or the NSS would have to be redesigned so that the beam was larger relative to the dimensions of the NSS. In addition, the small number of grains in the beam thickness are also likely to contribute to the discrepancies between the measured micro-scale NSS response and predictions from the FEA models that assume isotropic linear elastic behavior.

Despite the challenges in producing micro-scale NSS structures, loading of the specimens manually while observing them in an optical microscope showed that it was possible to activate the NSS produced by co-extrusion and thus the potential of this manufacturing method for producing NSS was validated. Subsequent quantitative measurements made in a nanoindenter revealed that the predicted force threshold for buckling of the beam was similar to the measured force, but the displacement range did not

agree with the predictions. Refinements in the manufacturing process to reduce extrusion deformations and additional quantitative testing is needed to characterize the behavior of micro-scale NSS.

#### CHAPTER 7: CONCLUSIONS

The main objectives of the current study were: (I) Using analytical and numerical models to study the combinations of NSS, specimen geometries and material properties that result in large energy absorption. To accomplish this a model system consisting of a single mechanically activated NSS was considered. (II) Experimentally validate this approach by testing specimens quasi-statically with the NSS placed in parallel with the matrix. (III) Extending the modeling and experimental validation to samples where the NSS was embedded in the matrix and (IV) demonstrate the viability of manufacturing micro-scale NSS using MFCX with a design similar to the one proposed by Klatt [13].

Chapter 4 presented the predictions and experimental results obtained for an idealized composite consisting of a single macro-scale NSS made of stainless steel that was placed in parallel with a polymeric matrix. Finite element models predicting the behavior of the specimens were validated experimentally and it was found that, when the stiffness of the structure was matched to the stiffness of the matrix, both the energy dissipation and stiffness were increased simultaneously. This is a significant finding because conventional composites containing positive stiffness inclusions exhibit a trade-off between stiffness and energy dissipation. Thus this result is the first experimental validation that a composite containing NSS activated by buckling can exhibit both higher energy dissipation and higher stiffness than the matrix.

This chapter provided a basic understanding of the energy dissipation mechanisms in polymer matrix NSS composites. It was observed that when the NSS was placed in parallel with the resin, the energy dissipation was the sum of the energy dissipated by the matrix and NSS. The stiffness in this configuration also followed a linear rule of mixtures so that the NSS generated a large stiffness increase relative to the low stiffness matrix. It was also shown that the energy dissipation and stiffness benefits are completely negated if the NSS is embedded in a high stiffness matrix relative to the stiffness of the NSS. The comparisons of the stiffnesses vs energy dissipations (Figure 4.3) was an important first experimental validation that the stiffness of the resin and the NSS should be matched to obtain the largest benefits.

Chapter 5 described the results obtained when an NSS with a modified geometry (NSS#2) was embedded in a polymeric matrix. Following a similar methodology to that used in Chapter 4, the specimens were tested in compression in different resins with varying stiffness. The predicted force versus displacement responses obtained from finite element modeling were validated experimentally for these specimens. It was found that there was a large stiffness and energy dissipation improvement when the stiffness of the NSS#2 was matched to the stiffness of the resin. In contrast, conventional, positive stiffness composites exhibit a trade-off between stiffness and energy dissipation.

When comparing the results from Chapter 5 for the NSS#2 embedded in a matrix to the results obtained from Chapter 4, it was observed that the energy dissipation no longer followed the additive behavior that was observed when the NSS was in parallel with the matrix. It was concluded that the three most important factors that generated an enhanced energy dissipation for embedded NSS#2 were: larger localized strain in the vicinity of the NSS when it activated, a larger localized strain rate, and increased hysteresis required to reach the same force due to the flat force versus displacement response of the NSS. Comparisons of the relationships between stiffness versus energy dissipated when the NSS#2 was activated inside the *low* (Figure 5.12), *medium* (Figure 5.18) and *high* (Figure 5.21) stiffness matrices, showed clearly seen that matching the stiffness of the NSS#2 and the resin is very important in order to obtain the desired benefit in both the energy dissipation and stiffness of the specimens.

Chapter 6 describes the design, manufacturing and testing of micro-scale NSS by co-extrusion. Much effort was placed on matching the viscosity of the extrusion compounds because it has been shown previously that this is a sufficient condition for obtaining successful co-extrusion with minimal distortion of the cross-section [18]. Torque and capillary rheometry techniques were used to characterize the viscosity of the compounds. However, co-extrusion of these compounds resulted in extrudates with significant extrusion distortion. Subsequent rheological characterization showed despite the apparent matching of viscosities using standard rheology methods, wall friction effects were significant during co-extrusion. It was determined that the actual viscosity of the SS-containing compound was lower than that for the CB-containing compound. Strategies for reducing the extrusion deformation were proposed.

Despite the deformation observed in the co-extruded NSS, testing of the microscale NSS under an optical microscope confirmed the NSS could be activated. Nanoindentation experiments were performed on the micro-scale NSS and the initial results showed a response that included a region of negative stiffness. These results are still preliminary and more testing needs to be performed on improved versions of the microscale NSS so that the behavior can be predicted using FEA.

Overall this work provided insight on the energy dissipation mechanisms in polymer-matrix composites containing NSS. Furthermore, it was demonstrated the simultaneous improvements in both the energy dissipation and stiffness in composites is possible with embedded NSS, when the stiffness of the polymer matrix and NSS are matched. Lastly, a viable manufacturing method utilizing co-extrusion was demonstrated that has the potential to produce NSS in sufficient quantities to allow implementation of these materials in real-world applications.

#### **CHAPTER 8:** FUTURE WORK

This section describes the most relevant work that can be performed in the future using the results obtained through this research. The important issues included here are: uniaxial dynamic testing of the macro NSS and resins, improvements to the co-extrusion process, testing of a large coextrusion chamber, and dynamic testing of micro-scale NSS embedded in a polymeric matrix.

## 8.1 Uniaxial dynamic testing of NSS and resins

A shaker table was installed and a testing setup was manufactured to measure the response of the NSS and resins when a vibration is applied. The complete testing setup is shown in Figure 8.1.



Figure 8.1. Uniaxial dynamic testing setup. a) Complete setup including the universal testing frame. b) Section showing the accelerometers and specimen.

The purpose of this test is to apply a uniform load to the specimens via a weight that is labeled "activation load". The weight provides a static load on the NSS that is large enough to push the beam close to its buckling point. The load can be varied by adding weights to account for matrices with different stiffnesses. Once the specimen is secured, two accelerometers measure the input and output accelerations, as shown in Figure 8.1-b. The shaker table can then be activated to apply a small cyclic load superimposed onto the static load to the specimens to determine the dynamic damping behavior of the material.

This test requires that the specimens be firmly attached to the bases and the weight. This can be done with metal plates that serve as bonding interfaces between the resin and the weight or the shaker table. The specimen can be glued to the metal plate and then a removable wax can be used to secure the plate to the weight or shaker table.

This testing would provide complementary dynamic data to the pseudo-static data obtained in this dissertation. These measurements could provide the first verification of improved dynamic damping and stiffness for a NSS + matrix systems. The setup was manufactured, assembled and preliminary testing was performed, but the complete testing and further data analysis were beyond the scope of this dissertation.

#### 8.2 Improvements in coextrusion and testing of micro-scale NSS

The most significant improvement that was identified to manufacture micro-scale NSS composites, is to improve the viscosity match of the SS and CB compounds. This should be done in order to obtain better geometrical quality of the micro-scale NSS. Improving the viscosity match of both compounds, while keeping the rest of the experimental procedures the same, can produce a large improvement in the quality of the coextruded structures. This could be done empirically by reducing the viscosity of the current formulation for the CB-containing compound while keeping the same viscosity for the SS-containing compound. Another option would be to measure the viscosity of the compounds using a parallel plate viscometer but increasing the testing temperature of the SS compound to avoid the wall slip problems observed during previous testing.

With an improved micro-scale NSS geometry, it would be very interesting to perform more nanoindentation testing and be able to obtain repeatable force versus displacement responses that shows negative stiffness behavior for several compression cycles. An alternative to the nanoindenter is to use a standard universal test frame equipped with the 250 N capacity load cell, which has a peak-to-peak noise close to 3 mN. To obtain valid measurements, it would be necessary to increase the force threshold to activate the NSS from the current value of 10 mN to about 50 mN. This could be done by cutting the extrudate in thicker slices, then the micro-scale NSS would be thicker and provide more resistance to deformation as illustrated in Figure 8.2. Increasing the thickness of the specimens would increase linearly the force required to compress them, facilitating accurate measurements with this load cell. The main benefit of testing the micro-scale NSS in the universal test frame is that the behavior of the specimens could be observed during testing using magnifying lenses. This is important since the buckling behavior of the beam is not always repeatable for co-extruded parts, due to the geometrical variations of the fabrication method.



Figure 8.2. Micro-scale NSS with different thicknesses. a) Thin micro-scale NSS requiring a small force to activate. b) Thicker micro-scale NSS requiring a larger force to activate.

Thicker micro-scale NSS were manufactured but the larger aspect ratio caused the specimens to tilt and fall onto their sides. In the case of the modified micro-scale NSS with a larger base, they did not fall, but fractures and beam deformation occurred because of the

weight of the specimens themselves was too large to survive the pyrolysis and sintering processes. This could be solved by adding supports for the micro-scale NSS during pyrolysis and sintering. This could be accomplished by placing the extrudate slices inside the crucible onto a bed of coarse alumina powder that is resistant to sintering. The coarse powder supports the structure during pyrolysis when it is particularly fragile, without chemically interacting with the steel.

Further improvements could be made to the micro-scale NSS if finer SS powder was used. SS powders with grain size between 2 - 5  $\mu$ m would allow the manufacture of micro-scale NSS with beam thickness close to 10  $\mu$ m. A smaller micro-scale NSS could be useful for damping high frequency vibrations. This is due to the fact that the maximum dimension of the micro-scale NSS has to be smaller than the wavelength of the vibration desired to damp, otherwise its beam would not buckle under the varying load.

## 8.3 Large coextrusion chamber

A large coextrusion chamber was fabricated in order to facilitate the feed rod manufacture and assembly, which is very time consuming and requires considerable skill. The large co-extrusion chamber is shown in Figure 8.3.



Figure 8.3. Large extrusion chamber. a) Top view showing the extrusion chamber and extrusion die. b) Whole assembly. (1) Load cell adapter. (2) Piston. (3) Brass plunger. (4) Extrusion chamber. (5) Heating elements. (6) Support base.

Currently the initial feed rod is manufactured manually with molds, which is also very time consuming. If the initial feed rod had a larger cross section, it could be manufactured quickly with a water jet cutter or a CNC milling machine. In either case, multiple layers of compound material could be cut at a time and later assembled, as shown in Figure 8.4. This is a similar technique to additive manufacturing, where a part is produced layer-by-layer until the three dimensional shape is obtained.



Figure 8.4. Proposed procedure for co-extrusion with the large co-extrusion chamber.

The large coextrusion chamber was intended to facilitate the manufacture of complex shapes such as double or triple beam NSS, but the extrusion volume is quite large and would consume too much material at the prototyping stage that was required for this dissertation and therefore it was not included in this study. Once the viscosity of the SS-and CB-containing compounds is completely matched and the results in the small extrusion chamber are satisfactory, the large extrusion chamber should be used.

## 8.4 Dynamic testing of immersed composite

Once the micro-scale NSS are manufactured and tested, they can be completely embedded into a polymeric matrix as shown in Figure 8.5. The matching of the stiffness of the resin and micro-scale NSS would require substantial FEA modeling to verify the desired behavior for the specimen.



Figure 8.5. Randomly oriented micro-scale NSS embedded into a polymeric matrix.

This specimen could then be immersed in a pressurized chamber filled with oil as shown in Figure 8.6.



Figure 8.6. Specimen immersed into oil inside a pressurized chamber. Taken from [39].

This chamber would have an acoustic emission source which is basically an immersed speaker. Also, it would have a sensor to measure the output after the wave travels through the medium and specimen. By comparing the output to the input signals, the transfer function can be determined and the damping behavior of the specimen can be compared to other reference specimens (*matrix*, *matrix* + *NSS*, *matrix* + *void* and *matrix* + *plate*).

It is important to note that in order to activate the micro-scale NSS, the pressure in the chamber can be modified. This would create a force on the matrix, which would be transferred to the micro-scale NSS that would in turn activate them.

Two parameters would be changed to determine the properties of the material: the hydraulic pressure applied in order to determine the correct set point to activate the micro-scale NSS; and the frequency applied to the specimens, which may be important due to the non-linear behavior of the polymeric matrix.

This test would produce measurements that are as similar as possible to a real-world scenario were the specimens are required to support a force statically (that works to activate the micro-scale NSS) and dynamically absorb vibrations. This would correspond to high stiffness and high damping simultaneously.

## **CHAPTER 9: APPENDIX**

# 9.1 Coextrusion process summary

Table 9.1 shows a summary of the coextrusion processes, testing procedures, methods for material characterization and parameters that can be varied in each step.

Mechanical Processing	Parameters	Testing and characterization	Possible defects
Polymer / ceramics compounding	<ul> <li>Particle size, geometry &amp; vol.%.</li> <li>Mixing temp.</li> <li>RPM</li> <li>Plasticizer compatibility</li> </ul>	- SEM - Capillary, torque and parallel plate rheometry	<ul> <li>Viscosity mismatch</li> <li>Non-uniform particle size</li> <li>Polymer debinding</li> </ul>
Composites Molding	<ul> <li>Mold release</li> <li>technique</li> <li>Temperature</li> <li>Compression speed</li> <li>Composition</li> </ul>	-Visual inspection	<ul> <li>Breakage while peeling</li> <li>Poor flow</li> <li>Voids</li> </ul>
Feed rod assembly	<ul> <li>Assembly technique</li> <li>Interlayer fusion</li> <li>(temperature &amp; pressure)</li> </ul>	-Visual inspection	<ul> <li>Voids</li> <li>Low tolerance due to manual assembly</li> </ul>
Co-extrusion	<ul> <li>Crosshead speed</li> <li>Die temperature</li> <li>Chamber temperature</li> <li>CB enclosing layer</li> <li>Viscosity mismatch</li> <li>Particle size</li> </ul>	-Visual inspection - Optical microscopy - Capillary, torque and parallel plate rheometry	<ul> <li>Sharkskin</li> <li>Shape deformation</li> <li>Rounded corners</li> </ul>

Table 9.1. Coextrusion summary

Table 9.1. Coextrusion summary (continued)

Mechanical Processing	Parameters	Testing and characterization	Possible defects
Polymer pyrolysis	<ul> <li>Thermal profile</li> <li>Final temperature</li> <li>Processing atmosphere</li> <li>Composition</li> <li>Part geometry</li> </ul>	- Visual observation - TGA	<ul> <li>Fractures</li> <li>Incomplete polymer removal</li> <li>Shape deformation</li> </ul>
Ceramics sintering	<ul> <li>Heat rate</li> <li>Green density</li> <li>Final temperature</li> <li>Particle size</li> <li>Composition</li> </ul>	<ul> <li>Density:</li> <li>pycnometer and</li> <li>Archimedes'</li> <li>SEM</li> </ul>	<ul> <li>Voids &amp; fractures</li> <li>Low densification</li> <li>Impurities</li> <li>Thermal expansion mismatch</li> </ul>
H <sub>2</sub> reduction (for metal NSS)	<ul> <li>H<sub>2</sub> concentration</li> <li>Flow rate</li> <li>Heat rate</li> <li>Final temperature</li> </ul>	<ul> <li>Density:</li> <li>pycnometer and</li> <li>Archimedes'</li> <li>SEM</li> </ul>	<ul> <li>Voids &amp; fractures</li> <li>Low densification</li> <li>Impurities</li> <li>Thermal mismatch</li> </ul>
Final part	Affected by all the previous parameters	<ul> <li>Dynamic E</li> <li>Tension tests</li> <li>Three-point bending</li> <li>Compression tests</li> <li>Micro-hardness testing</li> </ul>	All defects mentioned before

# 9.2 Results obtained for the NSS#2 embedded within a polymeric matrix

The results obtained for the different specimens tested in Chapter 5 are summarized in Table 9.2.

NSS#2 compressed by itself at a peak force of 35 N						
Specimen	Energy dissipated (mJ/cycle)	St dev	Stiffness (N/mm)	St dev		
NSS#2 by itself	0.20	0.01	20.59	0.13		
L matrix results taken at 10 mm/min and at a peak force of 30 N						
Specimen	Energy dissipated (mJ/cycle)	St dev	Stiffness (N/mm)	St dev		
L matrix	10.27	0.22	9.89	0.03		
L matrix + void	11.74	0.05	8.36	0.05		
L matrix + plate	7.28	0.11	16.99	0.03		
L matrix + NSS#2	7.91	0.19	13.11	0.07		
L matrix results taken at 10 mm/min and at a peak force of 35 N						
Specimen	Energy dissipated (mJ/cycle)	St dev	Stiffness (N/mm)	St dev		
L matrix	15.48	0.37	9.30	0.02		
L matrix + void	15.74	0.10	8.15	0.01		
L matrix + plate	10.16	0.18	16.13	0.03		
L matrix + NSS#2	17.04	0.32	8.73 - 12.45	0.05		
M matrix results taken at 10 mm/min and at a peak force of 35 N						
Specimen	Energy dissipated (mJ/cycle)	St dev	Stiffness (N/mm)	St dev		
M matrix	11.99	0.21	17.36	0.06		
M matrix + void	14.03	0.28	15.04	0.04		
M matrix + plate	7.71	0.09	29.38	0.16		
M matrix + NSS#2	9.03	0.16	20.50	0.30		

Table 9.2. Summary of results from Chapter 5

M matrix results taken at 10 mm/min and at a peak force of 45 N					
Specimen	Energy dissipated (mJ/cycle)	St dev	Stiffness (N/mm)	St dev	
M matrix	18.11	0.44	18.45	0.17	
M matrix + void	21.57	0.46	16.08	0.17	
M matrix + plate	11.89	0.24	31.81	0.20	
M matrix + NSS#2	20.72	0.32	16.63 - 20.79	0.12	
M matrix results taken at 1 mm/min and at a peak force of 45 N					
Specimen	Energy dissipated (mJ/cycle)	St dev	Stiffness (N/mm)	St dev	
M matrix	18.45	0.47	14.83	0.07	
M matrix + void	23.90	0.50	11.84	0.07	
M matrix + plate	12.68	0.12	16.55	0.13	
M matrix + NSS#2	20.37	0.07	12.20 - 16.02	0.06	
H matrix results taken at 10 mm/min and at a peak force of 35 N					
Specimen	Energy dissipated (mJ/cycle)	St dev	Stiffness (N/mm)	St dev	
H matrix	4.77	0.09	31.05	0.19	
H matrix + void	4.50	0.08	26.75	0.12	
H matrix + plate	3.65	0.07	44.41	0.28	
H matrix + NSS#2	4.03	0.07	30.31	0.10	
H matrix results taken at 10 mm/min and at a peak force of 70 N					
Specimen	Energy dissipated (mJ/cycle)	St dev	Stiffness (N/mm)	St dev	
H matrix	15.37	0.38	37.85	0.12	
H matrix + void	16.33	0.33	33.39	0.20	
H matrix + plate	11.51	0.25	55.85	0.37	
H matrix + NSS#2	16.21	0.24	29.85 - 32.52	0.08	

Table 9.2. Summary of results from Chapter 5 (continued)

#### **CHAPTER 10: REFERENCES**

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